

Volume Phase Transition Behaviors of Thermoresponsive Hydrogels

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Vollständiger Abdruck der von der TUM School of Natural Sciences der Technischen Universität München zur Erlangung eines

Doktors der Naturwissenschaften (Dr. rer. nat.)

genehmigten Dissertation.

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Prüfende der Dissertation:

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Die Dissertation wurde am 22.04.2024 bei der Technischen Universität München eingereicht und durch die TUM School of Natural Sciences am 10.05.2024 angenommen.

Dedicated to my parents
Bingmao Wang and Qilan Wang.

Abstract

The volume phase transition of thermoresponsive diblock polymer (DBC) thin films is receiving increasing attention in smart materials, due to their sensitive thickness changes responding to environmental perturbations, such as temperature, the composition of surrounding vapor, and the presence of salts. In this dissertation, the systematical studies are performed, focusing on co-nonsolvency-triggered phase collapse, KCl-modulated phase transition temperature shift and salts series driven co-nonsolvency behavior of DBC thin films, which consists of a nonionic poly(*N*-isopropylmethacrylamide) (PNIPMAM) and a zwitterionic poly(sulfobetaine) (PSB). To enable these scientific studies, neutron reflectometry, spectral reflectometry and Fourier-transform infrared spectroscopy are mainly used.

Zusammenfassung

Die Volumenphasenumwandlung von thermosensitiven Diblockpolymer (DBC) Dünnschichten erfährt zunehmend Aufmerksamkeit im Bereich der intelligenten Materialien. Dies liegt an ihrer empfindlichen Dickenänderung als Reaktion auf Umwelteinflüsse wie Temperatur, die Zusammensetzung der umgebenden Dämpfe und das Vorhandensein von Salzen. In dieser Dissertation werden systematische Studien durchgeführt, die sich auf den durch Co-Nonsolvenz ausgelösten Phasenzusammenbruch, die durch KCl modulierte Verschiebung der Phasenübergangstemperatur und das durch die Salz-Serie gesteuerte Co-Nonsolvenzverhalten von DBC-Dünnschichten konzentrieren. Diese bestehen aus einem nichtionischen Poly(*N*-isopropylmethacrylamid) (PNIPMAM) und einem zwitterionischen Poly(sulfobetain) (PSB). Zur Durchführung dieser wissenschaftlichen Studien werden hauptsächlich Neutronenreflektometrie, spektrale Reflektometrie und Fourier-Transform Infrarot spektroskopie eingesetzt.

Contents

Abstract	i
List of Abbreviations	vii
1. Introduction	1
2. Theoretical Background	7
2.1. Thermoresponsive polymer	7
2.1.1. Phase diagram of thermoresponsive polymer in solutions	7
2.1.2. Solubility of thermoresponsive polymers	8
2.1.3. Modulation of LCST and UCST	10
2.2. Co-nonsolvency effect	13
2.2.1. Polymer solution theory	13
2.2.2. Microscale mechanisms on co-nonsolvent effect	15
2.2.3. Conformation of thermoresponsive polymer in solution	19
2.3. Specific ion effect (SIE)	22
2.3.1. Hofmeister series	22
2.3.2. Classical theoretical ideas for SIE	23
2.3.3. SIE in polymer solutions	24
3. Characterization techniques	29
3.1. Neutron reflectometry (NR)	29
3.1.1. Basic principles of neutron reflection	30
3.1.2. NR setup and data process	31
3.1.3. Solvent content calculation	33
3.2. X-ray reflectometry (XRR)	34
3.2.1. X-ray interference in multilayer film	35
3.2.2. XRR setup	35

3.3.	Spectral reflectometry (SR)	36
3.3.1.	Decoupling method of film thickness and refractive index	37
3.4.	UV-Vis-NIR spectrophotometer	38
3.5.	Atomic force microscopy (AFM)	38
3.6.	Fourier-transform infrared spectroscopy (FTIR)	38
3.7.	Two-dimensional FTIR (2D FTIR) correlation analysis	40
3.7.1.	Acquisition of 2D infrared spectrum	40
3.7.2.	Mathematical processing of 2D correlation spectra	41
3.7.3.	2D FTIR correlation analysis	42
3.8.	Molecular dynamics simulation (MD)	43
4.	Sample preparation	45
4.1.	Materials	45
4.1.1.	Polymer synthesis	45
4.1.2.	Polymer solutions	48
4.2.	Substrate cleaning	48
4.3.	Spin-coating and drop-casting methods	49
4.4.	Sample environment	50
4.4.1.	“FlexiProb” and “custom designed FTIR” chambers	50
4.4.2.	Vapor generation system	50
4.4.3.	The applied vapor protocols	51
5.	Co-nonsolvency-triggered phase transition behavior	55
5.1.	Homopolymer thin films in water and mixed water/acetone vapor	56
5.2.	DBC thin films in water and mixed water/acetone vapor	59
5.2.1.	Experimental design	59
5.2.2.	Investigation of static equilibrium states	60
5.2.3.	Swelling and co-solvent switching kinetics	62
5.2.4.	Solvation process around the functional groups	66
5.3.	Conclusions	71
6.	KCl-modulated hydration and subsequent thermoresponsive behavior	73
6.1.	Swelling in D ₂ O vapor and temperature protocol	74
6.2.	KCl-modulated phase transition behavior of homopolymer thin films	74
6.3.	KCl-modulated phase transition behavior of PSBP- <i>b</i> -PNIPMAM thin films	77
6.3.1.	Swelling ratio response to the experimental protocol	77
6.3.2.	Polymer density and the migration of KCl	78
6.3.3.	Surface topography at ambient conditions	79

6.3.4.	Investigation of static equilibrium stages	79
6.3.5.	D ₂ O hydration and subsequent thermal stimulus kinetics	82
6.3.6.	Polymer–D ₂ O interactions around functional groups	86
6.4.	Conclusions	89
7.	Salt Series Driven Solvation Behavior in non-aqueous atmosphere	91
7.1.	Thin Film Response to a Stepwise Exchange of the Vapor Atmosphere. . .	93
7.2.	Thin Film Hydration and Switching Kinetics	96
7.2.1.	Kinetics of the swelling behavior	97
7.2.2.	Kinetics of solvent absorption	99
7.2.3.	Salt induced interactions between polymer and solvent	101
7.2.4.	Salt effect on the temporal sequence of solvation events	105
7.2.5.	Solvation shell and the DBC polymer conformation	110
7.3.	Conclusions	112
8.	Summary	113
A.	Supporting information for Chapter 5	117
B.	Supporting information for Chapter 6	121
C.	Supporting information for Chapter 7	125
	Bibliography	145
	List of Publications	169
	Acknowledgements	175

List of Abbreviations

2D	two-dimensional
AFM	atomic force microscopy
CAT	chain transfer agent
CP	cloud point
CP'	clearing point
CST	critical solution temperature
DBC	diblock copolymers
DLS	dynamic light scattering
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
DTGS	deuterated triglycerine sulfate
EG	ethylene glycol
FTIR	Fourier-transform infrared
ILL	Institut Laue-Langevin
LCST	lower critical solution temperature
MD	molecular dynamic
NMR	nuclear magnetic resonance
NR	neutron reflectometry

PAA	poly(acrylic acid)
PDEA	poly(<i>N,N</i> -diethylacrylamide)
PDMAM	poly(<i>N,N</i> -dimethylacrylamide)
PFS	pentafluorostyrene
PNIPAM	poly(<i>N</i> -isopropylacrylamide)
PNIPMAM	poly (<i>N</i> -isopropylmethacrylamide)
PS	poly(styrene)
PSB	poly(sulfbetain)
PSBP	poly(4-(<i>N</i> -(3-methacrylamidopropyl)- <i>N,N</i> -dimethylammonio)- butane-1-sulfonate)
PZ	polyzwitterion
RAFT	reversible addition-fragmentation chain transfer
RDF	radial distribution function
RH	room humidity
RT	room temperature
SANS	small-angle neutron scattering
SIE	specific ion effect
SLD	scattering length density
SR	spectral reflectometry
TEM	transmission electron microscopy
TFE	2,2,2-trifluoroethanol
THF	tetrahydrofuran
ToF	time-of-flight
UCST	upper critical solution temperature
VPT	volume phase transition

VPTT volume phase transition temperature

XRR X-ray reflectometry

Introduction

Numerous responsive polymer hydrogels feature volume phase transitions (VPTs) that result in swelling and contraction in response to even slight changes in the surrounding environment, such as varying temperature, [1]–[7] solvent composition, [8]–[13] salt concentration, [14]–[18] or pH value. [19]–[25] This stimuli-induced phase transition behavior of polymers has been widely studied for their potential applications, *e.g.*, in tissue engineering, [26]–[32] drug delivery, [28], [33]–[38] coatings [39]–[43] and soft robotics. [44]–[49] Among these polymer materials, thermoresponsive polymers are well-known for their pronounced sensitivity to small changes in temperature, which causes significant conformational changes (known as the “coil-to-globule” transition) via the absorption or release of water molecules. This coil-to-globule transition of responsive polymers allows materials to be switched between a well-solvated state and a poorly solvated state inducing, for instance, aggregation in solution, or volume changes of gels.

Poly(*N*-isopropylacrylamide) (PNIPAM), [50]–[53] and poly(*N*-isopropylmethacrylamide) (PNIPMAM) represent the class of non-ionic thermoresponsive polymers, which bears both, hydrophilic (amide) and hydrophobic (isopropyl) groups in its side chain. It shows a lower critical solution temperature (LCST) and becomes insoluble in water above its LCST ($\text{LCST}_{\text{PNIPAM}} \approx 32\text{ }^{\circ}\text{C}$ and $\text{LCST}_{\text{PNIPMAM}} \approx 44\text{ }^{\circ}\text{C}$), and thus, aqueous solutions turn turbid because of the aggregation of insoluble polymers. [50], [54] In contrast, many zwitterionic poly(sulfobetaine)s (PSBs) are thermoresponsive exhibiting an upper critical solution temperature (UCST) in an aqueous solution. [55]–[57] A representative of this polymer class is poly(4-(*N*-(3-methacrylamidopropyl)-*N,N*-dimethylammonio) butane-1-sulfonate) (PSBP) that has the polymethacrylamide backbone in common with PNIPAM and PNIPMAM. In addition to the moderately hydrophilic amide group, it features also the strongly hydrophilic ammonium and sulfonic acid groups, and becomes soluble in water above the clearing point (CP'_{PSBP}), resulting in a transparent aqueous solution. Note that the CP'_{PSBP} depends strongly on the molar mass. [55] While PSBP keeps the

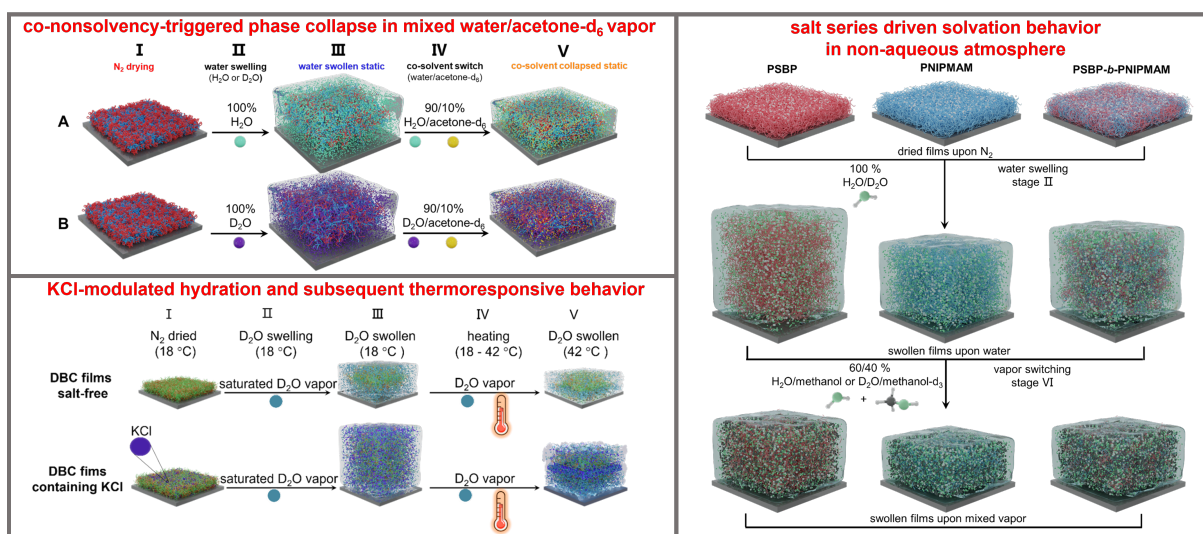
zwitterionic character over a broad pH window (pH 1-14), its solubility in water is highly sensitive to the type and concentration of added low molar mass salts in a nonlinear and complex fashion.[55]

The addition of co-solvents is one of the simplest and cheapest methods to modulate or adjust the phase transition behavior of thermoresponsive polymers. Moreover, it enables inversely to trigger the coil-to-globule transition under isothermal conditions.[8], [12] In a very particular scenario of solvent-induced switching, some water-miscible organic solvents added to aqueous solutions, including methanol,[58] dimethyl sulfoxide (DMSO),[9] dimethylformamide (DMF),[10] and tetrahydrofuran (THF),[59] may induce insolubility, although the polymer is soluble both in pure water and the pure organic solvent at the given temperature. This phenomenon is known as “co-nonsolvency behavior”. Whereas the co-nonsolvency of PNIPAM was the subject of many experimental and theoretical studies, such as homopolymer solutions,[60]–[62] micellar solutions,[63] crosslinked microgels,[64], [65] grafted polymer brushes[66]–[69] and has been recently extended to thin films,[70] investigations and understanding of the co-nonsolvency effect on PNIPAM are rather rare. Its co-nonsolvency behavior in certain water-alcohol mixtures in solution was demonstrated recently[71], [72] and was also confirmed for thin films.[73]–[75] However, co-nonsolvency studies on thermo-responsive polymer thin films using other organic co-solvents, such as acetone, have not been reported.[76] Acetone is a less polar and moreover an aprotic solvent, in contrast to methanol or ethanol. This difference substantially modifies the interaction with the polymer components, in particular with the zwitterionic moiety, which, a priori, prefers highly polar protic solvents.[55], [77], On the other hand, acetone is extensively used in biological and pharmaceutical research, where it acts as an excipient for pharmaceutical drugs.[9], [78] Importantly, for solutions, acetone has been shown to exhibit co-nonsolvency behavior for PNIPAM in mixtures with water.[59], [79], [80] Thus, in Chapter 5 of the present thesis, we broadened the range of co-solvents and explored the co-nonsolvency-triggered phase collapse of thermoresponsive diblock polymer (DBC, PSBP-*b*-PNIPAM) thin films exposed to mixed water/acetone vapors.

As the classical thermoresponsive polymers, the modulation of critical solution temperature (CST) is crucially important for PSBP and PNIPAM. The CP'_{PSBP} in aqueous solution increases initially with sodium salt concentration up to a maximum value, while further addition of salt decreases the CP'_{PSBP} strongly, often below the freezing point of water.[81], [82] Whereas, the salt effects on $LCST_{\text{PNIPAM}}$ of the homopolymer PNIPAM are not clear yet.[83] Still, a few studies on the modulation of the transition temperatures of DBCs containing PNIPAM by added salt were reported, in which a long PSBP block was combined with a short PNIPAM block.[82], [84] It was found, that $LCST_{\text{PNIPAM}}$ decreases slightly with increasing polymer concentration and does not

show significant sensitivity towards the added NaBr. Thereby, three or even four different solubility regimes of the DBC were realized by the addition of electrolytes to tune the CP'_{PSBP} and the cloud point of PNIPMAM (CP_{PNIPMAM}), respectively.[81] Compared to the previously used salt NaBr, K^+ being larger than Na^+ (0.138 nm *vs.* 0.099 nm) and Cl^- being smaller than Br^- (0.181 nm *vs.* 0.196 nm),[85] the difference in the size of the cation and the anion is notably smaller for KCl. Still, solid KCl has the same crystal structure (face-centered cubic) and a similar melting point, while previous studies showed that KCl in the solid state is also partially miscible with PSBs, though to a lesser extent than NaBr.[86] Thus, in Chapter 6 of the present thesis, we investigated KCl-modulated hydration and subsequent thermoresponsive behavior in an inverted block copolymer system, in which a shorter PSBP is combined with a much longer PNIPMAM, and studied the KCl impact of the varied relative block lengths on the swelling characteristics of PSBP-*b*-PNIPMAM thin films.

The presence of salts plays a widespread specific ion effect (SIE) on physicochemical properties.[87]–[89] Generally, the anions exhibit a more pronounced effect than cations, following a well-known trend described as the Hofmeister series.[16], [87], [89]–[94] Over the past decades, many experimental works attempted to decide the SIE via thermoresponsive polymers.[95]–[101] No doubt, PNIPAM is widely studied.[88], [94], [101]–[107] However, to the best of our knowledge, no literature has shown an investigation about the SIE on upper critical solution temperature (UCST-type) thermoresponsive polymers and its DBCs with LCST-type, especially in thin film geometry and in non-aqueous. Thus, in Chapter 7 of the present thesis, we prepared three types of thermoresponsive polymer thin film (UCST-type, LCST-type and UCST-*b*-LCST-type), namely PSBP, PNIPMAM and the PSBP-*b*-PNIPMAM respectively, and examined SIE driven solvation behavior in non-aqueous atmosphere with five potassium anions — CH_3COO^- , Cl^- , Br^- , I^- , NO_3^- . In this work, experimental methods are applied to investigate the film thickness of studied DBC thin films upon saturated pure water vapor or mixed water/acetone (methanol) vapor first by *in situ* spectral reflectometry (SR), to determine the desired sample preparation parameters, the composition of vapor, performed temperature, and the required loaded-salt concentrations. Then, to investigate the cooperated solvent content and the distribution of solvent molecules (or the salts) along the normal direction to the substrate upon the hydration or dehydration processes, the phase conformation conducted from scattering length density (SLD) profiles is determined in dependence on solvent composition and temperature using *in situ* time-of-flight neutron reflectometry (ToF-NR). In a more direct approach, the dynamics of polymer-solvent interactions around the DBC functional groups on a molecular scale are determined using *in situ* Fourier-transform infrared spectroscopy (FTIR). By tracking the emergence and decay of solvent-specific FTIR



This thesis is organized as follows: After a discussion on the physical properties of thermoresponsive polymers in solution, theoretical background information about the phase diagram and solubility of thermoresponsive polymer, as well as the co-nonsolvent effect and SIE, is given. Following this, the theoretical and practical aspects of the used characterization technologies are discussed, including ToF-NR, X-ray reflectometry (XRR), SR, UV-Vis-NIR spectrophotometer, atomic force microscopy (AFM) and FTIR. Besides, two computational methods (2D FTIR and MD correlation analysis) are introduced later. Subsequently, the synthesis of studied polymers and the thin film preparation procedure are given in detail. In the main part, the results from the employed experimental techniques are given and discussed. In Chapter 5, the co-nonsolvency effect on phase collapse of studied DBC thin films in mixed water/acetone-d₆ atmosphere is discussed. In Chapter 6, the specific salt effect of KCl on volume phase transition temperatures of studied DBC thin films in a pure D₂O atmosphere is investigated. Following this, the results on the co-nonsolvency behavior of studied DBC films loaded with specific ions are presented in

Chapter 7, where the co-nonsolvency behavior is triggered by a mixed water/methanol atmosphere. In the last part, the main findings presented in this thesis are summarized.

Theoretical Background

This chapter gives a brief overview of the thermoresponsive polymers, co-nonsolvent effect and specific ion effect (SIE), as well as the phase transition behavior in polymer solutions and the related models of macroscale mechanisms and theories.

2.1. Thermoresponsive polymer

2.1.1. Phase diagram of thermoresponsive polymer in solutions

Thermoresponsiveness refers to the phenomenon where small temperature changes near the phase transition temperature cause significant changes in the chemical, physical, or mechanical properties of polymers.[8], [26], [109], [110] Based on the phase diagram of the polymer-water system, as shown in Figure 2.1a and 2.1b, temperature-sensitive polymers can be classified into two types: those with a lower critical solution temperature (LCST) and those with an upper critical solution temperature (UCST).[84], [111]–[114] For LCST, the coexistence curve of the two phases in the polymer-solvent phase diagram takes the form of a concave parabolic line. The temperature corresponding to the lowest point of the curve is the LCST. Below the parabolic line, the polymer solution is a clear and transparent homogeneous phase, while above the parabolic line, the system separates into two phases, each being homogeneous. UCST is the opposite, exhibiting an upward convex shape in the coexistence curve.

LCST-type polymers

LCST-type polymers commonly exhibit a rapid, drastic, and reversible phase transition in response to temperature variations, due to the changes in solvent entropy of polymer chains in aqueous solutions.[114] The solubility decrease leads to the precipitation of poly-

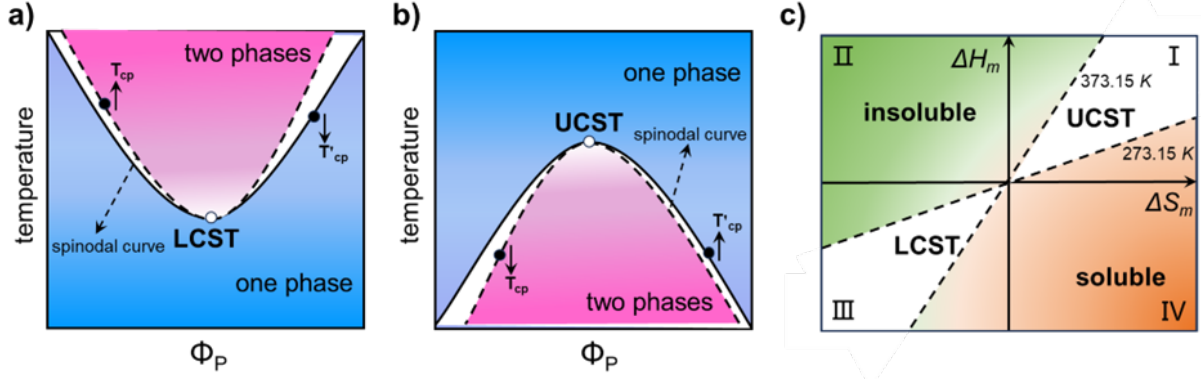


Figure 2.1.: Typical phase diagrams of a polymer solution with (a) LCST and (b) UCST behavior. (c) Thermodynamic map of polymer aqueous solution. Modified from reference [114].

mer chains at temperatures above the LCST and complete dissolution at temperatures below the LCST. One of the most well-known and extensively studied thermoresponsive polymers is poly(*N*-isopropylacrylamide) (PNIPAM) and its derivatives. PNIPAM exhibits different water solubilities during heating and cooling processes, undergoing a reversible phase transition from a hydrophilic coil state to a hydrophobic globule state within the LCST range of 30 - 35 °C.

UCST-type polymers

UCST-type polymers exhibit an opposite behavior to LCST-type, showing a phase separation during cooling. Based on the interactions between polymers, water-soluble UCST-type polymers can be mainly divided into two categories: zwitterionic UCST-type polymers and hydrogen-bonded UCST-type polymers. An example of zwitterionic polymers is the betaine-type polymers.[114] In these polymers, the side chain cation is a quaternary ammonium cation, and the anion group can be designed as sulfonate, carboxylate, phosphate, and other groups. Among the three classes of betaine-type polymers, the betaine-type polymer with strongly acidic sulfonate groups on the side chain carries a negative charge that is unaffected by the solution's pH. Therefore, the poly(sulfobetain)s (PSBs) are more prevalent in zwitterionic UCST-type polymers.

2.1.2. Solubility of thermoresponsive polymers

Basically, the phase separation behavior of thermoresponsive polymers is explained as an entropy-driven process and widely investigated from a thermodynamic perspective.[114] Gibbs free energy of the polymer dissolution process is expressed as:

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (2.1)$$

2.1. Thermoresponsive polymer

$$T_c = \Delta H_m / \Delta S_m \quad (2.2)$$

ΔH_m , ΔS_m , and T represent the mixing enthalpy, mixing entropy, and thermodynamic temperature of the polymer-water dissolution process, respectively. As listed in Table 2.1, based on the relationship between mixing enthalpy and mixing entropy, four types of polymer dissolution behaviors are distinguished. When $\Delta H_m > 0$ and $\Delta S_m < 0$, the polymer is insoluble in water ($\Delta G_m > 0$). When $\Delta H_m < 0$ and $\Delta S_m > 0$, the polymer is water-soluble ($\Delta G_m < 0$). When $\Delta H_m > 0$ and $\Delta S_m > 0$ (or $\Delta H_m < 0$ and $\Delta S_m < 0$), the system has a critical temperature T_c (see Eq. 2.2), corresponding to UCST and LCST dissolution behaviors, respectively.

For UCST-type polymers, when $T > T_c$ ($|T \cdot \Delta S_m| > |\Delta H_m|$ and $\Delta G_m < 0$), the polymer dissolves in water. When $T < T_c$ ($|T \cdot \Delta S_m| < |\Delta H_m|$ and $\Delta G_m > 0$), phase separation occurs in the polymer solution. Conversely, for LCST-type polymers, this pattern is reversed: when $T < T_c$, the polymer dissolves in water. Notably, ΔH_m and ΔS_m are also functions of temperature and one polymer may exhibit both LCST and UCST behaviors simultaneously.

Table 2.1.: Thermodynamic contributions and solubility of the polymer-solvent mixture. Modified from reference [114].

zone	ΔH_m mixing enthalpy	ΔS_m mixing entropy	$\Delta G_m < 0$ Gibbs free energy	polymer type
I	+	+	$T > T_c$	UCST
II	+	-	never	insoluble
III	-	-	$T < T_c$	LCST
IV	-	+	always	soluble

Based on the analysis shown in Table 2.1, Zhu and Zhao, *et al.*, proposed a ΔH_m - ΔS_m plot to map out the solubility of thermoresponsiveness of polymers in aqueous solutions, as shown in Figure 2.1c.[114] In this plot, each polymer can be in a zone according to ΔH_m and ΔS_m values. T_c is the slope of a straight line from the original point to its location. Zone I regroups polymers possessing a UCST. Zone II contains thermodynamically insoluble and thus non-thermoresponsive polymers. Zone III assembles polymers having an LCST. Zone IV contains soluble non-thermoresponsive polymers. It should be noted that Zones I and III are further limited by the liquid state of water between the freezing and boiling points of water under ambient conditions.

2.1.3. Modulation of LCST and UCST

The thermodynamic driving force comes from the breaking of hydrophobic to hydrophilic groups on the main chain or side chains of the polymer, leading to interactions between hydrophobic groups or changes in hydrogen bonding within the system, ultimately resulting in phase separation. Therefore, having a certain proportion of hydrophilic and hydrophobic groups in the structure is a key factor determining thermoresponsiveness. Thus, the critical solution temperatures (UCSTs or LCSTs) can be modulated by adjusting the balance between the hydrophilicity and hydrophobicity of the polymer.

Monomer substituents

For LCST, like PNIPAM, the LCST is around 32 °C. Various acrylamide-type polymers with different amide substituents have demonstrated that the LCST of PNIPAM can be adjusted by changing substituents on the nitrogen atom, as listed in Table 2.2a.[115] The monomers encompass cases with single and double nitrogen atom substitutions. Poly(*N,N*-dimethylacrylamide) (PDMAM) completely dissolves in water without an LCST. However, with an increase in the hydrophobicity of the alkyl substituents, the LCST decreases.

For UCST, Viet Hildebrand synthesized a series of new PSBs by systematically varying the substituents of the zwitterionic group and these PSBs show distinct UCST-type behavior in an aqueous solution.[116] As illustrated in Table 2.2b, the results show that increasing the spacer length separating the ammonium and the sulfonate groups of the zwitterion moiety from three to four carbons increased the T_{cp} markedly, whereas increasing the length of the spacer separating the ammonium group and the carboxylate ester group on the backbone from two to three carbons provoked the opposite effect. Moreover, the T_{cp} of the analogous polyzwitterions decreased in the order dimethylammonio > morpholinio > piperidinio alkanesulfonates.

Copolymerization

This method is to modulate the ratio of hydrophilic and hydrophobic groups within the polymer chain, and therefore the diblock copolymers (DBC) are composed of nonionic and zwitterionic blocks featuring LCSTs and UCSTs are widely studied. A study reports a series of DBCs by further copolymerizing NIPMAM monomers to the PSBP chains, and the critical solution transition temperatures (CSTs) measured upon heating are listed in Table 2.2c.[55], [117] By copolymerizing the LCST-block with the UCST-block, not only the UCSTs of PSBPs are changed, but the synthesized DBCs are bestowed two CSTs.

2.1. Thermoresponsive polymer

Table 2.2.: (a) Chemical structures and LCST-type T_{cp} of selected *N*-alkyl substituted polyacrylamides. Modified from reference [115]. (b) Chemical structures of the zwitterionic sulfobetaine methacrylate monomers and UCST-type T_{cp} of PSBs. Modified from reference [116]. (c) CSTs of UCST-type homopolymers PSBs and DBCs (PSBP-*b*-PNIPMAM) in H₂O solutions and D₂O solutions (n.d. = CST > CP_{LCST}). Modified from reference [117]

a)

	R	R'	abbreviation	LCST (°C)		R	R'	abbreviation	LCST (°C)
Poly (<i>N,N</i> -dimethylacrylamide)	Me	Me	PDMAM	soluble	Poly (<i>N</i> -isopropylacrylamide)	H	iPr	PNIPAM	32
Poly (<i>N</i> -ethylacrylamide)	H	Et	PEA	82	Poly (<i>N</i> - <i>n</i> -propylacrylamide)	H	nPr	PNNPAM	24
Poly (<i>N,N</i> -diethylacrylamide)	Et	Et	PDEA	32	Poly (<i>N</i> - <i>n</i> -butylacrylamide)	H	tBu	PTBA	insoluble

b)

sulfobetaine methacrylates

sample	cloud point (°C)		sample	cloud point (°C)		sample	cloud point (°C)		sample	cloud point (°C)	
	H ₂ O	D ₂ O		H ₂ O	D ₂ O		H ₂ O	D ₂ O		H ₂ O	D ₂ O
P-1 ₈₅	41	50	P-2 ₉₅	< 0	< 0	P-3 ₈₅	< 0	17	P-4 ₇₅	< 0	7
P-1 ₂₇₀	55	68	P-2 ₂₅₀	< 0	< 0	P-3 ₉₅	24	34	P-4 ₂₉₅	5	14
P-1 ₅₇₅	67	80	P-2 ₃₃₀	< 0	< 0	P-3 ₂₃₀	38	48	P-4 ₄₈₀	8	18
P-1 ₅₈₅	71	86	P-2 ₄₈₅	< 0	< 0	P-3 ₅₈₅	47	56	P-4 ₅₈₅	10	20

c)

sample	UCST transition (°C)		LCST transition (°C)		sample	UCST transition (°C)		LCST transition (°C)	
	H ₂ O	D ₂ O	H ₂ O	D ₂ O		H ₂ O	D ₂ O	H ₂ O	D ₂ O
PSBP ₄₀	60	66	—	—	PSBP ₄₀ - <i>b</i> -PNIPMAM ₁₉₀	35	38	43	43
PSBP ₅₀	67	76	—	—	PSBP ₅₀ - <i>b</i> -PNIPMAM ₁₅₅	40	n.d.	44	44
PSBP ₈₀	74	78	—	—	PSBP ₈₀ - <i>b</i> -PNIPMAM ₁₁₅	n.d.	n.d.	45	45
PSBP ₂₄₅	> 100	> 100	—	—	PSBP ₂₄₅ - <i>b</i> -PNIPMAM ₁₀₅	n.d.	n.d.	47	47
PSBP ₄₂₅	> 100	> 100	—	—	PSBP ₄₂₅ - <i>b</i> -PNIPMAM ₁₁₀	n.d.	n.d.	49	49

Solvent composition

The change in solvent composition alters the CST of the thermoresponsive polymers. For instance, Hia-Hsin Ko, *et al.*, studied the self-assembly of the thermoresponsive amphiphilic DBC (PMMA₂₁-*b*-PNIPAM₂₈₃) in different water/methanol mixtures, as shown in Figure 2.2a-c.[63] From turbidimetry measurements in Figure 2.2b and the T_{cp} in Figure 2.2c, T_{cp} decreases from 31.2 ± 0.2 °C in pure D₂O to 13.6 ± 0.2 °C in D₂O/CD₃OD (v/v = 70:30). Besides, the decrease in the light transmission becomes slightly broader with increasing CD₃OD volume fraction, and finite values are reached above T_{cp} . In methanol-rich solvent mixtures, the polymer solutions are clear and transparent in the temperature range from 15 to 55 °C. The samples with volume fractions of CD₃OD above 70 % do not exhibit T_{cp} within the temperature range accessible.

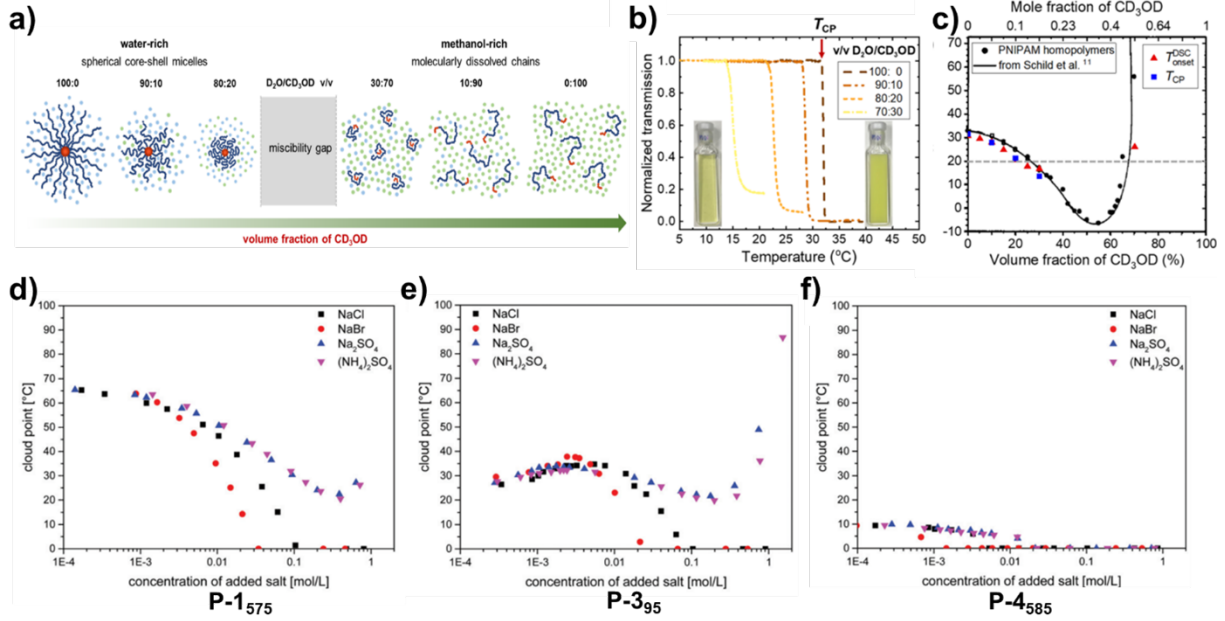


Figure 2.2.: (a) Schematic representation of the structures, (b) temperature-dependent light transmission and (c) identified cloud points of PMMA₂₁-*b*-PNIPAM₂₈₃ in D₂O/CD₃OD mixtures at 20 °C in dependence on the CD₃OD volume fraction. Adapted from reference [63]. Evolution of UCST-type T_{cp} of the PSBs in H₂O containing inorganic salts for (d) P-1₅₇₅, (e) P-3₉₅, (f) P-4₅₈₅ in Table 2.3. Adapted from reference [116].

Ion strength

Ion strength also plays a role in regulating the CSTs. For example, Viet Hildebrand, *et al.*, also investigated the effect of the added low molar mass electrolytes on the water-solubility of PSBs (P-1₅₇₅, P-3₉₅ and P-4₅₈₅ in Table 2.2).[116] The evolutions of T_{cp} in H₂O containing NaCl, NaBr, Na₂SO₄ and (NH₄)₂SO₄ are shown in Figure 2.2d - f. As a common feature, small amounts of added salt make a notable impact. The effect depends notably on the nature of the anion in the order $SO_4^{2-} < Cl^- < Br^-$, in agreement with the empirical Hofmeister series.[90], [118] PSBs of P-1 and P-4 are subject to a straightforward salting-in behavior. Their CSTs decreased continuously with increasing the amount of added salt following the same pattern, whereby salting-in effectivity increases in the order $(NH_4)_2SO_4 \approx Na_2SO_4 < NaCl < NaBr$. In the case of the latter two salts, the T_{cp} fell eventually below the freezing point, reaching this point for salt concentrations always lower than 0.1 M. In contrast, high concentrations (> 0.3 M) of sulfates induced a small increase in the T_{cp} .

2.2. Co-nonsolvency effect

2.2.1. Polymer solution theory

Polymer solution is a homogeneous and thermo-dynamically stable mixture formed by polymers dispersed in a solvent in a molecular state. The following introduces several important physical concepts about polymer solution systems.

Good, θ and poor solvent

Based on the types of interactions between polymer chains and solvent molecules, solvents can be classified as good, θ , and poor solvents.[119] In a good solvent, solvent molecules tend to surround the polymer chain, causing the polymer to adopt a swollen coil conformation. In the case, the interactions between polymer chains and solvent molecules dominate. For sufficiently large polymer chains, the mean square gyration radius of gyration (R_g), representing the spatial size, follows a scaling law:

$$R_g \sim N^{\frac{3}{5}} \quad (2.3)$$

where N is the polymerization degree of polymer chains. In a poor solvent, polymer chains aggregate under the attractive force, leading to a collapsed globule conformation. In the case, the effective attractive interactions between polymer chains prevail, and the scaling law for R_g follows:

$$R_g \sim N^{\frac{1}{3}} \quad (2.4)$$

θ solvent represents a special state between a good solvent and a poor solvent. In this state, various interactions are in balance without effective excluded volume interactions. The polymer chain adopts an ideal unperturbed coil state, and the scaling law for R_g follows:

$$R_g \sim N^{\frac{1}{2}} \quad (2.5)$$

The descriptions above only focus on the relationship between polymer chains and individual solvents. When polymer chains are in a binary solvent mixture, their structural properties exhibit a more diverse range of changes.

Cosolvent and co-nonsolvent

The variations in solvent composition of a binary mixture influence the conformation of dissolved polymer chains, as well as the phase transition diagram of polymer solutions. Two conformational transition behaviors have attracted widespread attention. The first phenomenon is known as the co-nonsolvent effect.[62], [120] It describes a situation where polymer chains are highly soluble and exhibit a swollen coil conformation in two individual good solvents, while undergo a transition from a swollen coil conformation to a collapsed globule conformation as mixing the two solvents in a certain proportion. As shown in Figure 2.3a, the PNIPAM-like polymer in mixed water/ethanol solutions is a typical experimental model exhibiting the co-nonsolvency effect.[62], [121]

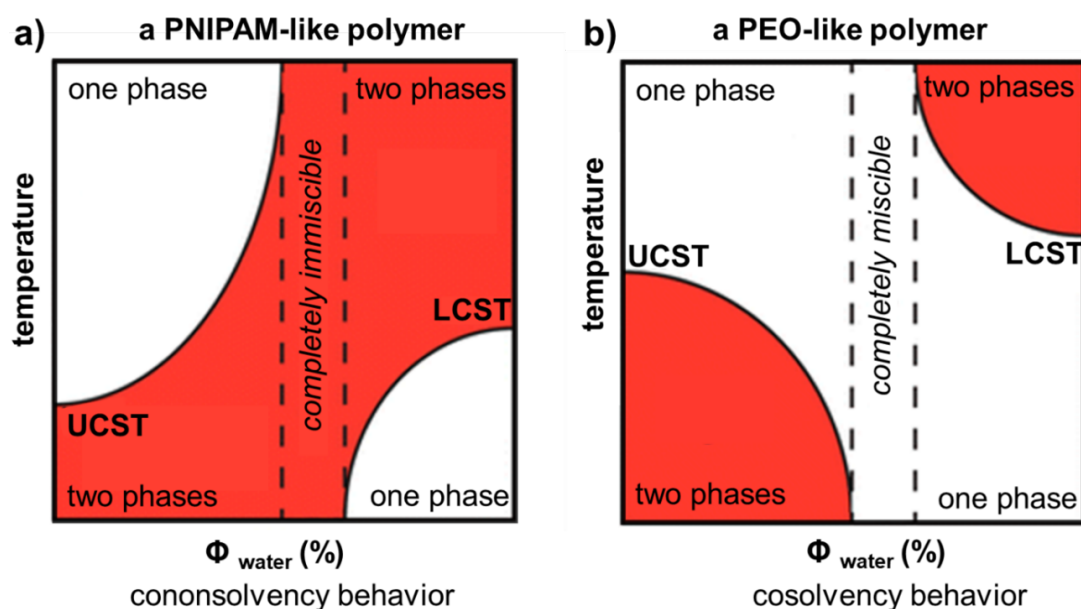


Figure 2.3.: Schematic representation of (a) co-nonsolvency and (b) cosolvency behaviors of polymers in mixed water/ethanol mixtures, showing variation of the phase transition line (UCST or LCST) between the mixed (one phase) and demixed (two phase) regions with increasing water fraction in water/ethanol mixtures. Modified from reference [62].

The second phenomenon is the cosolvent effect. It describes a situation where polymer chains might be poor soluble and exhibit a collapsed conformation in two individual poor solvents, while undergo a transition from a collapsed conformation to a swollen coil conformation in a mixed solvent composed of these two poor solvents.[62] A typical experimental model exhibiting the cosolvent effect is illustrated in Figure 2.3b by a PEO-like polymer mixed water/ethanol solutions.[62]

2.2.2. Microscale mechanisms on co-nonsolvent effect

Since Winnik and colleagues firstly observed that PNIPAM polymer chains exhibited flexible coil structures in two good solvents, water, and methanol in the 1990,[122] this phenomenon was termed the co-nonsolvency behavior.[123]–[127] Theoretical and simulation studies on co-nonsolvency behavior have predominantly focused on the coil-to-globule transitions of short single polymer chains in water/alcohol mixtures, but a consensus on the driving mechanisms and molecular interactions has not been reached. Currently, the literatures provide five main interpretations for the microscale mechanisms.

Preferential adsorption for cosolvents

Mukherji and colleagues investigated the conformational transition of a single PNIPAM chain in water/methanol mixture by molecular dynamics (MD) simulations, and found a widespread co-nonsolvent effect caused by the preferential adsorption of the methanol molecules onto the polymer chain, as shown in Figure 2.4a.[128] Subsequently, based on these simulation results, Sommer proposed the adsorption-attraction model, as depicted in Figure 2.4b.[68] By integrating the Alexander-de Gennes theory[129] and polymer-cosolvent bridging interactions, this model assume that a cosolvent molecule can be shared by two or more monomers, forming bridging cosolvent molecules. The formation of these bridging molecules enhances the interaction between polymer monomers and cosolvent, reduces the overall free energy, and triggers the collapse of the polymer chains at low cosolvent concentration. Bharadwaj and colleagues found that amphiphilic cosolvents, such as alcohols, preferentially adsorb onto polymers through a surfactant-like mechanism, thereby reducing the free energy of the polymer-solvent interface.[130] Additionally, the strong surfactant-like behavior of cosolvents enhances the co-nonsolvent effect and increases the preferential adsorption of cosolvents. To simplify calculations, attractive interactions between particles are neglected in the adsorption-attraction model. Therefore, further refinement of this model is still needed.

Cosolvent–solvent attractive interaction

Kawaguchi proposed that the interaction between two solvents lead to the coil-globule-coil transition of polymer chains.[11], [124], [132], [133] At low cosolvent concentrations, Zuo and colleagues demonstrated that the co-nonsolvent effect is generated by the strong water-cosolvent attraction, as illustrated in Figure 2.4c.[11], [134] At low cosolvent concentration, the solvent-cosolvent interactions reduce the amount of solvent available for dissolving the polymer chains, resulting in the collapse of polymer chains. Conversely, at

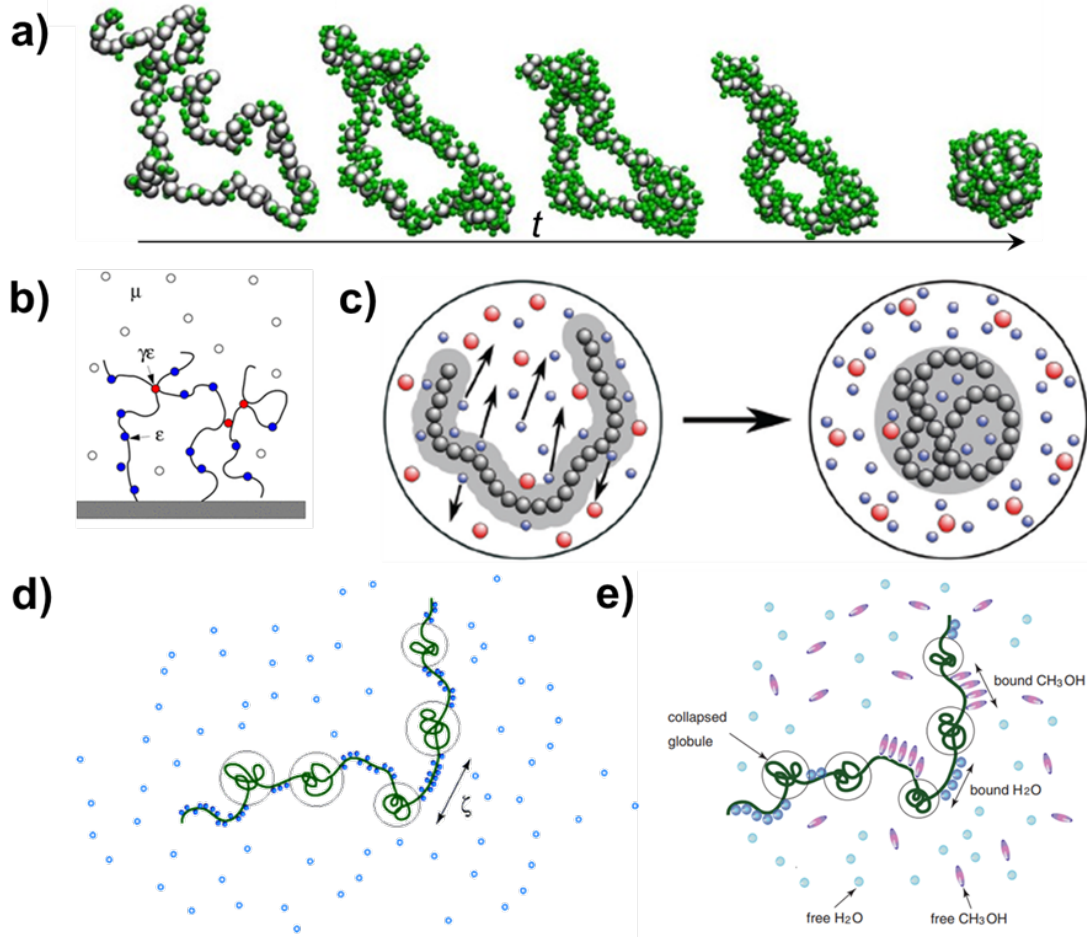


Figure 2.4.: (a) Preferential adsorption model: dynamics of polymer collapse for chain length $N_1 = 100$ at a cosolvent mole fraction $\chi_c = 0.1$. Modified from reference [128]. (b) Adsorption-attraction model: the preferential adsorption and bridging aspects. Modified from reference [68]. (c) Cosolvent-solvent attraction model: strong attractive solvent-cosolvent interactions lead to a decrease in overall solvation causing polymer collapse. Modified from reference [11]. (d) co-hydrogen bonding model: synergistic hydration. Modified from reference [131]. (e) Hydrogen bonding competition model: a pearl-necklace conformation generated from competition between PNIPAM-water and PNIPAM-methanol hydrogen bonding. Modified from reference [127].

high cosolvent concentrations, the excess cosolvent dissolves the polymer chains, causing the re-expand of polymer chains.

Co-hydrogen bonding competition

Tanaka introduced the concept of cooperative hydration based on the formation sequence of hydrogen bond between PNIPAM chains and water molecules in a binary system, and subsequently extended this concept to a ternary system involving PNIPAM chains and

a mixed water-methanol solvent.[127], [131] This model suggested that the competition of hydrogen bonds between polymer-water and polymer-methanol triggers the conformational transition of PNIPAM chains.

By introducing the positive correlation of neighboring hydrogen bonds along the PNIPAM chain in water, Tanaka attributed this positive correlation to the steric hindrance effect of the hydrophobic isopropyl groups. As depicted in Figure 2.4d, when water molecules overcome the steric hindrance and form hydrogen bonds with the amide groups, the adjacent water molecules are more likely to form hydrogen bonds with the amide group, resulting in a water sequence along the PNIPAM chain. In a mixed water/methanol solution, the functional groups on the PNIPAM chain not only form hydrogen bonds with water molecules but also with methanol molecules, leading to cooperative hydration between water hydrogen bonds and alcohol hydrogen bonds, as illustrated in Figure 2.4e. The stronger the cooperative hydration, the more intense the competition becomes. When the competition is fierce, both water and methanol molecules are unable to adequately interact with the PNIPAM chain to form hydrogen bonds, resulting in the collapse of the PNIPAM chain under hydrophobic interactions.

Formation of stoichiometric complexes

Han, Hammouda, *et al.*, integrated the re-entrance of poly(*N,N*-diethylacrylamide) (PDEA) in D₂O/*d*-ethanol mixtures (*i.e.*, the coil-to-spherical aggregates-to-coil transition) at 27 °C by small-angle neutron scattering (SANS).[135] By analyzing the SANS profiles, three Flory–Huggins interaction parameters ($\chi_{\text{PDEA } d\text{-ethanol}}$, $\chi_{\text{PDEA D}_2\text{O}}$, and $\chi_{d\text{-ethanol-D}_2\text{O}}$) are obtained. They found that, *d*-ethanol molecules have a strong interaction with D₂O as a small amount of *d*-ethanol is added to the system, and therefore *d*-ethanol molecules directly distribute into the water structure and makes a negative contribution to the dissolution of PDEA ($\chi_{d\text{-ethanol-D}_2\text{O}} \gg \chi_{\text{PDEA } d\text{-ethanol}}$ and $\chi_{\text{PDEA D}_2\text{O}}$). While the interactions between *d*-ethanol with water molecules become weaker as the addition of more *d*-ethanol, but still stronger than those between PDEA–D₂O and PDEA–*d*-ethanol, as illustrated in Figure 2.5a. Neither *d*-ethanol nor D₂O wants to help the dissolution of PDEA in the first place, until the structure of mixed solvents tends to be pure *d*-ethanol in the D₂O-poor region.

Zhang and Wu investigated the conformational changes of individual PNIPAM chains in various methanol/water mixtures by dynamic light scattering (DLS).[136] They observed that the (H₂O)_{5m}(CH₃OH)_n complexes formed between water and methanol molecules at low methanol molar concentration (χ_{methanol}), as illustrated in Figure 2.5b. However, the number of methanol molecules are not sufficient to interact with all water molecules, and free water molecules allow to dissolve PNIPAM chains. As $\chi_{\text{methanol}} = 17\%$, the

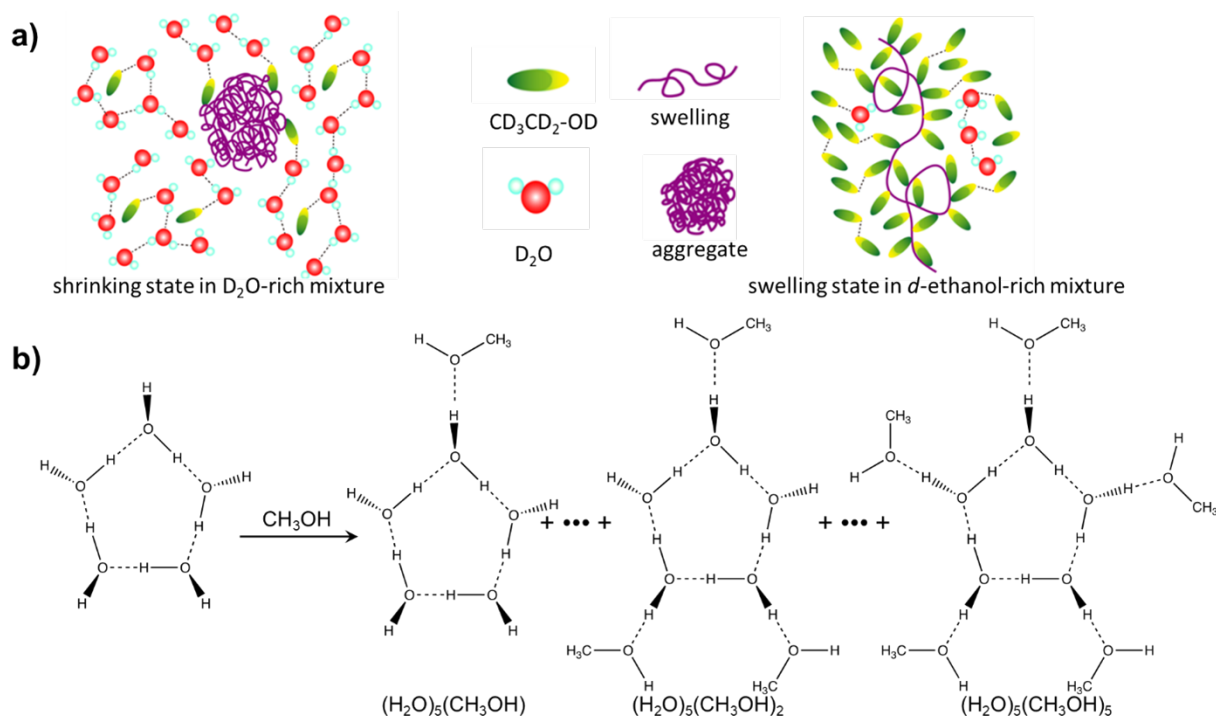


Figure 2.5.: (a) Schematic illustration of shrinking and swelling state in D_2O / d -ethanol mixture. Modified from reference [135]. (b) Schematic of the pentagon structure of pure water and its possible complexation with different numbers of methanol molecules. Modified from reference [136].

PNIPAM polymer chains dehydrated significantly due to the substantial formation of $(H_2O)_{5m}(CH_3OH)_n$ complexes, resulting in collapse. As $\chi_{\text{methanol}} > 50\%$, although the substantial $(H_2O)_{5m}(CH_3OH)_n$ complexes formed, a significant number of free methanol molecules in the solution dissolve the PNIPAM chains, leading to a re-expansion. Thus, corresponding to the good-poor-good solvent, the formed $(H_2O)_{5m}(CH_3OH)_n$ complexes realize a coil-globule-coil transition for the PNIPAM chains in the solution. Zhang and Wu proposed that the slight change in conformation of PNIPAM chains at $\chi_{\text{methanol}} = 17 - 50\%$ was attributed to the formation of $(H_2O)_{5m}(CH_3OH)_n$ complexes with specific stoichiometries ($m/n = 5/2, 5/3, 5/4$).

Hydrophobic effect

Nayar and colleagues analyzed the impact of cosolvents on the water solubility and hydrophobic interactions of non-polar solutes.[137] Besides, they studied the self-assembly or collapse behavior of water-soluble polymers upon hydrophobic effect through MD simulations. The results indicated that the direct interaction between cosolvents and non-polar solutes or water-soluble polymers strengthen hydrophobic interactions and contribute to

stabilizing collapsed globular structures.

Walter et al. analyzed the solvent structure around the main chain of PNIPAM hydrogels using hydrogen bond statistics and visualization techniques.[124] They found that methanol molecules strongly adhere to the main chain of PNIPAM due to the hydroxyl groups. As a result, the hydrophobic methyl groups of methanol face towards the bulk water. Therefore, the solvation shell exhibits hydrophobicity and collapses in a water-rich phase. With an increase in the methanol concentration, the hydrophobic effect disappears, and the PNIPAM hydrogel re-expand.

2.2.3. Conformation of thermoresponsive polymer in solution

Coil-globule transition of single polymer chain

Stockmayer, *et al.*, first predicted the conformational transition of polymer single chains based on the mean-field theory, and proposed that the attractive force between segments of a flexible polymer chain increases in the dissolved state, as the solvent quality deteriorates.[138] As a result, the segments come closer together, and the conformation of the polymer chain collapses from an extended random coil into a uniform, tightly packed globule. This phenomenon is referred to as the coil-globule transition.[141] However, due to the low solubility of the compact globule, it was challenging to observe stable single-chain globules experimentally.[139]–[141]

Until after 1995, Wu and others experimentally demonstrated the coil-globule transition predicted by Stockmayer’s early theory, by investigating the conformational changes of single PNIPAM chain in aqueous solution via DLS.[142], [143] In the study, the conformation of the single PNIPAM chain undergoes a transition as the temperature increases. As shown in Figure 2.6a, initially, the PNIPAM chain transforms from an extended random coil to a crumpled coil, then presents as a molten globule conformation, and finally transform into a fully collapsed globule conformation with further temperature increases.

Focusing on the dynamic process of the coil-globule transition, several different models were proposed. De Gennes first introduced the “expanding sausage model”, as shown in Figure 2.6b.[139] In “expanding sausage model”, the coil-globule transition process is described as: the polymer chain initially forms small chain segments or “blobs”, and then upon attraction force these gradually aggregated blobs force make the polymer chain shorter and thicker, resembling a “sausage-like” conformation, and eventually these blobs form a spherical structure if further aggregation. Halperin and Goldbart, proposed the “pearl-necklace model” for the coil-globule transition.[144] In “pearl-necklace model”, initially, the polymer chains locally aggregate forming small droplets referred to as “pearls”.

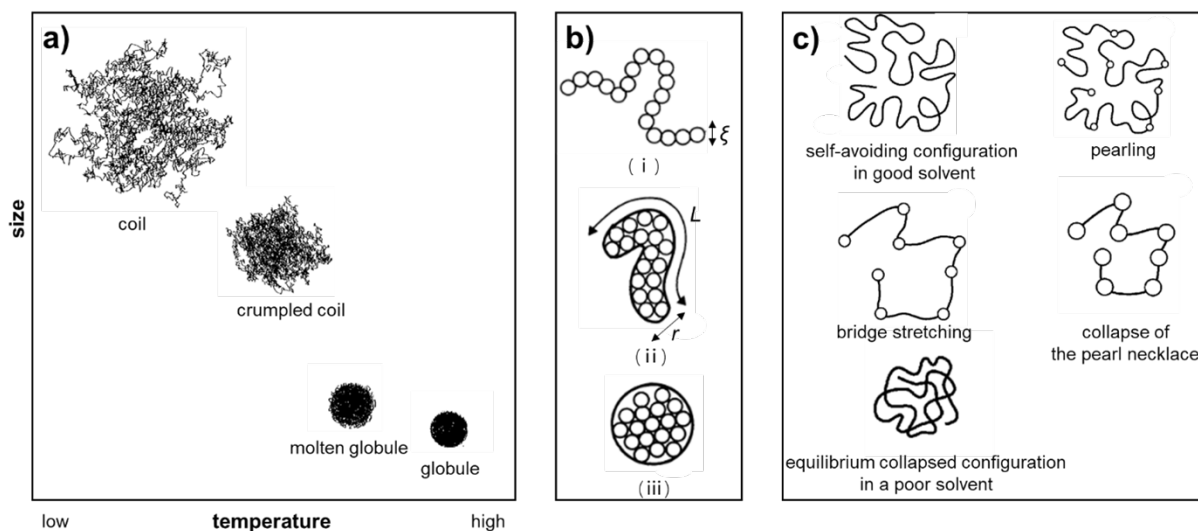


Figure 2.6.: (a) Schematic of four thermodynamically stable states of a homopolymer chain in the coil-to-globule and the globule-to-coil transitions. Modified from reference [142]. (b) Sausage model for successive folding stages during coil-to-globule transformation process: (i) the original coil (blobs with the size ξ), (ii) “sausage-like” conformation (length L and radius r) due to the blobs tend to stick to each other and (iii) a compact sphere (radius R_f). Modified from reference [139]. (c) Proposed sequence of states during the collapse of a flexible homopolymer: self-avoiding configuration in good solvent, pearling, bridge stretching, collapse of the pearl necklace and equilibrium collapsed configuration in a poor solvent. Modified from reference [144].

These pearls are connected by the remaining monomers that act as bridges, resembling a pearl necklace. Then, these small droplets grow by attracting the connecting monomers, leading to an increase in the size of the “pearls”. This growth is accompanied by the shortening of bridges and contraction of polymer chain. Eventually, the pearl necklace collapses, forming a spherical structure, as illustrated in Figure 2.6c. Subsequently, the coil-globule transition process aligns with the pearl-necklace model was supported by extensive studies.

Self-assembly of amphiphilic DBCs

According to the solubilities in water, DBCs can be classified into amphiphilic, amphiphilic-hydrophilic and amphiphilic-hydrophobic systems. Amphiphilic DBCs have hydrophilic and hydrophobic segments in their structure, which are connected by covalent bonds and allows to undergo self-assembly in specific solution. The morphologies of self-assembled

2.2. Co-nonsolvency effect

DBC's can also be explained using the theory of packing parameters (P), which commonly employed to illustrate the small molecules of surfactant. P is expressed as:[145]

$$P = \frac{v}{a_0 l_c} \quad (2.6)$$

Where, v , a_0 and l_c represent the volume of the hydrophobic tail, the contact area between the hydrophilic and hydrophobic parts, and the length of the hydrophobic tail, respectively. When $P < 1/3$, DBCs exhibit a spherical morphology. When $1/3 < P < 1/2$, DBCs typically show a worm-like morphology. When $1/2 < P < 1$, DBCs form vesicles. When $P > 1$, an inverted structure can be observed.

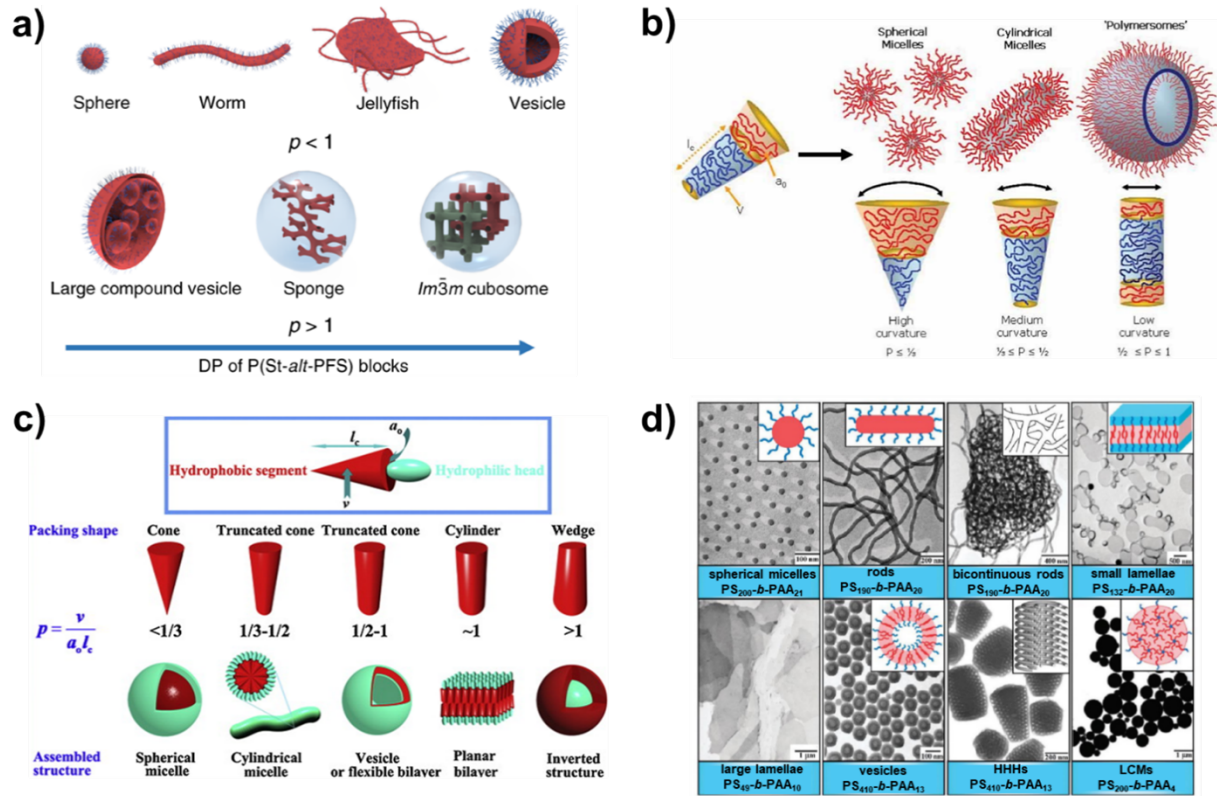


Figure 2.7.: (a) Schematic diagram of the relationship between the packing parameter P and the morphology of PDMA-*b*-P(St-*alt*-PFS) block copolymer. Adapted from reference [146]. (b) Various self-assembled structures, estimated through P , formed by amphiphilic block copolymers in a block-selective solvent. Adapted from reference [147]. (c) Superstructures assemblies varying from spherical micelle, through cylindrical micelle, and vesicle, to inverted structure when P changes from $< 1/3$, $1/3 - 1/2$, $1/2 - 1$, to > 1 . Adapted from reference [148]. (d) Transmission electron microscopy (TEM) micrographs and corresponding schematic diagrams of various morphologies formed amphiphilic PS-*b*-PAA copolymers. Modified from reference [149].

The variation of morphologies with the arrangement parameter P is illustrated in Figure

2.7. Wu, *et al.*, reported scalable preparation of amphiphilic alternating block copolymer particles with inverse bicontinuous mesophases via polymerization induced selfassembly.[146] As illustrated in Figure 2.7a, concentrated dispersion copolymerization of styrene (SS) and pentafluorostyrene (PFS) using a short poly(*N,N*-dimethylacrylamide) (PDMA₂₉) stabilizer block lead to the formation of well-defined, highly asymmetric PDMA₂₉-*b*-P(SS-*alt*-PFS)_x block copolymers with precise compositions and various morphologies, from simple spheres to ordered inverse cubosome mesophases. Ryan and Armes, *et al.*, explained the self-assembly of block copolymer solutions theoretically.[147] As shown in Figure 2.7b, when P is equal to $1/3$, spherical assemblies with larger curvature are mainly formed; when P is greater than or equal to $1/3$ and less than or equal to $1/2$, rod-shaped micelles can be obtained; when P is greater than or equal to $1/2$ and less than or equal to 1 , Mainly forms vesicles. In 2012, Li, *et al.*, used the small molecule surfactant as a model to study the P in self-assembly theory (see Figure 2.7c).[148] In 1999, Eisenberg and colleagues synthesized a series of poly(styrene)-*b*-poly(acrylic acid) (PSS-*b*-PAA) with varying lengths of hydrophobic and hydrophilic chains.[149] By altering the lengths of the hydrophobic and hydrophilic segments, a variety of polymer nano assemblies in solution are obtained, as shown in Figure 2.7d.

2.3. Specific ion effect (SIE)

2.3.1. Hofmeister series

The Hofmeister series is derived from Hofmeister's study, that intestates the evolutionary impact of different salts on the precipitation of proteins and other colloids.[92] The classical sequence is shown in Figure 2.8.[88], [90], [91], [107], [150]–[154] In fact, the Hofmeister series is not fixed. Depending on specific circumstances, not only changes occur in the order of certain ions, a reversal series or a curvature series also happen in studies. Besides, some ions are difficult to integrate into this series, such as guanidinium ions.

When the interaction between ions and water is predominant, anion specific effect is more pronounced than cation, due to a strong interaction between anions and water if the ion size and charge density are the same. However, when the interaction between ions or between ions and charged groups is predominant, the specific effect of cations and anions become similar. These descriptions are based on inorganic salt ions. For long-chain quaternary ammonium salts, the longer the alkyl chain of organic cations, the stronger ability to denature proteins. Besides, However, the geometric configuration of ions and the nature of the charged end groups of large molecules alter the position of ions in the series.

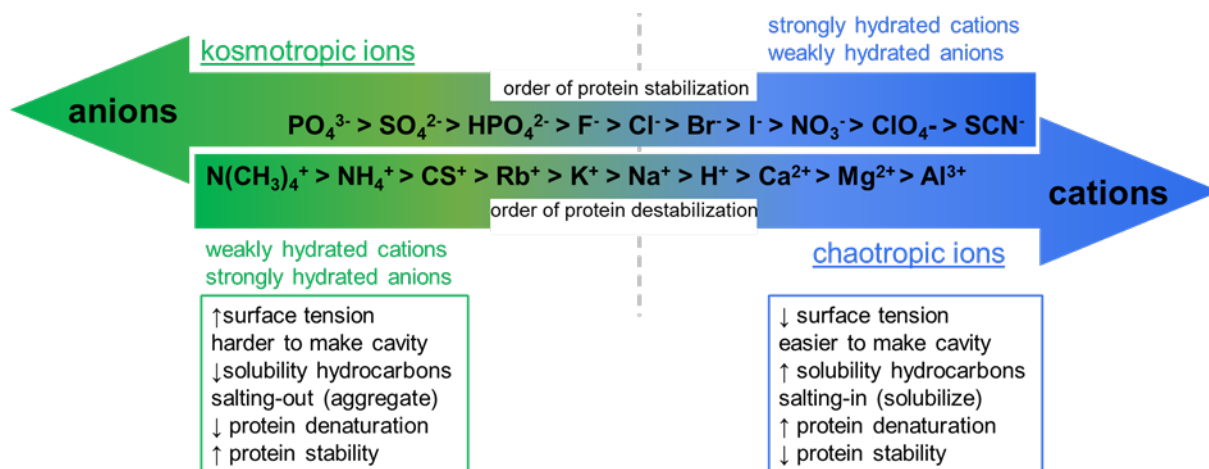


Figure 2.8.: Modern version of the cationic and anionic Hofmeister series and the accompanying physical properties including the salting-out and salting-in abilities. Modified from reference [154].

2.3.2. Classical theoretical ideas for SIE

Hydration theory

Hydration theory posits that ions attract surrounding solvent molecules to form a hydration layer.[155]–[158] In this process, the dissolved non-electrolyte polymer chains compete with ions to attract solvent molecules. If the hydration and solubility of non-electrolyte polymer chains, the precipitation of polymers from the solution occurs. Generally, the hydration of cations is stronger than that of anions, so cations dominate salting-in effect, while anions dominate salt-outting effect.[155] The solubility of polymers is a balance between two opposing hydration forces. The hydration number (the number of water molecules fixed by solvation for each ion) depends mainly on the type of hydration, including hydrophobic hydration, hydrophilic hydration, structure-disruptive hydration, and polarizing hydration. Since the hydration theory was proposed based on the assumption that, each ion interacts with limited water molecules and the dissolved salts do not affect the solvent properties, this theory cannot explain the salting-out effect.

Van der Waals force theory

The van der Waals force theory focus on short-range interactions, primarily involving interactions among ions, neutral molecules, and solvent molecules.[159]–[162] Except for the orientation forces (Keesom interactions) and induction forces (Debye interactions) that arise between permanent dipoles, ions, and induced dipoles, van der Waals forces also include dispersion forces generated by instantaneous dipoles. This dispersion forces rely

on the polarizability and ionization potential of ions, reflecting ion specificity. However, the van der Waals force theory is based on two-body perturbation theory, making them inapplicable in concentrated solutions.

Water dipole theory

The polarization theory posits that in the hydration layer of ions, the polarized water molecules arrange directionally: cations attract oxygen atoms with partial negative charges, and anions attract hydrogen atoms with partial positive charges.[163] Therefore, for both salting-in and salting-out effects on non-electrolyte solute, ions play a crucial role in enhancing or weakening the alignment of water molecules towards their direction. However, there is a challenge in the polarization theory: the individual water molecules having independent dipoles is not acknowledged if there are multiple interactions in the system. In fact, the hydration effect and dipole interactions coexist.

Electrostatic theory

The electrostatic theory posits that the ions dissolved in pure solvent or dissolved in a non-electrolyte's solution should be distinguished, as the polarity of the solute alters the dielectric constant of the solvent.[164], [165] The decrease in dielectric constant caused by the solute can lead to the occurrence of salting-out behavior, and vice versa. However, the static electricity theory cannot explain why ions with the same charge in different electrolytes produce different effects, nor why the system presents a transition behavior from salting-in to salting-out when the non-electrolyte is altered.

2.3.3. SIE in polymer solutions

SIE on PNIPAM in aqueous

SIE on the LCST of PNIPAM have been reported and related to the Hofmeister series.[94], [104], [107], [166], [167] In 2005, Cremer conducted a detailed study on the interaction between anions and PNIPAM.[94] Several typical interactions between anions and PNIPAM in aqueous solutions were proposed, including: (1) Hydrogen bonding between anions, polarized polymer, and water molecules; (2) Anions altering the surface tension between the hydrophobic part of the polymer and the aqueous solution; (3) Some anions directly adsorbing onto the amide bonds of the polymer. Simultaneously, Cremer and collaborators developed a corresponding model to fit the LCST data.[94] The specific formula is as follows:

$$T = T_0 + c[M] + \frac{B_{max}K_a[M]}{1 + K_a[M]} \quad (2.7)$$

2.3. Specific ion effect (SIE)

Where, T_0 represents the LCST without salt-adding. c ($^{\circ}\text{C}/\text{M}$) is a constant. $B_{\max}$ represents the maximum change in LCST caused by the adsorption of anions on the polymer chain, and the binding constant between anions and the polymer is denoted by K_a . The fit parameters for different anions are shown in Table 2.3.

Table 2.3.: Fitted values for K_a , $B_{\max}$, and c from LCST measurements of surface tension increments (σ) and entropy of hydrations (ΔS_{hydr}) for the anion. Modified from reference [94].

anion	σ (mN L/m mol)	ΔS_{hydr} (J/K mol)	$B_{\max}$ ($^{\circ}\text{C}$)	K_a (M^{-1})	C ($^{\circ}\text{C}/\text{mol}$)		
					initial	first step	second step
CO_3^{2-}	2.6	-245	—	—	-25.1	-29.0	-9.7
SO_4^{2-}	2.7	-200	—	—	-18.3	-23.1	-10.0
$\text{S}_2\text{O}_3^{2-}$	2.9	-180	—	—	-16.3	-20.3	-10.9
H_2PO_4^-	2.3	-166	—	—	-11.5	-14.7	-8.3
F^-	2.0	-137	—	—	-9.0		
Cl^-	1.6	-75	—	—	-5.3		
Br^-	1.3	-59	0.7	2.7	-3.7		
NO_3^-	1.1	-76	0.6	2.9	-3.5		
I^-	1.0	-36	1.1	4.3	-1.5		
ClO_4^-	1.4	-57	1.8	5.1	-6.4		
SCN^-	0.5	-66	1.6	4.3	-1.4		

By plotting ΔS_{hydr} or σ correlation coefficients against the corresponding c , a clear linear relationship can be observed, as shown in Figure 2.9a - c. For kosmotropic-type anions, the LCST exhibits a linear variation with salt concentration at low salt concentrations, and the slope c is controlled by the ΔS_{hydr} of anions. At higher salt concentrations, the phase transition involves two stages. On the one hand, the linear relationship between lower LCST with salt concentration, characterized by the slope c_1 , is controlled by ΔS_{hydr} (primarily associated with hydrogen bonding between polarized water molecules and the polymer). On the other hand, the linear relationship between the higher LCST and salt concentration, represented by the slope c_2 , is dominated by the surface tension increment. Due to the difficulty in removing the tightly hydrated solvation layer of kosmotropic-type anions, directly adsorption onto the polymer surface is impossible, resulting in a linear relationship between the LCST and salt. For chaotropic-type anions, the linear relationship part $c[M]$ between the LCST and salt concentration is primarily controlled by surface tension. Surface tension mainly affects the removal of the hydrophobic hydration layer (mainly related to isopropyl groups and the main chain). The adsorption parameters (K_a , $B_{\max}$) are mainly associated with the interaction strength between the anions and PNIPAM.

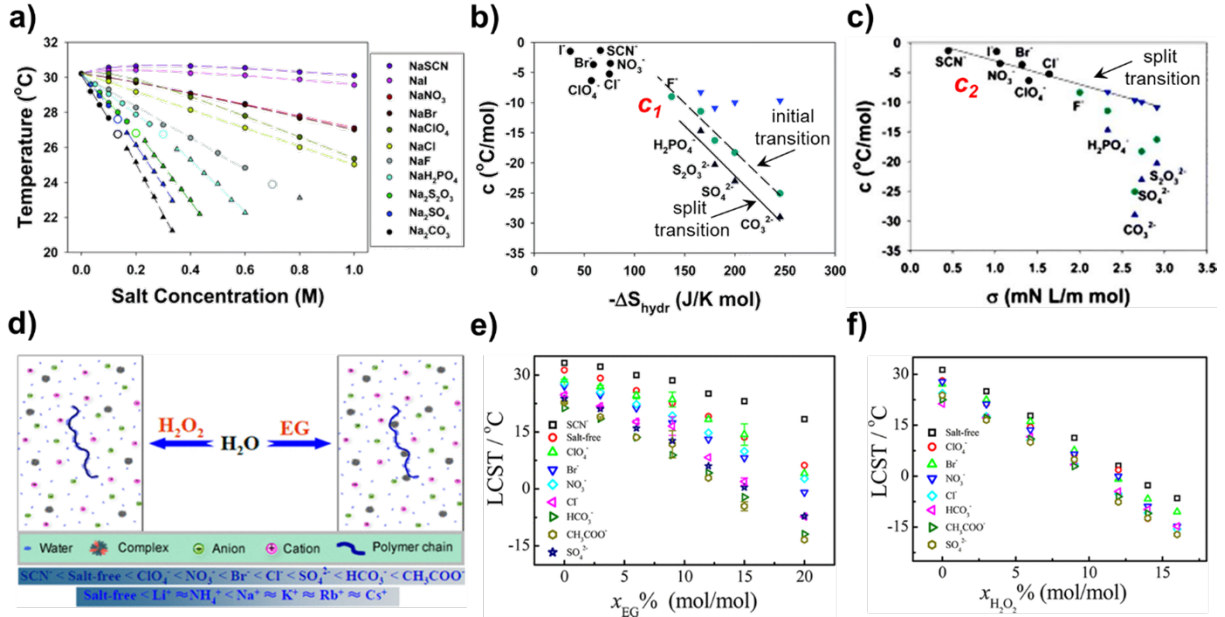


Figure 2.9.: (a) LCST values of PNIPAM measured for sodium salts at concentrations from 0 to 1.0 M. The dashed lines are curve fits to the Eq. 2.7. The relationship between c as a function of (b) ΔS_{hydr} and (c) σ , where circles represent the slope of LCST at lower salt concentration and equilateral and inverted triangles indicate the slope of LCST at higher salt concentration in the first stage and the second stage after stage, respectively. Modified from reference [94]. (d) Scheme of investigation of SIE on LCST of PNIPAM in H₂O-EG and H₂O-H₂O₂ mixtures. LCST values as a function of the molar fraction of (e) EG and (f) H₂O₂ with Na⁺ as the common cation. Adapted from reference [168].

SIE on PNIPAM in mixed binary solvents

Compared to the research on SIE in water, studies in mixed solvents are relatively fewer.[168]–[170] Due to the lower dielectric constants of mixed binary solvents, more ion pairs are formed.[171] Meanwhile, the complexes forming between solvent molecules influences the hydration of ions. For example, nuclear magnetic resonance (NMR) measurements indicate that in water-ethanol mixed solvents, the ability of monovalent anions forming ion pairs follows the Hofmeister series.[172] Zhang and Liu, *et al.*, investigated the SIE on LCST of PNIPAM in water-ethylene glycol (H₂O-EG) and water-hydrogen peroxide (H₂O-H₂O₂) solutions, as shown in Figure 2.9d - f.[168] H₂O₂ and EG molecules serve as both hydrogen bond donors and acceptors, and therefore hydrogen bond networks form in respective pure liquids. The results indicate that EG amplifies the Hofmeister effect, while H₂O₂ does not. The main reason for the amplification of the Hofmeister effect is attributed to the enhanced interaction between anions and the polymer chains in the presence of the co-solvent.

SIE on polyelectrolytes in aqueous

Schlenoff and Delgado investigated the dissolution process of polyelectrolytes (PZs) in aqueous solution containing the Hofmeister anion series, which provided a systematic way to tune PZs/ion interactions, as is illustrated in Figure 2.10.[173] The quaternary ammonium groups belong to a weakly hydrated group, and therefore bind more tightly to anions with weak hydration. This makes the anions with the weak hydration easier to break the coupling within and between amphiphilic polymer chains and facilitate dissolution. A consistent picture of PZs conformation illustrates the role and location of counterions (how they pair with the polymer chain) depend on their position in the Hofmeister series. At least four regimes of PZs conformation/interaction as a function of ionic strength were observed, the last showing no change in coil size (hydrodynamic radius) as a function of ionic strength for all monovalent salts in the concentration range 0.6 – 4 M.

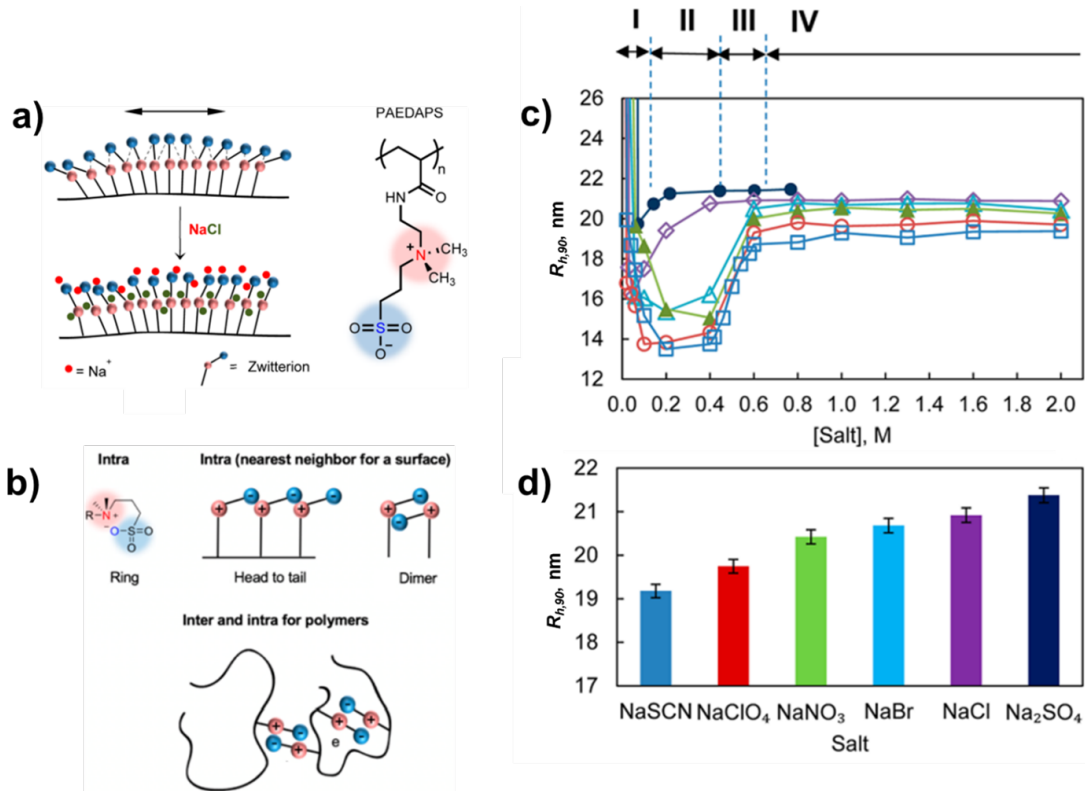


Figure 2.10.: Schematic illustration of (a) the interactions between ions and PZs and (b) possible intramolecular and intermolecular associations of zwitterion groups. (c) Dependence of $R_{h,90} \pm 0.5$ nm of PZs on Hofmeister salt concentrations of Na₂SO₄, NaCl, NaBr, NaNO₃, NaClO₄ and NaSCN at 25 °C and (d) average of R_h plateau from 0.8 to 2.0 M. Adapted from reference [173].

Characterization techniques

This chapter introduces all characterization techniques applied in this thesis, including neutron reflectivity (NR), X-ray reflectivity (XRR), spectral reflectometry (SR), UV-Vis-NIR spectrophotometer, atomic force microscopy (AFM) and Fourier-transform infrared (FTIR) spectroscopy. NR was conducted in two working modes (kinetic and static) to characterize the film in thickness change, surface roughness, absorbed solvent content, and especially in the solvent distribution along the normal direction of the film. XRR, as a supplementary method of NR, provides information about the density of films under room temperature (RT) and room humidity (RH). Spectral reflectance (SR) was applied to monitor the film thickness *in situ*. To determine the cloud points (T_{cp}) of the polymers in solutions, a UV-Vis-NIR spectrophotometer was used to measure the transmittance in dependence on the temperature. The surface topography of polymer films under RT and RH was characterized by AFM. FTIR followed the variations in characteristic peaks to analyze the solvation shell on a molecular level.

Two-dimensional FTIR (2D FTIR) correlation analysis was used to determine the temporal sequence of the fluctuation in spectral intensity, responding to the atmosphere perturbation. Furthermore, molecular dynamics (MD) simulation examined the accessibility of solvation shells near the hydrophilic groups.

3.1. Neutron reflectometry (NR)

NR is an advanced material characterization technology that obtains information such as structural components in the 0.5 - 500 nm scale range at the interface when the reflection angle equals the incident angle. By analyzing reflected neutrons by the interface, the information about the structure distribution and intrinsic properties of the thin films can be obtained. The variation of scattering length density (SLD) with depth is a crucial

parameter in neutron reflection and the SLD refers to the sum of the coherent scattering length products of various isotopes in a material. The relationship between these quantities is often deduced by analyzing the reflectivity curve. Due to the SLD difference between hydrogen and deuterium, NR allows us to determine the deuterium, that is useful in studying soft material films or interfaces.

3.1.1. Basic principles of neutron reflection

Neutron beams are refracted when they pass through a dispersive medium, and the refractive index (n_{neutron}) can be calculated from the optical reflection theory. The n_{neutron} of a medium (atomic number density ρ and coherent scattering length b_{coh}) is expressed as:

$$n_{\text{neutron}} = 1 - \frac{\lambda^2 \rho b_{\text{coh}}}{2\pi} + i\beta = 1 - \delta + i\beta \quad (3.1)$$

For an ideal planar medium with infinite thickness, the Fresnel reflectivity is expressed as:

$$R_F = \frac{\sin \theta - \sqrt{n^2 - \cos^2 \theta}}{\sin \theta + \sqrt{n^2 - \cos^2 \theta}} \quad (3.2)$$

The Fresnel reflectivity of neutrons at plane boundaries is conducted by the tangential component of the electric field vector and its continuous derivatives at sharp interfaces.[174], [175] Thus, the n_{neutron} of a layered structure can be modeled by applying the Fresnel equation successively at each interface. When $\beta \ll \delta$, the critical total reflection angle (θ_c) is expressed as:

$$\theta_c \approx \sqrt{2\delta} \quad (3.3)$$

Thus, the critical angle of total reflection depends on coherent SLD, which can be used to determine the density of the film. When the incident angle is $\theta > \theta_c$ ($R_F \ll 1$), the reflectance can be expressed as:

$$R \propto \frac{1}{Q^4} \quad (3.4)$$

While, for the rough surface, the Fresnel reflectance is corrected by the "Debye-Waller-like" factor,[176] and the reflectance $R(q)$ is expressed as:

$$R(q) = R_F(q) e^{-\frac{q^2 \sigma^2}{2}} \quad (3.5)$$

3.1. Neutron reflectometry (NR)

Here, $R_F(q)$ represents the Fresnel reflectance at an ideal interface, and σ is the root mean square parameter of the surface roughness. q is related to the reflection angle θ , illustrated as:

$$q = \frac{4\pi}{\lambda} \sin \theta \quad (3.6)$$

With an increase in roughness, the absolute intensity of the reflected beam and the contrast of interference oscillations gradually decreases with the increasing q . If the reflectance map exhibits better interference oscillation contrast only in certain regions of the q space, this can be attributed to the presence of density gradients in the thin film. The presence of density gradients effectively increases the number of interfaces in the thin film, leading to discontinuities in the reflectance patterns confined to specific regions in q space.[177]–[179] To accurately estimate interface roughness, reflectance measurements need to be conducted at larger q values, since reflectance is highly sensitive to roughness. To generate neutron reflectivity spectra for thin-film multilayer samples, the Parratt formalism is widely used, that the electric vector amplitudes for the incident, reflected, and transmitted waves match at each interface starting from the substrate bottom. The reflection amplitude at the substrate bottom is set to 0. Based on this, amplitudes are calculated layer by layer from the bottom, and the reflectivity at the air-film interface is ultimately computed. In this calculation, layer thickness, composition, density, interface roughness, and other parameters can be varied until a well-fitted result with the measured reflectivity curve is obtained.

3.1.2. NR setup and data process

In this thesis, all NR measurements were performed at the D17 vertical neutron reflectometer at Institut Laue-Langevin (ILL, Grenoble, France)[180] using the time-of-flight (ToF) mode. According to ToF mode, the time of arrival at the detector for each neutron allows to the calculation of its wavelength and energy.[181], [182] A schematic diagram of the applied instrument is shown in Figure 3.1.[180]

The experimental settings are described below and summarized in Table 3.1a. To monitor the vertical change in the composition of the polymer films on Si wafers, a broad range of neutron wavelengths ($\lambda = 2 - 27$) with a spectral resolution of $\Delta\lambda/\lambda = 10$ % was used. To cover a large scattering vectors q_z ($q_z = 0.01 - 0.25$ $^{-1}$), two fixed incident angles of $\alpha_i = 0.5^\circ$ and $\alpha_i = 2.5^\circ$ were applied for static measurements, while kinetic measurements were first performed at a fixed incident angle of $\alpha_i = 1.0^\circ$ for a good time resolution and then moved to $\alpha_i = 1.5^\circ$ to protect the detector from oversaturation. The thin film kinetics were followed with a time resolution of 5 s. A sample-detector distance of 3.1 m was

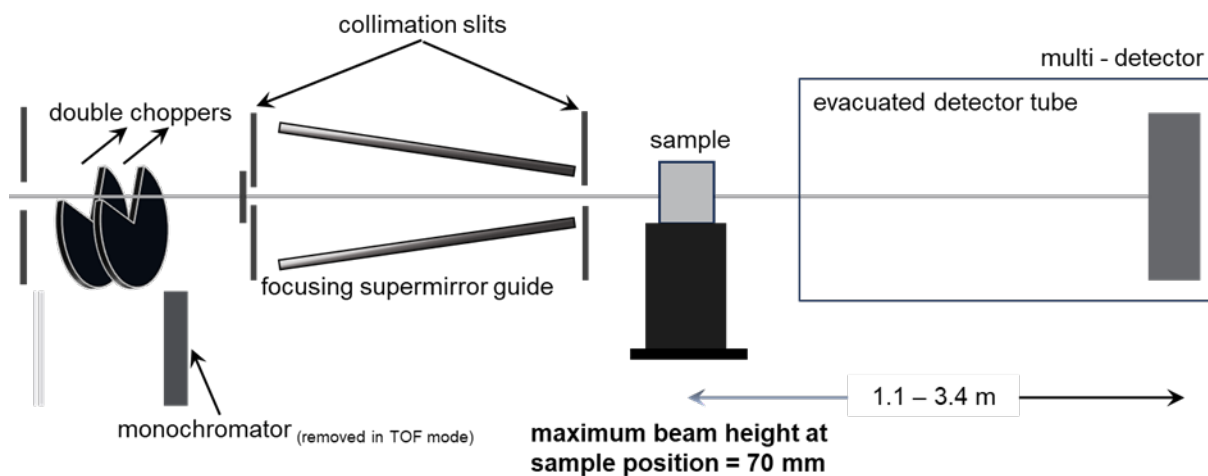


Figure 3.1.: Side view of the operational schematic of neutron reflectometer at D17 in TOF mode. The main components of the instrument include a neutron monochromator, a slit collimation system, a sample stage, and a detector. Modified from reference [180].

used for all static and kinetic measurements. Deuterated reagents (D_2O , acetone- d_6 , and methanol- d_3) are selected to enhance the SLD contrast, whereas, to protect the detector from oversaturation, the prepared films with small thicknesses are beneficial.

Table 3.1.: (a) The experimental settings applied in ToF-NR measurements. Summary of calculated theoretical SLD values of (b) neutron and (c) X-ray.

a)	incident angle (α_i)	static	kinetic	incident angle (α_i)	static	kinetic
	angle 1	0.5°	—	angle 3	—	1.0°
	angle 2	2.5°	—	angle 4	—	1.5°
$\lambda = 2 - 27\text{\AA}$; SDD = 3.1 m; time resolution ≈ 5 s						
b)	SLD _{neutron} $\times 10^{-6}$ ($\text{\AA}^{-2}$)				c)	SLD _{X-ray} $\times 10^{-6}$ ($\text{\AA}^{-2}$)
Si	2.07	PSBP ₈₀ -b-PNIPMAM ₁₁₅	0.701		H ₂ O	9.441
SiO ₂	3.47				D ₂ O	9.455
H ₂ O	-0.559				KCl	16.579
D ₂ O	6.393				PSBP ₅₀ -b-PNIPMAM ₁₅₅	9.914
acetone- d_6	5.389	PSBP ₅₀ -b-PNIPMAM ₁₅₅	0.808		PSBP ₅₀ -b-PNIPMAM ₁₅₅ with 5 mM KCl	10.082
methanol- d_3	4.279					
KCl	2.127					
KBr	1.456					
KNO ₃	3.260	PSBP ₅₀ -b-PNIPMAM ₁₅₅ with 10 mM KNO ₃	0.871			

As shown in Figure 3.2, all resulting neutron reflectivity curves in this thesis were modeled using the Motofit package (Andrew Nelson, Australian Nuclear Science and Technology Organiza), within the Igor Pro software (WaveMetrics, Portland, U.S.A.).[183]

3.1. Neutron reflectometry (NR)

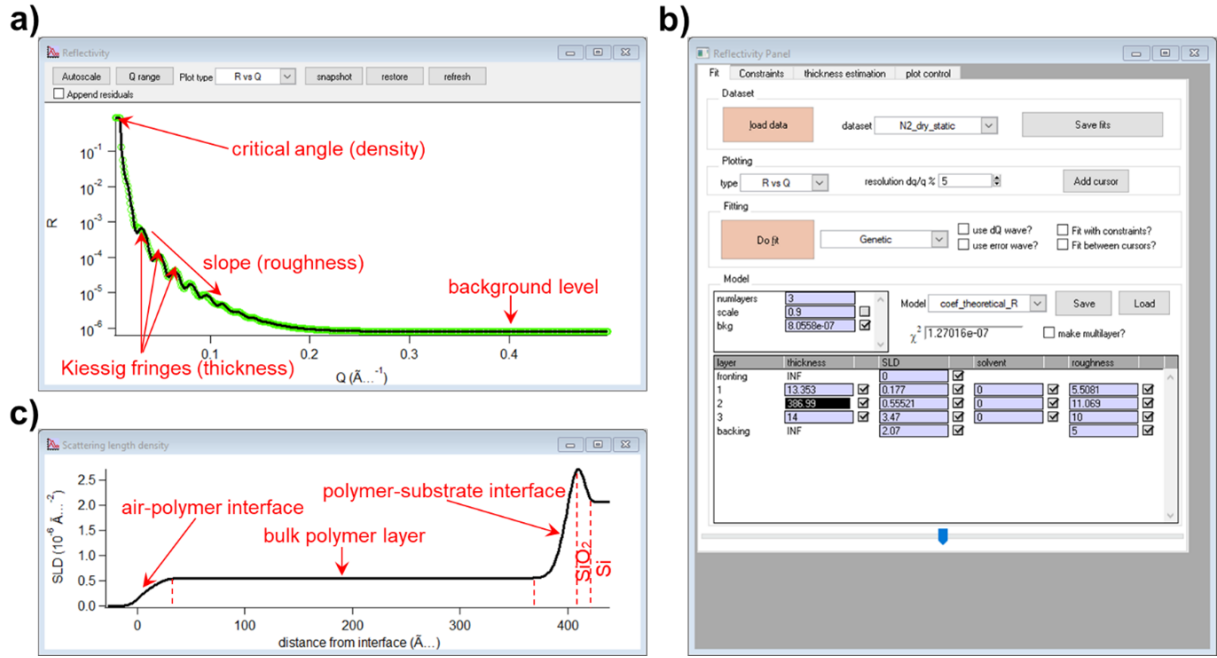


Figure 3.2.: Neutron data process within the Igor Pro software: (a) Neutron reflectivity curve with best fit, (b) profile of multi-layer modeling and (c) the resulting SLD profile.

3.1.3. Solvent content calculation

The absorbed solvent content can be calculated from the acquired SLD profile following the equations below.[76], [108], [184]

The overall solvent content is calculated by thickness and SLD as:

$$\Phi_{\text{solvent}}(t) = \frac{SLD_{\text{meas}}(t)}{SLD_{\text{solvent}}} \frac{SLD_{\text{polymer film}}}{SLD_{\text{polymer film}}} \quad (3.7)$$

Here, $SLD_{\text{means}}(t)$ represents the measured SLD at time t from an applied fitting model and $SLD_{\text{polymerfilm}}$ is the calculated SLD value of polymer film, as listed in Table 3.1b. Since we presume that the density is 1.0 g/cm^3 and 1.1 g/cm^3 for PSBP and PNIPMAM blocks respectively, the calculated density of DBC is 1.06 g/cm^3 . [185] Thus, the water content during the water swelling processes in chapters 5, 6 and 7 can be determined by Eq. 3.7 with temporal evolution of the bulk SLD.

For the vapor switching process shown in chapters 5 and 7 two solvent contents must be considered. Thus, the molar fraction $\chi_{\text{solvent-d}}(t)$ of deuterated solvents (acetone- d_6 in chapter 5 and methanol- d_3 in chapter 7) at time t is introduced as:

$$SLD_{\text{solvent}}(t) = (1 - \chi_{\text{solvent-d}}(t)) SLD_{\text{D}_2\text{O}} + \chi_{\text{solvent-d}}(t) SLD_{\text{solvent-d}} \quad (3.8)$$

We assume that the solvent content is related to the film thickness change via a volumetric conversion factor γ as:

$$\gamma = \frac{\frac{SLD_{meas}(t) - SLD_{polymer\ film}}{SLD_{solvent}(t) - SLD_{polymer\ film}}}{\frac{d_{ini}}{d_{meas}(t)} - 1} \quad (3.9)$$

Here, d_{ini} represents the initial film thickness and the $d_{meas}(t)$ represents the measured film thickness at time t . During vapor switching processes, the value of γ is approximated as 0.645 for Experiment A and 0.600 for Experiment B in chapter 5 and approximated as 0.5 for Br^- -loaded and 0.48 for NO_3^- -loaded DBC film in chapter 7. After implementing Eq. 3.9 in Eq. 3.8, the $\chi_{solvent-d}(t)$ at time t is calculated as below:

$$x_{solvent-d}(t) = \frac{\left(\frac{SLD_{meas}(t) - SLD_{polymer\ film}}{\gamma \left(\frac{d_{ini}}{d_{meas}(t)} - 1 \right)} \right) + SLD_{polymer\ film} - SLD_{D_2O}}{SLD_{solvent-d} - SLD_{D_2O}} \quad (3.10)$$

Thus, upon vapor switching processes, the overall absorbed solvent content is calculated by Eq. 3.7. As a result, the absorbed D_2O content and the deuterated solvent content upon vapor switching can be calculated.

3.2. X-ray reflectometry (XRR)

The wavelengths of X-rays are in the range of 0.01 to 10 nm, which characterized by short wavelength, high energy, and strong penetrating ability.[186], [187] According to Einstein's equation, the conversion relationship between the wavelength and energy of electromagnetic waves can be expressed as:[188]

$$E = h\nu = \frac{hc}{e\lambda} = \frac{1239.8}{\lambda}(eV) \quad (3.11)$$

Here, E , λ , e , h and c represent the electron volts (eV), wavelength (nm), elementary charge, Planck constant and speed of light, respectively. Thus, for an X-ray source of $CuK\alpha$, the $\lambda = 1.54$.

The relationship between X-rays and materials can be described by the complex refractive index (n_{X-ray}) of thin films:[189]

$$n_{X-ray} = 1 - \delta + i\beta \quad (3.12)$$

Here, δ represents the dispersion, and β represents the X-ray absorption of thin film. Due to the δ and β of the refractive index for all materials are extremely small ($\delta, \beta < 1$), the reflectance coefficient at normal incidence is very low, making it impractical to create single-layer film materials to achieve non-grazing incidence reflection of X-rays.

3.2.1. X-ray interference in multilayer film

As illustrated in Figure 3.3, the interface of multilayer film structure is formed by two layers. Layer 1 (absorption layer) has a relatively large refractive index (n_1), acting as the atomic layers in Bragg diffraction and providing scattering effects for X-rays. Layer 2 (spacer layer) has a smaller refractive index (n_2), serving to support the spacer layer. The total thickness is equivalent to the spacing in Bragg diffraction. Due to the different refractive indices of the absorption layer and the spacer layer, when X-rays are incident at a grazing angle, the multilayer film acts as an artificial lattice, achieving Bragg diffraction and satisfies the Bragg equation:

$$2d\sin\theta = m\lambda \quad (3.13)$$

where d , θ , λ and m represents the interplanar spacing, the angle of incidence, the wavelength of the incident wave and the order of Bragg diffraction, respectively. If a periodic multilayer film, the corresponding Bragg formula is expressed as:

$$m\lambda = 2(d_1 + d_2) \sqrt{\frac{n_1d + n_2d_2}{D_H + D_L} - (\cos \theta)^2} \quad (3.14)$$

$$\bar{n} = \frac{n_1d_1 + n_2d_2}{d_1 + d_2} \quad (3.15)$$

where, $\bar{n}$ represents the average refractive index of the absorption and spacer layers. d_1 , d_2 and $(d_1 + d_2)$, represent the thickness of the absorption layer, spacer layer and the period thickness, respectively. θ is the grazing incidence angle. According to this corresponding Bragg formula,[190] it is possible to design multilayer films.

3.2.2. XRR setup

XRR measurements in chapters 5 and 6 were performed with a diffractometer (D8 Advance, Bruker AXS, Germany), equipped with an X-ray source of $CuK\alpha$. A schematic diagram of the applied instrument is shown in Figure 3.3. The experimental settings are described as follows. To avoid over-illumination, a knife-edge collimator was placed above

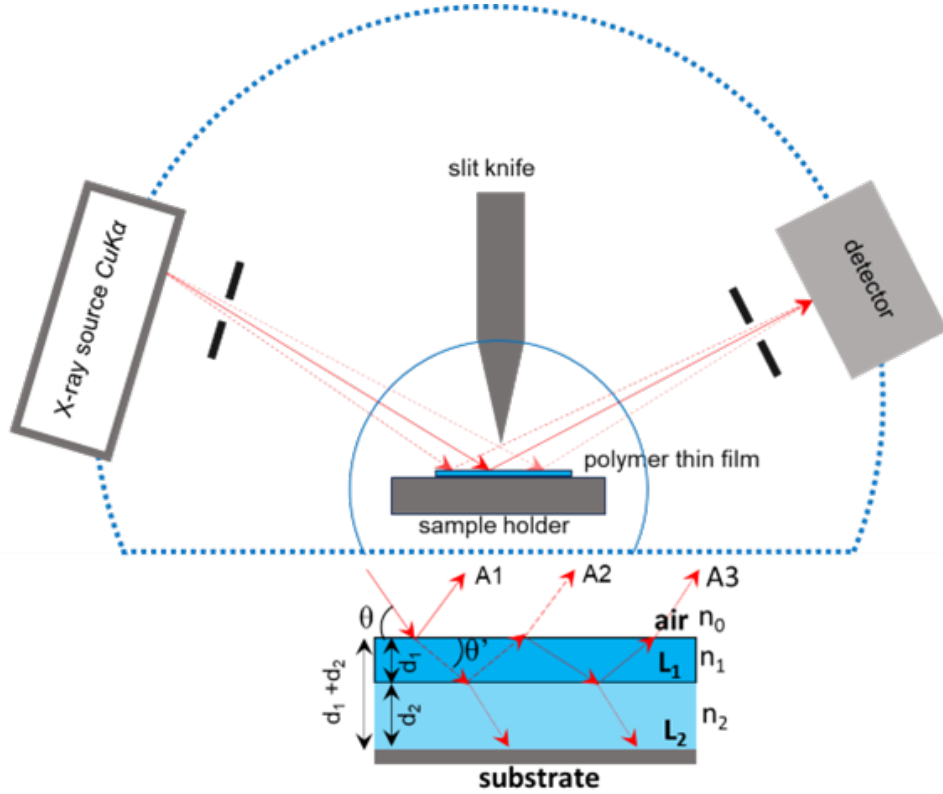


Figure 3.3.: Scheme of experimental XRR setup and multi-beam interference in a multilayer film.

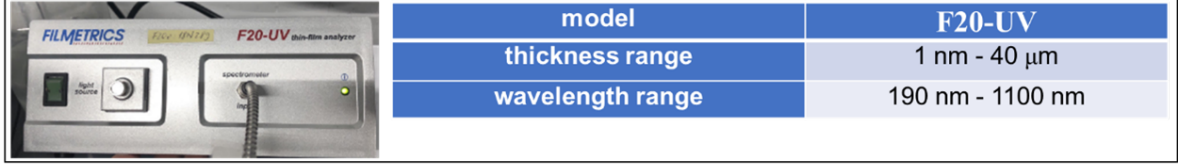
the samples at a very short distance. XRR measurements were carried out with the $\theta/2\theta$ configuration within the range of $2\theta = 0.04 - 4.00^\circ$. Similar to NR data process, the film thickness and composition of the thin films were also evaluated from the fits of the XRR curves via Igor Pro software with the Motofit package.[183] All XRR measurements were performed at ambient conditions (room temperature, $RT = 22^\circ C$ room humidity, $RH = 25 \pm 5\%$).

3.3. Spectral reflectometry (SR)

A spectral reflectance (SR) measurement device (Filmetrics F20 Thin Film Measurement System, KLA, Milpitas, U.S.A.) was used to detect the film thickness. As shown in Figure 3.4, the SR device includes parts of light source, spectrometer, reflection probe, light fiber and data recording software. By fixing the light source at 10 cm on the top of the sample chamber, where a CaF_2 window existed, the white light is allowed to pass through and reflect to the sample surface.

3.3. Spectral reflectometry (SR)

a) light source and spectrometer



b) reflection probe and light fiber



c) data recording

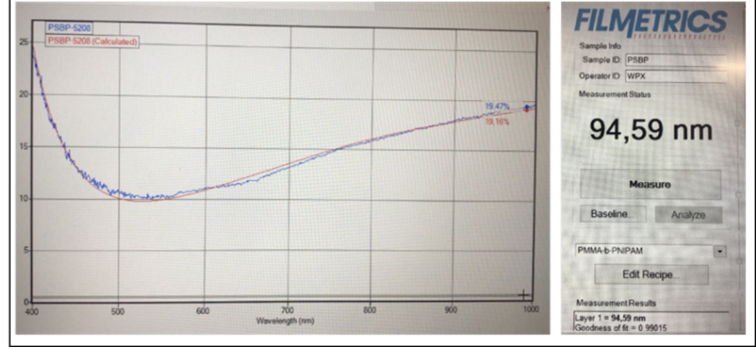


Figure 3.4.: Illustration of SR device, including the parts of (a) light source and spectrometer, (b) reflection probe and light fiber, and (c) data recording software.

3.3.1. Decoupling method of film thickness and refractive index

By fitting a multilayer model in the FILMeasure software (KLA, Milpitas, U.S.A.), the optical film thickness (d_{optical}) and refractive index (n_{film}) were obtained. Since d_{optical} is the product of the real geometric thickness (d_{film}) and n_{film} , the d_{film} can be determined. A more detailed explanation of the decoupling method of film thickness and refractive index is given below.[74], [75]

Since the d_{optical} and n_{film} are yielded by fitting the interference pattern formed between the reflected white light on Si-polymer and polymer-air interfaces, d_{optical} is calculated using n_{film} and d_{film} as:

$$d_{\text{optical}} = d_{\text{film}} n_{\text{film}} \quad (3.16)$$

After water swelling and subsequent co-solvent switching process, the n_{film} is introduced by the Lorentz-Lorenz effective medium approximation as:

$$\frac{n_{\text{film}}^2 - 1}{n_{\text{film}}^2 + 2} = \frac{d_{\text{ini}}}{d_{\text{film}}} \frac{n_{\text{DBC}}^2 - 1}{n_{\text{DBC}}^2 + 2} + \frac{d_{\text{film}} - d_{\text{ini}}}{d_{\text{film}}} \frac{n_{\text{D}_2\text{O}}^2 - 1}{n_{\text{D}_2\text{O}}^2 + 2} \quad (3.17)$$

Where, n_{DBC} , $n_{\text{H}_2\text{O}}$ and $n_{\text{D}_2\text{O}}$ represent the refractive index of DBC, H_2O and D_2O , respectively. Here, $n_{\text{DBC}} = 1.5$ for pure DBC and $n_{\text{H}_2\text{O}} = n_{\text{D}_2\text{O}} = n_{\text{acetone-d}_6} = n_{\text{methanol-d}_3} =$

1.33 for water and co-solvent. Since the volume fractions were determined using d_{ini}/d_{film} , and $(d_{film} - d_{ini})/d_{film}$, respectively, the d_{film} can be calculated with Eq. 3.16:

$$\frac{d_{optical}^2 - d_{film}^2}{d_{optical}^2 + 2d_{film}^2} = \frac{d_{ini}}{d_{film}} \frac{n_{DBC}^2 - 1}{n_{DBC}^2 + 2} + \frac{d_{film} - d_{ini}}{d_{film}} \frac{n_{D2O}^2 - 1}{n_{D2O}^2 + 2} \quad (3.18)$$

This decoupling method was applied to determine the real geometric thickness from all SR data.

3.4. UV-Vis-NIR spectrophotometer

In chapter 5, the T_{cp} of the polymers in mixed water-acetone solutions were determined by measuring their transmittance at 500 nm light in dependence on the temperature. Solutions in quartz cuvettes with an optical path length of 10 mm were measured by a Varian Cary 5000 UV-Vis-NIR spectrophotometer equipped with 6+6 cell Peltier thermostated cell holders, applying the heating rate of 0.5 Kmin⁻¹. The onset temperature of the transmission decay was considered as the cloud point temperature. First, stock solutions (10 gL⁻¹) of the polymer were prepared in pure solvents, which were mixed in the appropriate ratios to prepare the desired mixed water/acetone solutions. Solutions were stored at 4 °C overnight before the measurement.

3.5. Atomic force microscopy (AFM)

AFM is a testing method that can be used to study the surface morphology and properties of polymer films. As illustrated in Figure 3.5, AFM mainly studies the morphological information and mechanics of the surface of materials by detecting the interatomic interaction force between the sample surface and the probe. In chapter 6, an atomic force microscope (AFM, MFP-3D, Asylum Research) using a conical-shaped tip was applied to collect the AFM images of DBC thin films at the different static stages. All AFM measurements were performed at ambient conditions (RT = 22 °C, RH = 25 ± 5 %), and the images were recorded in tapping mode with a scanning area of 5 μm × 5 μm.

3.6. Fourier-transform infrared spectroscopy (FTIR)

When organic molecules are irradiated with infrared light, different chemical bonds or functional groups in the molecules will absorb light of specific frequencies, resulting a specific molecular vibrational mode in samples, as shown in Figure 3.6a. The frequency

3.6. Fourier-transform infrared spectroscopy (FTIR)

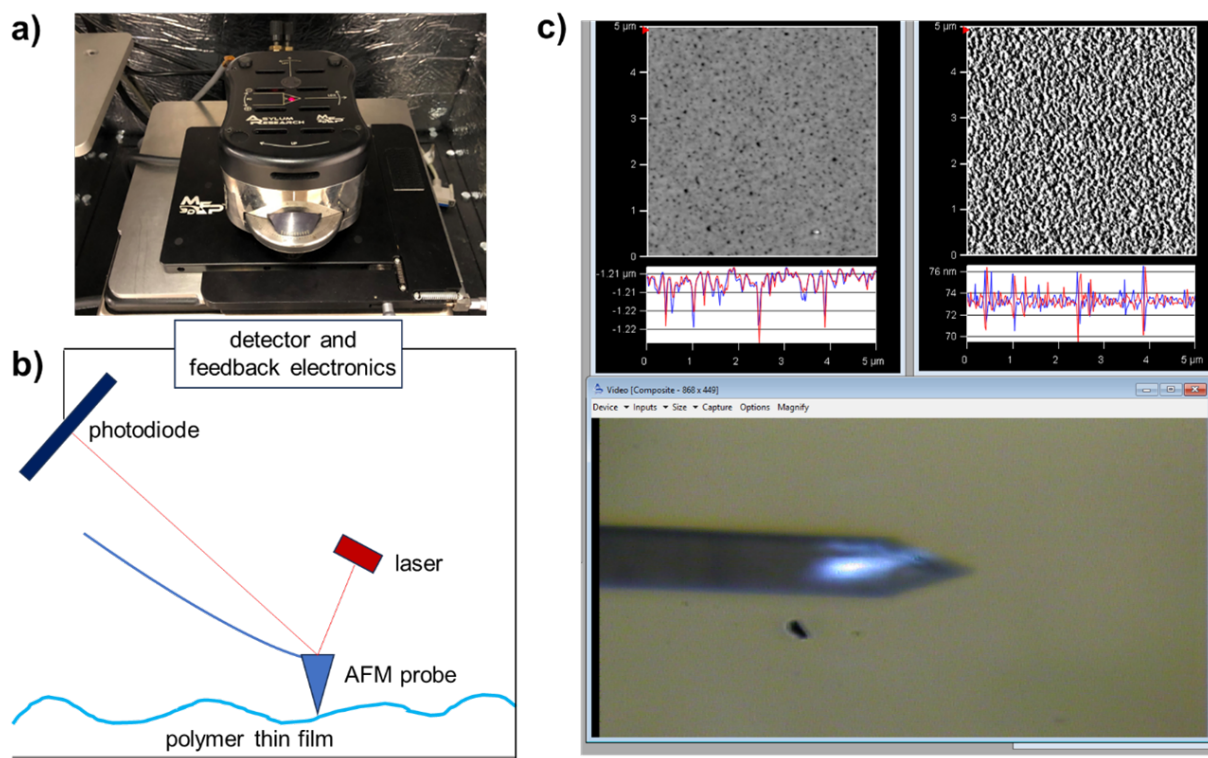


Figure 3.5.: Illustration of AFM device, including (a) top view stand-alone base, (b) the basic operation principle of AFM system, and (c) AFM images recording.

of the vibrations is associated with a particular normal mode of motion and a particular bond type. When an infrared light source (IR beam) passes through the beam splitter, it is divided into two infrared beams and directed to the fixed mirror and the movable mirror. After being reflected by the fixed mirror and the moving mirror, the optical path difference produced by the two infrared beams will cause destructive interference and constructive interference at different points in time. The interference phenomenon will eventually form an infrared beam with energy difference. Therefore, structural information of organic matter can be obtained by analyzing the infrared absorption spectrum. The principle working mode of Michelson interferometer is illustrated in Figure 3.6b.

To analyze the polymer films, FTIR spectra were obtained using a Bruker Equinox FTIR spectrometer, which is equipped with a KBr beam splitter and a deuterated triglycerine sulfate (DTGS) detector. The spectra were collected from 4000 to 600 cm^{-1} with a spectral resolution of 2 cm^{-1} . Data collection was carried out in transmission mode. This configuration allowed recording spectra *in situ*. The instrument was constantly purged with dry and CO_2 -free air to avoid small IR-active molecules, such as water and CO_2 in the IR beam pathway.

To ensure a clear intensity, the deuterated solvents (D_2O , acetone- d_6 and methanol- d_3)

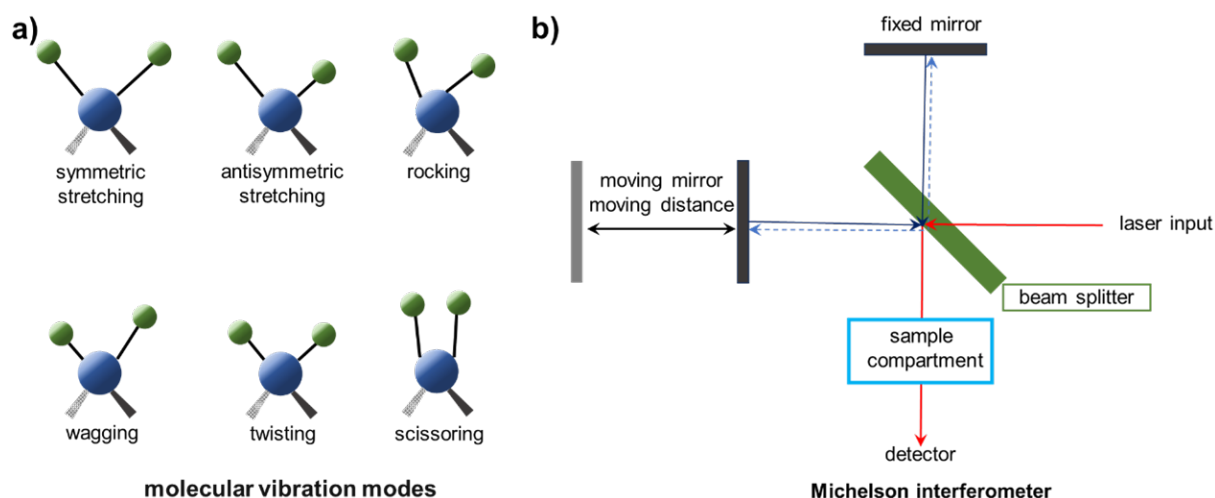


Figure 3.6.: Illustration of (a) molecular vibration modes, and (b) the principle working mode of Michelson interferometer.

are selected to avoid the overlap of specific FTIR bands and thicker rough films with a thickness of around 40 - 60 μm are beneficial.

3.7. Two-dimensional FTIR (2D FTIR) correlation analysis

3.7.1. Acquisition of 2D infrared spectrum

The commonly used experimental approach is based on detecting the dynamic changes in the spectroscopic signals of the sample system induced by external perturbations. When an external perturbation acts on a system, various chemical components of the system are selectively excited. The response to external perturbations often manifests as characteristic spectral changes, referred to as dynamic spectra. In infrared spectroscopy, typical changes observed in dynamic spectra include variations in absorption intensity, shifts in absorption peaks, and changes in directional absorption. By subjecting these dynamic spectra to some simple mathematical processing, a series of highly useful two-dimensional infrared spectra can be generated.

3.7.2. Mathematical processing of 2D correlation spectra

Dynamic spectrum

When the external perturbation acts on the system at time interval $t = T_{\min} - T_{\max}$, the dynamic spectrum is defined as:[100], [191]–[194]

$$\bar{y}(\nu, t) = \begin{cases} y(\nu, t) - \bar{y}(\nu) & T_{\min} \ll t \ll T_{\max} \\ 0 & \text{otherwise} \end{cases} \quad (3.19)$$

Where, $\bar{y}(\nu)$ is the reference spectrum of the system. Since the selection of reference spectra does not necessarily require consistency, we use the average value usually.

2D correlation function

The basic principle of 2D correlation spectroscopy is quantitative comparison of the variations in intensity observed by two optical variables, within the limited time intervals $t = T_{\min} - T_{\max}$, which is expressed as:

$$X(\nu_1, \nu_2) = \langle \tilde{y}(\nu_1, t) \bullet \tilde{y}(\nu_2, t') \rangle \quad (3.20)$$

The symbol $\langle \rangle$ represents any level of mathematical operation, known as the correlation function, which is conducted to determine the dependency of two selected quantities. Thus, the variation in optical intensity for two independent optical variables (ν_1, ν_2) is calculated. While $X(\nu_1, \nu_2)$ can also be expressed in complex form:

$$X(\nu_1, \nu_2) = \Phi(\nu_1, \nu_2) + i\Psi(\nu_1, \nu_2) \quad (3.21)$$

Here, the mutually perpendicular real and imaginary parts are called synchronous and asynchronous 2D correlation strengths, respectively.

The synchronous correlation spectrum $\Phi(\nu_1, \nu_2)$ characterizes the degree of coordination between two dynamic infrared signals. When the dynamic changes at wavenumbers ν_1 and ν_2 are completely identical, $\Phi(\nu_1, \nu_2)$ reaches the maximum value. When the two dynamic changes are orthogonal (*i.e.*, differ by $2\pi/2$), $\Phi(\nu_1, \nu_2)$ is 0. When the two dynamic changes are in phase opposition (*i.e.*, differ by π), $\Phi(\nu_1, \nu_2)$ is minimized. While the asynchronous correlation spectrum $\Psi(\nu_1, \nu_2)$ characterizes the extent of two dynamic infrared signals in difference that differ from each other. When the two dynamic signals are orthogonal, $\Psi(\nu_1, \nu_2)$ reaches the maximum or minimum, while in phase or out of phase, $\Psi(\nu_1, \nu_2)$ is 0.

Therefore, the 2D-IR correlation spectra can be obtained by calculating the synchronous correlation intensity $\Phi(\nu_1, \nu_2)$ asynchronous correlation intensity $\Psi(\nu_1, \nu_2)$ as functions of two independent wavenumber variables (ν_1, ν_2) .

Dynamic spectra convert to 2D correlation spectra

To remove the limitation on the waveform of external perturbation, Noda's generalized 2D correlation theory replaced the Fourier transform with Hilbert transformation, thereby reducing the processing time for 2D data.[100], [194] The applied waveforms, ranging from simple sinusoidal waves and pulse sequences to random noise or static physical changes, derived from various external perturbations.[194], [195]

In the Hilbert transform method, the synchronous correlation spectrum is calculated as follows:

$$\Phi(\nu_1, \nu_2) = \frac{1}{T_{max} - T_{min}} \int_{T_{min}}^{T_{max}} \tilde{y}(\nu_1, t) \bullet \tilde{y}(\nu_2, t) dt \quad (3.22)$$

The synchronous correlation spectrum reflects the degree of correlation between simultaneous changes in spectral intensity. Meanwhile, the asynchronous correlation spectrum is expressed as:

$$\Psi(\nu_1, \nu_2) = \frac{1}{T_{max} - T_{min}} \int_{T_{min}}^{T_{max}} \tilde{y}(\nu_1, t) \bullet \tilde{z}(\nu_2, t) dt \quad (3.23)$$

Here, $\tilde{z}(\nu_2, t)$ is the Hilbert transformation of signal $\tilde{y}(\nu_2, t)$, described as : Based on the Hilbert transform, $\tilde{z}(\nu_2, t)$ is orthogonal to $\tilde{y}(\nu_2, t)$. Therefore, the asynchronous spectrum reflects the correlation between the orthogonal quantities of intensity changes at two spectral coordinates. If the intensity changes are completely different or orthogonal, the asynchronous spectrum will exhibit peaks with maximum values. Thus, the asynchronous correlation spectrum reflects the dissimilarity in the intensity variations.

3.7.3. 2D FTIR correlation analysis

In chapter 7, to determine the temporal sequence of the fluctuation in spectral intensity of amide bands, 2D FTIR correlation analysis is employed to analyze only the first 30 FTIR spectra since the solvation events responding to the D₂O vapor perturbation mainly occur in the first 45 min. The 2D Shige developed by Shigeaki Morita (Kwansei-Gakuin University, Japan) was applied to generalize the 2D FTIR analysis, and the Origin program is further used to plot the resulting 2D synchronous and asynchronous maps combined with the corresponding FTIR spectra. The resulting synchronous and asynchronous maps are marked as Φ and Ψ respectively, and two independent wavenumber axes are set as ν_1

and ν_2 (ν_1 refers to the y-axis and ν_2 refers to the x-axis). The positive correlation and negative correlation are colored in red and blue respectively.

Further analysis procedures are described as follows based on Noda's rule.[191], [196], [197] If the cross peak shows the same coloration in both synchronous and asynchronous maps ($\Phi(\nu_1, \nu_2) > 0, \Psi(\nu_1, \nu_2) > 0$ or $\Phi(\nu_1, \nu_2) < 0, \Psi(\nu_1, \nu_2) < 0$), the event at ν_1 will vary prior to that at ν_2 . Reversely, if $\Phi(\nu_1, \nu_2) > 0, \Psi(\nu_1, \nu_2) < 0$ or $\Phi(\nu_1, \nu_2) < 0, \Psi(\nu_1, \nu_2) > 0$, the event at ν_1 will vary after that at ν_2 .

3.8. Molecular dynamics simulation (MD)

MD is a commonly used method to study molecular hydration. Based on the disruption and recombination of hydrogen bond, the hydration of the entire molecular chain can be dynamically simulated. Besides, the structural and dynamic changes in water molecules over time can be reflected. Basically, within a ranging from 0 - 0.02 ps, the stretching and bending vibrations of -OH groups can be captured, and within tens to hundreds ps, motion translation of individual water molecules or a few molecules can be captured. While, beyond hundreds ps, the hydration of solute molecules in water solution can be captured. Theoretical MD method assumes that the structural perturbation caused by solute molecules in water is short ranged. Therefore, this approach remains limited to simulations within the first hydration layer, typically within the range of 3.5 - 4.0 . If comes to the movement of water molecules, such as their reorientation, it goes beyond the scope of MD.

In chapter 7, MD were performed by Tianle using the Forcite module with the Compass force field. The time step was set at 1 fs, and equilibration of the solution models was achieved in the NPT ensemble by applying a Berendsen barostat to maintain a pressure of 0.001 Gpa with a decay rate of 0.1 ps over 20 ps while utilizing a Nose thermostat at 298 K.[198], [199] Following equilibration steps, production runs were conducted in an NVT ensemble for 200 ps duration to ensure equilibrium within the solution system. More parameters for the simulation model are presented below.

Quantum chemical calculations were performed using the Dmol3 module with B₃LYP functional, custom Grimme DFT-D parameters, and DNP 4.4 basis set in the Material Studio package.[200], [201] All molecules (KCH₃COO, KCl, KBr, KI, KNO₃, H₂O, CH₃OH, PSBP (4-unit)-*b*-PNIPMAM (6-unit)) utilized ESP charges after ultra-fine optimization and were simulated in a solvent environment using the conductor-like screening model (COSMO). The *k*-points were set to Gamma (1 × 1 × 1), and convergence tolerance was set at 1.0 × 10⁻⁵ Ha for energy and 2.0 × 10⁻³ Ha/ ⁻¹ for maximum force and maximum displacement of 5.0 × 10⁻³ . Several solution models were constructed to simulate the Hofmeister effect of potassium salts on solvation shells near the studied

DBC chains in a pure H₂O, pure CH₃OH and mixed H₂O/CH₃OH (6:4 v./v.) atmosphere. Each system was designed to maintain a mole ratio of 112: 5: 944 for potassium salts, DBC chains, and solvent molecules, respectively.

Sample preparation

This chapter gives a full overview of the sample preparation routine. The first part introduces all materials and polymers used in the thesis, as well as the preparation of polymer solutions. The second part describes the pre-treatment of the silicon substrates. The third part presents the preparation process of polymer film by spin-coating and drop-casting methods. The last part introduces the sample environment, including the used sample chambers, the vapor generation system, and the vapor protocols.

4.1. Materials

In the thesis, without further introductions, all used deionized water was purified by a Millipore Milli-QPlus water purification system (resistivity $18 \text{ M}\Omega \times \text{cm}$). For preparation for polymer solution, 2,2,2-trifluoroethanol (TFE, Roth, 99.8 % and potassium salts (KCH_3COO , KCl , KBr , KI , KNO_3 , Sigma-Aldrich) were used as received. For the substrate cleaning, the sulfuric acid (H_2SO_4 , Aldrich, 95 - 98 % and hydrogen peroxide (H_2O_2 , Roth, 30 % were used as received. For the gas flow system, deuterated water (D_2O , Deutero, 99.95 % , deuterated acetone (acetone- d_6 , Merck, 99.9 %) and deuterated methanol (CD_3OH , Deutero, 99.95 %) were used as received.

4.1.1. Polymer synthesis

The synthesis of the used homopolymers (PSBP and PNIPMAM) and DBCs is described in the following sections. The chemical structures are shown in Figure 4.1. All polymers are provided by Prof. André Laschewsky and Dr. Viet Hildebrand, as well as polymer information summarised in Table 4.1.

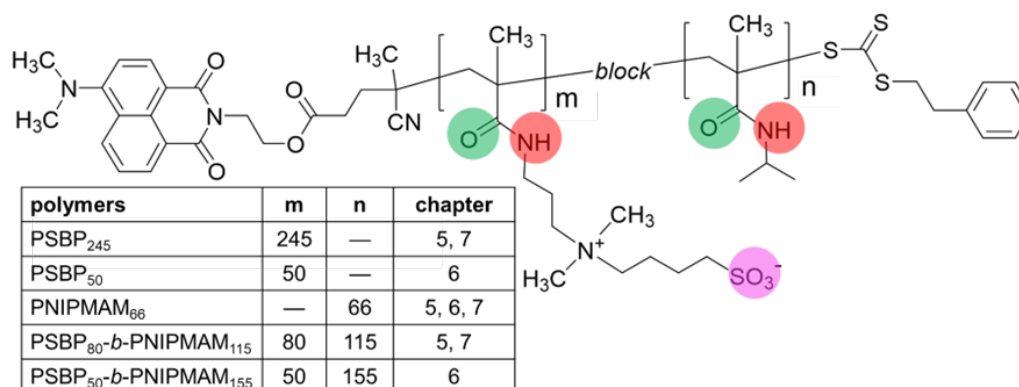


Figure 4.1.: Chemical structure of the studied polymers. The chromophore-labeled end groups were incorporated to support the molecular analysis.[81] The functional groups of S-O asymmetric stretching vibration, amide *I* band and amide *II* band are labeled by purple, green and red circle respectively.

PSBP₅₀ and PSBP₂₄₅

The reference homopolymer PSBP₅₀ and PSBP₂₄₅ were synthesized by the reversible addition-fragmentation chain transfer (RAFT) polymerization method, as described before.[55] In the procedure, the chromophore-labeled chain transfer agent (*R*)-2-(6-(dimethylamino)-1,3-dioxo-1H-benzo[*de*]-isoquinolin-2(3H)-yl)ethyl 4-cyano-4 (((phenethylthio) carbonothio-yl) thio) pentanoate (CTA, 0.1 g, 0.16 mmol) is applied as reversible addition-fragmentation chain transfer, and dissolved in trifluoro ethanol (TFE, 9 ml), together with monomer 4-((3-methacrylamidopropyl)dimethylammonio)butane-1-sulfonate (SBP, 5.0 g, 0.016 mmol) and initiator 4,4'-azobis(4-cyanopentanoic acid) (V501 (Wako, crystallized from methanol), 0.009 g, 0.03 mmol)). After polymerized at 75 °C, the mixture is cooled to room temperature and precipitated into methanol. Then, the homopolymer of PSBP is collected as a yellow powder after dried in vacuo.

Table 4.1.: Summary of information on studied polymers.

polymers	M_n (theoretical) [g · mol ⁻¹]	M_n (¹ H NMR) [g · mol ⁻¹]	M_n (UV/Vis) [g · mol ⁻¹]	UCST [°C]	LCST [°C]	UCST [°C]	LCST [°C]
				D ₂ O	D ₂ O	H ₂ O	H ₂ O
PSBP ₂₄₅	75,100	—	88,800	> 100	—	> 100	—
PSBP ₅₀	16,200	16,800	29,500	76	—	67	—
PNIPMAM ₆₆	9,000	9,100	7,400	—	32	—	30
PSBP ₈₀ - <i>b</i> -PNIPMAM ₁₁₅	39,100	35,700	45,700	> 42	42	> 42	42
PSBP ₅₀ - <i>b</i> -PNIPMAM ₁₅₅	36,000	34,400	49,900	41	43	37	43

PNIPMAM₆₆

Homopolymer PNIPMAM₆₆ was synthesized following an established procedure.[82] Monomer NIPMAM (Sigma-Aldrich, 97 % , crystallized from hexane), 10.5 g, 83 mmol), initiator (V501 (Wako, crystallized from methanol), 0.046 g, 0.164 mmol), and RAFT chain transfer agent (CTA, 0.500 g, 0.84 mmol),[202] were dissolved in trifluoroethanol (37 ml). After purging with N₂ for 30 min, the yellow reaction mixture was polymerized at 75 °C. After 19 h, the reaction was stopped by cooling to ambient temperature and allowing air into the vessel.

The mixture was precipitated from trifluoroethanol into diethyl ether thrice. The polymer was collected by filtration and dried under a high vacuum. Polymer PNIPMAM₆₆ was obtained as a yellow solid (yield 6.6 g, 60 %). Purity was checked by ¹H NMR spectroscopy and elemental analysis. Theoretically, expected number average molar mass $Mn_{theo} = 9 \text{ kg mol}^{-1}$ ($DP_n = 66$), as calculated from the monomer conversion and the molar ratios of monomer and CTA engaged. Molar mass analysis was performed by multiple methods as described in our previous study:[82] Apparent number average molar mass from size exclusion chromatography (SEC, eluent 0.1 wt LiBr in DMF, calibration by PMMA standards) $Mn_{app} = 5 \text{ kg mol}^{-1}$ (monomodal distribution, dispersity $D = 1.3$), number average molar mass via end group analysis by vis spectroscopy in trifluoroethanol normalizing to the absorbance at 444 nm of the naphthylamide chromophore in the *R*-group of the RAFT agent $Mn_{UV-R} = 9 \text{ kg mol}^{-1}$, number average molar mass via end group analysis by ¹H NMR normalizing to the signal of the *R*-group of the RAFT agent $Mn_{NMR} = 9 \text{ kg mol}^{-1}$, number average molar mass via end group analysis by ¹H NMR normalizing to the signal of the *Z*-group of the RAFT agent $Mn_{NMR-Z} = 10 \text{ kg mol}^{-1}$, *Z/R* end group ratio = 0.9 (*i.e.*, end group fidelity $\approx 90 \%$).

PSBP₅₀ -*b*-PNIPMAM₁₅₅ and PSBP₈₀ -*b*-PNIPMAM₁₁₅

DBC of PSBP₅₀ -*b*-PNIPMAM₁₅₅ and PSBP₈₀ -*b*-PNIPMAM₁₁₅ were synthesized by chain extension of PSBP₅₀ or PSBP₈₀ with NIPMAM, respectively. The synthesis of macro-chain-transfer agent PSBP₅₀ or PSBP₈₀ as described above. PSBP₈₀ (macro-CAT, 1.500 g, 0.0061 mmol), monomer NIPMAM (3.110 g, 24 mmol), and initiator V-501 (0.0034 g, 0.012 mmol) were dissolved in TFE (8 mL), purged with N₂ for 30 min, and sealed. Then, the yellow orange reaction mixture was polymerized at 75°C for 90 h. The reaction was stopped by allowing air into the flask and cooling to ambient temperature. After withdrawing a small amount for the analysis of monomer conversion by ¹H NMR, the reaction mixture was precipitated into diethyl ether (repeated thrice). The DBC PSBP₈₀-

b-PNIPMAM₁₁₅ was isolated by filtration and dried under high vacuum. PSBP₅₀-*b*-PNIPAM₁₅₅ was synthesized analogously.

4.1.2. Polymer solutions

In Chapter 5, the used polymers of PSBP₂₄₅ and PNIPMAM₆₆ and PSBP₈₀-*b*-PNIPMAM₁₁₅ are dissolved in TFE with a concentration of $c = 20$ mg/mL for SR and ToF-NR measurements. While, in order to obtain a good signal-to-noise ratio in FTIR spectroscopy measurements, the concentration of the solution of PSBP₈₀-*b*-PNIPMAM₁₁₅ in TFE was increased to $c = 35$ mg/mL to result in a thick film. In Chapter 6, the salt solution (KCl dissolved in deionized H₂O, $c_{\text{salt}} = 50$ mM) or deionized H₂O was mixed with the polymer solution (PSBP₅₀, PNIPMAM₆₆, and PSBP₅₀-*b*-PNIPMAM₁₅₅ dissolved in TFE, $c_{\text{polymer}} = 20$ mg/mL) at a volume ratio of 1:9, respectively. In Chapter 7, three types of polymers (PSBP₂₄₅, PNIPMAM₆₆, and PSBP₈₀-*b*-PNIPMAM₁₁₅) were dissolved in TFE with a concentration of $c_{\text{polymer}} = 22.22$ mg/mL, and the potassium salts were dissolved in deionized H₂O with a concentration of $c_{\text{salt}} = 100$ mM, before further use. The salt-loaded (or salt-free) polymer solutions were prepared by mixing three types of polymer solutions with the five kinds of salt solutions (or deionized H₂O) at a volume ratio of 1:9.

4.2. Substrate cleaning

For SR, AFM and XRR measurements, the Si wafers were cut into a size of 20 mm $\times$ 20 mm. The Si wafers were cleaned in an acid bath (54 mL deionized H₂O, 84 mL H₂O₂, 198 mL H₂SO₄) at 80 °C for 20 min, then rinsed with deionized water and dried under an N₂ stream. Subsequently, the cleaned Si wafers were treated with an oxygen plasma (2000 W for 10 min) before being coated with prepared polymer solutions.

For ToF-NR measurements, pre-cut silicon wafers with a size of 70 mm $\times$ 70 mm were cleaned in an acid bath at 75 °C for 15 min, then rinsed with deionized water three times and dried by compressed N₂ gas. After drying under an N₂ stream, the wafers were saved in a plastic sample box before further use.

For FTIR measurements, the wafers were first cut into a size of 10 mm $\times$ 10 mm, and then treated with an oxygen plasma (2000 W for 10 min), and used after exposure to air for 25 min.

4.3. Spin-coating and drop-casting methods

Polymer thin films for SR, ToF-NR, AFM, and XRR measurements are prepared by spin-coating. The drop-casting method is used to prepare films for FTIR measurements. Figure 4.2 presents the preparation procedures.

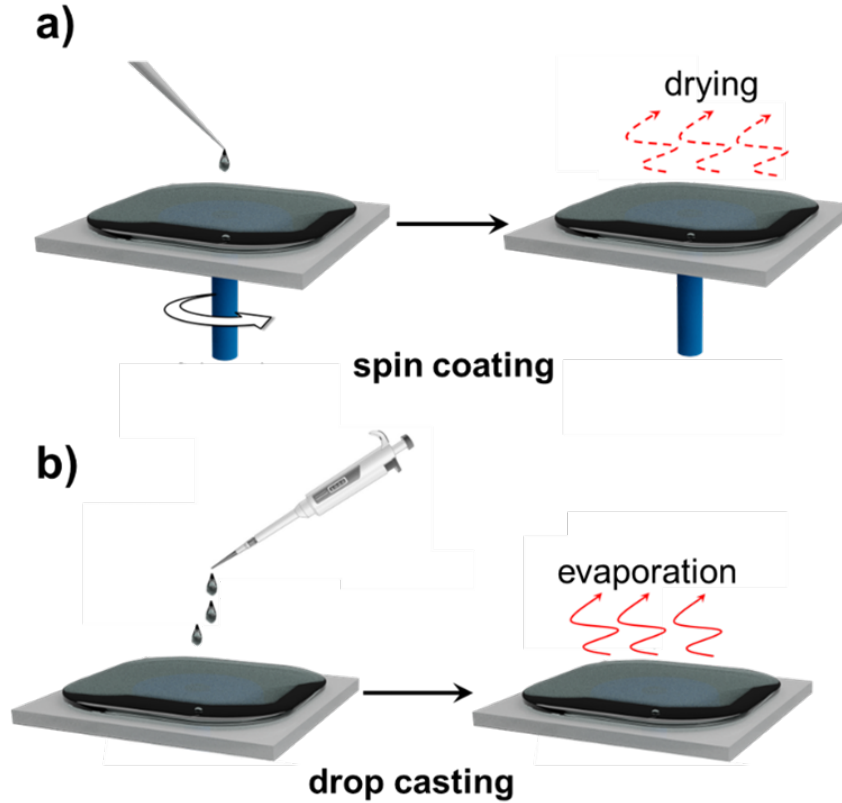


Figure 4.2.: Scheme of sample preparation procedures: (a) Spin-coating method and (b) drop-casting method. Modified from references [76], [108].

In Chapter 5, the spin-coating parameters are set to 3000 rpm for 300 s for all samples, and the resulting thickness for all samples is around 65 nm. The DBC solution ($V = 8.0 \mu\text{L}$ each) is drop-cast on the Si substrates for FTIR spectroscopy, and the films with a thickness of more than $40 \mu\text{m}$ are obtained after solvent evaporation at 25°C for 24 h.

In Chapter 6, the mixed solutions mentioned above are stirred overnight at room temperature, and then the cleaned Si wafers are coated with prepared polymer solutions by spin-coating (3000 rpm and 300 s for SR, AFM, and XRR measurements, 2500 rpm and 60 s for ToF-NR measurements). After spin-coating, all samples are annealed under solvent vapor for 15 min at room temperature, as a result, all samples have initial thicknesses in the range of $d_{ini} \approx 25 - 35 \text{ nm}$. While, for every sample used in FTIR spectroscopy measurement, $60 \mu\text{L}$ of the mixed DBC solution mentioned above is drop-casted on the Si wafer, and the solvent is removed by storing the samples in a desiccator for 24 h, resulting

in films with a thickness of 40 - 60 μm .

In Chapter 7, after coating with the prepared solutions (300 μL for SR and 2 mL for ToF-NR), the polymer films are prepared by spin-coating (2000 rpm and 90 s for SR and 3500 rpm and 120 s for ToF-NR measurements). After that, all samples are annealed under solvent vapor for 15 min at room temperature. As a result, the prepared polymer thin films have a thickness of around 80 - 100 nm for SR measurements ($d_{\text{ini}} \approx 91 - 98$ nm for PSBP, 83 - 91 nm for PNIPMAM, and 98 - 101 nm for PSBP-*b*-PNIPMAM), and around 30 - 35 nm for ToF-NR measurements.

In all chapters, for a good FTIR signal-to-noise ratio, 60 μL of prepared solutions is drop-casted on the Si wafer and then transferred to a desiccator to heal naturally. The obtained polymer films with a thickness of 4 - 6 μm for FTIR measurements are prepared by the drop-casting method.

4.4. Sample environment

4.4.1. “FlexiProb” and “custom designed FTIR” chambers

The “Flexiprob” chamber was designed by Tobias Widmann via the software SolidWorks 2019 and developed in close collaboration with Dr. Lucas P. Kreuzer, as shown in Figure 4.3a.[203] This 3D-printed aluminum chamber (PROTIQ GmbH, Blomberg, Germany) was used for ToF-NR and SR measurements. During the measurement, the sample was fixed into a 3D-printed aluminum chamber, which allowed a continuous and saturated D_2O vapor stream across the sample surface. The 3D-printed aluminum chamber is equipped with a CaF_2 window on top, which allows a white-light source passed through. By located the white-light source 10 cm above from the thin films, SR spectra were recorded with a spectral reflectance measurement device, namely a Filmetrics F20 Thin Film Measurement System (KLA, Milpitas, U.S.A.), and the resulting data was analyzed via the FILMeasure software (KLA, Milpitas, U.S.A.).

Compared to the 3D-printed aluminum chamber ($V_{\text{internal}} = 1.4$ L), the custom-made copper chamber ($V_{\text{internal}} = 15$ mL) had a smaller internal volume, as insulated in Figure 4.3b. The customized copper chamber is equipped with two highly transmissive ZnS windows, that ensure a high light transmittance, which was used for FTIR measurement.

4.4.2. Vapor generation system

Two methods are applied to generate the vapor, including a custom-made gas flow system and an injection method, as shown in Figure 4.4a and b respectively.[76], [204] For both methods, a thermal bath (JULABO FP50 HL) was connected to both chambers to achieve

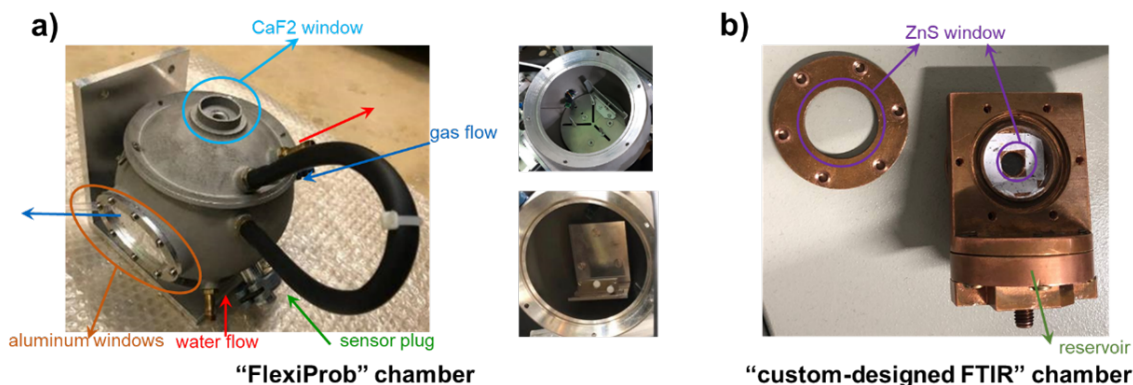


Figure 4.3.: Illustration of used sample chambers: (a) A 3D-printed aluminum chamber and (b) a “custom designed FTIR” chamber. Modified from references [76], [108].

a defined temperature and stable heating rate of the generated D_2O vapor, and an SHT31 humidity and temperature sensor (Sensirion AG, Staefa, Switzerland) was plugged or fixed into the chambers to monitor the real-time temperature and the humidity change.

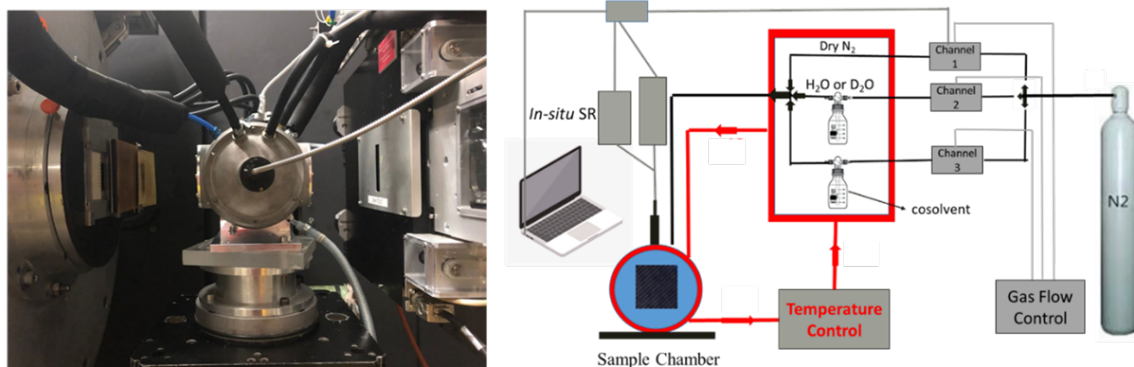
For all ToF-NR and FTIR measurements and the SR measurements in chapter 5 and 7, a humid atmosphere was generated via a custom-made gas flow system.[76], [184] The 3D-printed aluminum chamber was used for ToF-NR and SR measurements,[203] while the custom-made copper chamber was used for FTIR measurements. An ideal simplified diagram of vapor exchanging setup / *in situ* SR setup and thermo control system is shown in Figure 4.4a. The custom-made gas flow system is applied to control and change the N_2 flow through three different channels. The first channel is for pure N_2 , the second one connected to the water bottle, and the third one connects to the co-solvent bottle. All of the solvents are changed to stream under the N_2 flow and then are introduced into the sample chamber. The temperature of all the parts in the red line was controlled constantly by the thermos control system. The *in situ* SR setup is installed on the lid of chamber.

Except for the custom-made gas flow system, for the SR measurements in chapter 6 , the relative humidity was generated based on an injection method. As shown in Figure 4.4b, the relative humidity was generated by injecting 10 mL D_2O into a solvent reservoir located below the sample holder.

4.4.3. The applied vapor protocols

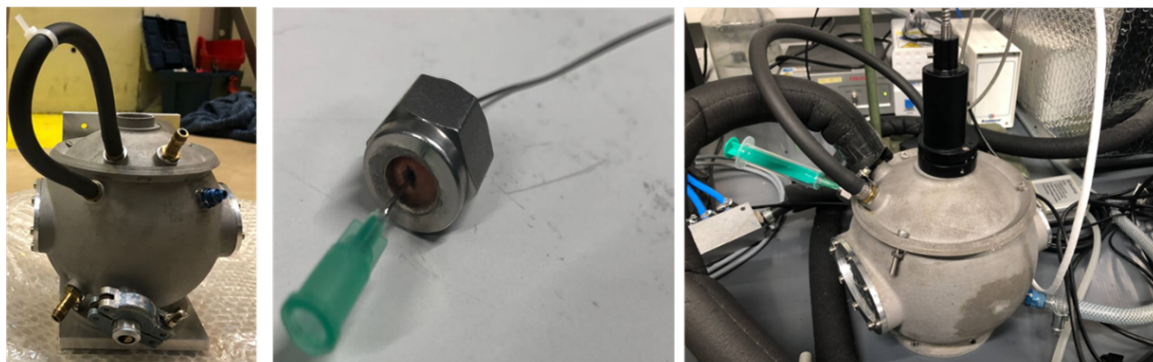
In chapter 5, as shown in Figure 4.5a, the as-prepared DBC thin film was dried under a N_2 gas flow, Then, as N_2 was replaced by a saturated H_2O stream or a D_2O stream, the water vapor swelling process begins. after a swelling process, the gas flow is switched from

a)



custom-made gas flow system

b)



injection method

Figure 4.4.: Illustration of vapor generation methods: (a) Custom-made gas flow system with temperature control system, beamtime chamber and *in situ* SR measurements and (b) injection method realized by a removable, well-sealed encapsulated component with a long needle. Modified from references [76], [108].

a saturated water vapor stream to a saturated binary mixed stream (H_2O /acetone- d_6 or D_2O /acetone- d_6), which is composed of (H_2O or D_2O): acetone- $\text{d}_6 = 9:1$ v/v. Finally, an equilibrated state under mixed stream terminates the measurement protocol.

In chapter 6, as shown in Figure 4.5b, after drying under an N_2 stream, the N_2 is replaced by a saturated D_2O vapor. However, after reached a swelling ratio plateau, the saturated D_2O vapor temperature is increased slowly from $T = 18^\circ\text{C}$ to $T = 42^\circ\text{C}$ with a temperature rate of $8^\circ\text{C}/\text{h}$, to provide sufficient time for movement or rearrangement of polymer segments. Then, the thermo-responsive behavior is investigated upon heating. The final D_2O swollen stage at $T = 42^\circ\text{C}$ ends the measurement protocol.

In chapter 7, as shown in Figure 4.6a, for stepwise vapor exchanging protocol, after drying under an N_2 stream, the samples are exposed to a saturated H_2O vapor (flow rate = $1\text{ L}/\text{min}$, set as 100 %). Then, the saturated H_2O vapor was stepwise replaced by a methanol vapor in 10 % increments until a saturated methanol vapor was generated. Each

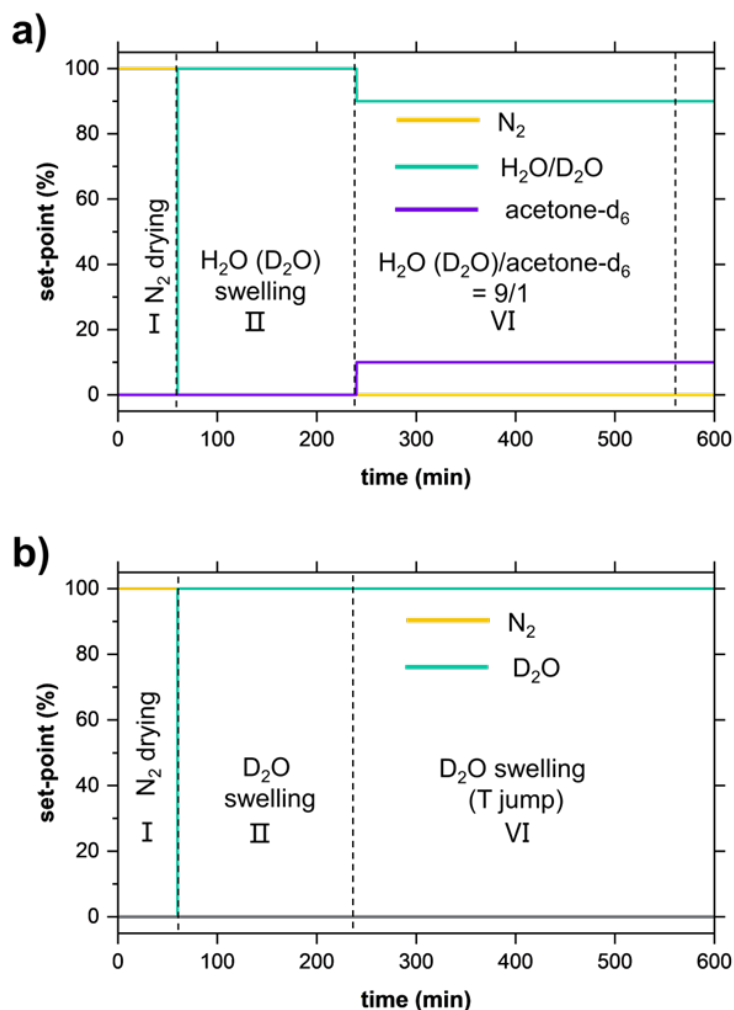


Figure 4.5.: Applied vapor protocols of (a) H₂O(D₂O)/acetone-d₆ exchanging in chapter 5 and (b) D₂O swelling in chapter 6. The flow rate is set as a set-point (100 % represents the flow rate = 1 L/min) and plotted in yellow, green, and purple for N₂, H₂O/D₂O, and acetone-d₆, respectively.

step goes for 2h. For the mixed water/methanol vapor switching protocol (Figure 4.6b), all samples are dried under a N₂ flow before exposure under a saturated water vapor (H₂O for SR, or D₂O for ToF-NR and FTIR). Once a plateau upon water hydration is reached, the saturated water vapor is switched to a saturated mixed vapor (H₂O/methanol for SR, or D₂O/methanol-d₃ = 6/4 for ToF-NR and FTIR). Then, the final equilibrium ends the measurement protocol; For the methanol vapor switching protocol (Figure 4.6c) for SR measurements, the dried samples are directly exposure to a saturated methanol vapor, and then the final equilibrium ends the measurement protocol.

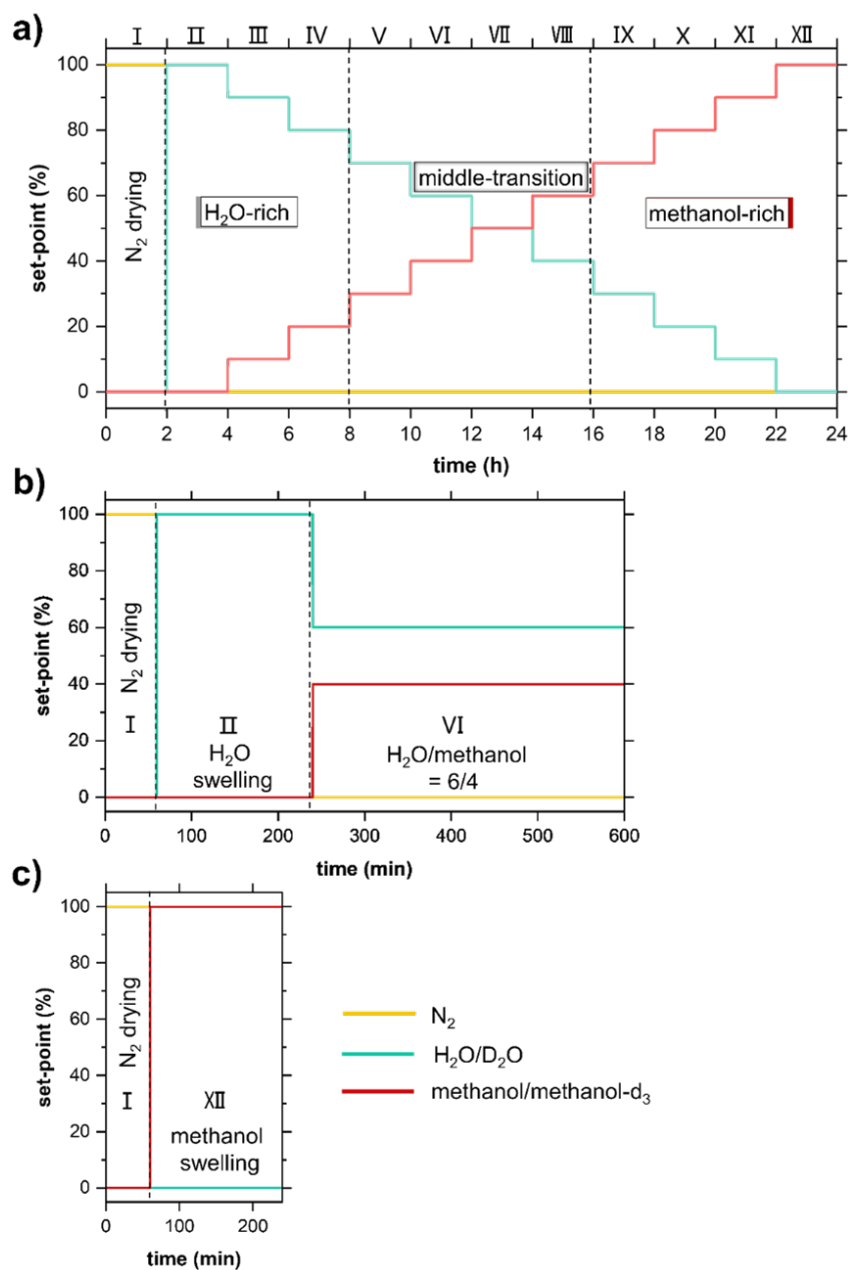


Figure 4.6.: Applied vapor protocols in chapter 7 of (a) H_2O /methanol stepwise exchanging, (b) H_2O /methanol exchanging and (c) methanol swelling. The flow rate is set as a set-point (100 % represents the flow rate = 1 L/min) and plotted in yellow, green, and red for N_2 , H_2O/D_2O , and methanol/methanol- d_3 , respectively.

Co-nonsolvency-triggered phase transition behavior

This chapter is based on the publication “Poly(sulfobetaine)-Based Diblock Copolymer Thin Films in Water/Acetone Atmosphere: Modulation of Water Hydration and Co-nonsolvency-Triggered Film Contraction” (P. Wang, C. Geiger, L. P. Kreuzer, T. Widmann, J. Reitenbach, S. Liang, R. Cubitt, C. Henschel, A. Laschewsky, C. M. Papadakis and P. Müller-Buschbaum, *Langmuir* **2022**, 38, 6934-6948; DOI: 10.1021/acs.langmuir.2c00451). Reproduced with permission.[76] Copyright 2022 American Chemical Society.

Introduction

The polymer’s solubility in a mixture of two individually good solvents decreases or even vanishes,[62] which provides various interesting possibilities for applications. Examples include switches,[73] molecular drive motors,[205] smart microchip membranes,[206] as well as intelligent systems for the uptake, transport, and release of nanoparticles.[207]

An interesting polymer is PNIPMAM. It shows a thermoresponsive LCST-behavior in solution features some characteristic differences to PNIPAM.[110], [208]–[214] Its co-nonsolvency behavior in certain water-alcohol mixtures in solution was demonstrated recently[71], [72] and was also confirmed for thin films.[73]–[75] However, co-nonsolvency studies on thin thermoresponsive polymer films are still rare and in particular limited to lower alcohols, while studies using other organic co-solvents, such as acetone, have not been reported.

In this chapter, I broaden the range of co-solvents and explore the co-nonsolvency behavior of thin films exposed to mixed water/acetone vapors. I study PNIPMAM as a nonionic thermoresponsive homopolymer and a zwitterionic PSBP, that is also thermoresponsive. Based on the understanding of the homopolymer films, the focus of the study is on films

from DBCs (PSBP₈₀-*b*-PNIPMAM₁₁₅) containing both blocks. The chemical structure of the investigated polymers is shown in Section 4.1. The PSB block in the studied DBC is changed to PSBP, as its UCST-behavior is more stable with respect to the *CP* compared of the hitherto employed PSB blocks.[84] This change in the DBC enables the use of a rather symmetrical copolymer made of two blocks of about equal size. In addition, I explore now the use of acetone as organic co-solvent instead of lower alcohols used in earlier studies. On the one hand, acetone is a less polar and moreover, an aprotic solvent, in contrast to methanol or ethanol. This difference substantially modifies the interaction with the polymer components, in particular with the zwitterionic moiety, which, a priori, prefers highly polar protic solvents.[77], [215] On the other hand, acetone is extensively used in biological and pharmaceutical research, where it acts as an excipient for pharmaceutical drugs.[9], [78] Importantly, for solutions, acetone has been shown to exhibit co-nonsolvency behavior for PNIPAM in mixtures with water.[59], [79], [80] Hence, we anticipate a similar behavior for PNIPMAM. Accordingly, the investigation of PSBP-*b*-PNIPMAM films immersed in water/acetone vapor could lay the foundation for potential biomedical applications, such as drug carriers,[216], [217] delivery agents,[207] and optical sensor.[218]

To gain a deeper understanding of the swelling behavior in water vapor and of a possible co-nonsolvency transition of PSBP-*b*-PNIPMAM thin films in water/acetone mixed vapor, the chapter is structured as follows: Investigation a co-nonsolvency behavior for PNIPMAM and PSBP homopolymer in mixed water-acetone systems of low acetone content, both in dilute solution as well as in thin films. Subsequent, investigation a co-nonsolvency behavior for PSBP-*b*-PNIPMAM thin films in two series of mixed water/acetone vapors (a mixed H₂O/acetone-d₆ atmosphere and a mixed D₂O/acetone-d₆ atmosphere. The vapor protocol introduced in Section 4.3.

In present chapter, the water swelling behavior and the solvation exchange triggered transition are probed *in situ* by simultaneous ToF-NR and SR, as well as by FTIR. Details to ToF-NR, SR, and FTIR can be found in the Chapter 3 . For realizing *in situ* measurements, corresponding sample environments described in Section 4.4. The thin film samples are prepared according to Section 4.3.

5.1. Homopolymer thin films in water and mixed water/acetone vapor

Since acetone is a non-solvent for PSBP and a powerful precipitant, the clouding behavior of the block copolymer solutions is dominated by the PSB block. Thus, any possible co-nonsolvency effect of the PNIPMAM block is covered by the precipitation of PSBP

setting in at much lower acetone contents. Thus, only the anticipated co-nonsolvency behavior of PNIPMAM in water-acetone mixtures is verified for dilute solutions. Figure 5.1 displays the CP determined when adding gradually acetone to the PNIPMAM dissolved in water. The decrease in CP of PNIPMAM solutions are somewhat less marked than reported for PNIPAM in mixed water-acetone solutions, while the general shape of the co-nonsolvency curve of PNIPMAM closely resembles to the one of PNIPAM i.e., the curvatures and minima (at a mole fraction of about 0.14 of acetone) are very similar.[59] The CP initially decreases from about 44 °C, which is in good agreement with previous studies on PNIPMAM of comparable molar masses,[110] to a minimum of about 34 °C for a volume fraction of 0.4, above which the CP rises steeply. For volume fractions of acetone above 0.6, no CP could be observed. Compared to the reported co-nonsolvency behavior of PNIPMAM in lower alcohols, the effect is less pronounced though still significant.[59], [62], [219] Importantly, a distinct reduction of the CP to 41 °C is already obtained for acetone contents as low as 0.1.

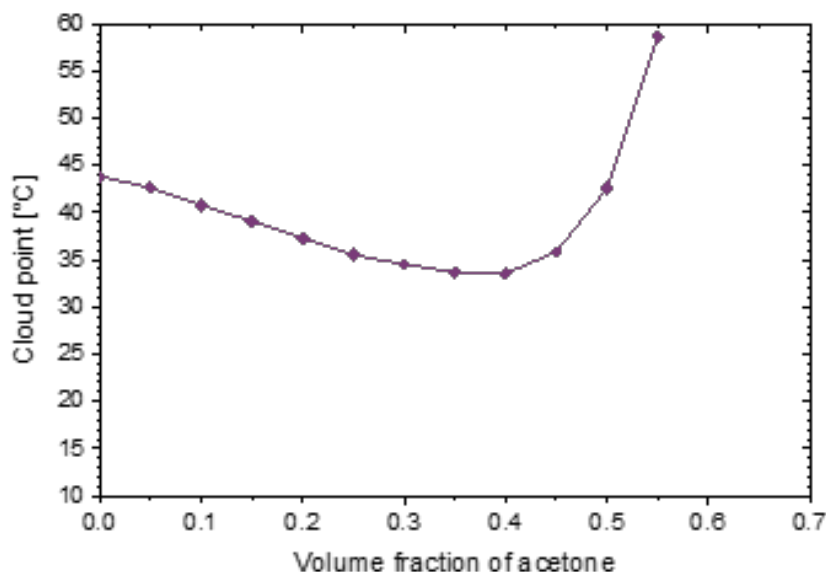


Figure 5.1.: T_{CP} of PNIPMAM₄₉₂ in aqueous solutions (10 g L⁻¹) containing increasing fractions of acetone. The line connecting the symbols is as guide to the eye. Reproduced with permission.[76] Copyright 2022 American Chemical Society.

Subsequently, the swelling of both homopolymer films is studied by measuring the swelling ratios d/d_{ini} (film thickness d extracted from SR measurements divided by the initial film thickness d_{ini}) as a function of time during the H₂O vapor swelling and H₂O/acetone-d₆ vapor switching, as well as the acetone-d₆ vapor swelling as reference points (see Figure 5.2). PSBP₂₄₅ reaches a higher swelling ratio in a shorter time compared with PNIPMAM₆₆ during H₂O vapor swelling (at $t = 120$ min reach to 1.67 for PSBP₂₄₅ and at $t = 135$ min

reach to 1.15 for PNIPMAM₆₆). In addition, PSBP₂₄₅ reaches equilibrium faster during H₂O/acetone-d₆ vapor switching (at $t = 200$ min for PSBP₂₄₅ and at $t = 285$ min for PNIPMAM₆₆).

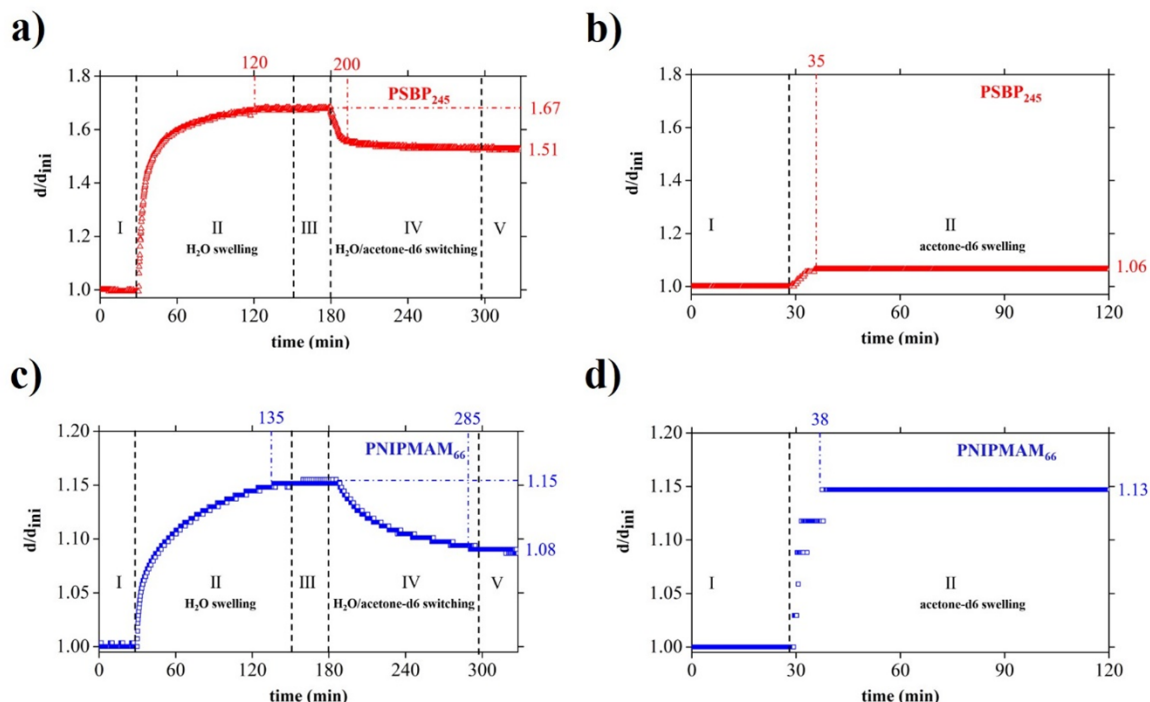


Figure 5.2.: Swelling ratio d/d_{ini} (a,c) in H₂O and H₂O/acetone-d₆ = 9:1 v/v mixed vapors and (b,d) in pure acetone-d₆ vapors, as function of time for (a,b) PSBP₂₄₅ and (c,d) PNIPMAM₆₆. The live SR data is plotted as red triangles for PSBP₂₄₅ and blue squares for PNIPMAM₆₆. Reproduced with permission.[76] Copyright 2022 American Chemical Society.

During acetone-d₆ vapor swelling, both reach almost simultaneously the maximum swelling ratio at a faster speed. Interestingly, PNIPMAM₆₆ realizes almost the same swelling ratio in acetone vapor as in the H₂O vapor swelling process, but the non-continuous thickness change in acetone vapor prove that the swelling behavior is different from that in H₂O vapor. In contrast, the swelling of PSBP₂₄₅ in acetone-d₆ vapor is much weaker compared with H₂O vapor swelling and H₂O/acetone-d₆ vapor switching. These findings demonstrate that the film contraction for PSBP is due to acetone-d₆ acting as a poor solvent, whereas for PNIPMAM, acetone acts as a co-nonsolvent in mixed saturated water/acetone-d₆ vapor atmosphere notwithstanding its modest content (H₂O: acetone-d₆ = 9:1 v/v). Since there is a small amount of water left bound in the films even after the drying procedure with N₂ and water mixes well with acetone, the PSBP thin film is still slightly swollen in pure acetone-d₆ vapor.

5.2. DBC thin films in water and mixed water/acetone vapor

5.2.1. Experimental design

The concept of the two performed experiments (Experiment A: H₂O swelling followed by acetone-d₆ addition, and Experiment B: D₂O swelling followed by acetone-d₆ addition) on the DBC is shown in Figure 5.3.

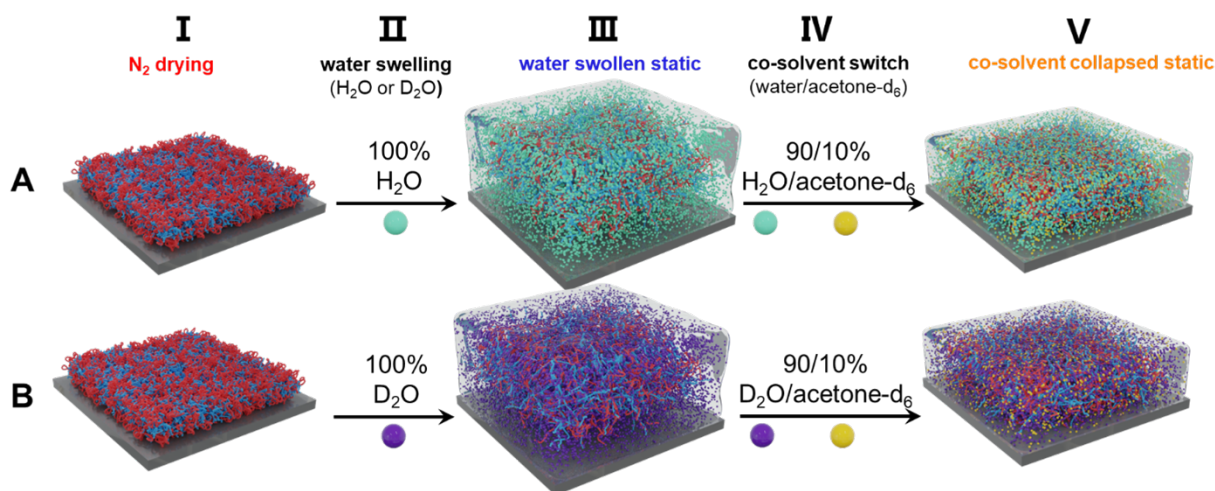


Figure 5.3.: Experimental design applied for ToF-NR, SR and FTIR studies on the DBC films. The individual states for Experiment A (H₂O : acetone-d₆ = 9:1 v/v) and Experiment B (D₂O : acetone-d₆ = 9:1 v/v) are labelled accordingly: N₂ dried state (*I*), water vapor swelling state (*II*), water vapor swollen static state (*III*), water/acetone-d₆ vapor switching state (*IV*), and acetone-d₆ vapor contracted static state (*V*). Reproduced with permission.[76] Copyright 2022 American Chemical Society.

The vapor swelling and solvent exchange behavior are studied by a series of static as well as *in situ* ToF-NR, SR and FTIR experiments, to follow the initial absorption of water, and the subsequent substitution of water by acetone-d₆ inside the DBC film on mesoscopic and molecular length scales. After drying the as-prepared DBC thin film under a N₂ gas flow for 30 min, the established N₂ dried state (state *I*) of the DBC film is characterized by static ToF-NR measurement. Then, as N₂ is replaced by a saturated H₂O stream in Experiment A, and by a D₂O stream in Experiment B, the water vapor swelling (state *II*) process begins, which is followed *in situ* with a kinetic ToF-NR measurement. During a swelling process (duration 3 h), the increase in film thickness is followed *in situ* with ToF-NR. This final swollen state of the DBC film (state *III*) is also probed with static ToF-NR. The subsequent investigation of the solvent exchange behavior (state *IV*) is followed again with *in situ* ToF-NR. For this step, the gas flow is switched from a

saturated water vapor stream to a saturated binary mixed stream ($\text{H}_2\text{O}/\text{acetone-d}_6$ for Experiment A and $\text{D}_2\text{O}/\text{acetone-d}_6$ for Experiment B), which is composed of (H_2O or D_2O): $\text{acetone-d}_6 = 9:1$ v/v. In the case of co-nonsolvency behavior, this change of the vapor composition is expected to trigger the collapse of the polymer coils in the previously swollen film. In this state, the DBC film (state V) is investigated again with a static ToF-NR measurement, which terminates the measurement protocol. Simultaneously to the ToF-NR measurements, SR measurements are performed during this entire protocol to independently measure the film thickness. To further study the mechanism of the solvent exchange triggered transition and the interaction between solvent molecules and polymer chains, the process is monitored *in situ* by FTIR spectroscopy following the same measurement protocol.

5.2.2. Investigation of static equilibrium states

The thin film thickness and SLD are monitored *in situ* by static ToF-NR measurements during the three static equilibrium states (I, III, V). ToF-NR experiments can provide information about the thin film composition in the direction normal to the substrate surface, and therefore, enable the investigation of the solvent distribution along the film normal. Furthermore, the water and acetone-d_6 content can be calculated from the SLD profile, as explained in Section 3.1.

Figure 5.4) shows a zoom-in of the low q_z region of the static ToF-NR data for both experiments together with the best fits and the respective SLD profiles. From the SLD profiles, values such as film thickness and SLD are obtained (in Table A.1), Appendix A. The static reflectivity curves of both Experiments A and B (Figure 5.4a and c) show clear differences between the different states. Compared to the N_2 dried state (red curve), the spacing of the fringes of the water vapor swollen film is reduced (dark blue), indicating an increase in the film thickness. Similarly, the increase of the fringe spacing upon acetone-d_6 addition (yellow) illustrates that a film shrinkage occurs. Moreover, the incorporation of a solvent with higher SLD value compared to the DBC film shifts the q_z position of the critical edge,[220] *i.e.*, the absorption of D_2O shifts the critical edge towards higher q_z values.

As displayed in Table A.1 (Appendix A), the dry DBC films in both experiments A and B exhibit a thickness of about 66 nm. The differences in the strength of the Kiessig fringes for the dry films used in experiments A and B, shown in Figure 5.4 are caused by a difference in surface roughness. Furthermore, the SLD value of the dry DBC film is slightly lower than the theoretical DBC value. We noted this phenomenon already in previous work, and attributed it to residual H_2O inside of the films, which cannot be removed.[75]

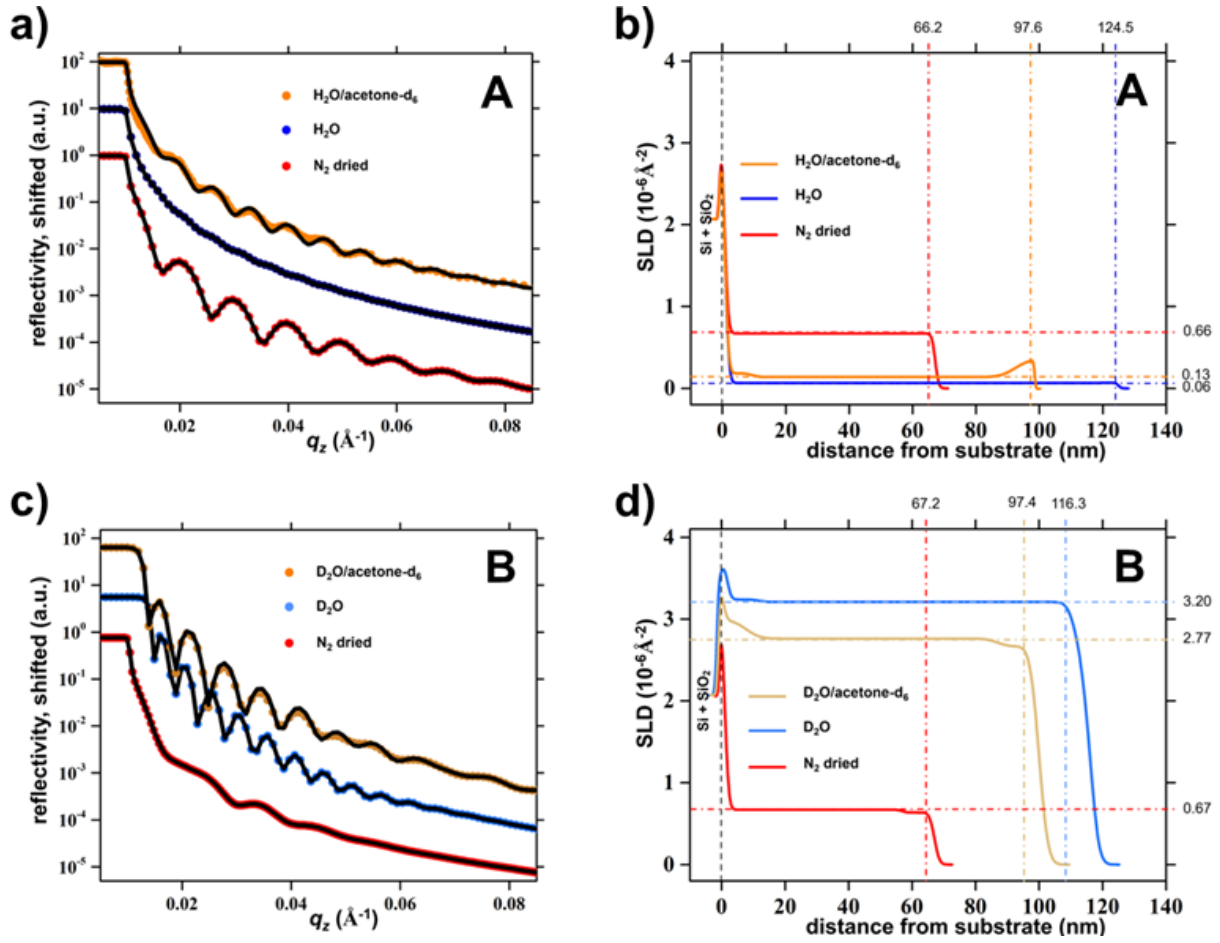


Figure 5.4.: (a, c) Static ToF-NR data at low q_z values (symbols) and (b, d) determined SLD profiles of (a, b) Experiment A (H₂O : acetone-d₆ = 9:1 v/v) and (c, d) Experiment B (D₂O : acetone-d₆ = 9:1 v/v). The N₂ dried state (I), water vapor swollen static state (III) and acetone-d₆ vapor contracted static state (V) are colored in red, blue, and yellow, respectively. The best fits obtained via a three-layer model are presented as black solid lines in (a) and (c). The SLD profiles between substrate and polymer layer are separated by dash-dotted lines in (b) and (d). The thickness and SLD values are listed on corresponding axis in (b) and (d). The entire q -range static reflectivity curves with the best fits are shown in Figure A.1 (Appendix A). Reproduced with permission.[76] Copyright 2022 American Chemical Society.

After the water vapor swelling in experiments A and B, the thickness and water content of both DBC films are increased. The film thickness in Experiment A increases from 66 nm to 124 nm, and the SLD value decreases from 0.66 to 0.06, indicating a strong hydration of the thin film. Similarly, the film thickness in Experiment B increases from 67 nm to 116 nm, and the SLD value increases from 0.67 to 3.20, also indicating a strong hydration of the thin film. Compared with state III (dark blue SLD curves), in state V (yellow SLD curves), the thickness in both Experiments A and B is reduced, while the SLD increases

in Experiment A but decreases in Experiment B. The reason is the diffusion of acetone-d₆ ($SLD_{D_2O} > SLD_{\text{acetone-d}_6} > SLD_{H_2O}$) molecules into the film, and exchange of the water molecules at the same time. Acetone enrichment layers at the polymer/vapor interface are observed in both experiments. Furthermore, it is observed that acetone-d₆ impacts deeper inside the film for a D₂O-swollen DBC thin film.

Based on Eq. 3.7) and 3.10, the water and acetone-d₆ content for the three static states are calculated (Table A.1, Appendix A). When comparing the water and acetone-d₆ contents in both experiments, it is found that the absorption and release of water molecules are synchronized with the swelling and collapse processes of the DBC films. Moreover, the water release is also accompanied by the uptake of acetone-d₆ molecules. Interestingly, the H₂O content in the swollen static state ($\phi_{H_2O} = 53 \pm 1 \%$) is significantly higher than the D₂O content ($\phi_{D_2O} = 45 \pm 1 \%$). This also suggests that the polymer films have a higher affinity towards H₂O than D₂O. However, in the collapsed static state, the films contain within the error margins the same amount of H₂O and D₂O molecules, as well as a similar amount of absorbed acetone-d₆ molecules in both scenarios. This finding not only confirms that a pronounced co-nonsolvency behavior can be triggered even by a small amount of acetone-d₆, but also suggests that the solvation shell in the contracted state is similar for both Experiments A and B.

5.2.3. Swelling and co-solvent switching kinetics

in situ ToF-NR measurements are applied to monitor the kinetic processes in both protocols, water vapor swelling (state *II*) and water/acetone-d₆ vapor switching (state *IV*), with a time resolution of 5 s. In addition, SR measurements are implemented, which can provide the continuous thickness information not only for the kinetic states but also for the static ones. The kinetic data are acquired over a time of 180 min. Selected kinetic ToF-NR curves with the corresponding fits (black solid lines) are shown in Figure A.2 (Appendix A).

The increase of SLD due to an uptake of D₂O molecules during the D₂O vapor swelling (Figure A.2c) and the incorporation of acetone-d₆ molecules during the H₂O/acetone-d₆ vapor switching (Figure A.2b) lead to a shift of the position of the critical edge towards higher q_z values. No obvious shift of q_z is seen in case of the tiny difference in the SLD values between D₂O and acetone-d₆ (Figure A.2d). Comparing water vapor swelling (*II*) with water/acetone-d₆ vapor switching (*IV*), the Kiessig fringe minima move in opposite directions as highlighted by the arrows in Figure A.2. Thickness and SLD values for the kinetic processes are determined from a three-layer model fit to the ToF-NR data and plotted in Figure 5.5 together with the SR data.

Compared to water swelling as presented in state *II* of Figure 5.5a and b, not only the

5.2. DBC thin films in water and mixed water/acetone vapor

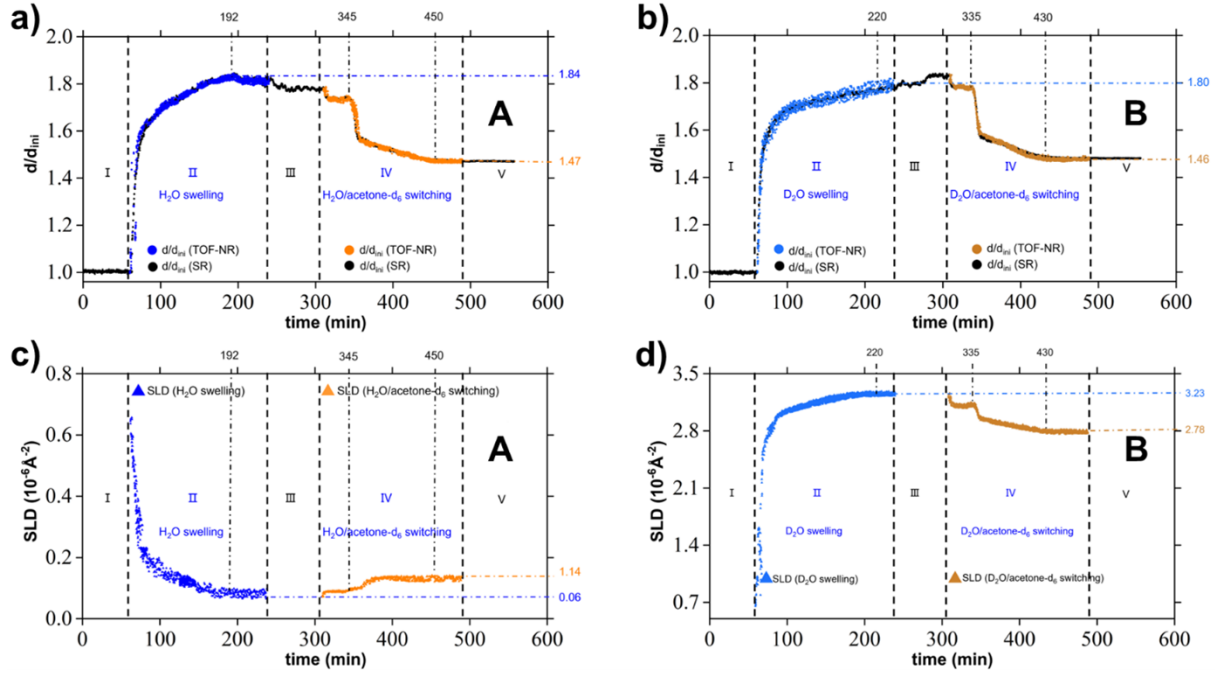


Figure 5.5.: (a,b) Swelling ratio d/d_{ini} and (c,d) bulk SLD, as function of time for Experiments A ($\text{H}_2\text{O} : \text{acetone-d}_6 = 9:1$ v/v) and B ($\text{D}_2\text{O} : \text{acetone-d}_6 = 9:1$ v/v) with indicated states *I-V*. The real-time SR data are plotted as black dots in (a) and (b). The swelling ratio and bulk SLD obtained from kinetic ToF-NR data are plotted as blue dots and triangles for water vapor swelling, and as with yellow dots and triangles for the water/acetone- d_6 vapor switching. Reproduced with permission.[76] Copyright 2022 American Chemical Society.

maximum reached swelling ratio (1.84 for Experiment A and 1.80 for Experiment B) is slightly higher, but also the time until equilibrium is reached (after $t = 192$ min for Experiment A and $t = 220$ min for Experiment B) is shorter for the H_2O vapor swelling. We explain this by the stronger affinity of the DBC to H_2O than to D_2O molecules. This affinity leads to a higher thickness of the H_2O swollen films caused by a larger segment spacing between the polymer chains due to incorporated water molecules. Concerning the SLD values, the characteristic times are similar in both experiments. However, details of the curve shapes differ between thickness and SLD increase. This difference is attributed to a rearrangement of the polymer chains for accommodating water molecules, and to an H/D exchange taking place at the PNIPMAM amide groups. The findings are consistent with previous studies on the swelling behavior of DBCs based on PNIPMAM or PNIPAM in H_2O and D_2O atmosphere.[75], [184] Note that, after the equilibrium is reached, a slight decrease in thickness by 3 nm is observed for Experiment A, while the SLD value remains unchanged. This finding indicates a rearrangement of polymer chains after the absorption of large amounts of water.

The kinetics of water/acetone- d_6 vapor switching (state *IV* in Figure 5.5) show a similar

two-step contraction in the swelling ratio and SLD for both experiments A and B. In addition, a similar final equilibrium swelling ratio is reached after applying the acetone-d₆ vapor switching (1.47 for Experiment A, and 1.46 for Experiment B), although the initial (isotope sensitive) swelling ratios in state *III* are differed. Looking to the two-step contraction in more detail, first the films weakly contract almost at the time as they are exposed to the mixed water/acetone-d₆ vapor. After a brief equilibration phase, a second fast, but much stronger contraction occurs. Afterwards, the films shrink slowly over an extended time span until the final equilibrium value is reached after about 8 h.

When comparing the times at which each contraction sets in and when equilibrium is reached, it becomes evident that the co-nonsolvency effect differs for the films depending on the used water isotope species. The initial weak contraction happens immediately and is accompanied by a change in the SLD in the same time span after acetone-d₆ is introduced. Thus, a rapid uptake of acetone-d₆ and a quick release of water takes place in this scenario. The zwitterionic PSBs show a more pronounced H/D isotope sensitivity than PNIPMAM,[75], [81], [82], [113], [220] and the film contraction happens immediately for homopolymer PSBP thin films, but slowly for homopolymer PNIPMAM thin films in H₂O/acetone-d₆ mixed vapor (see Figure 5.2). Therefore, we attribute the first, weaker contraction to the PSBP block and the second, stronger contraction to the PNIPMAM block. Compared to the second, stronger shrinkage in mixed H₂O/acetone-d₆ vapor in the course of Experiment A, the second contraction in D₂O/acetone-d₆ solvent mixture in the course of Experiment B starts earlier (after $t = 345$ min for Experiment A and $t = 335$ min for Experiment B). We attribute this difference to the higher affinity of the PSBP block to H₂O, delaying the release of H₂O. This assumption is supported by the finding that the SLD reaches a stable value in Experiment B not only later than in Experiment A, and that the variation is also synchronous with the evolution of the swelling ratio.

The water content ($\phi_{\text{H}_2\text{O}}$ for Experiment A and $\phi_{\text{D}_2\text{O}}$ for Experiment B) and acetone-d₆ content ($\phi_{\text{acetone-d}_6}$ for both Experiments) are calculated for both kinetic processes (states *II* and *IV*). Both are plotted as a function of time in Figure 5.6.

The equilibrium values of water content ($\phi_{\text{H}_2\text{O}} = 52$ % for Experiment A and $\phi_{\text{D}_2\text{O}} = 44$ % for Experiment B) and acetone-d₆ content ($\phi_{\text{acetone-d}_6} = 5$ % for Experiment A and $\phi_{\text{acetone-d}_6} = 6$ % for Experiment B) in both experiments match well with the static results listed in Table A.1 (Appendix A. During the water vapor swelling process, a faster and stronger H₂O uptake is observed compared with the D₂O uptake. This further confirms that the studied DBC thin film has a stronger affinity towards H₂O than towards D₂O as explained before.

During the water/acetone-d₆ vapor switching process, a two-step release of water and a two-step uptake of acetone-d₆ is observed. This finding agrees with the two-step con-

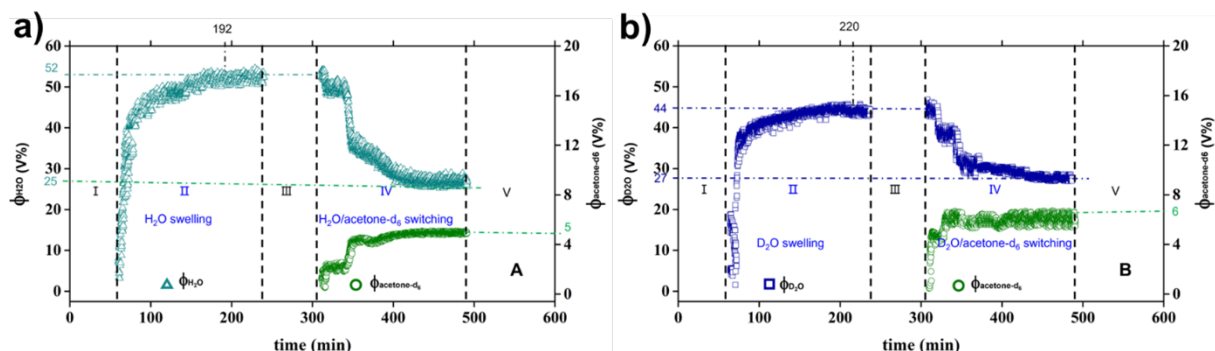


Figure 5.6.: Calculated water and acetone- d_6 contents as function of time for (a) Experiment A ($H_2O : acetone-d_6 = 9:1$ v/v) and (b) Experiment B ($D_2O : acetone-d_6 = 9:1$ v/v). H_2O (ϕ_{H_2O}), D_2O (ϕ_{D_2O}) and acetone- d_6 contents ($\phi_{acetone-d_6}$) are presented in cyan triangles, dark blue squares, and green circles, respectively. Reproduced with permission.[76] Copyright 2022 American Chemical Society.

traction in the swelling ratio, illustrated in Figure 5.5. It implies that the co-nonsolvency behavior is induced by a molecular substitution mechanism. The inter substitutions differ between different isotope species, as reflected in the different time scales of the second contraction step happening and an unusual slight fluctuation in $\phi_{acetone-d_6}$. As shown in Figure 5.6, the first pronounced water release occurs on a short time scale. It is triggered by an immediate pronounced absorption of acetone- d_6 in both experiments A and B, without any delay in time. We attribute this initial pronounced change to the PSBP block because of the pronounced isotope sensitivity of PSBs.[75] Since the increased strength of hydrogen bonds of H_2O over D_2O not only affects the stability of the hydration shell, but also decreases the mobility of H_2O species, the starting time of the second, stronger contraction step in mixed H_2O /acetone- d_6 vapor in Experiment A is slightly delayed compared to the D_2O /acetone- d_6 vapor mixture in Experiment B. This agrees well with the change observed in the swelling ratio. In addition, the whole process of the second step of solvent exchange in both experiments lasts for a longer time compared to the first one, in agreement with a previous report on related systems.[75], [184] This finding corroborates our understanding that the second contraction step is caused by the PNIPMAM block, and that the second step is followed by a third slower process when approaching the final equilibrium due to an internal rearrangement of the polymer chains.

In respective of the experiment, the equilibrium value ϕ_{H_2O} is like ϕ_{D_2O} at end of both water/acetone- d_6 switching processes, as well as the thickness and the final $\phi_{acetone-d_6}$ values. In addition, during the second, stronger contraction step, not only most of the water is released from the longer PNIPMAM block. We note also that D_2O is expelled faster than H_2O : ϕ_{H_2O} reaches equilibrium approximately at $t = 430$ min, while ϕ_{D_2O} reaches equilibrium at approximately at $t = 380$ min. This difference indicates a different

competition of the polymer chains between the absorption of acetone-d₆ and the hydration by H₂O or D₂O. Anyhow, the very sensitive co-nonsolvency behavior caused by a small number of acetone-d₆ molecules results in drastic changes in thickness and water content. Such sensitivity makes the studied DBC thin films attractive as candidates for *e.g.*, biopharmaceutical systems involving small amounts of acetone as co-solvent, as well as for molecular detection systems of acetone.

5.2.4. Solvation process around the functional groups

For the detection of direct water/acetone-d₆ - polymer interactions, Fourier transform infrared (FTIR) spectroscopy is used, following the same experimental design (Experiment A and Experiment B). By tracking the hydroxyl peaks of water molecules (O-H stretching vibration (around 3410 cm⁻¹) in H₂O molecules, and O-D stretching vibration (around 2540 cm⁻¹) in D₂O molecules), the characteristic peaks of acetone-d₆ (carbonyl peak C=O stretching vibration (around 1740 cm⁻¹) and methyl peak C-D symmetric vibration (around 1245 cm⁻¹)), which are convenient to avoid the overlap of peaks originating from the PNIPMAM block, can reveal information about the build-up and depletion of the hydration shell in the DBC films. Figure 5.7 shows the temporal evolution of the overall FTIR spectra after background and baseline correction. For clarity, enlarged FTIR spectra of the characteristic peaks of acetone-d₆ are presented in Figure A.3 (Appendix A).

During the water vapor swelling process, as marked with black arrows in Figure 5.7a and c, the build-up of the hydration shell is reflected in the height increase and area expansion of hydroxyl peaks assigned to water molecules. Similarly, the height decreases and area reduction of hydroxyl peaks during the acetone-d₆-induced switching process in Figure 5.7b and d represent the depletion of the hydration shell and the expulsion of water. As is expected, the opposite behavior of the characteristic peaks assigned to acetone-d₆ molecules is found due to the uptake of acetone-d₆, which is in good agreement with the results from the ToF-NR data.

Relative H₂O and D₂O contents are calculated by determining the peak areas of the O-H and O-D stretching vibrations, respectively. Furthermore, the acetone-d₆ content is obtained by determining the peak area of the C=O stretching vibration, as this peak has a minor overlap with neighboring other signals as compared with the C-D symmetric vibration. The derived values are plotted in Figure 5.8. A Gaussian fit and normalization to the three-folded peak of the CH₃isopropyl asymmetric stretching vibration (around 2970 cm⁻¹) are applied. The peak mainly derived from isopropyl groups of PNIPMAM block and methyl ammonium groups of PSBP block. The first one is affected neither by water vapor swelling nor the water/acetone-d₆ vapor switching.[75] In contrast, the second one is affected slightly by water vapor swelling, and undergoes only minor changes

5.2. DBC thin films in water and mixed water/acetone vapor

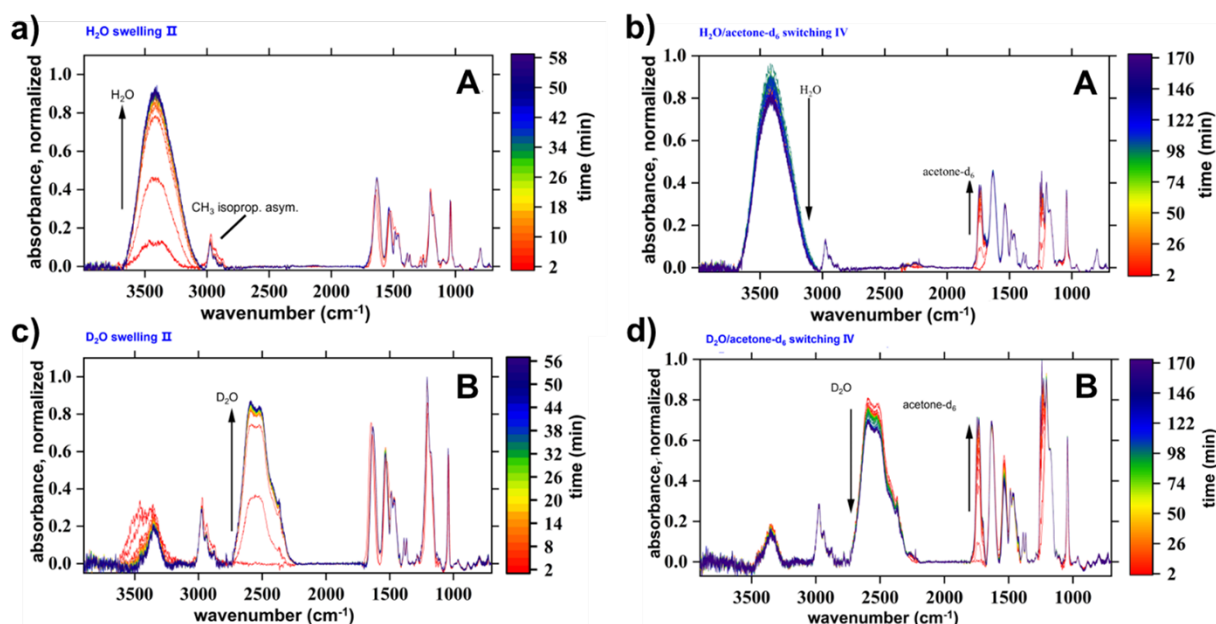


Figure 5.7.: FTIR spectra for Experiment A upon (a) H₂O vapor swelling, (b) H₂O/acetone-d₆ = 9:1 v/v vapor switching, and for Experiment B upon (c) D₂O vapor swelling, d) D₂O/acetone-d₆ = 9:1 v/v vapor switching. The time resolved FTIR spectra (curves recorded from red to purple) cover 60 min for the water vapor swelling process, and 180 min for the acetone-d₆ vapor switching process. The relevant characteristic peaks are indicated, and the emergence and decay of solvent-specific signals are marked with black arrows. Reproduced with permission.[76]
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compared with the peak changes of O-H and O-D stretching vibrations. Thus, it is approximated as constant in normalization.

In general, the temporal evolution of the water and acetone-d₆ contents is very similar to the behavior observed in the kinetic ToF-NR data analysis (seen in Figure 5.6) during the entire process. The observed D₂O uptake is not only faster during the water vapor swelling process, but also an obvious two-step mechanism is seen during the water/acetone-d₆ vapor switching process. This two-step process involves a first fast and pronounced step within a period of about 15 min, and a second slower step after more than 2 h of applying the solvent vapor switch, stretching over a longer time of about 60 - 90 min (Figure 5.8). This observation indicates that both blocks show separate and different solvation exchange behaviors. Moreover, compared to the acetone-d₆ absorption in Experiment A, in Experiment B a higher absorption level (0.08 for Experiment A and 0.15 for Experiment B) is reached in the final equilibrium. In agreement with the finding in Figure 5.6, the onset of the second changes occurs earlier in Experiment B than in Experiment A (Figure 5.8), indicating that the H₂O hydration shell of the DBC thin films has a higher stability than the D₂O hydration shell. For the H₂O vapor swelling process, the OH-peak intensity

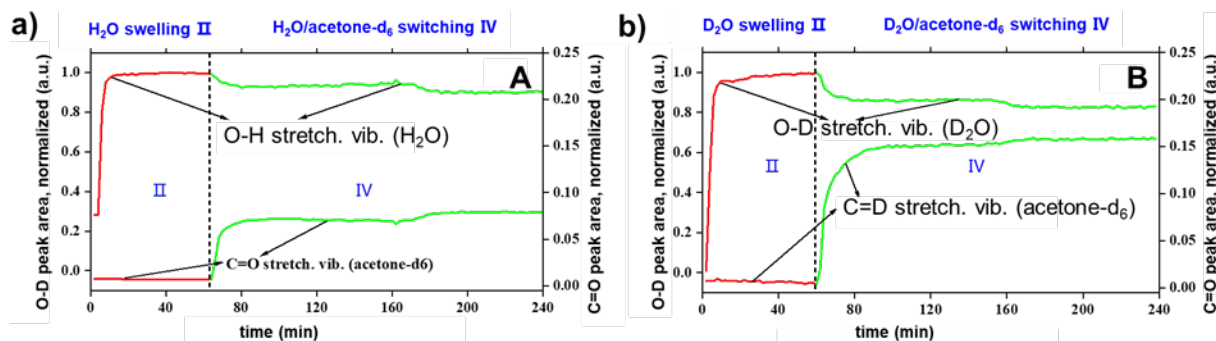


Figure 5.8.: Integrated FTIR peak areas of solvent-specific signals as a function of time. (a) O-H stretching vibration (around 3410 cm^{-1}) and C=O stretching vibration (around 1740 cm^{-1}) are assigned to H₂O and acetone-d₆ in Experiment A. (b) O-D stretching vibration (around 2540 cm^{-1}) and C=O stretching vibration (around 1740 cm^{-1}) are assigned to D₂O and acetone-d₆ in Experiment B. Each peak area is normalized to the three-folded peak area of the asymmetric CH₃ isopropyl stretching vibration. Reproduced with permission.[76] Copyright 2022 American Chemical Society.

at the starting point is not zero, due to un-removable H₂O molecules inside the thin N₂-dried films, as described before.[75] This is not only seen in FTIR spectra (Figure 5.7a) but also in the kinetic ToF-NR data (Figure 5.6a). A direct comparison of absolute values from the IR spectra and from the ToF-NR measurements is not possible.

In contrast to the ToF-NR measurements, the FTIR spectra offer not only the possibility to detect the water uptake and acetone-d₆ release. They also provide insight into the local chemical surroundings of the functional groups within the thin films. The shift in the peak positions allows for analyzing changes of the different solvation states, and thus, to gain further information on the mechanisms of the solvent exchange. The peak shifts of the characteristic signals of the amide groups present in both blocks are known to result from the formation and breakage of hydrogen bonds, which are related to the hydrophilic surroundings, as found before for PNIPAM.[73]–[75], [184] The carbonyl group bonding to one or two water/acetone-d₆ species (namely amide *I* band) is located in the wavenumber range $\nu = 1630 - 1650\text{ cm}^{-1}$, and the amide proton bonding to one water/co-solvent species (namely amide *II* band) is located in the wavenumber range $\nu = 1510 - 1540\text{ cm}^{-1}$. The peak position of the anionic SO₃[−] group (namely S-O asymmetric stretching vibration), which is characteristic for the PSB block, is located within the wavenumber range $\nu = 1035 - 1045\text{ cm}^{-1}$. It responds to the bond energy changes upon hydration.[75] The temporal evolutions of the peak positions of the amide *I* band, amide *II* band and the S-O asymmetric vibration band are analyzed for each FTIR spectrum during both kinetic processes using Gaussian fits. The results are displayed in Figure 5.9.

Upon water vapor swelling (state *II*), the position of the S-O asymmetric vibration signal

5.2. DBC thin films in water and mixed water/acetone vapor

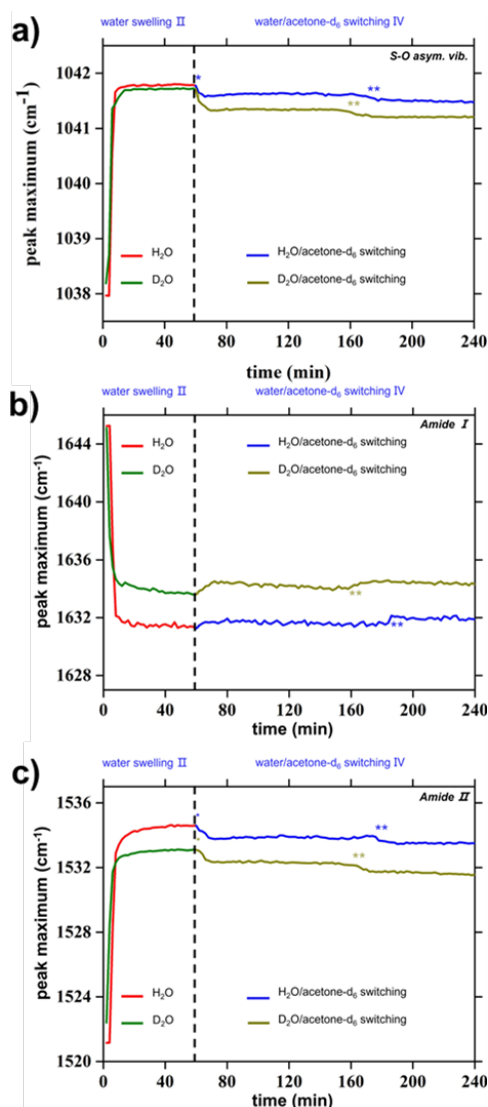


Figure 5.9.: Temporal evolution of FTIR peak position shifts of (a) the asymmetric S-O stretching vibration ($\nu = 1035 - 1045 \text{ cm}^{-1}$) representative for the PSBP block and (b) amide *I* band ($\nu = 1630 - 1650 \text{ cm}^{-1}$) as well as (c) amide *II* band ($\nu = 1510 - 1540 \text{ cm}^{-1}$) representing the overall behavior due to presence of secondary amide groups in both blocks. Reproduced with permission.[76] Copyright 2022 American Chemical Society.

shifts towards higher wavenumbers, since the anionic SO_3^- group acts as the hydrogen bond donor. The same trend is observed for the amide *II* signal. However, the peak shift of the amide *I* signal is opposite to the one of the amide *II*, since the carbonyl group ($\text{C}=\text{O}$) acts as the hydrogen bond acceptor and the amide proton (N-H) also acts as the hydrogen bond donor. All observed peak shifts during the water hydration process match well earlier reports on related polymers.[74], [75], [184]

During the water vapor swelling, the shift of the S-O asymmetric vibration signal reaches

a similar equilibrium wavenumber in both Experiments A and B, irrespective of using H₂O or D₂O (Figure 5.9a). In contrast, the peak position shifts of the amide *I* and amide *II* bands occurring upon H₂O vapor swelling are always more pronounced than those upon D₂O swelling (Figures 5.9b and c). This observation confirms that the amide group plays an important role in the hydration process and corroborates that the DBC films forms a stronger hydration shell in H₂O compared to D₂O. The shift of the S-O asymmetric vibration signal is explained by an increased space for bond vibration and rotation due to the incorporated water. After water hydration, all peak position shifts reach equilibrium, corresponding to the swollen static state (state *III*).

The water/acetone-d₆ vapor switching (state *IV*) is initiated as soon as acetone-d₆ vapor is introduced into the system, resulting in a distinct two-step transition. This consists of a nearly instantaneous first transient reverse shift of the peak positions (marked with single star in Figure 5.9), followed by a delayed second reverse shift (marked with a double star in Figure 5.9). In the D₂O/acetone-d₆ mixture, the second backshift happens earlier than in the H₂O/acetone-d₆ mixture, like observations made with ToF-NR. Thus, the two-step solvent exchange process and a more stable hydration shell of H₂O compared to D₂O are also observed here. When comparing the magnitude between the two steps in the backshift of the amide *I* and amide *II* peak positions, no pronounced differences are found, since the amide group exists in both blocks, PSBP and PNIPMAM. Whereas, comparing with our previous co-nonsolvency study in water/methanol vapors,[22], [61] the magnitude in second backshift of the amide *I* and amide *II* peak positions is relatively weak, which is addressed to the use of aprotic acetone instead of protic methanol.

Concerning the SO₃⁻ group exclusively located in the PSBP block, we note that the first peak backshift of the S-O asymmetric vibration peak is slightly more prominent than the second one. This finding supports our assumption that the PSB block dominates the first step of the solvation exchange behavior, while the PNIPMAM block dominates the second step. Moreover, the peak backshift in the S-O asymmetric vibration signal takes also place in two steps and does not present just a single shift upon acetone-d₆ vapor switching. Thus, the solvation exchange processes assigned to both blocks mutually affect each other, disposing of comparable hydration capacities. Since a two-step thickness contraction of the films along with the continuous loss of water and adsorption of acetone-d₆, a steric squeezing will restrict the bonding vibration and rotation of the S-O asymmetric vibration, resulting in a two-step weakening of the oscillation frequency. Accordingly, the polymer chains in the studied DBC films undergo several conformational transitions when swollen in water vapor or in water/acetone-d₆ mixed vapors, respectively, as shown in Figure A.4 (Appendix A).

5.3. Conclusions

For the first time, mixed water/acetone vapor induced co-nonsolvency is found in thin thermoresponsive polymer films. In case of PSBP, the film contraction is caused by acetone-d₆ acting as a non-solvent, whereas for PNIPMAM, acetone induces co-nonsolvency in mixed saturated water/acetone-d₆ atmosphere. In case of PSBP₈₀-*b*-PNIPMAM₁₁₅, a complex two-step contraction mechanism is seen. The PSBP block pre-dominates the first step and the PNIPMAM block dominates the second step, during which the solvation exchange processes assigned to both blocks mutually affect each other. Remarkably, a co-nonsolvency effect is established for the nonionic PNIPMAM block, both in mixed water-acetone solutions as well as in mixed vapor swollen films. The zwitterionic and the nonionic blocks of the DBC show a separate but interlinked solvent exchange behavior in water/acetone-d₆ vapor atmosphere. Besides studying the affinity of the DBC thin film towards water or deuterium water, the sensitivity and stability of the formed hydration shell exposed to mixed water/acetone-d₆ vapor atmosphere is revealed. The co-nonsolvency effect is seen in the less polar and moreover aprotic solvent acetone, in contrast to methanol or ethanol studied before. In particular, the newly studied films contract more drastically at a lower concentration of the trigger co-solvent.

KCl-modulated hydration and subsequent thermoresponsive behavior

This chapter is based on the publication “KCl-Modulated Hydration and Subsequent Thermoresponsive Behavior of Poly(sulfobetaine)-Based Diblock Copolymer Thin Films” (P. Wang, C. Geiger, J. Reitenbach, A. Vagias, L. P. Kreuzer, S. Liang, R. Cubitt, V. Hildebrand, A. Laschewsky, C. M. Papadakis and P. Müller-Buschbaum, *Macromolecules* **2023**, 56, 4087-4099; DOI: 10.1021/acs.macromol.3c00484). Reproduced with permission.[108] Copyright 2023 American Chemical Society.

Introduction

Characteristically, the CP_{PSBP} in aqueous solution increases initially with sodium salt concentration up to a maximum value, while further addition of salt decreases the CP_{PSBP} strongly, often below the freezing point of water.[81], [82] So far, the salt effects on $LCST_{PNIPMAM}$ of the homopolymer PNIPMAM are not clear yet.[83] Still, a few studies on the modulation of the transition temperatures of DBCs containing PNIPMAM by added salt were reported, in which a long PSBP block was combined with a short PNIPMAM block.[82], [84] It was found, that $LCST_{PNIPMAM}$ decreases slightly with increasing polymer concentration and does not show significant sensitivity towards the added NaBr. Thereby, three or even four different solubility regimes of the DBC were realized by the addition of electrolytes to tune the CP_{PSBP} and the $CP_{PNIPMAM}$, respectively.⁸¹ In addition, the micellar size and shape both change by varying the PNIPMAM block length.[83], [84]

In this chapter, I investigate the inverted block copolymer system, in which a shorter PSBP₅₀ is combined with a much longer PNIPMAM₁₅₅ and study the impact of the varied relative block lengths on the swelling characteristics of its thin films in the presence of

KCl. A particularity of the chosen DBC, PSBP₅₀-*b*-PNIPMAM₁₅₅, is that the LCST-type transition temperature of the PNIPMAM-block in D₂O ($CP \approx 43\text{ }^{\circ}\text{C}$ at 50 g L^{-1}) is very close to the UCST-type transition temperature of the PSBP-block ($CP \approx 41\text{ }^{\circ}\text{C}$) in terms of thermoresponsivity.[117] In addition to the KCl-loaded DBC thin films of PSBP₅₀-*b*-PNIPMAM₁₅₅, I also prepare the analogous films of the homopolymers PSBP₅₀ and PNIPMAM₆₆ for comparison.

In this chapter, *in situ* ToF-NR is applied to study the effect of salt addition on the D₂O absorption behavior of the DBC thin films during swelling and heating. Meanwhile the real-time thickness is detected by *in situ* SR. The solvation-induced phase transition upon D₂O hydration and subsequent heating is probed *in situ* by FTIR spectroscopy. Besides, the migration and/or aggregation of KCl domains inside the DBC thin films are characterized by XRR) and AFM.

6.1. Swelling in D₂O vapor and temperature protocol

The experimental protocol applied for *in situ* SR, ToF-NR, and FTIR measurements of salt-free and KCl-loaded DBC (PSBP₅₀-*b*-PNIPMAM₁₅₅) thin films is illustrated in Figure 6.1. The applied vapor protocol is described in Section 4.4. During the neutron measurements, the established three static states (stage *I*, *III*, *V*) are characterized by static ToF-NR measurement and two dynamic processes (stage *II*, *IV*) are followed by *in situ* ToF-NR. The ToF-NR parameters are listed in Section 3.1. During the heating process (stage *IV*), the saturated D₂O vapor temperature is increased slowly from $T = 18\text{ }^{\circ}\text{C}$ to $T = 42\text{ }^{\circ}\text{C}$ with a temperature rate of $8\text{ }^{\circ}\text{C/h}$, to provide sufficient time for movement or rearrangement of polymer segments. Simultaneously with the ToF-NR measurements, SR characterization is performed over the entire procedure to independently corroborate the film thickness. In addition, to investigate the interaction mechanism between solvent molecules and polymer chains at the molecular level, the process is monitored via *in situ* FTIR spectroscopy.

6.2. KCl-modulated phase transition behavior of homopolymer thin films

To obtain first insights into the influence of KCl on the swelling in D₂O vapor and the subsequent thermoresponsive behavior, the DBC thin films and the corresponding homopolymers are studied by *in situ* SR measurements. Figure 6.2 displays the swelling ratio (d/d_{ini}) as a function of time following the experimental protocol of Figure 6.1. The samples for SR measurements have initial thicknesses in the range of $d_{ini} \approx 25 - 35\text{ nm}$.

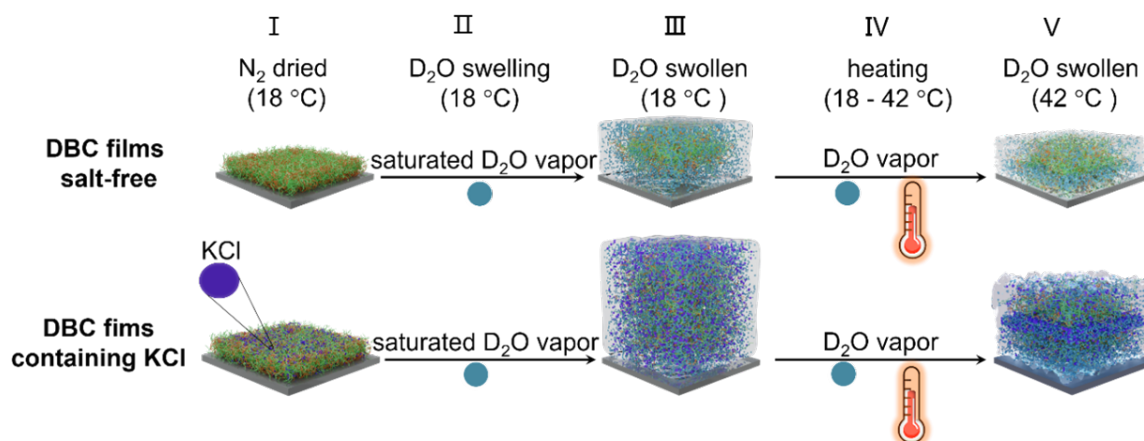


Figure 6.1.: Experimental protocol applied for SR, ToF-NR, and FTIR studies on salt-free and KCl-loaded DBC or homopolymer thin film samples. Distinct sequential stages and kinetic processes are labeled as follows: N₂ dried stage at $T = 18\text{ }^{\circ}\text{C}$ (I), D₂O swelling kinetics at $T = 18\text{ }^{\circ}\text{C}$ (II), D₂O swollen stage at $T = 18\text{ }^{\circ}\text{C}$ (III), kinetics during heating from $T = 18$ to $T = 42\text{ }^{\circ}\text{C}$ (IV), and D₂O swollen stage at $T = 42\text{ }^{\circ}\text{C}$ (V). Reproduced with permission.[108] Copyright 2023 American Chemical Society.

As shown in Figure 6.2, all the samples present a fast thickness increase during the D₂O swelling (stage II). For all polymers, the reached swelling ratio is higher for KCl-loaded films than for the corresponding salt-free films (by a factor of 1.09 for PSBP, of 1.13 for PNIPMAM, and of 1.33 for the DBC). Thus, the added salt enhances the D₂O swelling stronger for the DBC than for the homopolymer films, due to the higher molecular weight of the PNIPMAM block compared to the homopolymer PNIPMAM. Compared to our recent study on NaBr-modulated D₂O swelling of DBC films,[221] we note (i) a larger final swelling ratio upon D₂O hydration for KCl-loaded DBC films, as well as (ii) a stronger increment in the swelling ratio relative to their corresponding salt-free counterparts (the maximal equilibrium swelling ratio was 1.4 for KCl-loaded DBC films, and the analogous increase factor was 1.10 for NaBr-loaded samples).

As shown in Figure 6.2, once the heating has started, the swelling ratios of all the films undergo first an increase but after longer heating, PNIPMAM homopolymer films and DBC films undergo a partial contraction. However, the thermoresponsive behavior is quite different. Both PSBP homopolymer films, with and without KCl, show a maximum after 10 min (Figure 6.2a), and then a plateau is observed. In the case of both PNIPMAM homopolymer films (Figure 6.2b), the swelling ratio of the KCl-loaded film reaches its maximum faster than the salt-free film, and then both films contract. Concerning both DBC films (Figure 6.2c), the swelling ratios reach their maximum at the same time as the corresponding PSBP homopolymer film, and then remain in a short plateau before

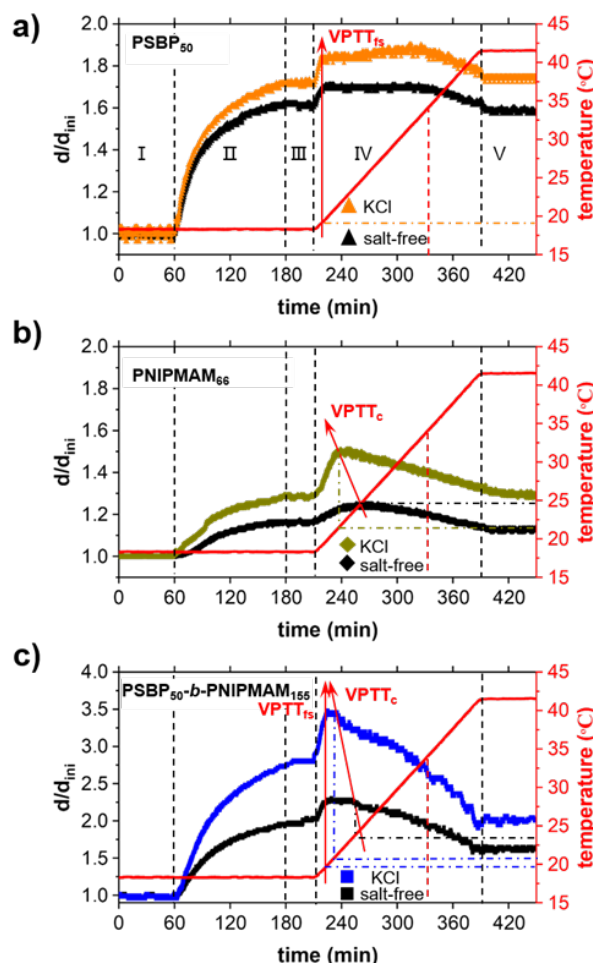


Figure 6.2.: Swelling ratio d/d_{ini} obtained from SR measurements as a function of time for (a) PSBP₅₀, (b) PNIPMAM₆₆, and (c) PSBP₅₀-*b*-PNIPMAM₁₅₅ thin films with the stages I-V indicated according to Figure 6.1. The evolution of the temperature is plotted as red solid lines with a red dotted line indicating the time at which the relative humidity starts to decrease, as shown in Figure B.1 (Appendix B). Reproduced with permission.[108] Copyright 2023 American Chemical Society.

contraction sets in. Interestingly, like PNIPMAM homopolymer films, the KCl-loaded DBC film starts to contract earlier than the salt-free film does.

Both PSBP homopolymer films reach a maximum for the same temperature, labeled as $VPTT_{fs} = 18.6\text{ }^{\circ}\text{C}$ (marked by the red arrow in Figure 6.2a and listed in Table B.1a, Appendix B). This proves that KCl does not affect the $VPTT$ of PSBP homopolymer. This finding contrasts with the previous observations in dilute aqueous solution, where the addition of salts significantly affected the CP'_{PSBP} . [55], [81], [117] In addition, both PSBP films (KCl-loaded and salt-free) keep an equilibrated film thickness for 120 min after crossing $VPTT_{fs}$. This suggests that the subsequent response is temperature indepen-

dent. Even a continuously rising temperature does not modify the swelling characteristics of these thin films, thereby confirming that the further swelling of the PSBP thin films during the heating process is mainly due to the UCST-type phase transition of PSBP. We also notice that a film contraction happens at higher temperatures ($T > 33\text{ }^{\circ}\text{C}$). This can be explained by the decreasing relative humidity caused by the elevated temperature (see Figure B.1, Appendix B). However, during the heating process, both PNIPMAM homopolymer films feature a strong time- and salt-dependent evolution. The KCl-loaded film further swells for about 35 min, while the salt-free film swells for another 60 min. This behavior indicates that the further swelling of the PNIPMAM films is mainly due to the increase in temperature, which leads to the intensified motion of the polymer segments. The PNIPMAM films contract differently with increasing temperature after passing the $VPTT$, labeled as $VPTT_c$ (marked by the red arrow in Figure 6.2b and listed in Table 2.1a, Appendix B), which is attributed to the LCST-type phase transition of PNIPMAM. Notably, the $VPTT_c$ of KCl-loaded PNIPMAM film shifts towards lower temperatures compared to the salt-free film, in agreement with the studies of the salt effect on aqueous solutions of the PNIPMAM-analog PNIPAM. Interestingly, both PNIPMAM films contract steadily without an intermediate plateau as shown by the PSBP homopolymer films. This behavior is attributed to the decreased relative humidity at high temperatures.

6.3. KCl-modulated phase transition behavior of PSBP-*b*-PNIPMAM thin films

6.3.1. Swelling ratio response to the experimental protocol

As shown in Figure 6.2c, the thermoresponsive behavior of the DBC films during the entire heating process can be seen as the joint result of contributions of the PSBP and PNIPMAM blocks, throughout both the “further-swelling” and subsequent “film contraction” periods. When comparing the swelling ratio and the $VPTT$ between the DBC and the homopolymer films (KCl-loaded or salt-free), a stronger variation (increase and subsequent decrease) in the swelling ratio of the DBC films is observed, as well as $VPTT_{fs}$ and $VPTT_c$ (marked by red arrows in Figure 6.2c and listed in Table B.1a, Appendix B) appear. Both $VPTT_{fs}$ and $VPTT_c$ shift towards lower temperatures compared to the $UCST_{PSBP}$ and $LCST_{PNIPMAM}$ reported in aqueous solution, reflecting an impact of high polymer concentration in thin-film geometry.[222] Besides, the $VPTT_{fs}$ of the DBC films shifts slightly to higher temperatures compared to the PSBP homopolymer films, while the $VPTT_c$ shifts slightly to lower temperatures compared to the PNIPMAM homopolymer films. In analogy to the PSBP films, both the salt-free and salt-loaded DBC

films show a brief equilibrium phase after achieving the same $VPTT_{fs}$ (see Table B.1a, Appendix B), but their appearance and duration are salt-dependent. This brief “further-swelling” period likely originates from the UCST-type phase transition of the PSBP blocks. Similarly, above the $VPTT_c$, the films subsequently contract with the same kinetic trends as for the PNIPMAM homopolymer films, indicating that the LCST-type phase transition of the PNIPMAM blocks dominates this particular “film contraction” period of the DBC films. Looking at the “film contraction” period of the DBC films (with and without salt) in more detail, there are still some small fluctuations in thickness at high temperatures. These are attributed to the PSBP block contraction caused by the elevated temperature, as described before. However, the shift of $VPTT$ markedly differs from the previous study on the NaBr-modulated phase transition behavior of PSBP-*b*-PNIPMAM with inverted relative block sizes.[221] For the latter, the $VPTT_c$ of PNIPMAM did not shift in thin-film geometry, while the $VPTT_{fs}$ of PSBP shifted similarly to the salt effect found in aqueous solutions.[55], [81], [117] The different VPT behavior of the DBC films is probably a consequence of the much smaller relative block length of the PSBP block in the present study in the DBC. Thus, our findings provide the first evidence that the swelling response of such PSBP-*b*-PNIPMAM double thermoresponsive thin films in presence of a monovalent salt depends also on the relative block lengths.

6.3.2. Polymer density and the migration of KCl

To investigate the polymer density and the migration of KCl within the DBC thin films after the D₂O swelling and subsequent heating processes, XRR measurements are performed following the description in Section 3.1. The XRR data with the corresponding best fits as well as the related SLD profiles are shown in Figure B.2 (Appendix B). After N₂ drying at $T = 18\text{ }^{\circ}\text{C}$, both as-prepared films show a uniform and flat SLD profile, which demonstrates the presence of homogenous DBC films on the Si substrates. For the DBC without salt, the SLD profile is slightly lower than the theoretically calculated bulk SLD (see Table 3.1 in 3.1). This may originate from a less dense chain packing in the thin film than expected, and/or from remaining H₂O molecules in the film ($SLD_{H_2O} < SLD_{DBC}$ for X-rays). We note that the SLD increases close to the bulk SLD at the substrate interface, indicating that a chain conformation close to the bulk is assumed at the substrate. The KCl-loaded DBC film exhibits a larger surface roughness than the salt-free sample. After D₂O swelling at $T = 42\text{ }^{\circ}\text{C}$ (stage V), the SLD profiles show a layered shape, indicating a reorganization of the film.

The presence of salt increases the complexity of the SLD profile, since the SLD value is increased in the middle of the DBC layer. This observed value is very close to the

calculated theoretical SLD of the DBC containing 5 mM KCl (see Table 3.1 in 3.1). This finding implies that the KCl salt is heterogeneously distributed along the surface normal and is enriched in the intermediate section of the film. In addition, the SLD at the film surface is reduced also in the presence of KCl, which can be explained by pore formation in the surface-near film zone in analogy to the salt-free DBC film.

6.3.3. Surface topography at ambient conditions

Since the XRR data implies that the sample surfaces have changed after the experiment, AFM is used to monitor the surface topography at ambient conditions after the three static stages were reached (stage *I*, *III*, and *V*). When comparing the three AFM images for each DBC thin film shown in Figure B.3 (Appendix B), a change in the surface topography is observed after the hydration by D₂O. The film surface is smoother than it is in the as-prepared samples (see *RMS* roughness values S_q in in Figure B.3 (Appendix B)). Such changes are attributed to the rearrangement of the polymer chains after D₂O hydration, as seen in our previous studies.[76], [221]

In both films, small aggregates are formed after the heating process, for which the size is larger in the KCl-loaded than in the salt-free DBC film. These findings reconfirm that the presence of an inorganic salt such as KCl significantly changes the topography of organic DBC films. This might be one reason why KCl affects the thermoresponsive behavior of PSBP-*b*-PNIPMAM in thin-film geometry. Irreversible changes on the surface microstructure are obtained that do not fully “erase” even though the sample is returned to room temperature after the heating.

6.3.4. Investigation of static equilibrium stages

Static ToF-NR measurements are performed to characterize the film thickness and the SLD values at the static stages for the salt-free and KCl-loaded DBC thin films following the experimental protocol in Figure 6.1. By analyzing the obtained SLD profiles, information on film composition and the D₂O distribution along the film normal is obtained. The D₂O content is calculated according to the description in Section 3.1.

The static NR curves with the best fits, as well as the obtained SLD profiles, are shown in Figure 6.3. A two-layer model is used to fit the static NR data of the N₂ dried films at $T = 18\text{ }^{\circ}\text{C}$ (stage *I*) and D₂O swollen films at $T = 18\text{ }^{\circ}\text{C}$ (stage *III*) for both DBC films (with and without salt). The static data of the D₂O swollen films at $T = 42\text{ }^{\circ}\text{C}$ (stage *V*) is fitted by a three-layer model for the salt-free sample but requires a four-layer model for the KCl-loaded sample. The variations in the Kiessig fringes spacing and q_z position of the critical edge illustrate the change in film thickness and SLD values (*i.e.*

the incorporated D₂O content). The corresponding SLD profiles are displayed in Figures 6.3b and d and the results are listed in Table B.2 (Appendix B). For example, compared to the NR curves measured in the dry stage *I* (purple symbols), a reduction in the fringe spacing and a shift in the critical edge towards higher Q_z values is observed for the D₂O swollen films at $T = 18\text{ }^{\circ}\text{C}$ (stage *II*, green symbols). The corresponding SLD profiles visualize the increase in the film thickness (58 nm for the salt-free and 94 nm for the KCl-loaded film, see Table B.2, Appendix B) and the absorption of D₂O molecules (46 % (V %) for the salt-free and 77 % (V %) for KCl-loaded film, see Table B.2, Appendix B) respectively. Although the water sensitivity of salt-free PSBP-*b*-PNIPMAM thin films was documented in our previous study,[76] such a strong water swelling behavior accompanied by drastic water absorption in a KCl-loaded sample has not been realized. This finding demonstrates that the presence of KCl strongly promotes the D₂O absorption ability of the DBC film, which in turn facilitates the migration or aggregation of KCl inside the thin film upon the subsequent heating. This behavior might be related to a more effective plasticizing effect, thus lowering the very high glass transition temperature of the dry polyelectrolyte block. Similarly, an increase in the fringe spacing and a shift in the critical edge towards lower q_z values in the NR data for the D₂O swollen films at $T = 42\text{ }^{\circ}\text{C}$ (stage *III*, pink symbols) demonstrate the contraction of both DBC films and the release of D₂O molecules, respectively. In the two NR curves of the N₂ dry films (stage *I*, purple symbols), a big difference in the amplitude of the Kiessig fringes is observed, similar to the XRR data, which is caused by a significant difference in surface roughness.[76] This finding confirms that the surface roughness of salt-loaded DBC films prepared by spin-coating is generally higher than that of salt-free DBC films, as is seen in the AFM data. In addition, a higher bulk SLD value of the KCl-loaded DBC film is observed due to the presence of KCl (see Table 3.1 in Section 3.1). As shown in Figures 6.3b and d, a D₂O enrichment layer exists in all SLD curves at the polymer-substrate interface. Because the hydrophilic SiO₂ layer on the Si substrate attracts D₂O molecules towards this interface, an increased SLD results. Such water enrichment was already found in other thermoresponsive polymer films.[76], [184]

In the D₂O swollen films at $T = 42\text{ }^{\circ}\text{C}$ (stage *V*, pink lines in Figures 6.3 b and d) major changes in the SLD profiles are found. Without salt, the polymer film forms two layers with a less dense near-to-air interface part. For the KCl-loaded DBC film, an enrichment of salt in the middle of the DBC film occurs together with the pores formed in the near-to-air interface part. Thus, after hydration and heating, the PSBP-*b*-PNIPMAM contraction causes a heterogeneous salt distribution. These structural changes are partially preserved after bringing the films back to ambient temperature, as seen by XRR and AFM. Taking the consistency of variations in the SLD profiles between XRR and NR data

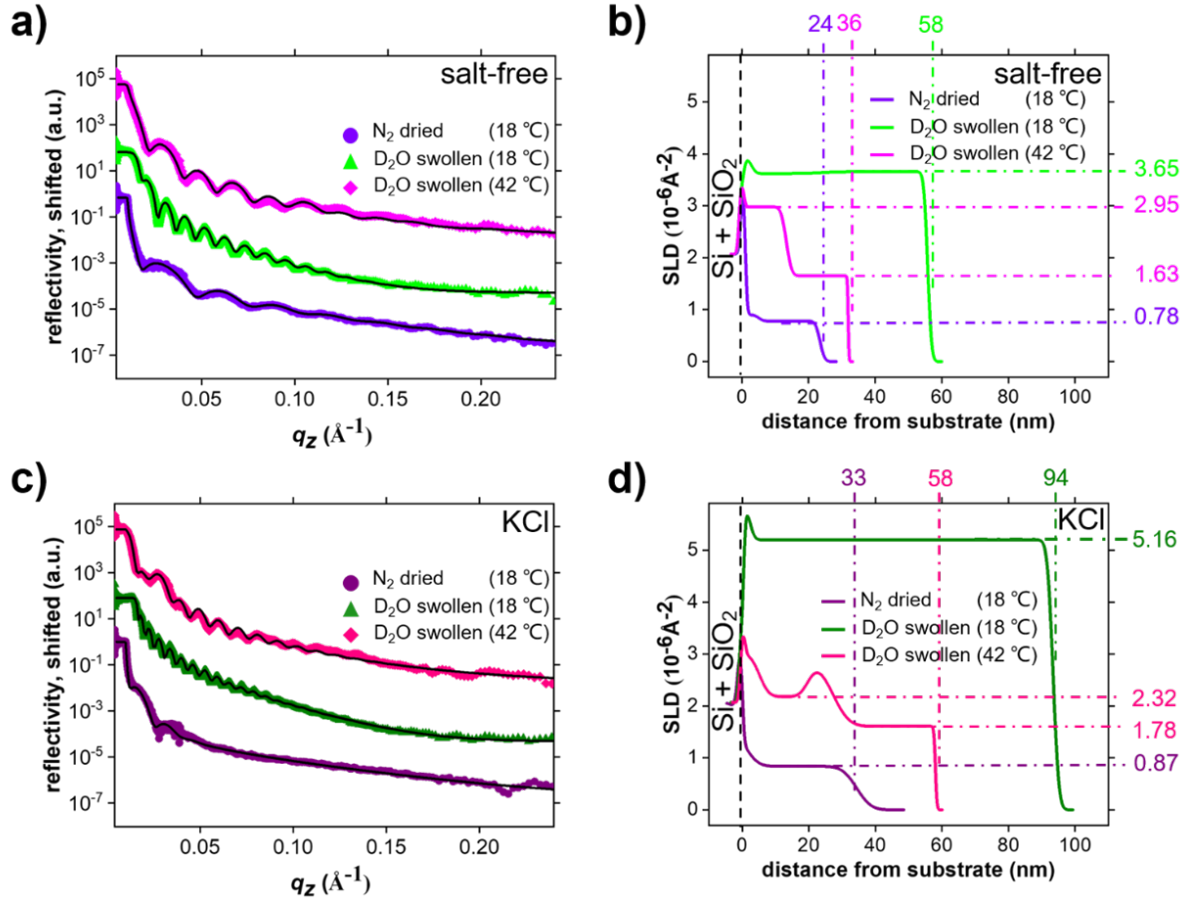


Figure 6.3.: (a, c) Static ToF-NR data (symbols) and (b, d) derived SLD profiles for (a, b) salt-free DBC thin film and (c, d) KCl-loaded DBC thin film. The reflectivity curves and corresponding SLD profiles at N_2 dried ($T = 18\text{ }^\circ\text{C}$) static stage (I), D_2O swollen ($T = 18\text{ }^\circ\text{C}$) static stage (III), and D_2O swollen ($T = 42\text{ }^\circ\text{C}$) static stage (V) are colored in purple, green and pink respectively. The black solid lines in the NR graphs represent the best fit. The black dashed lines in the SLD profile graphs indicate the substrate surface and related thickness and SLD values are listed on the corresponding axes. Reproduced with permission.[108] Copyright 2023 American Chemical Society.

for each DBC thin film as well as their respective environment into account, we attribute this partially preserved internal morphology changes to the migration or aggregation of KCl inside the thin-film geometry. The subsequent D_2O release and film contraction is partially obstructed by the KCl distribution, as the SLD values of the sublayers near the polymer-air interface are always lower than the SLD values of the sublayers near the polymer-substrate interface. This assumption is also supported by the data summarized in Table B.2 (Appendix B): After the heating process, the D_2O content decreases from 46 % to 25 % for the salt-free film and decreases from 77 % to 28 % for the KCl-loaded

film. In agreement, the swelling ratio decreases from 2.4 to 1.5 for the salt-free film and decreases from 2.8 to 1.7 for the KCl-loaded film, which is very close to the SR results.

6.3.5. D₂O hydration and subsequent thermal stimulus kinetics

For further understanding, both kinetic processes of the DBC thin films are monitored with *in situ* ToF-NR measurements. Selected kinetic NR curves (symbols) with their corresponding fits (black solid lines) are shown in Figure 6.4a, as well as the SLD profiles during the “film contraction” period. Equally to the static NR fits, a two-layer model is selected for the batch fitting of the kinetic NR data to describe the D₂O swelling for both DBC films. A three-layer model and a four-layer model are applied to fit the kinetic NR data during heating for the salt-free and KCl-loaded films, respectively.

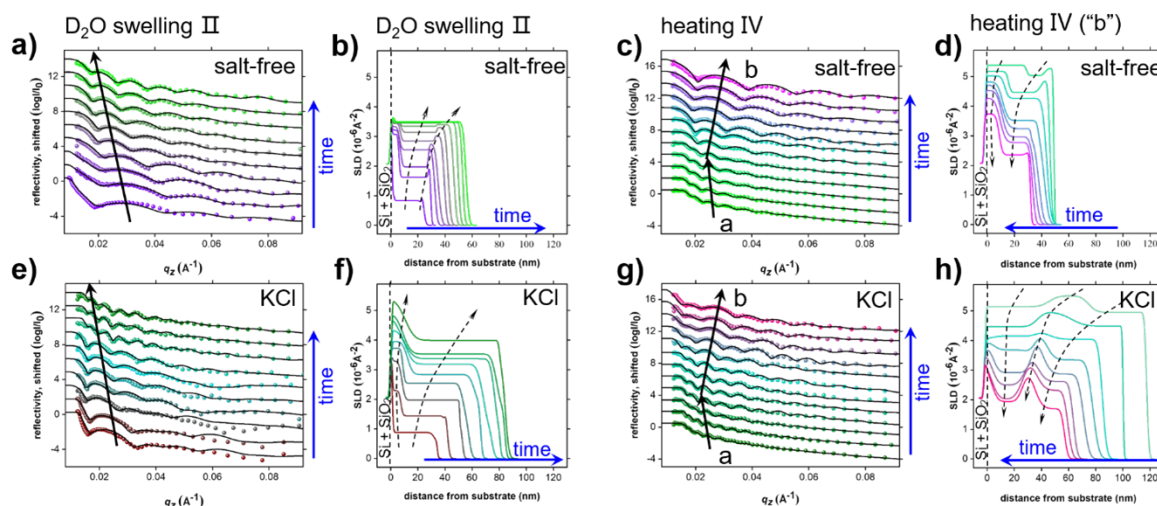


Figure 6.4.: Selected kinetic NR data (symbols) with corresponding fits (black solid lines) during (a, e) D₂O swelling (II) and (c, g) heating (IV) processes, as well as (b, f) corresponding SLD profiles during D₂O swelling (II) and (d, h) part of corresponding SLD profiles during the “film contraction” period for the (a, b, c, d) salt-free DBC and (e, f, g, h) KCl-loaded DBC thin films. For D₂O swelling processes the selected curves are taken at $T = 0, 2, 5, 10, 15, 20, 30, 50, 75$, and 100 min. For heating processes, the selected curves are taken at $T = 0, 5, 10, 20, 30, 40, 50, 60, 80, 100, 120$, and 150 min. The curves are vertically shifted for clarity. The blue time bar arrows are drawn for clarity; the color gradient indicates the kinetic transition between different static stages. The shift of the Kiessig fringe maxima is marked with black arrows. Concerning the ToF-NR curves in stage IV, the “a” and “b” represent the “further-swelling” and the “film contraction” periods upon heating respectively. The vertical black dashed lines indicate the surface of the substrate in the SLD profiles. Dashed black arrows in the SLD profiles indicate temporal evolution. Reproduced with permission.[108] Copyright 2023 American Chemical Society.

Upon D₂O swelling (stage *II*), the Kiessig fringe maxima move towards lower q_z values over time for both DBC films, as highlighted by the black arrows in Figures 6.4a and e, which represents the increase in the film thickness due to an uptake of D₂O molecules. During the heating processes (stage *IV*), the movement of Kiessig fringe maxima exhibits a non-monotonic variation and reverses over time, as marked with black arrows in Figures 6.4c and g. While the Kiessig fringe minima first shift slightly towards lower q_z values for a short time (see highlighted black arrows of “a”), they then shift towards higher q_z values (see highlighted black arrows of “b”). This observation indicates that for all heating processes the thickness of the DBC films first increases (“further-swelling” period) and then decreases (“film contraction” period), as found also in the SR results (Figure 6.2). The corresponding SLD profiles obtained from the selected reflectivity curves during D₂O swelling (stage *II*) are shown in Figures 6.4b and f. A two-layer SLD profile is gradually formed during D₂O swelling (stage *II*). For the salt-free DBC film, the D₂O hydration goes fast in the layer near the polymer-substrate interface at the beginning ($t < 10$ min), and then gradually expands towards the entire polymer layer. Especially, a high SLD is observed at the layer near the polymer-air interface. After 60 min, the SLD of the polymer layer reaches an equal value to the polymer-air interface, while the thickness still increases slowly. In contrast, both SLD profiles at the layers (near the polymer-substrate interface and polymer layer) expand fast and synchronously for the KCl-loaded DBC film, and this expansion trend is still maintained even after 100 min. Different from the observation in the SLD profiles of the salt-free DBC film, an SLD plateau at the layer near the polymer-air interface disappears in the SLD profiles of the KCl-loaded DBC film. This phenomenon is explained by the temporal evolution of the swelling ratio D₂O content extracted from the NR data.

The corresponding SLD profiles obtained from the selected reflectivity curves during the “film contraction” period (marked with black arrows of “b” in Figures 6.4c and g) are shown in Figures 6.4d and h. During the “film contraction” period, with time (*i.e.*, temperature increase accompanied by a continuous contraction of the thin films), a two-layer SLD profile is gradually formed for the salt-free DBC film. In contrast, the formation of a three-layer substructure is seen for the KCl-loaded DBC film at $T = 42^\circ\text{C}$ (see Figures 6.3b and d) due to the redistribution of the salt. As highlighted by the dotted black arrows in Figures 6.4d and h, the contraction in the SLD profiles for each sample always starts at the layer near the polymer-air interface, and gradually expands towards the layer near the polymer-substrate interface. In agreement with the static ToF-NR and XRR data, the SLD values of the layers near the polymer-air interface are always lower than the SLD values of the layers close to the polymer-substrate interface. These observations prove that the film contraction of both samples is accompanied by a release of D₂O molecules

and that a substantial D₂O loss occurs near the polymer-air interface. In other words, after the films are swollen with D₂O, the PNIPMAM blocks near the polymer-air interface respond more quickly to the increased temperature compared with the PNIPMAM blocks near the substrate. This behavior can also explain that the surface morphology after heating differs so much from the surface morphology after D₂O swelling (see AFM images in Figure B.3, Appendix B). Different from the evolving SLD profiles of the salt-free DBC film, an enrichment layer of KCl is formed between the two SLD layers described above, which becomes more pronounced as the film contracts. Considering the higher theoretical SLD value of KCl (see Table 3.1 in Section 3.1), we note that near the sample surface, a substantial D₂O loss causes the dramatic shrinkage of the film. This in turn makes the KCl that was originally dispersed in the layer near the surface migrate or aggregate towards the interior of the thin film, to form eventually a salt-rich section in the middle of the DBC film.

By analyzing all kinetic ToF-NR data, the thickness and the calculated D₂O content for both processes are determined (Figure 6.5). As expected, the swelling ratio and the D₂O content at the end of swelling agree with the static values (Table B.2, Appendix B). Moreover, the temporal evolution of the swelling ratio is consistent with the SR results. A higher swelling ratio and D₂O content of the KCl-loaded DBC film compared to the salt-free DBC film are confirmed for both kinetic processes. This finding is ascribed to the strong hygroscopic contribution of KCl. A short “further-swelling” period and a subsequent “film contraction” period are observed for the swelling ratio and D₂O content. Thus, for both scenarios, the change in thickness is achieved by modulating the uptake or release of D₂O molecules via the hygroscopic effect of KCl in the thin-film geometry. Typically, compared to the $VPTT_c$ at which the thin films start to contract and the D₂O contents begin to decrease, the finding that the presence of KCl exhibits the ability to lower the $VPTT_c$ of the PNIPMAM block is reconfirmed (see Table B.1b, Appendix B). Besides, the general effect of the release of D₂O molecules caused by the elevated temperature is also observed in the ToF-NR. However, differences are seen compared with the SR data, which is reflected in an accelerated process (*i.e.*, drastic, and very fast film contraction).

In the studied scenarios, the most significant advantage of *in situ* ToF-NR measurements is that it offers the possibility to compare the real-time D₂O content inside both films, as shown in Figure 6.5b. Compared to the times at which the swelling ratio or D₂O content reach the equilibrium upon D₂O swelling for each sample, the D₂O content reaches equilibrium earlier than the swelling ratio for the salt-free sample, while the D₂O content and swelling ratio reach equilibrium almost simultaneously for the KCl-loaded sample. We attribute the former phenomenon to the rearrangement of the polymer segments for

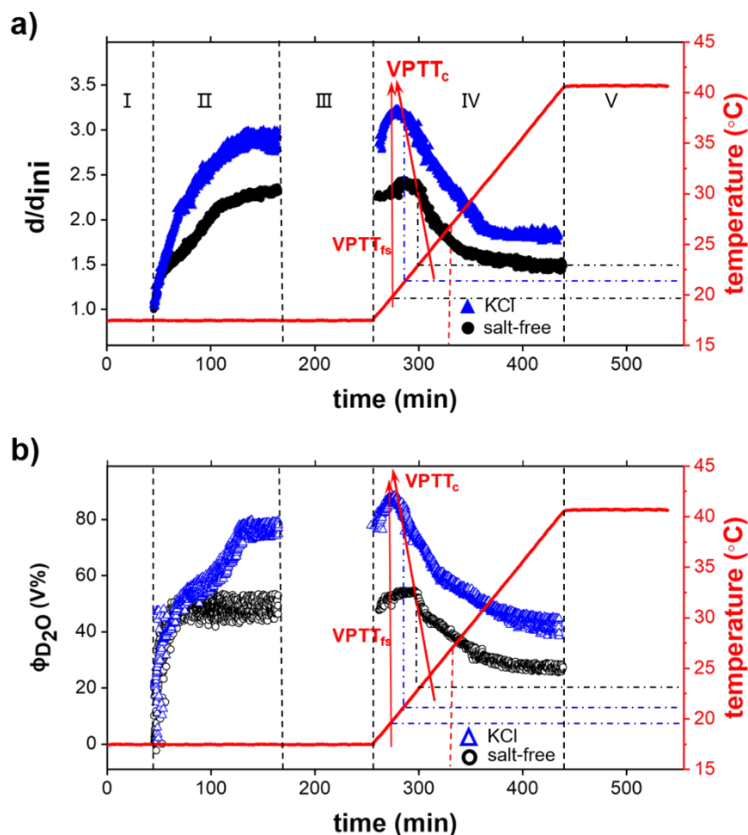


Figure 6.5.: (a) Swelling ratio d/d_{ini} obtained from ToF-NR measurements and (b) calculated D₂O content as a function of time for both KCl-loaded and salt-free DBC thin films with indicated stages *I-V*. The swelling ratio and D₂O content are plotted as blue solid triangles and hollow blue triangles, respectively, for the salt-free sample. They are plotted as black solid dots and hollow black dots, respectively, for the KCl-loaded sample. The temporal evolution of the temperature for ToF-NR measurements is plotted as the red solid lines with a red dotted line at the time when the relative humidity starts to decrease, as shown in Figure B.1 (Appendix B). The shift of the *VPTTs* (refers to as $VPTT_{fs}$ and $VPTT_c$) are indicated as the red arrows and the small dash lines crossing the temperature evolution curve indicate the actual transition temperatures. Reproduced with permission.[108] Copyright 2023 American Chemical Society.

accommodating D₂O molecules. This is consistent with our previous studies on the D₂O swelling behavior of PSB-*b*-PNIPMAM thin films.[76], [221] In addition, we address the latter phenomenon to the hygroscopic effect of KCl in thin-film geometry, which is also demonstrated in our previous study on the NaBr-dependent phase transition behavior of PSB-*b*-PNIPMAM thin films in D₂O vapor.[221] Since the most stable stage is reached for rearranged polymer chains after the D₂O swelling at 18 °C (stage *III*), the variation of both swelling ratio and D₂O content are always synchronized in the subsequent heating

process (IV), which again illustrates that the thermoresponsive behavior of swollen DBC thin films on thickness is achieved by modulating the uptake or release of D₂O molecules.

6.3.6. Polymer–D₂O interactions around functional groups

On a molecular level, the build-up and reduction of the hydration shell inside the DBC thin films give insights into the polymer-D₂O interactions. Therefore, FTIR is performed to track the local hydration and dehydration processes around specific functional groups, following the experimental protocol in Figure 6.1. The temporal evolution of the resulting FTIR spectra after background and baseline corrections is shown in Figure 6.6. As an overlap exists among some FTIR bands during the heating processes (see black arrows in Figures 6.6b and d), Figure B.4 (Appendix B) presents enlarged FTIR spectra for clarity. As marked by black arrows in Figures 6.6a and c, the hydroxyl band of the O-D

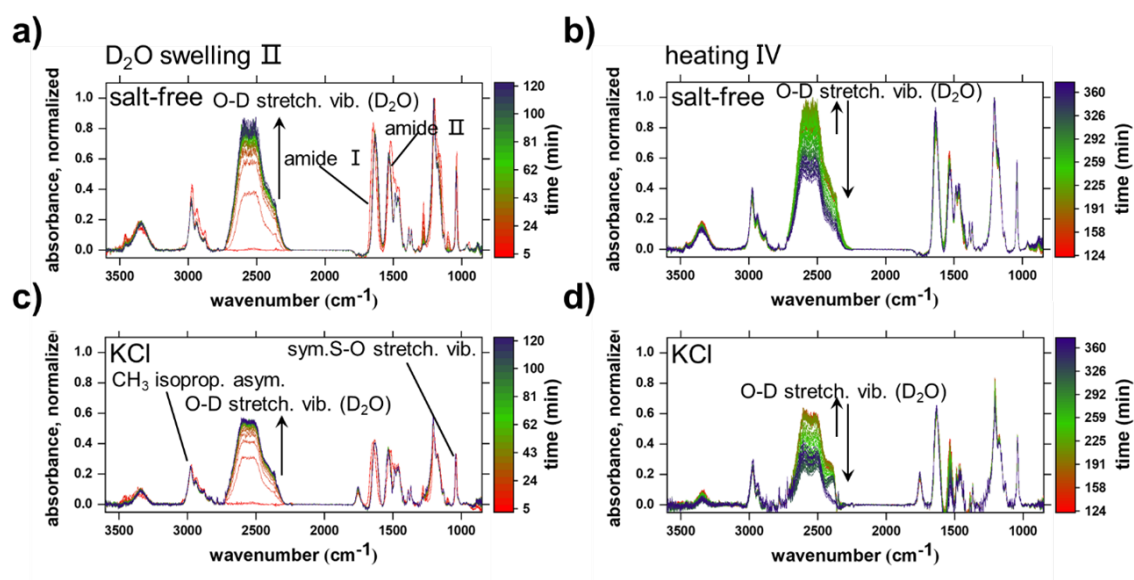


Figure 6.6.: FTIR spectra of (a, b) salt-free DBC thin film and (c, d) KCl-loaded DBC thin film upon (a, c) D₂O swelling (stage II) and (b, d) subsequent heating (stage IV). The temporal evolution of the resulting FTIR spectra is recorded during 120 min (red to purple) for the D₂O swelling processes, and during 240 min (red to purple) for the subsequent heating processes. The characteristic D₂O bands are indicated by vertical arrows. The single black arrow in (a, c) highlights the growth of the D₂O signal, while the two oppositely oriented black arrows with different lengths in (b, d) highlight the initial continued weak increase and the subsequent strong decay of the D₂O signal. Reproduced with permission.[108] Copyright 2023 American Chemical Society.

stretching vibration (wavenumber about $\nu = 2540 \text{ cm}^{-1}$) increases in height and area upon D₂O swelling due to the formation of a hydration shell. Analogously, during the

heating processes, the hydroxyl peak (marked with black arrows in Figures 6.6b and d) shows a two-step variation, in form of an initial slight increase (short arrow) followed by a substantial decrease (long arrow). This finding is attributed to the initial weak growth and the subsequent depletion of the hydration shell during heating, corroborating the results from the SR and ToF-NR data. In general, the relative D₂O content through the whole experimental protocol can be estimated by integrating the peak area of O-D stretching vibrations and then normalizing to the three-shouldered peak of the CH₃isopropyl asymmetric stretching vibrations (wavenumber about $\nu = 2970 \text{ cm}^{-1}$). The derived values for both DBC films are plotted in Figure 6.7a. The peak of CH₃isopropyl asymmetric stretching vibration is chosen for normalization for the same reason we pointed out before.[76] As expected, the changes of the D₂O content derived from the FTIR data are similar to the ones observed in the ToF-NR data (Figure 6.5b). Compared to the salt-free sample, the D₂O content of the KCl-loaded sample is higher throughout the entire process but reaches equilibrium later during the D₂O swelling process. Moreover, $VPTT_c$ of the KCl-loaded DBC film is lower than of the salt-free sample (see Table B.1b, Appendix B). These observations reconfirm that KCl inside PSBP-*b*-PNIPMAM thin films promotes D₂O absorption and lowers $VPTT$ of the PNIPMAM block. The $VPTT_{fs}$ is not observed in the FTIR data due to the thicker films studied (4 - 6 μm). Compared with a thin-film geometry, the stronger intermolecular force derived from the exacerbated entanglement between zwitterionic PSBP chains in a relatively thick-film geometry (*i.e.* increased polymer concentration) causes a shift of the $VPTT_{fs}$ towards higher temperatures compared to the $VPTT_{fs}$ values of the thin DBC films (25 - 35 nm) utilized in SR and ToF-NR. In addition to the films' D₂O content, the FTIR spectra can also inform about the hydration changes of specific functional groups. By plotting the temporal evolution of the peak shifts of their characteristic signals, the local chemical surrounding of functional groups can be analyzed. In addition to the peak shifts of the strongly hydrophilic anionic SO₃⁻ group (Figure 6.7b), the peak shifts of the signals of the moderately hydrophilic secondary groups (namely the amide *I* and amide *II* bands in the spectra of Figure 6.6) are also plotted in Figure 6.7c and d, respectively. The amide groups, which exist in both, the PSBP and PNIPMAM blocks, form hydrogen bonds that are dependent on the humidity and temperature, as observed in our previous studies on PNIPAM or PNIPMAM.¹⁸⁸ While, the amide *I* band mainly informs on the carbonyl group (C=O symmetric stretching vibrations, located in the wavenumber range $\nu = 1630 - 1650 \text{ cm}^{-1}$), the amide *II* band mainly refers to the amides' protons (N-H bending vibration, located in the wavenumber range $\nu = 1520 - 1540 \text{ cm}^{-1}$). As the carbonyl groups act as hydrogen-bond acceptors whereas the amide protons act as hydrogen bond donors, the peak position of the amide *I* band shifts towards higher wavenumbers upon

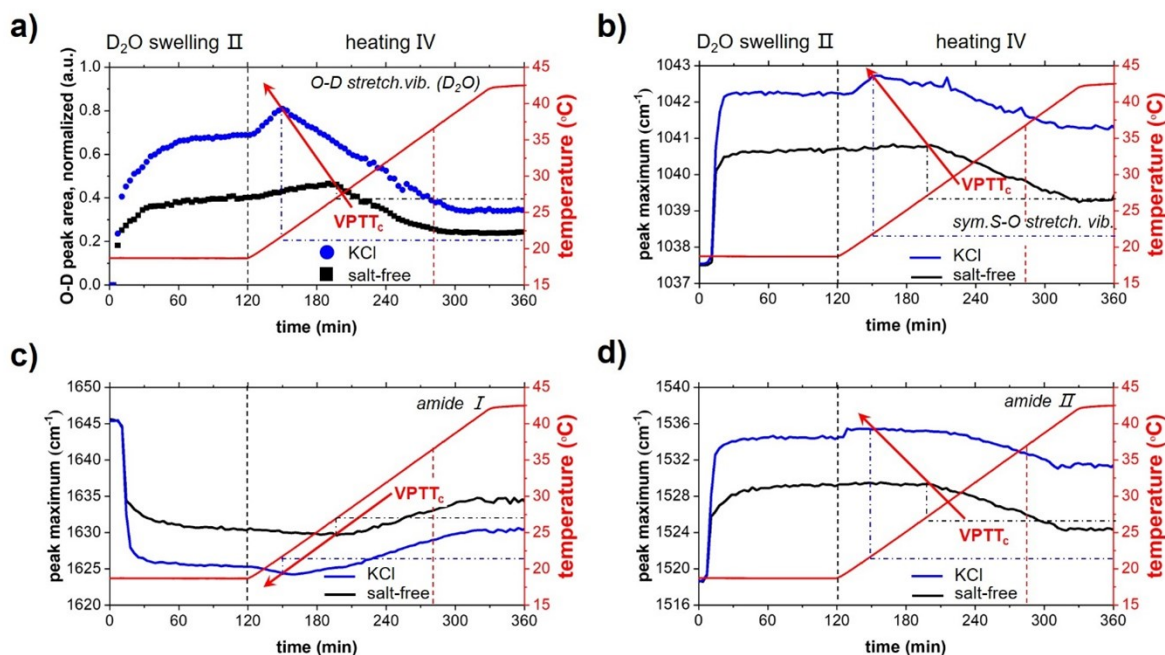


Figure 6.7.: (a) Normalized FTIR peak areas of O-D stretching vibration and temporal evolution of FTIR peak position shifts of (b) the symmetric S-O stretching vibration, (c) amide *I* band and d) amide *II* band as a function of time. The data for the peak areas and peak position shifts are colored in blue for the KCl-loaded DBC thin film, and in black for the salt-free DBC thin film. The temporal evolution of the temperature for FTIR measurements is plotted as red solid lines with a red dotted line marking the point where the relative humidity starts to decrease, as shown in Figure B.1 (Appendix B). The shift of the $VPTT_c$ is indicated as the red arrows and the small dash lines crossing the temperature evolution curve indicate the actual transition temperatures. Reproduced with permission.[108] Copyright 2023 American Chemical Society.

D₂O swelling (stage *II*), but the peak position of amide *II* band shifts towards lower wavenumbers. The anionic SO₃⁻ groups, too, act as hydrogen bond donors. Thus, the peak position of the symmetric S-O stretching vibration (located in the wavenumber about $\nu = 1038 \text{ cm}^{-1}$) also shifts towards higher wavenumbers upon D₂O swelling. All aforementioned peaks show up at the same location and shift in the same direction as noted in the literature.[76] Although the positions of these characteristic peaks evolve in different directions (to lower or higher wavenumbers), the shift upon D₂O swelling during stage *II* as well as the initially continued shift and subsequent backshift upon heating during stage *IV* is always more pronounced for the KCl-loaded than for the salt-free DBC film. In addition, the $VPTT$ at which the backshift occurs during the heating process of the KCl-loaded DBC film is always lower compared to that of the salt-free DBC film in any scenario. These observations are consistent with the other findings, *e.g.* the thickness change in SR and ToF-NR data, and the D₂O content derived from the ToF-NR and

FTIR data. Thus, the enhanced water uptake observed with KCl in thin-film geometry and its ability to lower the $VPTT_c$ of the PNIPMAM blocks is demonstrated by FTIR on a molecular level as well. Before the backshift of the peaks of the DBC films, the red-shift of both amide signals is hardly visible, while a clear red-shift occurs for the signal of the more hydrophilic charged SO_3^- group. This supports the finding from SR data, that during the heating processes, the UCST-type phase transition of PSBP blocks has a stronger contribution to the further swelling of the thin films, compared to the intensified motion of PNIPMAM blocks introduced by a temperature increase. Similarly, the backshifts of both amide signals as the temperature increases after passing $VPTT_c$ indicate that the LCST-type phase transition of PNIPMAM blocks mainly contributes to the contraction of the thin films upon heating. Logically, the backshift of the anionic SO_3^- group observed in Figure 6.7b, also reflects the partial reduction of its hydration shell. Even so, the magnitude of the backshift is quite small compared to both amide signals (the wavenumber shifts by around 1 cm^{-1} back for the band of the SO_3^- group, while it shifts by around 9 cm^{-1} and 7 cm^{-1} back for the amide *I* and amide *II* bands, respectively). Notwithstanding, the effect of density loss of D_2O molecules caused by the elevated temperature ($T > 37^\circ\text{C}$) also inevitably exists for FTIR measurements (see Figure B.1 Appendix B).

6.4. Conclusions

The addition of KCl leads to a pronounced boosting of the water uptake in the thin-film geometry. Under good solvency conditions at $T = 18^\circ\text{C}$, the KCl-loaded samples always exhibit a higher swelling ratio compared to the salt-free samples, both for DBC and the reference homopolymer films. The presence of KCl increases the equilibrium thickness by 185 % and the D_2O content by 77 % upon D_2O hydration. Upon subsequent heating, an initial “further-swelling” period and a subsequent marked “film contraction” period with separate $VPTTs$ (refers to $VPTT_{fs}$ and $VPTT_c$) are observed for both the salt-free and the KCl-loaded DBC films. Both $VPTTs$ are shifted towards lower temperatures compared to the clearing points found in aqueous solutions. This is mainly attributed to the high polymer concentration in thin-film geometry. Based on comparisons with the salt effect for the respective homopolymer thin films, the “further-swelling” period of the DBC thin films is attributed to the UCST-type phase transition of the PSBP block, whereas the “film contraction” period is attributed to the LCST-type phase transition of PNIPMAM block. The presence of KCl only affects the $VPTT_c$ of the PNIPMAM blocks in thin-film geometry, but not the $VPTT_{fs}$ of the PSBP block. Upon subsequent heating, the migration or aggregation of KCl inside the thin film is observed, resulting in

the formation of a salt-rich zone. Analyzing the stage of hydration around the hydrophilic functional groups located in both the PSBP and the PNIPMAM blocks, the increasing hydration during the “further-swelling” period is attributed to the PSBP blocks, while this block is not involved in the reduction of the hydration during the subsequent “film contraction” period.

Salt Series Driven Solvation Behavior in non-aqueous atmosphere

The following chapter is based on the upcoming publication “Salt Series Driven Solvation Behavior of Thermoresponsive Polymer Thin Films in Water and Subsequent Mixed Water/Methanol Atmosphere” by P. Wang, T. Zheng, J. Reitenbach, S. A. Wegener, L. F. Huber, L. P. Kreuzer, S. Liang, R. Cubitt, Y. Cheng, T. Xu, V. Hildebrand, A. Laschewsky, C. M. Papadakis and P. Müller-Buschbaum.

Introduction

Over the past decades, many studies investigated the specific ion effect for thermoresponsive polymers on the LCST behavior in aqueous solution.[223]–[229] Among the numerous polymers investigated, PNIPAM is probably the best-studied one.[227], [230]–[237] For example, Delfi *et al.*[234] reported that the LCST and particle size of PNIPAM nano-gels are highly correlated with the Hofmeister series. Qian *et al.*[233] showed a direct interaction between the cations and PNIPAM by MD simulations and demonstrated that the anions shift the LCST down following the Hofmeister series from kosmotropes to chaotropes. Bergbreiter and co-workers[231] further revealed that the effect of the anion on the LCST of PNIPAM can be ascribed to three types of interactions of anions with the polymer and its hydrating water molecules, including (i) the hydrophobic hydration of the molecule associated with surface tension, (ii) direct binding of the anion to the amide group and (iii) hydrogen bonding of the amide and its destabilization through polarization by the anion. More recently, PNIPMAM has been explored as an alternative to PNIPAM, due the similarity of their hydrophilic and hydrophobic groups.[238]

Other than by the addition of salts, the thermoresponsiveness of polymers in water can also be modulated by the addition of organic co-solvents. A particularity arises for the

LCST behavior of PNIPAM as well as of PNIPMAM, which exhibits co-nonsolvency for a number of polar solvents, including methanol as the most studied example,[239] but also ethanol,[240] acetone,[241] DMSO,[241] or DMF.[242] Although all of those are good solvents for both polymers, their addition to water decreases the polymer solubility.[240], [243] The reasons for co-nonsolvency behavior are controversially discussed and seem complex, in particular as the term comprises several thermodynamic scenarios.[243] In the simplest one, the transition in the ternary phase diagram between solubility in water via an insoluble region to solubility in the co-solvent is due to an LCST-transition that shows a minimum at intermediate contents of the co-solvent in the mixture. In the second scenario, the sequence solubility - insolubility - solubility is characterized by the occurrence and steep drop of an LCST-transition with increasing co-solvent content resulting eventually in a region of insolubility. This is followed by the occurrence of a UCST-transition that steeply falls with further increase of the co-solvent content, thus reestablishing the polymer's solubility.[244] While the latter scenario seems to be the more widespread case, co-nonsolvency of PNIPAM and PNIPMAM in water-methanol mixtures follows the former scenario. A third thermodynamic scenario,[245] namely co-nonsolvency in combination with UCST-behavior in both the water-rich and the co-solvent rich regimes, where the UCST becomes exceedingly high at intermediate co-solvent contents, but is much lower or even absent in pure water and in the pure co-solvent, has been observed only in exceptional cases up to now.[246], [247]

Notwithstanding that the reasons for co-nonsolvency are still under debate, a frequently proposed explanation evokes that the added co-solvent disrupts (or enhances) the water structure. Accordingly, the addition of salts (be they kosmotropes or chaotropes) can be expected to modify the co-nonsolvency (or co-solvency) behavior of PNIPAM and PNIPMAM markedly.[248], [249] Within this line of reasoning, Abdelhamid and co-workers,[250] reported the specific effects of different anions on the cononsolvency behavior of PNIPAM microgels in water/ethanol mixtures. The addition of salts induced the particles to collapse, and promoted the system partly destabilization when the V_{ethanol} (ethanol volume ratio) was $< 20\%$, while the system was driven to complete destabilization as $V_{\text{ethanol}} > 20\%$.

To the best of our knowledge, salt effects on co-nonsolvency behavior of UCST-type thermoresponsive polymers or on DBCs that combine two thermoresponsive blocks with LCST- and UCST-type behavior, have not been investigated yet, especially not in thin film geometry for polymer-rich systems in a vapor environment. Addressing such a scenario, we select PNIPMAM as LCST-type polymer, and PSBP as UCST-type polymer for our investigations, as the latter bears the poly(methacrylamide) backbone and hydrophilic amide groups in common with PNIPMAM. Also, salt effects on the UCST-transition of PSBP

in dilute solution have been investigated in some detail,[251] and the co-nonsolvency behavior of structurally closely related DBCs has already been addressed.[247], [252] Hence, in the present work, PSBP, PNIPMAM and PSBP-*b*-PNIPMAM (Figure 4.1) are chosen as representatives of UCST, LCST and UCST-*b*-LCST type thermoresponsive polymers, to examine the salt effect on the solvation behavior of thin films in pure water vapor and in mixed water/methanol vapor. We focus on the potassium salts CH₃COOK, KCl, KBr, KI and KNO₃, whose anions cover a large part of the Hofmeister series from kosmotropic to chaotropic behavior.

The results include two sections. In the first section, the salt effects (CH₃COOK, KCl, KBr, KI, and KNO₃) on the film thickness (PSBP, PNIPMAM, and PSBP-*b*-PNIPMAM) are investigated by *in situ* SR measurements, responding to a stepwise exchanged vapor atmosphere starting with 100 % water vapor and ending with 100 % methanol vapor. In each step, 10 vol% of CH₃OH vapor replaces successively H₂O vapor as illustrated in Figure 4.6a. In the second section, the salt effects on initial swelling in pure water vapor and subsequent rapid film contraction in a mixed water/methanol vapor are investigated further with *in situ* SR, ToF-NR and FTIR measurements. The applied vapor switching protocol is illustrated in Figure 4.6b. To echo the study of swelling in pure methanol vapor in the first section, a further *in situ* SR measurement is performed following the vapor protocol in Figure 4.6c. Besides, 2D FTIR is used to determine the perturbation sequence of hydration events responding to the pure water vapor, and MD simulations are used to observe the salt effect on accessibility of solvation shells and the conformation transition of PSBP-*b*-PNIPMAM chains.

7.1. Thin Film Response to a Stepwise Exchange of the Vapor Atmosphere.

Figure 7.1 displays the swelling ratio as a function of time following a stepwise exchanged vapor protocol (Figure 4.6a). Based on the relative mixing ratio, the process can be divided into three regimes (H₂O-rich, transition, and CH₃OH-rich). As shown in Figure 7.1, the overall trend of the swelling/deswelling behavior of the PSBP, PNIPMAM, and PSBP-*b*-PNIPMAM films basically depends on the vapor composition. The added salts amplify the swelling/deswelling behavior, but do not alter the overall trend. If the swelling ratio increases with added methanol, we classify the phenomena as a positive response, and refer to it as a positive cosolvent effect (Figure 7.1b). In the opposite case (Figure 7.1a and 7.1c), we classify it as a negative response and refer to it as a negative cosolvent effect. Since the relative swelling/deswelling degree of each type of salt-loaded sample depends on the type of anions, especially during the H₂O-rich and middle tran-

sition regimes, we compare the anion specificity of the effects with their position in the Hofmeister series, which is known to govern the solution behavior of such polymers. Furthermore, the phenomenon that the loaded salts enhance the swelling ratio, is attributed to a salt-induced solvation effect, otherwise, to a salt-induced desolvation effect. Accordingly, the observed behavior is considered as an interplay between the cosolvent and salt effects. The interplay of the two effects within the three different regimes on the PSBP, PNIPMAM, and PSBP-*b*-PNIPMAM films is discussed below.

In the H₂O-rich regime (stages *II-IV*, where $V_{\text{methanol}} < 30\%$), the swelling ratio remains almost constant for PSBP, while it increases for PNIPMAM, and decreases for PSBP-*b*-PNIPMAM, respectively. This behavior indicates that at low V_{methanol} , the added methanol influences the PSBP film only weakly, while it presents a positive cosolvent effect for PNIPMAM and a negative cosolvent effect for PSBP-*b*-PNIPMAM. Thus, in the H₂O-rich regime, the salt effect mainly dominates the swelling behaviors for the PSBP film, and a positive cosolvent effect results in enhanced swelling for the PNIPMAM film, while a negative cosolvent effect results in the collapse of the DBC film. A balance between the salt and cosolvent effects results in an equilibrated thickness for each stage. The extent of the salt-mediated equilibrated thickness values follows the order $\text{CH}_3\text{COO}^- > \text{Cl}^- > \text{Br}^- > \text{I}^- > \text{NO}_3^-$ in the case of PSBP, which approximately inverts the order of the Hofmeister series that governs salting-in efficiency of these anions for PSBP in aqueous solution.[251], [253] The corresponding orders of anions effects are $\text{Br}^- > \text{CH}_3\text{COO}^- > \text{Cl}^- > \text{I}^- > \text{NO}_3^-$ for PNIPMAM, and $\text{CH}_3\text{COO}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^- > \text{I}^-$ for the DBC. Hence, they also seem to follow to a certain extent an inverted Hofmeister correlation, but with polymer-specific variations. Note, that the salt-loaded films reach a higher thickness than corresponding salt-free films, illustrating a salting-in effect for each type of polymer, promoting water swelling, as addressed in previous studies.[254] Besides, for the films loaded with the same anion or without salt, the equilibrated thicknesses at a specific mixing ratio (*i.e.*, as a function of V_{methanol}) are higher for PSBP-*b*-PNIPMAM than for PNIPMAM, but lower than for PSBP. This finding indicates a stronger water absorption by PSBP films than by PNIPMAM films of similar thickness.

During the transition regime (stages *V-VIII*, where $30\% < V_{\text{methanol}} < 70\%$), the swelling ratios undergo discrepant transitions for the PSBP and PNIPMAM films. Once V_{methanol} exceeds 30%, all PSBP samples contract dramatically (however, at different rates). This observation implies that a negative cosolvent effect emerges and overrides the salt effect, since no thickness plateau is reached responding to a stepwise exchange in 2 h. Nevertheless, the decreased swelling ratios still obey the salt series that are found in the H₂O-rich regime. Differently, when V_{methanol} exceeds 40%, all PNIPMAM films undergo a continuous contraction with a short inevitable re-swelling, which starts when transitioning

7.1. Thin Film Response to a Stepwise Exchange of the Vapor Atmosphere.

between adjacent stages (*i.e.*, V_{methanol} instantaneously increases) and is unobtrusive in the PSBP and DBC films. Interestingly, once V_{methanol} reaches 40% (VI), the Br^- -loaded PNIPMAM film collapses rapidly after the reswelling, causing a pass down of swelling ratio over the CH_3COO^- -loaded film, whereas the Cl^- -loaded film reswells more, causing a surpass of swelling ratio over the I^- -loaded film. As a result, the order of the anion mediated effect in the transition regime is changed for PNIPMAM films from $\text{Br}^- > \text{CH}_3\text{COO}^- > \text{Cl}^- > \text{I}^- > \text{NO}_3^-$ to $\text{CH}_3\text{COO}^- > \text{Br}^- > \text{Cl}^- > \text{I}^- > \text{NO}_3^-$. Therefore, we conclude that the positive cosolvent effect is transformed into the negative cosolvent effect as V_{methanol} exceeds 40%, and afterward, the negative cosolvent effect overrides the salt effect since no thickness plateau is reached responding to a stepwise exchange in 2 h.

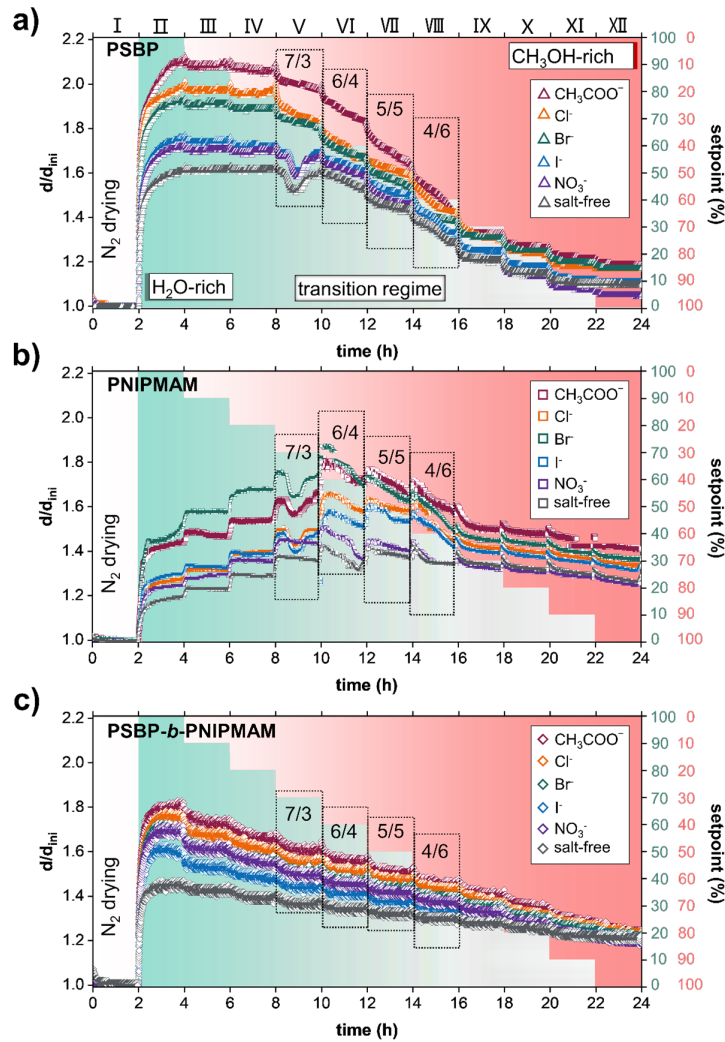


Figure 7.1.: Evolution of the swelling ratio (d/d_{ini}) obtained from SR measurements as a function of time for (a) PSBP, (b) PNIPMAM, and (c) PSBP-*b*-PNIPMAM thin films following a stepwise exchanged saturated vapor.

Even so, the transient positive cosolvent effect caused by a sudden V_{methanol} increase is not shieldable during the transition regime (stages *V-VIII*). Notably, part of the PSBP (I^- -, NO_3^- -loaded and salt-free) and PNIPMAM (Br^- -, CH_3COO^- -, Cl^- - and I^- -loaded) curves suffer from a downward inverted peak in stage *V*, but basically return to the degree of swelling before. In contrast, the DBC films collapse stepwise and synchronously at a similar rate as produced in stages *III* and *IV*, and continue to follow the salt series of the H_2O -rich regime. Besides, concerning an approximate equilibrium of thickness at each stage, we conclude that although the negative cosolvent effect dominates the entire regime, a balance with the salt effect exists at each stage, which enables a near-linear collapse with a control of the thickness by the loaded specific anion species.

During the CH_3OH -rich regime (stages *IX-XII*, where $V_{\text{methanol}} > 70\%$), all PSBP films pursue the trend of shrinking thickness from the transition regime. This can even lead to partial overlap or crossover of the swelling ratios for different loaded salts. As a result, the order of the salt-induced effects weakly changes to $\text{CH}_3\text{COO}^- > \text{Cl}^- \approx \text{Br}^- > \text{I}^- \approx \text{NO}_3^-$, *i.e.*, the effects induced by Cl^- and Br^- become nearly the same. Differently, all PNIPMAM samples collapse nearly simultaneously by inheriting the trends (*i.e.*, approximately constant differences among swelling ratios) seen in the stages before, and continue to follow the initial anion series. All DBC films continue the near-linear contraction, promoting swelling ratios to coincide at one point. Thus, for the DBC films, the changed salt series observed in the transition regime still remains, but the distinction is no longer significant in pure methanol vapor. Since all salt-loaded samples present a stepwise equilibrated thickness, we conclude that at high V_{methanol} , the negative cosolvent effect dominates the swelling behavior. Interestingly, the hitherto observed salt-induced solvation effect of NO_3^- for PSBP and PNIPMAM is replaced in pure methanol vapor by a weak salt-induced desolvation effect.

7.2. Thin Film Hydration and Switching Kinetics

For each polymer, the present study highlights a notable salt effect in stage *II*. Furthermore, a strong negative cosolvent effect in stage *VI* for PNIPMAM is observed, where the mixing ratio of $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ is 6/4. To further study the salt effect on the solvation behavior in H_2O and in a subsequently mixed $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ vapor (*i.e.*, upon the negative cosolvent effect), as well as the salt effect on the polymer-solvent interactions, *in situ* SR, ToF-NR, and FTIR measurements are conducted to characterize the time-resolved film thickness changes, the solvent contents, and the local polymer-solvent interactions. The experimental protocol is illustrated in Figure 7.2.

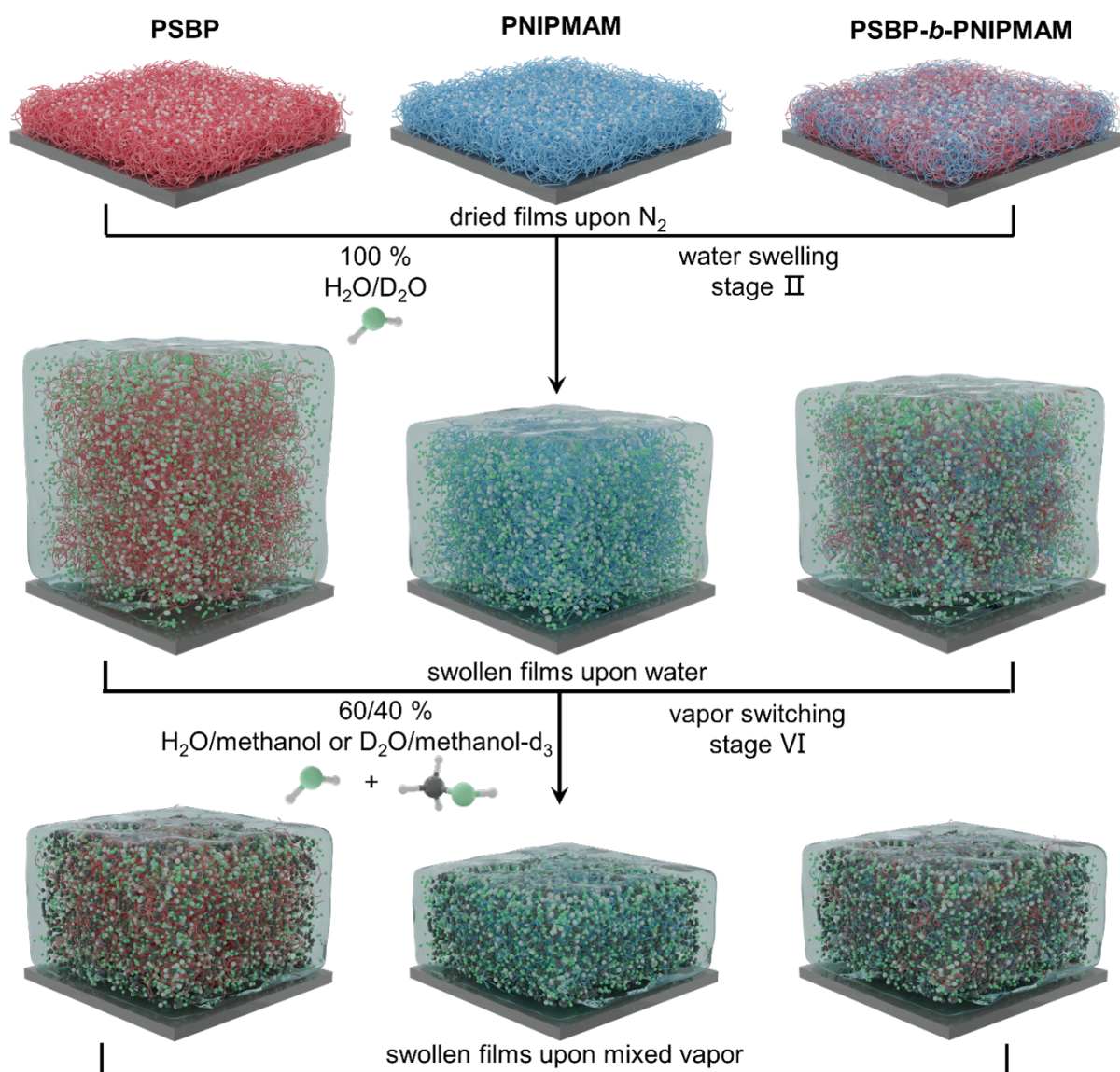


Figure 7.2.: Experimental protocol applied for SR, ToF-NR, and FTIR studies on PSBP, PNIPMAM and PSBP-*b*-PNIPMAM thin films. Two kinetic processes are labeled: water swelling (H_2O or D_2O = 100 %, stage *II*) and vapor switching (H_2O /methanol or D_2O /methanol- d_3 = 60/40 %, stage *VI*).

7.2.1. Kinetics of the swelling behavior

All samples are investigated by *in situ* SR measurements upon H_2O hydration and the subsequent $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ switching process. To echo the study in a CH_3OH -rich regime, further exploration of the salt effect in pure methanol vapor is performed following the vapor exchange protocol in Figure 4.6c. In agreement with the findings at stage *II* (see Figure 7.1), once exposed to an H_2O vapor, all samples swell strongly to a defined threshold (Figure 7.3), depending on the loaded salt, which differs in the anion species. Further-

more, the swelling ratios of each type of polymer thin film obey the salt series introduced in the H₂O-rich regime as discussed above. Again, the loaded salts provoke a salt-induced solvation effect, enhancing the water absorption.

In mixed H₂O/CH₃OH vapor (stage *VI*), all samples contract but undergo several distinguishable multistep transitions depending on the polymer type. As illustrated in Figure 7.3a, all PSBP films undergo a spontaneous collapse within the first 5 min, followed by a nearly linear contraction period (50 - 70 min). Afterwards, they contract slowly to a final equilibrated state. Compared to the stepwise collapses at stages *V* and *VI* in Figure 7.1a, the CH₃COO⁻, Cl⁻, and Br⁻-loaded PSBP films tend to reproduce the two-step variations to a larger extent in a shorter time. Importantly, except for the changes in swelling ratio, both the duration of the middle near-linear or subsequent slow contraction, as marked by the black arrows, also obey the original order that resembles an inverted Hofmeister series. Conversely, all PNIPMAM films reswell strongly in the first 20 min of stage *VI* due to the positive cosolvent effect, but then contract slowly due to the negative cosolvent effect until a plateau is reached, as shown in Figure 7.3b. Thus, a positive cosolvent effect coexists with a negative cosolvent effect. Moreover, the order of the anion effects encountered in pure H₂O vapor is no more followed (*i.e.*, Cl⁻ loses its priority position over I⁻ and NO₃⁻ in mixed H₂O/CH₃OH vapor).

For all DBC films in Figure 7.3c, not only a weak reswelling is seen during the first 7 min of stage *VI*, but also the two-step collapse is found (weaker than PSBP and stronger than PNIPMAM). Thus, the behavior of the DBC films upon vapor switching shows superposed contributions of both the PSBP and PNIPMAM blocks. Interestingly, in this switching experiment, the anion effects follow the order CH₃COO⁻ > Cl⁻ > Br⁻ > NO₃⁻ > I⁻, *i.e.*, it mirrors the Hofmeister series. Again, compared to the salt-free samples, the higher swelling ratio for salt-loaded samples illustrates a significant salt-induced solvation effect even in a mixed H₂O/CH₃OH atmosphere.

In pure CH₃OH vapor (stage *XII*), although all films are slightly swollen, the salt effects are very small (the swelling ratios do not differ more than 0.17 for PSBP, 0.14 for PNIPMAM, and 0.10 for PSBP-*b*-PNIPMAM). Unlike the swelling behavior in pure H₂O vapor, all films swell instantaneously in CH₃OH vapor to a high ratio, and then contract rapidly to their equilibrium thickness. This finding implies that the films experience a process of instantaneous absorption and subsequently rapid release of methanol molecules, which might be the reason for the positive cosolvent effect. Obviously, the relaxation time and thickness changes do not depend only on the anion species, but also on the polymer type (with PNIPMAM > DBC > PSBP). Despite the difficulty in distinguishing the anion-specific effects due to partial overlapping or interspersing, the salt series in pure CH₃OH vapor are determined as: CH₃COO⁻ > Cl⁻ > Br⁻ > I⁻ > NO₃⁻ for PSBP, CH₃COO⁻

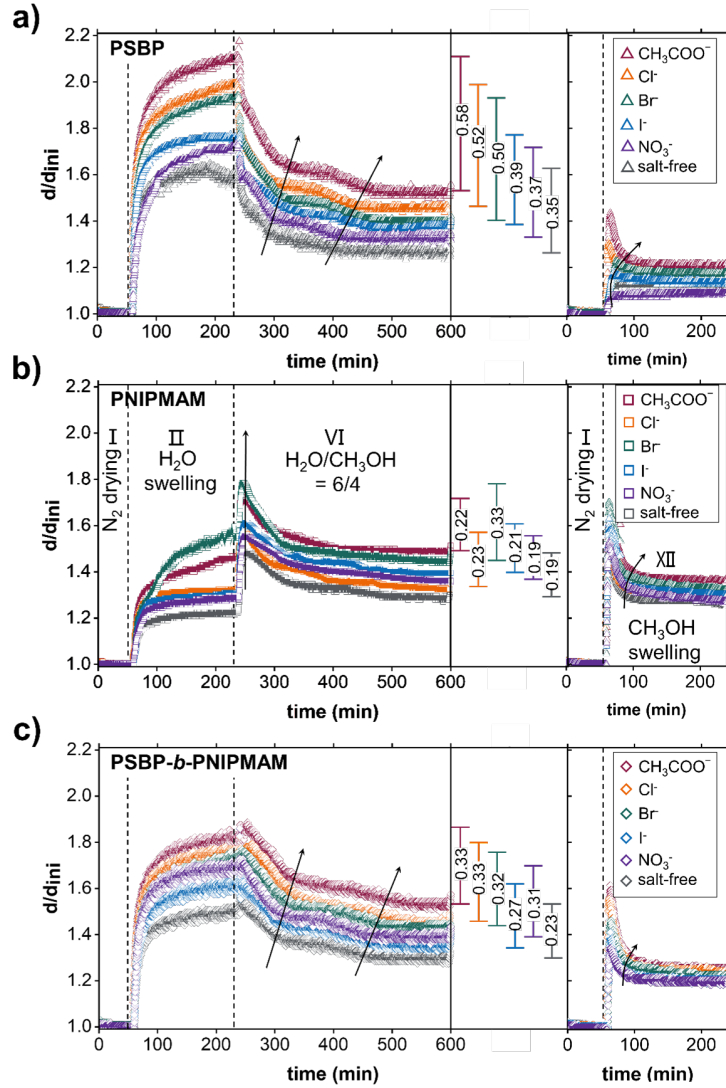


Figure 7.3.: Evolution of the swelling ratio d/d_{ini} obtained from SR measurements as a function of time for (a) PSBP, (b) PNIPMAM, and (c) PSBP-*b*-PNIPMAM thin films with the stages: N_2 drying (I), H_2O swelling (II), H_2O /methanol = 6/4 (VI), and methanol swelling (XII). The largest absolute changes in swelling ratio at stage VI are listed on the corresponding drop scale bar. The black arrows indicate the positions where the swelling ratios mutate.

$> Br^- > Cl^- > I^- > NO_3^-$ for PNIPMAM and $CH_3COO^- > Cl^- > Br^- \approx I^- > NO_3^-$ for the DBC. Again, a weak salt-induced desolvation effect of NO_3^- is observed in pure CH_3OH vapor for NO_3^- -loaded PSBP and DBC films.

7.2.2. Kinetics of solvent absorption

With static and kinetic ToF-NR measurements we examine the solvent absorption. Due to the limited availability of neutron beamtime, we focus on the Br^- and NO_3^- -loaded DBC

films. Moreover, D_2O and CD_3OH are selected to enhance the scattering length density (SLD) contrast for the neutron scattering experiment, whereas the film thicknesses are chosen such that they are appropriate for ToF-NR (34 nm for Br^- and 31 nm for NO_3^- -loaded). The static NR curves with the best fits, as well as the obtained SLD profiles, are shown in Figure C.1, in the Appendix C. A three-layer model, consisting of a substrate-polymer interface, a bulk polymer layer, and a polymer-air interface, is used to fit the ToF-NR data. Table C.1, presents the calculated theoretical SLD values of all involved materials. The method to calculate the SLD of the polymers is described in the “ToF-NR” section in the Appendix C. Comparing the NR curves between N_2 drying static and D_2O swelling static (Figure C.1a and b), the Kiessig fringe spacing decreases, and the critical edge shifts towards higher q_z values, illustrating the increase in film thickness and SLD values (*i.e.*, the incorporated D_2O content), as seen in the corresponding SLD profiles (Figure C.1c and d). In contrast, the corresponding SLD profiles of vapor switching static curves demonstrate a decrease in both, thickness and SLD values (Figure C.1c and d). Following the Eq. 3.7-3.10 described in the Section 3.1, the absorbed solvent content (D_2O and CD_3OH) is calculated and given in Table C.1. In agreement with the SR results, the Br^- -loaded DBC film not only realizes a higher swelling ratio and a larger D_2O absorption in both scenarios compared to the NO_3^- -loaded DBC film, but also has a larger CD_3OH content in stage *VI*.

Figure 7.4 presents the findings from the kinetic ToF-NR data analysis of both salt-loaded DBC samples. As expected, swelling ratio, SLD values, and solvent contents (D_2O and CD_3OH) are higher for the Br^- -loaded DBC film than for the NO_3^- -loaded one. Analogous to the SR results, the effect of the presence of Br^- on the solvation behavior of the DBC film is stronger than NO_3^- , matching the observed salt series as discussed before. Upon D_2O hydration (stage *II*), a synchronous fluctuation that appears in the swelling ratio, SLD profiles, and D_2O content, is ascribed to the rearrangement of polymer chains induced by the rapid water absorption.[247], [252], [254] Attractively, upon vapor switching (stage *VI*), the two DBC films exhibit an asynchronous variation in the CD_3OH content, while a synchronous variation in the D_2O content is found (Figures 7.4c and d). Once the mixed D_2O/CD_3OH vapor replaces the D_2O vapor, a fast release of D_2O molecules accompanied by rapid absorption of CD_3OH molecules is observed in 10 -15 min. In the following 70 min before reaching the final equilibrium, the CD_3OH content of the Br^- -loaded film decreases more slowly than for the NO_3^- -loaded film, while both their D_2O contents increase slightly. This behavior explains why the Br^- -loaded film presents a higher swelling ratio than the NO_3^- -loaded one at the first near-linear contraction in Figures 7.3c and 7.4a. Considering the large difference between both CD_3OH contents and the small difference between both D_2O contents, we infer that the presence of the anions

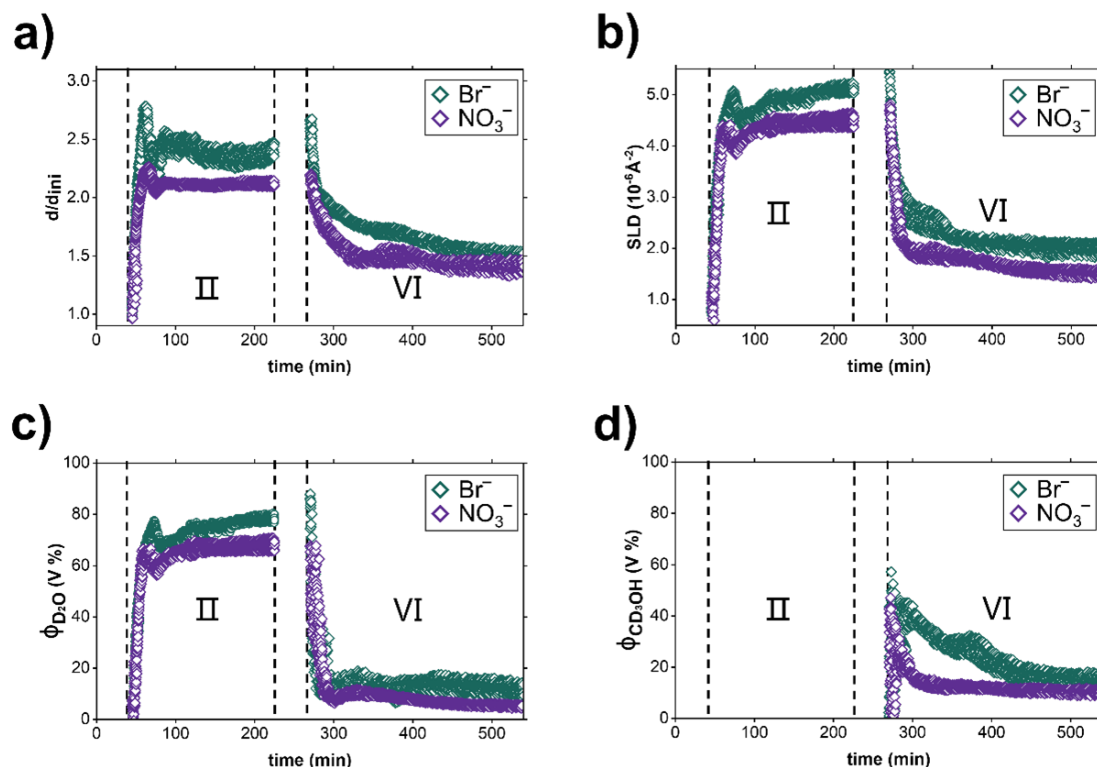


Figure 7.4.: Evolution of the (a) swelling ratio d/d_{ini} , (b) obtained bulk SLD, (c) calculated D₂O and (d) methanol-d₃ contents obtained from ToF-NR data as a function of time for Br^- - (green) and NO_3^- -loaded (purple) PSBP-*b*-PNIPMAM thin films at two stages: D₂O swelling (II) and vapor switching (D₂O/methanol-d₃ = 6/4, VI).

mainly affects the methanol absorption, resulting in different film thicknesses during this stage of the kinetic process.

7.2.3. Salt induced interactions between polymer and solvent

FTIR spectroscopy is performed to track the formation or reduction of solvation shells on a molecular level. Again, the deuterated solvents D₂O and CD₃OH are selected to avoid the overlap of specific IR bands. The prepared films are thicker than in the previous experiments with thicknesses of around 4 - 6 μm , to ensure sufficient intensity of the IR signals. The FTIR spectra are exemplified in Figure 7.5 for the Cl^- -loaded films, to explain the observed changes. For clarity, Figure C.3-C.5 and Figure C.6-C.8 present the resulting full, enlarged FTIR spectra of all PSBP, PNIPMAM, and DBC samples. Besides, all FTIR bands assigned to polymers are listed in Table 7.1.

Upon D₂O hydration (Figure 7.5a, c, and e), the height and area of the hydroxyl band of D₂O ($\nu_{\text{as}}(\text{O-D}_2) \approx 2540 \text{ cm}^{-1}$) increase while they decrease for the one of H₂O ($\nu_{\text{as}}(\text{O-}$

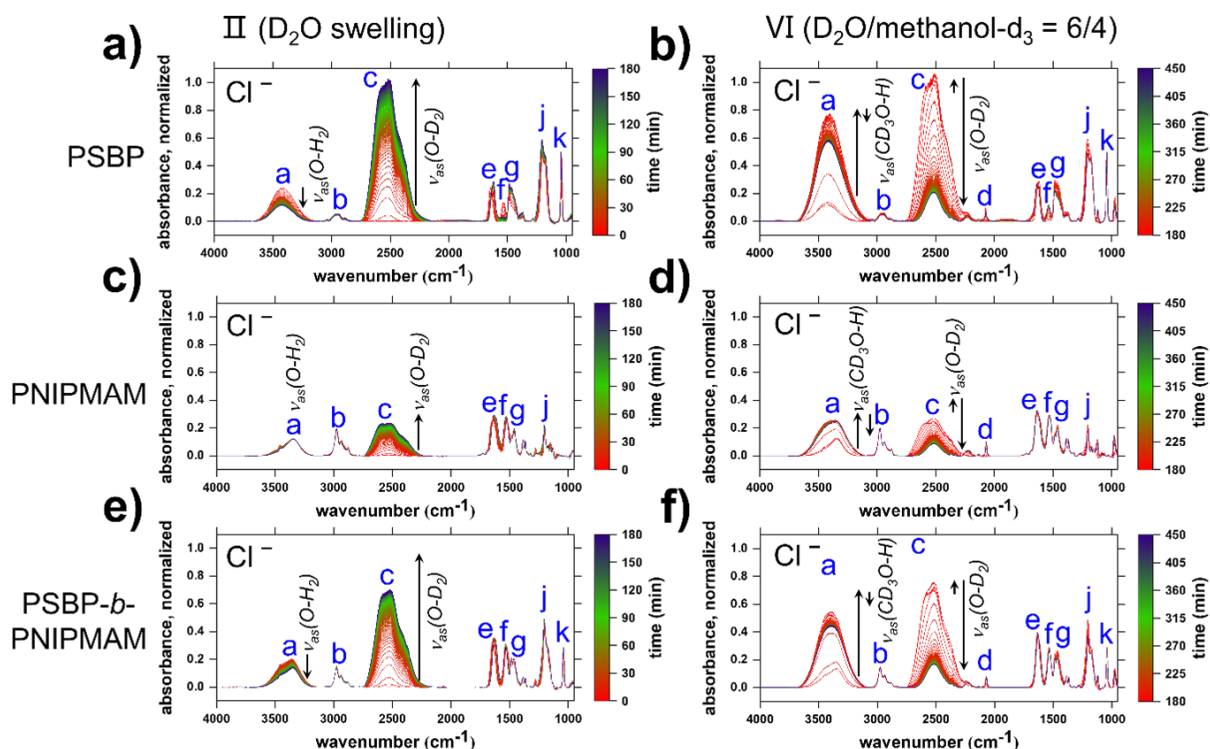


Figure 7.5.: FTIR spectra of Cl^- -loaded (a, b) PSBP, (c, d) PNIPMAM, and (e, f) PSBP-*b*-PNIPMAM film upon (a, c, e) D₂O swelling (stage II) and (b, d, f) subsequent vapor switching (stage VI). The characteristic bands listed in Table 7.1 are indicated by blue lower-case letters. The black arrows highlight the growth or decay of characterized signals.

H_2) $\approx 3400 \text{ cm}^{-1}$). This observation indicates that the absorbing D₂O molecules replace the residual H₂O being already present in the films. Analogously, upon vapor switching, the reversed changes of both hydroxyl bands illustrate the concomitant D₂O release and CD₃OH absorption. The emergence of a peak *d* ($\nu_{\text{as}}(\text{C-D}_3\text{OH})$, specifically attributed to the CD₃OH) corroborates the absorption of CD₃OH. As seen in the enlarged spectra of Cl^- -loaded PSBP (marked by black arrows in Figure C.6c), the amide *I* band shifts towards lower wavenumbers as the carbonyl groups act as hydrogen-bond acceptors, while the amide *II* band disappears accompanied by an increase of the amide *II'* band due to an H/D exchange (N-H to N-D) upon D₂O hydration. The introduction of CD₃OH prompts the reverse change, as shown in Figure C.6d. Differently, the amide *II* band shifts towards higher wavenumbers for Cl^- -loaded films of PNIPMAM (Figure C.7c) and then shifts reversely (Figure C.7d), as the amide protons act as hydrogen-bond donors. An increase followed by an equivalent decrease in the amide *II'* signal (Figure C.7d) indicates an H/D exchange provoked by the absorbed CD₃OH molecules, fading out over time. As marked by the black arrows in Figure C.8c and d, the variations in the amide *II* and *II'* bands positions and heights of the DBC films result from superposed contributions of the two

blocks. The findings described above also apply to other salt-loaded samples for each type of polymer. Besides, the FTIR peaks resulting from CH_3COO^- ($\nu \approx 1590 - 1550 \text{ cm}^{-1}$) and NO_3^- ($\nu \approx 1410 - 1370 \text{ cm}^{-1}$) are marked in the static FTIR spectra (Figure C.9). Although the absorbed D_2O and CD_3OH contents can be partly distinguished via their hydroxyl bands in the static FTIR spectra, it remains challenging to determine a trend for the salt series. The observations from the kinetic FTIR study are plotted in Figure 7.6, including the temporal evolution of the relative D_2O and CD_3OH contents (Figure 7.6a-*i*, b-*i* and c-*i*) as well as the peak shifts of characteristic signals (Figure 7.6a-*ii*, *iii*, b-*ii*, *iii* and c-*ii*, *iii*, *iv*).

Upon D_2O hydration, the trend of the salt effects on the absorbed D_2O amount varies somewhat between the different polymer films, in agreement with the observations by the SR measurements (see Figure 7.1). While the order of the effects may be formally described by an inverted Hofmeister series for the DBC ($\text{CH}_3\text{COO}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^- > \text{I}^-$) and -at least approximately- also for PSBP ($\text{CH}_3\text{COO}^- > \text{Cl}^- > \text{Br}^- > \text{I}^- > \text{NO}_3^-$), the deviations from such an analogy are rather pronounced for PNIPMAM ($\text{Br}^- > \text{CH}_3\text{COO}^- > \text{Cl}^- > \text{I}^- > \text{NO}_3^-$). The three consecutive steps of D_2O absorption in the PSBP films (Figure 7.6a-*i*) are attributed to the strong water absorption ability of the polyelectrolyte, which might cause a mismatch between the rates of water absorption and polymer chain conformation changes. Upon vapor switching, the salt effects are easily determined from the equilibrated CD_3OH contents (stage *VI* in Figure 7.6a,d,c-*i*). The determined salt series from the D_2O uptake behavior remains unchanged in the CD_3OH uptake in the presence of nearly equal amounts of D_2O content, in agreement with findings from ToF-NR. The short reswelling process during the first 10 min of stage *XII* is also clearly observed in the CD_3OH content.

To reveal the salt effects on the local chemical surroundings, a Gauss fit is performed to FTIR data to detect the peak shifts of the characteristic signals (amide *I* band and anionic SO_3^- group for PSBP, amide *I* and *II* bands for PNIPMAM and all three bands for DBC). For the amide bands, either the peak shifts upon D_2O hydration or the subsequent backshifts upon vapor switching, follow the same trends identified before as a function of salt type. Interestingly, the shift of the amide *II* band of PNIPMAM films at stage *VI* (Figure 7.6b-*iii*) features a small overshoot and is partially reversed to reach a similar position as upon D_2O hydration. This observation coincides with the increase in height and area of the amide *II'* band in Figure C.7, which is followed by an equivalent decrease subsequently. As no further shift appears for the amide *I* band (Figure 7.6b-*ii*), we infer that the reswelling process (positive cosolvent effect) in mixed $\text{D}_2\text{O}/\text{CD}_3\text{OH}$ vapor is due to an H/D exchange at the amide group. Besides, for the Br^- -loaded PNIPMAM film, an up/down change, that makes the Br^- -loaded curve crossing the CH_3COO^- -loaded curve,

Table 7.1.: Detailed band assignments of three types of polymer thin films upon dynamic processes.

detailed band assignments of PSBP, PNIPAM, PSBP- <i>b</i> -PNIPAM in thin film geometry according to FTIR spectrum						
	PSBP		PNIPAM		PSBP- <i>b</i> -PNIPAM	
	wavenumber/cm ⁻¹	assignment	wavenumber/cm ⁻¹	assignment	wavenumber/cm ⁻¹	assignment
a	3658 – 3145 methanol-d ₃ H ₂ O	$\nu_{as}(CD_3O-H)$ $\nu_{as}(O-H_2)$	3600 – 3135 methanol-d ₃ H ₂ O	$\nu_{as}(CD_3O-H)$ $\nu_{as}(O-H_2)$	3640 – 3155 methanol-d ₃ H ₂ O	$\nu_{as}(CD_3O-H)$ $\nu_{as}(O-H_2)$
b	3090 - 2790	$\nu_{as}(N-H)$ $\nu_{as}(C-H_3)$ $\nu_{as}(C-H_2)$ $\nu_{as}(C-H)$ $\nu_{sym}(C-H_3)$ $\nu_{sym}(C-H_2)$	3045 - 2850	$\nu_{as}(N-H)$ $\nu_{as}(C-H_3)$ $\nu_{as}(C-H_2)$ $\nu(C-H)$ $\nu_{sym}(C-H_3)$ $\nu_{sym}(C-H_2)$	3060 - 2850	$\nu_{as}(N-H)$ $\nu_{as}(C-H_3)$ $\nu_{as}(C-H_2)$ $\nu(C-H)$ $\nu_{sym}(C-H_3)$ $\nu_{sym}(C-H_2)$
c	2755 – 2235 D ₂ O	$\nu_{as}(O-D_2)$	2750 – 2185 D ₂ O	$\nu_{as}(O-D_2)$	2750 – 2185 D ₂ O	$\nu_{as}(O-D_2)$
d	2100 – 2020 methanol-d ₃	$\nu_{as}(C-D_3OH)$	2100 – 2020 methanol-d ₃	$\nu_{as}(C-D_3OH)$	2120 – 2020 methanol-d ₃	$\nu_{as}(C-D_3OH)$
e	1750 – 1575 amide I	$\nu_{as}(C=O\cdots H-N)$ $\nu_{as}(C=O\cdots D-O-D)$ $\nu_{as}(C=O\cdots H-O-D_3C)$	1755 – 1570 amide I	$\nu_{as}(C=O\cdots H-N)$ $\nu_{as}(C=O\cdots D-O-D)$ $\nu_{as}(C=O\cdots H-O-D_3C)$	1700 – 1575 amide I	$\nu_{as}(C=O\cdots D-N)$ $\nu_{as}(C=O\cdots D-O-D)$ $\nu_{as}(C=O\cdots H-O-D_3C)$
f	1575 – 1510 amide II	$\delta(N-H\cdots O=C)$ $\delta(N-H\cdots O-D_2)$ $\delta(N-H\cdots H-O-D_3C)$	1570 – 1495 amide II	$\delta(N-H\cdots O=C)$ $\delta(N-H\cdots O-D_2)$ $\delta(N-H\cdots H-O-D_3C)$	1575 – 1505 amide II	$\delta(N-H\cdots O=C)$ $\delta(N-H\cdots O-D_2)$ $\delta(N-H\cdots H-O-D_3C)$
g	1510 – 1340 amide II'	$\delta(N-D\cdots O-H/D)$ $\delta_{as}(C-H_3)$ $\delta_{as}(C-H_2)$	1495 – 1410 amide II'	$\delta(N-D\cdots O-H/D)$ $\delta_{as}(C-H_3)$ $\delta_{as}(C-H_2)$	1505 – 1405 amide II'	$\delta(N-D\cdots O-H/D)$ $\delta_{as}(C-H_3)$ $\delta_{as}(C-H_2)$
h	1410 - 1350	$\delta_{sym}(C-H_3)$ $\delta_{sym}(C-H_2)$	1410 - 1335	$\delta_{sym}(C-H_3)$ $\delta_{sym}(C-H_2)$	1405 - 1335	$\delta_{sym}(C-H_3)$ $\delta_{sym}(C-H_2)$
i	1305 – 1265 amide III	—	1295 – 1235 amide III	—	1305 – 1265 amide III	—
j	1265 - 1080	CH ₃ skeletal CH ₂ skeletal CH ₃ rocking CH ₂ rocking	1235 - 1005	CH ₃ skeletal CH ₂ skeletal CH ₃ rocking CH ₂ rocking	1265 - 1100	CH ₃ skeletal CH ₂ skeletal CH ₃ rocking CH ₂ rocking
k	1080 - 1010	$\delta(-SO_2-O-)$	—	—	1070 - 1010	$\delta(-SO_2-O-)$

is not observed in the amide II shift. This finding implies that the solvation shells at the amide I band mainly affect the PNIPAM contraction. As for the peak of the anionic SO₃[−] group (Figure 7.6a-iii and 7.6c-iv) which is exclusive for the side chains of PSBP, the loaded salts push its initial position towards higher wavenumbers as a general effect, while reducing the peak shift compared to the salt-free control. However, no specific salt effect is observed. This finding suggests indiscriminate ionic interactions between SO₃[−] and loaded K⁺, which impairs the ability of the SO₃[−] group to act as a hydrogen-bond donor. In all cases, a significant salt-induced solvation effect is observed in the FTIR data of each type of polymer thin film, including solvent contents and peak shifts.

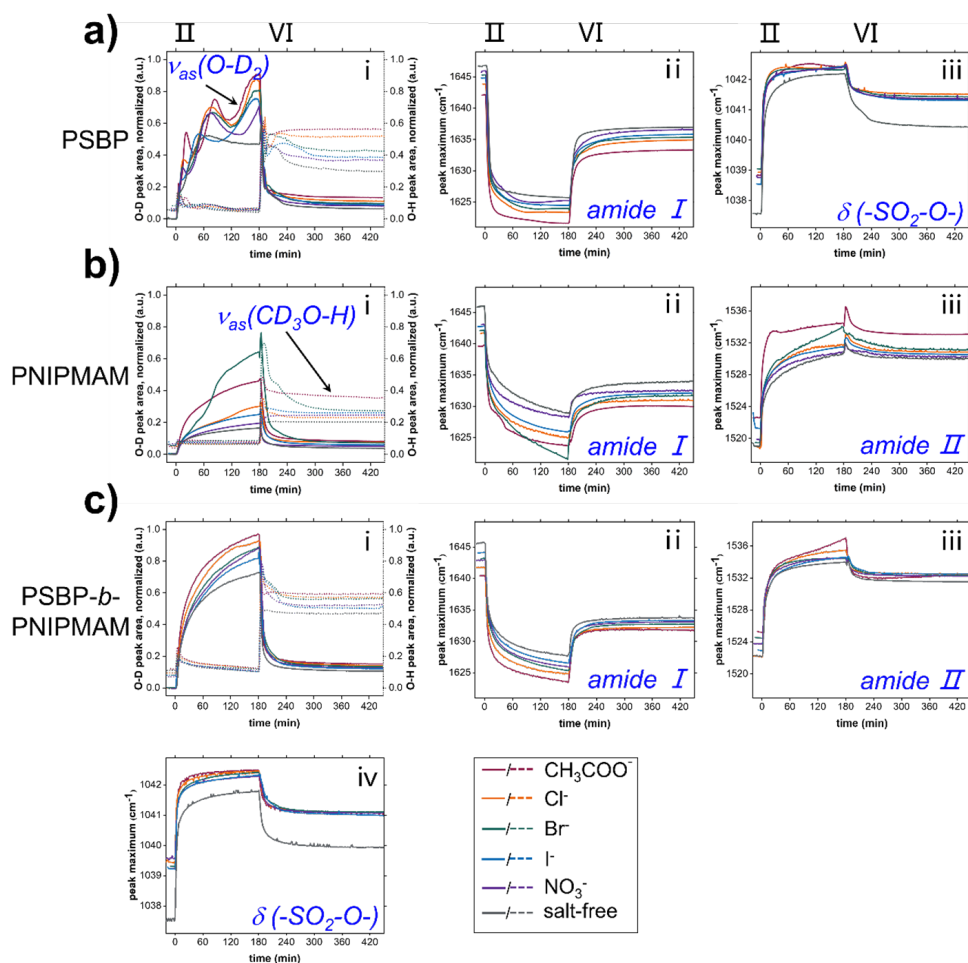


Figure 7.6.: Temporal evolution of normalized peak areas of O-D and O-H stretching vibrations, and peak position shifts of the amide *I* band, amide *II* band and the symmetric S-O stretching vibration for (a) PSBP, (b) PNIPMAM and (c) PSBP-*b*-PNIPMAM thin films. The peak areas of O-H stretching vibrations in Figures *i* are plotted as dotted lines corresponding to the right y-axis, to distinguish them from O-D stretching vibrations.

7.2.4. Salt effect on the temporal sequence of solvation events

Figure 7.7 presents the 2D FTIR correlation contour maps of the different Cl^- -loaded polymer samples during the first 45 min upon D_2O hydration, during which period most of the solvation events occur that respond to the D_2O vapor, as marked by black arrows in the spectra on top of the synchronous maps. The observed decrease of the amide *I* signal is attributed to the breaking of intermolecular hydrogen bonds ($\text{C}=\text{O}\cdots\text{H}-\text{N}$), while the observed increase is attributed to the generation of amide *I*- D_2O hydrogen bonds ($\text{C}=\text{O}\cdots\text{D}-\text{O}-\text{D}$). Similarly, the increase in the amide *II* band in PNIPMAM and DBC films (Figure 7.7b, c) is attributed to the generation of amide *II*- D_2O hydrogen bonds ($\text{N}-\text{H}\cdots\text{O}-\text{D}_2$), while the decrease is attributed to the breaking of intermolecular hydrogen

bonds ($\text{N-H}\cdots\text{O}=\text{C}$). In agreement with the findings from the FTIR spectra, the amide II fluctuation in PSBP (Figure 7.7a) is attributed to the generation of amide II - D_2O hydrogen bonds ($\text{N-H}\cdots\text{O-D}_2$) and a H/D exchange, while the latter one contributes to the increase in amide II' band ($\text{N-D}\cdots\text{O-H/D}$). Note that the 2D plot only reveals the spectral fluctuation hidden by peak shift, but not the intensity change. Thus, the event that occurred at the amide II band in PSBP only represents the generation of $\text{N-H}\cdots\text{O-D}_2$ bonds, whereas the one that occurred at the amide II' band represents a H/D exchange. Corresponding to the described solvation events, strong autopeaks develop in the respective synchronous map diagonals.

As shown in the off-diagonal region ($\nu_1 > \nu_2$, Figure 7.7), the cross-peaks are marked by gray dotted lines in both synchronous and asynchronous maps. According to Noda's rule[255]–[257] and the analysis of Cl^- -loaded samples described in the Appendix C, the concluded sequence of solvation events is depicted as $1545 > 1620 > 1450 > 1655 \text{ cm}^{-1}$ for Cl^- -loaded PSBP film. It is depicted as $1605 > 1542 > 1665, 1500 \text{ cm}^{-1}$ for Cl^- -loaded PNIPMAM film, and depicted as $1605 > 1545 > 1667, 1505 > 1465 \text{ cm}^{-1}$ for Cl^- -loaded DBC film. For a comparative analysis, two types of contour maps of all salt-loaded and salt-free PSBP (Figure C.10), PNIPMAM (Figure C.11), and DBC (Figure C.12) samples are plotted in the Appendix C. The salt effect on the temporal sequences of the assigned solvation events is summarized in Table 7.2 for all samples. As at stage VI , each sample undergoes multi-responses to this vapor switching step as described by the normalized peak areas of the group-specific IR-bands (Figure 7.6a,b,c-*i*), resulting in a disordered separation and distribution of cross-peaks in the asynchronous maps. Therefore, 2D FTIR correlation analysis is not used to analyze the solvation sequence at stage VI .

Except for CH_3COOK , the loaded salts do not change the temporal sequence of solvation events in the PSBP films that is depicted as $1545 > 1620 > 1450 > 1655 \text{ cm}^{-1}$. This sequence indicates that upon water absorption, the water shell surrounding the chemical groups responsible for the amide II band in the PSBP film builds-up faster than the one surrounding the groups responsible for the amide I band. Later an H/D exchange follows. As a result, the hydrated water molecules break the intermolecular hydrogen bonds, leading to an expansion of the polymer chains. As listed in Table 7.2, the temporal sequence of solvation events is depicted as $1560 > 1620 > 1450 > 1545, 1655 \text{ cm}^{-1}$ for the CH_3COO^- -loaded PSBP film, as two autopeaks ($\nu = 1580$ and 1560 cm^{-1}) are detected in the synchronous map (Figure C.10a). These are attributed to the hydration of CH_3COO^- as mentioned in the analysis of the static FTIR spectra. This finding implies that the hydration of CH_3COO^- is faster than of the amide groups, and makes the amide I band response prior to that of the amide II bands. Significantly, as listed in Table 7.2, depending on the loaded anion species, the temporal sequence of solvation events

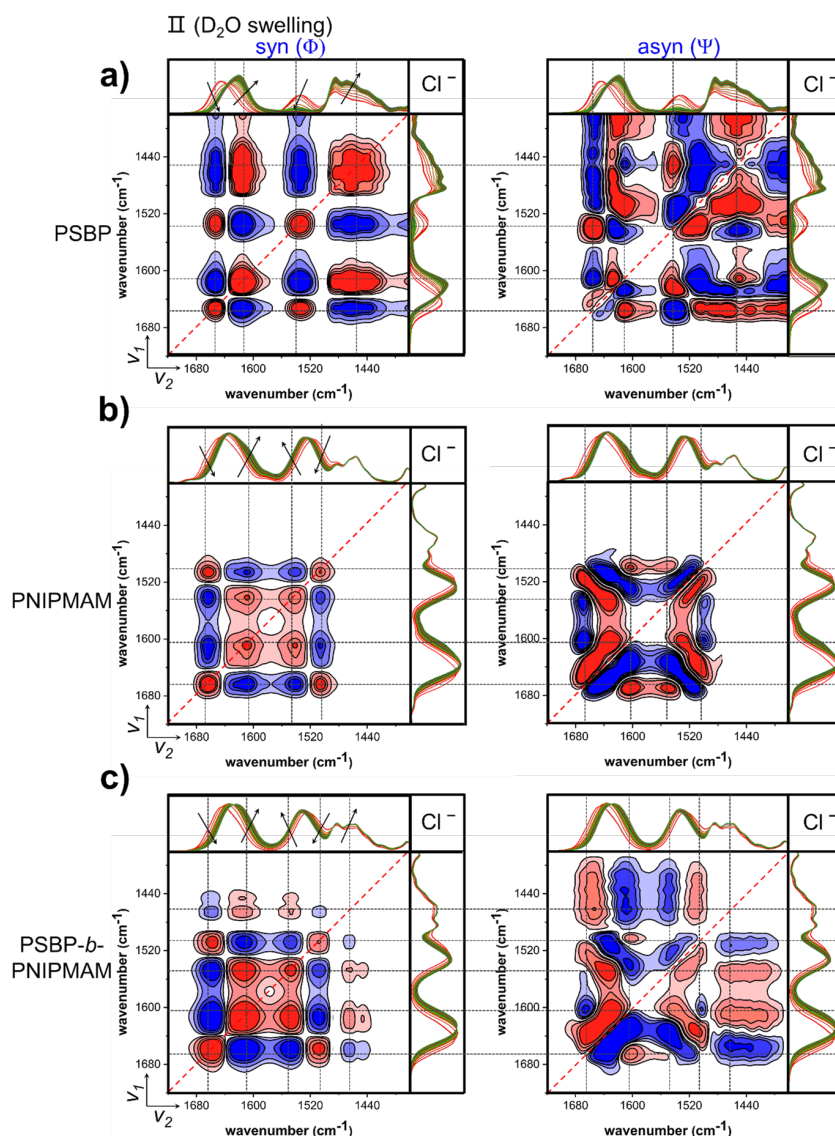


Figure 7.7.: 2D FTIR correlation contour maps of Cl^- -loaded (a) PSBP, (b) PNIPMAM and (c) PSBP-*b*-PNIPMAM thin films. Synchronous and asynchronous maps are marked as Φ and Ψ respectively. The positive correlation and negative correlation are colored in red and blue respectively.

differs among the various salt-loaded PNIPMAM films. The same temporal sequences of $1605 > 1542 > 1665$, 1500 cm^{-1} are found for Cl^- , I^- , and NO_3^- -loaded PNIPMAM films, indicating that the amide *I* related group responds faster than the amide *II* related one. A weak autopeak ($\nu = 1460 \text{ cm}^{-1}$), assigned to the amide *II'* band, is detected in CH_3COO^- -loaded and salt-free synchronous maps, but a strong peak is found in the Br^- -loaded synchronous map (Figure C.11c). Unexpectedly, the observed sequences indicate that response of the amide *II'* band is faster than the responses of the amide *I* and amide

Table 7.2.: Temporal sequence of the solvation events.

temporal sequence of solvation events in amide bands of PSBP, PNIMAM, PSBP- <i>b</i> -PNIPMAM					
	D ₂ O swelling	strong autopeaks			
		amide I		amide II	amide II'
		$\nu_{as}(C=O\cdots H-N)$	$\nu_{as}(C=O\cdots D-O-D)$	$\delta(N-H\cdots O-D_2)$	$\delta(N-D\cdots O-H/D)$
		$\approx 1655\text{ cm}^{-1}$	$\approx 1620\text{ cm}^{-1}$	$\approx 1545\text{ cm}^{-1}$	$\approx 1450\text{ cm}^{-1}$
PSBP	CH ₃ COO ⁻	1560 > 1620 > 1450 > 1545, 1655 $CH_3COO\cdots D_2O > \nu_{as}(C=O\cdots D-O-D) > \delta(N-D\cdots O-H/D) > \delta(N-H\cdots O-D_2), \nu_{as}(C=O\cdots H-N)$			
	Cl ⁻	1545 > 1620 > 1450 > 1655 $\delta(N-H\cdots O-D_2) > \nu_{as}(C=O\cdots D-O-D) > \delta(N-D\cdots O-H/D) > \nu_{as}(C=O\cdots H-N)$			
	Br ⁻	1545 > 1620 > 1450 > 1655 $\delta(N-H\cdots O-D_2) > \nu_{as}(C=O\cdots D-O-D) > \delta(N-D\cdots O-H/D) > \nu_{as}(C=O\cdots H-N)$			
	I ⁻	1545 > 1620 > 1450 > 1655 $\delta(N-H\cdots O-D_2) > \nu_{as}(C=O\cdots D-O-D) > \delta(N-D\cdots O-H/D) > \nu_{as}(C=O\cdots H-N)$			
	NO ₃ ⁻	1545, 1620 > 1450 > 1655 $\delta(N-H\cdots O-D_2), \nu_{as}(C=O\cdots D-O-D) > \delta(N-D\cdots O-H/D) > \nu_{as}(C=O\cdots H-N)$			
	salt-free	1545 > 1620 > 1450 > 1655 $\delta(N-H\cdots O-D_2) > \nu_{as}(C=O\cdots D-O-D) > \delta(N-D\cdots O-H/D) > \nu_{as}(C=O\cdots H-N)$			
PNIPMAM		strong autopeaks			
		amide I		amide II	amide II'
		$\nu_{as}(C=O\cdots H-N)$	$\nu_{as}(C=O\cdots D-O-D)$	$\delta(N-H\cdots O-D_2)$	$\delta(N-H\cdots O=C)$
		$\approx 1665\text{ cm}^{-1}$	$\approx 1605\text{ cm}^{-1}$	$\approx 1542\text{ cm}^{-1}$	$\approx 1500\text{ cm}^{-1}$
	CH ₃ COO ⁻	1460 > 1542 > 1605 > 1665, 1500 $\delta(N-H\cdots O-H/D) > \delta(N-D\cdots O-D_2) > \nu_{as}(C=O\cdots D-O-D) > \nu_{as}(C=O\cdots H-N) > \delta(N-H\cdots O=C)$			
	Cl ⁻	1605 > 1542 > 1665, 1500 $\nu_{as}(C=O\cdots D-O-D) > \delta(N-H\cdots O-D_2) > \nu_{as}(C=O\cdots H-N), \delta(N-H\cdots O=C)$			
	Br ⁻	1460 > 1542, 1605 > 1665 $\delta(N-H\cdots O-H/D) > \delta(N-H\cdots O-D_2), \nu_{as}(C=O\cdots D-O-D) > \nu_{as}(C=O\cdots H-N)$			
PSBP- <i>b</i> -PNIPMAM	I ⁻	1605 > 1542 > 1665, 1500 $\nu_{as}(C=O\cdots D-O-D) > \delta(N-H\cdots O-D_2) > \nu_{as}(C=O\cdots H-N), \delta(N-H\cdots O=C)$			
	NO ₃ ⁻	1605 > 1542 > 1665, 1500 $\nu_{as}(C=O\cdots D-O-D) > \delta(N-H\cdots O-D_2) > \nu_{as}(C=O\cdots H-N), \delta(N-H\cdots O=C)$			
	salt-free	1460 > 1665, 1500 > 1605, 1542 $\delta(N-H\cdots O-H/D) > \nu_{as}(C=O\cdots H-N), \delta(N-H\cdots O=C) > \nu_{as}(C=O\cdots D-O-D), \delta(N-H\cdots O-D_2)$			
		strong autopeaks			
		amide I		amide II	amide II'
		$\nu_{as}(C=O\cdots H-N)$	$\nu_{as}(C=O\cdots D-O-D)$	$\delta(N-H\cdots O-D_2)$	$\delta(N-H\cdots O=C)$
		$\approx 1667\text{ cm}^{-1}$	$\approx 1605\text{ cm}^{-1}$	$\approx 1545\text{ cm}^{-1}$	$\approx 1505\text{ cm}^{-1}$
PSBP- <i>b</i> -PNIPMAM	CH ₃ COO ⁻	1505 > 1605, 1667 > 1580, 1545, 1465 $\delta(N-H\cdots O=C) > \nu_{as}(C=O\cdots D-O-D), \nu_{as}(C=O\cdots H-N) > CH_3COO\cdots D_2O, \delta(N-H\cdots O-D_2), \delta(N-D\cdots O-H/D)$			
	Cl ⁻	1605 > 1545 > 1667, 1505 > 1465 $\nu_{as}(C=O\cdots D-O-D) > \delta(N-H\cdots O-D_2) > \nu_{as}(C=O\cdots H-N), \delta(N-H\cdots O=C) > \delta(N-D\cdots O-H/D)$			
	Br ⁻	1605 > 1545 > 1667, 1505 > 1465 $\nu_{as}(C=O\cdots D-O-D) > \delta(N-H\cdots O-D_2) > \nu_{as}(C=O\cdots H-N), \delta(N-H\cdots O=C) > \delta(N-D\cdots O-H/D)$			
	I ⁻	1605 > 1545 > 1667, 1505 > 1465 $\nu_{as}(C=O\cdots D-O-D) > \delta(N-H\cdots O-D_2) > \nu_{as}(C=O\cdots H-N), \delta(N-H\cdots O=C) > \delta(N-D\cdots O-H/D)$			
	NO ₃ ⁻	1605 > 1400, 1545 > 1667, 1505 > 1465 $\nu_{as}(C=O\cdots D-O-D) > NO_3\cdots D_2O, \delta(N-H\cdots O-D_2) > \nu_{as}(C=O\cdots H-N), \delta(N-H\cdots O=C) > \delta(N-D\cdots O-H/D)$			
	salt-free	1605 > 1545 > 1667, 1505 > 1465 $\nu_{as}(C=O\cdots D-O-D) > \delta(N-H\cdots O-D_2) > \nu_{as}(C=O\cdots H-N), \delta(N-H\cdots O=C) > \delta(N-D\cdots O-H/D)$			

the symbol of ">" refers to the change priority of spectral fluctuation

II bands, while the responses of the of amide I and II bands to hydration are faster than the breaking of intermolecular hydrogen bonds for CH₃COO⁻- and Br⁻-loaded samples but slower for the salt-free sample. These observations demonstrate that upon water absorption, the water shell surrounding the groups responsible for the amide I band in the PNIPMAM films builds up faster than the hydration shell around the ones producing the amide II band. As a result, the intermolecular hydrogen bonds break. When a preferential H/D exchange exists, the amide I and amide II bands show a similar response

priority in their sequences. These differences in the PNIPMAM solvation sequences may be correlated to the findings for the salt series as determined by SR and FTIR, namely that the CH_3COO^- - and Br^- anions provoke a pronounced effect, and that the relative effect of Br^- crosses that of CH_3COO^- at one point, while the Cl^- , I^- and NO_3^- anions induce very similar effects.

Except for CH_3COOK , the loaded salts do not change the temporal sequence of solvation events in the PSBP films that is depicted as $1545 > 1620 > 1450 > 1655 \text{ cm}^{-1}$. This sequence indicates that upon water absorption, the water shell surrounding the chemical groups responsible for the amide *II* band in the PSBP film builds-up faster than the one surrounding the groups responsible for the amide *I* band. Later an H/D exchange follows. As a result, the hydrated water molecules break the intermolecular hydrogen bonds, leading to an expansion of the polymer chains. As listed in Table 7.2, the temporal sequence of solvation events is depicted as $1560 > 1620 > 1450 > 1545, 1655 \text{ cm}^{-1}$ for the CH_3COO^- -loaded PSBP film, as two autopeaks ($\nu = 1580$ and 1560 cm^{-1}) are detected in the synchronous map (Figure C.10a). These are attributed to the hydration of CH_3COO^- as mentioned in the analysis of the static FTIR spectra. Such finding implies that the hydration of CH_3COO^- is faster than of the amide groups, and makes the amide *I* band response prior to that of the amide *II* bands. Significantly, as listed in Table 7.2, depending on the loaded anion species, the temporal sequence of solvation events differs among the various salt-loaded PNIPMAM films. The same temporal sequences of $1605 > 1542 > 1665, 1500 \text{ cm}^{-1}$ are found for Cl^- , I^- , and NO_3^- -loaded PNIPMAM films, indicating that the amide *I* related group responds faster than the amide *II* related one. A weak autopeak ($\nu = 1460 \text{ cm}^{-1}$), assigned to the amide *II'* band, is detected in CH_3COO^- -loaded and salt-free synchronous maps, but a strong peak is found in the Br^- -loaded synchronous map (Figure C.11c). Unexpectedly, the observed sequences indicate that response of the amide *II'* band is faster than the responses of the amide *I* and amide *II* bands, while the responses of the of amide *I* and *II* bands to hydration are faster than the breaking of intermolecular hydrogen bonds for CH_3COO^- - and Br^- -loaded samples but slower for the salt-free sample. These observations demonstrate that upon water absorption, the water shell surrounding the groups responsible for the amide *I* band in the PNIPMAM films builds up faster than the hydration shell around the ones producing the amide *II* band. As a result, the intermolecular hydrogen bonds break. When a preferential H/D exchange exists, the amide *I* and amide *II* bands show a similar response priority in their sequences. These differences in the PNIPMAM solvation sequences may be correlated to the findings for the salt series as determined by SR and FTIR, namely that the CH_3COO^- - and Br^- anions provoke a pronounced effect, and that the relative effect of Br^- crosses that of CH_3COO^- at one point, while the Cl^- , I^- and NO_3^- anions

induce very similar effects.

For all DBC samples, the hydration events basically follow the sequence of $1605 > 1545 > 1465 \text{ cm}^{-1}$, indicating that the amide *I* band response is faster than the one of the amide *II* band, while the amide *II'* band response is slowest. As for DBC films, in addition to the CH_3COO^- autopeak ($\nu = 1580 \text{ cm}^{-1}$) in Figure C.12a, an autopeak ($\nu = 1400 \text{ cm}^{-1}$) is seen and attributed to the hydration of NO_3^- (Figure C.12e). Besides, with CH_3COO^- present, the amide *I* band loses its priority, while with NO_3^- present, the amide band *II* reaches priority. These differences can explain that the salt effect of CH_3COO^- in the DBC film is less pronounced than in the PSBP and PNIPMAM films. Moreover, it can explain that NO_3^- has a priority to I^- in the DBC salt series. We also find that the response of amide *II'* band takes precedence in PNIPMAM films but lags in PSBP films over the amide *I* and *II* bands, and that the autopeaks assigned to amide *II'* band show up in Cl^- , I^- , NO_3^- -loaded PSBP film but not in PNIPMAM films. Taking these observations together, we conclude that the response of the PNIPMAM block is faster than the response of the PSBP block in the DBC films upon water hydration.

7.2.5. Solvation shell and the DBC polymer conformation

To examine the salt effect on the accessibility of solvation shells near the hydrophilic groups, radial distribution function (RDF) profiles between solvation shells and DBC chains are calculated as shown in Figure 7.8. We restrict the MD calculations to a single DBC chain, featuring 4 SBP repeating units and 6 NIPMAM repeating units exposed to pure H_2O atmosphere (Figure C.13), pure CH_3OH atmosphere (Figure C.14), and mixed $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ atmosphere (Figure C.15).

In a pure H_2O vapor atmosphere (Figure 7.8a), the first H_2O shell is observed at $\sim 1.5 \text{ \AA}$ and $\sim 2.2 \text{ \AA}$ respectively for CH_3COO^- - and Cl^- -loaded DBC chains, while the second H_2O shell is observed for both at $\sim 2.7 \text{ \AA}$. In addition, the first H_2O shell is observed at $\sim 2.7 \text{ \AA}$ for Br^- , I^- and NO_3^- -loaded DBC chains after an RDF overlap at $\sim 2.5 \text{ \AA}$. Yet before the overlap, a shift towards the right is following the tendency $\text{Br}^- > \text{NO}_3^- > \text{I}^-$, as well as the intensity decrease in the RDF profiles. These findings indicate that the hydration water shells not close to the hydrophilic groups follow the anion sequence of $\text{CH}_3\text{COO}^- < \text{Cl}^- < \text{Br}^- < \text{NO}_3^- < \text{I}^-$. As shown in Figure C.16, by integrating the corresponding relative intensity peak area, the accessibility of the water shell to the DBC chains obeys the anion order $\text{CH}_3\text{COO}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^- > \text{I}^-$ of the salt series found in the SR, TOF-NR, and FTIR data analysis. In a pure CH_3OH atmosphere (Figure C.16), the corresponding intensity peak area decreases, indicating that there are fewer methanol molecules than water molecules nearby the polymer chain. The observation that a first methanol shell is observed at $\sim 2.1 \text{ \AA}$ for Cl^- -loaded and at $\sim$

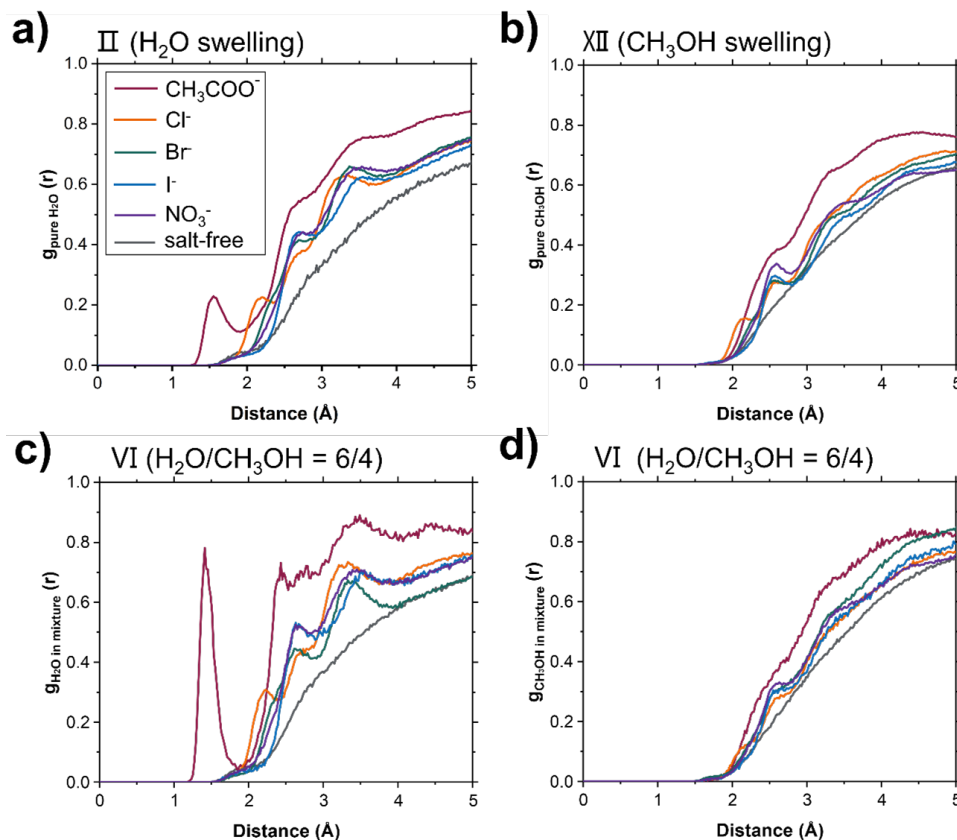


Figure 7.8.: Radial distribution function (RDF) profiles for H₂O shell a) in pure H₂O and c) mixed atmosphere, and for methanol shell b) in pure methanol and mixed atmosphere.

2.6 Å for the other salt-loaded DBC chains, indicates that the presence of Cl[−] allows the methanol shell to be closer to the hydrophilic groups. Considering the integrated relative peak areas of the intensity in Figure C.16, the salt series of CH₃COO[−] > Cl[−] > Br[−] > NO₃[−] > I[−] is still valid for the accessibility of the methanol shell to the salt-loaded DBC chain. Analogously, in a mixed H₂O/CH₃OH atmosphere, when comparing the integrated relative peak areas of the intensity in Figure C.16, the accessibility of the water shell follows the order CH₃COO[−] > Cl[−] > Br[−] > NO₃[−] > I[−], while the methanol shell follows the slightly modified order CH₃COO[−] > Cl[−] ≈ Br[−] ≈ NO₃[−] ≈ I[−]. Nevertheless, in each scenario, the loaded anions shift the formed solvation shell significantly closer to the DBC chains, especially in the cases of CH₃COO[−] and Cl[−].

The conformation transitions of the salt-free DBC chains in each case are illustrated by the snapshots from the MD simulations at 0 and 20 ps. As shown in Figure C.17, the DBC chain undergoes a significant coil-to-globe transition from 0 to 20 ps, as the intermolecular hydrogen bonds are replaced by polymer-water hydrogen bonds upon H₂O hydration. In contrast, in the pure CH₃OH atmosphere (Figure C.18), the DBC chain extends slightly due to the less cooperative methanol molecules. As both water and methanol molecules

form hydrogen bonds with the hydrophilic groups in a mixed $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ atmosphere (Figure C.19), the DBC chains also expand slightly, but are surrounded by a built-up methanol-water shell.

7.3. Conclusions

The salt effect of 5 potassium salts, namely CH_3COOK , KCl , KBr , KI , and KNO_3 , on the solvation behavior of thin films of the thermoresponsive zwitterionic polymer PSBP (UCST-type), the polar non-ionic one PNIPMAM (LCST-type), and their diblock copolymer (DBC) PSBP-*b*-PNIPMAM (UCST-*b*-LCST type), is systematically studied via complementary experimental methods (SR, ToF-NR, and FTIR) in pure water and mixed water/methanol vapor atmospheres. Salt-free samples are studied as references. Complementary computational methods (2D FTIR analysis and MD simulations) explain the salt effects on the response sequence of solvation events and the accessibility of solvation shells. For all combinations of polymers and salt, marked solvation effects are found. These vary however, for the different polymer types examined, and show also some polymer-anion pair specificities. Moreover, the kinetics of the solvation events vary markedly for the various hydrophilic moieties involved, such as the sulfonate and the amide groups. For thin PSBP films, the efficiency of the salt effects on the solvation behavior of may be approximatively described by an inverted Hofmeister series as $\text{CH}_3\text{COO}^- > \text{Cl}^- > \text{Br}^- > \text{I}^- > \text{NO}_3^-$, with CH_3COO^- featuring the strongest and NO_3^- showing the smallest effect, with respect on film thickness and solvent content. The order of salt effects found for the DBC films matches even better an inverted Hofmeister series, with $\text{CH}_3\text{COO}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^- > \text{I}^-$. However, in the case of PNIPMAM thin films, such a description seems not appropriate, as the observed order in the salt series changes from $\text{Br}^- > \text{CH}_3\text{COO}^- > \text{Cl}^- \approx \text{I}^- > \text{NO}_3^-$ to $\text{CH}_3\text{COO}^- > \text{Br}^- > \text{Cl}^- > \text{I}^- > \text{NO}_3^-$ when the V_{methanol} exceeds 40 %. The cosolvent effect depends on the response property (positive or negative) of the thin films. The reached equilibrated state is explained by the balance between cosolvent and salt effects. In pure water vapor, the salt effects are mainly manifested in the change of the water absorption, visualized in the temporal sequence of solvation events and the accessibility of the hydration water shells. In contrast, in the specific mixed water/methanol (6/4) vapor, they are mainly manifested in the regulation of the methanol absorption under a retained moisture, visualizing in the examined water/methanol contents and a built-up methanol-water solvation shell.

Summary

A wealth of research on stimuli-responsive polymers provides vast potential applications in the fabrication of modern intelligent and microdevices, due to the significant changes in their physical or chemical properties under small environmental stimuli, while the focus has primarily been on temperature-sensitive polymers. Compared to extensive studies on aspects such as molecular design, synthesis, and applications, only limited research on the response mechanisms, predominantly concentrated on homopolymer in solution, was conducted. Rare exploration focusing on block copolymers and multiblock polymers was proposed, especially in 2D thin film geometry. The intrinsic response mechanisms of thermoresponsive polymers are constrained by various factors, such as the self-assembled structures, hydrophilic groups, response times and enthalpy changes, *etc.* Additionally, there are limitations in instrumental detection. Therefore, in the present thesis, the basic understanding framework of co-nonsolvency-triggered phase collapse, specific salt-modulated phase transition temperature shift, and specific ion effect on co-nonsolvency behavior of DBC thin films are examined in experiments by *in situ* methods.

The experimental part in the present work is composed of the setup and computational method. For the setup part, two sample chambers (the “Flexiprob” chamber and custom-designed FTIR chamber) were designed, which allowed controlling of the vapor composition by connecting to a gas flow system and controlling of the temperature by connecting to a temperature control system. The former with three channels realized the switch of saturated vapor of water, acetone, and methanol at will in any desired combination and proportion. The latter not only ensures the constant temperature of solvents, generated vapor, and samples but also realizes a slow temperature change from $T = 18\text{ }^{\circ}\text{C}$ to $T = 42\text{ }^{\circ}\text{C}$ with a temperature rate of $8\text{ }^{\circ}\text{C}/\text{h}$ to provide sufficient time for movement or rearrangement of polymer segments. The “Flexiprob” chamber with two freely removable sample holders (vertical one and horizontal one) is a benefit to *in situ* NR with aluminum windows and SR measurements with a CaF_2 window on tap, due to being lightweight and

small, which makes it ideal for installation at neutron beamlines and in the laboratory. Accordingly, equipped with two highly transmissive ZnS windows, the customized copper FTIR chamber not only provided the samples with a desired surrounding environment but also realized a temperature control by fixing it on a large copper holder. For the computational method, 2D FTIR correlation analysis is used to investigate the salt effect on the sequence of hydration events, and MD simulations are applied to explain the Hofmeister effect on the accessibility of hydrated solvation shells.

In situ ToF-NR with a time resolution of 5 s is an advanced material characterization technique applied in the soft matter field. The information about components at the interface can be obtained by analysis of the corresponding SLD profiles, such as the distribution of polymer layers, the interface thickness, the solvent absorption, and distribution along the normal direction. Besides, ToF-NR allows to determine the deuterium due to the SLD difference between hydrogen and deuterium. *In situ* SR with a time resolution of 10 s and *in situ* FTIR with a time resolution of 95 s or 210 s were performed at laboratory conditions, to detect the temporal evaluation of film thickness and track the building-up or reduction of solvation shells, respectively.

For a first fundamental understanding, the swelling behavior of PSBP-*b*-PNIPMAM thin films is systematically investigated in saturated H_2O or D_2O vapors, respectively. Additionally, a subsequent solvent exchange in mixed saturated water/acetone ($(H_2O$ or $D_2O)$: acetone- $d_6 = 9:1$ v/v) vapors are studied. This is described in Chapter 5. For the first time, mixed water/acetone vapor-induced co-nonsolvency is found in thin thermo-responsive polymer films. In the case of PSBP, the film contraction is caused by acetone- d_6 acting as a non-solvent, whereas, for PNIPMAM, acetone induces co-nonsolvency in a mixed saturated water/acetone- d_6 atmosphere. In the case of the DBC PSBP-*b*-PNIPMAM, a complex two-step contraction mechanism is seen. The PSBP block pre-dominates the first step and the PNIPMAM block dominates the second step, during which the solvation exchange processes assigned to both blocks mutually affect each other.

In general, the studied DBC achieves three different and stable static thicknesses upon swelling and solvation exchange, which can be used in applications devoted to nano-scale switches. Remarkably, a co-nonsolvency effect is established for the nonionic PNIPMAM block, both in mixed water-acetone solutions as well as in mixed vapor swollen films. The zwitterionic and the nonionic blocks of the DBC show a separate but interlinked solvent exchange behavior in a water/acetone- d_6 vapor atmosphere. Besides studying the affinity of the DBC thin film towards water or deuterium water, the sensitivity and stability of the formed hydration shell exposed to mixed water/acetone- d_6 vapor atmosphere are revealed. Importantly, the co-nonsolvency effect is seen in the less polar and aprotic solvent acetone. In particular, the studied films contract more drastically at a lower concentration

of the trigger co-solvent. The findings that a water isotope sensitivity is present during the water swelling and that a marked co-nonsolvency behavior is triggered by only a small amount of acetone molecules, which is much less harmful than methanol.

In the second part of this thesis, the specific salt(KCl)-modulated D₂O swelling and subsequent thermoresponsive behavior of PSBP-*b*-PNIPMAM thin films and the respective homopolymer thin films (PSBP and PNIPMAM) are systematically studied. This is described in Chapter 6. By complementary scattering and IR-spectroscopic methods. Under good solvency conditions at $T = 18\text{ }^{\circ}\text{C}$, the KCl-loaded samples always exhibit a higher swelling ratio compared to the salt-free samples, both for DBC and the reference homopolymer films. The presence of KCl increases the equilibrium thickness by 185 % and the D₂O content by 77 % upon D₂O hydration. Those indicate that adding KCl leads to a pronounced boosting of the water uptake in the thin-film geometry. Upon subsequent heating, an initial “further-swelling” period and a subsequent marked “film contraction” period with separate $VPTT_s$ (refers to $VPTT_{fs}$ and $VPTT_c$) are observed for both the salt-free and the KCl-loaded DBC films. Both $VPTT_s$ are shifted towards lower temperatures compared to the CPs found in aqueous solutions. This is mainly attributed to the high polymer concentration in thin-film geometry. Based on comparisons with the salt effect for the respective homopolymer thin films, the “further-swelling” period of the DBC thin films is attributed to the UCST-type phase transition of the PSBP block, whereas the “film contraction” period is attributed to the LCST-type phase transition of PNIPMAM block. The presence of KCl only affects the $VPTT_c$ of the PNIPMAM blocks in thin-film geometry, but not the $VPTT_{fs}$ of the PSBP block. Upon subsequent heating, the migration or aggregation of KCl inside the thin film is observed, resulting in the formation of a salt-rich zone. Analyzing the stage of hydration around the hydrophilic functional groups located in both the PSBP and the PNIPMAM blocks, the increasing hydration during the “further-swelling” period is attributed to the PSBP blocks, while this block is not involved in the reduction of the hydration during the subsequent “film contraction” period.

Compared with our earlier study on the NaBr-modulated thermo-responsive hydration behavior of the related DBC PSBP-*b*-PNIPMAM, the two blocks inside the DBC films of PSBP-*b*-PNIPMAM loaded with KCl show opposite thermal responses, especially concerning shifts in the $VPTT$. The added KCl only affects the $VPTT_c$ of the PNIPMAM block but not the $VPTT_{fs}$ of the PSBP block in thin-film geometry. Furthermore, we observe as a novum the formation of a KCl-rich interlayer. This interlayer reveals that (i) separate layers are present in the DBC thin films, which each absorbs a different amount of D₂O and (ii) the KCl ions originally dispersed into the sublayer near the surface migrate or accumulate in the interior of the thin film. At present, it is not clear, to what extent

this substructure formation is a result of the relatively smaller size of the zwitterionic polymer block, which has a priori a high affinity to accommodate ions, and the resulting reduced uptake capacity. This is the first evidence to prove that the relative block length of two blocks inside the DBC affects the thermoresponsive behavior and the studied DBC provides a new perspective on the salt effect on thin-film geometry.

The first two Chapters 5 and 6 focus on the phase transition behavior of PSBP-*b*-PNIPMAM thin films in a mixed vapor composition at constant temperature and specific salt effects on $VPTT_s$ in pure D₂O vapor, as well as respective PSBP and PNIPMAM homopolymers, Chapter 7 describes the salt effect of potassium salts (CH₃COOK, KCl, KBr, KI and KNO₃) on solvation behavior of respective PSBP (UCST-type), PNIPMAM (LCST-type) and PSBP-*b*-PNIPMA (UCST-LCST type) thin films, in water and subsequent exchanging or switching of mixed water/methanol atmosphere. The complementary computational methods (2D FTIR analysis and MD simulations) explain the salt effect on the response sequence of solvation events and the accessibility of solvation shells. Meanwhile, the parallelly studied salt-free samples explore the salt-induced solvation effect. For each type of polymer, the salt effect depends on the difference in phase transition upon mixed vapors, while the cosolvent effect depends on the response property (positive or negative) of thin films. The reached equilibrated state is explained by the balance between the two effects. In pure water atmosphere, the salt effect is mainly manifested in the modulation of water absorption visualizing in the temporal sequence of solvation events and the accessibility of the hydrated water shells, whereas, in specific mixed water/methanol (6/4) atmosphere, it mainly manifested in the regulation of methanol absorption under retained moisture visualizing in the examined water/methanol contents and a built-up methanol-water shell.

In summary, the present thesis demonstrates a sensitive water hydration behavior of the investigated orthogonally dual thermoresponsive DBC thin films, and provides a basic understanding of solvent exchanging mechanism triggered nonsolvent behavior and salt enrichment induced layer separation and $VPTT$ shift. Remarkably, those behaviors can be modulated by the addition of ions following the salt series, which is beneficial to designing stimuli-responsive materials with customized properties. In parallel, the thin film geometry enables new possibilities. Multiple and reproducible thin film regimes are established that can be tuned by the vapor composition and salt additives, making the studied DBC films promising candidates for a wider range of potential applications, such as humidity sensors, multifunction switches, controlled release systems, and biopharmaceutical systems.

Appendix A

Supporting information for Chapter 5

This chapter is based on the publication “Poly(sulfobetaine)-Based Diblock Copolymer Thin Films in Water/Acetone Atmosphere: Modulation of Water Hydration and Co-nonsolvency-Triggered Film Contraction” (P. Wang, C. Geiger, L. P. Kreuzer, T. Widmann, J. Reitenbach, S. Liang, R. Cubitt, C. Henschel, A. Laschewsky, C. M. Papadakis and P. Müller-Buschbaum, *Langmuir* **2022**, 38, 6934-6948; DOI: 10.1021/acs.langmuir.2c00451). Reproduced with permission.[76] Copyright 2022 American Chemical Society.

In appendix A, will be presented:

- Full static ToF-NR data at entire q -range values.
- Table for a summary of static data.
- Selected NR curves from kinetic ToF-NR data.
- Enlarged FT-IR spectra of the characteristic peaks of acetone- d_6 .
- Scheme of the conformation of polymer chains.

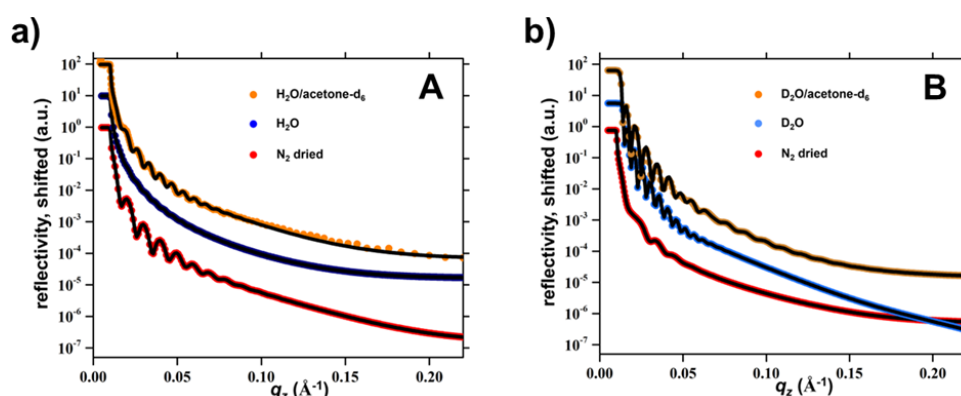


Figure A.1.: The entire q -range static ToF-NR data including large q_z values of (a) Experiment A and (b) Experiment B in Chapter 5. The best fits obtained via a three-layer model are presented as black solid lines. Reproduced with permission.[76] Copyright 2022 American Chemical Society.

Table A.1.: Film thickness d , normalized film thickness d/d_{ini} and bulk SLD, as well as the solvent content during the three static states in Experiments A ($\text{H}_2\text{O} : \text{acetone-d}_6 = 9:1 \text{ v/v}$) and Experiment B ($\text{D}_2\text{O} : \text{acetone-d}_6 = 9:1 \text{ v/v}$) in Chapter 5. Reproduced with permission.[76] Copyright 2022 American Chemical Society.

A	N₂ dried static I	H₂O vapor swollen static III	acetone-d₆ vapor contracted static V
d (nm)	66 ± 1	124 ± 2	97 ± 2
d/d_{ini}	1.0	1.88 ± 0.04	1.47 ± 0.04
$\text{SLD} \times 10^{-6} (\text{\AA}^{-2})$	0.66 ± 0.01	0.06 ± 0.01	0.13 ± 0.01
H ₂ O content $\phi_{\text{H}_2\text{O}}$ (vol%)	2 ± 1	53 ± 1	27 ± 1
acetone-d ₆ content $\phi_{\text{acetone-d}_6}$ (vol%)	—	—	5 ± 1
B	N₂ dried static I	D₂O vapor swollen static III	acetone-d₆ vapor contracted static V
d (nm)	67 ± 2	116 ± 1	97 ± 1
d/d_{ini}	1.0	1.75 ± 0.04	1.46 ± 0.07
$\text{SLD} \times 10^{-6} (\text{\AA}^{-2})$	0.67 ± 0.01	3.20 ± 0.01	2.77 ± 0.01
D ₂ O content $\phi_{\text{D}_2\text{O}}$ (vol%)	—	45 ± 1	28 ± 1
acetone-d ₆ content $\phi_{\text{acetone-d}_6}$ (vol%)	—	—	6 ± 1

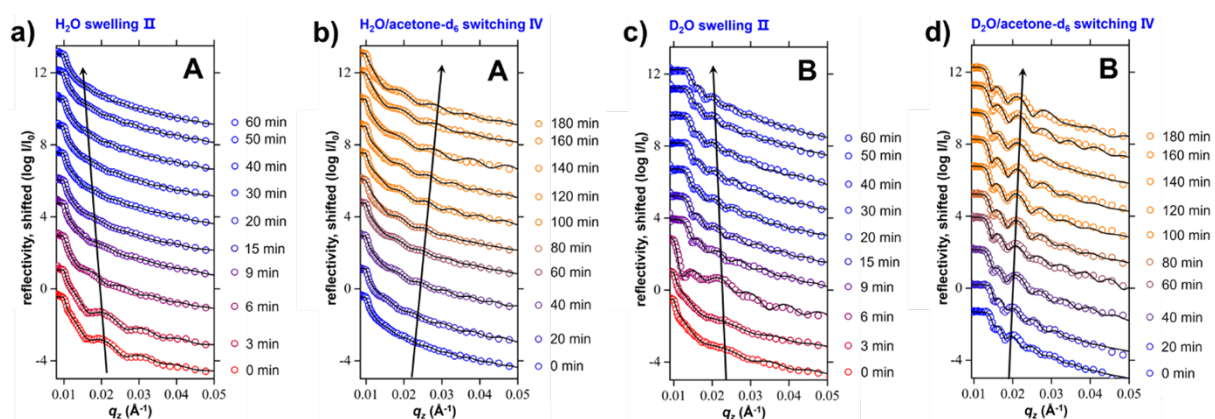


Figure A.2.: Selected NR curves from kinetic ToF-NR data (symbols) with automated batch three-layer fits (black solid lines) during the two kinetic processes in Experiments A and B in Chapter 5. The black arrows indicate the shift of the Kiessig fringe maxima. Reproduced with permission.[76] Copyright 2022 American Chemical Society.

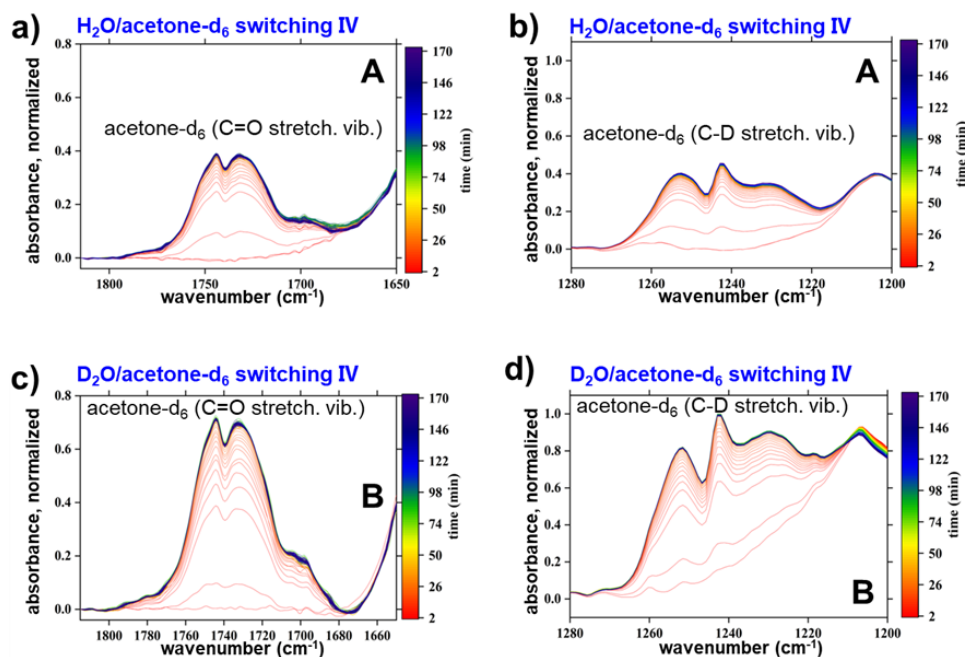


Figure A.3.: Enlarged FTIR spectra of the characteristic peaks of acetone- d_6 during the water/acetone- d_6 switching process in Chapter 5. The relevant characteristic peaks are indicated. Reproduced with permission.[76] Copyright 2022 American Chemical Society.

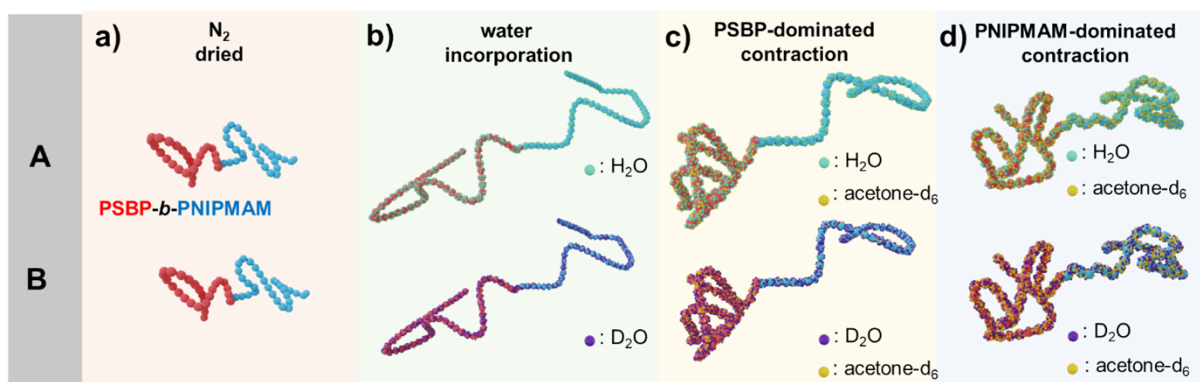


Figure A.4.: Model of the conformation of polymer chains for Experiment A and Experiment B in the DBC films (a) during the N_2 dried state (state I), (b) after water incorporation (state III), (c) during the PSBP dominated contraction (initial phase of state IV) and (d) after the PNIPMAM dominated contraction (reaching state V) in Chapter 5. Reproduced with permission.[76] Copyright 2022 American Chemical Society.

Appendix B

Supporting information for Chapter 6

This chapter is based on the publication “KCl-Modulated Hydration and Subsequent Thermoresponsive Behavior of Poly(sulfobetaine)-Based Diblock Copolymer Thin Films” (P. Wang, C. Geiger, J. Reitenbach, A. Vagias, L. P. Kreuzer, S. Liang, R. Cubitt, V. Hildebrand, A. Laschewsky, C. M. Papadakis and P. Müller-Buschbaum, *Macromolecules* **2023**, 56, 4087-4099; DOI: 10.1021/acs.macromol.3c00484). Reproduced with permission.[108] Copyright 2023 American Chemical Society.

In appendix B, will be presented:

- Temporal evolution of temperature and relative humidity.
- XRR data.
- Table for the summary of the $VPTT_s$ during heating processes.
- Calculated static ToF-NR data.
- AFM topography images.
- Enlarged FTIR spectra of the D₂O characteristic signal.

Table B.1.: Summary of the $VPTT_s$ during the heating (IV) processes, (a) obtained from the SR measurements, and (b) obtained from SR, ToF-NR, and FTIR in Chapter 6. Reproduced with permission.[108] Copyright 2023 American Chemical Society.

a)	salt-free		KCl	
	$VPTT_{fs}$	$VPTT_c$	$VPTT_{fs}$	$VPTT_c$
PSBP ₅₀	18.6 °C	—	18.6 °C	—
PNIPMAM ₆₆	—	24.7 °C	—	21.7 °C
PSBP ₅₀ - <i>b</i> -PNIPMAM ₁₅₅	19.3 °C	23.0 °C	19.3 °C	20.8 °C
b)	salt-free		KCl	
	$VPTT_{fs}$	$VPTT_c$	$VPTT_{fs}$	$VPTT_c$
SR	19.3 °C	23.0 °C	19.3 °C	20.8 °C
ToF-NR	19.5 °C	23.0 °C	19.5 °C	21.0 °C
FTIR	—	26.2 °C	—	21.0 °C

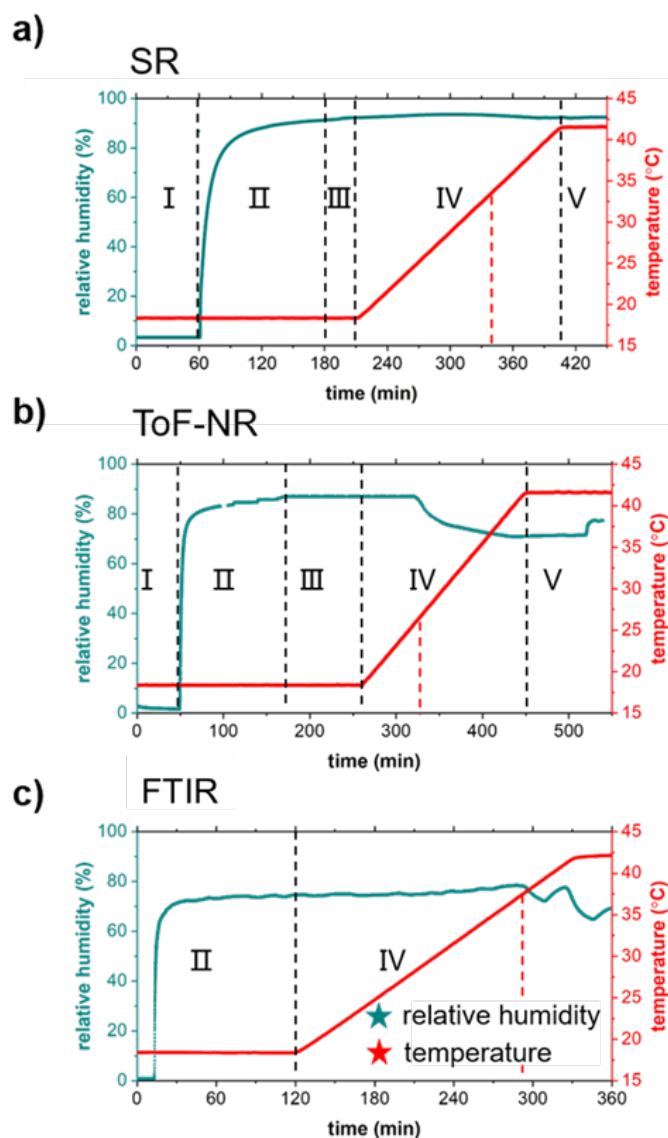


Figure B.1.: Temperature and relative humidity as a function of time for (a) SR, (b) ToF-NR, and (c) FTIR measurements with indicated stages and kinetics *I-V* in Chapter 6. The red dotted lines indicate the temperatures at which the relative humidity starts to decrease. Reproduced with permission.[108] Copyright 2023 American Chemical Society.

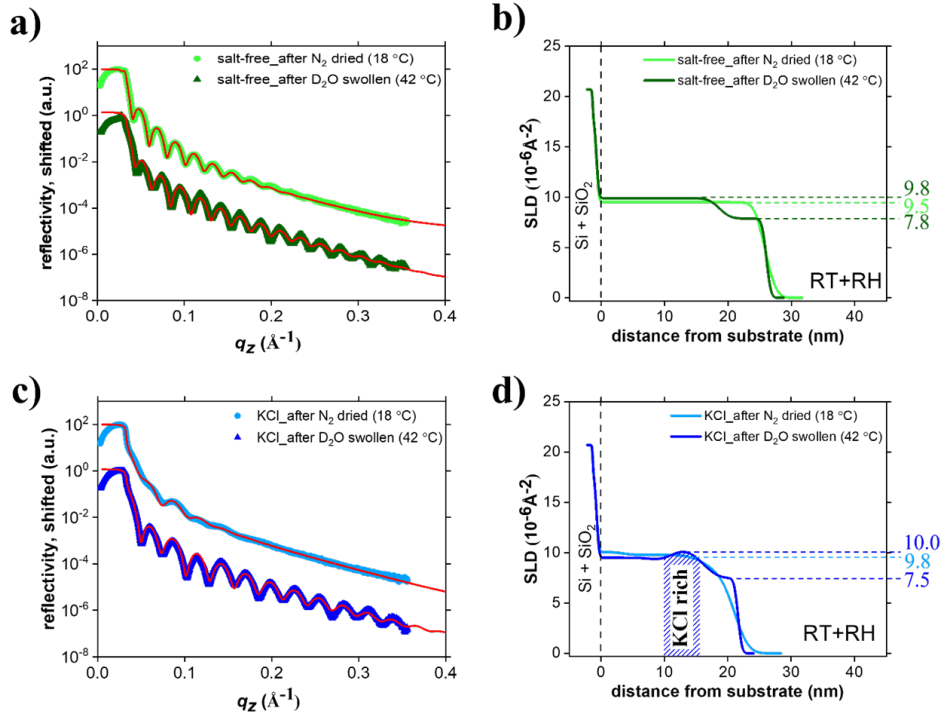


Figure B.2.: (a, c) X-ray reflectivity curves (symbols) and (b, d) determined X-ray SLD profiles of the salt-free DBC thin film (green) and the KCl-loaded DBC thin film (blue) after N_2 drying at $T = 18^\circ\text{C}$ (light colors) and after D_2O swelling at $T = 42^\circ\text{C}$ (dark colors) in Chapter 6. Reproduced with permission.[108] Copyright 2023 American Chemical Society.

Table B.2.: Film thickness d , swelling ratio d/d_{ini} , bulk SLD, and D_2O content of both salt-free and KCl-loaded DBC thin films during the three static stages in Chapter 6. Reproduced with permission.[108] Copyright 2023 American Chemical Society.

salt-free	N_2 dried (18°C) I	D_2O swollen (18°C) III	D_2O swollen (42°C) V
d (nm)	24 ± 2	58 ± 1	36 ± 2
d/d_{ini}	1.0	2.40 ± 0.04	1.50 ± 0.08
$\text{SLD} \times 10^{-6} (\text{\AA}^{-2})$	0.78 ± 0.02	3.65 ± 0.04	2.27 ± 0.02
D_2O content $\phi_{\text{D}_2\text{O}}$ (vol%)	—	46 ± 1	25 ± 1
KCl	N_2 dried (18°C) I	D_2O swollen (18°C) III	D_2O swollen (42°C) V
d (nm)	33 ± 1	94 ± 1	58 ± 2
d/d_{ini}	1.0	2.85 ± 0.04	1.76 ± 0.07
$\text{SLD} \times 10^{-6} (\text{\AA}^{-2})$	0.81 ± 0.03	5.16 ± 0.05	2.41 ± 0.07
D_2O content $\phi_{\text{D}_2\text{O}}$ (vol%)	—	77 ± 1	28 ± 1

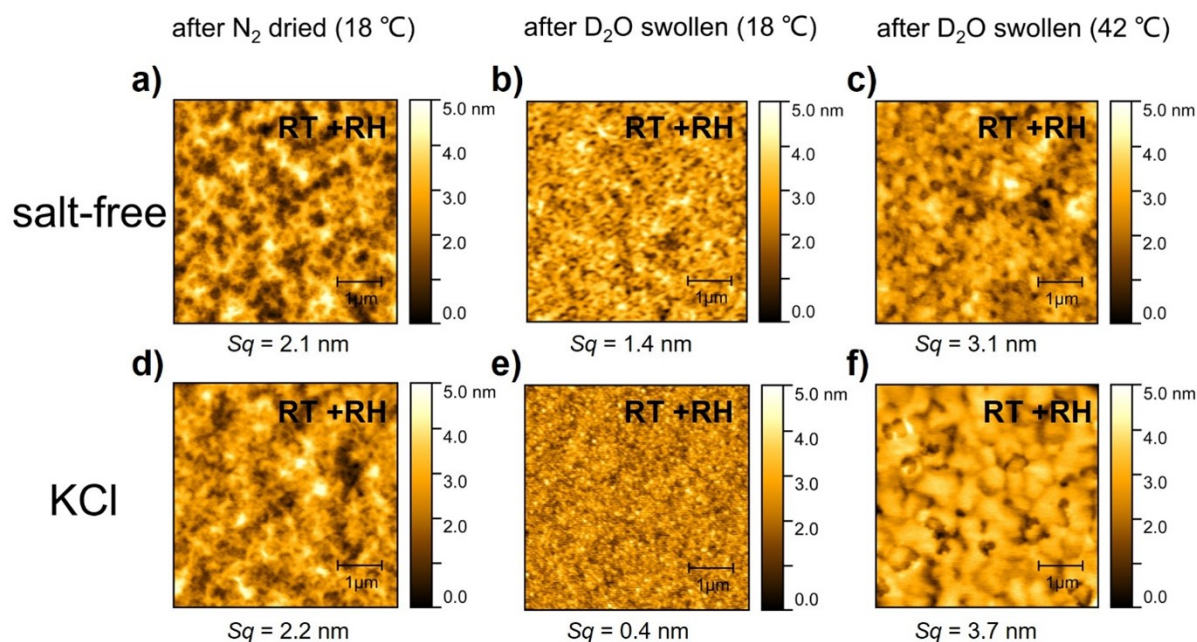


Figure B.3.: AFM images of both, salt-free and KCl-loaded DBC thin films after three static stages in Chapter 66. The RMS roughness values S_q are given below the corresponding AFM images. Reproduced with permission.[108] Copyright 2023 American Chemical Society.

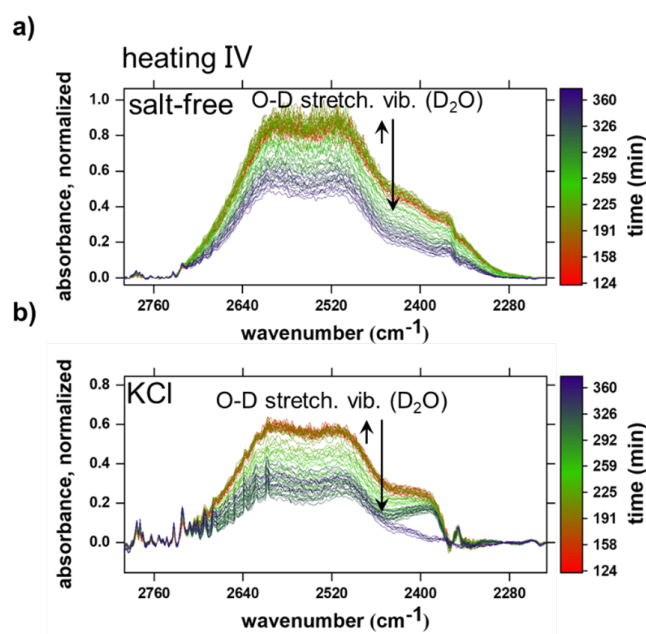


Figure B.4.: Enlarged FTIR spectra of the D_2O characteristic signal upon heating for (a) salt-free DBC thin film and (b) KCl-loaded DBC thin film in Chapter 6. Reproduced with permission.[108] Copyright 2023 American Chemical Society.

Appendix C

Supporting information for Chapter 7

The following chapter is based on the upcoming publication “Salt Series Driven Solvation Behavior of Thermoresponsive Polymer Thin Films in Water and Subsequent Mixed Water/Methanol Atmosphere” by P. Wang, T. Zheng, J. Reitenbach, S. A. Wegener, L. F. Huber, L. P. Kreuzer, S. Liang, R. Cubitt, Y. Cheng, T. Xu, V. Hildebrand, A. Laschewsky, C. M. Papadakis and P. Müller-Buschbaum.

In appendix C, will be presented:

- Static ToF-NR data.
- Kinetic ToF-NR data of methanol-d₃ molar faction and overall solvent content.
- Static and kinetic FTIR spectra.
- 2D FTIR correlation contour maps.
- Snapshots of the simulation boxes.
- Peak areas of RDF profiles and conformations of DBC chains.
- Anionic radii and static NR data.

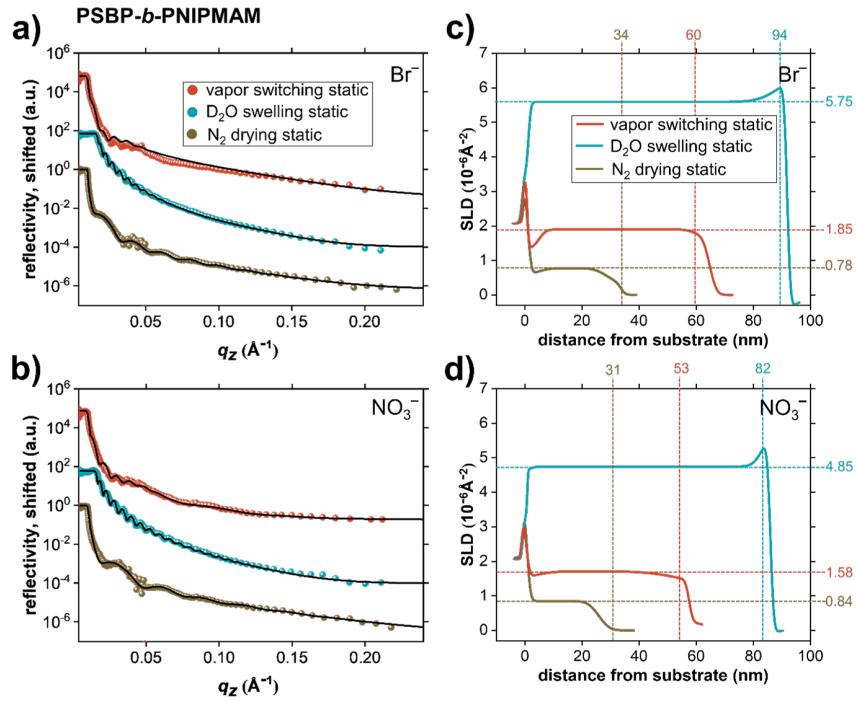


Figure C.1.: (a,b) Static ToF-NR data (symbols) and (c,d) determined SLD profiles of Br^- - and NO_3^- -loaded PSBP-*b*-PNIPMAM thin films in Chapter 7. The best fits obtained via a three-layer model are presented as black solid lines in (a,b).

Table C.1.: Film thickness d , swelling ratio d/d_{ini} , bulk SLD, and D_2O and methanol- d_3 content of both Br^- - and NO_3^- -loaded PSBP-*b*-PNIPMAM thin films at the three static stages in Chapter 7.

Br^-	N_2 drying I	D_2O swelling II	vapor switching VI
d (nm)	34 ± 3	94 ± 3	60 ± 3
d/d_{ini}	1.0	2.76 ± 0.03	1.76 ± 0.05
$\text{SLD} \times 10^{-6} (\text{\AA}^{-2})$	0.78 ± 0.02	5.75 ± 0.05	1.85 ± 0.03
D_2O content $\phi_{\text{D}_2\text{O}}$ (vol %)	—	78 ± 2	15 ± 4
methanol- d_3 content $\phi_{\text{methanol-d}_3}$ (vol %)	—	—	20 ± 4
NO_3^-	N_2 drying I	D_2O swelling III	vapor switching VI
d (nm)	31 ± 2	82 ± 4	53 ± 2
d/d_{ini}	1.0	2.64 ± 0.04	1.70 ± 0.02
$\text{SLD} \times 10^{-6} (\text{\AA}^{-2})$	0.84 ± 0.02	4.85 ± 0.07	1.58 ± 0.06
D_2O content $\phi_{\text{D}_2\text{O}}$ (vol %)	—	67 ± 3	9 ± 1
methanol- d_3 content $\phi_{\text{D}_2\text{O}}\text{methanol-d}_3}$ (vol %)	—	—	13 ± 2

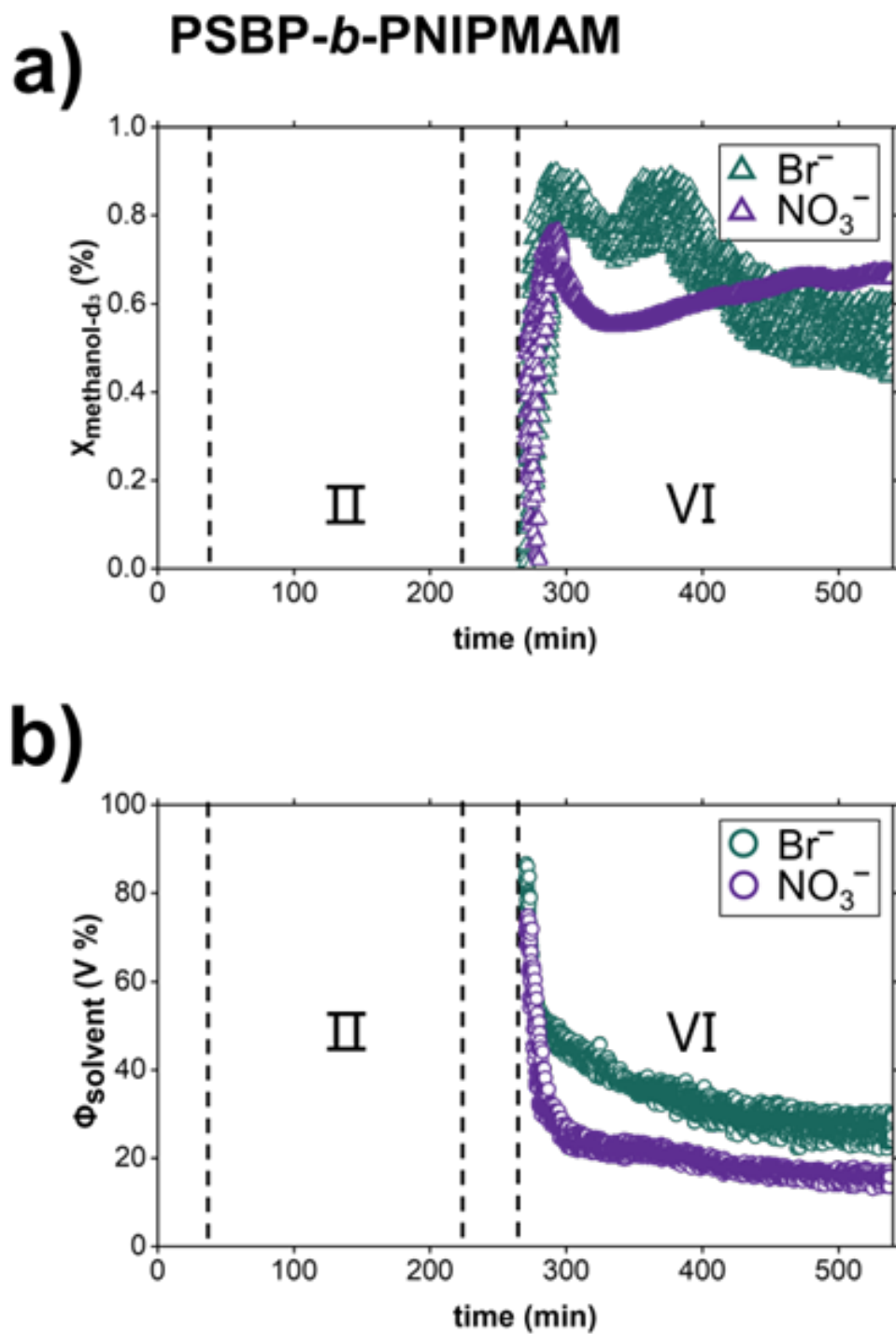


Figure C.2.: Evolution of the (a) determined methanol- d_3 molar fraction $\chi_{\text{methanol-d}_3}$, (b) the overall solvent content obtained from ToF-NR data as a function of time for Br^- - (green) and NO_3^- -loaded (purple) PSBP-*b*-PNIPMAM thin films with the stages in Chapter 7.

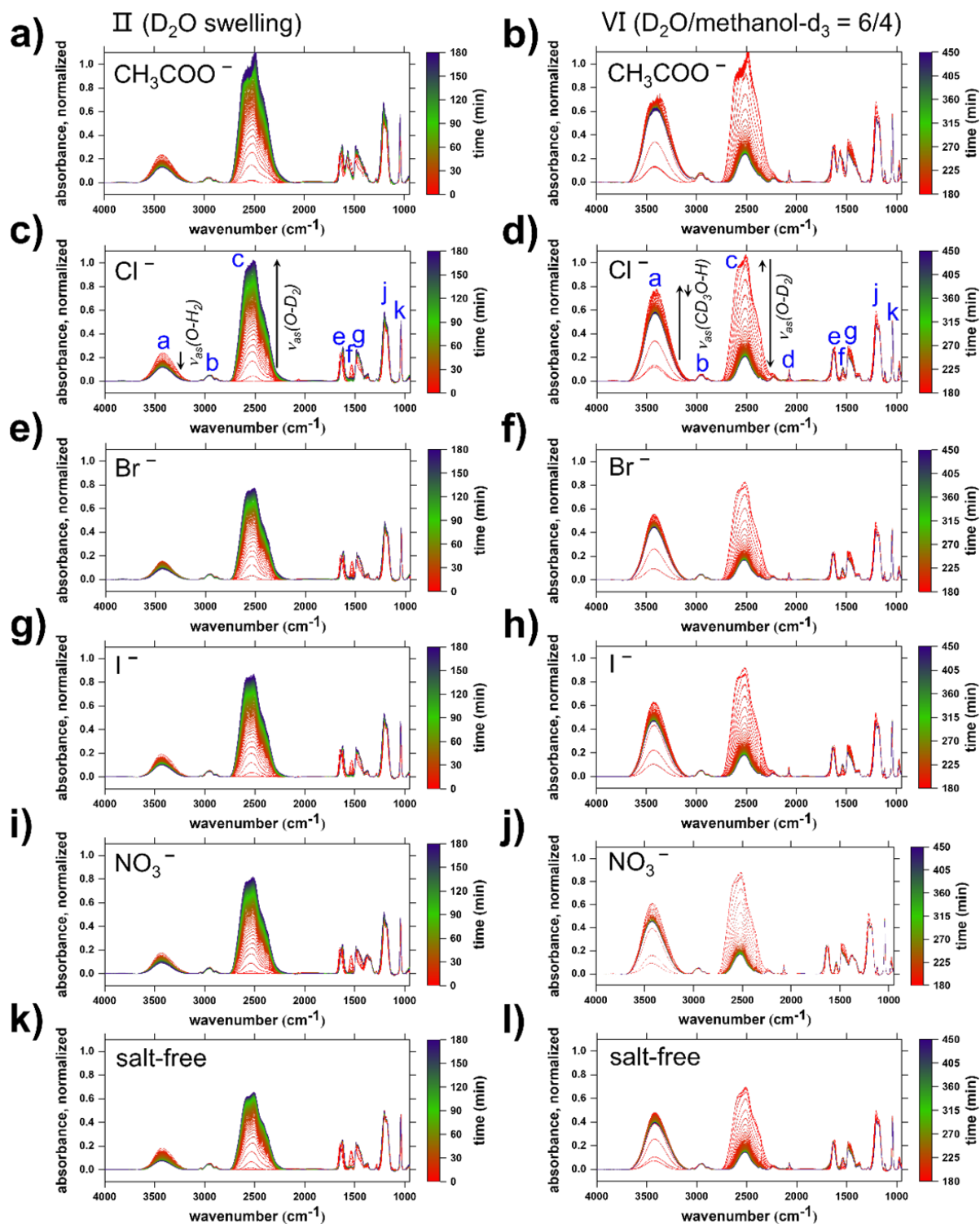


Figure C.3.: FTIR spectra of (a, b) CH_3COO^- , (c, d) Cl^- , (e, f) Br^- , (g, h) I^- , (i, j) NO_3^- loaded and (k, l) salt-free PSBP thin films in Chapter 7. The black arrows highlight the change of corresponding characterized signals.

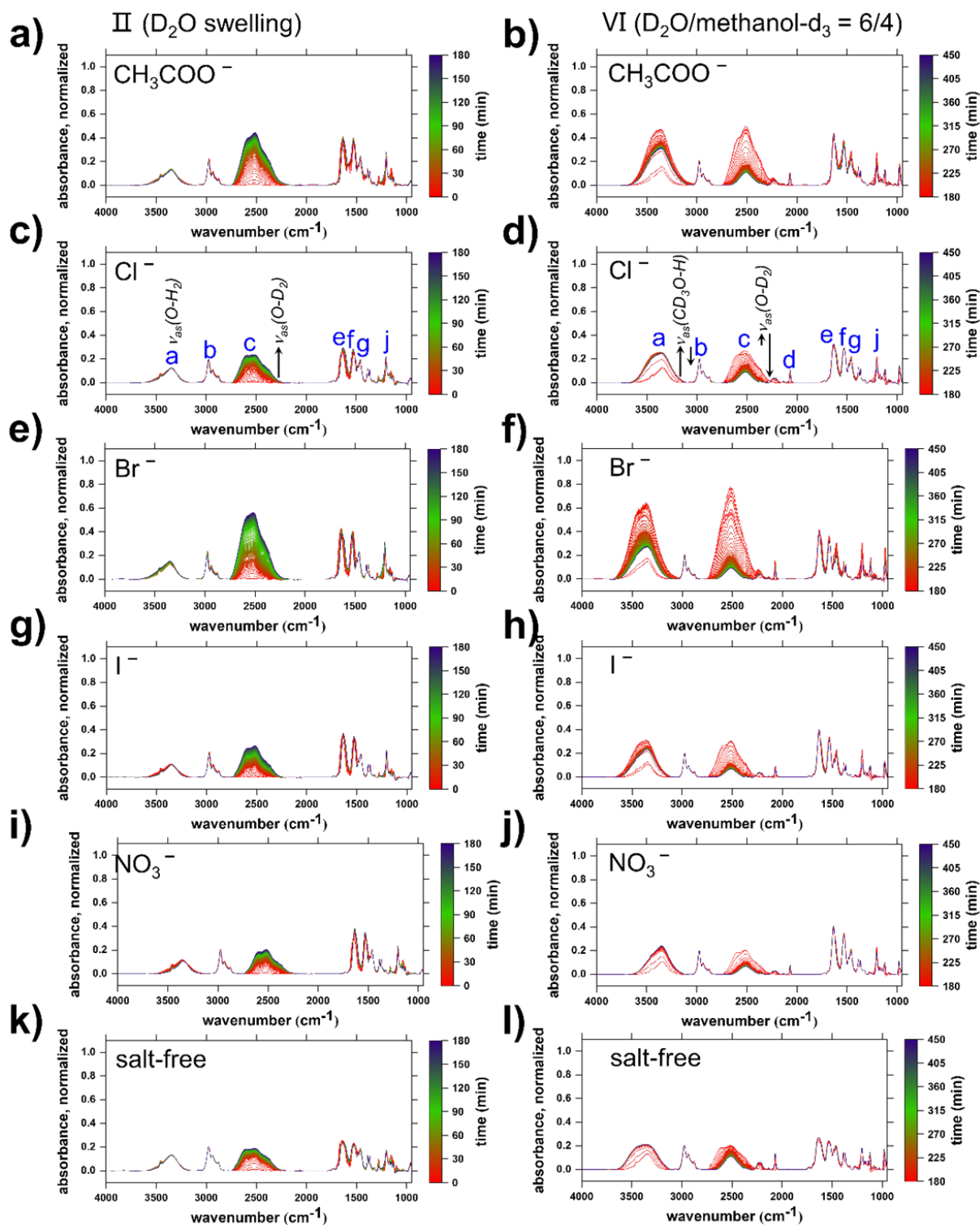


Figure C.4.: FTIR spectra of (a, b) CH_3COO^- , (c, b) Cl^- , (e, f) Br^- , (g, h) I^- , (i, j) NO_3^- -loaded and (k, l) salt-free PNIPMAM thin films in Chapter 7. The black arrows highlight the change of corresponding characterized signals.

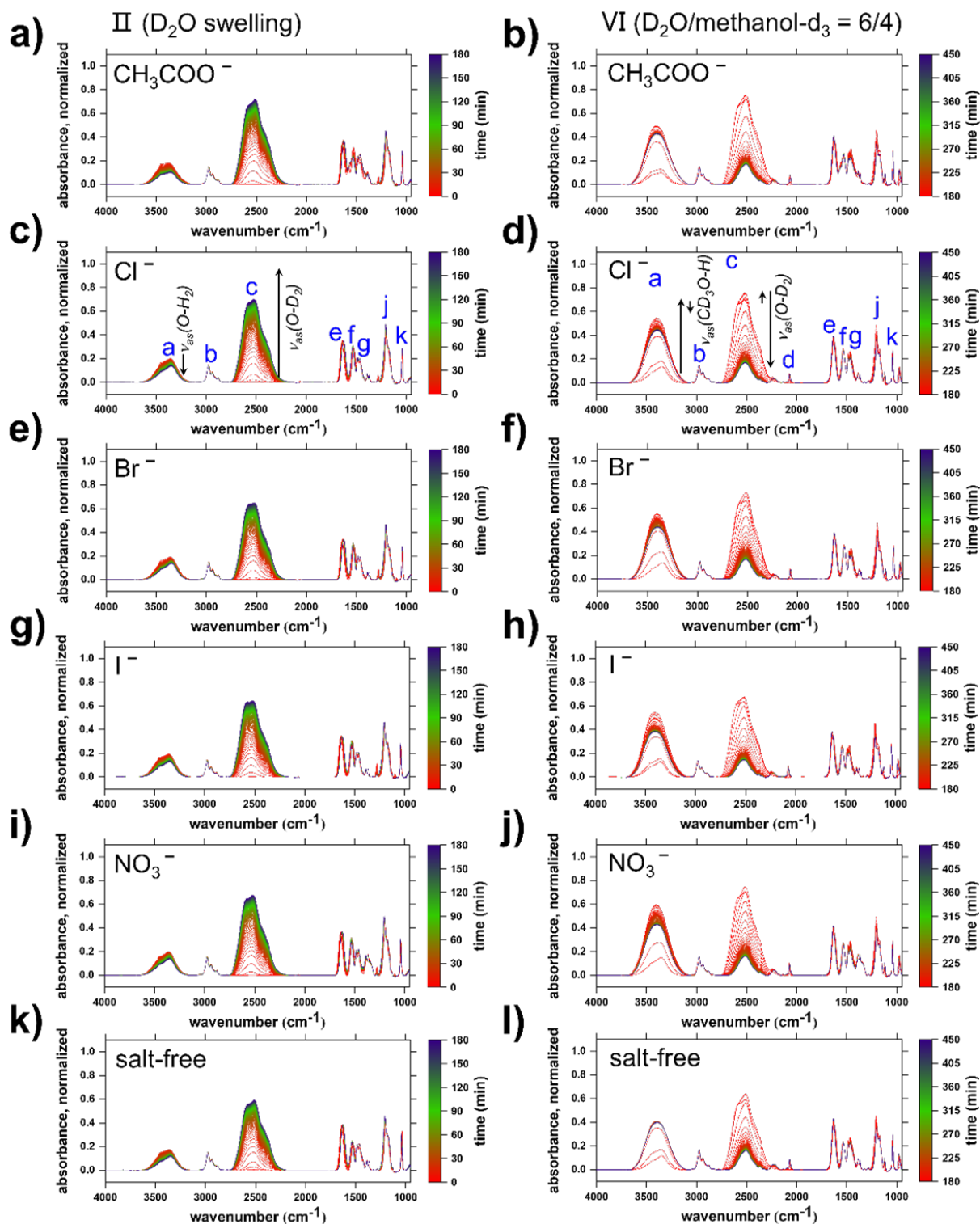


Figure C.5.: FTIR spectra of (a, b) CH_3COO^- , (c, b) Cl^- , (e, f) Br^- , (g, h) I^- , (i, j) NO_3^- -loaded and (k, l) salt-free PSBP-*b*-PNIPMAM thin films in Chapter 7. The black arrows highlight the change of corresponding characterized signals.

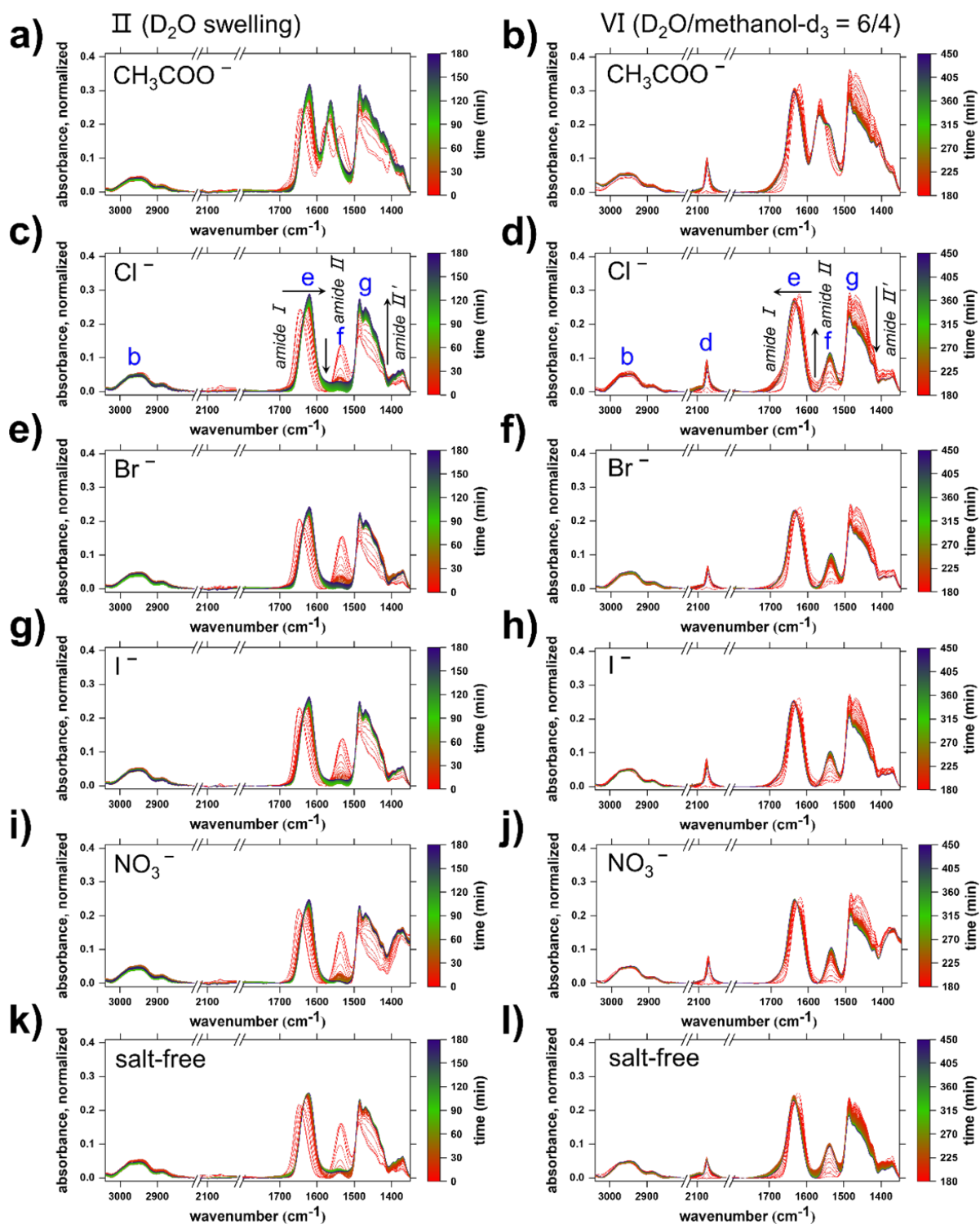


Figure C.6.: Enlarged FTIR spectra of (a, b) CH_3COO^- , (c, b) Cl^- , (e, f) Br^- , (g, h) I^- , (i, j) NO_3^- -loaded and (k, l) salt-free PSBP thin films in Chapter 7. The black arrows in (c and d) highlight the change of corresponding amide groups.

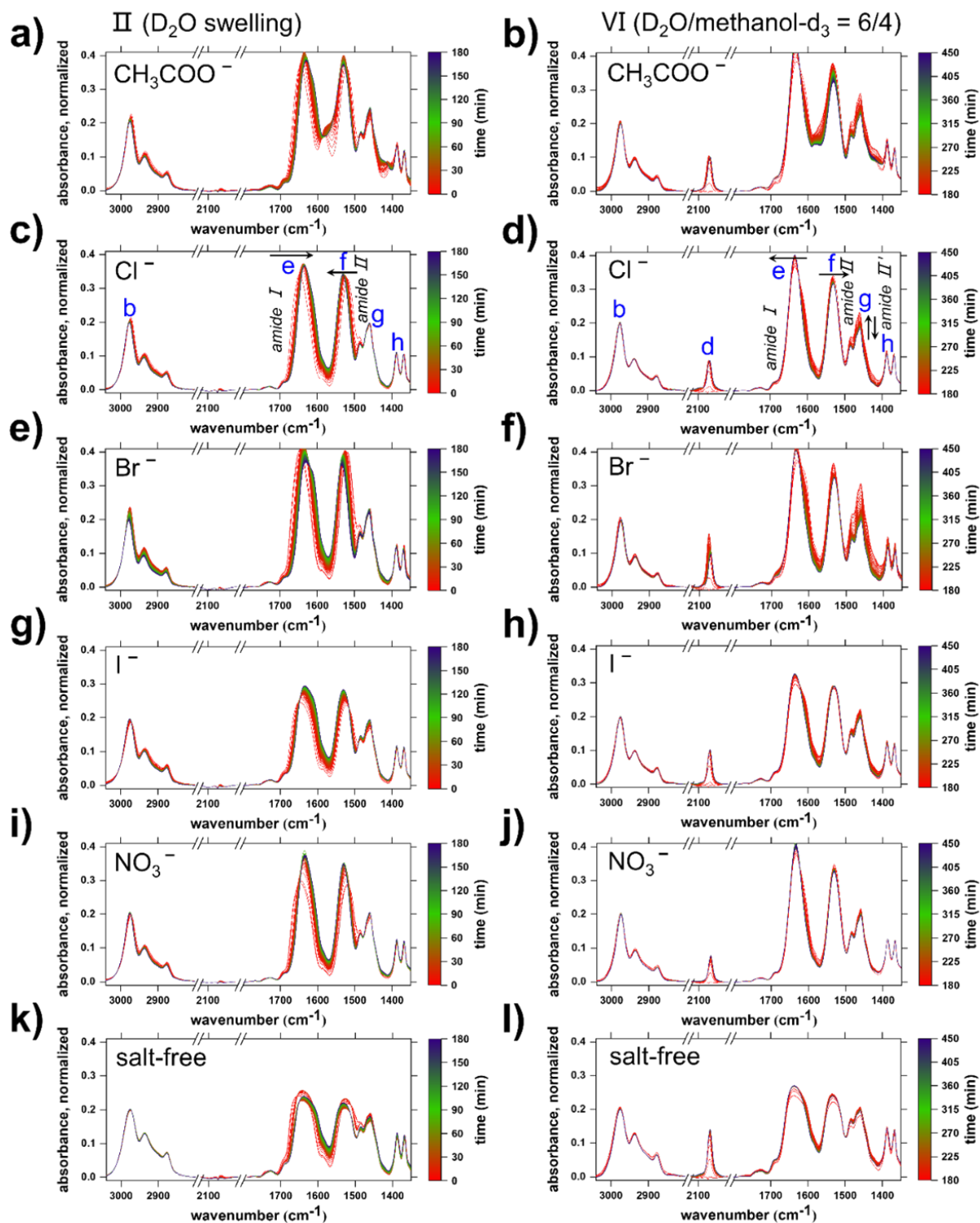


Figure C.7.: Enlarged FTIR spectra of (a, b) CH_3COO^- , (c, b) Cl^- , (e, f) Br^- , (g, h) I^- , (i, j) NO_3^- -loaded and (k, l) salt-free PNIPMAM thin films in Chapter 7. The black arrows in (c and d) highlight the change of corresponding amide groups.

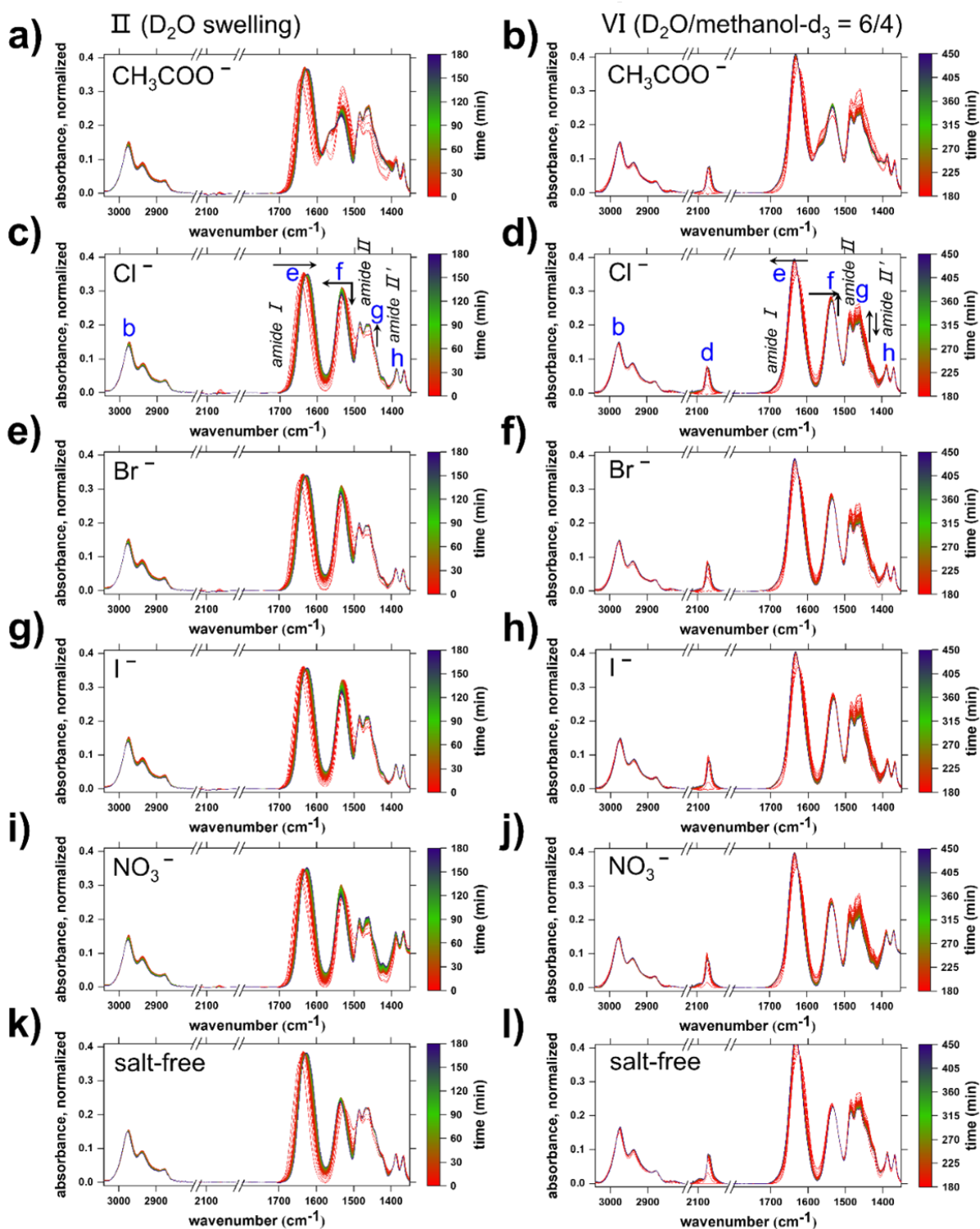


Figure C.8.: Enlarged FTIR spectra of (a, b) CH_3COO^- , (c, b) Cl^- , (e, f) Br^- , (g, h) I^- , (i, j) NO_3^- -loaded and (k, l) salt-free PSBP-*b*-PNIPMAM thin films in Chapter 7. The black arrows in (c and d) highlight the change of corresponding amide groups.

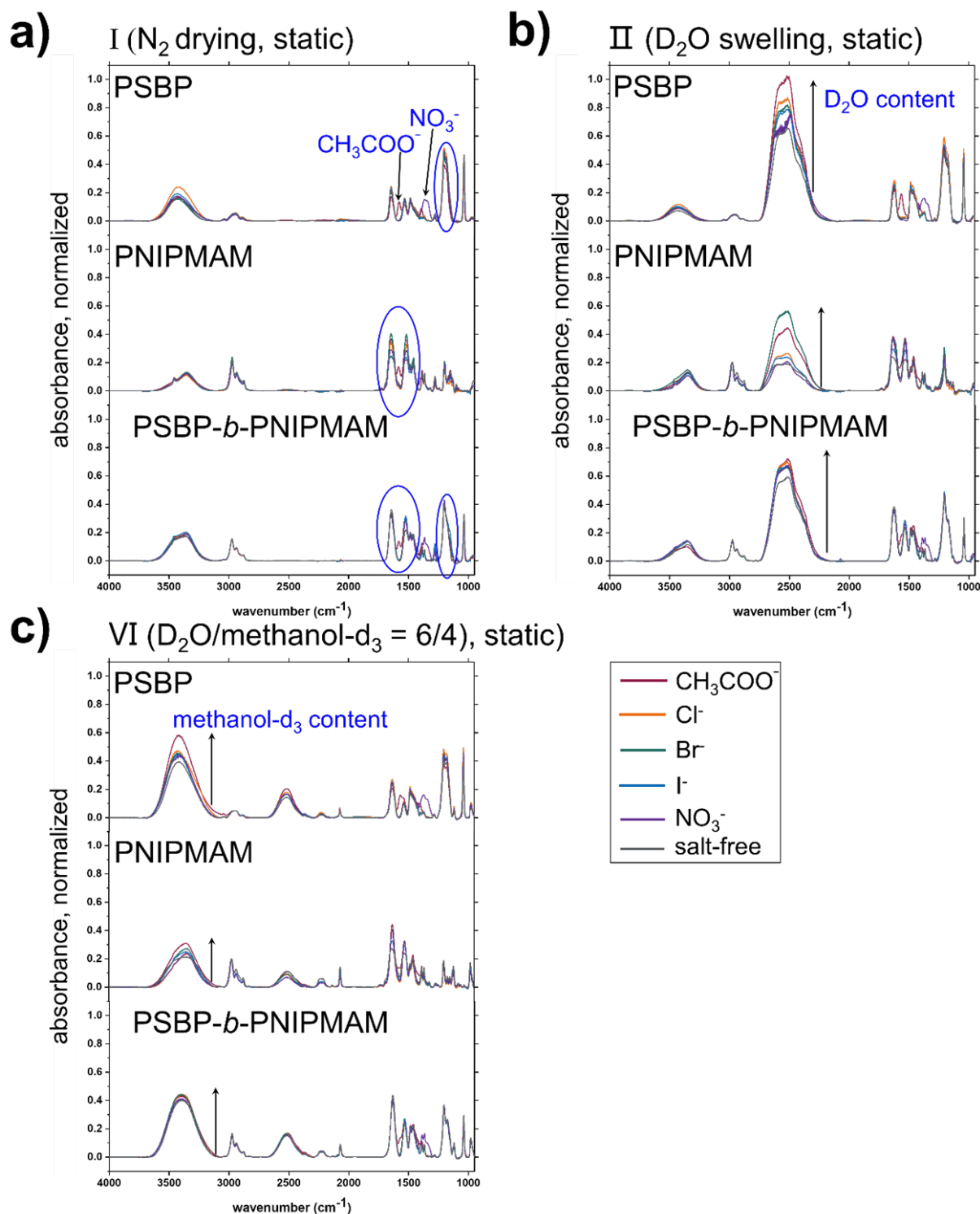


Figure C.9.: Static FTIR spectra of salt-loaded and salt-free PSBP, PNIPMAM and PSBP-*b*-PNIPMAM thin film in Chapter 77. The spectra of the CH₃COO⁻, Cl⁻, Br⁻, I⁻, NO₃⁻-loaded and salt-free samples are colored in red, orange, green, blue, purple, and grey respectively.

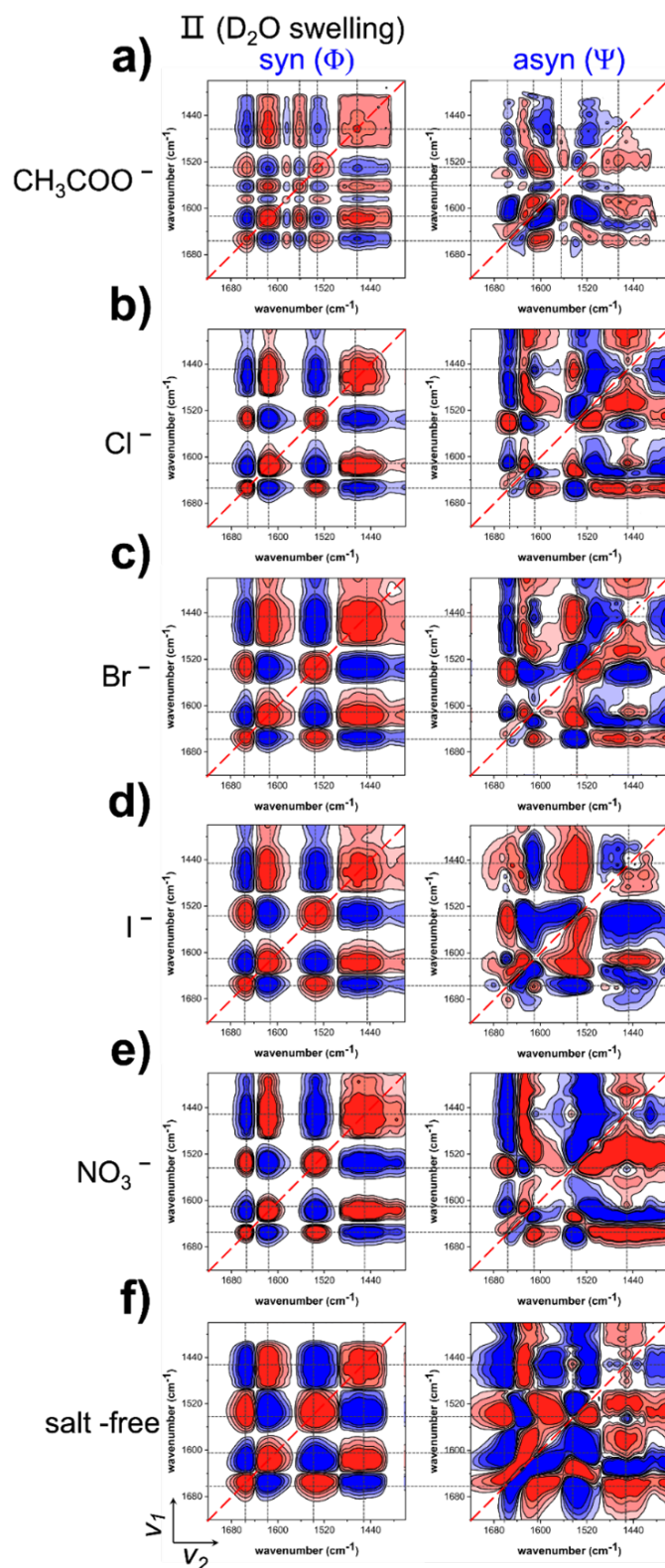


Figure C.10.: 2D FTIR correlation contour maps of (a) CH_3COO^- , (b) Cl^- , (c) Br^- , (d) I^- , (e) NO_3^- -loaded and (f) salt-free PSBP thin films in Chapter 7.

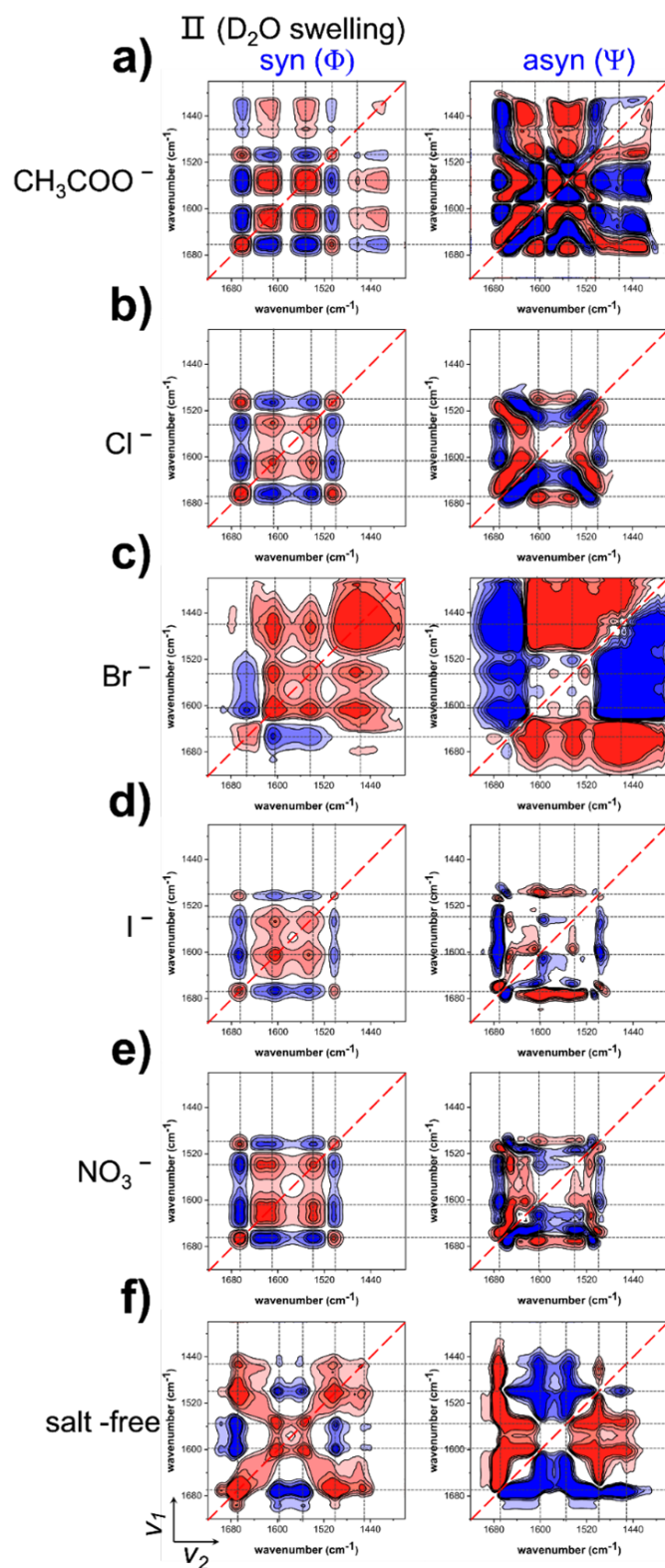


Figure C.11.: 2D FTIR correlation contour maps of (a) CH_3COO^- , (b) Cl^- , (c) Br^- , (d) I^- , (e) NO_3^- -loaded and (f) salt-free PNIPMAM thin films in Chapter 7.

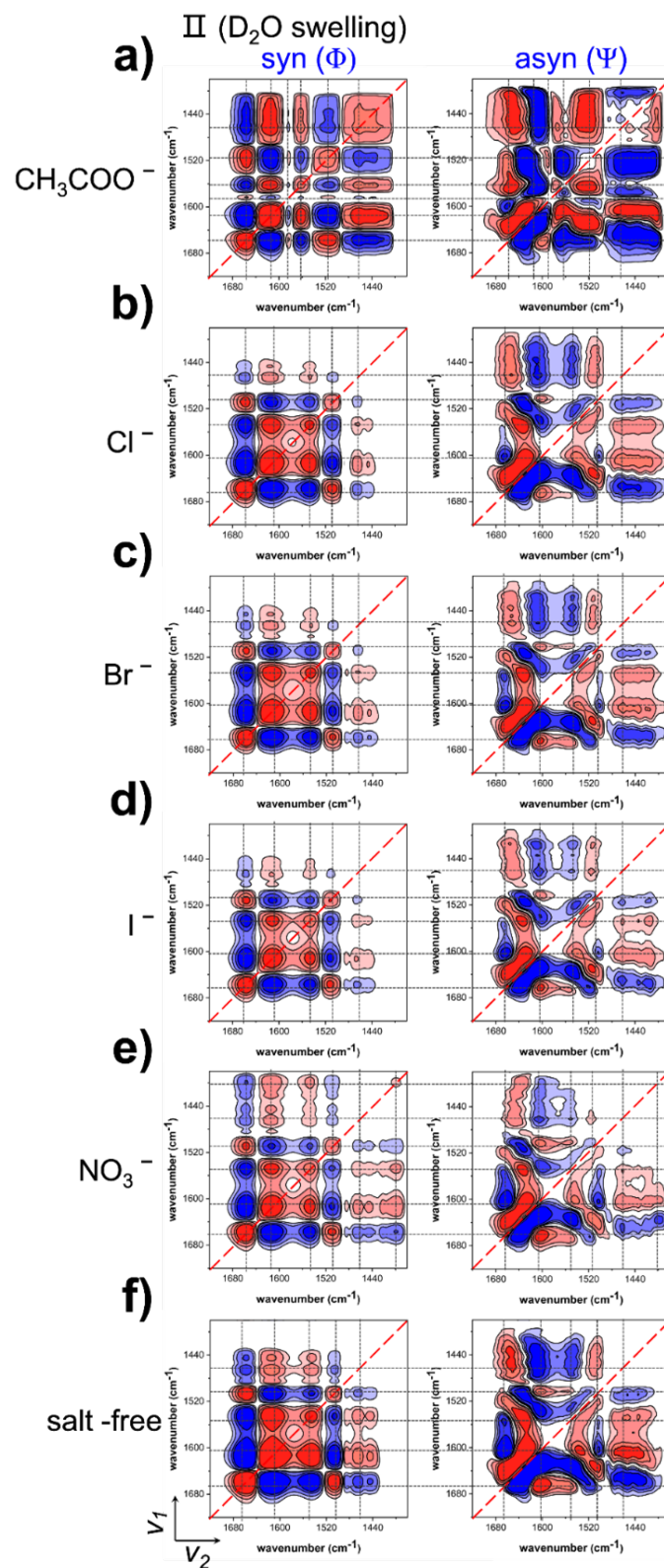


Figure C.12.: 2D FTIR correlation contour maps of (a) CH_3COO^- , (b) Cl^- , (c) Br^- , (d) I^- , (e) NO_3^- -loaded and (f) salt-free PSBP-*b*-PNIPMAM thin films in Chapter 7.

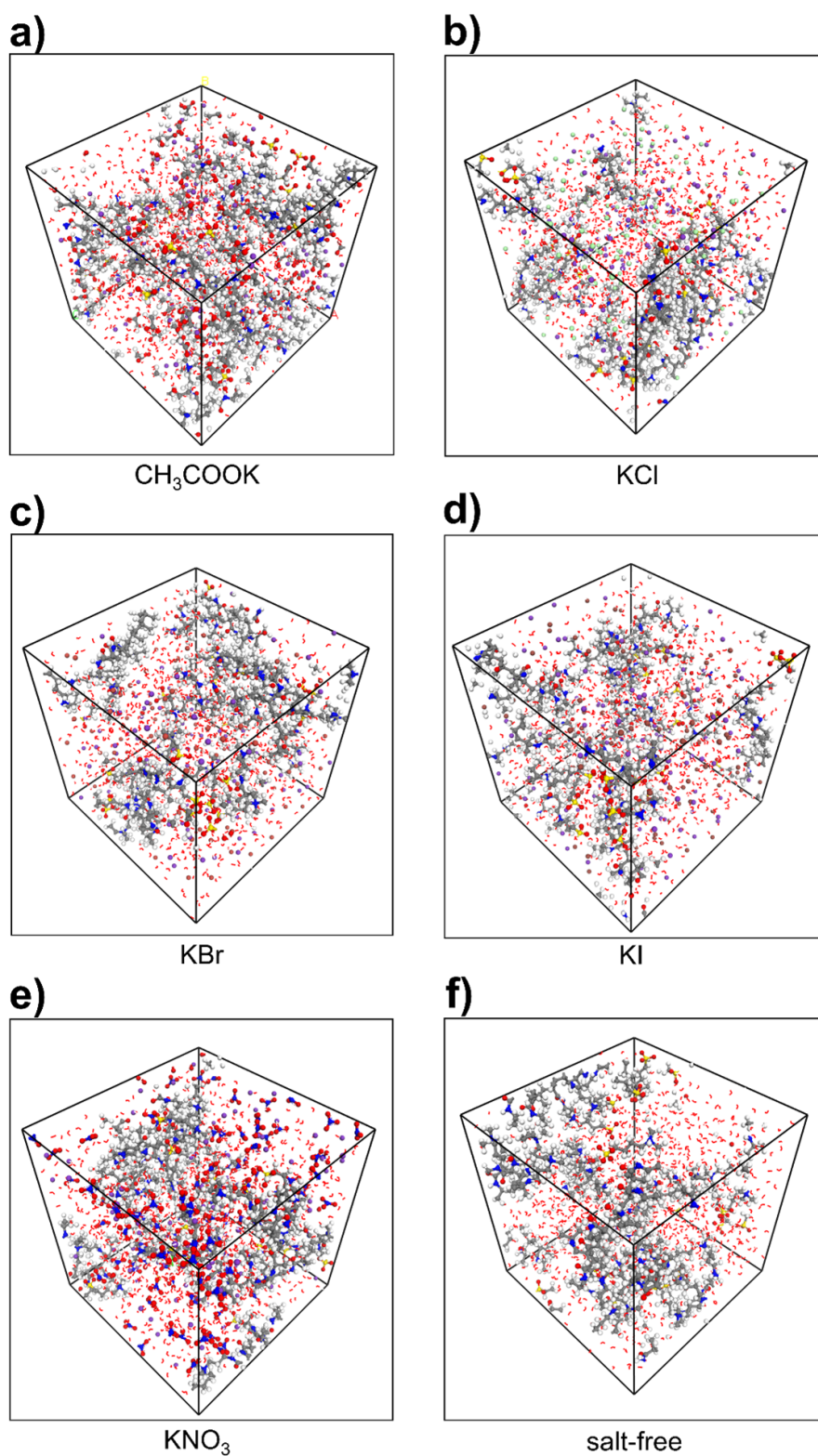


Figure C.13.: Snapshots of the employed simulation boxes for (a) CH₃COO⁻, (b) Cl⁻, (c) Br⁻, (d) I⁻, (e) NO₃⁻-loaded and (f) salt-free PSBP-*b*-PNIPMAM chains in pure H₂O atmosphere in Chapter 7.

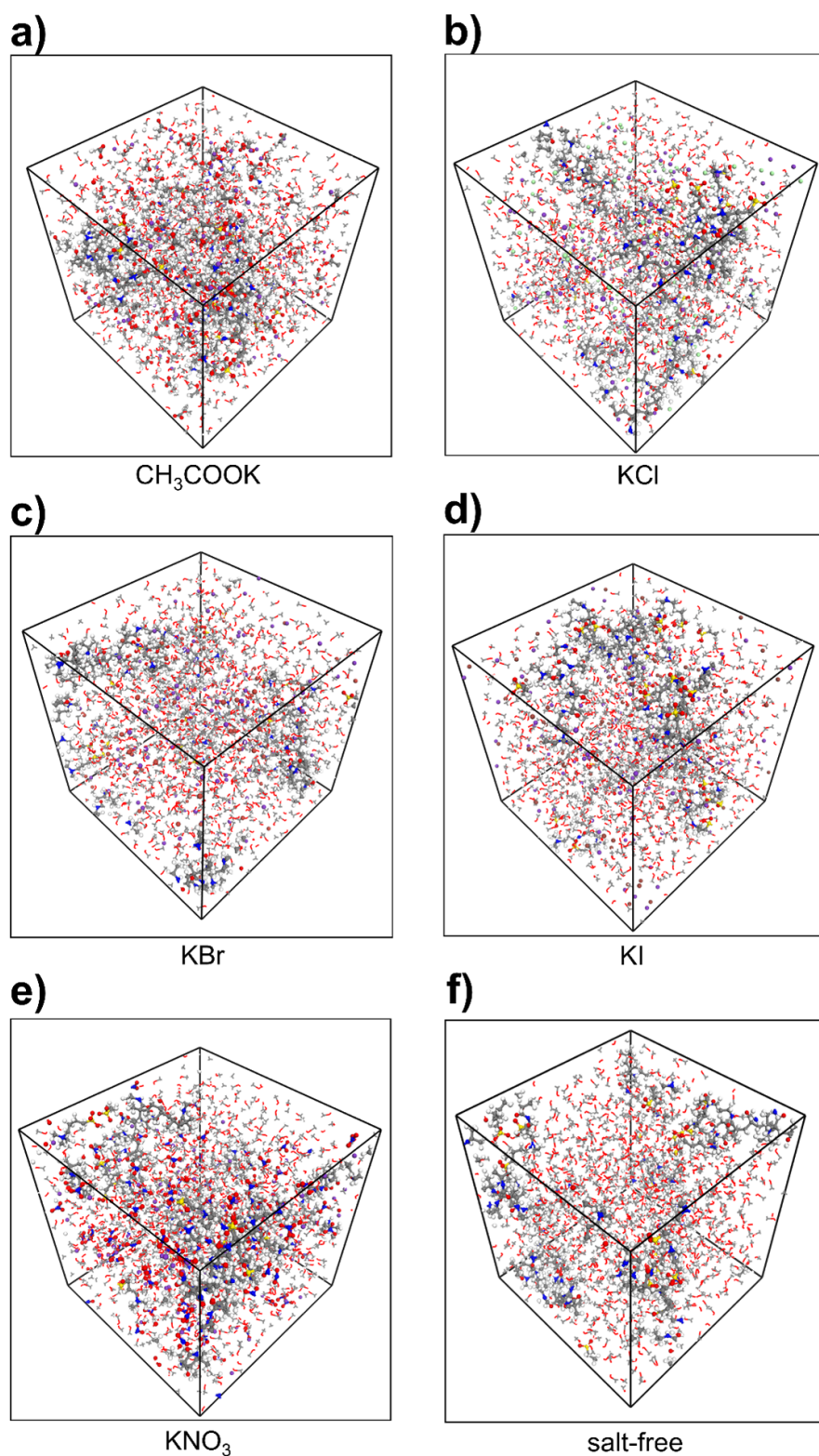


Figure C.14.: Snapshots of the employed simulation boxes for (a) CH_3COO^- , (b) Cl^- , (c) Br^- , (d) I^- , (e) NO_3^- -loaded and (f) salt-free PSBP-*b*-PNIPMAM chains in pure methanol atmosphere in Chapter 7.

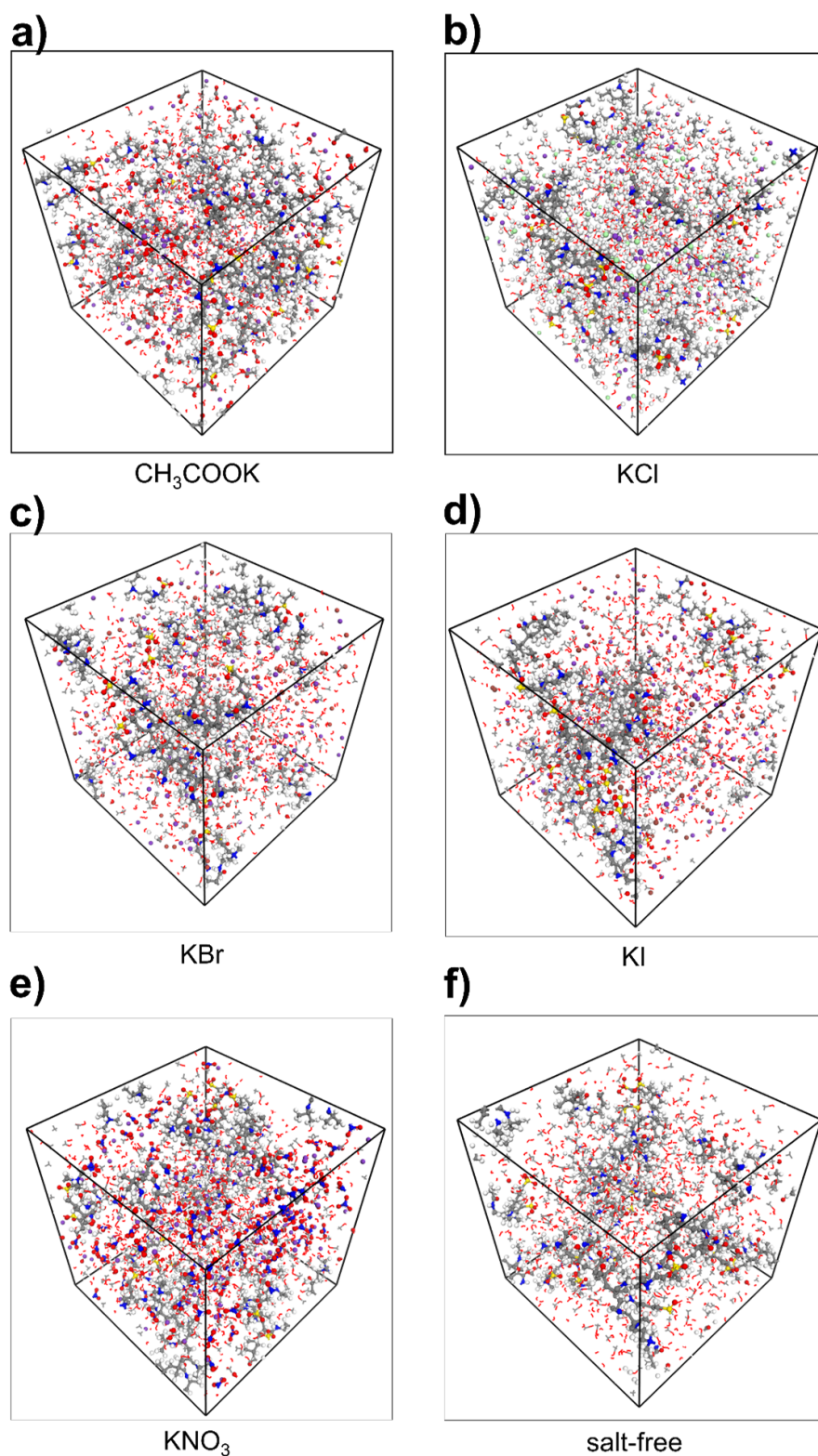


Figure C.15.: Snapshots of the employed simulation boxes for (a) CH_3COO^- , (b) Cl^- , (c) Br^- , (d) I^- , (e) NO_3^- -loaded and (f) salt-free PSBP-*b*-PNIPMAM chains in mixed atmosphere ($\text{H}_2\text{O}/\text{methanol} = 6/4$) in Chapter 7.

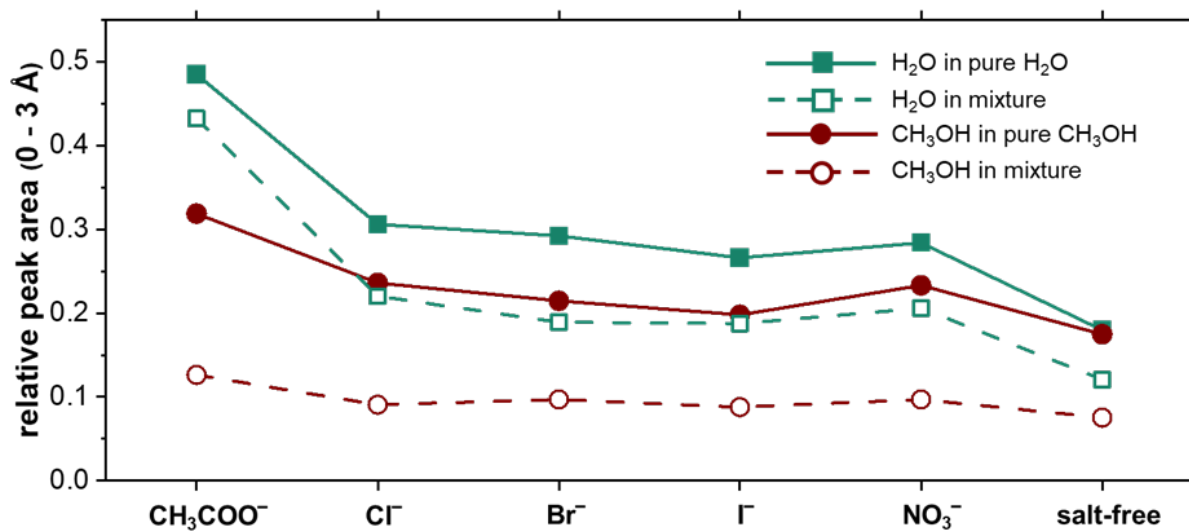


Figure C.16.: Peak areas of RDF profiles from 0 ~ 3 Å. The relative accessibility is plotted as green squares of H_2O shells and red circles for methanol shells, connected by solid lines in pure atmosphere and by dash lines in mixed atmosphere respectively in Chapter 7.

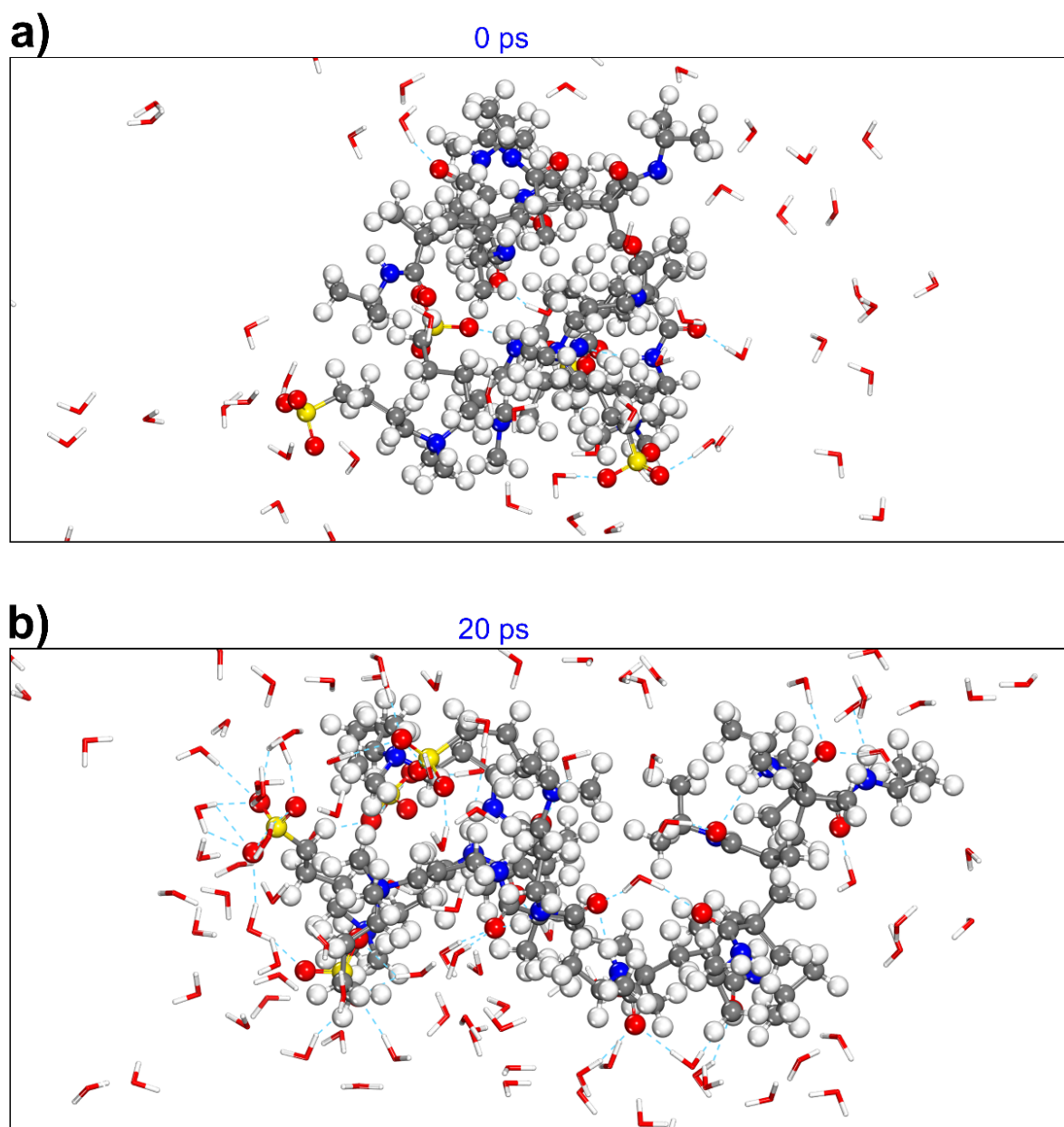


Figure C.17.: Snapshots illustrating the conformations of salt-free PSBP-*b*-PNIPMAM chains in pure H₂O atmosphere at (a) 0 ps and (b) 20 ps in Chapter 7. The atoms of N, O and S are colored dark blue, red and yellow respectively. The dashed lines in light blue represent the formed hydrogen bonds.

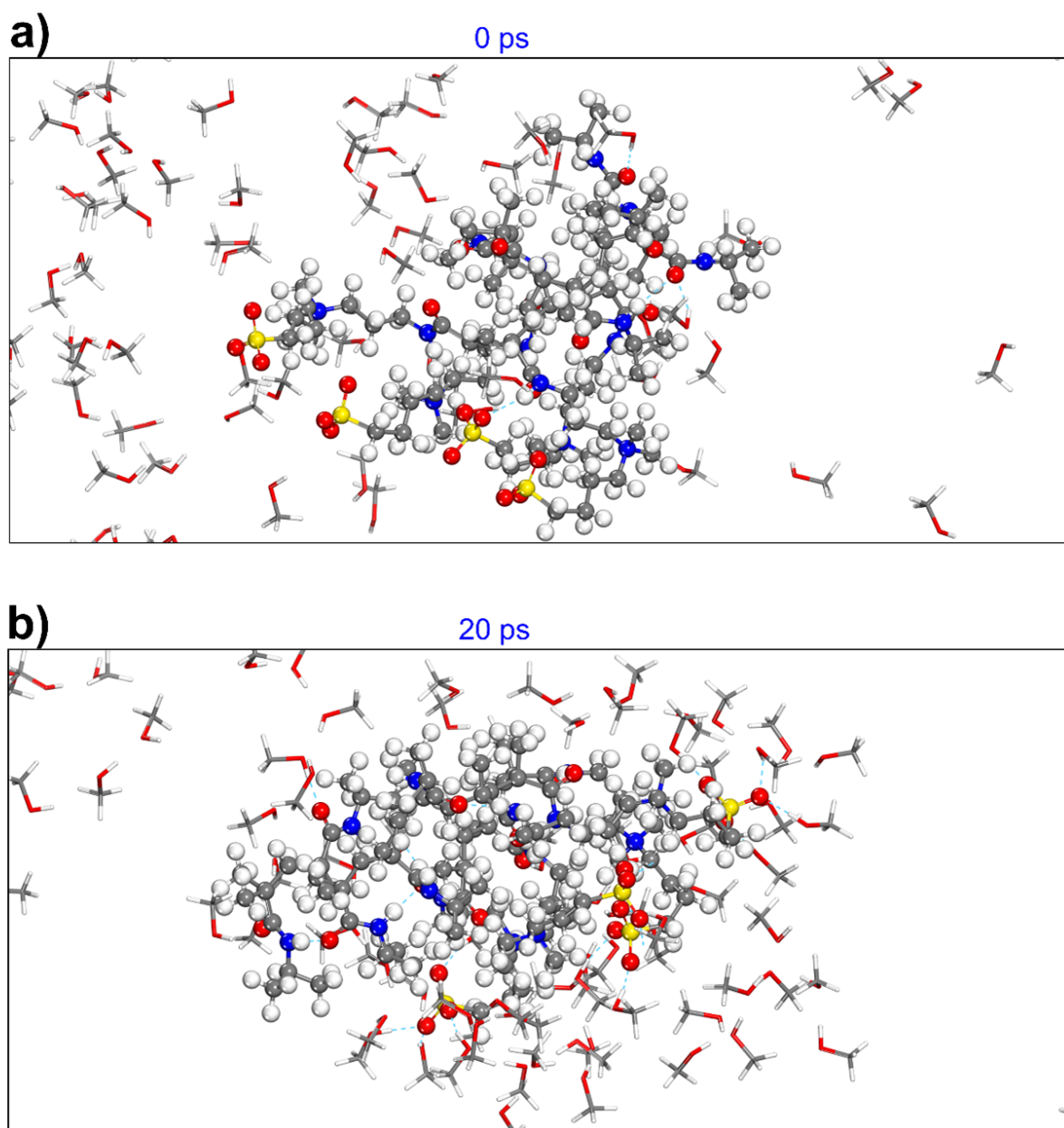


Figure C.18.: Snapshots illustrating the conformations of salt-free PSBP-*b*-PNIPMAM chains in a pure methanol atmosphere at (a) 0 ps and (b) 20 ps in Chapter 7. The atoms of N, O and S are colored dark blue, red and yellow respectively. The dashed lines in light blue represent the formed hydrogen bonds.

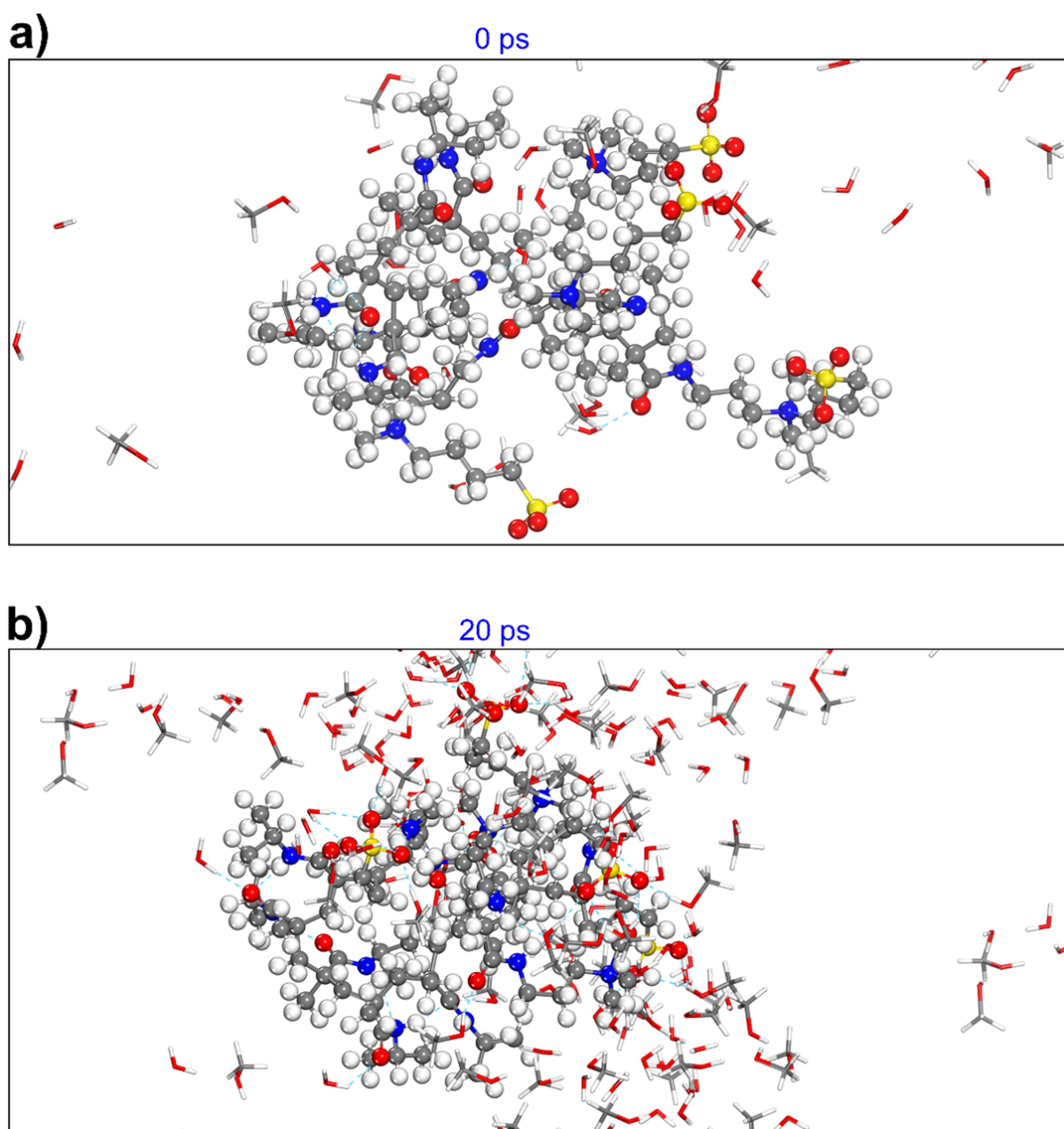


Figure C.19.: Snapshots illustrating the conformations of salt-free PSBP-*b*-PNIPMAM chains in a mixed atmosphere ($\text{H}_2\text{O}/\text{methanol} = 6/4$) at (a) 0 ps and (b) 20 ps in Chapter 7. The atoms of N, O and S are colored dark blue, red and yellow respectively. The dashed lines in light blue represent the formed hydrogen bonds.

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List of Publications

First Author Journal Articles Related to Thesis

- **P. Wang** C. Geiger, L. P. Kreuzer, T. Widmann, J. Reitenbach, S. Liang, R. Cubitt, C. Henschel, A. Laschewsky, C. M. Papadakis, P. Müller-Buschbaum
Poly(sulfobetaine)-Based Diblock Copolymer Thin Films in Water/Acetone Atmosphere: Modulation of Water Hydration and Co-nonsolvency-Triggered Film Contraction
Langmuir **38**, 6934-6948 (2022)
(DOI: 10.1021/acs.langmuir.2c00451)
- **P. Wang** C. Geiger, J. Reitenbach, A. Vagias, L. P. Kreuzer, S. Liang, R. Cubitt, V. Hildebrand, A. Laschewsky, C. M. Papadakis, P. Müller-Buschbaum
KCl-Modulated Hydration and Subsequent Thermoresponsive Behavior of Poly(sulfobetaine)-Based Diblock Copolymer Thin Films
Macromolecules **56**, 4087-4099 (2023)
(DOI: 10.1021/acs.macromol.3c00484)

Coauthor Journal Articles not Related to Thesis

- L. P. Kreuzer, C. Geiger, T. Widmann, **P. Wang**, R. Cubitt, V. Hildebrand, A. Laschewsky, C. M. Papadakis, P. Müller-Buschbaum
Solvation Behavior of Poly(sulfobetaine)-Based Diblock Copolymer Thin Films in Mixed Water/Methanol Vapors
Macromolecules **54**, 7147-7159 (2021)
(DOI: 10.1021/acs.macromol.1c01179)

- C. Geiger, J. Reitenbach, L. P. Kreuzer, T. Widmann, **P. Wang**, R. Cubitt, C. henschel, A. Laschewsky, C. M. Papadakis, P. Müller-Buschbaum
PMMA-b-PNIPAM Thin Films Display Cononsolvency-Driven Response in Mixed Water/Methanol Vapors
Macromolecules **54**, 3517-3530 (2021)
(DOI: 10.1021/acs.macromol.1c00021)
- C. Geiger, J. Reitenbach, C. henschel, L. P. Kreuzer, T. Widmann, **P. Wang**, G. mangiapia, J. F. moulin, A. Laschewsky, C. M. Papadakis, P. Müller-Buschbaum
Ternary Nanoswitches Realized with Multiresponsive PMMA-b-PNIPMAM Films in Mixed Water/Acetone Vapor Atmospheres
Advanced Engineering Materials **23**, 2100191 (2021)
(DOI: 10.1002/adem.202100191)
- M. K. Włodarczyk-Biegun, M. Villiou, M. Koch, C. Muth, **P. Wang**, J. Ott, and A. del Campo*
Melt Electrowriting of Graded Porous Scaffolds to Mimic the Matrix Structure of the Human Trabecular Meshwork
ACS Biomaterials Science & Engineering **8**, 3899-3911 (2022)
(DOI: 10.1021/acsbiomaterials.2c00623)
- J. Reitenbach, C. Geiger, **P. Wang**, A. Vagias, R. Cubitt, D. Schanzenbach, A. Laschewsky, C. M. Papadakis, P. Müller-Buschbaum
Effect of Magnesium Salts with Chaotropic Anions on the Swelling Behavior of PNIPMAM Thin Films
Macromolecules **56**, 567-577 (2023)
(DOI: 10.1021/acs.macromol.2c02282)

Conference Contributions

- *Thermoresponsive polymers*
E13 summer school, Nassfeld, 18 – 21 July 2023
- *2D FTIR and MD simulations study on Hofmeister series driven phase transition behavior of DBC thin films*
Project meeting (Technical University of Munich and University of Potsdam) 2023, Garching, 30 June 2023

- *KCl modulated Hydration and Subsequent Thermoresponsive Behavior of Poly(sulfobetaine)-Based Diblock Copolymer Thin Films*
5th internal biannual science meeting of the MLZ, Grainau, 19 – 22 Jun 2023
- *KCl modulated D₂O Hydration and Subsequent Thermoresponsive Behavior of Poly(sulfobetaine)-Based Diblock Copolymer Thin Films*
DPG Spring Meeting of the Condensed Matter Section 2023, Dresden, 26 – 31 March 2023
- *Hofmeister Series Driven Solvation Behavior of Thermoresponsive Polymer Thin Films in Water and Subsequent Mixed Water/Methanol Atmosphere*
Project meeting (Technical University of Munich and University of Potsdam) 2022, Garching, 14 December 2022
- *Spectral reflectometry (SR)*
E13 summer school, Nassfeld, 18 – 21 July 2022

Posters

- P. Wang, L. P. Kreuzer, C. Geiger, T. Widmann, S. Liang, P. Müller-Buschbaum
Effect on Conformational Transformation of Methyl Side Group in Poly(sulfobetaine)-Based Thermo-responsive Block Copolymer Thin Films
MLZ User Meeting 2019, München, 10-11 December 2019
- P. Wang, L. P. Kreuzer, C. Geiger, T. Widmann, S. Liang, A. Laschewsky, C. M. Papadakis, R. Cubitt, P. Müller-Buschbaum
Co-Nonsolvency Transition of PNIPMAM-based Diblock Copolymer Thin Films in a Series of Binary Mixtures
MLZ User Meeting 2020, 08 – 09 December 2020
- P. Wang, L. P. Kreuzer, C. Geiger, T. Widmann, S. Liang, A. Laschewsky, C. M. Papadakis, R. Cubitt, P. Müller-Buschbaum
Investigation of Cononsolvency Phase Transition of Poly(sulfobetaine)-based Diblock Copolymer Thin Films
Osmolyte and Cosolvent Effects in Stimuli-Responsive Soft Matter Systems 2021, 25 – 26 February 2021

- P. Wang, L. P. Kreuzer, C. Geiger, T. Widmann, S. Liang, A. Laschewsky, C. M. Papadakis, R. Cubitt, P. Müller-Buschbaum
Investigation of Cononsolvency Phase Transition of Poly(sulfobetaine)-based Diblock Copolymer Thin Films
 DPG spring Meeting 2021, 22 – 24 March 2021
- P. Wang, L. P. Kreuzer, C. Geiger, T. Widmann, S. Liang, A. Laschewsky, C. M. Papadakis, R. Cubitt, P. Müller-Buschbaum
Co-Nonsolvency Transition of PNIPMAM-based Block Copolymer Thin Films in Water/Acetone Mixtures
 ACS spring Meeting 2021, 05 – 30 April 2021
- P. Wang, L. P. Kreuzer, C. Geiger, T. Widmann, S. Liang, A. Laschewsky, C. M. Papadakis, R. Cubitt, P. Müller-Buschbaum
Co-nonsolvency Triggered thin Films Contraction of Poly(sulfobetaine) based Diblock Copolymer Thin Films in Water/Acetone Atmosphere
 MLZ User Meeting 2021, 07 – 08 December 2021
- P. Wang, C. Geiger, L. P. Kreuzer, T. Widmann, S. Liang, V. Hildebrand, A. Laschewsky, C. M. Papadakis, P. Müller-Buschbaum
Co-Nonsolvency Transition of PNIPMAM-based Diblock Copolymer Thin Films in a Series of Binary Mixtures
 The 16th International Conference on Surface X-ray and Neutron Scattering (SXNS16), 11 – 14 January 2022
- P. Wang, C. Geiger, L. P. Kreuzer, T. Widmann, S. Liang, V. Hildebrand, A. Laschewsky, C. M. Papadakis, P. Müller-Buschbaum
Co-Nonsolvency Transition of PNIPMAM-based Diblock Copolymer Thin Films in a Series of Binary Mixtures
 DPG Spring Meeting 2022, 04 – 09 September 2022
- P. Wang, C. Geiger, L. P. Kreuzer, T. Widmann, S. Liang, V. Hildebrand, A. Laschewsky, C. M. Papadakis, P. Müller-Buschbaum
Co-Nonsolvency Transition of PNIPMAM-based Diblock Copolymer Thin Films in a Series of Binary Mixtures
 MLZ User Meeting 2022, 08 – 09 December 2022

- P. Wang, C. Geiger, J. Reitenbach, A. Vagias, L. P. Kreuzer, S. Liang, R. Cubitt, V. Hildebrand, A. Laschewsky, C. M. Papadakis, P. Müller-Buschbaum
KCl modulated D₂O Hydration and Subsequent Thermoresponsive Behavior of Poly(sulfobetaine)-Based Diblock Copolymer Thin Films
8th European Conference on Neutron Scattering, Munich, 20 – 23 March 2023
- P. Wang, C. Geiger, J. Reitenbach, A. Vagias, L. P. Kreuzer, S. Liang, R. Cubitt, V. Hildebrand, A. Laschewsky, C. M. Papadakis, P. Müller-Buschbaum
KCl modulated D₂O Hydration and Subsequent Thermoresponsive Behavior of Poly(sulfobetaine)-Based Diblock Copolymer Thin Films
MLZ User Meeting 2023, Munich, 04 – 05 December 2023

Acknowledgments

Four and a half years have passed in the blink of an eye, and my Ph.D. thesis has reached the final stage, signaling the conclusion of my doctoral journey. Starting from the autumn of 2019 and ending in the spring of 2024, these four and a half years have been a turning point in my life, worthy of savoring slowly over a lifetime. On the occasion of my thesis nearing completion, I want to express sincere gratitude to those who have taught me, helped me, and encouraged me throughout this journey.

I would like to sincerely thank my supervisor, Prof. Dr. Peter Müller-Buschbaum for giving me the opportunity to work on a Ph.D. project at E13 chair. Over these years of academic life, Prof. Dr. Peter Müller-Buschbaum has provided significant assistance and guidance in the process of my research. He has not only given me a clear direction for my projects but has also offered detailed guidance on experimental details, helping me to navigate through intricacies. He provided me with the chance to perform measurements at multiple international large-scale facilities, like ILL, MLZ, PSI and Elettra, from which I learned different things and had excellent experiences. Meantime, I was grateful for the opportunity to join many conferences, workshops, and summer schools to present my posters and talks. Under the guidance of Prof. Dr. Peter Müller-Buschbaum, I have learned how to think independently, organize a beamtime team successfully, and process papers efficiently. Except for the academic activities, many memorable moments spent with Peter in life are unforgettable, from the Oktoberfest to the E13 barbecue, E13 hiking, and Bavarian Curling and Chinese food. Thank you, Peter!

I am also grateful to have Prof. Dr. Christine M. Papadakis as my mentor. I benefited greatly from the collaboration with her and would like to thank her for many suggestions to improve my understanding of the topic and comments to improve my writing of papers. Especially, I would like to thank Christine for allowing me to work in her lab and sharing

me with the polymers. Thank you, Christine!

This thesis is the product of many collaborations. I would like to thank Prof. Dr. André Laschewsky and Dr. Viet Hildebrand from the University of Potsdam. The conducted research would not have been possible without the challenging synthesis and characterization of the polymers, especially, the assistance from Prof. Dr. André Laschewsky during the preparation of manuscripts. I also would like to thank my colleagues for developing the “FlexiProb” chamber and gas flow system. With those excellent setups, the projects were proposed possibly. Thank you, Tobias Widmann, Dr. Lucas Philipp Kreuzer, Christina Geiger and Julija Reitenbach. Also, a special thanks go to the neutron community at ILL, with support from the neutron community, the neutron measurements and data analysis were successfully performed. Thank you, Dr. Robert Cubitt, Dr. Thomas Saerbeck, Dr. Samantha Micciulla, and Dr. Philipp Gutfreund. I also would like to thank the contributions from High Performance Computing Center of Shanghai University and Shanghai Engineering Research Center of Intelligent Computing System for providing the computing resources and technical support, especially, the assistance from Prof. Dr. Ya-jun Cheng and Tonghui Xu.

I am deeply thankful to the Hydrogel Subgroup. Thank you, Christina Geiger, Dr. Lucas Philipp Kreuzer, Julija Reitenbach, Dr. Apostolos Vagias and Morgan Le Dû. It’s my great honor and luck to meet with you and work together with you. You are the guides in my laboratory life and the cornerstone of my PhD academic products. Furthermore, I would like to thank Dr. Suzhe Liang. Your amazing job on Blender highlights my manuscripts. I would like to thank Tianle Zheng for your contributions to molecular dynamic simulations. I also would like to thank Dr. Xinyu Jiang for the AFM measurements. I am also grateful to work together with nice group colleagues as beamtime members. Thank you, Christina Geiger, Dr. Lucas Philipp Kreuzer, Tobias Widmann, Julija Reitenbach, Dr. Apostolos Vagias, Anna-Lena Oechsle, Suo Tu, Fabian Apfelbeck, Linus Huber and Simon Wegener, as well as the colleagues from Heinz Maier-Leibnitz (FRM II), Thank you, Marcell Wolf, Garvey, Christopher, Markos Skoulatos and Dr. Robert Georgii. Special thanks go to Carola Kappauf and Marion Waletzki, for their support in document work and organizing the group activities. I am also thankful to Reinhold Funer, who provided help with fixing the office table and the instrument holders. In addition, I would like to express my gratitude to all the members of the Chair of Functional Materials for the positive and pleasant working atmosphere. It was a great time to be at the chair with all of you during all these years.

The China Scholarship Council (CSC) and the Deutsche Forschungsgemeinschaft (DFG) are acknowledged for the financial support of the project.

Finally, I want to express my gratitude to my parents. Thank you for your unwavering support and contributions throughout my educational journey, being my solid pillar. I also extend deep thanks and respect to the family members who have cared for me with warmth. I appreciate their encouragement and support, which have enabled me to successfully complete my Ph.D. study. I feel immensely proud to have grown up in such a joyful, loving family.

Grateful for all the encounters and sincerely wish everyone well. Using limited words to express my gratitude, for the days ahead are long! This writing is dedicated to all those who have crossed paths with me, and to all the experiences. It is with you that my life has become so vibrant and exciting.

