Chapter 3

Miscibility Behavior and Interactions
of Linear and Four-Arm Poly(*tert*-butyl acrylate)/Polybenzoxazines Blends

Abstract

The linear poly(*tert*-butyl acrylate) (PtBA) and the four-arm PtBA were prepared by atom transfer radical polymerization (ATRP). The characterized data of the linear and four-arm PtBA are reported from analyses by gel permeation chromatography (GPC). Polymer blends prepared from PtBA and polybenzoxazines (PBZZ) were investigated by differential scanning calorimetry (DSC), Fourier-transform infrared spectra (FT-IR) and high-resolution solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy. Each of the blends showed one composition-dependent glass transition temperature (T_g), indicating that both the blends are homogeneous on a scale of 20-40 nm. Furthermore, T_g of the four-arm PtBA/PBZZ blends is higher than that of the linear PtBA/PBZZ blends with the same composition. Experimental results showed that the hydrogen bonding interaction of the four-arm PtBA/PBZZ blends is greater than the corresponding linear PtBA/PBZZ blends by FT-IR. The proton spin–lattice relaxation time in the rotating frame ($T_{1\rho}^H$) determined by high resolution solid state ^{13}C NMR for resolved of the two polymers in the blend changes significantly with thermal history, indicating inhtergeneity on a 3-nm scale. All components of linear or four-arm PtBA/PBZZ systems were shown to separate into heterogeneous phases even through the material exhibits only a single broad T_g by DSC.

3.1   *Introduction*

With the fast development of materials science, the interest in the synthesis and characterization of star polymeric materials has increased so dramatically that they have been a consistent area of exploration in the pursuit of structure property relationships. Star polymers have different hydrodynamic properties and higher degrees of chain end functionality compared to linear polymers of similar composition. They have also found applications in various areas where they serve as additives but they can also be used as such. For instance, star block copolymers with polystyrenepoly(2-vinylpyridine) (PS_6P2VP_6) arms were shown to exhibit improved processability and mechanical properties [1]. The polystyrene stars of Phillips [2] are examples of commercial star polymers.

There are essentially two methods to get access to star polymers: either by linking a given number of linear chains to a central corn ("arm-first" method) or by growing branches from an active core ("core-first" method). In the "arm first" method, living linear macromolecules are initially synthesized. Star formation then occurs in one of two ways: a difunctional comonomer is used to provide cross-linking through propagation [3] or a multifunctional terminating agent is added connecting a precise number of arms to a central core molecule [4]. The former technique produces macromolecules with a large number of arms while in the latter case separation techniques are used to isolate stars from uncoupled linear polymers. In the "core first" method, multifunctional initiators are used to grow chains from a central core resulting in macromolecules with well-defined structures in terms of both arm number and length. Furthermore, the reaction consists solely of stars in the absence of linear polymers.

During the past decade, atom transfer radical polymerization (ATRP) has made possible the synthesis of well-defined star polymers as well as of novel nonlinear polymers such as simple comb, branched, and graft copolymers. ATRP provides control over chain length and functionality by an equilibrium between a dormant alkyl halide and a free radical mediated by

an interchange between copper (I)/copper (II) salts and the organic polymeric chain ends.

It is well-known that interactions play an important role in the wide range of material properties. The method for preparation of polymer blends in this article is utilizing benzoxazine monomer. Polybenzoxazine, as a recently developed phenolic resin, which can overcome many shortcomings associated with traditional phenolic resins, has many fascinating characteristics such as outstanding performance, low cost, and acceptable processing characteristics by the conventional techniques that are being used industrially [5, 6]. Furthermore, these polybenzoxazines have many excellent properties, which easily surpass the phenolic resins, such as excellent mechanical properties, heat resistance, good electronic properties, low water absorption, relatively low dielectric constant, dimensional stability, and amazingly high T_g, even with rather low cross-link density [7-9]. Benzoxazine monomers can be easily prepared from inexpensive raw materials like phenols, formaldehyde, and primary amines. Accordingly, they have a tremendous flexibility in molecular design for monomers and consequently a versatile performance for polymers. Moreover, they can be polymerized without using strong acid or basic catalysts and without producing byproducts through the heterocyclic ring opening, affording polybenzoxazines. A possible explanation for these unusual properties is the formation of extensive hydrogen bonding networks.

In this study, we prepared the four-arm stars initiator at first. Polymers were prepared by ATRP. Then, the linear PtBA and four-arm PtBA were mixed with BZZ and heated to yield thermosetting polymer blends, respectively. It is of interest to see whether hydrogen bonding interactions are changed in the linear and four-arm PtBA/PBZZ blends. The characterized data are observed by gel permeation chromatography (GPC), ^{1}H NMR spectroscopy, differential scanning calorimetry (DSC), Fourier transform infrared (FT-IR) spectroscopy and high-resolution solid-state ^{13}C NMR spectroscopy.

3.2 Experimental Section

3.2.1 Materials

Bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl)isopropane (BZZ) was kindly supplied by Shikoku Chemicals Co. and used as received. *tert*-Butyl acrylate (tBA) was distilled from calcium hydride and stored under N_2. Copper (I) bromide (CuBr) was purified by washing with glacial acetic acid overnight, followed by absolute ethanol and ethyl ether, and then dried under vacuum. Methyl 2-bromopropionate (MBrP), 2-bromopropionyl bromide, Amberlite IR-120 (H form) cation exchange resin, pentaerythritol, triethylamine (TEA), and *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA) were all used as received. All solvents were distilled prior to use.

3.2.2 Characterization

Nuclear magnetic resonance spectroscopy (NMR). ^{1}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 Ultrastyragel columms (100, 500, and 10^3 Å) connected in series in order of increasing porn size-using THF 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

-60 °C from the first scan and then scanned between -60 and 230°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^{-1} were collected with a KBr disk at room temperature. The THF 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 ^{13}C NMR. High-resolution solid-state ^{13}C NMR experiments were carried out at 25 ℃ using a Bruker DSX-400 Spectrometer operating at a resonance frequency of 100.47 MHz for ^{13}C. The high-resolution solid-state ^{13}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°-τ-spin lock pulse sequence prior to CP. The data acquisition was performed at a delay time (τ) ranging from 0.1 to 12 ms with a contact time of 1.0 ms.

3.2.3 Synthesis of Tetrafunctional Initiator

The tetrafunctional initiator was synthesized as described in the previous paper by Matyjaszewski et al. [10]. Under argon, pentaerythritol tetrakis(2-bromopropionate) (4BrPr) was prepared by adding 2-bromopropionyl bromide (21.00 g, 9.90×10^{-2} mol) with 40 mL of dry CHCl$_3$ into a stirring mixture of triethylamine (10.00 g, 9.90×10^{-2} mol) and pentaerythritol (3.10 g, 2.30×10^{-3} mol) in 100 mL of dry CHCl$_3$ in an ice bath for 4 h. After complete addition of the acid bromide, the reaction flask was stirred at room temperature

overnight. The mixture was transferred to a 1 L separatory funnel with 300 mL of diethyl ether and extracted consecutively with 3×200 mL of $NaHCO_3$ and 3×200 mL of H_2O. The organic phase was dried over $MgSO_4$ and filtered and the solvent removed by rotary evaporation. The product, a white solid, was recrystallized directly from the diethyl ether phase and dried in a vacuum. (2.8 g, 18 %). ^{1}H NMR ($CDCl_3$), δ: 4.17-4.41 (m, 12H), 2.62 (s), 1.81 (d, 12H) ppm. E_{LEM}. A_{NAL}. Calcd. for $C_{17}H_{24}Br_4O_8$: C, 30.21%; H, 3.58%.

3.2.4 Polymerization Procedures

For a Typical Monofunctional tBA Polymerization. CuBr (0.39 g, 2.73×10^{-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. Acetone (10 mL) and tBA (40.00 mL, 2.70×10^{-1} mol) were added, both of which were deoxygenated and added via syringes that had been purged with nitrogen. The complexing agent, PMDETA (0.56 mL, 2.73×10^{-3} mol), was added, and the solution was stirred until the Cu complex had formed. The solution changed from cloudy and colorless to clear and light green. After complex formation, MBrP (0.61 mL, 5.50×10^{-3} mol) was added to the flask, an initial sample was removed, and the flask was placed in an oil bath thermostated at 60 °C. After 7 h, GPC analysis showed the polymer had a number-average molecular weight (M_n) = 5,000 g mol^{-1} and a polydispersity index (PDI) = 1.07.

For a Typical Four-Arm Polymerization of tBA. CuBr (1.05 g, 7.30×10^{-3} mol) and 4BrPr (2.47 g, 3.60×10^{-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 tBA (16.83 mL, 1.13×10^{-1} mol) and anisole (4 mL) via purged syringes. After 10 min, the PMDETA (1.53 mL, 7.30×10^{-3} mol) was added and the copper complex formed. The solution was brown/green and heterogeneous. The flask was placed in an oil bath thermostated at 60 °C. After 7 h, a M_n = 4,890 g mol^{-1} and a PDI = 1.06 were determined by GPC.

Purification of PtBA. A 50 mL scale reaction using the above PtBA procedure was purified by dissolving the reaction mixture in approximately 300 mL of additional acetone, washing with DOWEX MSC macroporous ion-exchange resin for about 1 h, and filtering the solution through a column of alumina. Both the resin and the alumina serve to remove the copper catalyst from the polymer. The acetone was removed by evaporation, and the polymer was then dissolved in a minimum amount of diethyl ether (~50 mL), after which it was precipitated into a 10-fold excess of a 50 water: 50 MeOH (vol %). After decanting off the solvent, the polymer was redissolved in diethyl ether, and the precipitation procedure was repeated two more times. The final polymer was dissolved in diethyl ether and transferred to a tared container, and the solvent was removed under vacuum. Three resonances were present in the ^{1}H NMR spectra (CDCl$_3$): a sharp one for the *tert*-butyl group (s, δ = 1.5 ppm) and two broad ones for the backbone protons (δ =1.85 ppm and δ= 2.35 ppm).

3.2.5 Blend Preparation

To blends of BZZ with the linear or four-arm PtBA were dissolved in THF at room temperature and stirred for 6–8 h. The solution was allowed to evaporate slowly at 25 ℃ for 1 day in an aluminum foil and dried at 60 ℃ for 1 day to ensure total elimination of the solvent. The blends were cured at 180 ℃ for 4 hours to attain a complete curing reaction. The curing reaction of benzoxazine monomers is shown in Scheme 3.1.

3.3　Results and Discussion

3.3.1 DSC Analyses

The most widely used criterion for the judgment of the miscibility behaviour of polymer blend is the existence of a single glass transition temperature (T_g). The T_g of the linear or four-arm PtBA/PBZZ blends dependence on composition is shown in Figure 3.1. Each blend showed a composition-dependent T_g, showing that these are fully miscible blends with a homogeneous amorphous phase. A single T_g of all blends higher than that of either individual polymer was observed. This large positive deviation reveals that obvious hydrogen bonding must exist between PtBA and PBZZ polymers. It has been generally suggested that the T_g relationship to the composition of the miscible polymer blends follows the Kwei equation:

$$T_g = \frac{W_1 T_{g1} + k W_2 T_{g2}}{W_1 + k W_2} + q W_1 W_2 \qquad (1)$$

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 =0.18 and q = 80 of the four-arm PtBA/PBZZ blends and k =0.18 and q = 10 of the linear PtBA/PBZZ blends were obtained from the non-linear least-squares 'best fit' values (Figure 3.2). Here q is a parameter corresponding to the strength of hydrogen-bonding in the blend, reflecting a balance between the breaking of the self-association and the forming of the inter-association hydrogen bonding. These positive q values of 80 and 10 were obtained, indicating a obvious inter-association hydrogen bonding interaction between the linear or four-arm PtBA and PBZZ. Further, the inter-association hydrogen bonding interaction of the four-arm PtBA/PBZZ blends is greater than that of the linear PtBA/PBZZ blends.

3.3.2 FT-IR Analyses

FTIR spectroscopy has been successfully applied in polymer blends possessing intermolecular interaction through hydrogen bonding. Chemical structures of PtBA and PBZZ

are shown in Scheme 3.2, containing IR carbonyl vibrations from the free and hydrogen-bonded of PtBA with PBZZ. Figure 3.3 shows the infrared spectra of the carbonyl stretching measured at room temperature ranging from 1675 to 1765 cm^{-1} for different compositions of the linear and four-arm PtBA/PBZZ blends. For the tBA unit, the IR carbonyl stretching absorptions by free and hydrogen-bonded carbonyl groups are at 1730 and 1705 cm^{-1}, respectively. It clearly shows that the fraction of hydrogen bonded carbonyl in the four-arm PtBA/PBZZ systems is greater than that of the linear PtBA/PBZZ systems as shown in Figure 3.3. By quantitative measuring the absorptivity ratio of the hydrogen bonded to the free carbonyl bands in a blend system, we can determine the fraction of hydrogen bonded carbonyl of the PtBA by using the $a_R = a_{HB}/a_F = 1.5$ [11, 12]. Through least-squares curve-fitting within the carbonyl stretching region using two Gaussian bands. The parameters of the infrared carbonyl band are summarized in Table 1, where the hydrogen bonded carbonyl fraction of the 50 linear PtBA/50 PBZZ or the 50 four-arm PtBA/50 PBZZ are the biggest. Figure 3.4 plots the fraction of hydrogen bonded carbonyl from the linear or four-arm PtBA vs. the PBZZ weight fraction of these two blend systems. The result suggests that the hydrogen bonding strength within the four-arm PtBA/PBZZ blends is stronger than the corresponding linear blends, but it is weak. Further, the hydrogen bonding of intra-association and inter-association of the pure PBZZ is greater than that of inter-association of the PtBA/PBZZ blends (Scheme 3.2).

3.3.3 Solid-state NMR Analyses

In addition FT-IR, evidence on interactions in polymer blends can also be obtained from solid-state NMR spectroscopy as demonstrated by changes in chemical shift and/or line shape. Figure 3.5 shows the selected ^{13}C CP/MAS spectra of various linear and four-arm PtBA/PBZZ blends. Peak structural assignments (see Scheme 3.2) of ^{13}C CP/MAS spectra of PtBA and PBZZ are shown in Figure 3.5. Figure 3.6 shows the carbonyl resonance of the PtBA (174 ppm) and the PBZZ C-2 resonance (127 ppm) against the PBZZ content.

According to the chemical shifts of hydroxyl (C-2) from the PBZZ in linear and four-arm PtBA/PBZZ blends, they are difficult to distinguish the difference. Nevertheless, according to the chemical shifts of the carbonyl from the PtBA, changes in four-arm PtBA/PBZZ blends are greater than those from the corresponding linear PtBA/PBZZ blends. The result suggests that the hydrogen bonding strength within the four-arm PtBA/PBZZ blends is stronger than the corresponding linear blends, but it is weak. This result is also consistent with the observed glass transition temperature difference between linear and four-arm PtBA/PBZZ blends. Further, the interaction between PBZZ and PBZZ affects the hydrogen bonding interactions between PtBA and PBZZ (Scheme 3.2).

Solid-state NMR spectroscopy has been used to better understand the phase behavior and miscibility of polymer 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}C/MAS experiments. The $T_{1\rho}^H$ values were calculated from Eq. (2).

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

where τ is the delay time used in the experiment, and M_τ is the corresponding resonance.

Figure 3.7 shows plots of $\ln(M_\tau/M_0)$ vs. τ, for the PBZZ C-2 resonance (127 ppm) at polymer 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 3.2 lists the results of the $T_{1\rho}^H$ values for the polymer blends. Composition-dependent $T_{1\rho}^H$ values are obtained for all polymer blends, suggesting that all polymer blends are heterogeneous to a scale where the spin-diffusion occurs within the time $T_{1\rho}^H$.

3.4   Conclusions

The linear and four-arm PtBA polymers were prepared by ATRP. The linear and four-arm PtBA/PBZZ blends were investigated by using DSC, FT-IR, and high-resolution solid-state ^{13}C NMR. All polymer blends have a single T_g, indicating that both the blends are homogeneous on a scale of 20-40 nm. The positive q value of the four-arm PtBA/PBZZ blends is higher than that of the linear PtBA/PBZZ blends. The fraction of the hydrogen bonded carbonyl from four-arm PtBA/PBZZ blends is greater than the linear PtBA/PBZZ blends based on FT-IR analyses, but it is weak. Further, the interaction between PBZZ and PBZZ affects the hydrogen bonding interactions between PtBA and PBZZ. Measurements of $T_{1\rho}^{H}$ reveal that all blends possess multiple composition- dependent $T_{1\rho}^{H}$ values, indicating all blends are heterogeneity on a scale smaller than 20 nm.