

## Chapter 2

### Miscibility Behavior and Interactions

#### of Poly(hydroxyethyl methacrylate)/Poly(vinylpyrrolidone) Blends and Poly(hydroxyethyl methacrylate)-b-Poly(vinylpyrrolidone) Diblock Copolymer

#### **Abstract:**

Atom transfer radical polymerization (ATRP) and conventional radical polymerization have been used to direction prepare poly(hydroxyethyl methacrylate)-b-poly(vinylpyrrolidone) (PHEMA-b-PVP) of controlled molecular weight and low polydispersity. The characterized data of PHEMA-b-PVP diblock copolymers are reported from analyses by gel permeation chromatography (GPC). The miscibility behaviour and interactions in the system of the PHEMA-b-PVP diblock copolymers and PHEMA/PVP blends were observed. Experimental results showed that the glass transition temperatures ( $T_g$ ) of the diblock copolymers by differential scanning calorimetry (DSC) were higher than that of the blends. The  $q$  values of the diblock copolymers and the blends are positive, and increase with the increase of molecular weight of PVP. This large positive deviation reveals that strong hydrogen bonding must exist between PHEMA and PVP polymers. Fourier transform infrared (FT-IR) spectroscopy showed that inter-association interaction of the diblock copolymers was greater than that of the blends. Measurement of the proton spin–lattice relaxation time in the rotating frame, ( $T_{1\rho}^H$ ), reveal that each of the diblock copolymers and the blends has one composition-dependent  $T_{1\rho}^H$ , indicating that both the diblock copolymers and the blends are homogeneous on a scale of 1-3nm. Furthermore, the calculated domain sizes of the diblock copolymers are smaller than those of the corresponding blends.

## 2.1 Introduction

Block copolymers composed of segments with different properties have been of considerable interest. Some fundamental research and practical technologies to clarify or improve the block copolymers have been carried out [1, 2]. These complex nanostructures have shown promise for utilization in environmental, biomedical, and materials applications, including the sequestration of pollutants, drug delivery, gene therapy, coatings, and composites.

Although the atom transfer radical polymerization (ATRP) can polymerize a relatively broad range of monomers such as styrenes, acrylates, methacrylates, and acrylonitrile, etc., not all alkenes can be successfully polymerized by ATRP. ATRP has not yet been successful in polymerizing vinyl acetate, olefins, etc., presumably due to either relatively strong carbonhalogen bonds or low radical reactivities. Several efforts to overcome this limitation have been made. First, CRPs were combined with different polymerization methods to prepare novel block copolymers, i.e., with cationic polymerization [3], ROMP [4], condensation [5], and anionic polymerization [6]. Another approach is to combine CRP with conventional radical polymerization. Priddy et al. reported a method to prepare copolymers by combining conventional radical polymerization and TEMPO-based CRP [7]. Destarac and Boutevin reported a similar approach, the use of difunctional initiator using conventional radical polymerization and ATRP for the formation of block copolymers of styrene with *n*-butyl acrylate [8]. Matyjaszewski et al. report four different methods for the synthesis of block copolymers using ATRP and conventional radical polymerization [9].

2-Hydroxyethyl methacrylate (HEMA) is a commercially important monomer that is widely used in manufacture of soft contact lenses and intraocular lenses [10]. HEMA copolymers exhibit excellent biocompatibility and good blood compatibility [11]. Other biomedical applications for HEMA-based materials include an embedding substrate for the examination of cells using light microscopy [12], and inert matrices for the slow release of

drugs [13].

Poly(vinylpyrrolidone) (PVP) is a water-soluble tertiary amide and a strong Lewis base that possesses good biocompatibility, and devices based on hydrogels of this material have found several medical applications. PVP was chosen for this study because the amide group is known to be a stronger hydrogen-bond acceptor than the carbonyl group of poly(methyl methacrylate) (PMMA) or the ether group of poly(ethylene oxide) (PEO).

In this article, we report the preparation of diblock copolymers of HEMA and *N*-vinyl-2-pyrrolidone (NVP) by ATRP and conventional radical polymerization. The homopolymers of HEMA have been first prepared using ATRP from 2,2'-azobis[2-methyl-*N*-(2-(2-bromoisobutyryloxy)ethyl)propionamide] (AMBEP) initiator. By lowering the polymerization temperature and carefully controlling the polymerization procedure to minimize the oxidation of Cu (I) to Cu (II), we obtained well-behaved polymerizations occurring at reasonable rates to yield well-defined polymers of narrow molecular weight dispersities. The initially prepared homopolymers then served as macroinitiators for the growth of diblock copolymers from combinations of NVP monomers by conventional radical polymerization. Then, PHEMA was blended with PVP, respectively. It is of interest to see whether hydrogen bonding interactions are changed in PHEMA-*b*-PVP diblock copolymers and PHEMA/PVP blends. The characterized data are observed by gel permeation chromatography (GPC), <sup>1</sup>H NMR spectroscopy, differential scanning calorimetry (DSC), Fourier transform infrared (FT-IR) spectroscopy and high-resolution solid-state <sup>13</sup>C NMR spectroscopy.

## 2.2 Experimental Section

### 2.2.1 Materials

2,2'-Azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] was provided by WAKO Chemicals. and used as received. *N*-vinyl-2-pyrrolidone (NVP) was distilled from calcium hydride and stored under N<sub>2</sub>. 2-Hydroxyethyl methacrylate (HEMA) was distilled under reduced pressure before use. Copper (I) chloride (CuCl) was purified by washing with glacial acetic acid overnight, followed by absolute ethanol and ethyl ether, and then dried under vacuum. Triethylamine (TEA), (1-bromoethyl) benzene (BrB), 2-bromoisobutyryl bromide and 2,2'-bipyridine (bpy) were all used as received. Silica-60 gel was purchased from Merck (Germany) and was used as supplied for removal of the spent ATRP catalyst. All solvents were distilled prior to use. The polyvinylpyrrolidone (PVP) with molecular weight of  $M_w = 11,000 \text{ g mol}^{-1}$  was purchased from Acros Chemical Company, Inc.

### 2.2.2 Characterization

*Nuclear magnetic resonance spectroscopy (NMR)*. <sup>1</sup>H NMR spectra were recorded as solutions on a Bruker AM500 (500MHz) spectrometer, with the solvent proton signal as a standard.

*Elemental analysis (EA)*. Elemental analysis was carried out on a Heraus CHN-Rapid Elemental Analyzer.

*Gel permeation chromatography (GPC)*. Molecular weights and molecular weight distributions were determined by GPC. GPC was conducted on a Waters 510 HPLC–equipped with a 410 Differential Refractometer, a UV detector, and three Ultrastyrigel columns (100, 500, and 10<sup>3</sup> Å) connected in series in order of increasing pore size–using DMF as an eluent at a flow rate of 0.6 mL/min. The molecular weight calibration curve was obtained using polystyrene standards.

*Differential scanning calorimetry (DSC)*. Glass transition temperatures ( $T_g$ ) were measured by DSC from Du-Pont (model 910 DSC-9000 controller). Heating rates were 20

°C/min, and a temperature range of 30-220 °C in nitrogen atmosphere. Approximately 4-6 mg sample was weighted and sealed in an aluminum pan. The sample was the quickly cooled to 0 °C from the first scan and then scanned between 0 and 220°C at a scan rate of 20 °C /min. The  $T_g$  was taken as the midpoint of the heat capacity transition between the upper and lower points of deviation from the extrapolated glass and liquid lines.

*Fourier transform infrared spectroscopy (FT-IR).* FT-IR spectra were obtained on a Nicolet Avatar 320 FT-IR Spectrometer, 32 scans at a resolution of 1 cm<sup>-1</sup> were collected with a KBr disk at room temperature. The MeOH solution containing the sample was cast onto a KBr disk and dried under containing similar to that used in bulk preparation. The sample chamber was purged with nitrogen in order to maintain the film dryness.

*High-resolution solid-state <sup>13</sup>C NMR.* High-resolution solid-state <sup>13</sup>C NMR experiments were carried out at 25 °C using a Bruker DSX-400 Spectrometer operating at a resonance frequency of 100.47 MHz for <sup>13</sup>C. The high-resolution solid-state <sup>13</sup>C NMR spectra were acquired by using the cross-polarization (CP)/magic angle spinning (MAS)/high-power dipolar decoupling (DD) technique. A 90° pulse width of 3.9 ms with 3 s pulse delay time and an acquisition time of 30 ms with 2048 scans were used. A magic angle sample-spinning rate of 5.4 KHz was used to avoid absorption overlapping. The proton spin–lattice relaxation time in the rotating frame ( $T_{1\rho}^H$ ) was determined indirectly via carbon observation using a 90°- $\tau$ -spin lock pulse sequence prior to CP. The data acquisition was performed at a delay time ( $\tau$ ) ranging from 0.1 to 12 ms with a contact time of 1.0 ms.

### **2.2.3 Synthesis of Difunctional Initiator**

The initiator was synthesized as described in the previous paper by Matyjaszewski et al. [9]. 2,2'-Azobis[2-methyl-*N*-(2-(2-bromoisobutyryloxy)ethyl)propionamide] (AMBEP) was prepared by adding 2-bromoisobutyryl bromide (5.63 mL,  $4.34 \times 10^{-2}$  mol) into a stirring mixture of 2,2'-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] (5.00 g,  $1.73 \times 10^{-2}$  mol)

and triethylamine (6.02 mL,  $4.34 \times 10^{-2}$  mol) in 150 mL of dry  $\text{CHCl}_3$  in an ice bath for 1 h. After complete addition of the acid bromide, the reaction flask was stirred at room temperature for 3h. The mixture was transferred to a 500 mL separatory funnel and extracted consecutively with  $3 \times 200$  mL of  $\text{H}_2\text{O}$ . The organic phase was dried over  $\text{MgSO}_4$  and filtered and the solvent removed by rotary evaporation. The product, a white solid, was recrystallized directly from the diethyl ether/ethyl acetate and dried in a vacuum. (3.00 g, 39.2%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 7.18 (s, 2H), 4.32 (t, 4H), 3.67 (q, 4H), 1.90 (s, 12H), 1.35 (s, 12H) ppm.  $E_{\text{LEM}}$ .  $A_{\text{NAL}}$ . Calcd. for AMBEP: C, 40.89%; H, 5.90%; N, 9.44%.

## 2.2.4 Polymerization Procedures

*For a Typical Monofunctional HEMA Polymerization.*  $\text{CuCl}$  (0.10 g,  $1.00 \times 10^{-3}$  mol) was added to a dry round-bottom flask (rbf) equipped with a stir bar. After sealing it with a rubber septum, the flask was degassed and backfilled with nitrogen three times and then left under nitrogen.  $\text{MeOH}$  (1 mL) and HEMA (8.00 mL,  $6.60 \times 10^{-2}$  mol) were added, both of which were deoxygenated and added via syringes that had been purged with nitrogen. The complexing agent, bpy (0.47 g,  $2.73 \times 10^{-3}$  mol) in 1 mL of  $\text{MeOH}$ , was added, and the solution was stirred until the Cu complex had formed. After complex formation, (1-bromoethyl) benzene (BrB) (0.41 mL,  $3.00 \times 10^{-3}$  mol) was added to the flask and the flask was placed at room temperature for 24 h. Purification was achieved by passing the methanolic reaction solution through a silica column to remove the Cu (II) catalyst. The blue catalyst adsorbed onto the silica to yield a colorless aqueous solution. The  $\text{MeOH}$  was removed by vacuum distillation to produce white polymer. Finally, precipitation is into cold diethyl ether. Conversions of greater than 80% were routinely obtained, as judged by  $^1\text{H}$  NMR. Analysis using DMF GPC indicated a  $M_n$  of  $4,320 \text{ g mol}^{-1}$  and a  $M_w/M_n = 1.15$ .

*For a Typical difunctional HEMA Polymerization.* The AMBEP initiator (1.60 g,  $2.74 \times 10^{-3}$  mol) and  $\text{CuCl}$  (0.27 g,  $2.74 \times 10^{-3}$  mol) were added to a 50 mL rbf containing a stir bar. The flask was degassed and back-filled with nitrogen three times before introducing

deoxygenated HEMA (4.66 g,  $35.6 \times 10^{-3}$  mol) and MeOH (20 mL) via purged syringes. After the flask was in ice bath for 10 min, the bpy (1.29 g,  $6.80 \times 10^{-3}$  mol) was added and the copper complex formed. After 20 min, the reaction flask was stirred at room temperature for 24 h. Purification was achieved by passing the methanolic reaction solution through a silica column to remove the Cu (II) catalyst. The blue catalyst adsorbed onto the silica to yield a colorless aqueous solution. The MeOH was removed by vacuum distillation to produce white polymer. Finally, precipitation is into cold diethyl ether. Conversions of greater than 70% were routinely obtained, as judged by  $^1\text{H}$  NMR. Analysis using DMF GPC indicated a  $M_n$  of  $4,500 \text{ g mol}^{-1}$  and a  $M_w/M_n = 1.13$ .

*For polymerization of diblock copolymer.* The PHEMA-b-PHEMA (1.50 g,  $1.66 \times 10^{-4}$  mol) was added to a 50 mL rbf containing a stir bar. The flask was degassed and back-filled with nitrogen three times before introducing deoxygenated NVP (3.50 mL,  $3.20 \times 10^{-2}$  mol) via purged syringes. After 20 min, the flask was placed in an oil bath thermostated at  $70 \text{ }^\circ\text{C}$ . After 24 h, the produce is precipitated into cold ether. Conversions of greater than 50% were routinely obtained, as judged by  $^1\text{H}$  NMR. Analysis using DMF GPC indicated a  $M_n$  of  $10,300 \text{ g mol}^{-1}$  and a  $M_w/M_n = 1.30$ .

### **2.2.5 Blend Preparation**

Desired composition containing PHEMA and PVP was dissolved in MeOH at a concentration of 5 wt% and stirred for 6–8 h. The solution was allowed to evaporate slowly at  $25 \text{ }^\circ\text{C}$  for 1 day on a Teflon plate and dried at  $90 \text{ }^\circ\text{C}$  for 3 days to ensure total elimination of the solvent.

## 2.3 Results and Discussion

### 2.3.1 Polymer Characterization

The synthesis of the diblock copolymer and homopolymer are shown in Scheme 2.1. As shown in Scheme 2.1, the synthesis of the diblock copolymer includes two major steps. First, the PHEMA-b-PHEMA is made by ATRP using AMBEP initiator. Second, the PHEMA-b-PVP is made by conventional radical polymerization. The (1-bromoethyl) benzene was considered less likely to produce a significant “end-group” effect when assessing the water solubility of the HEMA homopolymers (Scheme 2.1). Moreover, the morpholine protons also provide a useful  $^1\text{H}$  NMR label for end-group analysis. These discrepancies were due to large systematic errors incurred in the GPC analyses: not only are polystyrene calibration standards unlikely to be reliable for the analysis of methacrylic polymers, but DMF is only a marginal solvent for polystyrene, which leads to a significant over-estimation of the true molecular weight of the well-solvated HEMA homopolymers. This latter problem was reported by Armes et al. [14]. The synthesis details and characterization data for various HEMA polymers are summarized in Table 2.1. By comparing the GPC data obtained using this protocol with the  $\text{DP}_n$ 's calculated from endgroup analysis using  $^1\text{H}$  NMR spectroscopy, it is clear that the GPC calibration error is reduced to around 300–400%. Moreover, the polydispersities are below 1.25. Table 2.2 shows the synthesis details and characterization data for PHEMA-b-PVP copolymers. The polydispersities are below 1.4, suggesting that diblock copolymer by conventional radical polymerization is controllable.

### 2.3.2 DSC Analyses

The most widely used criterion for the judgment of the miscibility behaviour of the diblock copolymers and the blends is the existence of a single  $T_g$ . The  $T_g$  of the diblock copolymers or blends dependence on composition is shown in Figure 2.1. Each diblock copolymer and blend showed a composition-dependent  $T_g$ , showing that these are fully miscible diblock copolymers and blends with a homogeneous amorphous phase. A single  $T_g$



of all diblock copolymers and blends higher than that of either individual polymer was observed. This large positive deviation reveals that strong hydrogen bonding must exist between PHEMA and PVP polymers. It has been generally suggested that the  $T_g$  relationship to the composition of the miscible diblock copolymers and blends follows the Kwei equation:

$$T_g = \frac{W_1 T_{g1} + kW_2 T_{g2}}{W_1 + kW_2} + qW_1W_2 \quad (1)$$

where  $w_1$  and  $w_2$  are weight fractions of the components,  $T_{g1}$  and  $T_{g2}$  represent the corresponding glass transition temperatures, and  $k$  and  $q$  are fitting constants. In this study,  $k = 1$  and  $q = 185$  of the diblock copolymers and  $k = 1$  and  $q = 80$  of the blends were obtained from the non-linear least-squares ‘best fit’ values (Figure 2.2). Here  $q$  is a parameter corresponding to the strength of hydrogen bonding in the systems, reflecting a balance between the breaking of the self-association and the forming of the inter-association hydrogen bonding. These positive  $q$  values of 185 and 80 were obtained, indicating a strong inter-association hydrogen bonding interaction between PHEMA and PVP.

### 2.3.3 FT-IR Analyses

FTIR spectroscopy has been successfully applied in the diblock copolymers and the blends possessing intermolecular interaction through hydrogen bonding. Chemical structures of PHEMA and PVP are shown in Scheme 2.2, containing IR carbonyl vibrations from the free and hydrogen-bonded of PHEMA with PVP. Fig 2.3 shows a scale-expanded infrared spectrum in the range 2700–4000  $\text{cm}^{-1}$  of the diblock copolymers and the blends at room temperature. The pure PHEMA shows two bands in the hydroxyl-stretching region of the infrared spectrum, corresponding to free hydroxyl at 3521  $\text{cm}^{-1}$  and the hydrogen-bonded hydroxyl–carbonyl of the PHEMA at 3419  $\text{cm}^{-1}$ , respectively. The frequency difference between the hydrogen-bonded hydroxyl absorption and free hydroxyl absorption ( $\Delta \nu$ ) is a rough estimate of the average hydrogen bonding strength and its enthalpy in a hydrogen bonding blend system [15]. In this study, the  $\Delta \nu$  of the pure PHEMA is 102  $\text{cm}^{-1}$ .

Figure 2.3 also illustrates that the hydrogen-bonded hydroxyl and carbonyl group absorbance of PHEMA shifts to a lower wavenumber with increase of the PVP content. Moreover, the intensity of the free hydroxyl group decreases gradually with an increase of PVP content. This result reflects a new distribution of hydrogen bond formation resulting from the competition between the hydroxyl–carbonyl group of pure PHEMA and the hydroxyl of PHEMA and the carbonyl of PVP. It also reveals that the interaction of the hydroxyl of PHEMA and the carbonyl of PVP become dominant in PVP-rich blends. Therefore, it is reasonable to assign the band at  $3354\text{ cm}^{-1}$  to the hydrogen bonding interaction between the hydroxyl of PHEMA and carbonyl group of PVP. Hydrogen bonding interaction between hydroxyl of PHEMA and carbonyl of PVP ( $\Delta\nu = 169\text{ cm}^{-1}$ ) is stronger than the hydroxyl–carbonyl interaction of the pure PHEMA ( $\Delta\nu = 102\text{ cm}^{-1}$ ) and this is consistent with the observed positive  $q$  value in the Kwei equation.

Figure 2.4 shows the infrared spectra of the carbonyl stretching measured at room temperature ranging from  $1675$  to  $1765\text{ cm}^{-1}$  for different compositions of the diblock copolymers and the blends. As mentioned above, the carbonyl stretching of pure PHEMA splits into two bands, absorption by the free and hydrogenbonded carbonyl groups at  $1730$  and  $1710\text{ cm}^{-1}$ , respectively. Meanwhile, the carbonyl stretching of PVP also splits into two bands at  $1680$  and  $1665\text{ cm}^{-1}$ , corresponding to the free and the hydrogen-bonded carbonyl groups, which can also be well fitted to a Gaussian function. The fraction of hydrogen bonded carbonyl of the PVP by using the  $a_R = a_{HB}/a_F = 1.3$  [16]. The parameters of the infrared carbonyl band are summarized in Table 2.3. Figure 2.5 plots the fraction of hydrogen bonded carbonyl from the diblock copolymers or the blends vs. the PVP weight fraction of these two systems. According to the Painter-Coleman association model PCAM [17], we can determine the values of equilibrium constants describing the self-association, inter-association and other thermodynamic properties. Figure 2.5 shows that the inter-association equilibrium constant of the diblock copolymers is greater than that of the blends. Further, the inter-association

interaction of the diblock copolymers is greater than that of the blends, which is consistent with previous Kwei equation.

### 2.3.4 Solid-state NMR Analyses

In addition FT-IR, evidence on interactions in the diblock copolymers and the blends can also be obtained from solid-state NMR spectroscopy as demonstrated by changes in chemical shift and/or line shape. Figure 2.6 shows the selected  $^{13}\text{C}$  CP/MAS spectra of various PHEMA-b-PVP and PHEMA/PVP blends. Peak structural assignments (see Scheme 2.1) of  $^{13}\text{C}$  CP/MAS spectra of PHEMA and PVP are shown in Figure 2.6. According to the chemical shifts of carbonyl from the PVP (175 ppm) and those of the hydroxyl from the PHEMA (60 ppm) in the diblock copolymers and the blends, they are difficult to distinguish the difference. Nevertheless, the NMR spectra provide evidence of the existence of inter-association interaction between PHEMA and PVP.

Solid-state NMR spectroscopy has been used to better understand the phase behavior and miscibility of the diblock copolymers and the blends. A single  $T_g$  based on DSC analysis implies that the mixing of two blending components is in a scale of about 20–40 nm. The dimension of mixing smaller than 20 nm can be obtained through measurement of the spin–lattice relaxation time in the rotating frame ( $T_{1\rho}^H$ ). The  $T_{1\rho}^H$  values of the blends were measured through the delayed-contact  $^{13}\text{C}$ /MAS experiments. The  $T_{1\rho}^H$  values were calculated from Eq. (2).

$$\ln(M_\tau / M_0) = -\tau / T_{1\rho}^H \quad (2)$$

where  $\tau$  is the delay time used in the experiment, and  $M_\tau$  is the corresponding resonance.

Figure 2.7 shows plots of  $\ln(M_\tau/M_0)$  vs.  $\tau$ , for the PHEMA resonance (60 ppm) at the diblock copolymers and the blends. It is noted that the experimental data were in good agreement with Eq. (2). From the slope of the fitting line, the  $T_{1\rho}^H$  value can be determined.

Table 2.4 lists the results of the  $T_{1\rho}^H$  values for the diblock copolymers and the blends.

A single composition-dependent  $T_{1\rho}^H$  was obtained for each of the diblock copolymers and the blends. Furthermore, the  $T_{1\rho}^H$  values of the blends are intermediate between those of the two pure polymers and those of the diblock copolymer are above that of the pure PVP. It suggests that diblock copolymers and the blends are homogeneous to a scale where the spin-diffusion occurs within the time  $T_{1\rho}^H$ .

The upper spatial scale of the spin-diffusion path length  $L$  can be estimated from the following expression:

$$L = (6DT_{1\rho}^H)^{1/2} \quad (3)$$

where  $D$ , which is typically assumed to be  $10^{-16} \text{ m}^2\text{s}^{-1}$ , is the effective spin-diffusion coefficient depending on the average proton to proton distance as well as the dipolar interaction (Table 2.4). Therefore, the upper limit of the domain sizes for the blends is estimated to be 1.2-1.6 nm and that of the domain sizes for the diblock copolymers is estimated to be 0.9-1.5 nm. It can be seen that the diblock copolymers has relatively smaller domain sizes than the corresponding blends, indicating that the degrees of homogeneity of the diblock copolymers are relatively higher than those of the blends. The diblock copolymers, in general, has greater fraction of the hydrogen bonded carbonyl than the corresponding blends due to the smaller radius of gyration of the former [17].

## 2.4 Conclusions

Diblock copolymers and homopolymers were prepared by ATRP. PHEMA-b-PVP and PHEMA/PVP blends were investigated by using DSC, FT-IR, and high-resolution solid-state  $^{13}\text{C}$  NMR. All these diblock copolymers and blends have a single  $T_g$ . The  $T_g$  of the diblock copolymers is higher than that of the blends. The  $q$  values of diblock copolymers and the blends are positive. The  $q$  value of the diblock copolymers is higher than that of the blends. The inter-association interaction of the diblock copolymers is greater than that of the blends based on FT-IR analyses. Measurements of  $T_{1\rho}^H$  reveal that all systems possess a single composition-dependent  $T_{1\rho}^H$ , indicating all diblock copolymers and blends are homogeneity. Moreover, the calculated domain sizes of the diblock copolymers have relatively smaller than those of the corresponding blends.

