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ORIGINAL PAPER

Competitive mechanism of poly(ethylene glycol) with poly(vinyl methyl ether) in complexing water molecules revealed with elastic light scattering spectroscopy

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Abstract By using elastic light scattering (ELS) spectroscopy, dependences of lower critical solution temperature (LCST) of poly(vinyl methyl ether) (PVME)/poly(ethylene glycol) (PEG) solutions on concentration (C_{PEG}) and molecular weight of PEG were analyzed. It was found that the onset temperature of phase separation (T_p) decreased with increasing C_{PEG} or molecular weight of PEG in the solutions. It indicated that PEG was competitive with PVME in complexing water molecules. The presence of PEG disturbed the hydration layer around PVME, facilitating the aggregation of PVME chains at lower temperature. Moreover, the ELS spectra revealed the aggregation and dissociation of molecular chains in PVME/PEG solutions during one heating and cooling cycle. PVME chains aggregated above the microphase transition temperature. With further increasing temperature, PVME aggregates started to contract, and then kept stable. During cooling, the chain aggregates were not immediately swelled but gradually swelled, and began to dissociate when the solution temperature was further decreased. Finally, the conformation of the molecular chains returned to its original state.

Keywords Elastic light scattering spectroscopy · Phase separation · Poly(vinyl methyl ether) · Poly(ethylene glycol)

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Introduction

It is well-known that aqueous solutions of some water-soluble polymers exhibit phase separation above their lower critical solution temperature (LCST). Poly(vinyl methyl ether) (PVME) has a LCST at moderate temperature of around 35 °C, which makes it suitable for industrial and medical applications [1–3]. In order to control the phase separation temperature, many studies have been carried out on the PVME aqueous solutions with different kinds of additives [4]. Schild et al. [5, 6] revealed that the LCST of PVME gradually increased with a rise of methanol concentration, while Horne et al. [2] investigated the effects of electrolytes, urea and alcohols on the phase separation of PVME. Recently, the influence of the addition of a second solvent to the binary water/PVME system on liquid/liquid phase separation has been extensively studied [7–9]. Furthermore, Maeda et al. examined the effects of inorganic [10] ions and tetraalkylammonium [11] ions on the LCST of PVME by infrared and Raman spectroscopy. The role of salt in the phase behavior of PVME aqueous solution was also explored by Durme et al. [12], Gu and Wu [4], and Guo et al. [13].

However, the study of phase transition of mixed aqueous solution containing two polymers is rather few. Karayanni and Staikos [14] reported the phase separation behavior of PVME aqueous solution in the presence of poly(acrylic acid) (PAA). They found that the cloud point of the PVME/PAA aqueous solutions was gradually displaced to higher temperature (>33 °C) when the PAA concentration increased. Starovoytova et al. [15] investigated thermotropic phase transition in D_2O solutions of PVME/poly(*N*-isopropylmethacrylamide) (PIPMAm) mixtures, and found that the phase transition of PVME component was not affected by the presence of PIPMAm. So far, the knowledge of the phase transition process in polymer mixtures on molecular level is less satisfactory.

Poly(ethylene glycol) (PEG), an uncharged hydrophilic polymer, is completely miscible with water in all proportions for a very wide range of degrees of polymerization duo to the fact that PEG chains may be modeled in a hexagonal water structure [16] with hydrogen bonds between water and polar groups of the polymer, forming highly linked networks [17]. To reveal the influence of PEG on the phase transition of PVME aqueous solution in molecular terms, the information about aggregation of the molecular chains is necessary.

Naturally, a question is raised. That is, which characterization tool is competent for such a study? Although the changes of chain conformation and the aggregation process of molecules can be monitored by laser light scattering [18] and ^{1}H NMR [19] or small-angle neutron scattering [20], expensive equipments and complicated testing processes are needed. Recently, we found that resonance light scattering (RLS) is a promising technique to follow temperature-induced phase transition [21, 22] and macromolecular aggregation [23] owing to its high sensitivity, convenience in performance, simplicity and rapidity. RLS spectra can be collected by simultaneously scanning the excitation and emission monochromators of a conventional spectrofluorimeter with $\Delta\lambda = 0$ nm [24, 25]. According to the literature [26], the scattering acquired with the same procedure as that of RLS includes two parts: conventional Rayleigh light-scattering (in the initial stage of

phase separation) [27] and large particle scattering (in the mid-late stage of phase separation) [28]. These two kinds of scatterings are all ascribed to elastic light scattering (ELS), which possesses many merits of RLS [29] and is able to describe the aggregation process in polymer solution by a single parameter related to the degree of aggregation: ELS intensity (I_{ELS}).

In order to gain deeper insight into the inherent mechanism of the effect of PEG on phase transition of PVME solution, this work applies ELS spectroscopy to investigate the aggregation of macromolecular chains during phase transition by inspecting the change in size of the aggregates from the ELS intensity variances. Accordingly, the dependences of the LCST of PVME/PEG solutions on the concentration (C_{PEG}) and molecular weight of PEG are obtained. Molecular chain aggregation in PVME/PEG solutions are traced by studying the temperature and concentration dependent ELS spectra during cyclic heating and cooling.

Experimental

Materials and sample preparation

PVME was purchased from Sigma-Aldrich as a 50 wt% aqueous solution. Its average molecular weight characterized by gel permeation chromatography (GPC) is 71150 g/mol (M_w) and 35770 g/mol (M_n), respectively. The polymer was used without any purification. PEG 2000 (polydispersity (PDI) = 1.05), 4000 (PDI = 1.06), 6000 (PDI = 1.05), 10000 (PDI = 1.04), and 20000 (PDI = 1.05) samples were purchased from Shanghai Chemical Reagent Co. of China and used as supplied without additional purification. All the solutions were prepared by dissolving appropriate amount of PVME and PEG with doubly distilled and deionized water. Prior to the measurements, the solutions were incubated for 1 day below the LCST for equilibration.

Apparatus

Elastic light scattering measurements were performed on a Cary Eclipse fluorescence spectrophotometer (Varian Inc.) equipped with a Xenon flash lamp, R928 photomultiplier detector, dual monochromators, and a single-cell Peltier holder. The latter is an electronically controlled thermostatting single cell accessory capable of controlling the temperature within ±0.1 °C. By using this unit, the variable-temperature measurements within 0–100 °C were carried out. ELS spectra were recorded from 200 to 700 nm with synchronous scanning at $\lambda_{ex} = \lambda_{em}$ (i.e., $\Delta\lambda = 0$ nm). UV–Vis absorption spectra of PVME/PEG solutions were collected by a UV-3150 spectrophotometer (Shimadzu Co.). The slit width was 1 nm during the measurements.

Procedures

The sample solution was put into the single-cell Peltier holder where the temperature was set at 25 °C. After 20 min, ELS spectra were measured by

synchronous scanning at $\Delta\lambda = 0$ nm. Then, the sample was heated from room temperature to 41.5 °C at a heating rate of 0.5 °C/min, during which there was a time interval of 10 s for each increase of 0.5 °C. The subsequent cooling was also conducted at a rate of 0.5 °C/min. The slit (ex/em) width was 1.5 nm/2.5 nm for the measurements of temperature dependences of ELS intensities (at the maximum scattering wavelength) of PVME ($C_{PVME} = 7.5$ g/L) and PVME/PEG solutions (PEG6000, $C_{PEG} = 5.0$ g/L, and $C_{PVME} = 7.5$ g/L) during one heating and cooling cycle, and temperature dependences of ELS intensities (at the maximum scattering wavelength) of PVME ($C_{PVME} = 7.5$ g/L) solutions with different concentrations and molecular weights of PEG during heating. Besides, the slit (ex/em) width of other measurements was 5 nm/5 nm.

Results and discussion

ELS and absorption spectra of PVME/PEG aqueous solutions

It is known that three concentration domains are presented for polymer random coils in solution, corresponding, respectively, to separated chains, overlapping chains and concentrated solution regime [30, 31]. Thereinto, the overlap concentration, C^*, from dilute to semidilute regimes is defined as the concentration at which the polymer coils touch one another [30]. In this work, the overlap concentrations of PVME and PEG in solutions are evaluated by $C^* = 3\,M/(4\pi N_A R_g^3)$ [30, 32], where M refers to the polymer molecular weight, N_A and R_g are Avogadro's number and the radius of gyration, respectively. The value of R_g is estimated from the mean square end-to-end distance (r^2) by using $R_g^2 = r^2/6$, where $r^2 = C_\infty N'(2l_{C-C}^2)$ for PVME and $r^2 = C_\infty N'(l_{C-C}^2 + 2l_{C-O}^2)$ for PEG [33–35]. The characteristic ratio C_∞ is 10.0 for PVME and 4.1 for PEG, N' is the number of the repeat unit, and the lengths of C–C (l_{C-C}) and C–O (l_{C-O}) bonds are 1.54 and 1.43 Å, respectively [34, 36]. Accordingly, the overlap concentration of PVME solutions is estimated to be 29.56 g/L, and that of PEG6000 solutions is 161.06 g/L. Herein, we only investigate the phase separation process in the dilute PVME/PEG solutions during heating.

Because the estimation for overlapping concentration is based on Θ condition of dilute solution and its value should be varied with temperature and solvent affinity in the present systems, the overlapping concentration in the present work should be lower than that obtained from theoretical calculation. Figure 1 shows the ELS and absorption spectra of PVME aqueous solution at 25 °C. PVME exhibits absorption band below 360 nm, whereas the absorbance approaches zero in the range over 400 nm. From the ELS spectrum of PVME solution, it is found that the maximum scattering wavelength, λ_{max}, of PVME solution is 379 nm, located at the red side of the absorption band of the solution. It implies that the maximum scattering peak becomes perceivable where the absorption decreases, ascribed to ELS [26].

Figure 2 presents the ELS and absorption spectra of PVME/PEG solution at 25 °C. From the inset, we can see that PEG exhibits absorption band below 220 nm, and the absorbance approaches zero in the range over 220 nm. From the ELS spectrum of PEG solution, it is found that λ_{max} of PEG solution appears at 364 nm,

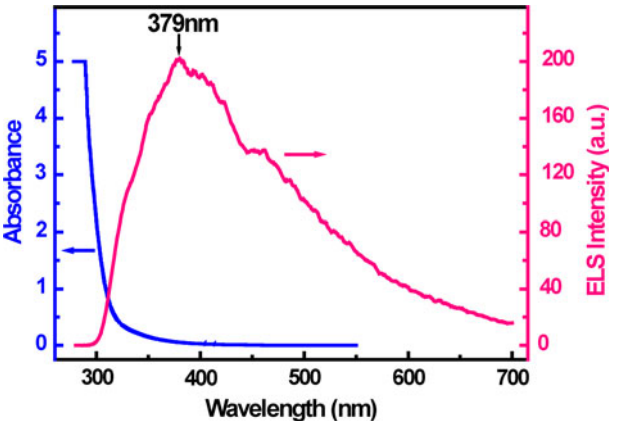

Fig. 1 ELS and absorption spectra of PVME aqueous solution (C_{PVME} = 7.5 g/L) at 25 °C

which is located at the red side of the absorption band of the solution. Besides, the PVME/PEG solution exhibits absorption band below 360 nm, whereas the absorbance approaches zero in the range over 400 nm. Moreover, λ_{max} of PVME/PEG solution is 371 nm, which also occurs at the red side of the absorption band of the solution. Therefore, the scattering of PVME/PEG solution is ascribed to ELS. By comparing Figs. 1 and 2, we find that the maximum scattering wavelength shifts from 379 to 371 nm, and the maximum scattering intensity of PVME/PEG solution is higher than that of PVME solution. This can be explained by the fact that the absorbance of PVME component causes the red-shift of λ_{max} of PEG solution, and then superposition of the two scattering peaks of PVME and PEG components makes λ_{max} of the studied system appear at 371 nm. In addition, it can be seen from Figs. 1 and 2 that the maximum scattering wavelength of pure PVME solution is close to that of pure PEG solution, and the superposition of two scattering peaks of PVME and PEG components makes the maximum scattering intensity of PVME/PEG solution higher. Thus, the higher maximum scattering intensity of PVME/PEG solution is caused by the increase of scattering intensity of system due to the addition of PEG in solution.

For the ternary solutions containing water and two kinds of polymer in this work, the interaction between different molecules includes the following three aspects: the intermolecular interaction of PVME–water, PEG–water, and PVME–PEG. It is known that the polarity of PEG is stronger than PVME. The pure PEG solution does not exhibit a LCST transition from room temperature to 100 °C during heating. However, for pure PVME solution, the onset of phase separation is located in the temperature range of 32–35 °C. The molecular interaction for PVME-water is weaker than that for PEG-water. At room temperature, the reason that PVME can be dissolved in water is that the hydrophilic ether groups of PVME are able to form hydrogen bonds with the neighboring water molecules so as to construct the hydration layer around PVME chains. Therefore, the intermolecular interaction of PVME–water and PEG–water play a major role in dilute solution, the interaction of

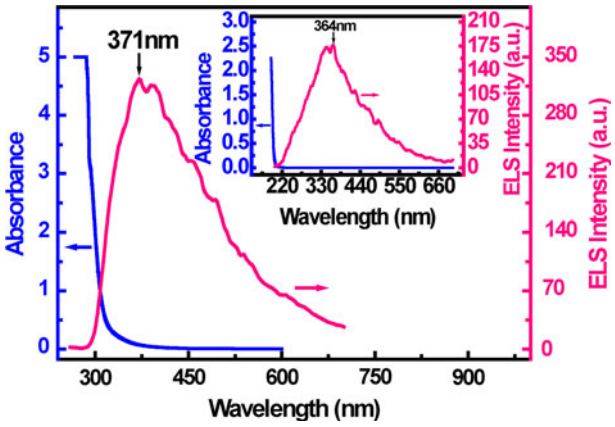

Fig. 2 ELS and absorption spectra of PVME/PEG solution (PEG6000, $C_{PEG} = 5.0$ g/L, and $C_{PVME} = 7.5$ g/L) at 25 °C. The *inset* gives the ELS and absorption spectra of PEG solution (PEG6000, $C_{PEG} = 5.0$ g/L) at 25 °C

PVME–PEG is weak [34]. Moreover, the stronger polarity of PEG makes it compete with PVME in complexing water molecules to form hydrogen bonding [34].

Figure 3a displays the ELS spectra of PVME/PEG solutions with lower PEG concentrations at 25 °C. The spectral characteristics of all the solution systems are similar. It can be seen that I_{ELS} is greatly enhanced with an increase in PEG concentration, and λ_{max} of solutions exhibits no shift (at 371 nm). According to the references [22, 26, 37], the intensity of ELS depends on the number of the scattering particles per unit volume and the volume of one particle. So the increase of I_{371} should be due to the rise in molecular number of PEG per unit volume, along with increasing the concentration. Figure 3b shows the ELS spectra of PVME/PEG solutions with higher PEG concentrations at 25 °C. I_{371} decreases with further increasing concentration of PEG in PVME/PEG solutions. As PEG can form hydrogen bonding with water molecules, PEG competes with PVME in complexing water molecules, which might induce the contraction of PVME coils in the case of high concentration of PEG. This means that the volume of PVME scattering particles decreases, thus further resulting in the decrease of peak intensity in Fig. 3b.

Temperature dependence of ELS spectra of PVME/PEG solutions

Temperature dependent ELS spectra of PVME/PEG solution were recorded during heating (Fig. 4). I_{ELS} increases with increasing temperature, and λ_{max} appears at 371 nm. As the scattering spectra in Fig. 4 are collected at the initial stage of heating, then the temperature approaches to or is lower than the onset temperature of phase separation of PVME/PEG solution. The molecular chains just start to aggregate, the aggregates' size is smaller; the chain aggregation is still not significant. Thus, it is seen that the peak position of light scattering keeps unchanged with temperature. The increase in I_{ELS} results from the fact that the main chains of

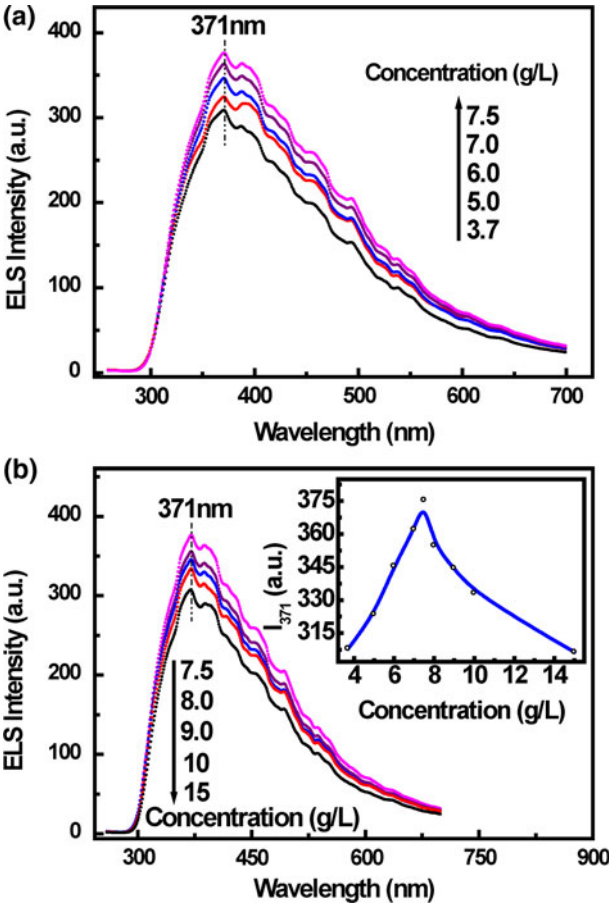

Fig. 3 **a** ELS spectra of PVME/PEG6000 solutions ($C_{PVME} = 7.5$ g/L) with different PEG concentrations ($C_{PEG} = 3.7$–7.5 g/L) at 25 °C. **b** ELS spectra of PVME/PEG6000 solutions ($C_{PVME} = 7.5$ g/L) with different PEG concentrations ($C_{PEG} = 7.5$–15 g/L) at 25 °C. The *inset* gives the C_{PEG} dependence of ELS intensity (at 371 nm, I_{371}) of PVME/PEG6000 solutions ($C_{PEG} = 3.7$–15 g/L, $C_{PVME} = 7.5$ g/L)

PVME (methyl groups) dehydrate during heating. When water molecules that cluster around the C–H groups break away, the network structure of the PVME chain disrupts, and the conformation of C–H main chains may change accordingly [38], inducing collapsion and partial aggregation of PVME chains. Considering the sensitivity of detection, the maximum scattering wavelength is selected for the further work [39].

Figure 5 shows the temperature dependence of normalized ELS intensities (at λ_{max}) of PVME and PVME/PEG solutions during heating. The normalized intensity (I_N) is obtained from $I_N = (I - I_{min})/(I_{max} - I_{min})$, where I_{min} and I_{max} are the minimum and maximum values of ELS intensities at the maximum scattering wavelength. It can be seen that the change trends of the normalized intensities of PVME and PVME/PEG solutions with increasing temperature are similar. I_N is

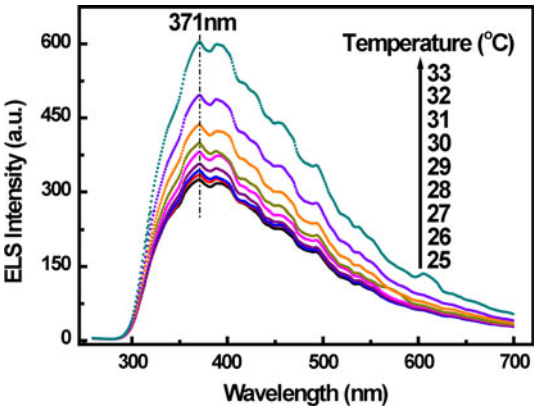

Fig. 4 ELS spectra of PVME/PEG solution (PEG6000, $C_{PEG} = 5.0$ g/L, and $C_{PVME} = 7.5$ g/L) recorded during heating

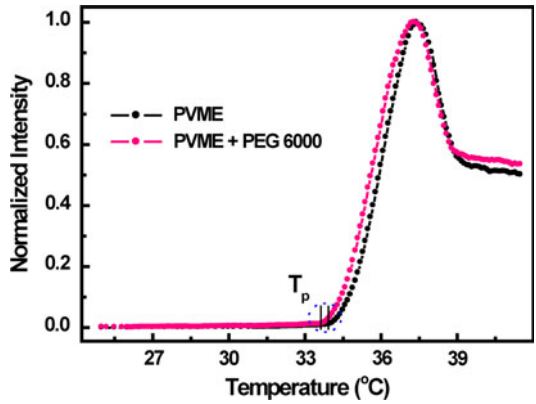

Fig. 5 Temperature dependences of normalized ELS intensities (at the maximum scattering wavelength) of PVME ($C_{PVME} = 7.5$ g/L) and PVME/PEG solutions (PEG6000, $C_{PEG} = 5.0$ g/L, and $C_{PVME} = 7.5$ g/L) during heating. The normalized intensity (I_N) is obtained from $I_N = (I - I_{min})/(I_{max} - I_{min})$, where I_{min} and I_{max} are the minimum and maximum values of ELS intensities at the maximum scattering wavelength

almost constant at the initial stage of heating, and then presents a sharp increase within higher temperature regime, corresponding to a drastic change in polymer concentration in the polymer-rich phase [40]. Afterward, I_N reaches the maximum and then begins to decrease. Finally, the I_N reaches a plateau, suggesting that the phase transition has completed. Moreover, there is no precipitation of PVME on the bottom of sample cell in our experiments, and the solutions become turbid above the LCST and the aggregates of PVME exist in form of the suspended particles, which dose not influence the ELS measurements. In such a manner, the normalized ELS intensity at λ_{max} exhibits its feasibility in serving as an indication of phase separation extent of PVME and PVME/PEG solutions.

As the pure PEG aqueous solution does not exhibit a LCST transition from room temperature to 100 °C during heating and the interaction of PVME–PEG is very weak, the aggregation of PEG chains in PVME/PEG solutions do not occur within the temperature range of research. During the phase separation, main chains of PVME begin to dehydrate, and their conformation undergoes a "coil–globule" transition, inducing dehydration of the hydrophilic side groups [38]. These changes of the main chains make the I_N begin to gradually increase, which can be considered as the signal of the onset of phase separation. Subsequently, ether oxygens that have

strong hydrogen bonding with water below LCST are wrapped by the hydrophobic C–H groups of the main chains and dehydrate [4], and the molecular chains aggregate, leading to sharp increase of the aggregates' size. Therefore, we conclude that aggregation of molecular chains accounts for the drastic increase of I_N. The decrease of I_N after it reaches the maximum is due to the further contraction of the PVME aggregates in solution [41]. By comparing the curves in Fig. 5, it is seen that the contraction amplitude of PVME aggregates in PVME solution is larger than that in PVME/PEG solution. This may be caused by two factors: (i) the presence of PEG suppresses the interchain aggregation of PVME chains, namely, PVME chains form small-scale aggregates at elevated temperature due to the restriction of PEG chains [34]; and (ii) the existence of weak interaction between PVME and PEG molecules could also decrease the contraction amplitude of PVME aggregates in PVME/PEG solution [34]. In addition, it is found that the onset temperature of phase separation (T_p) of PVME/PEG solution is lower than that of PVME solution. This means that the presence of PEG promotes the dehydration of PVME chains [34]. As a result of the fact that PEG can form hydrogen bonding with water molecules [42–44], PEG competes with PVME in complexing water molecules, which induces the shift of T_p of PVME/PEG solution to lower temperature [34].

To gain an in-depth understanding of the competitive mechanism of PEG with PVME in complexing water molecules, dependence of phase separation of PVME/PEG solutions on C_{PEG} was studied (Fig. 6a). When the concentration of PEG is high, the normalized ELS intensity of PVME/PEG solutions begins to increase at lower temperature. Obviously, the onset temperature of phase separation decreases with increasing the concentration of PEG. Moreover, it is seen that the contraction amplitude of PVME aggregates in PVME/PEG solution decreases with increasing concentration of PEG. From Fig. 6a, the onset temperature of phase separation of PVME/PEG solutions can be ascertained. Accordingly, the dependence of the temperature of phase separation, T_p, of PVME/PEG solutions on C_{PEG} is given in Fig. 6b. It is observed that T_p decreases with increasing C_{PEG} in dilute solutions. Since PVME forms hydrogen bonds with water molecules, it binds a certain number of water molecules to construct the hydration layer [45, 46]. The presence of PEG disturbs the hydration layer around PVME, so that some of the hydrophobic groups are exposed, leading to the onset of collapse and aggregation of PVME chains [34]. The increase of C_{PEG} facilitates the aggregation of PVME chains at lower temperature because PEG is competitive with PVME in complexing water molecules [34].

Figure 7a presents the ELS spectra of PVME/PEG solutions with PEG of lower molecular weights at 25 °C. I_{ELS} increases with increasing molecular weight of PEG, and λ_{max} of PVME/PEG solutions is located at 371 nm. The increase of ELS intensity is attributed to the increase of the length of PEG chains with the same molar concentration. The ELS spectra of PVME/PEG solutions with PEG of higher molecular weights at 25 °C are shown in Fig. 7b. The inset gives the molecular weight (PEG) dependence of I_{371} of PVME/PEG solutions. It is found that I_{371} firstly decreases, and then changes slightly with further increasing molecular weight of PEG. This is probably ascribed to the contraction of PVME coils with the continual increase of length of PEG chains. At room temperature, the peak intensity

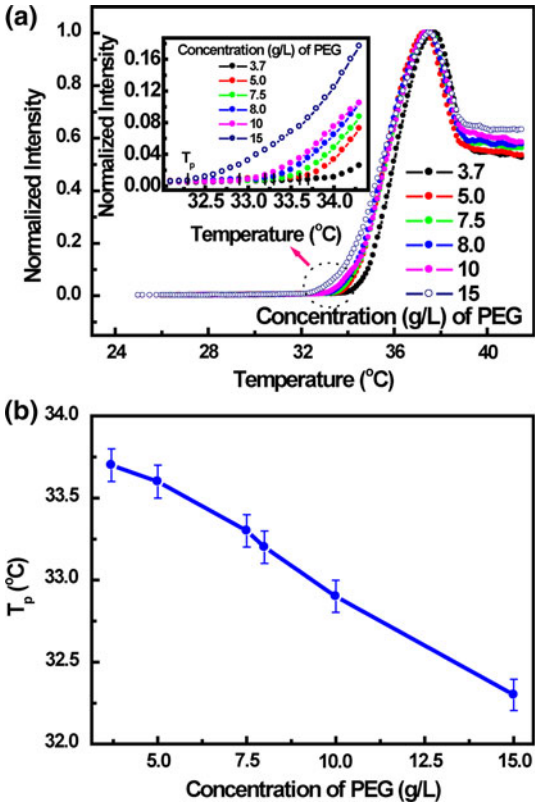

Fig. 6 **a** Temperature dependences of normalized ELS intensities (at 371 nm) of PVME/PEG6000 solutions (C_{PEG} = 3.7–15 g/L, C_{PVME} = 7.5 g/L) during heating. **b** Dependence of the temperature of phase separation, T_p, of PVME/PEG6000 solutions on C_{PEG}

of solutions in Fig. 7 correlates with the length of PEG chain. When the temperature is raised to the LCST of solution, the phase separation (PVME chains begin to aggregate) occurs. At this time, the intensity of ELS primarily depends on the size of aggregates. With increasing temperature further, polymer concentration in the polymer-rich phase increases drastically. During phase separation, PVME chains aggregate continually, so the aggregates' size increases, which induces the increase of peak intensity.

To understand the influence of molecular weight of PEG on phase separation of PVME/PEG solutions, the temperature dependences of ELS intensities of PVME/PEG solutions with PEG of different molecular weights were collected. It is seen from Fig. 8a that the I_N keeps invariant at the beginning of heating. When the temperature increases to the LCST of PVME, the I_N increases abruptly as a result of collapsion and aggregation of PVME chains [41]. In addition, it is observed that the onset temperature of phase separation decreases with increasing molecular weight of PEG. When the molecular weight of PEG is lower than 6000 g/mol, the contraction amplitude of PVME aggregates increases with increasing molecular weight of PEG. For this change, the weak interaction between PVME and PEG may play a major role, owing to the small size of PEG. When the molecular weight of PEG is higher than 6000 g/mol, due to the larger size, the PEG chains that complex with water molecules can suppress the interchain aggregation of PVME chains [34],

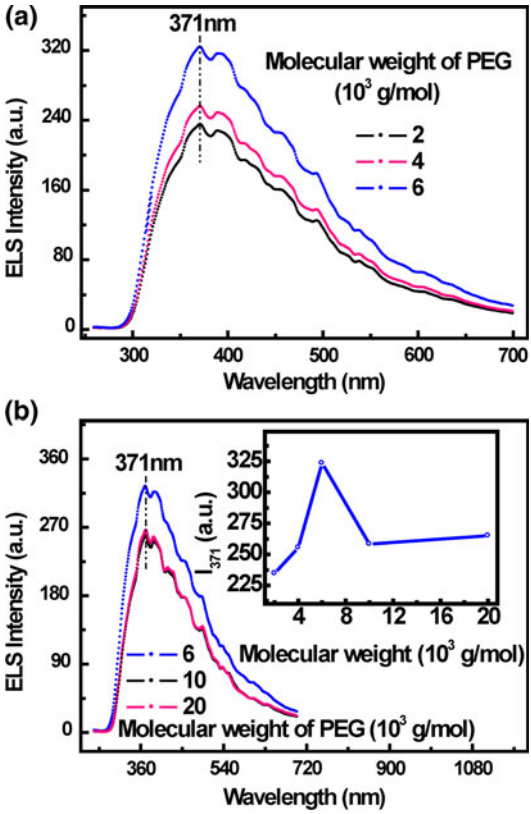

Fig. 7 **a** ELS spectra of PVME/PEG solutions ($C_{PVME} = 7.5$ g/L) with PEG of different molecular weights (PEG2000, $C_{PEG} = 1.7$ g/L; PEG4000, $C_{PEG} = 3.3$ g/L; PEG6000, $C_{PEG} = 5.0$ g/L) at 25 °C, and **b** ELS spectra of PVME/PEG solutions ($C_{PVME} = 7.5$ g/L) with PEG of different molecular weights (PEG6000, $C_{PEG} = 5.0$ g/L; PEG10000, $C_{PEG} = 8.3$ g/L; PEG20000, $C_{PEG} = 16.7$ g/L) at 25 °C. The *inset* gives the molecular weight (PEG) dependence of I_{371} of PVME/PEG solutions

inducing the decrease of the contraction amplitude of PVME aggregates during heating. From the inset of Fig. 8a, T_p of PVME/PEG solutions can be obtained from the inflection points of curves.

In addition, Fig. 8b shows the change of temperature of phase separation of PVME/PEG solutions with the molecular weight of PEG. The decrease of T_p with a rise in molecular weight of PEG may originate from: (i) competition with PVME in complexing water molecules; and (ii) the disturbance and influence on the cooperativity between the neighboring water molecules that are hydrogen-bonded onto the PVME chains [34]. Figure 9 displays the temperature dependences of normalized ELS intensities (at 371 nm) of PVME/PEG solutions with PEG of different molecular weights ($C_{PEG} = 5.0$ g/L) during heating. It can be seen that T_p decreases with increasing molecular weight of PEG in solutions, which is similar to that in Fig. 8. All these demonstrate that molecular weight of PEG has effect on the temperature of phase separation of PVME/PEG solutions, and the results are consistent with those reported in the Ref. [34].

To have knowledge of the effect of PEG on the dissociation process of PVME aggregates in solution, ELS spectra of the PVME/PEG solution during cooling were recorded. Figure 10 presents the temperature dependences of normalized ELS intensities (at λ_{max}) of PVME and PVME/PEG solution during cooling. Compared

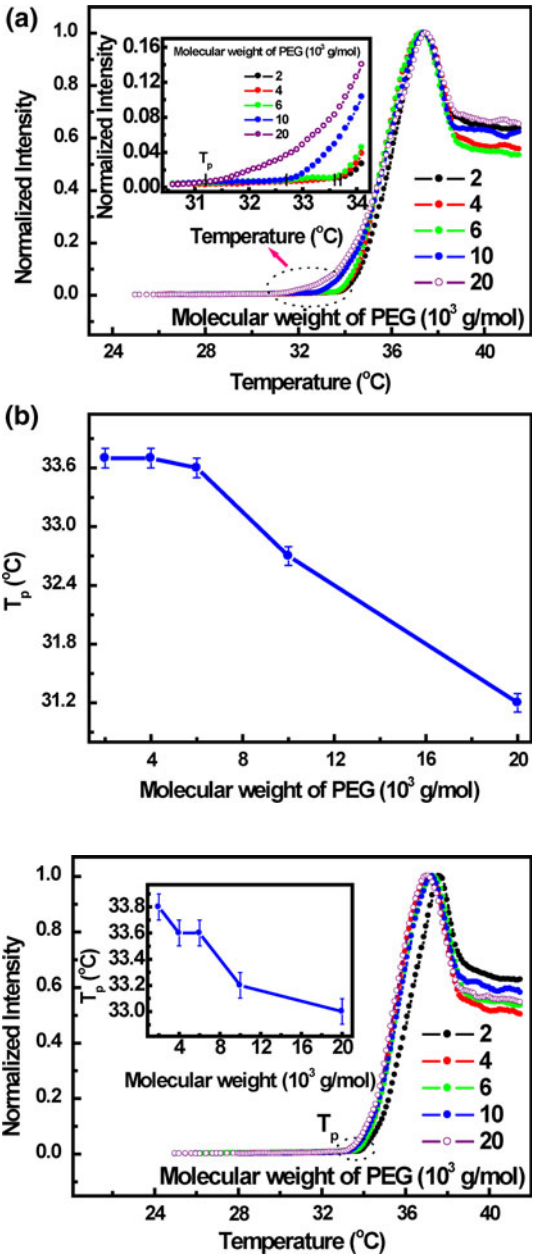

Fig. 8 **a** Temperature dependences of normalized ELS intensities (at 371 nm) of PVME/PEG solutions ($C_{PVME} = 7.5$ g/L) with PEG of different molecular weights (PEG2000, $C_{PEG} = 1.7$ g/L; PEG4000, $C_{PEG} = 3.3$ g/L; PEG6000, $C_{PEG} = 5.0$ g/L; PEG10000, $C_{PEG} = 8.3$ g/L; PEG20000, $C_{PEG} = 16.7$ g/L) during heating. **b** Temperature of phase separation, T_p, of PVME/PEG solutions as a function of molecular weight of PEG

Fig. 9 Temperature dependences of normalized ELS intensities (at 371 nm) of PVME/PEG solutions ($C_{PVME} = 7.5$ g/L) with PEG of different molecular weights ($C_{PEG} = 5.0$ g/L) during heating, the inset gives the molecular weight (PEG) dependence of the temperature of phase separation of PVME/PEG solutions

with the curves in Fig. 5 that are collected during heating, it is seen that those in Fig. 10 shift to lower temperature regime, in the case of identical concentration. In addition, the transition temperature from aggregation to complete dissociation of PVME chains in PVME/PEG solution is lower than that in PVME solution. This can be explained by the fact that some water molecules are complexed with PEG in the

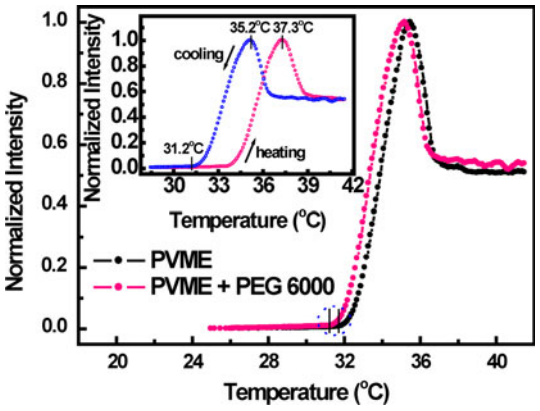

Fig. 10 Temperature dependences of normalized ELS intensities (at the maximum scattering wavelength) of PVME ($C_{PVME} = 7.5$ g/L) and PVME/PEG solutions (PEG6000, $C_{PEG} = 5.0$ g/L, and $C_{PVME} = 7.5$ g/L) during cooling. The inset gives the temperature dependences of normalized ELS intensities (at 371 nm) of PVME/PEG solutions (PEG6000, $C_{PEG} = 5.0$ g/L, and $C_{PVME} = 7.5$ g/L) during one heating and cooling cycle

cooling process. It is hard for the solvent to disrupt the intrachain and interchain quasi-hydrogen bonds between different chain segments when they are overlapped in the collapsed state [47]. As a result, lower transition temperature of PVME/PEG solution is observed during cooling.

The inset of Fig. 10 gives the temperature dependences of normalized ELS intensities (at 371 nm) of PVME/PEG solutions during one heating and cooling cycle. By comparing the curves of heating and cooling processes, it can be seen that the two curves do not overlap and the hysteresis occurs during cooling. The following two factors should take the responsibility: (i) the formation of intrachain and interchain quasi-hydrogen bonds between different chain segments when they are overlapped in the collapsed state [47]; and (ii) the rate of disengagement of polymer chains from the swollen phase-liquid interface [48–50]. The quasi-hydrogen bonds can be gradually removed during cooling. As a result of the interchain interaction that is established in the collapsed state at higher temperature, the chain aggregates are not swelled at the initial stage of cooling, but swelled gradually with decreasing temperature. When the swelling reaches a certain extent, the chain aggregates begin to dissociate. Finally, the conformation of molecular chains returns to its original state at lower temperature. Besides, in combination with Figs. 5 and 10, it is seen that there is also a hysteresis in PVME solution without PEG in one heating-and-cooling cycle, and the hysteresis loops of PVME solution with or without PEG are similar. Therefore, it is considered that there is no obvious effect of PEG on the hysteresis loop.

Conclusions

In this work, ELS spectroscopy was used to investigate the competitive mechanism of PEG with PVME in complexing water molecules. Accordingly, the onset

temperatures of phase transition of PVME/PEG solutions with various concentrations and molecular weights of PEG were identified. The presence of PEG was found to disturb the hydration layer around PVME, facilitating aggregation of PVME chains at lower temperature.

Moreover, the ELS spectra provided information about aggregation and dissociation process of PVME chains in PVME/PEG solutions. When the solution was heated above the LCST, PVME chains simultaneously underwent intrachain contraction and interchain association/entanglement, forming large and dense aggregates whose size increased with the solution temperature [51]. With further increasing temperature, the PVME aggregates started to contract, and then kept stable. On the other hand, cooling led to swelling and dissociation of aggregates. At the initial stage of cooling, the chain aggregates were not immediately swelled, but gradually swelled with decreasing temperature. When the swelling reached a certain extent, the aggregates began to dissociate and the hysteresis gradually disappeared. Finally, the conformation of the molecular chains returned to its original state at lower temperature.

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