

# Reexamination of the Miscibility of Stereoregular Poly(methyl methacrylate) with Poly(vinyl phenol)

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**ABSTRACT:** Previously, isotactic, atactic, and syndiotactic poly(methyl methacrylates) (PMMA) (designated as iPMMA, aPMMA, and sPMMA) were mixed with poly(vinyl phenol) (PVPh) separately in tetrahydrofuran (THF) to make three polymer blend systems. According to calorimetry data, iPMMA was found to be miscible with PVPh; however, partial miscibility or immiscibility was found between aPMMA (or sPMMA) and PVPh. According to the article by C. J. T. Landry and D. M. Teegarden, *Macromolecules*, 1991, 24, 4310, THF is the reason for causing aPMMA and PVPh to phase separate, but 2-butanone instead produces miscible blends. Therefore, in this article these three polymer systems were investigated again using 2-butanone as solvent. Films were prepared under specific conditions to minimize the effect of aggregation in PMMA. The formation of hydrogen bonding between PMMA and PVPh and the attendant changes in the aggregation of PMMA segments were determined in the solid states by means of FTIR. Based on the results of calorimetry, iPMMA and aPMMA were found to be miscible with PVPh. For iPMMA/PVPh blends, different degrees of hydrogen bonding were observed based on DSC data and FTIR spectra when compared to previous study. An elevation of the glass transition temperatures ( $T_g$ s) of aPMMA/PVPh blends above weight average was detected and the  $T_g$  values were fitted well by the Kwei equation. But partial miscibility was still found between sPMMA and PVPh on account of the observation of two  $T_g$ s in most compositions. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1425–1431, 2002

**Key words:** polymer blends; stereoregular; PMMA; PVPh

## INTRODUCTION

It has been known for years that the stereoregularity of polymer chains influences polymer–polymer miscibility. Because of its availability in both syndiotactic and isotactic forms, poly(methyl methacrylate) (PMMA) has been frequently used

in investigations of the effect of tacticity on miscibility. Several articles<sup>1–8</sup> have shown that the tacticity of PMMA influences blend compatibility when PMMA is blended with a chemically different polymer. Because of differences in the molecular weights and preparation methods of samples, the results are sometimes not consistent. Because atactic PMMA (aPMMA) is mainly syndiotactic, the results of aPMMA and syndiotactic PMMA (sPMMA) are often similar.

The miscibility between dissimilar polymers can be enhanced by favorable intermolecular interactions. Among the various secondary interaction forces commonly encountered, hydrogen

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bonding has been the subject of many investigations.<sup>9</sup>

In a previous investigation,<sup>10</sup> isotactic PMMA (iPMMA), aPMMA, and sPMMA were blended with poly(vinyl phenol) (PVPh) in tetrahydrofuran (THF) to make three polymer blend systems. All the films were transparent after preparation. iPMMA was found to be more miscible with PVPh than aPMMA or sPMMA. The results were corroborated by glass-transition temperature ( $T_g$ ) measurements and Fourier transform infrared (FTIR) spectra. There is a single  $T_g$  for each composition in the blends of iPMMA and PVPh. Therefore, iPMMA forms miscible blends with PVPh. However, there are two  $T_g$ 's for one composition of aPMMA/PVPh or sPMMA/PVPh blends. Therefore, partially miscible blends are formed between aPMMA (or sPMMA) and PVPh. Also from FTIR spectra, the degree of hydrogen bonding of iPMMA with PVPh is the highest among these three blends. Similar results were reported by Dong and Ozaki.<sup>11</sup> They investigated the miscibility of aPMMA and PVPh with FTIR and Fourier transform Raman spectroscopy. Although both techniques provide evidence for the formation of hydrogen bonds between the hydroxyl groups of PVPh and the ester groups of aPMMA, the blends show only a limited degree of hydrogen-bonding interactions when cast from THF solutions. A comparison of the blends with those cast from a ketone solution and changes in the hydrogen-bonded fractions after thermal cycles indicate that the blends are partially miscible mixtures. However, with prolonged heating above  $T_g$  of aPMMA and PVPh, the blends gradually approach the complete miscibility predicted by an association model.<sup>9</sup>

Moreover, according to Landry and Teegarden,<sup>12</sup> when aPMMA and PVPh were cast from THF, a phase-separated mixture was obtained. However, when aPMMA and PVPh were prepared by melt mixing or cast from 2-butanone, they were found to be miscible. This research was motivated by the results of refs. 11 and 12. Reexamining the miscibility of stereoregular PMMA and PVPh was, therefore, pursued in this laboratory.

In this study, iPMMA, aPMMA, and sPMMA with almost the same molecular weights were blended with PVPh in 2-butanone to be cast into films.  $T_g$ 's of the polymers were measured calorimetrically, and FTIR spectra of the polymers were made so that the degree of hydrogen bonding could be studied between different tactic PM-

MA and PVPh. In this article, the miscibility of the prepared blends is investigated on the basis of the  $T_g$  data. A discussion of the connection between the degree of hydrogen bonding, miscibility, and  $T_g$  is also included.

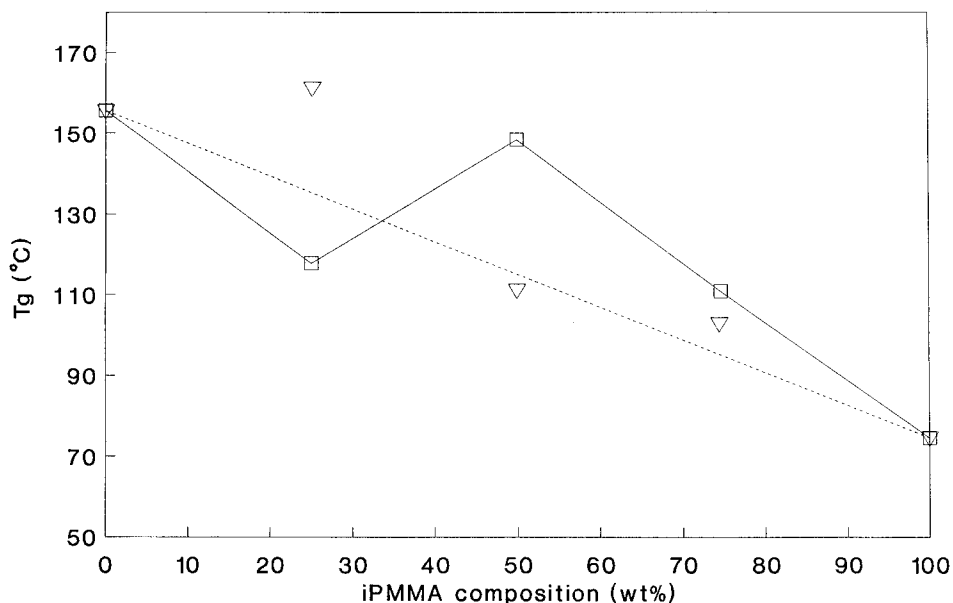
## EXPERIMENTAL

### Materials and Film Preparation

iPMMA, aPMMA, and sPMMA were purchased from Polysciences, Inc. (Warrington, PA). According to the supplier information, the weight-average molecular weights ( $M_w$ 's) of the iPMMA, aPMMA, and sPMMA were the same, about 100,000 g/mol.  $M_w$  of PVPh was about 30,000 g/mol.

The polydispersities (weight-average molecular weight/number-average molecular weight) of the three PMMAs were not measured and, therefore, are not reported here. However, the molecular weight distribution effect is believed to have been minimal in this study in comparison with the effect of tacticity. We did not characterize the tacticity of PMMA by NMR. Therefore, a simple estimation of the fractions of meso (m) and racemic (r) diads was employed. The meso diad fractions of PMMA were previously computed.<sup>13</sup> The m and r fractions of iPMMA, aPMMA, and sPMMA were 68.7 and 31.3%, 33.8 and 66.2%, and 9.3 and 90.7%, respectively. The error of estimation was 5–8%. The validity of the estimation was proven by a comparison of the m and r fractions of aPMMA with Li and Brisson's data.<sup>14</sup> They used the same molecular weight aPMMA from Polysciences. In their report, they characterized the tacticity of aPMMA to be 16% isotactic, 45% heterotactic, and 39% syndiotactic. When converted to m and r fractions, the m fraction percentage was  $16 + 45/2 = 38.5$ , and the r fraction percentage was  $36 + 45/2 = 61.5$ . Our computed m and r values (33.8 and 66.5%) are in agreement with theirs within the error of estimation.

Thin films of individual polymers and their blends were made by solution casting onto glass plates. 2-Butanone was used as a solvent for most compositions, but for PMMA toluene was used instead. 2-Butanone and toluene were American Chemical Society reagents purchased from Aldrich Chemical Company, Inc. (Milwaukee, WI) and Fisher Scientific (Fair Lawn, NJ), respectively. For blends, PVPh was mixed with each



**Figure 1**  $T_g$ 's of iPMMA/PVPh blends with the cast solvents (□) 2-butanone and (▽) THF.

tactic PMMA in weight ratios of about 1/3, 1/1, and 3/1. The final drying step for all the films took place in a vacuum oven for about 1 day at 92–128°C. Then, the films were cooled down to room temperature slowly in air. The as-cast films were later used for differential scanning calorimetry (DSC) and FTIR studies.

#### DSC and FTIR Spectroscopy

$T_g$ 's of the polymer blends were determined with a DuPont 2000 thermal analyzer (Dupont [through the agency of Lih Yuan Enterprise Co., Ltd., Taiwan]) coupled to a mechanical cooling system. The scanning range was 30–200°C, and a heating rate of 20°C/min was used in every measurement. The experiments were performed in two consecutive scans in the ambient environment of nitrogen gas at a flow rate of about 90–110 mL/min. In the first thermal scan, the samples remained at 200°C for 1 min. Then, the samples were cooled to 30°C with a cooling rate of 20°C/min. The inflection point of the specific heat jump of the second thermal scan was taken to be  $T_g$ . The cooling rate was proven to be fast enough to produce virtually the same results as quenching.

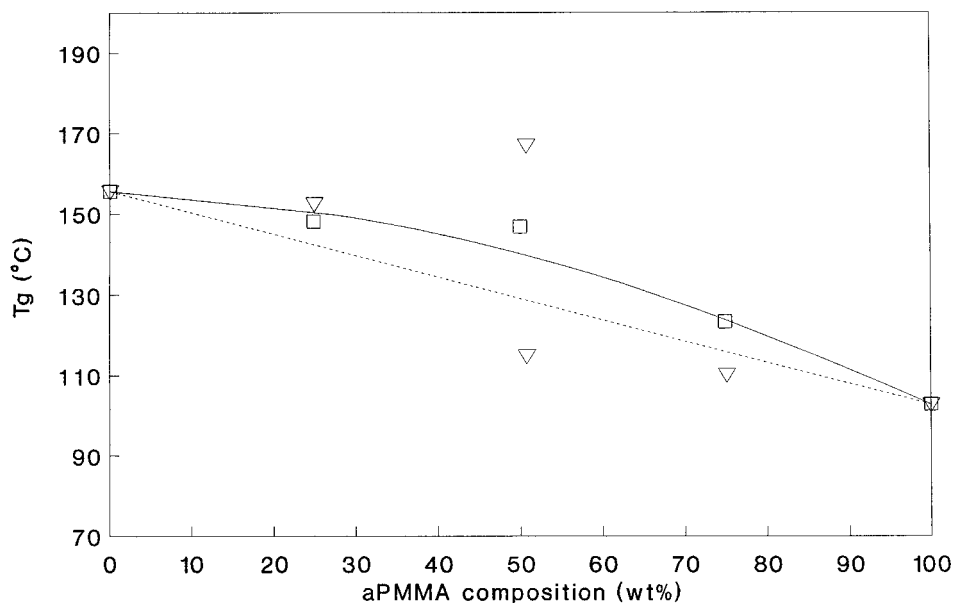
The as-cast polymers were ground with KBr powder to make samples for FTIR studies, and some films were cast directly onto KBr windows and subjected to thermal treatments similar to

those used for the DSC samples. Spectra were obtained with 64 scans at a resolution of 4  $\text{cm}^{-1}$  at room temperature. The wave-number range was 400–4000  $\text{cm}^{-1}$ .

## RESULTS AND DISCUSSION

### $T_g$

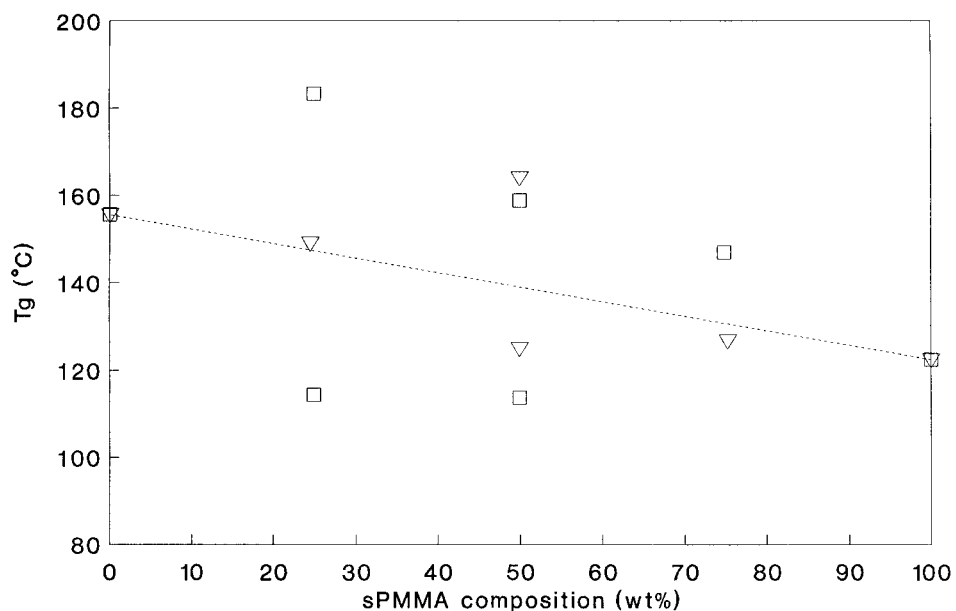
For brevity, the thermal scans of the three polymer blends are not shown. All the  $T_g$  values of the three polymer blends versus the PVPh composition are shown in Figures 1–3 for iPMMA, aPMMA, and sPMMA, respectively. Previous results<sup>10</sup> for the same system cast from THF are also included and are shown in Figures 1–3 for comparison. The dashed lines in all three figures represent weight-average predictions. As plotted in Figure 1, each iPMMA/PVPh blend cast from either 2-butanone or THF shows a single  $T_g$ , indicating that iPMMA forms miscible mixtures with PVPh. However, the degree of hydrogen bonding between iPMMA and PVPh (reflected approximately by the difference between  $T_g$  and the weight average) is not always the same for either solvent-cast blend. The degree of hydrogen bonding in the 75/25 iPMMA/PVPh blend is about the same, regardless of the cast solvent. As for the 50/50 iPMMA/PVPh blends, the 2-butanone-cast



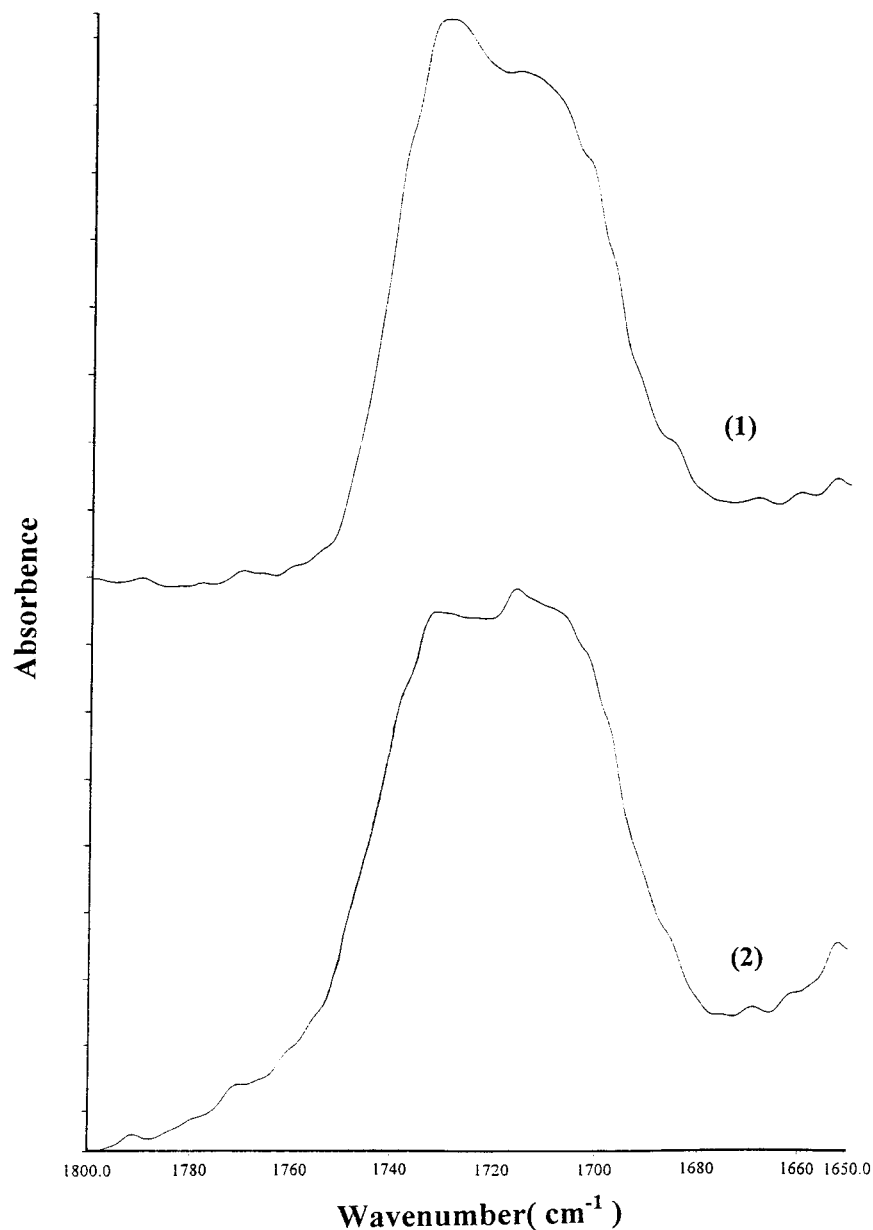
**Figure 2**  $T_g$ 's of aPMMA/PVPh blends with the cast solvents (□) 2-butanone [(—) Kwei equation with  $q = 49.0$ ] and (▽) THF.

blend has a higher  $T_g$  than the THF-cast blend, indicating a higher degree of hydrogen bonding. However, the opposite is true for the 25/75 iPMMA/PVPh blend. The THF-cast blend has a higher degree of hydrogen bonding than the 2-butanone blend according to the observation of a higher  $T_g$ . Figure 2 shows the  $T_g$  values of

aPMMA/PVPh blends. Previous THF-cast results show immiscibility in the 50/50 aPMMA/PVPh blend. This study (with 2-butanone as the solvent) shows that aPMMA forms miscible blends with PVPh for all the studied compositions. Except for the 50/50 aPMMA/PVPh blend, the results from the two solvents are about the same.



**Figure 3**  $T_g$ 's of sPMMA/PVPh blends with the cast solvents (□) 2-butanone and (▽) THF.



**Figure 4** FTIR spectra of 25/75 sPMMA/PVPh blends that were (1) THF-cast and (2) 2-butanone-cast.

An elevation of  $T_g$  (i.e., above the additivity rule) was observed because of hydrogen bonding that occurred between aPMMA and PVPh in 2-butanone-cast blends. Several empirical equations have been proposed to describe the composition dependence of miscible blends that involve strong specific interactions. Three articles<sup>15–17</sup> offer theoretical insight into the underlying reason for the experimental observations. In the limiting case, these equations reduce to a simple expression:<sup>18</sup>

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

where  $W_1$  and  $W_2$  denote the weight fractions of components 1 and 2, respectively;  $T_g$ ,  $T_{g1}$ , and  $T_{g2}$  are the glass-transition temperatures of a blend and polymers 1 and 2, respectively; and  $q$  is a parameter that depends on the net polymer–polymer interaction (i.e., hydrogen bonding in this article). The following results were obtained from the fitting of  $T_g$  values of miscible aPMMA/PVPh blends in Figure 2 with eq. (1). The  $q$  value was

estimated to be 49.0, larger than the  $q$  value of 17.0 in aPMMA/poly(styrene-*co-p*-hydroxystyrene) blends.<sup>13</sup> In ref. 13, a copolymer of styrene and hydroxystyrene (i.e., vinyl phenol) containing 15 mol % vinyl phenol (the copolymer abbreviated as PHS-15) was used for blending with aPMMA instead. The reason for the larger  $q$  value observed in PVPh blends than in PHS-15 blends is obviously the greater availability of OH groups in PVPh segments.

Figure 3 shows the results for sPMMA/PVPh blends. For 2-butanone-cast blends, only one composition has a single  $T_g$ , and the other two compositions show two  $T_g$ 's, indicating partial miscibility or immiscibility. However, for the THF-cast blends, one composition is not miscible, and the rest are miscible. For blends with about 50 or 75% sPMMA, the data from the two solvents are not so different, and the difference is only in the degree of hydrogen bonding. However, a large difference was observed in the blends with 25% sPMMA. The THF-cast blend is miscible, but the 2-butanone-cast blend is not miscible. The reason for this is the greater difference in the degree of hydrogen bonding after casting.

### Solvent Effects

The observation of phase separation in the THF-cast aPMMA/PVPh blend and probably the sPMMA/PVPh blend is due to so-called solvent effects. The solvent effects on the miscibility and morphology of polymer blends have been studied for several polymer blend systems, such as polystyrene/poly(vinyl methyl ether).<sup>19</sup> However, most investigations have focused on blends in which strong specific intermolecular interactions were scarcely involved. For such solvent-cast blends, it may be assumed that the different mobility is related to changes in the solvent-polymer interaction parameters ( $\Delta\chi$ ). For a solvent with a high  $\Delta\chi$  value ( $\Delta\chi = |\chi_{12} - \chi_{13}|$ , where  $\chi_{12}$  and  $\chi_{13}$  are solvent-polymer interaction parameters of the two constituent homopolymers), poor miscibility is observed, and vice versa. Therefore, it is appropriate to choose a solvent in which the two polymers have nearly the same solvent-polymer interaction parameters. It seems that little has been reported on the effects of solvents on the phase-separation dynamics and morphology of solvent-cast blends with strong specific intermolecular interactions.<sup>12</sup> Light scattering methods have been used for monitoring the phase-separation process during solvent evaporation of poly-

mer A/polymer B/solvent ternary systems,<sup>20,21</sup> but investigations have been restricted to polymers without specific interactions. When 2-butanone is used instead of THF, aPMMA/PVPh blends turn out to be miscible; however, partial miscibility is still found between sPMMA and PVPh. In summary, although the presence of an intermolecular hydrogen-bond structure in PMMA/PVPh blends supplies a possibility of miscibility, other factors, such as solvent properties and polymer tacticity, may also affect the phase structure of the blends obtained.

### Connection Between $T_g$ and FTIR Spectra

Although not shown, the effect of self-aggregation of iPMMA or sPMMA in the blends is believed to be minimal on the basis of IR spectra. Because our focus is on the connection between  $T_g$  and the degree of hydrogen bonding only, the IR spectra in the carbonyl absorption regions are presented. The 25/75 sPMMA/PVPh blends are used as examples for demonstrating that the differences in the  $T_g$ 's of the blends prepared from different solvents are due to different degrees of intermolecular hydrogen bonding. The results are shown in Figure 4. Recall that the 2-butanone-cast blend has two  $T_g$ 's, but the THF-cast blend has one  $T_g$  (as presented in Fig. 3). It is not surprising that when sPMMA is blended with PVPh in a 1/3 weight ratio from 2-butanone, the prepared blends have a lower degree of intermolecular hydrogen bonding than those cast from THF. This low degree of hydrogen bonding in the 2-butanone-cast 25/75 sPMMA/PVPh blends causes phase separation, as detected in the DSC scan. Similarly, according to IR spectra (not shown here), a lower fraction of hydrogen-bonded carbonyl groups are detected in the 2-butanone-cast 25/75 iPMMA/PVPh blend in comparison with the THF-cast blend. However, miscibility is still maintained at this blend according to the calorimetry data.

### CONCLUSIONS

On the basis of calorimetry data, iPMMA and aPMMA are miscible with PVPh when cast from 2-butanone. However, there is partial miscibility between sPMMA and PVPh. According to a comparison with the results of a previous study that used THF as a solvent, 2-butanone is a better choice for making aPMMA/PVPh blends miscible.

$T_g$ 's of aPMMA/PVPh blends are fitted well by the Kwei equation with a  $q$  value of 49.0, indicating strong intermolecular hydrogen bonding. With the help of IR spectra, the effect of hydrogen bonding is clearly demonstrated to be the driving force for the observed miscibility in the studied blends. In summary, although the presence of an intermolecular hydrogen-bond structure in PMMA/PVPh blends supplies a possibility of miscibility, other factors, such as solvent properties, polymer tacticity, and self-aggregation of polymer, may also affect the phase structure of the blends obtained.

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