

Water sorption on a thin film of stereocontrolled poly(*N*-ethylacrylamide) and poly(*N,N*-diethylacrylamide)

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Abstract. The tacticity effects on the water-vapor sorption of the thin films of poly(*N*-ethylacrylamide) (PNEAm) and poly(*N,N*-diethylacrylamide) (PNdEAm) are investigated by the quartz crystal microbalance method and infrared spectroscopy. The quantity of sorbed water on the spin-coated films of isotactic-rich PNEAm is larger than that of atactic one. For PNdEAm, the syndiotactic-rich polymer film absorbs more water. The amide I or C=O stretching band of the polymers are monitored during water sorption on the spin-coated films. The result indicates that the water-sorption site is also influenced by the tacticity of the polymers. The annealing of these films wipes out the tacticity dependence of water sorption, indicating that the water-sorption sites in the spin-coated films are voids around C=O groups that are made by evaporation of solvent during spin-coating (so-called, the “solvent-imprint” effect). The isotactic-rich PNEAm is more influenced by the solvent-imprint effect than the syndiotactic-rich one, while an opposite tendency is found for PNdEAm.

1 Introduction

Controlling the water sorption of polymer thin films is important for designing soft biomaterials. In fact, when a foreign material such as a synthetic polymer comes into contact with blood, the water sorption is the first event before protein sorption [1]. Thermoresponsive polymers have attracted keen interest of scientists in this field [2], because of their potentials for developing intelligent soft biomaterials. Poly(*N*-substituted acrylamide) is a representative of thermosensitive polymers in aqueous media [3]. In general, the thermo-responsiveness of acrylamide polymers is concerned with lower critical solution temperature (LCST) type phase behaviour in the aqueous media. Poly(*N*-isopropylacrylamide) (PNiPAm) is the most popular thermoresponsive polymer and has extensively been studied [2-6]. The interaction between the polymer chain and water is a fundamental factor to induce the thermo-responsiveness of the polymers. In this context, the effects of salt and co-solvent on the phase behaviour have been investigated. On the other hand, several experimental results have implied that the intramolecular interaction among the side chains plays an important role in its phase behaviour. This is clearly shown when the phase separation behaviour of PNiPAm is compared with poly(*N,N*-diethylacrylamide) (PNdEAm). The co-solvent effect on the phase behaviour of PNiPAm is different from that of PNdEAm; the addition of methanol to the aqueous solutions causes the rise of the cloud point (T_c) for PNdEAm [7], but the

decrease of T_c for PNiPAm [8]. The tacticity dependence of T_c is also opposite for these two polymers: The increase of the *meso* diad (*m*) fraction in the polymer chain causes the rise of T_c for PNdEAm [9,10], but the decrease of T_c for PNiPAm [11,12]. These phenomena cannot be explained only by taking account of the interaction between the side chain and water, and thus we have to also consider the contribution of the intramolecular interaction among the side chains [13]. A remarkable difference in the chemical structures of PNdEAm is the lack of the N–H group. The side chains of PNiPAm can form an intramolecular C=O···H–N hydrogen bond (H-bond), whereas those of PNdEAm cannot. In the previous paper [14], we revealed that the tacticity dependence on the water solubility of the dimer model of PNiPAm is owing to the changes in the intramolecular interaction between the diastereomers. This clearly indicates that the intramolecular C=O···H–N H-bond of the amide groups affects the solubility of the polymer in water.

In this paper, we have examined how the tacticity of polymers affects the water-vapor sorption of the thin films of poly(*N*-ethylacrylamide) (PNEAm) and PNdEAm.

2 Experimental

Chemicals were from WACO, TCI, and Aldrich. The stereospecific free radical polymerization was carried out.

The preparation of *N*-ethylacrylamide can be found in elsewhere [15]. *N,N*-diethylacrylamide was kindly provided by Kojin and purified by distillation under reduced pressure. The polymerizations were carried out in the absence or presence of Yttrium(III) trifluoromethanesulfonate (Y(OTf)₃ Lewis acid) [12,16]. Chemical structures of PNEAm and PNdEAm were shown in figure 1. The weight-average molecular weight (M_w) and polydispersity (M_w/M_n) were determined by a size exclusion chromatography. The *m* content was determined by ¹H NMR [12,16,17]. The cloud point (T_c) of a 1 wt % aqueous solution was estimated by the transmittance curve [12].

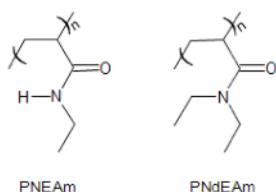


Fig. 1. Chemical structures of PNEAm and PNdEAm.

IR spectra were recorded at a resolution of 2 cm⁻¹ with a co-addition of 512 scans on a Jasco FT/IR-615 spectrometer equipped with a liquid-nitrogen cooled HgCdTe (MCT) detector. CaF₂ plates were used as a window material. Quartz crystals (9 MHz) with Cr/Au electrodes and the electronic circuit oscillators (QSET - 9E-H) were purchased from Tama-devise co. ltd. The Sauerbrey equation was used for correlating changes in the oscillation frequency of the QCM sensor with the mass deposited on it [19].

Polymers dissolved in acetone (0.2 wt%) were spin-coated on CaF₂ and QCM sensors with 2000 rpm, and then the samples were dried in a desiccator overnight before being placed in a vacuum chamber. The chamber was vacuumed by a rotary pump (LS63P, Edwards). The vapor pressure of water was monitored by a strain-gauge manometer (D357-26 strain-gauge with D395-57 monitor, Edwards). The experiment was carried out at room temperature. After the system was vacuumed, the needle valve was opened to introduce the D₂O vapor.

3 Results and Discussion

Table 1 compiles the characterization of prepared samples and their notations. For both PNEAm and PNdEAm, the polymerization in the presence of Y(OTf)₃ yields an isotactic-rich polymer, which contains a high *meso* diad (*m*) configuration in the main chain. The T_c of the aqueous solution of PNdEAm increases with

Table 1. Characterization of polymer samples

Sample	<i>m</i> %	$M_n / \text{g mol}^{-1}$	M_w / M_n	$T_c / ^\circ\text{C}$
PNEAm				
E- <i>m</i> 47	47	2.4×10^4	2.6	78
E- <i>m</i> 78	78	1.4×10^4	1.6	70
PNdEAm				
D- <i>m</i> 55	55	3.1×10^4	3.3	32
D- <i>m</i> 90	90	3.6×10^4	2.4	40

increasing *m* content as reported previously [10]. The tacticity dependence of T_c for PNEAm, on the other hand, is similar to that observed for PNiPAm [12], which is opposite to that for PNdEAm. These results indicate that an isotactic-rich PNdEAm is hydrophilic, whereas an isotactic-rich PNEAm is hydrophobic.

3.1. Tacticity dependence on the quantity of water sorption for the polymer films

Figure 2 shows the water-vapor sorption of the thin films of PNEAm with different tacticity (E-*m*47 and E-*m*78) at each water-vapor pressure. For the spin-coated film as prepared, the water sorption of E-*m*78 is a little greater than that of E-*m*47. When the 0.2 μg of D₂O is sorbed on 1.0 μg of PNEAm, one monomer unit of the polymer interacts with one water molecule on an average. The difference between the quantity of water sorption between E-*m*78 and E-*m*47 is about 0.03 μg/μg (0.015 D₂O molecule per monomer unit) at any vapor pressure. Even though the difference is not quite big, the result seems to be counter intuitive, because T_c of the aqueous solutions insists that E-*m*78 is more hydrophobic. After annealing the films at 140 °C for 15 min, the water sorption on the film was measured. For E-*m*47, the quantity of sorbed water is almost identical between the films before and after annealing, while that for E-*m*78 markedly decreases. This may be caused by a solvent-imprint effect on the spin-coated film of E-*m*78. In the previous paper [19], we concluded from the IR measurement of stereocontrolled PNiPAm that solvents around the amide groups of the polymer evaporate quickly before the reorientation of the amide groups occurs, in which a portion of the carbonyl groups would be left isolated. If the water-sorption site is concerned with these free carbonyl groups, the result obtained here suggests that the solvent-imprint effect of E-*m*78 is more prominent.

The water sorption of PNdEAm films as a function of water-vapor pressure is represented in figure 3. The fraction of water molecule per one monomer unit is about 0.6 on an average at where 0.1 μg of D₂O is sorbed on 1.0 μg of PNdEAm. The quantity of the sorbed water on the PNdEAm film is smaller by twice than that on the PNEAm film. This implies that PNdEAm is more hydrophobic than PNEAm. In fact, T_c of PNdEAm in water is lower by 30-40 °C than that of PNEAm. It is worth noting that the functional type for the water sorption isotherm of PNdEAm seems to be different from that of PNEAm.

For the spin-coated films, the water sorption of D-*m*55 is slightly greater than that of D-*m*90. Interestingly, the result is in good harmony with that for the PNEAm films, because D-*m*55 has a lower T_c and absorbs more water than D-*m*90 in a solid state. The annealing effects on the PNdEAm film also show a similar tendency with those of PNEAm. The quantity of sorbed water of D-*m*90 is almost identical between the films before and after annealing, while that for D-*m*55 discernibly decreases. It is worth reminding that for PNEAm the annealing effect of E-*m*47 on the water sorption is small in contrast to E-

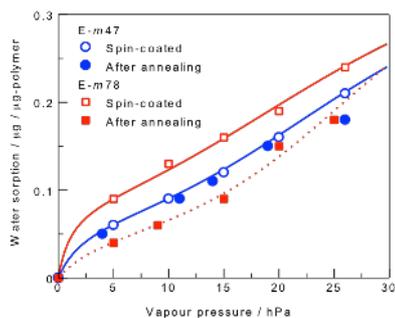


Fig. 2. Water sorption of PNEAm films. The line was drawn as guides for the eyes.

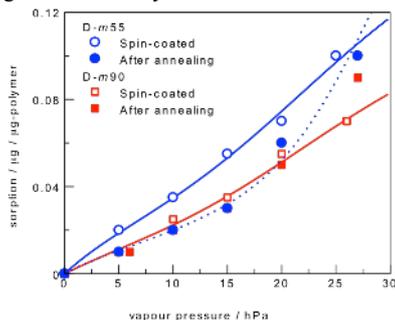


Fig. 3. Water sorption of PNdEAm films. The line was drawn as guides for the eyes.

m78. The result supports again the existence of solvent-imprint effects in a spin-coated film of acrylamide polymers. Moreover, the solvent-imprint effect is always large for a polymer that has a lower T_c in aqueous media, *i.e.* for a polymer that has poor solubility to water.

3.2. Water-sorption sites in PNEAm films

IR spectra of the polymer thin films at each water-vapor pressure were measured in order to investigate the water-sorption site. Figure 4 shows changes in the amide I envelope of PNEAm depending upon the water-vapor pressure. There are at least three bands in this region at 0 hPa (Dry); 1675, 1650, and 1625 cm^{-1} . These bands are associated with the proton accepting number of the C=O groups (n_H). According to the previous papers [13,20], the bands at 1675, 1650, and 1625 cm^{-1} are assignable to $n_H = 0, 1, \text{ and } 2$, respectively. It is worth noting that the bands due to $n_H = 1$ and 2 contain contributions not only from an intermolecular H-bond between the C=O group and water (C=O \cdots H-O) but also from an intramolecular C=O \cdots H-N H-bond among the side chains of the polymer. For both *E-m47* and *E-m78*, the relative intensity of the 1675 cm^{-1} band decreases with increasing vapor pressure, while that of the 1625 cm^{-1} band increases (figure 4). This indicates that D₂O molecules sorbed in the film form a H-bond with C=O groups of the polymer. The relative intensity of the 1625 cm^{-1} band for *E-m78* at 20 hPa is a little stronger than that for *E-m47*, indicating that the amount of H-bonded C=O groups with $n_H = 2$ for *E-m78* is larger. This is in good agreement with the QCM results; the quantity of water sorption of *E-m78* is larger than that of *E-m47*. Further, the result supports the hypothesis that the solvent-imprint effect for *E-m78* is more emphasized than that for *E-m47*. It is interesting

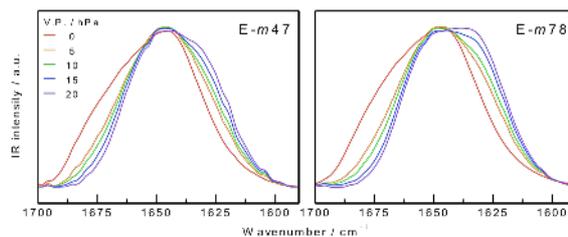


Fig. 4. Amide I envelope of *E-m47* and *E-m78* spin-coated films at each water-vapor pressure.

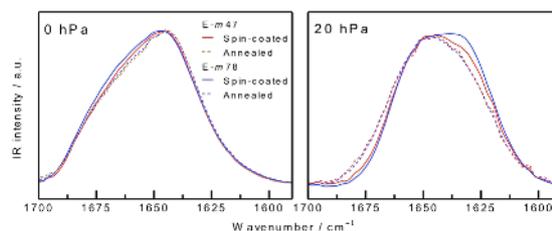


Fig. 5. Amide I envelope of *E-m47* and *E-m78* after annealing the films.

that the difference in the amide I envelopes between the two polymers at 0 hPa is smaller than that at 20 hPa. This may be attributed to the fact that the relative intensity of a free amide I band is much smaller than that of a H-bonded amide I band, *i.e.* H-bonding at a C=O group enlarges the relative strength of the amide I mode.

The annealing of the films marginally modifies the amide I envelope at a dry state (0 hPa of water vapor), but causes the reduction of the relative intensity near 1625 cm^{-1} when the vapor pressure increases (see figure 5). After annealing the films, the amide I envelopes of *E-m47* and *E-m78* are almost identical even at 20 hPa. By carefully inspecting the spectra shown in the left panel of figure 5, the band at 1675 cm^{-1} for *E-m78* at 0 hPa before annealing is stronger than that for *E-m47*. It is therefore considered that the capacity of water-sorption depends upon the amount of the free C=O groups ($n_H = 0$) in the film. After annealing, the shoulder near 1675 cm^{-1} of the amide I band of *E-m78* decreases its relative intensity, and the band profile becomes almost identical with that for *E-m47*. This can explain well the QCM results that the quantity of water sorption of *E-m78* decreases after annealing. The amount of free C=O groups of *E-m78* may be reduced by forming an intramolecular H-bond during the annealing process, and then the quantity of water-sorption sites decreases. It is suggested by the QCM results that the quantities of water sorption for *E-m47* and *E-m78* films after annealing are almost same at a vapor pressure higher than ~ 20 hPa (figure 2). Again, the QCM and IR results are well correlated.

As mentioned above, QCM results indicate that at 25 hPa of vapor pressure one monomer unit of PNEA interacts with one water molecule on an average. C=O groups are generally capable to accept two protons at least. Thus, we inferred that the water-sorption of the PNEAm films is caused by forming a direct H-bonding between C=O groups and water.

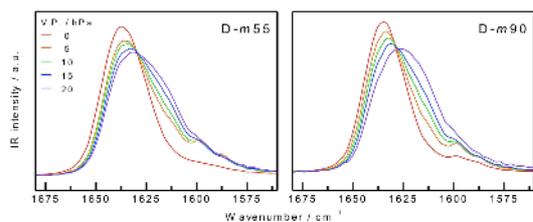


Fig. 6. Dependence of the C=O stretching envelope of D-*m*55 and D-*m*90 spin-coated films on the water-vapor pressure.

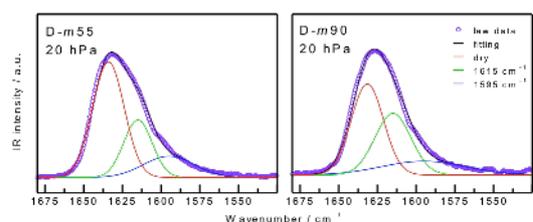


Fig. 7. C=O stretching envelope of D-*m*55 and D-*m*90 after annealing the films.

3.3. Water-sorption sites in PNdEAm films

Figure 6 represents the changes in the C=O stretching envelope of PNdEAm depending upon the water-sorption. In contrast to PNEAm, the IR spectrum of D-*m*55 is markedly different from that of D-*m*90 even at 0 hPa (dry state). The peak of dry D-*m*55 and D-*m*90 films is located at 1637 and 1634 cm^{-1} , respectively. This indicates that the interaction among the C=O groups in the dry D-*m*90 film is slightly stronger than that in the dry D-*m*55 [21]. The interaction in a dry PNdEAm film should be attributed to a dipole interaction among the neighbouring amide groups. When the water-vapor pressure becomes high, a shoulder on the low wavenumber side of the main peak increases its relative intensity. According to the previous paper [21], the hydration of the C=O groups of PNdEAm gives rise to the bands at 1616 and 1595 cm^{-1} , which are associated with the weakly and strongly hydrated C=O groups, respectively. Therefore, the result obtained here indicates that the water molecules directly interacts with the C=O groups in the polymer after being absorbed by the films. Figure 7 shows the curve fitting results of D-*m*55 and D-*m*90 at 20 hPa of water vapor. The peaks of the bands due to hydration are fixed at 1616 and 1595 cm^{-1} , respectively. The curve-fitting results suggest that the relative intensity of the 1595 cm^{-1} band for D-*m*55 is stronger than that for D-*m*90. On the other hand, the 1616 cm^{-1} band of D-*m*90 is more emphasized. The hydration of the C=O groups of D-*m*90 may be more interfered by the interaction among the C=O groups. In the current state, it is difficult to find a clear correlation between the quantity of sorbed water and the water-sorption sites of PNdEAm, unlike those we found for PNEAm.

4 Conclusion

For PNEAm films, the QCM and IR results suggest that the majority of water molecules in the films exist around the C=O groups and form a H-bond with those. The

amount of water-sorption for the spin-coated films of PNEAm and PNdEAm are markedly influenced by the tacticity of polymers, which is possibly induced by the solvent-imprint effects. The solvent-imprint effect is always large for the polymer that has poor solubility to water. The annealing treatment makes the tacticity effects small. The results obtained here suggest that the solvation structure and polymer chain geometry of PNEAm and PNdEAm in solution are varied depending on the tacticity.

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