



Effects of Inert Diluent Segment and Hydrogen Bonding in Poly(styrene-co-methacrylamide) Copolymers

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Abstract

A series of random poly(styrene-co-methacrylamide) (PS-co-PMAAM) copolymers were prepared by free radical polymerization of styrene and methacrylamide monomers. The PS and PMAAM units of the copolymer do not have any specific interaction based on the Kwei equation and the infrared spectroscopy result, indicating that the styrene plays strictly as an inert diluent segment on the PMAAM main chain. This result offers an opportunity to enhance the miscibility and specific interaction between the amide group of PMAAM and the functional group of second polymer by reducing the strong self-association of the PMAAM.

Introduction

Since the combined entropy contribution to the free energy involved in mixing two polymers is negligibly small, specific intermolecular interactions are generally required for the miscibility of polymer blends. For example, the immiscible blend of polystyrene can be enhanced by introducing a functional group to polystyrene capable of forming intermolecular association with second functional polymers such as poly(styrene-co-acetoxystyrene)/phenolic [1], poly(styrene-co-vinylphenol) (PSOH)/poly(caprolactone) (PCL) [2], poly(styrene-co-vinylphenol)/poly(methyl methacrylate) [3] blends. However, in a special case, the incorporation of inert styrene into the poly(vinylphenol) (PVPh) main chain actually enhances the miscibility with a second functional polymer by reducing the stronger self-association of the pure PVPh such as PSOH/poly(acetoxystyrene) [4] and PSOH/poly(bisphenol-A carbonate) [5] blend systems. Therefore, a homopolymer and a random copolymer may form a miscible blend as a result of attractive intermolecular interaction or intramolecular repulsion effects between co-monomeric units.

Polystyrene offers some advantages due to its easy processing ability allowing for the availability of items like plates, tubes, dishes, beads at a fairly low cost. However, poor hydrophilic interaction of polystyrene render poor with biological systems in aqueous environment. In order to solve this problem, the introduction of certain functional groups on the polystyrene is a necessary requirement to transform it into a material capable of interacting with proteins dissolved in aqueous medium. Therefore, in this study, a series of poly(styrene-co-methacrylamide) (PS-co-PMAAM) copolymers were prepared by free radical polymerization of

styrene and methacrylamide monomers. The polymethacrylamide (PMAAM) is the largest synthesized water soluble polymer in the world, which provides many applications in construction, biological and texture industries. However, the nature of strong self-association hydrogen bonding of the pure PMAAM makes it difficult to form miscible blend systems with a second polymer containing functional group such as poly(ethylene-oxide). Therefore, the incorporation of an inert diluent segment such as styrene into the PMAAM main chain is able to reduce the self-association hydrogen bonding and thus enhances the miscibility with second functional polymers. In this study, we will focus our attention on the syntheses and fundamental characterization of PS-co-PMAAM copolymers.

Experimental

Samples

Styrene and methacrylamide monomers were purchased from Aldrich Chemical Company that were purified by distillation under vacuum and nitrogen atmosphere before their polymerization. The azobisisobutyronitrile (AIBN) radical initiator was recrystallized from ethyl alcohol prior to use. 1,4 dioxane was distilled under vacuum and then used as solvent in the solution copolymerization experiments.

Syntheses of Poly(styrene-co-methacrylamide) Copolymers

Solution copolymerization of styrene with methacrylamide in 1,4 dioxane was performed at 80 °C under nitrogen atmosphere in a glass reaction flask containing a condenser. AIBN (1 wt% based on monomer) was employed as an initiator. The mixture was stirred about 24 hours, and then

poured into excess isopropyl alcohol under vigorous agitation to precipitate the product. The crude copolymer product was purified by redissolving in 1,4 dioxane and the solution was added dropwise into a large excess of isopropyl alcohol. This procedure was repeated several times and the residual solvent of the final product was removed by the vacuuming at 70 °C for 1 day to yield the pure white poly(styrene-co-methacrylamide). The chemical composition of the copolymer was measured by using ^1H and ^{13}C NMR spectra in CDCl_3 .

Blend Preparations

Blends of PMAAM/PEO = 50/50 were prepared by water solution casting and PMAAM34.5/PEO = 50/50 were prepared by THF solution containing 5 wt% polymer mixture which were stirred for 6–8 h and cast on a Teflon dish, respectively. The solution was allowed to evaporate slowly at room temperature for 1 day. The blend films were then dried at 50 °C for 2 days.

Characterizations

Nuclear Magnetic Resonance. ^1H and ^{13}C NMR spectra were recorded on Bruker ARX300 spectrometer using CDCl_3 and D_2O solvent for the poly(styrene-co-methacrylamide) and pure polymethacrylamide, respectively.

Gel Permeation Chromatograph (GPC). Weight average (M_w), number average molecular weights (M_n) and polydispersity index (M_w/M_n) were determined by a Water 510 Gel Permeation Chromatograph (GPC).

Differential Scanning Calorimetry. The glass transition temperature of the blend was performed using a DSC from Du-Pont (DSC-9000) with a scan rate of 20 °C/min and the temperature range of 30–260 °C. The measurement was made using 5–10 mg sample on a DSC sample cell after the sample was quickly cooled to 30 °C from the melt of the first scan. The T_g was obtained as the inflection point of the heat capacity jump.

Infrared Spectroscopy. Infrared spectra of copolymer films were determined by using the conventional NaCl disk method. The THF solution containing the blend was cast onto a NaCl disk. The film used in this study was thin enough to obey the Beer–Lambert law. FTIR measurement was recorded on a Nicolet Avatar 320 FT-IR spectrophotometer and 32 scans were collected with a spectral resolution of 1 cm^{-1} . The sample containing hydroxyl groups is moisture sensitive; a pure nitrogen flow was used to purge the IR optical box in order to maintain dry sample films. IR analyses recorded at elevated temperatures were performed by using a cell mounted inside the temperature-controlled compartment of the spectrometer.

Results and Discussion

The ^{13}C spectra of the pure PS and the PS-co-PMAAM copolymer containing 14.7 mol% of methacrylamide are shown in Figure 1. The pure PS has six resonance peaks and all the peak assignments are also assigned in Figure 1(a). The PS-co-PMAAM copolymer clearly shows its related resonance peaks in Figure 1(b) in addition to the amide carbon (C-8) at 180 ppm and the methyl carbon at 20 ppm (C-7). As a result, we can confirm that the methacrylamide monomer has indeed been incorporated into the PS main chain. Figure 2 shows ^1H NMR spectra of pure polystyrene, PS-co-PMAAM copolymer containing 14.7 mol% of methacrylamide and pure PMAAM. For the pure PS homopolymer, the multiple resonance of aromatic protons (3,4,5.), methylene (1) and methine (2) protons are located at 6.62–6.88, 1.53 and 2.06 ppm, respectively. For the pure PMAAM, proton resonance absorptions of methyl (6) and methylene (7) at the mole ratio of 3 : 2 is located at 1.08 and 1.70 ppm, respectively. The areas of methyl, methylene, methane and aromatic protons of the PS-co-PMAAM copolymer were employed to characterize its composition. The chemical shifts and their corresponding areas of these PS-co-PMAAM copolymers are summarized in Table 1, which can be used to calculate the copolymer composition of these copolymers. Table 2 lists the monomer feed ratio, copolymer composition yield and molecular weights. The reactivity ratio was calculated using the methodology of Kelen and Tudos [6, 7] by Equation (1)

$$\eta = \left(r_1 + \frac{r_2}{\alpha} \right) \xi - \frac{r_2}{\alpha}, \quad (1)$$

where

$$\eta = \frac{G}{(\alpha + F)} \quad \text{and} \quad \xi = \frac{F}{(\alpha + F)}.$$

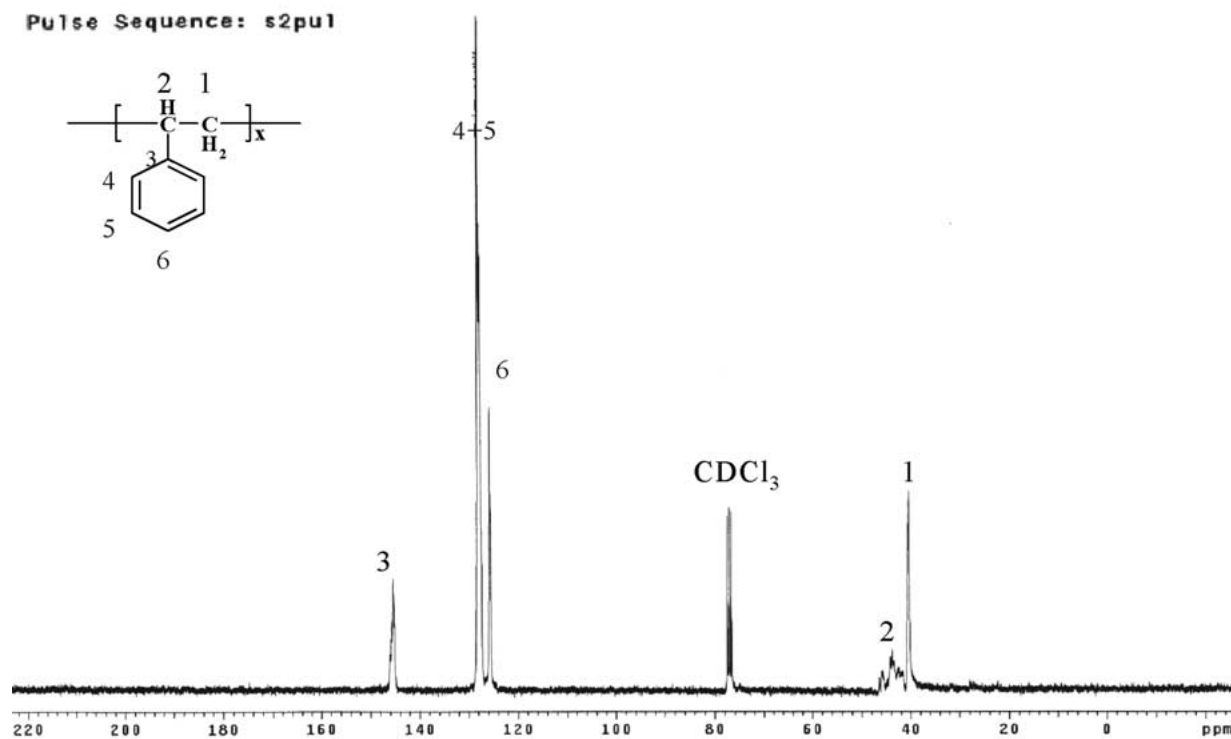
F and G can be obtained by the quantities of x and y , where $x = M_1/M_2$ is the ratio of molar concentration of monomer 1 and 2, and $y = dM_1/dM_2$ is the mole ratio of these monomers in the copolymer, $F = x^2/y$ and $G = x(y - 1)/y$. Parameter α is suitably obtained by Equation (2):

$$\alpha = \sqrt{F_m F_M}, \quad (2)$$

where F_m and F_M are the lowest and highest F from the experimental data. Plotting of η versus ξ , we can obtain r_2 and r_1 from the intercept and slope. The results are shown in Figure 3 from which values of $r_{ps} = 2.89$ and $r_{pas} = 2.04$ are calculated.

Figure 4 shows the DSC thermograms of the pure PS, pure PMAAM and several PS-co-PMAAM copolymers. The pure PS and PMAAM show single glass transition temperatures at about 100 °C and 251 °C, respectively. Compared with the chemical structure of PMAAM and PMMA, the methoxy group of PMMA is replaced by the amine group in PMAAM and results in significant glass transition temperature increase due to the formation of strong hydrogen bonding of the pure PMAAM. Taking into account the chemical structures of PS and PMAAM, these two homopolymers

(a) PS



(b) PS-co-PMAAM

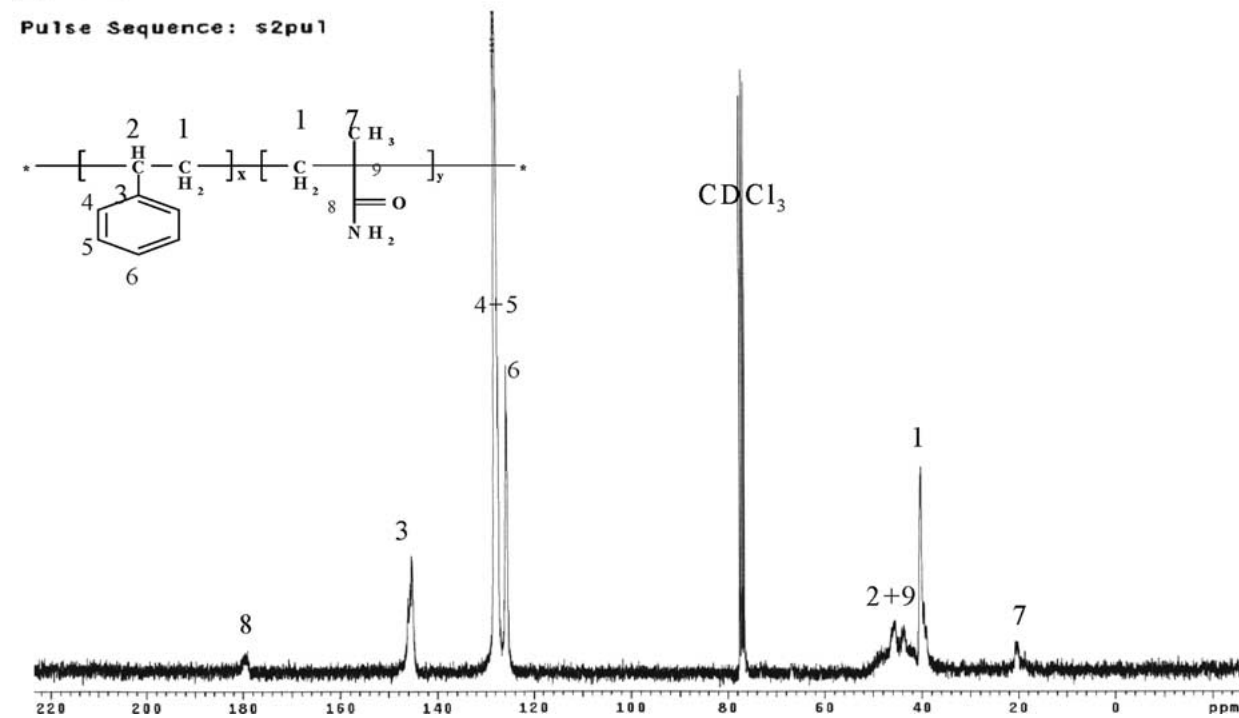


Figure 1. Spectral characteristics by ^{13}C NMR analysis of the pure PS and PMAAM14.7.

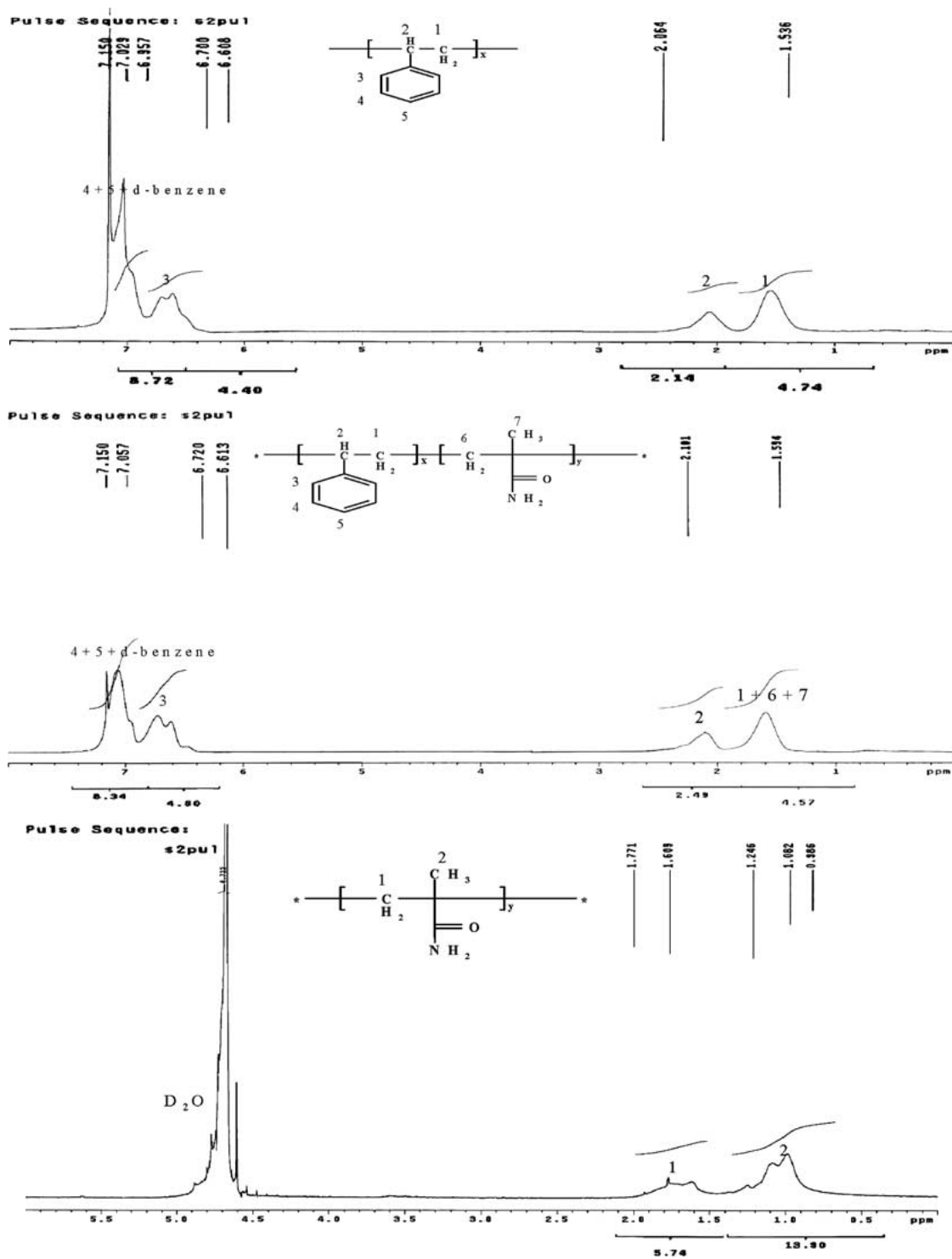


Figure 2. ¹H NMR spectra of the pure PS, PMAAM14.7 and pure PMAAM.

Table 1. The chemical shift of ¹H NMR of poly(styrene-co-methacrylamide) copolymers

Aberration	Styrene+MAAM (ppm)		Styrene (ppm)	Styrene+MAAM Area	Styrene Area	Styrene/MAAM	
PMAAM1.4	1.59	2.10	6.62	4.57	2.49	4.60	2.30/0.03
PMAAM2	1.61	2.10	6.74	4.16	2.43	3.77	1.88/0.04
PMAAM8.4	1.61	2.10	6.74	3.83	2.29	3.53	1.77/0.16
PMAAM14.7	1.61	2.10	6.76	3.79	2.50	3.25	1.63/0.28
PMAAM34.5	1.72	2.11	6.88	3.56	3.07	2.35	1.18/0.62

Table 2. Information on poly(styrene-co-methacrylamide) in this study

Polymer	Monomer feed (mol%)		Polymer composition (mol%)		Mn	Yield (%)
	Styrene	MAAM	Styrene	MAAM		
PS	100	0	100	0	25800	38.8
PMAAM1.4	96.5	3.5	98.6	1.4	24360	30.0
PMAAM2	92.1	7.9	98	2	19340	19.6
PMAAM8.4	84.5	15.5	91.6	8.4	42700	4.7
PMAAM14.7	76.6	23.4	85.3	14.7	23909	10.5
PMAAM34.5	65.6	34.4	65.6	34.5	16400	11.4
PMAAM71	29.0	71.0	29.0	71.0	ND	38.5
PMAAM	0	100	0	100	11000	68.0

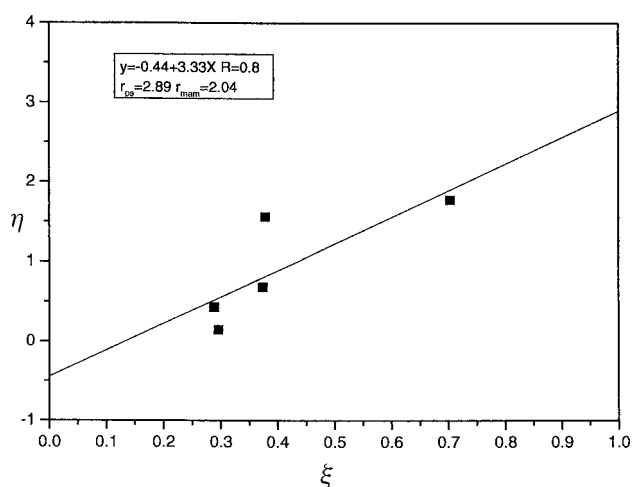


Figure 3. Kelen-Tudos plot for PS-co-PMAAM copolymers.

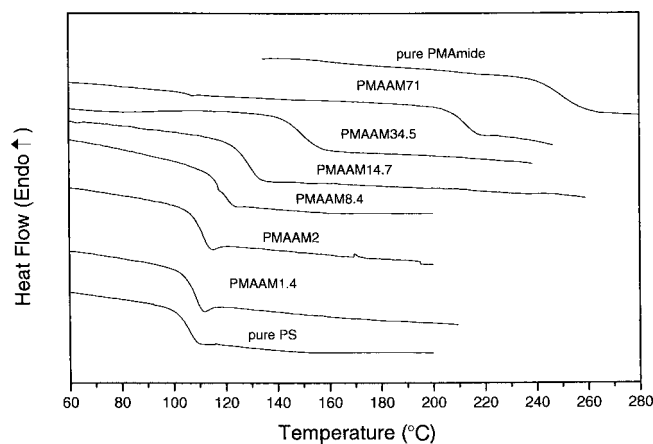
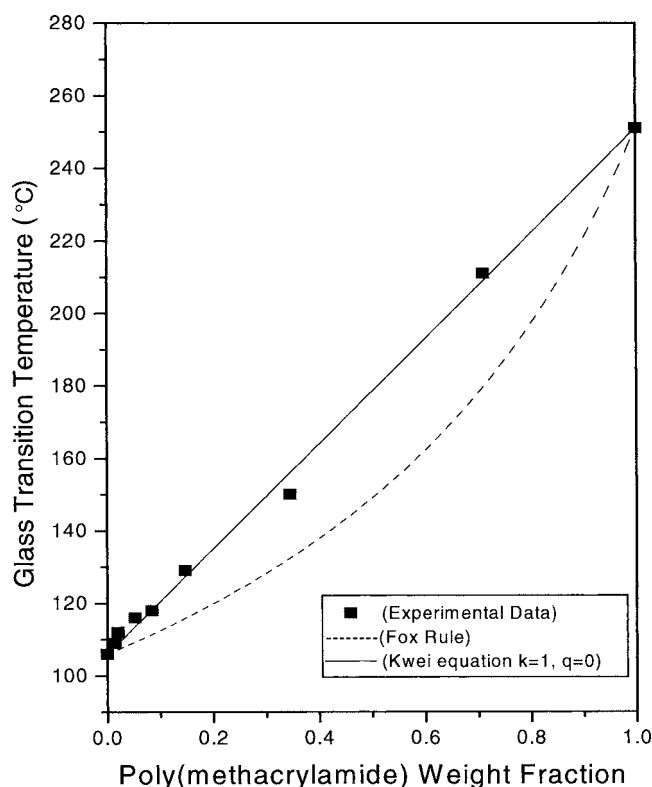


Figure 4. DSC thermograms of pure PS, pure PMAAM and PS-co-PMAAM with different PMAAM contents: (a) pure PS; (b) PMAAM1.4; (c) PMAAM2; (d) PMAAM8.4; (e) PMAAM14.7; (f) PMAAM34.5; (g) PMAAM71; (h) pure PMAAM.

should be immiscible due to large solubility parameter difference as would be expected. In addition, the difference in reactivity ratio in this system does not favor to form a random copolymer. However, all these PS-co-PMAAM copolymers show a single glass transition temperature, indicating that these copolymers are mostly in short blocks. Therefore, the incorporation of styrene monomer into the


 Figure 5. T_g versus composition curves based on: (■) experimental data, (---) Fox equation, and (—) Kwei equation.

methacrylamide main chain can be considered as statistical. Over the years, a number of equations have been offered to predict the variation of the glass transition temperature of a miscible blend or a copolymer as a function of composition. The most popular equation is the Kwei Equation [8] as follows (3):

$$T_g = \frac{W_1 T_{g1} + k W_2 T_{g2}}{W_1 + k W_2} + q W_1 W_2, \quad (3)$$

where W_1 and W_2 are weight fractions of the compositions, T_{g1} and T_{g2} represent the corresponding glass transition temperatures, and k and q are fitting constants. Figure 5 shows the dependence of the T_g on the composition of the PS-co-PMAAM copolymer where the Fox equation do not fit the experiment data well. Clearly, the Kwei equation is able to fit

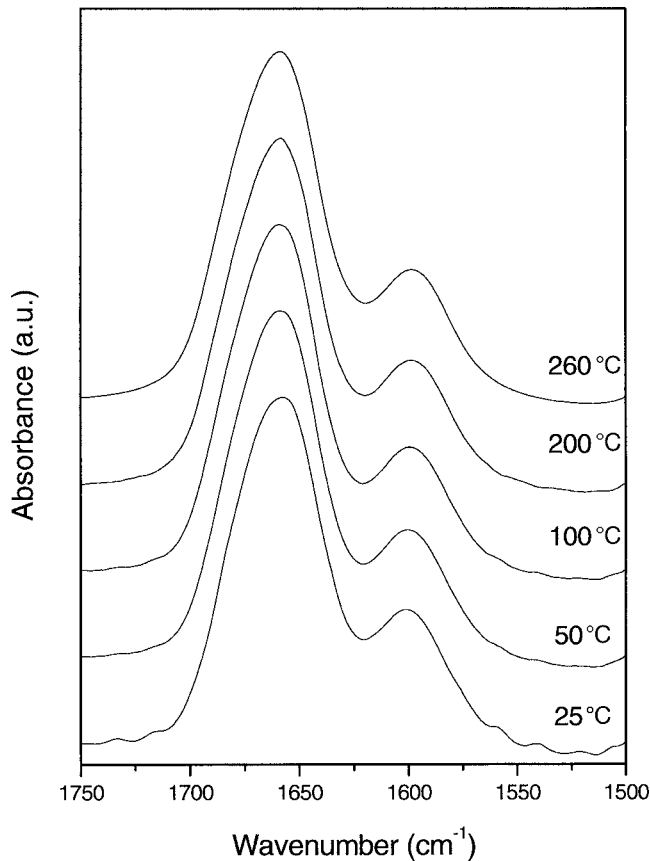


Figure 6. FTIR spectra of pure PMAAM in the amide I and amide II regions recorded as a function of temperature.

well the experiment data and the best fit of $k = 1$ and $q = 0$ are obtained, which is the same as the simple additive rule. Where q is a parameter corresponding to the strength of hydrogen bond in the copolymer, reflecting a balance between the breaking of the self-association and the forming of the inter-association hydrogen bonding. In this study, the T_g of this copolymer obeys the simple additive rule ($q = 0$), indicating that the PS and PMAAM polymer chain does not have any specific interaction such as hydrogen bonding in this copolymer system. This result implies that the polystyrene plays strictly as an inert diluent segment on the PMAAM polymer chain. In order to support this claim, we will turn our attention on the infrared spectra.

For convenience, we firstly focus on the infrared spectra of pure PMAAM. Figure 6 shows FTIR spectra of the group of the pure PMAAM measured at different temperatures from 25°C to 260°C between 1550 cm^{-1} and 1750 cm^{-1} . The carbonyl absorption of amide occurs at lower frequencies than the normal carbonyl absorption due to the resonance effect that has been widely discussed. The pure PMAAM shows two bands at 1650 and 1600, corresponding to the amide I band (C=O stretching vibrations) and the amide II band (N-H bending vibration), respectively. In generally, the amide II band has an intensity of one-half to one-third of the carbonyl absorption band. The absorption of hydrogen bonded carbonyl group of pure PMAAM (amide I band in Figure 6) shifts only slightly to higher wavenumber with increasing temperature, implying that the

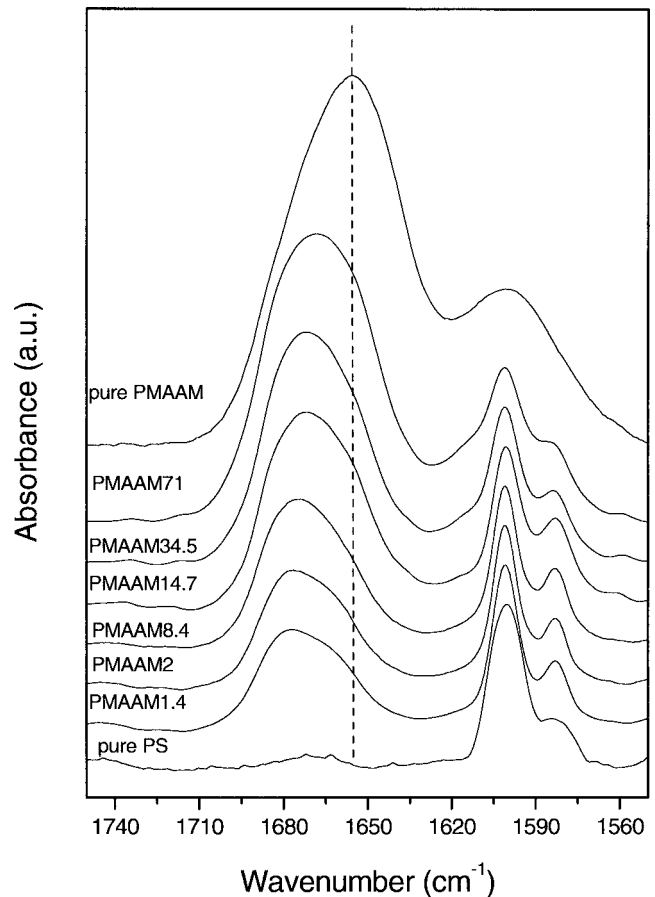


Figure 7. The IR spectra at 1550 cm^{-1} –1750 cm^{-1} of pure PS, pure PMAAM and PS-co-PMAAM copolymers with different PMAAM contents at room temperature.

hydrogen bonding strength is slightly and gradually broken down with the increase of temperature due to the strong hydrogen bonding strength existing in the pure PMAAM. Even though the temperature is above the glass transition temperature of the pure PMAAM (260°C), the absorption of the amide group is almost the same since the amide group can bond to produce strong dimers with an *s-cis* conformation and in polymers with an *s-trans* conformation. Now, we turn our attention on the infrared spectra of the PS-co-PMAAM copolymer. Figure 7 shows scale-expanded infrared spectra in the range 1550 cm^{-1} –1750 cm^{-1} of several PS-co-PMAAM copolymers at room temperature. Clearly, the absorption of the amide group shifts significantly to high wavenumber with the increase of the PS content. In a biological aqueous system, the absorption of the amide group protein in dilute solution also shifts to higher frequency. In this copolymer system, the absorption of the amide group also shifts to higher frequency with the incorporation of the inert diluent segment such as styrene into the PMAAM chain. This result is consistent with previous Kwei equation that PS and PMAAM do not form any specific interaction. The inert diluent segment of styrene into the PMAAM will change the *s-cis* conformation of the pure PMAAM and results in the higher wavenumber shift. Therefore, we can confirm that the styrene indeed acts as an inert diluent segment for the PMAAM polymer,

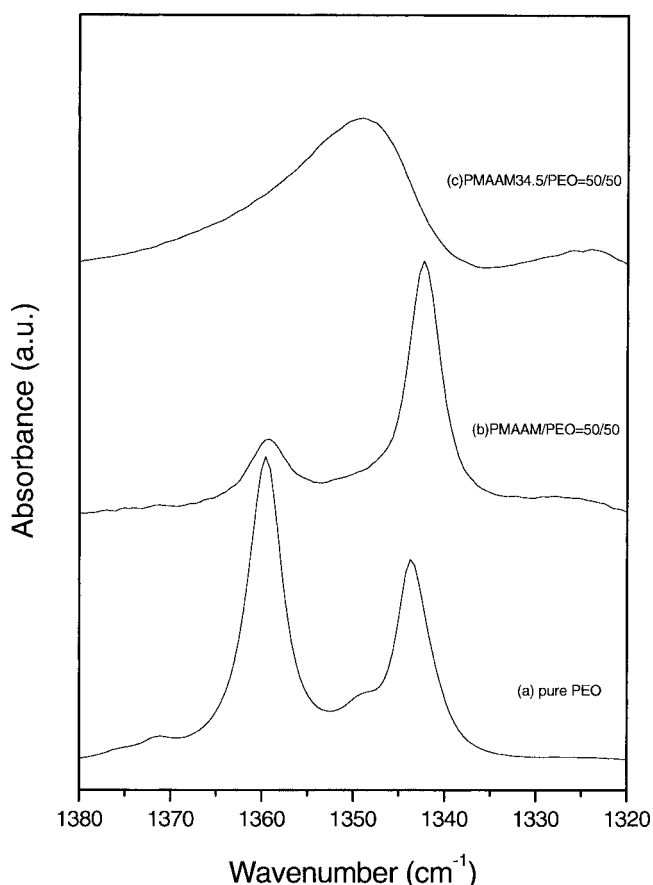


Figure 8. FTIR spectra recorded at room temperature at 1320 cm^{-1} – 1380 cm^{-1} region for (a) pure PEO, (b) PMAAM/PEO = 50/50 blend, (c) PMAAM34.5/PEO = 50/50 blend.

which provides a special route in forming miscible polymer blend systems. For example, compared with the pure PMAAM/PEO blend and PS-co-PMAAM (with 34.5 mol% of PMAAM)/PEO blend systems, Figure 8 shows infrared spectra in the 1320 cm^{-1} to 1380 cm^{-1} region of the pure PEO, PMAAM/PEO blend and PS-co-PMAAM/PEO blend. The bands observed at 1360 and 1343 cm^{-1} represent the crystalline phase of the pure PEO [9]. These bands disappear in the PS-co-PMAAM/PEO blend, and are replaced by a broad band roughly centered at 1350 cm^{-1} corresponding to the amorphous phase. However, the PMAAM/PEO blend still possesses the crystalline phase of PEO, indicating that the PS-co-PMAAM provides much more hydrogen bonds than the pure PMAAM with PEO phase. Coleman et al. [10] has reported that the self-association equilibrium constant of the amide group is higher than the inter-association equilibrium constant between the amide group and the ether group of PEO and thus limits the miscibility between these two segments. In this study, the incorporation of the inert styrene into the PMAAM main chain is able to decrease the strong PMAAM self-association hydrogen bonding that is even more efficient than by increasing the temperature.

In summary, the miscibility of homopolymer/random copolymer blend depends on the attractive intermolecular interaction and intramolecular repulsion effects between co-

monomeric units. For example, in this study, the polystyrene is immiscible with PEO as would be expected due to large solubility parameter difference. In addition, the PMAAM is also immiscible with PEO due to the strong self-association hydrogen bonding of PMAAM. However, the PMAAM34.5 is miscible with PEO due to the intramolecular repulsion effect between the PS and PMAAM and results in the attractive intermolecular interaction such as hydrogen bonding between the amide group of PMAAM and the ether group of PEO. We have demonstrated that the miscibility enhancement of the self-association of polymer such as poly(vinylphenol) or poly(methacrylamide) with a second polymer can be achieved by incorporating an inert diluent segment.

Conclusions

A series of poly(styrene-co-methacrylamide) (PS-co-PMAAM) copolymer prepared through free radical polymerization of styrene and methacrylamide monomers have been synthesized. The styrene and the methacrylamide segment does not have any specific interaction such as hydrogen bonding based on the Kwei equation and the infrared spectroscopy, implying that the styrene moiety plays strictly as an inert diluent in the PMAAM main chain. This result offers an opportunity to enhance the miscibility between the amide group of PMAAM and the ether group of PEO by incorporating an inert diluent to reduce the strong self-association hydrogen bonding of pure PMAAM and thus increases the standard inter-association equilibrium constant between PMAAM/PEO blend.

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