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A Novel Application of Hybrid Two-Dimensional Correlation Infrared Spectroscopy: Exploration of the Reversibility of the Pressure- and Temperature-Induced Phase Separation of Poly(*N*-isopropylacrylamide) and Poly(*N*-isopropylmethacrylamide) in Aqueous Solution

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ABSTRACT: We have demonstrated a novel application of hybrid two-dimensional (2D) correlation spectroscopy in exploring the reversibility of phase separation (or transitions). Pressure-induced phase separation and temperature-induced phase transitions have been studied for poly(*N*-isopropylacrylamide) (PNiPA) and poly(*N*-isopropylmethacrylamide) (PNiPMA) in aqueous solutions using Fourier transform infrared (IR) and hybrid 2D correlation spectroscopy. Here we show that pressure-dependent sample−sample (SS) hybrid 2D correlation IR spectroscopy reveals for PNiPA a reversible phase separation with a differential rate of concentration change and separation pressure and a reversible phase separation with similar dynamics for PNiPMA, but involving irreversible hydrogen/deuterium exchange. Subtle differences in concentration dynamics have been revealed clearly by the hybrid SS 2D IR correlation analysis; these include the minor irreversibility of amide I in PNiPA, resulting from the loss of a very few coil populations, and in PNiPMA, resulting from the irreversible H/D exchange. Such events are not apparent from the transition plots constructed on the basis of one-dimensional data analysis.

Introduction

Poly(*N*-isopropylacrylamide) (PNiPA) and poly(*N*-isopropylmethacrylamide) (PNiPMA) are normally used as model polymers to understand the fundamental physics of the polymer coil-to-globule collapse.[1] Because of their high solubility in water, their application in drug delivery and bioseparation has also been reported.[2−4] These polymers show a sharp transition in their aggregation state upon a change in temperature, and both their macroscopic thermodynamic properties and molecular interactions have been investigated extensively using a wide variety of techniques.[5−7] Infrared (IR) studies on the thermally induced coil−globule transition of PNiPA solutions have been carried out by several research groups.[8−11] IR spectroscopy has been shown to be a suitable method for observing changes not only in the hydration of the polymer chain of PNiPA but also in the interactions and microenvironments of the amide and isopropyl groups in the polymer. Maeda et al.[8] have reported hydration changes of PNiPA during coil−globule transition by using transmission Fourier transform IR (FT-IR) spectroscopy; Katsumoto et al.[11] investigated the conformational change of PNiPA during the coil−globule transition using attenuated total reflection IR spectroscopy and density functional theory calculations.

Although many investigations have focused on the kinetics of pressure-induced phase separation of polymers in solutions,[12−15] reports specifically on these polymers are scarce.[16] Meersman et al.[16] reported an IR study on the pressure-induced phase separation and hydration variations of PNiPA in aqueous solution. The pressure-dependent IR spectra of PNiPA demonstrated significantly different spectral changes in comparison with the temperature-dependent spectra.[16] Meersman et al. showed that although both pressure and temperature induce a phase separation, the underlying mechanisms are fundamentally different.[16] High pressure was found to enhance the hydration of the hydrophilic amide group, whereas increasing temperature above the lower critical solution temperature causes the well-known dehydration of the hydrophilic and hydrophobic moieties, which drives the coil-to-globule transition and subsequent aggregation.

The thermally induced coil−globule transition of PNiPA and PNiPMA is usually reversible.[5,9] However, the reversible kinetics of the phase transition of PNiPA and PNiPMA induced by temperature, and especially the phase separation induced by pressure, have not been investigated extensively at the microstructure level. Here we investigate their reversibility using IR spectroscopy and hybrid two-dimensional (2D) correlation spectroscopy. Hybrid 2D correlation spectroscopy was proposed in 2002, and it deals with the 2D correlation analysis between two separately obtained data matrices.[17] Three possible types of hybrid 2D correlations has been mentioned: In the first type, 2D correlation spectra are calculated by using different sets of spectral data of one sample obtained under two unrelated perturbations,[17,18] such as temperature and pressure. In the second type, 2D correlation spectra are constructed by using spectral variations measured under conjunct or related perturbations. The third type treats 2D correlation spectra generated by using two independent spectral data sets collected under the

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same perturbation but different conditions.[17] Using this approach allows direct exploration of the dynamic correlation between two different perturbations or two processes [sample−sample (SS) hybrid 2D correlation spectrum] or structural correlation induced by two different perturbations [variable−variable (VV) hybrid 2D correlation spectrum]. By using SS hybrid 2D correlation, furthermore, can potentially explore the latent correlation between different perturbations or processes, and the relationship of process dynamics can be studied by examining the similarity or subtle difference of their trace patterns along the spectral variable. However, since soft modeling techniques relying heavily on inferences are mostly effectively utilized in conjunction with concrete scientific reasoning and physical reality, overinterpretation of correlation results without sound justification should be carefully avoided.[21]

It is well-known that a conventional synchronous 2D correlation spectrum always shows a symmetric pattern along the diagonal line, in the cases of both VV 2D[19−22] and SS 2D[23,24] correlation spectra. In contrast, a hetero-2D correlation spectrum[25−28] and a hybrid 2D[17,18] correlation spectrum do not yield a completely symmetric synchronous spectrum because of the dissimilarity involved in the two spectral data sets. Therefore, it is possible to explore the similarity and/or difference between two systems or processes by use of hybrid 2D correlation spectroscopy. In exploring the reversibility of polymer process, an asymmetry along the diagonal line in the SS hybrid 2D cross product would indicate a dissimilarity in any of the following aspects: (i) recovery degree of the concentration of the original components, (ii) transitional temperature or pressure, or (iii) the rate of concentration change during the phase transition.

Here we demonstrate the potential of SS hybrid 2D correlation IR spectroscopy in analyzing the reversibility of the phase separation and coil−globule transition in polymers induced by pressure and temperature. Instead of generating hybrid 2D maps with two spectral data sets measured under two independent perturbations, we created hybrid 2D correlation maps by using two spectral data sets measured at same perturbation in two opposite processes, heating and cooling or compression and decompression, which can be regarded as example of case III in hybrid 2D correlation[17] or one of useful variants of the heterocorrelation methods.[21] The general usefulness of SS hybrid 2D correlation spectroscopy in exploring the reversibility of processes has been assessed by analyzing the pressure- and temperature-induced phase separation or transitions in polymers.

Experimental Section

Materials. Poly(*N*-isopropylacrylamide) (PNiPA) and poly(*N*-isopropylmethacrylamide) (PNiPMA) were obtained by free-radical polymerization of the corresponding monomers in dimethylformamide.[16] Azobis(isobutyronitrile) was used as an initiating agent. The monomers were polymerized for 7 h at 70 °C under nitrogen. Finally, they were precipitated from the reaction mixture by diethyl ether and then purified on a NAP-25 column by eluting with water. The polymer was dried under vacuum to constant weight at room temperature.

FTIR Spectroscopy. For the IR spectral measurements, PNiPA and PNiPMA were dissolved in deuterated water (Cambridge Isotopes Inc., Andover, MA) at a concentration of 50 mg/mL and left overnight to achieve complete deuteration of all solvent accessible protons. The polymer solution was injected in a temperature cell (Graseby Specac, UK) with CaF_2 windows separated by a 50 μm Teflon spacer, creating an airtight chamber. The cell was then placed into a computer-controlled heating jacket (Graseby Specac, UK). The heating/cooling rate was 0.2 °C/min. High pressures were obtained with a diamond anvil cell (Diacell Products Ltd., UK). Barium sulfate was used as an internal pressure standard. In the case of PNiPMA, pressure was varied at an approximate rate of 200 and 300 MPa/h for compression and decompression, respectively. For PNiPA, the respective values are 300 and 400 MPa/h. All pressure experiments were performed at room temperature.

IR spectra were recorded with a Bruker IFS66 FTIR spectrometer equipped with a liquid nitrogen cooled MCT detector. The sample compartment was continuously purged with dry air. After registration with a resolution of 2 cm^{-1}, 250 interferograms were coadded.

Data Analysis and Calculation of 2D Correlation Spectra. An IR spectrum of water vapor was subtracted from all spectra before smoothing. The data manipulation, subtraction, truncation, and baseline corrections of IR spectra were performed using the GRAMS program package (Galactic Inc. Corp.). The spectral smoothing was made using the RAZOR program (Spectrum Square Associates, Inc., Ithaca, NY), also running under the GRAMS software. The smoothing was carried out by the method of maximum entropy using a Lorentzian line shape of 20 cm^{-1} full width at half-height.

Software for the SS hybrid 2D correlation analysis was developed by one of the authors (Y. Wu) based on Matlab 6.0 (Math Works Inc., Natick, MA). The procedure for its use has been described elsewhere.[17,18]

Results and Discussion

Reversibility of Pressure-Induced Phase Transition of PNiPA. Figure 1a shows the pressure dependence of the carbonyl vibrational band of PNiPA in D_2O solution. In a previous study, we showed that although it is a fundamentally different mechanism, pressure can induce a phase separation similar to that induced by temperature.[16] The main spectral changes that occur with pressure are varied and can be summarized as follows: a strong band at 1625 cm^{-1}, which is generally attributed to the vibrational mode of the carbonyl group that forms either an intermolecular $C{=}O{\cdots}D{-}O{-}D$ hydrogen bond[1,8] or an intramolecular $C{=}O{\cdots}D{-}N$ hydrogen bond,[29] decreases with increasing pressure. At the same time, two new components with vibrational bands at 1650 and 1600 cm^{-1} appear. The band at ∼1650 cm^{-1} was assigned to the vibrational mode of free C=O in PNiPA by Katsumoto et al., based on its low sensitivity to the hydration,[11] and the band at around 1600 cm^{-1} has been suggested to result from the strongly intrachain hydrogen-bonded species of $C{=}O{\cdots}D{-}N$ between polymers in the globule state[32] or doubly hydrogen-bonded carbonyl with water.[16] Figure 1b depicts the pressure-dependent IR spectra of PNiPA measured in the decompression process. We note that the spectra show an intensity decrease at 1650 and 1600 cm^{-1} and an intensity increase at 1625 cm^{-1}, which are opposite to the effects induced by the compression.

Figure 2 shows a synchronous SS hybrid 2D correlation spectrum constructed from the IR spectra of PNiPA measured in the compression (*x*-axis) and decompression (*y*-axis) processes. In the present case, SS hybrid 2D correlation spectroscopy is the pressure−pressure correlation spectroscopy. Usually, a strong correlation is observed in a SS 2D correlation spectrum between two groups of samples that have high concentrations of the same species.[23] The strong positive correlation in the low-pressure region ($p < 182$ MPa) indicates the existence of a single component (which shows an absorption band at 1625 cm^{-1}) at high concentration, suggesting the recovery of the coil structure in the decompression process.

However, a slight asymmetry of the two sides along the diagonal line in the low-pressure region ($p < 182$ MPa) of the SS hybrid 2D correlation spectrum can be observed. This asymmetry reveals that the concentration of the coil species may

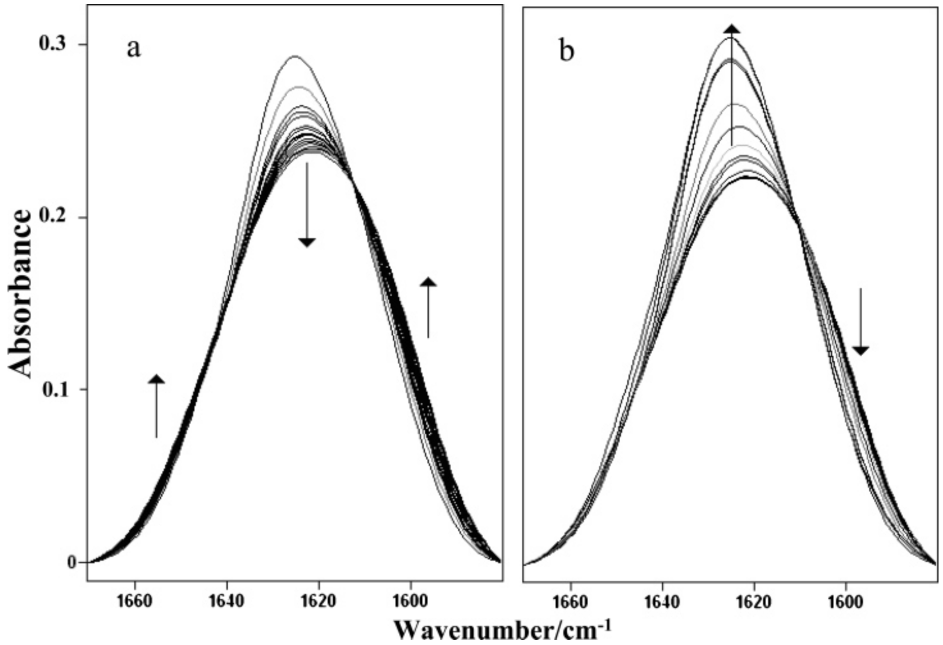

Figure 1. FT-IR absorption spectraof PNiPA in D_2O solution as a function of pressure: compression (a) and decompression (b). The pressure was varied between 10 and 1084 MPa with an interval of about 100 MPa.

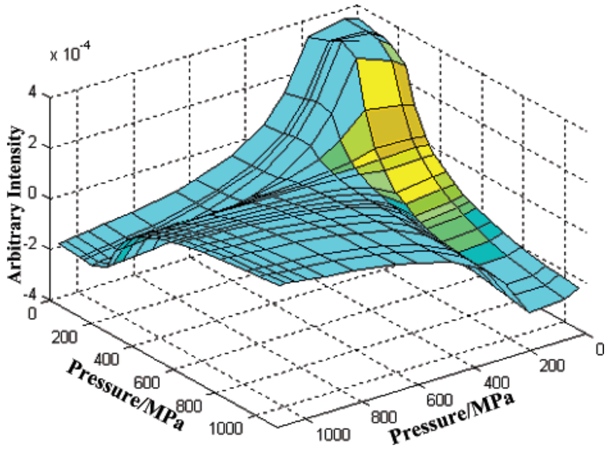

Figure 2. A synchronous SS hybrid 2D correlation IR spectrum of PNiPA constructed from the two IR spectra data sets shown in Figure 1.

be slightly lower after the compression−decompression cycle in comparison with that in the initial state. An asymmetry along the diagonal line in the intermediate pressure region ($182 < p < 600$ MPa) of the SS hybrid 2D correlation spectrum strongly suggests the existence of differences in concentration kinetics between the compression and decompression processes. Thus, differences may exist either in the separation pressure or in the rate of concentration change (as defined by the slope of the slice spectra in the intermediate pressure region) induced by pressure during the phase separations or remixing. However, generally, the asymmetry in all regions of pressure in Figure 2 is not very significant; therefore, it does not impede the general reversibility of PNiPA induced by decompression. Thus, pressure-dependent hybrid SS 2D correlation IR spectroscopy reveals a reversible phase separation with slight differences in the rate of concentration change and transition pressure of PNiPA.

The differences in concentration dynamics between the compression and decompression processes are illustrated more clearly in the slice spectra shown in Figure 3a,b, which are extracted from the SS hybrid 2D correlation spectrum in Figure 2 along the *x*-axis (compression) and the *y*-axis (decompression).

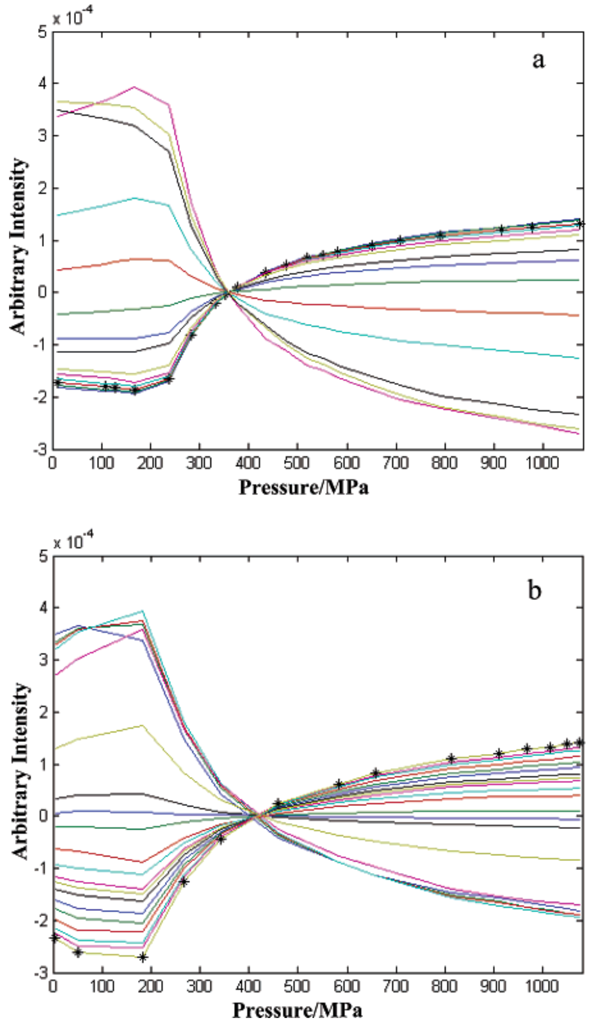

Figure 3. Slice spectra extracted along the two axes from the SS hybrid 2D correlation IR spectrum in Figure 2: (a) compression process (*x*-axis); (b) decompression process (*y*-axis).

The slice spectra in Figure 3a for the pressure increase show a turn at a pressure of 238 MPa and a midpoint around 300 MPa.

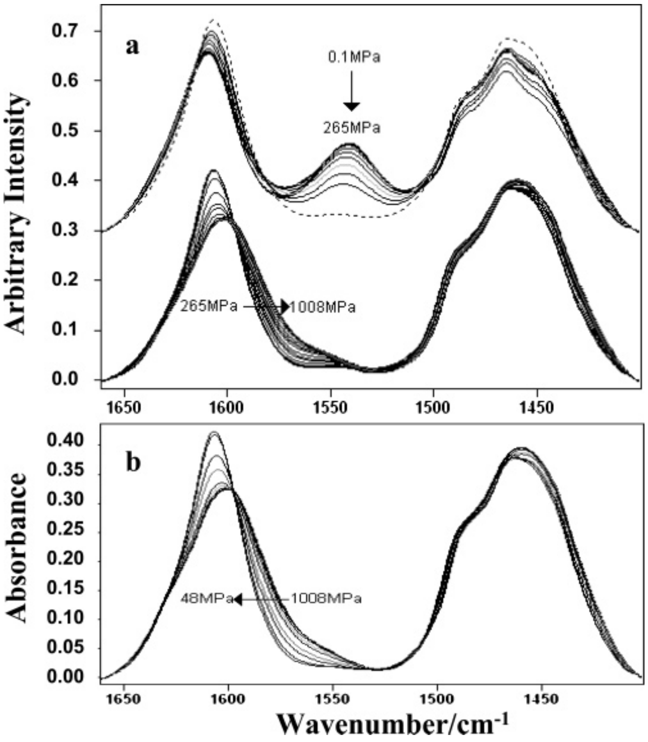

Figure 4. Pressure-dependent IR spectra of PNiPMA in the region of 1660−1400 cm^{-1}: (a) compression and (b) decompression processes. The pressure was varied between 0.1 and 1008 MPa with an interval of about 100 MPa.

As revealed previously by light microscopy, at 168 MPa a phase separation, corresponding to the lower critical solution pressure of PNiPA, is observed.[16] The reason for this finding has been explained previously and can be summarized as follows: the initial phase separation involves only a fraction of the polymer chains, a fraction that is too small to be detected by FT-IR spectroscopy. As the pressure further increases, more chains will undergo phase separation, and the concentration of the polymer in the polymer-rich phase will start to increase,[31,32] producing significant structural variation in IR spectra. Therefore, the illustration in the slice spectra of Figure 3b shows a hysteresis for PNiPA in decompression. A significant turn is observed at a pressure of 182 MPa in Figure 3b with a pressure decrease, which is slightly lower than the transition pressure in the compression process. Meanwhile, the rate of concentration change, as indicated by the slopes (dI/dP) of the correlation lines during the phase transition does not show much difference between parts a and b of Figure 3. This observation suggests that very similar dynamics of phase separation are observed for PNiPA between compression and decompression.

Reversibility of Pressure-Induced Phase Separation of PNiPMA Involving Enhanced H/D Exchange. Figure 4a shows pressure-dependent IR spectra of PNiPMA as a function of increasing pressure. PNiPMA differs from PNiPA by the presence of a methyl group attached to the α-carbon of the vinyl backbone.[6] The substitution of the methyl group for the hydrogen atom in the polymer chain of PNiPMA decreases the electron density on the C═O bond in comparison with those of PNiPA[6] and, therefore, results in the low-frequency shift of the amide I band to 1609 cm^{-1} in PNiPMA. Therefore, the prominent IR bands in Figure 4a can be attributed to the amide I band (1609 cm^{-1}), amide II band (1541 cm^{-1}), and the deuterated amide II band, amide II′ (1465 cm^{-1}). Note that the amide II band is absent in the spectra of PNiPA. Its presence in the case of PNiPMA indicates that in this polymer not all protons have been exchanged.

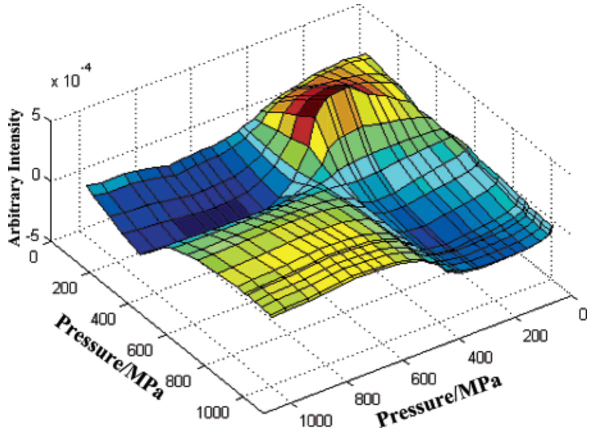

Figure 5. A synchronous SS hybrid 2D correlation IR spectrum of PNiPMA constructed from the two IR spectra data sets shown in Figure 4. The used spectral region is 1660−1560 cm^{-1}.

An enhanced H/D exchange can be observed clearly in the compression process of PNiPMA. As shown in the IR spectra displayed in the upper part of Figure 4a, the amide II band (1545 cm^{-1}) disappears at a pressure of 265 MPa, indicating that complete deuteration of PNiPMA occurs in D_2O solution under pressure. The slow kinetics of H/D exchange in PNiPA was observed many years ago by Scarpa et al. as a result of locking of the exchangeable hydrogens in N−H···O═C bond and a change of water in the neighborhood of the pendant residues of the polymer.[29] And the methylation appears in PNiPMA may accentuate this and suggest a stronger screening of the amide groups from the solvent in these random coil molecules. This adds further support to the idea that under pressure the polymer chain becomes increasingly solvated.[16] Pressures higher than 265 MPa induce a downward shift of the amide I′ band, as shown in the IR spectra at the bottom part of Figure 4a. Analogous to the band assignments and the corresponding pressure-induced structural variations of PNiPA,[16] this shift can also be attributed to the formation of the stronger double hydrogen bond between the side C═O groups of PNiPMA with water, i.e., to the stronger hydration of PNiPMA.[16] We note that an opposite upward shift of the amide I′ band can be observed in the IR spectra measured in the decompression process (Figure 4b), indicating a loss of the additional hydrogen bonding between C═O and water during decompression; i.e., partial dehydration occurs with the pressure decrease. However, the IR spectra of PNiPMA in Figure 4b do not show an appearance of the amide II band at all, which reveals that the pressure-enhanced H/D exchange of PNiPMA is irreversible, as expected.

A synchronous SS hybrid 2D IR correlation spectrum constructed from the IR spectral data sets in amide I region (1660−1560 cm^{-1}) of PNiPMA measured in the compression and decompression processes is shown in Figure 5. As with the hybrid 2D correlation spectrum in Figure 2, strong correlations are observed in the low-pressure region (p < 327 MPa), indicating a population gain of the original coil species in the decompression process. However, a greater asymmetry along the diagonal line is observed in this low-pressure region in comparison with that of PNiPA. This high asymmetry is mainly attributable to the complete but irreversible H/D exchange of PNiPMA induced by the pressure increase. Note, however, that the spectral region which we employed to construct SS 2D correlation spectra is only limited in the amide I (or I′) region

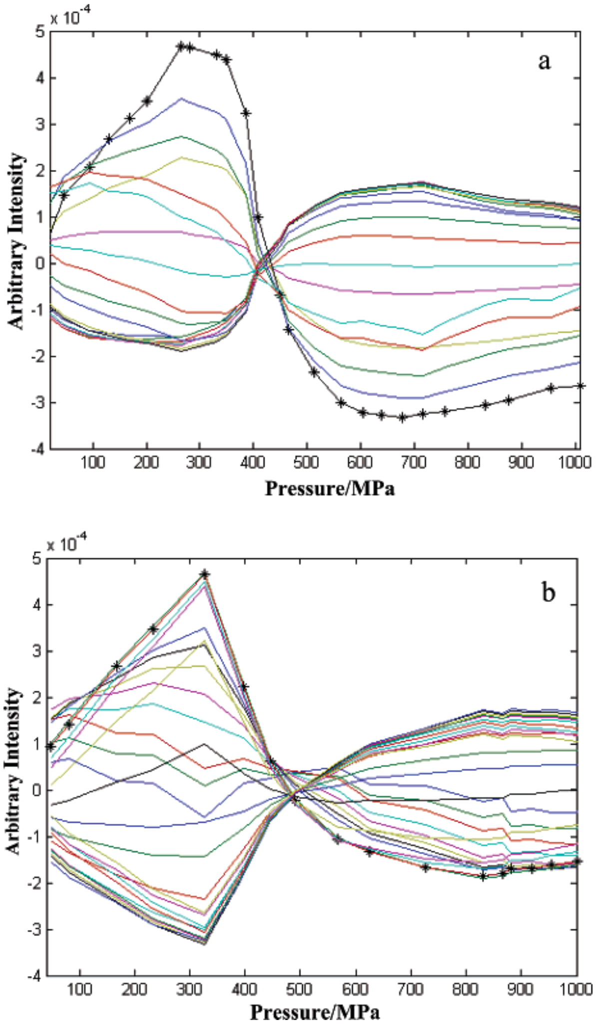

Figure 6. Slice spectra extracted along the two axes from the SS hybrid 2D correlation IR spectrum in Figure 5: (a) compression process (*x*-axis); (b) decompression process (*y*-axis).

(1660−1560 cm^{-1}). This limitation suggests that even minor irreversibility of amide I due to H/D exchange, which is not easily distinguished in original one-dimensional (1D) spectra, can be revealed clearly by hybrid 2D correlation analysis. In this case, hybrid 2D correlation spectroscopy does show its power in revealing a subtle reversible of phase separation in a polymer, which can be further applied to the studies of aggregation−dissociation and folding−refolding of proteins. In addition, it is interesting to observe that the asymmetry of the SS hybrid 2D correlation spectrum along the diagonal line in the intermediate pressure region is less pronounced than that seen in Figure 2 for PNiPA, indicating very similar transition dynamics between the compression and decompression processes of PNiPMA.

Slice spectra along the two axes give a clearer demonstration of the concentration-changing dynamics in the two processes. The slice spectra in Figure 6a for the compression show two significant turns at pressures of 265 and 348 MPa, respectively. The former value corresponds to the pressure of complete deuteration of PNiPMA in the D_2O solution, while the latter corresponds to the phase separation (or transition) of PNiPMA induced by pressure.[6] On the other hand, only one significant turn is observed at a pressure of 327 MPa in the slice spectra of Figure 6b for the decompression process, which may correspond to the significant dehydration of PNiPMA. The decompression-induced phase transition of PNiPMA shows only a small hysteresis of transition pressure (327 MPa vs 348 MPa). This difference is not significant. Taken together with the minor asymmetry along the diagonal line, this observation indicates the reversibility of the phase separation with similar dynamics in both directions.

Reversibility of Temperature-Induced Phase Transition of PNiPMA. Figure 7a shows the temperature-induced spectral changes in the carbonyl group-stretching region of PNiPMA. A significant band shift of the amide I′ band from 1609 to 1628 cm^{-1} is observed with the increase in temperature. As in the case of PNiPA,[8,11] the band shift of amide I′ observed here can be assigned to the loss of coil structure (1609 cm^{-1}) and the gain of a globule structure (1628 cm^{-1}). The reversible band shift from 1628 to 1609 cm^{-1} observed in Figure 7b for the cooling process indicates the reversal of the thermally induced coil−globule transition.

Figure 8 shows a synchronous SS hybrid 2D correlation spectrum constructed from the temperature-dependent IR spectra of PNiPMA in the heating and cooling processes. The temperature ranges for both processes are between 25 and 65 °C with an interval of 1 °C. Strong positive correlations are found at sample coordinates (T < 41 °C and T > 55 °C), while strong negative peaks are seen at the two corners (25, 65 °C and 65, 25 °C). The strong positive correlation values in the low-temperature region (T < 41 °C) indicate the strong correlation of the same amide I′ component in the temperature-dependent IR spectra, which illustrates the high recovery of the coil species during cooling. However, the asymmetry along the diagonal line in the middle-temperature region (41 < T < 55 °C) reveals that differences in the concentrational dynamics exist between the heating and cooling processes.

The concentrational dynamics are revealed more clearly by the slice spectra in Figure 9a (along the axes of heating) and Figure 9b (along the axes of cooling). The transition onset temperature of the coil−globule transition (T) can be observed at 45 °C (Figure 9a), and its value is close to that determined by turbidity measurements.[6] For the reverse process, the corresponding T can be observed at 41 °C (Figure 9b). Differentiation in the concentration changing rates is also revealed by the slopes (dI/dT) of the slice spectra in the intermediate temperature regions of Figure 9. The hysteresis of transition temperature can be attributed to the fact that the globule−coil transition is a more time-consuming process than the coil−globule transition because of the slow expansion of the polymer chain in the knotted globule state.[33] It has been proposed that knots may be formed in the globule state; therefore, this process could cause very slow chain expansion during the globule−coil transition.[33] Although knots are considered to be formed in isolated polymer chains (i.e., under dilute conditions),[33] it is also possible that even in more concentrated situations entanglement between chains can occur. Different changing rates in the slopes (dI/dT) observed in the slice spectra in the intermediate-temperature region between parts a and b of Figure 9 indicate different changing rates of the concentration during the transition. The steeper changing rate in Figure 9a compared to that in Figure 9b indicates a faster transition process in heating than in cooling.

Although not much hysteresis was observed between the compression and decompression processes of PNiPMA due to the attached methyl group in the main chain, it is possible that the knotted globule state or entanglement may occur in the temperature-induced transition. Thus, the effects of pressure and temperature on the PNiPMA solution may differ. Ongoing

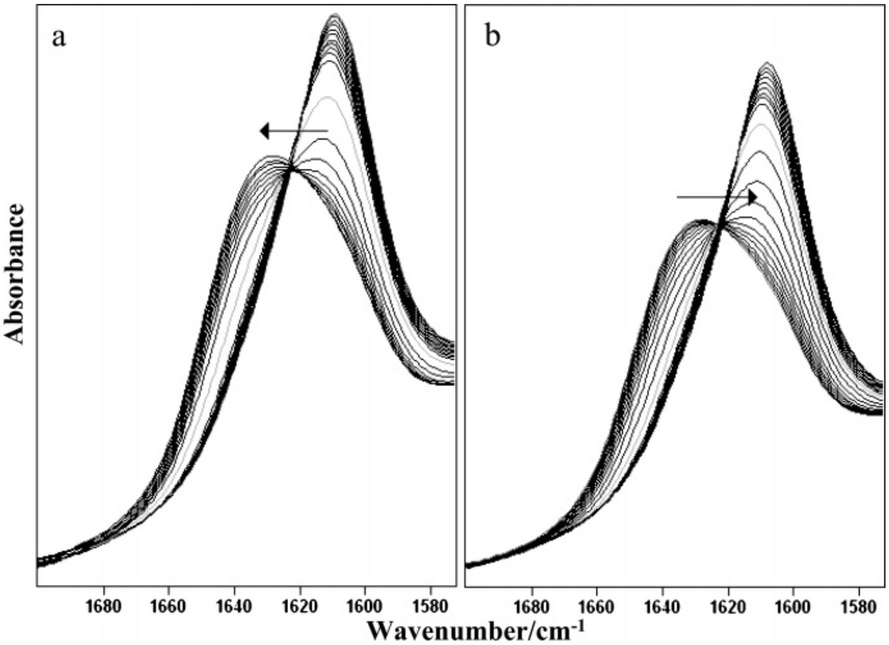

Figure 7. Temperature-dependent IR spectra of PNiPMA in the region of 1700−1570 cm^{-1}: (a) heating and (b) cooling. The temperature was changed between 25 and 65 °C with an interval of 2 °C.

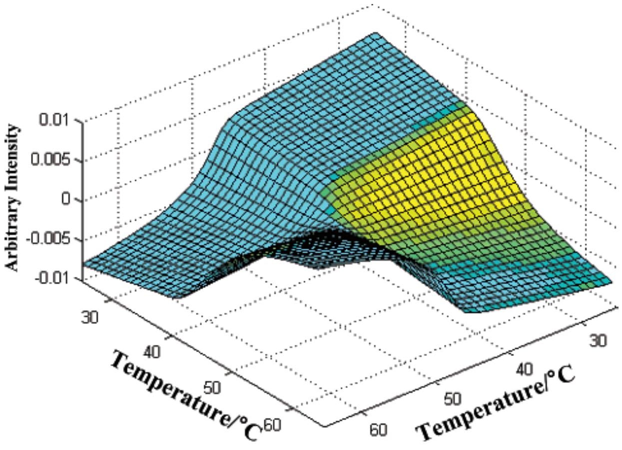

Figure 8. A synchronous SS hybrid 2D correlation IR spectrum of PNiPMA constructed from the two IR spectra data sets partially shown in Figure 7. The temperature was changed between 25 and 65 °C in increments of 1 °C.

efforts will address comparisons of pressure- and temperature-induced structural variations of PNiPMA.

Conclusions

The present study has demonstrated a novel application of SS hybrid 2D spectroscopy in exploring the reversibility of the temperature- or pressure-induced phase separation and transition of PNiPA and PNiPMA in aqueous solution. The synchronous SS hybrid 2D correlation spectrum constructed from the pressure-dependent IR spectra of PNiPA measured in the compression and decompression processes indicates an almost full recovery of the coil structure with differences in the rate of concentration change and separation pressure. On the other hand, there was a high asymmetry in the lower-pressure region ($p <$ 327 MPa) of the SS hybrid 2D correlation spectra constructed from the pressure-dependent IR spectra of PNiPMA in the two opposite pressure-induced processes. This high asymmetry illustrates a recovery of the original coil structure with similar concentration dynamics, even involving an irreversible deuteration of PNiPMA.

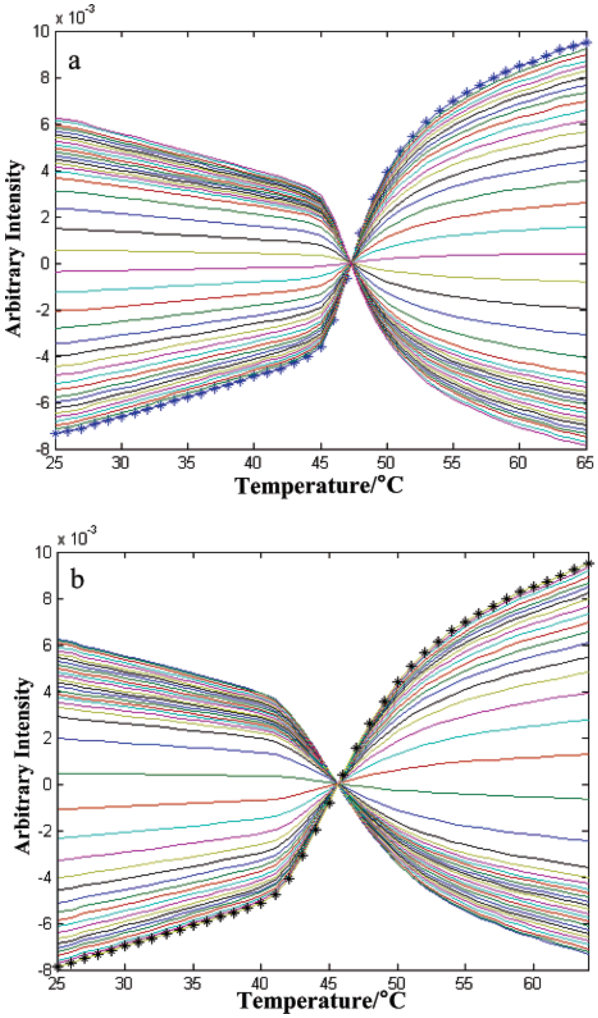

Figure 9. Slice spectra extracted along the two axes from the SS hybrid 2D correlation IR spectrum shown in Figure 8: (a) heating process (*x*-axis); (b) cooling process (*y*-axis).

In addition, there was a high symmetry at the lower temperature (T < 41 °C) and a high asymmetry along the diagonal line in the intermediate-temperature region (41−55 °C) of the temperature-dependent SS hybrid 2D correlation spectrum constructed from the IR spectra of PNiPMA in the heating and cooling processes. This shift with temperature from symmetry to asymmetry illustrates a completely reversed coil−globule transition with different transition dynamics. It should be emphasized that such events are not apparent from the transition plots constructed on the basis of 1D data analysis. In this way, SS hybrid 2D correlation spectroscopy holds great potential in exploring reversibility of the phase separation (or transition), in both component recovery and concentration dynamics of polymers. This approach can be further applied to investigations of protein aggregation−dissociation or folding−refolding.

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