Hydrogen-Bonding Interactions Mediate the Phase Behavior of an A–B/C Block Copolymer/Homopolymer Blend Comprising Poly(Methyl Methacrylate-b-vinylpyrrolidone) and Poly(Vinylphenol)

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ABSTRACT: We have investigated a new type of A–B/C blend, formed between poly(methyl methacrylate-b-vinylpyrrolidone) and poly(vinylphenol) (PMMA-b-PVP/PVPh), that displays unusual phase behavior. In this blend, the PMMA (A) and PVP (B) blocks within the PMMA-b-PVP (A–B) copolymer are miscible; although PVPs (C) experiences attractive interactions \( (\xi \leq 0) \) through hydrogen bonding, with both the PVP and PMMA blocks, its interaction with the former block is significantly stronger than that with the latter \( (\xi_{BC} \gg \xi_{AC}) \). We investigated the miscibility and phase behavior of this novel A–B/C blend through the use of FTIR spectroscopy, DSC, \(^{13}\)C CP/MAS solid-state NMR spectroscopy, and TEM. The proton spin–lattice relaxation time in the rotating frame \( (T_1\rho) \), which we determined using \(^{13}\)C NMR spectroscopy, indicates that phase separation occurs for blends containing ca. 20–60 wt % PVPh. TEM images indicated clearly that the morphology of phase separation consists of a matrix of homogeneous mixed PVP/PVPh and micellar domains of excluded PMMA. This special phase behavior and miscibility is due mainly to the diversity of interactions that exist between the PMMA/PVPh and PVP/PVPh units.

Introduction

In recent years, there has been growing interest in the study of blends of diblock (A–B) copolymers mixed with homopolymers (C) because of the unusual phase behavior exhibited in such blending systems.\(^1\)\(^-\)\(^10\) Different kinds of A–B/C-type blend systems have been investigated extensively. One is the blend system comprising an immiscible A–B diblock copolymer \( (\chi_{AB} > 0) \) and a homopolymer C in which C is immiscible with block A \( (\chi_{AC} > 0) \) but interacts favorably with block B \( (\xi_{BC} \leq 0) \). Hellmann et al.\(^1\)\(^,\)\(^2\) and Kwei et al.\(^8\)\(^,\)\(^9\) have theoretically analyzed the relationships between the microphases and macrophases in a number of such blends and have compared their calculated structures with morphological observations. The other blend system comprises an immiscible A–B diblock copolymer \( (\chi_{AB} > 0) \) and a homopolymer C that is miscible with both blocks A and B; in such a system, C acts as a “nonselective polymer solvent” for both blocks A and B. The poly(styrene-b-hydroxy-styrene)/poly(vinyl methyl ether) (PS-b-PHOST/PVME) blending system is a typical example: when the PVME content is 50% or higher, it functions as a common solvent for the two blocks and results in a single phase.\(^8\) Balsara et al. also demonstrated a special A–B/C blend system of poly(ethylene-b-propylene)/polyisobutylene (PE-b-PIB),\(^10\) wherein \( \chi_{AC} \) is positive and a decreasing function of temperature, while \( \chi_{BC} \) is negative and an increasing function of temperature. These interactions lead to an order–disorder transition and macrophase separation at specific temperature range.

In this paper, we report a different A–B/C diblock copolymer/homopolymer system in which the value of \( \chi_{AB} \) is negative (A and B are miscible) and blocks A and B both experience attractive interactions (hydrogen-bonding interactions, \( \xi_{AC} \) and \( \xi_{BC} \)) with C, but \( \xi_{BC} \gg \xi_{AC} \). To investigate the miscibility and phase behavior in this blend system, we synthesized poly(methyl methacrylate-b-vinylpyrrolidone) (PMMA-b-PVP; \( M_\text{w} = \) 46,000 g/mol) and blended it with poly(vinylphenol) (PVPh). Indeed, we synthesized the PMMA-b-PVP block copolymer for the first time through a combination of atom transfer radical polymerization (ATRP) and conventional radical polymerization. Although ATRP has many advantages over other polymerization methods when used for block copolymerization, including a high tolerance toward a wide range of monomers and functional groups,\(^11\) it has not yet been applied successfully for polymerizing vinylpyrrolidone, vinyl acetate, or olefins. One approach to overcoming this limitation is to combine ATRP with conventional radical polymerization through the use of difunctional initiators.\(^12\)\(^,\)\(^13\)

We have reported previously that PVPh is totally miscible with PVP over the entire range of blend compositions because of strong hydrogen bonding between the hydroxyl groups of PVPh and the carbonyl groups of PVP.\(^14\)\(^,\)\(^15\) In addition, Zhang et al. reported that PVPh/PMMA blends are miscible because of the hydrogen-bonding interactions that exist between PVP’s hydroxyl groups and the carbonyl groups of PMMA.\(^16\)\(^,\)\(^17\) Furthermore, according to the Painter–Coleman association model,\(^18\)\(^,\)\(^19\) the interassociation equilibrium constant of the PVPh/PVP blend \( (K_\Lambda = 6000; \text{ determined from studies of a model compound})\(^20\)\(^,\)\(^21\) is significantly higher than that of the PVPh/PMMA blend \( (K_\Lambda = 37.4)\).\(^18\) This result implies that the formation of hydrogen bonds between PVP and PVPh should dominate over that between PVP and PMMA in PMMA-b-PVP/PVPh blends.

We investigated the interactions and phase behaviors of this A–B/C-type blend of PMMA-b-PVP and PVPh through the use of differential scanning calorimetry (DSC), Fourier transform infrared (FTIR) spectroscopy, high-resolution \(^{13}\)C CP/MAS NMR spectroscopy, and transmission electron microscopy (TEM). Measurements of the proton spin–lattice relaxation time in the rotating frame \( (T_1\rho) \), determined through \(^{13}\)C NMR spectroscopic analyses, indicated that phase separation exists within blends containing 20–60 wt % PVP. Transmission
electron microscopy images clearly indicated that the morphology of this phase transition consists of a matrix phase of mixed PVP and PVPh and micellar domains of excluded PMMA.

**Experimental Section**

**Materials.** All monomers were distilled from CaH₂ and stored under argon at ~30 °C. Triethylamine was also distilled from CaH₂ prior to use. CuBr was purified according to a literature procedure. All solvents were distilled prior to use. 2-Bromoisobutyric acid (98%, Aldrich), N,N,N′,N′′-pentamethyldiethylenetriamine (PMDETA; 99%, Acros), and Amberlite IR-120 (H form) cation exchange resin were used as received. Poly(vinylphenol) (PVPh; N,N′-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (98%, WAKO), N,N,N′,N′′-pentamethyldiethylenetriamine (PMDETA; 99%, Acros), and Amberlite IR-120 (H form) cation exchange resin were used as received. Poly(vinylphenol) (PVPh; N,N′-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (98%, WAKO), N,N,N′,N′′-pentamethyldiethylenetriamine (PMDETA; 99%, Acros), and Amberlite IR-120 (H form) cation exchange resin were used as received. Poly(vinylphenol) (PVPh; N,N′-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (98%, WAKO), N,N,N′,N′′-pentamethyldiethylenetriamine (PMDETA; 99%, Acros), and Amberlite IR-120 (H form) cation exchange resin were used as received. Poly(vinylphenol) (PVPh; N,N′-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (98%, WAKO), N,N,N′,N′′-pentamethyldiethylenetriamine (PMDETA; 99%, Acros), and Amberlite IR-120 (H form) cation exchange resin were used as received. Poly(vinylphenol) (PVPh; N,N′-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (98%, WAKO), N,N,N′,N′′-pentamethyldiethylenetriamine (PMDETA; 99%, Acros), and Amberlite IR-120 (H form) cation exchange resin were used as received. Poly(vinylphenol) (PVPh; N,N′-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (98%, WAKO), N,N,N′,N′′-pentamethyldiethylenetriamine (PMDETA; 99%, Acros), and Amberlite IR-120 (H form) cation exchange resin were used as received. Poly(vinylphenol) (PVPh; N,N′-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (98%, WAKO), N,N,N′,N′′-pentamethyldiethylenetriamine (PMDETA; 99%, Acros), and Amberlite IR-120 (H form) cation exchange resin were used as received.

**Synthesis of 2,2′-Azobis[2-methyl-N-(2-(2-hydroxyethyl)propionamide)] (AMBEP),** 2-Bromoisobutyryl bromide (5.63 mL, 43.4 mmol) was added dropwise over 1 h to a stirred mixture of 2,2′-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (5.00 g, 17.3 mmol) and triethylamine (6.02 mL, 43.4 mmol) in CHCl₃ (150 mL) under argon in an ice bath. The reaction was then stirred at room temperature for 3 h before being washed with water (3 × 150 mL) and dried (MgSO₄). After filtration, evaporation of CHCl₃ gave a white product, which was recrystallized from diethyl ether/ethyl acetate (3.83 g, 50.4%). 1H NMR (CDCl₃) δ: 7.18 (s, 2H), 4.32 (t, 4H), 3.67 (q, 4H), 1.90 (s, 12H), 1.35 (s, 12H).

**Synthesis of Poly(methyl methacrylate-b-vinyl pyrrolidone) Copolymer.** Block copolymers of methyl methacrylate (MMA) with N-vinyl-2-pyrrolidone (NVP) were prepared through radical polymerization using azo-PMMa as initiator [monomers-to-azo-PMMa ratio = 200:1 (mol/mol)]. The copolymerization was conducted in benzene at 90 °C reflux for 24 h under an argon atmosphere. Before vacuum drying, the PMMA-b-PVP was precipitated repeatedly from methylene chloride solution into cold diethyl ether and purified through Soxhlet extraction with THF for 24 h to remove any unreacted azo-PMMa macroinitiator. The isolated yield of purified PMMA-b-PVP copolymer was 38%.

**Blend Preparation.** Blends of various PMMA-b-PVP/PVPh compositions were prepared through solution casting. DMF solutions containing a 5 wt % polymer mixture were stirred for 6–8 h and then cast on a Teflon dish. The solution was left to evaporate slowly 80 °C for 1 day. The blend films were then dried under vacuum at 120 °C for 2 days.

**Characterization. Gel Permeation Chromatography.** Molecular weight and molecular weight distributions were determined through gel permeation chromatography (GPC) using a Waters 510 HPLC, equipped with a 410 differential refractometer, a refractive index (RI) detector, and three Ulltrastyragel columns (100, 500, and 10⁵) connected in series in order of increasing pore size, with DMF as eluent at a flow rate of 0.6 mL/min. The molecular weight calibration curve was obtained using polystyrene standards.

**Differential Scanning Calorimetry.** Thermal analyses were performed using a DuPont 910 DSC-9000 controller at a scan rate of 20 °C/min over the temperature range from 30 to 250 °C under a nitrogen atmosphere. The sample (ca. 5–10 mg) was weighed and sealed in an aluminum pan, quickly cooled to room temperature from the first scan, and then scanned between 30 and 250 °C at a scan rate of 20 °C/min. The glass transition temperature 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.

**Infrared Spectroscopy.** FTIR spectra were recorded using a Nicolet Avatar 320 FTIR spectrometer and NaCl disks; 32 scans were collected at a resolution of 1 cm⁻¹. The DMF solution containing the sample was cast onto a NaCl disk and dried under conditions similar to those used in the bulk preparation. The sample chamber was purged with nitrogen to maintain film dryness.

**Solid-State NMR Spectroscopy.** High-resolution solid-state ¹³C NMR spectroscopy experiments were performed at 25 °C using a Bruker DSX-400 spectrometer operating at a resonance frequency of 100.47 MHz. High-resolution solid state ¹³C NMR spectra were acquired using the magic-angle spinning (MAS)/high-power dipolar decoupling (DD) technique, with a 90 °C pulse width of 3.9 μs, a pulse delay time of 3 s, an acquisition time of 30 ms, and 2048 scans. 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 (T₁(p)) was determined indirectly via carbon observation using a 90 °C r-spin lock pulse sequence prior to CP. The data acquisition was performed at delay times (τ) ranging from 0.1 to 12 ms with a contact time of 1.0 ms.
Transmission Electron Microscopy. TEM analysis was performed using a Hitachi H-7500 electron microscope operated at 100 kV. Ultrathin sections of the samples were prepared using a Leica Ultracut UCT microtome equipped with a diamond knife. Slices of ca. 700 Å thickness were cut at room temperature. Some of the sliced samples were stained with the vapor from an aqueous solution of RuO4. The contrast between poly(methyl methacrylate) and the two other polymers increased in these samples because poly(methyl methacrylate) is selectively unstained.

Results and Discussion

Block Copolymer Characterization. PMMA-b-PVP diblock copolymer was synthesized as indicated in Scheme 1. The molecular weight distribution of the block copolymer, as measured using GPC (Figure 1), indicates that the value of \( M_d / M_n \) of PMMA was 1.26; the polydispersity of the block copolymer of methyl methacrylate and vinylpyrrolidone was 1.53. The number-average molecular weight of the PMMA block was 21,000 g/mol, and that of the block copolymer was 46,000 g/mol. Parts a and b of Figure 2 display the \(^1\)H NMR spectra of the azo-PMMA macroinitiator and block copolymer. The latter spectrum features peaks that are characteristic of the resonances of both the PMMA and PVP blocks. The DSC analyses of the azo-PMMA macroinitiator and the PMMA-b-PVP copolymer were also conducted for thermal characterization. The value of \( T_g \) of azo-PMMA is 106 °C. Only one glass transition for the PMMA-b-PVP diblock copolymer was observed at 130 °C, indicating that the diblock copolymer is miscible between PMMA and PVP, which is in agreement with results reported in the literature.\(^{23,24}\)

Blends of PMMA-b-PVP and PVPh. Fourier Transform Infrared Spectroscopic Analyses. Scheme 2 summarizes the signals observed for the free and hydrogen-bonded hydroxyl and carbonyl vibrations in the IR spectra of both PMMA and PVP mixed with PVPh. Figure 3 displays the FTIR spectra, recorded at room temperature in the region 2700–4000 cm\(^{-1}\) (OH stretching), of PVPh and various PMMA-b-PVP/PVPh blends; the OH stretching signals of PMMA/PVPh (50/50) and PVP/PVPh (50/50) blends are also included for comparison. Under ambient conditions, the pure PVPh self-associated through the formation of intermolecular hydroxyl multimers. As indicated in Figure 3i, the hydroxyl band of the pure PVPh consists of two components: a relatively narrow band at 3525 cm\(^{-1}\) from the free hydroxyl groups and a broad band centered at 3360 cm\(^{-1}\) representing a wide distribution of hydrogen-bonded hydroxyl groups. Here, we focus on the variation of hydrogen-bonded hydroxyl groups. The hydroxyl groups of PVPh that form hydrogen bonds with PVP and PMMA underwent frequency shifts to 3250 cm\(^{-1}\) (Figure 3a) and 3390 cm\(^{-1}\) (Figure 3j), respectively. From parts b–h of Figure 3, we observe in general that the hydroxyl groups of PVPh form hydrogen bonds with PVP more preferentially at lower PVPh content (i.e., the signal of the hydrogen-bonded hydroxyl groups appears mainly at 3250 cm\(^{-1}\)). At higher PVPh contents, the hydroxyl groups of PVPh also form hydrogen bonds with the PMMA blocks (i.e., the signal of the hydrogen-bonded hydroxyl groups broadens).

Figure 4 presents FTIR spectra of the carbonyl stretching region, ranging from 1630 to 1780 cm\(^{-1}\), of PMMA-b-PVP and its blends at room temperature. Two types of signals for carbonyl...
stretching appear for the pure PMMA-

b-PVP: the amide carbonyl stretching band of the PVP at 1680 cm$^{-1}$ and the carbonyl stretching band of PMMA at 1730 cm$^{-1}$. When the PVPh content in the blend is increased, a new band appears at 1660 cm$^{-1}$, reflecting the presence of intermolecular hydrogen bonding between the PVP and PVPh units. In contrast, no peak shifting and no new peaks developed for PMMA carbonyl group stretching in these blends containing a PVPh content below 60 wt %; this result implies that the PMMA carbonyl groups interact only insignificantly with PVPh when the PVPh content is less than 60 wt %.

Table 1 summarizes all of these curve fitting results, i.e., the fraction of hydrogen-bonded carbonyl groups of PVP and PMMA as a function of PVPh content.

It is clear that the PVPh hydroxyl groups begin to form hydrogen bonds with PMMA when the PVPh content is greater than 60 wt %.

These FTIR spectra are consistent with the predictions made using the Painter–Coleman association model (PCAM). According to the PCAM, the interassociation equilibrium constant of the PVPh/PVP blend ($K_A = 6000$ determined using a model compound) is significantly greater than that of the PVPh/PMMA blend ($K_A = 37.4$). The FTIR spectra confirm the tendency predicted by the PCAM, i.e., that the hydrogen bond formation between PVP and PVPh predominates over that between PVPh and PMMA in the PMMA-

b-PVP/PVPh blends.

Thermal Analyses. Figure 5 displays DSC thermograms of PMMA-

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of the glass transition temperature \(T_g\) of PVPh is 150 °C (0/100); the PMMA-b-PVP block copolymer has only one glass transition, at 130 °C (100/0). For PMMA-b-PVP/PVPh blends, each composition exhibits a single glass transition, indicating that blends of these compositions are macroscopically miscible, except for the blend containing 50 wt % of PVPh, for which we observed two glass transitions. The lower one, at ca. 110 °C, can be assigned as reflecting a PMMA phase that had separated from the mixed phase of miscible PVP and PVPh. Presumably, this phenomenon results from the more favored formation of hydrogen bonds between PVP and PVPh than between PMMA and PVPh, as the FTIR spectra revealed.

Figure 6 displays the dependence of the value of \(T_g\) on the composition of the blends. We observed that the values of \(T_g\) were all higher than those of the individual polymers; large positive deviations indicate that strong interactions exist within the blends. The typical Fox and Gordon—Taylor equations are not suitable for describing this complicated blend system (data not shown here). Actually, the behavior of the values of \(T_g\) of PMMA/PVPh and PVP/PVPh has been reported based on the linear rule (Figure 6d)\(^2\)\(^5\)\(^6\) models, respectively. Kim et al. recently proposed\(^2\)\(^7\) the configurational entropy model to predict the glass transition behavior of polymer blends that feature specific interactions between the components:

\[
\ln\left(\frac{T_g^{12}}{T_g^1}\right) = \frac{\beta \left(1 - \gamma_{\text{spe}} \ln\left(\frac{z-1}{e}\right)\right)}{\frac{1}{R_1} \ln \phi_1 + \frac{1}{R_2} \ln \phi_2} + \frac{1}{\phi_1} \ln \left(\frac{T_g^2}{T_g^1}\right)
\]  

(1)

where \(T_g^1, T_g^2, \text{ and } T_g^{12}\) are the values of \(T_g\) of the pure polymers 1 and 2 and of their blend, respectively; \(\phi_i, R_1, \text{ and } R_2\) are the volume fraction and degree of polymerization, respectively, of polymer \(i; z\) is the lattice coordination number, \(\beta = zR(M_u \Delta C_p)\), where \(R, M_u, \text{ and } \Delta C_p\) are the gas constant, the molecular weight of the repeat unit, and the isobaric specific interaction of polymer 1, respectively; \(\gamma_{\text{spe}}\) is a proportionality constant representing the specific interactions, such as hydrogen-bonding, dipole—dipole, or ionic interactions, between the two polymers. Kim et al. reported a value of \(\gamma_{\text{spe}}\) of 288.1 for blends of PVP and PVPh, but this value is not appropriate for use with PMMA-PVP/PVPh blends, as indicated in Figure 6. A value of \(\gamma_{\text{spe}}\) of 900 fits well at relatively lower PVPh contents (<20 wt %), but increased deviation occurs between the predicted and experimental data upon increasing the PVPh content. At lower PVPh contents (<20 wt %), the value of \(T_g\) increased significantly, presumably because of nanoconfinement of PVP/PVPh with a PMMA corona phase as a result of hydrogen bonding predominantly between PVP and PVPh (Scheme 3). Upon further increasing the PVPh content (<60 wt %), segregation transition of the PMMA domain occurred to further reduce the value of \(T_g\). Total miscibility on the macro- and microscales is expected at relatively higher PVPh contents (e.g., 80 wt %), i.e., a mixed phase of miscible PMMA, PVP, and PVPh, because the hydroxyl groups of PVPh also interact with the carbonyl groups of PMMA, as evidenced from FTIR spectroscopic analyses. As a result, the value of \(T_g\) at this composition can be predicted well using a combination of the linear rule of PMMA/PVPh (Figure 6d) and the entropy configurational model of PVP/PVPh.

**Figure 6.** Plots of \(T_g\) vs composition based on (●) experimental data and (a, b) the entropy configuration models of PVP/PVPh with (a) \(\gamma_{\text{spe}} = 900\) and (b) \(\gamma_{\text{spe}} = 288\), (c) a combination of (b) and (d) for PMMA-b-PVP/PVPh, and (d) the linear rule of PMMA/PVPh.

**Figure 7.** \(^{13}\)C CP/MAS spectra recorded at room temperature for PMMA-b-PVP/PVPh blends of different compositions (weight ratios).
PVPh with a value of $\gamma_{\text{spe}}$ of 288.1 (Figure 6b), as indicated in Figure 6c.

These DSC results suggest that phase transition occurs because PMMA is a significantly weaker hydrogen bond acceptor than is PVP. Added PVPh preferentially forms hydrogen bonds with PVP, rather than with PMMA, and thus, the PMMA blocks are excluded from the PVP/PVPh phase. To further investigate this phase behavior in detail, we measured the spin–lattice relaxation times ($T_1$) in the rotating frame to examine the homogeneity of the PMMA-b-PVP/PVPh blends on the molecular scale (i.e., below 20 nm).

$^{13}$C CP/MAS Spectroscopic Analyses. Solid-state NMR spectroscopy is often used to better understand the phase behavior and interactions within polymer blends. Figure 7 displays the $^{13}$C CP/MAS spectra of pure PVPh, PMMA-b-PVP, and PMMA-b-PVP/PVPh blends at various compositions. The signal for the resonance of the phenolic carbon atom of PVPh at 153 ppm underwent a gradual downfield shift upon blending with PMMA-b-PVP. The shift was ca. 2.5 ppm for a blend containing 80 wt % PMMA-b-PVP, indicating that specific interactions exist between PVPh and the block copolymer; this finding is consistent with the results of our FTIR spectroscopic analyses.

As we discussed earlier, our DSC analyses revealed that phase separation occurred for the 50/50 PMMA-b-PVP/PVPh blend on a scale of ca. 20–40 nm; we chose to study, through measurement of proton spin–lattice relaxation times in the rotating frame ($T_1\rho^H$), whether phase separation also occurred for other compositions on an even smaller scale (<20 nm). We measured the values of $T_1\rho^H$ of the blends through delayed-contact $^{13}$C CP/MAS experiments, using eq 2:

$$\ln(M_t/M_0) = -\tau/T_1\rho^H$$

where $\tau$ is the spin-lock time used in the experiment, and $M_0$ and $M_t$ are the intensities of the peaks initially and at time $\tau$, respectively. Parts a–f of Figure 8 present the values of $\ln(M_t/M_0)$ plotted against $\tau$. We estimated the homogeneities of these polymer blends through quantitative analyses based on the PMMA-b-PVP carbonyl carbon atom's resonance at 177 ppm (Figure 8a–c) and the PVPh phenolic carbon atom's resonance at 153 ppm (Figure 8d–f). We obtained single-exponential decays in $T_1\rho^H$ for pure PMMA-b-PVP, the 20/80 PMMA-b-PVP/PVPh blend, and pure PVPh (Figure 8a, c, e, and f), suggesting that the block copolymer, the 20/80 PMMA-b-PVP/PVPh blend, and PVPh are homogeneous on the scale at which spin diffusion occurs within the time $T_1\rho^H$. In contrast, the $T_1\rho^H$ decays of the carbonyl and phenolic carbon atoms’ resonance of the 80/20 PMMA-b-PVP/PVPh blend were not single-exponential (Figure 8b and d); in addition to a main decay, there also exists a slow decaying component, indicating that two domains, with distinct mobilities, were present in this blend on a scale below 20 nm.

From the slopes of fitted lines, we determined the values of $T_1\rho^H$, which are listed in Table 2, for various compositions of PMMA-b-PVP/PVPh blends. Blends containing less than 10 wt % of PVPh display homogeneous single-exponential behavior. When the PVPh content increases to 20 wt %, nonexponential
60 wt % of PVPh was present in the blend, segregation transition exhibits good miscibility between its two blocks. When ca. 20–60 wt % of these PMMA-PMMA-PVP/PVPh blends. Pure PMMA-PMMA-PVP/PVPh blend contained ca. 20–60 wt % because hydrogen bonds began to form between the PMMA and PVPh units (from Table 1).

Figure 9. Transmission electron micrograph of the solution-cast film of the 70/30 (wt %) PMMA-PMMA-PVP/PVPh blend stained with RuO₄. The dark region (matrix) corresponds to a mixed phase of PMMA and PVPh; the white region (micelles) corresponds to excluded PMMA.

Conclusions
We have investigated the phase behavior, mediated by hydrogen-bonding interactions, of novel A–B/C-type PMMA-PMMA-PVP/PVPh blends. We synthesized the PMMA-PMMA-PVP copolymer by combining atom transfer radical polymerization with conventional radical polymerization. FTIR spectra provided evidence that the PVP carbonyl groups are significantly stronger hydrogen bond acceptors than are the PMMA carbonyl groups. Furthermore, DSC revealed that phase transition existed in this A–B/C blend system. FTIR and ¹³C CP/MAS NMR spectra provided additional evidence confirming that phase transition occurred for the blends containing ca. 20–60 wt % of PVP/PVPh. TEM imaging clearly indicated that the morphology of the segregation transition consisted of a matrix of a homogeneous mixed PMMA-PVP/PVPh phase and micellar domains of excluded PMMA. The blends became homogeneous again when the PVP/PVPh content was greater than 60 wt % because hydrogen bonds also formed between the PMMA and PVPh units. In conclusion, the diversity of attractive interactions (Δ) between the PMMA and PVPh and the PVP and PVPh moieties appears to be a major factor influencing the phase behavior of this A–B/C blend system.

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