Intermolecular Interaction in Aqueous Solution of Binary Blends of Poly(acrylamide) and Poly(ethylene glycol)

Ting Lü,[1,2] **Guorong Shan,**[1] **Songmin Shang**[2]

[1]*State Key Laboratory of Chemical Engineering, Department of Chemical Engineering, Zhejiang University, Hangzhou 310027, China*
[2]*Institute of Textiles and Clothing, The Hong Kong Polytechnic University (HKPolyU), Hong Kong, China*

ABSTRACT: The interaction between poly(acrylamide) (PAM) and poly(ethylene glycol) (PEG) in their solid mixture was studied by Fourier transform infrared spectroscopy (FTIR); and their interaction in aqueous solution was investigated by nuclear magnetic resonance spectroscopy (NMR). For the solid PAM/PEG mixtures, an induced shift of the >C=O and >N─H in amide group was found by FTIR. These results could demonstrate the formation of intermolecular hydrogen bonding between the amide group of PAM and the ether group of PEG. In the aqueous PAM/PEG solution system, the PAM and PEG associating with each other in water, i.e., the amide group of PAM interacting with the ether group of PEG through hydrogen bonding was also found by ^{1}H NMR. Furthermore, the effects of different molecular weight of PAM on the strength of hydrogen bonding between PAM and PEG in water were investigated systemically. It was found that the hydrogen bonding interaction between PAM and PEG in water did not increase with the enlargement of the PAM molecular weight as expected. This finding together with the viscosity reduction of aqueous PAM/PEG solution with the PAM molecular weight increasing strongly indicated that PAM molecular chain, especially having high molecular weights preferred to form spherical clews in aqueous PEG solution. Therefore, fewer amide groups in PAM could interact with the ether groups in PEG. Based on these results, a mechanism sketch of the interaction between PAM and PEG in relatively concentrated aqueous solution was proposed. The fact that the phase separation of aqueous PAM/PEG solution occurs while raising the temperature indicates that this kind of hydrogen bonding between PAM and PEG in water is weak and could be broken by controlling the temperature. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 2572–2581, 2010

Key words: Poly(acrylamide); Poly(ethylene glycol); interaction; phase separation

INTRODUCTION

Hydrogen bond is very important in a noncovalent interaction system such as in an aqueous two-phase system which is widely used for separating in a biological system, like containing proteins,[1–5] and for preparing water-soluble polymer via aqueous two-phase polymerization.[6–10] The hydrogen bond could act as a linkage to hold the various water-soluble polymers together and increase the compatibility between different polymer solution. As the hydrogen bond is sensitive to temperature, the phase behavior may vary because of the break of hydrogen bonding while raising the temperature of the homogeneous aqueous solution.[11]

As early in the 1960s, the fact that poly(acrylic acid) (PAA) could form an association complex with poly(oxyethylene) (POE) through hydrogen bond in water was confirmed via viscometric method and the pH change accompanied the complex formation.[12] PAA was the proton donor, and POE was the proton acceptor. In the last few decades, many efforts have been devoted to investigate the interaction between water-soluble polymers in water. By attracting the pyrene group to PEG at both chain ends, the fluorescence was used to probe the complexation between PEG and PAA or poly(methacrylic acid) (PMAA) in aqueous solution.[13,14] It was found that the carboxyl of PMAA or PAA could interact with the ether group of PEG by hydrogen bond to form interpolymer association. The interaction between PMAA and PEG was stronger because of the hydrophobic effect contributed by the methyl group. The interaction between POE and dansyl-labeled PAA or PMAA was also studied by fluorescence method and similar result was obtained.[15] Staikos et al.[16] compared the interactions between PAA/poly(acrylamide) (PAM), and PAA/poly(N-isopropyl acrylamide) (PNIPAM) in aqueous solution by viscometric method. As the PAM molecules are very hydrophilic, the hydrogen bond between PAA and PAM is almost the unique interaction, and

Correspondence to: G. R. Shan (shangr@zju.edu.cn) and S. M. Shang (tcshang@inet.polyu.edu.hk).

the association between PNIPAM and PAA is more compact because of the hydrophobic effect of the isopropyl. They also studied the effects of various comonomers on the interaction between PAA copolymer and PEG in water.[17] Weiss and Lu[18] introduced the viscosity enhancement factor R to express the interaction between various polymers. Moreover, infrared spectra, NMR spectroscopy, and the differential scanning calorimetry (DSC) were also effectively applied to characterize the hydrogen bonding association.[19–24]

PAM is amorphous and water-soluble polymer with attractive properties for applications in membrane technology and biomedical devices.[25] The combination of PAM and PEG in blends may allow control over its selectivity and mechanical properties. For instance, adjusting the blend composition could effectively control the surface structure of membrane,[26] but also improve the tenacity of PAM to be applied in the immobilization of enzyme.[27] The compatibility between PAM and PEG in solid mixture was studied by DSC method,[25] and was concluded that the polymer system of PAM100,000/PEG2,000 could be partially miscible in the range of compositions. However, by determining the ultrasonic velocity, viscosity, density, and refractive index of the polymer solution blends, the calculated interaction parameter indicated that PAM20,000/PEG6,000 and PAM20,000/PEG4,000 are completely immiscible over the entire composition range at 30°C.[28] Ramanathan and Ravichandran[29] speculated that both polymer-water and polymer–polymer interactions exist in aqueous PAM5,000,000/PEG600 solution through the ultrasonic velocity studies, but the specific interaction behavior between PAM/PEG was not clarified.

In the present research, the interaction between PAM and PEG in their solid mixture has been studied by infrared spectroscopy, and that in water has been investigated systemically by NMR spectroscopy for better understanding the intermolecular interaction in an aqueous two-phase polymerization system (PAM/PEG/H$_2$O system). Moreover, we also examined the phase behavior of the PAM/PEG blended aqueous solution at various temperatures. This article focused on the interaction mechanism between PAM and PEG in water, and a sketch map for the interaction was established.

EXPERIMENTAL

Materials

Acrylamide (AM, Acros Organics), poly(acrylamide) with the weight-average molecular weight of 1,000, 10,000, 100,000 and 3,000,000 (PAM, Acros Organics), and poly(ethylene glycol) with the weight-average

molecular weight of 1,000, 2,000, 4,000, 10,000, and 20,000 (PEG, Acros Organics) were used as received without any purification. Deionized water was used throughout this work.

Characterization

The PAM and PEG were dissolved and blended in water, and then dried to constant mass in a vacuum at 40°C for 1 week. These dried powder samples blended with KBr were pressed to the plate for FTIR measurement (NICOLET 5700 FTIR spectrometer). The ^{1}H NMR experiments were carried out at room temperature with DMX (500 MHz) NMR spectrometer. The samples were usually completely dissolved in pure water (H$_2$O), and kept the aqueous PAM/PEG solution in the homogeneous region at room temperature. The points of the sample composition were shown in the phase diagram of PAM/PEG/water system (Fig. 1) which was determined by cloud point method.[30] The heavy water (D$_2$O) kept in a sealed capillary was cast into the NMR tube and used as the external criterion. The viscosity of aqueous PAM/PEG solution was determined with an Ubbelohde capillary viscometer (the volume of small ball is about 4.2 mL, the diameter of the capillary is about 0.6 mm) at 30°C. The weight concentration of the PAM or PEG water solution was 4%, and then blended proportionately with each other for the viscosity measurement. The phase separation evolution of the aqueous PAM/PEG solution was photographed by a digital optical microscope (NIKON ECLIPSE E600POL) with a heating platform (ED600). The aqueous PAM/PEG solution was filled up and sealed in a thinnest transparent cell, and then was cast on the heating platform.
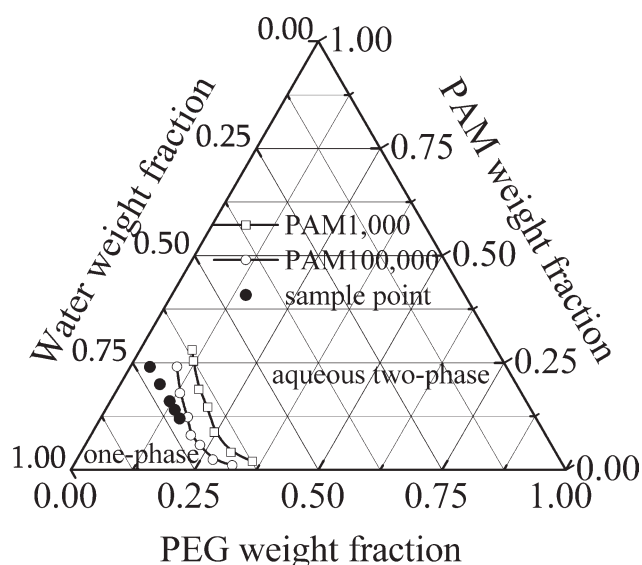
Figure 1 Phase diagram for the PAM/PEG/water system.

HO⎯CH₂⎯CH₂⎯(O⎯CH₂⎯CH₂)ₙ⎯OH

PEG

⎯(CH₂⎯CH)ₙ⎯
            |
            C=O
            |
            NH₂

PAM
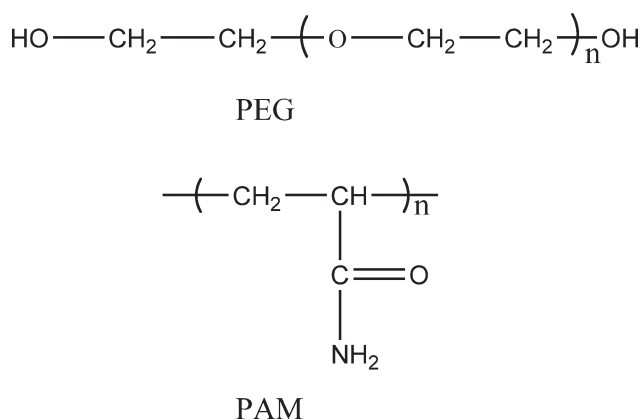
**Scheme 1** Molecular structure of PEG and PAM.

RESULTS AND DISCUSSION

Interaction between PAM and PEG in solid mixture

The PAM and PEG chemicals structures are illustrated in Scheme 1. The two absorption bands in PAM, the $>C=O$ stretching near 1650 cm^{-1} and the $>N—H$ stretching around 3000–3500 cm^{-1}, are particularly sensitive to the hydrogen bonding. The infrared spectra of PAM, PEG, and their mixtures in the 1400–2000 cm^{-1} region, are shown in Figure 2(a). It can be seen that the $>C=O$ of the pure PAM appear at 1653 cm^{-1}. However, the stretching vibration of $>C=O$ shifted to 1665 cm^{-1} when one-third or one-half weight of PEG was blended with PAM. These results could be explained that the hydrogen bonding between $>C=O$ and $>N—H$ within the pure PAM was broken to release free $>C=O$. The new intermolecular hydrogen bond interaction between PAM and PEG was set up that would be the main reason of the band shifting, i.e., the hydrogen bonding between $>N—H$ and $>C=O$ within the pure PAM is substituted by that between the $>N—H$ of PAM and PEG. More direct evidence for the hydrogen bonding between PAM and PEG is provided by the spectral changes of the $>N—H$ stretching vibration. Figure 2(b) shows the FTIR spectra for the PAM, PEG and their mixtures in the $>N—H$ stretching region. There are two kinds of $>N—H$ stretching absorption for the pure PAM including symmetrical and anisomerous stretching. The primary amine band is centered at 3430 cm^{-1}, and a weaker amine band appears at about 3224 cm^{-1}. The broad band absorption indicates a distribution of environments for the $>N—H$ group, e.g., free $>N—H$, $>N—H$ hydrogen bonded with $>C=O$, and $>N—H$ hydrogen bonded with itself. When one-third weight of PEG was blended with PAM, the broad $>N—H$ band shifted slightly to lower frequency centered at 3425 and 3209 cm^{-1}. It is believed that this small shift was probably due to a

decrease in the concentration of free $>N—H$ and the $>N—H$ hydrogen bonded with amide, whose absorption frequencies are somewhat higher than that of $>N—H$ hydrogen bonded with PEG. With the PEG content increasing to one-half weight, the hydrogen bonded $>N—H$ band shifted to 3412 and 3203 cm^{-1} respectively, which further suggests that the hydrogen bonding happens between amide groups in PAM and PEG.

The effects of PEG molecular weight on the FTIR spectra of the PAM/PEG blends at a weight ratio of 1 : 1 are shown in Figure 3. With the PEG molecular weight increasing from 1,000 to 20,000, the positions of $>C=O$ at 1665 cm^{-1} do not appear obvious shift [Fig. 3(a)]. It is known that the number of terminal
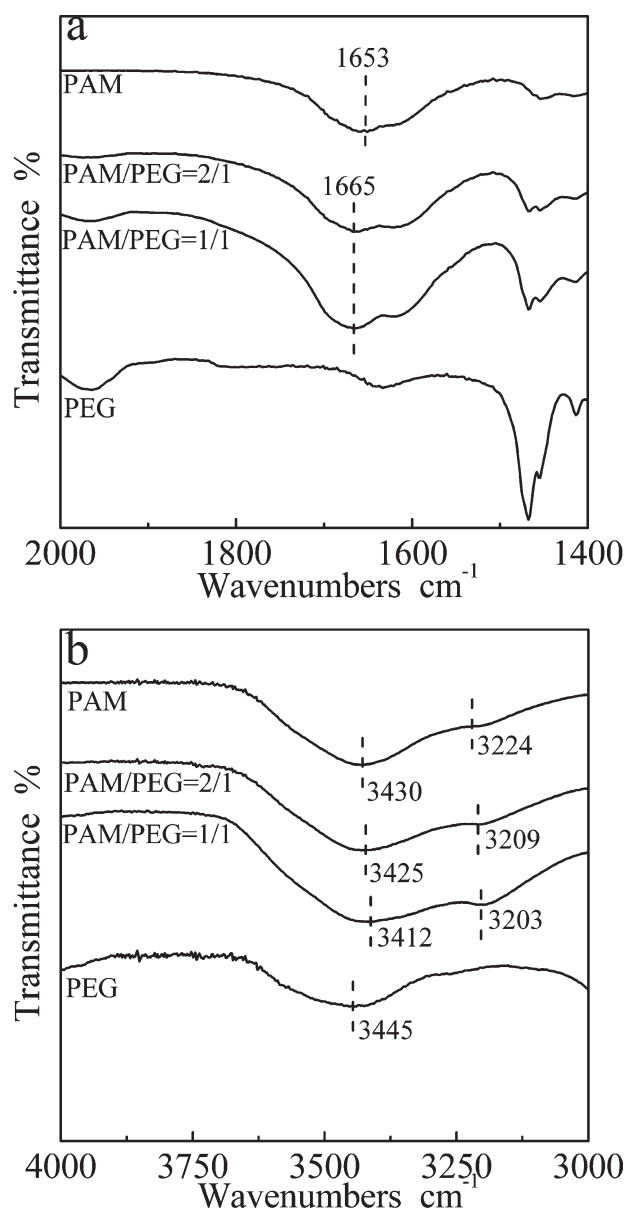
Figure 2 FTIR spectra of PAM3,000,000, PEG20,000, and their mixture (weight ratio).
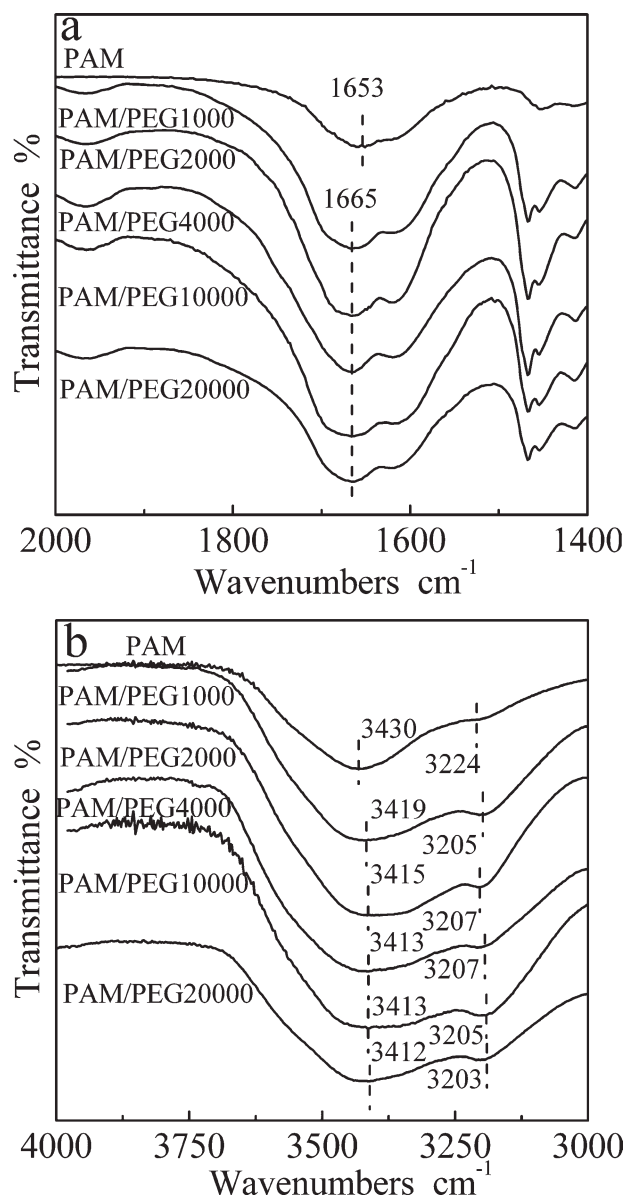
Figure 3 FTIR spectra of PAM and the mixtures of PAM and the different molecular weight of PEG (weight ratio = 1 : 1).

hydroxyl in PEG is very few and decreases significantly with the increase of PEG molecular weight; on the contrary, the ether number in PEG increases slightly. Therefore, if the hydrogen bonding happens between amide group in PAM and terminal hydroxyl group in PEG, the interaction between PEG and PAM should become weaker with the PEG molecular weight increasing. However, in Figure 3(b), the frequency of hydrogen bonded >N—H do not show any significant increase, but even slight decrease with the PEG molecular weight increasing from 1,000 to 20,000. This result indicated that the hydrogen bond between PAM and PEG happened between the amide groups in PAM and the ether groups in PEG.

These findings could give additional support to the results that the PAM and PEG are partially miscible in solid composition.[25] However, the solid blends of PAA and PEG are miscible over the entire range of composition as a result of the hydrogen bonding between the carboxyl and ether groups.[24] In light of the above, the hydrogen bonding interaction between PAM and PEG is obviously weaker than that between PAA and PEG. This result coincides with the theory that the proton donor ability of amide groups in PAM is poorer than that of carboxyl groups in PAA.

Interaction between PAM and PEG in water

The interaction between PAM and POE in dilute aqueous solution was studied by fluorescence method. It was found that mixing of the dansyl-labeled PAM and POE led to no change in emission intensity, hence amide groups do not seem to associate with the ether groups of POE.[31] Moreover, the interaction between hydrolyzed PAM and POE in dilute aqueous solution was also not observed, whereas the hypersensitive research method of fluorescence.[32] This may attribute to the intense interaction between POE or PAM and water in diluted aqueous solution. It is known that the ether groups of PEG interact with water molecules with hydrogen bond and this kind of hydrogen bonding could be broken while the temperature rises to nearly 100°C. Figure 4(a) gives the chemical shift (3.581 ppm) of the ether groups in aqueous PEG solution. No apparent change of the chemical shift of the ether groups is observed with the PEG concentration increasing from 8 to 20%. It appears that the interaction between PEG molecule chains in water is very small. Day and Robb[33] regarded that the PAM chain sections prefer to interact with water rather than other chain sections of PAM in diluted aqueous solutions, and therefore, the hydrogen bonding between PAM molecular chains do not exist widely. However, just as shown in Figure 4(b), the chemical shifts of amide of PAM shift to low fields appreciably with increasing concentration of PAM in water. It means that the extensive intermolecular hydrogen bonding between PAM molecules occurs and even the physical crosslinking through hydrogen bonding appears in a relatively concentrated aqueous solution. For a PAM/PEG aqueous solution, based on above discussion, it could be concluded that hydrogen bonding may exist between PAM and PEG in their relatively concentrated blended water solution.

To clarify the interaction between PAM and PEG in water, a set of ^{1}H NMR experiments was carried out. The spectra of PAM, PEG, and their blends in water are shown in Figure 5(a–c). Figure 5(a) is the magnified NMR spectra, in which the carbon

(a)

(b)
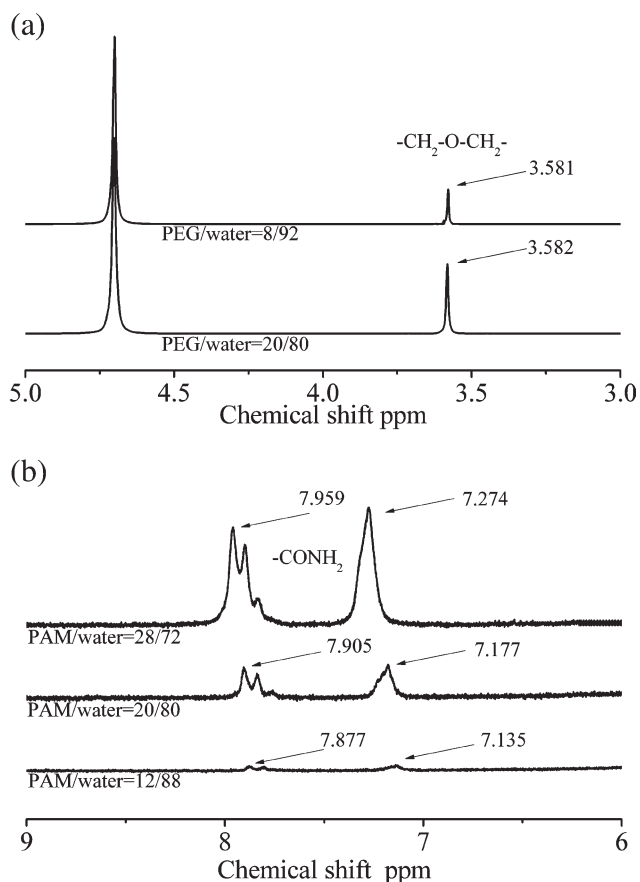
Figure 4 ^{1}H NMR spectra of the PEG20,000 water solution and the PAM1,000 water solution at different concentrations.

hydrogen appears two peaks around 2 ppm. The amides of PAM also display two peaks, which is corresponded with the report that chemical shift can be observed between 7 and 8 ppm.[34] In Figure 5(b), it could be seen clearly that the chemical shift of the ether hydrogen of aqueous PEG solution is at 3.581 ppm, and shifted to 3.946 ppm while PAM was added into it. The most pronounced peak at 4.699 ppm is water. Moreover, in Figure 5(c), the amide peaks of PAM in the PAM/PEG water solution become smoother than that of the PAM water solution. It is believed that wider and more even amide peaks are the results of hydrogen bonding between amide and ether groups, which make the amide hydrogen suffering more influence from the ether groups. Thus, it is suggested that hydrogen bonding happens between the amide groups of PAM and ether groups of PEG in relatively concentrated aqueous solution. In Figure 6, with the PAM fraction increasing, the chemical shift of the ether hydrogen of PEG moved to the low field gradually (from 3.582 to 3.967 ppm). These results could give further evidence that the PAM interacts with PEG in water through hydrogen bonding between the amide

groups in PAM and the ether groups in PEG rather than the hydroxyl groups at PEG chain ends.

Figure 7 shows the ^{1}H NMR spectra of the PEG water solution, the various PEG/PAM blended water solutions with different PAM molecular weights (1,000–100,000) and the PEG/AM blended water solution. In Figure 7(a), it is evident that the chemical shift of the ether group of the PEG/AM blend is nearly same as that of the pure PEG water solution, even though the chemical shift of the ether groups in aqueous PEG/PAM1,000 solution shifts from 3.581 to 3.946 ppm. It means that the proton

(a)

(b)

(c)
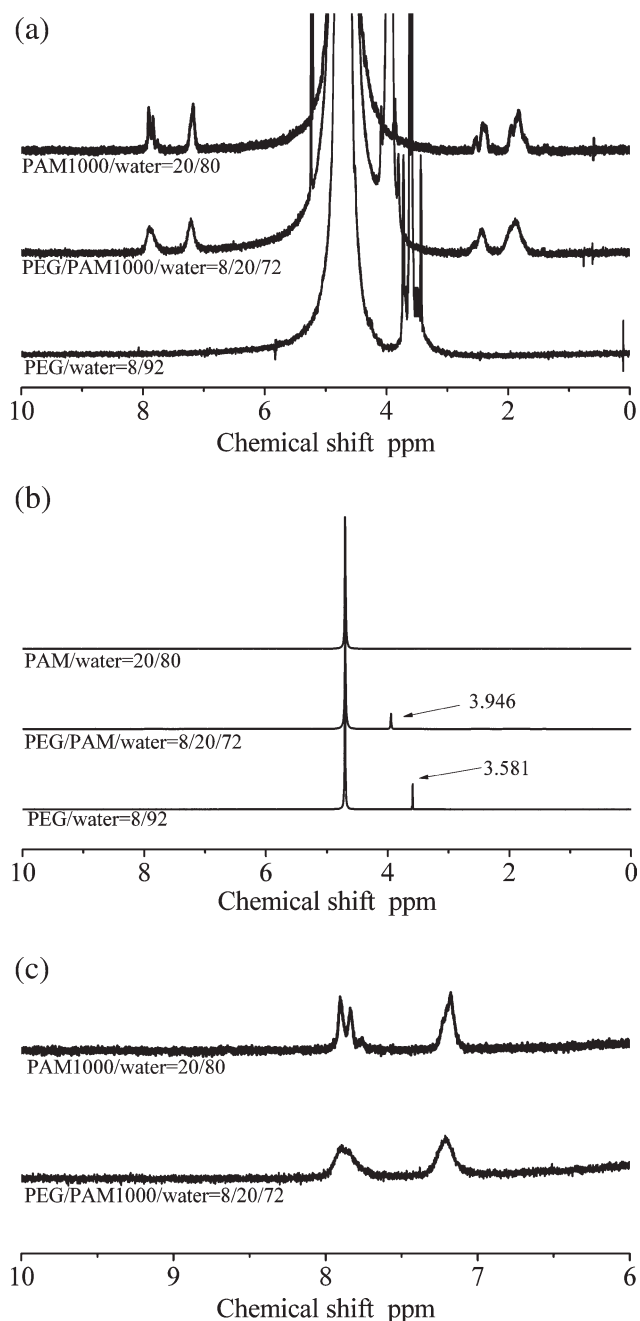
**Figure 5** ^{1}H NMR spectra of PAM1,000, PEG20,000, and their blends in water.
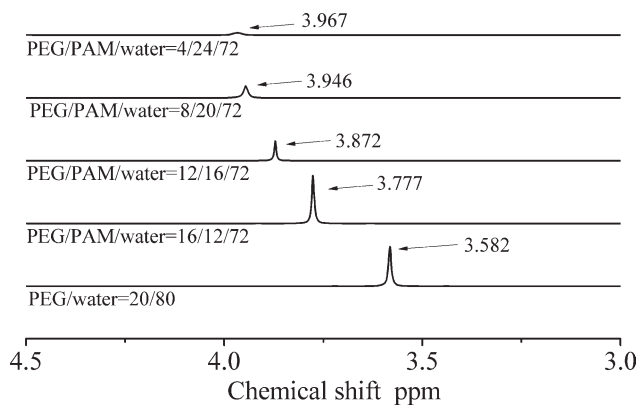
**Figure 6** ^{1}H NMR spectra of PAM1,000, PEG20,000, and their blends with various weight ratios in water.

donor analogue of low molecular weight, AM, nearly does not interact with PEG. Similar result was obtained while studying the interaction between acetic acid and PEG in water.[13,14] In another word, the driving force toward the formation of a hydrogen bond between an ether group in PEG and an amide group of AM in aqueous solution is very small, and a stable complex could only be formed by the cooperative interaction of many such groups. As a result, it can be speculated that the interaction between PAM and PEG would be strengthened with increasing molecular weight of PAM like that of PAA and POE in water.[12,15] However, the chemical shifts for the ether groups of the various PEG/PAM blended water solution with different PAM molecular weights (from 10,000 to 100,000) do not reveal significant difference compared to that of the aqueous PEG/PAM1,000 solution shown in Figure 7(a), where the concentrations of PAM, PEG, and water are 20, 8, and 72%, respectively. To a certain extent, the chemical shift of the ether groups even reduces with increasing PAM molecular weight while increasing PEG to 14% and decreasing PAM to 14% as shown in Figure 7(b). In a relatively concentrated aqueous PAM solution, PAM especially with high molecular weight is a strong self-associated polymer, and many amide groups interact with each other through hydrogen bonding. Thus, the results in Figure 7 strongly suggest that the PAM molecular chains with high molecular weight prefer to aggregate with each other and even form compact spherical clews with the addition of PEG, and then the PEG molecular chains are congregated and entwisted around the PAM clew through hydrogen bonding between amide and ether groups. As a result, fewer amide groups could interact with PEG, and the chemical shifts of ether groups of PEG do not show apparent increase and even decrease.

In Figure 8(a) it is shown that the peaks of the amide groups of the PEG/AM water solution are inten-

sive between the chemical shift 6.5 and 8 ppm. In the contrast, the peaks for the amide groups of the PEG/PAM water solution shift to lower filed between 7 and 8 ppm. The positions of the amide groups in aqueous PEG/PAM (AM) solution [Fig. 8(a)] is conformity with that in pure PAM (AM) water solution with the PAM molecular weight increasing, as shown in Figure 8(b). However, all the amide peaks of PAM with different molecular weight in aqueous PEG/PAM solution is more smooth and flat than that in aqueous PAM solution, indicating the hydrogen bonding between PAM and PEG in water. As described earlier, the hydrogen bodings between PAM and water, PEG and water usually exist in aqueous PAM/PEG solution. Therefore, the interactions in a relatively concentrated aqueous PAM/PEG solution are very complex. The competitions may exist among three kinds of interactions regarding PAM, including the interactions between PAM and PEG, between PAM and PAM, between PAM and water, respectively. In other words, the addition of PEG into aqueous PAM solution leads to partial hydrogen bonding between PAM/PAM and PAM/water to be substituted by
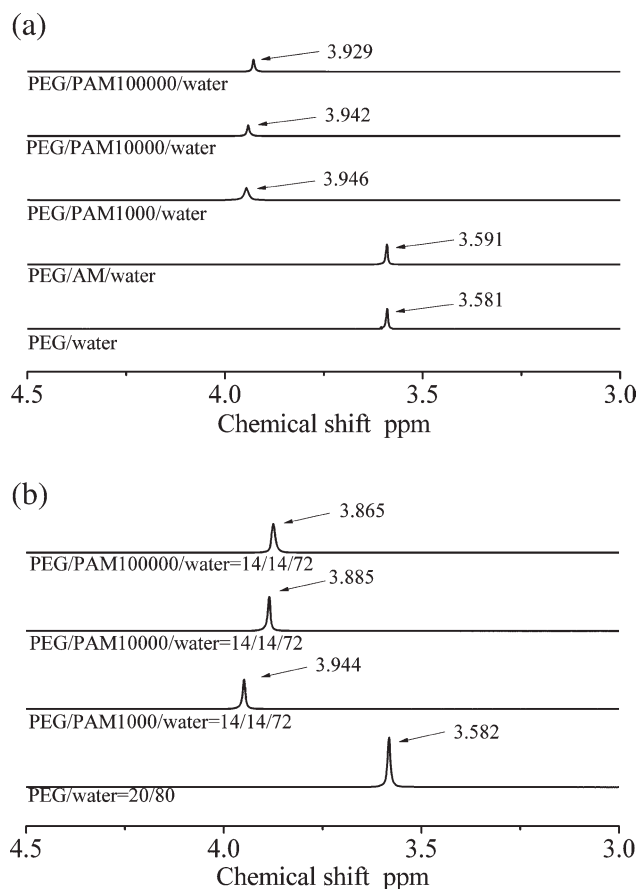
Figure 7 ^{1}H NMR spectra of the PEG water solution, the PEG/PAM (AM) blends water solution with various PAM molecular weights: (a) PAM/PEG = 20% : 8%, (b) PAM/PEG = 14% : 14%.

(a)

(b)
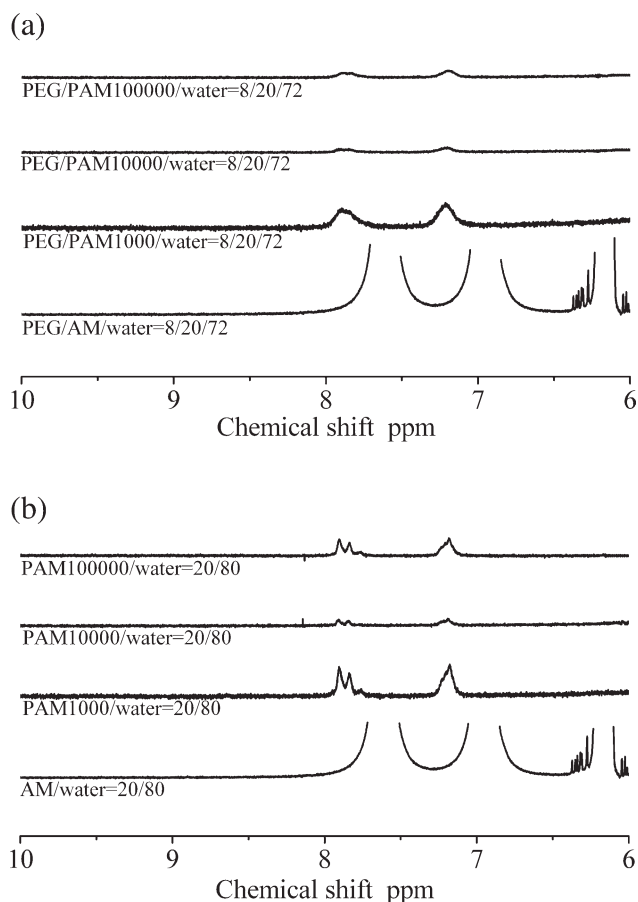
Figure 8 ¹H NMR spectra of the PEG/PAM (AM) water solution and the PAM (AM) water solution with various PAM molecular weights.

the hydrogen bonding between PAM/PEG. The facts that the chemical shifts of the two amide groups are almost unchanged in various PEG/PAM water solutions suggest that the intensions of three kinds of hydrogen bonding are approximate. This result was in agreement with the conclusion that polymer–polymer interactions were not dominant in aqueous PAM/PEG solution.[29]

Figure 9 gives the viscosity change factor R of the blends of the PAM and PEG at various molar ratios in water. For an ideal solution of two polymers without any specific interactions between the polymers, its ideal viscosity, η_{id}, can be calculated as a weight-average of the viscosities of the individual components, $\eta_{id} = \frac{w_1\eta_1 + w_2\eta_2}{w_0}$, Where η_1 and η_2 are the viscosities of the polymers at concentration w_1 and w_2, $w_0 = w_1 + w_2$.[18] For an actual solution mixed with two polymers, its viscosity η_{exp}(experimentally measured viscosities) would be usually different from the value of η_{id}, and therefore, R $(R = \frac{\eta_{exp} + \eta_{id}}{\eta_{id}})$ could be applied to characterize the viscosity change degree. It is clearly shown in Figure 9, after introducing PEG into aqueous PAM solution, the values of R deviate from zero more and

more with increasing PAM molecular weight. This result is again to verify that the greater molecular weight of PAM is more easily forming compact clew, which would result in more reduction of viscosities. Silberberg et al.[35] found that the viscosity of diluted aqueous PAM solution did not increase significantly with its concentration increasing, and even decreased with increasing concentration at higher temperature. They attributed it to the formation of more compact or spherical PAM clews with increasing concentration of PAM. Thus, it is believed that only small parts of the amide groups could interact with the ether groups of PEG in a relatively concentrated solution. Therefore, the hydrogen bonding between PAM and PEG cannot be strengthened by increasing the molecular weight of PAM. This result from Figure 9 would also be a further support to the results of Figures 7 and 8.

The phase separation of two water-soluble polymers in water was reported early,[30] the polymer concentration of phase separation for the PAM/PEG/water system was not high when using high molecular weight polymers. Huraux et al.[26] studied the final film morphology of the polymer blend film prepared via drying the aqueous PEG/PAM solution at a constant temperature in which process the phase separation occurred. The essential cause of the phase separation was the increase of polymer concentration; but the effect of temperature on the phase behavior was not involved in these studies. In a familiar aqueous two-phase system such as dextran/PEG/water, the temperature was reported to have little effects on the phase diagram from 4–40°C.[36] However, in the PEG/PAM water solution
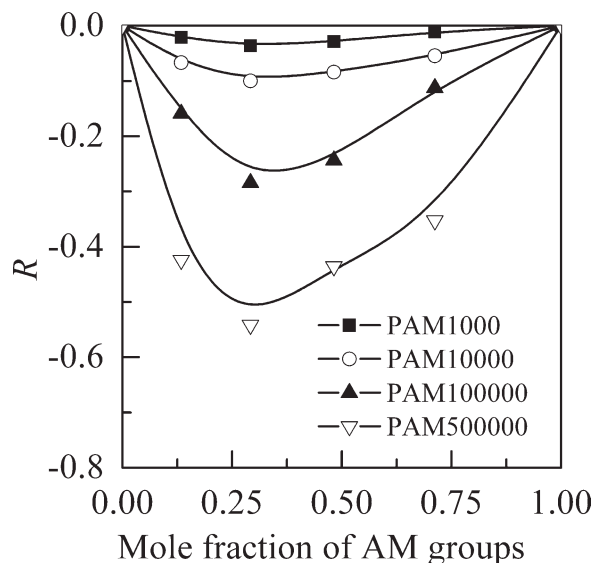
Figure 9 Viscosity change factor (R) vs. molar fraction of AM unit under various PAM molecular weight (PAM+PEG20,000 = 4%, T = 30°C).
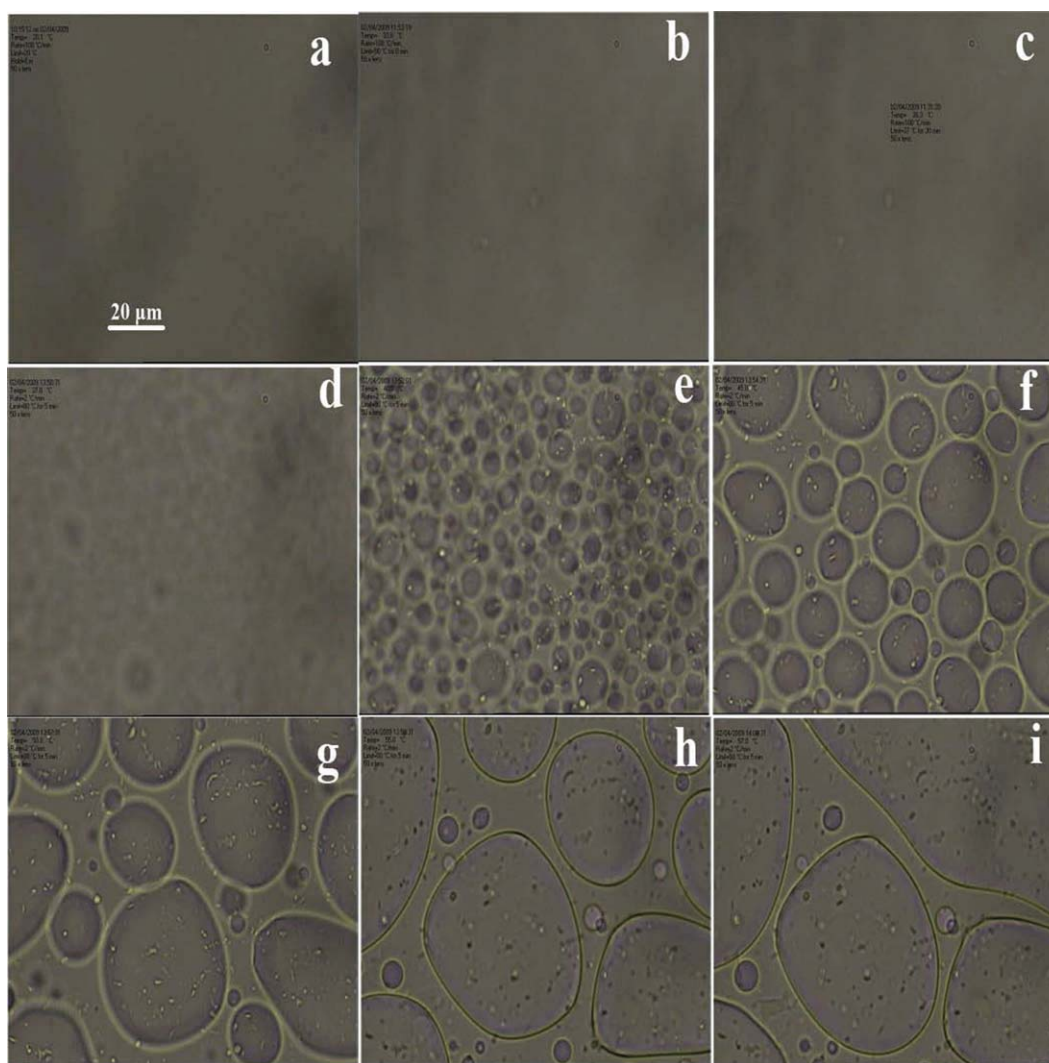
Figure 10 Phase behavior of aqueous PEG20,000/PAM1,000 solution with temperature rising observed by the optical microscopy, and all the images were magnified 500 times: (a) 20°C, (b) 34°C, (c) 36°C, (d) 37°C, (e) 40°C, (f) 45°C, (g) 50°C, (h) 55°C, and (i) 57°C. (PAM1,000 14%, PEG20,000 14%, H_2O 72%). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

as described above, hydrogen bonding is the main interaction between PAM and PEG in relative concentrated aqueous solution. As the hydrogen bonding could enhance the compatibility between various polymers, thus, if the hydrogen bonding is broken via raising temperature, the compatibility between different polymers in aqueous solution would decrease and the phase separation might occur.

Figure 10 shows the phase behaviors of aqueous PAM/PEG solution with temperature rising from 20 to 57°C at a rate of 2°C/min. It could be seen clearly that the aqueous PAM droplets started to separate gradually from the aqueous PAM/PEG solution, grow and aggregate ceaselessly to form larger droplets. It seems that the effect of temperature on the phase behavior was significant. This result indicates that the hydrogen bonding between PAM and PEG

in water could be broken by raising temperature. Bailey et al.[12] found that the interaction between PAA and POE in water could not be broken by either raising temperature or adding urea into it. This could be the reason why the phase separation phenomenon of aqueous PAA/POE solution had been not reported by varying the temperature. These phenomena again confirm that the interaction between PAM and PEG is significantly weaker than that between PAA and POE in water. Contrarily, the aqueous droplets disappeared gently by naturally cooling the temperature from 57 to 20°C. It means that the hydrogen bonding between PAM and PEG could be formed once again when the temperature is cooled down. Thus, the phase behavior of aqueous PAM/PEG solution can be well controlled by controlling temperature. The results achieved in this
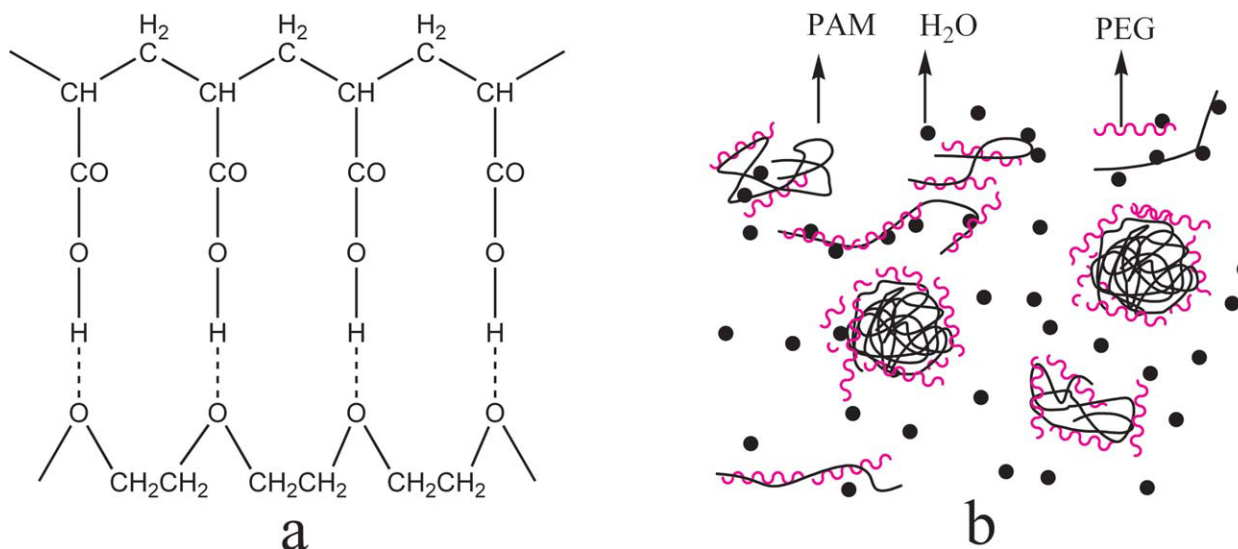
Scheme 2 Sketch map of the interaction mechanism: (a) interaction between PAA and PEG in water, (b) interaction between PAM and PEG in water. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

study would be significant, such as it could be applied to better separate and purify many substances like proteins. It could also be used to synthesize the microporous materials whose interspaces derived from the induced phase separation process.[37]

Interaction mechanism

Sivadasan et al.[38] stated that when at a very high concentration of polymer, the local concentration of PAA molecules around the PAM chains was high and possibly most of these molecules participated in hydrogen bonding with PAM to form a rather cross-linked structure. Many researchers[13–15] summarized that the PAA (or PMAA) and PEG (or POE) associations were through the hydrogen bonding between carboxyl and ether groups one by one represented by the structure described in Scheme 2(a). However, these phenomena could not be verified in the system of aqueous PAM/PEG solution, possibly because the interaction between PAM and PEG is significantly weaker than that between PAA and PEG as discussed before. Because of the intense solvation of these two polymers in dilute solutions, no interaction between PAM and PEG occurred in protic solvent was observed. However, the PAM molecular chain can interact with PEG through the hydrogen bonding between their amide and ether groups in the relatively concentrated aqueous solution. At the same time, the PAM molecular chains prefer to entwist to form clews especially at the high molecular weight. Therefore, the interaction between PAM and PEG is not the one by one hydrogen bonding interaction between amide and ether like that between PAA and PEG, but the PEG molecular

chains aggregate around the PAM clews through hydrogen bonding between ether groups and partial amide groups of PAM as shown in Scheme 2(b).

CONCLUSIONS

The hydrogen bonding between PAM/PEG solid blend has been successfully investigated by using FTIR analyses. The FTIR results reveal that hydrogen bonding exists between PAM and PEG. The interaction between PAM and PEG in water has been studied by ^{1}H NMR. Although the interaction between AM and PEG in water could not be detected, the interassociation between amide groups of PAM and ether groups of PEG in water is confirmed through the ^{1}H NMR studies. However, the hydrogen bonding between PAM and PEG could not be strengthened with the increase of PAM molecular weight, which is distinct from the system of aqueous PAA/ PEG solution. The viscosity reduction of the aqueous PAM/PEG solution increases with the PAM molecular weight increasing, which indicates that PAM molecular chain, especially having high molecular weights preferred to form spherical clews in aqueous PEG solution. Phase separation occurred when raising the temperature of the aqueous PAM/PEG solution, which indicated that the hydrogen bonding between PAM and PEG in water could be broken via controlling the temperature. Based on these results, an interaction mechanism of PAM and PEG in relatively concentrated aqueous solution was proposed.

References

1. Abbott, N. L.; Blankschtein, D.; Hatton, T. A. Macromolecules 1991, 24, 4334.
2. Abbott, N. L.; Blankschtein, D.; Hatton, T. A. Macromolecules 1992, 25, 3917.
3. Abbott, N. L.; Blankschtein, D.; Hatton, T. A. Macromolecules 1992, 25, 3932.
4. Abbott, N. L.; Blankschtein, D.; Hatton, T. A. Macromolecules 1992, 25, 5192.
5. Abbott, N. L.; Blankschtein, D.; Hatton, T. A. Macromolecules 1993, 26, 825.
6. Song, B. K.; Cho, M. S.; Yoon, K. J.; Lee, D. C. J Appl Polym Sci 2003, 87, 1101.
7. Cho, M. S.; Yoon, K. J.; Song, B. K. J Appl Polym Sci 2002, 83, 1397.
8. Shan, G. R.; Cao, Z. H. J Appl Polym Sci 2009, 111, 1409.
9. Lü, T.; Shan, G. R. J Appl Polym Sci 2009, 112, 2859.
10. Chen, D. N.; Liu, X. G.; Yue, Y. M.; Zhang, W. D.; Wang, P. X. Eur Polym J 2006, 42, 1284.
11. Kuo, S. W. J Polym Res 2008, 15, 459.
12. Bailey, J. F. E.; Lundberg, R. D.; Callard, R. W. J Polym Sci Part A: Polym Chem 1964, 2, 845.
13. Oyama, H. T.; Tang, W. T.; Frank, C. W. Macromolecules 1987, 20, 474.
14. Oyama, H. T.; Tang, W. T.; Frank, C. W. Macromolecules 1987, 20, 1839.
15. Bednar, B.; Li, Z. M.; Huang, Y. H.; Chang, L.-C. P.; Morawetz, H. Macromolecules 1985, 18, 1829.
16. Staikos, G.; Bokias, G.; Karayanni, K. Polym Int 1996, 41, 345.
17. Bokias, G.; Staikos, G.; Iliopoulos, I.; Audebert, R. Macromolecules 1994, 27, 427.
18. Lu, X. Y.; Weiss, R. A. Macromolecules 1991, 24, 5763.
19. Kuo, S. W.; Lin, C. L.; Chang, F. C. Macromolecules 2002, 35, 278.
20. Xu, J. W.; He, C. B.; Toh, K. C.; Lu, X. H. Macromolecules 2002, 35, 8846.
21. Cheuk, K. K. L.; Lam, J. W. Y.; Li, B. S.; Xie, Y.; Tang, B. Z. Macromolecules 2007, 40, 2633.
22. Cheuk, K. K. L.; Li, B. S.; Lam, J. W. Y.; Xie, Y.; Tang, B. Z. Macromolecules 2008, 41, 5997.
23. Chen, W. C.; Kuo, S. W.; Lu, C. H.; Jeng, U. S.; Chang, F. C. Macromolecules 2009, 42, 3580.
24. Lu, X. Y.; Weiss, R. A. Macromolecules 1995, 28, 3022.
25. Silva, M. E. S. R. E.; Machado, J. C.; Mano, V.; Silva, G. G. J Polym Sci Part B: Polym Phys 2003, 41, 1493.
26. Huraux, K.; Narita, T.; Fretigny, C.; Lequeux, F. Macromolecules 2007, 40, 8336.
27. Huang, B.; Sun, J. Z.; Li, W.; Zhou, Q. Y.; Lu, Y. J Chem Eng Chin Univ 2003, 17, 431.
28. Swamy, T. M. M. J Appl Polym Sci 2007, 104, 2048.
29. Ravichandran, S.; Ramanathan, K. Polym-Plast Technol Eng 2008, 47, 164.
30. Iliopoulos, I.; Frugier, D.; Audebert, R. Polym Prepr 1989, 30, 371.
31. Maltesh, C.; Somasundaran, P.; Pradip., R. A.; Gundiah, S. Macromolecules 1991, 24, 5775.
32. Koussathana, M.; Lianos, P.; Staikos, G. Macromolecules 1997, 30, 7798.
33. Day, J. C.; Robb, I. D. Polymer 1981, 22, 1530.
34. Bovey, F. A.; Tiers, G. V. D. J Polym Sci Part A: Polym Chem 1963, 1, 849.
35. Silberberg, A.; Eliassaf, J.; Katchalsky, A. J Polym Sci 1957, 23, 259.
36. Haghtalab, A.; Asadollahi, M. A. Fluid Phase Equilib 2000, 171, 77.
37. Liang, C. D.; Dai, S. Chem Mater 2009, 21, 2115.
38. Sivadasan, K.; Somasundaran, P.; Turro, N. J. Colloid Polym Sci 1991, 269, 131.