

Effect of Tacticity of Poly(methyl methacrylate) on the Miscibility with Poly(vinyl pyrrolidone)

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ABSTRACT: Isotactic, atactic, and syndiotactic poly(methyl methacrylates) (PMMA) (designated iPMMA, aPMMA, and sPMMA) with approximately the same molecular weight were mixed separately with poly(vinyl pyrrolidone) (PVP) primarily in chloroform to make three polymer blend systems. Differential scanning calorimetry (DSC) was used to study the miscibility of these blends. The results showed that the tacticity of PMMA has a definite impact on its miscibility with PVP. The aPMMA/PVP and sPMMA/PVP blends were found to be miscible because all the prepared films showed composition-dependent glass-transition temperatures (T_g). The glass-transition temperatures of the aPMMA/PVP blends are equal to or lower than weight average and can be qualitatively described by the Gordon–Taylor equation. The glass-transition temperatures of the other miscible blends (i.e., sPMMA/PVP blends) are mostly higher than weight average and can be approximately fitted by the simplified Kwei equation. The iPMMA/PVP blends were found to be immiscible or partially miscible based on the observation of two glass-transition temperatures. The immiscibility is probably attributable to a stronger interaction among isotactic MMA segments because its ordination and molecular packing contribute to form a rigid domain. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 3190–3197, 2001

Key words: tacticity; poly(methyl methacrylate); poly(vinyl pyrrolidone); miscibility

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 frequently been used in the investigation of the effect of tacticity on miscibility. Several articles^{1–8} 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 the preparation methods of the samples, the results sometimes are not consistent. Since atactic PMMA is mainly syndiotactic, results for atactic material are often similar to syndiotactic material.

Most previous studies^{1–8} concentrated on a few blends, such as poly(vinylidene fluoride) (PVDF), poly(ethylene oxide) (PEO), and poly(vinyl chloride) (PVC) with stereoregular PMMA. However, few studies focused on other polymers blended with stereoregular PMMA. Recently, da Silva and Tavares⁹ investigated the behavior of poly(methyl methacrylate)/poly(vinyl pyrrolidone) (PMMA/PVP) blends by solid-state nuclear magnetic resonance (NMR), using proton spin-lattice relaxation time in the ro-

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tating frame ($T_{1\rho}^H$). Based on their observation, miscibility was detected for all the proportions studied as a consequence of the interaction process of blend components.

Poly(vinyl pyrrolidone) (PVP) is a water-soluble tertiary amide and a strong Lewis base. As a result, it is susceptible to the formation of hydrogen bonds with substances containing hydrogen donor groups. It has been shown to form a large number of polymers, such as poly(vinyl chloride) and poly(epichlorohydrin),¹⁰ poly(vinyl fluoride),¹¹ poly(2-hydroxyethyl methacrylate),¹² poly(hydroxy ether of bisphenol A),¹³ and poly(vinyl phenol).¹⁴ Not surprisingly, PMMA has been shown to be miscible or partially miscible with those polymers aforementioned miscible with PVP.

We were motivated by the results of da Silva et al.⁹ and also, to our knowledge, there have been no reports of the tacticity effect of PMMA on miscibility with PVP. On the basis of their results,⁹ it is concluded that aPMMA is miscible with PVP. Although da Silva et al. did not specify the tacticity of PMMA, commercial PMMA is often considered to be atactic. Therefore, a systematic study of the effect of tacticity of PMMA on its miscibility with PVP is worthwhile and was pursued in our laboratory.

In this article, isotactic, atactic, and syndiotactic PMMA with approximately the same molecular weight, were blended with PVP mostly in chloroform to cast into films. The glass-transition temperatures (T_g) of the polymers were measured calorimetrically. In this report, the miscibility of the prepared blends is investigated based on the data of T_g .

EXPERIMENTAL

Materials and Film Preparation

Isotactic, atactic, and syndiotactic PMMA (designated *i*, *a*, and *s*PMMA in this study) were purchased from PolySciences (Warrington, PA). According to the supplier information, the molecular weights (M_w) of iPMMA, aPMMA, and sPMMA are the same, $\sim 100,000$ g/mol. The polydispersities (M_w/M_n) of the three PMMA were not measured and therefore are not reported. However, the molecular weight distribution effect is believed to be minimal in the current study when compared with the effect of tacticity. We did not characterize the tacticity of PMMA by nuclear

Table I Meso and Racemic Fractions of Tactic PMMA

	<i>m</i> (%)	<i>r</i> (%)
iPMMA	68.7	31.3
aPMMA	33.8	66.2
aPMMA ^a	38.5	61.5
sPMMA	9.3	90.7

Error of estimation = 5–8%.

^aFrom Li and Brisson.¹⁶

magnetic resonance (NMR). Therefore, a simple estimation of the fractions of meso (*m*) and racemic (*r*) diads was used. The meso diad fractions of PMMA were computed previously¹⁵ and are listed in Table I. Validation of the estimation is proved by comparing the *m* and *r* fractions of aPMMA with Li and Brisson's data.¹⁶ These investigators 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 (also listed in Table I), *m* fraction (%) = $16 + 45/2 = 38.5$ and *r* fraction (%) = $39 + 45/2 = 61.5$. Our computed *m* and *r* values (33.8% and 66.5%) are in agreement with theirs within the error of estimation.

Two different sources of PVP were used to blend with PMMA. PVP1 was obtained from Riedel-de Haën Germany laboratory chemicals and had an M_v value of $\sim 10,000$ g/mol. PVP2 was purchased from Aldrich Chemical Company (Milwaukee, WI), and its M_w value was 55,000 g/mol. PVP1 or PVP2 was mixed with each tactic PMMA individually in chloroform at room temperature in several weight ratios to form blends. In addition, PVP1 was blended with aPMMA in tetrahydrofuran (THF) for comparison. At room temperature, the solution of aPMMA/PVP1 in THF showed some opacity. When the solution was heated to $\sim 60^\circ\text{C}$, it became clear, indicating a complete dissolution of aPMMA and PVP1. sPMMA and PVP1 did not dissolve well in THF, even at high temperatures ($>60^\circ\text{C}$). Some orange precipitates formed with subsequent heating ($\sim 70\text{--}80^\circ\text{C}$). The formation of precipitates was probably due to interaction between sPMMA and PVP1. Therefore the pursuit of using THF as another solvent was stopped.

Thin films of individual polymers and their blends were made by solution casting onto glass plates. Chloroform, or sometimes THF as in the

forementioned situation, was used as the solvent, but for PMMA toluene was used instead. Chloroform, THF, and toluene were all ACS reagents purchased from Fisher Scientific (Fair Lawn, NJ). The final drying step for all the films took place in a vacuum oven for ~16 h at 92–155°C, which was above the T_g of the individual polymers. Then the films were cooled down to room temperature slowly by air. The as-cast films were later used for differential scanning calorimetry (DSC) studies. The applied drying and vacuuming conditions were proved to be enough for eliminating all residual solvent, since no solvent peak was detected by DSC.

Differential Scanning Calorimetry

The T_g of the polymer blends were determined using a DuPont 2000 thermal analyzer with a mechanical cooling accessory system. Experiments were performed in two consecutive scans in an ambient environment of nitrogen gas at a flow rate of 100–110 mL/min. At the end of the first thermal scan, the samples remained at 220°C for 1 min. The samples were then cooled to 20°C at a rate of 20°C/min and were scanned a second time. A scanning temperature of 20–220°C and a heating rate of 20 °C/min were used in each scan. The inflection point of the specific heat jump of the second thermal scan was taken as the glass-transition temperature. Although our previous publication¹⁵ used an ice-water bath in the end of the first thermal scan to obtain T_g of the quenched samples. The cooling rate of 20°C/min used in this study produced almost the same T_g as quenching within experimental error.

RESULTS AND DISCUSSION

Because most of the solvent used was chloroform and, only in one blend system was THF used for comparison as well. Therefore, when no solvent name is given in this section, it refers to chloroform. However, it is denoted clearly when THF was used as the solvent.

Glass-Transition Temperature

The T_g values of three tactic PMMA/PVP1 blends are listed in Table II. For the aPMMA/PVP1 and sPMMA/PVP1 blends, only one T_g was detected for each blend composition. It can be concluded

Table II Glass-Transition Temperatures of Chloroform-Cast PMMA/PVP1 Blends

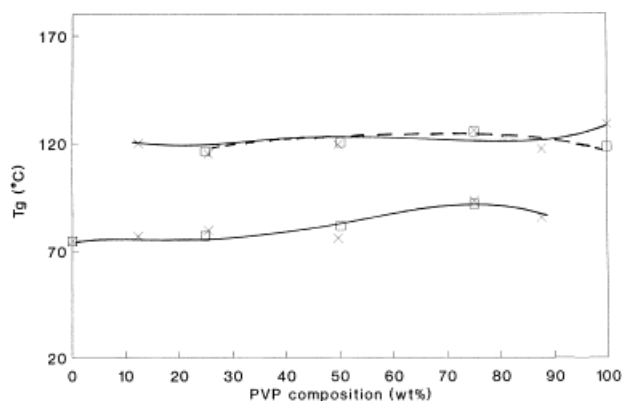
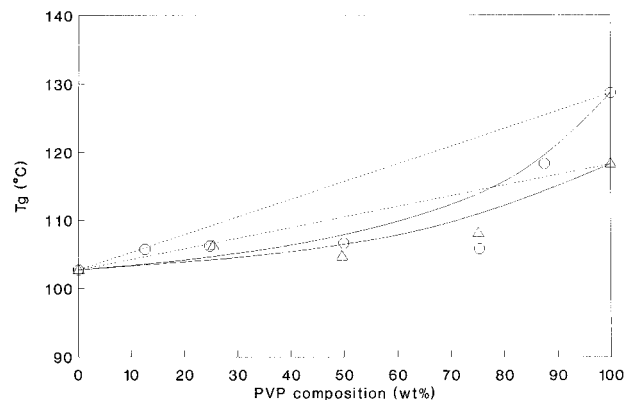
	T_g (°C)	ΔT_g (°C)
1. iPMMMA/PVP1		
100/0	74.6	20
87.7/12.3	76.8, 119.8	12, 14
74.5/25.5	79.5, 115.0	16, 13
50.3/49.7	75.9, 119.3	19, 17
24.9/75.1	93.1, 125.8	12, 14
12.4/87.6	85.4, 117.2	14, 17
2. aPMMA/PVP1		
100/0	102.7	12
87.5/12.5	105.7	9
75.3/24.7	106.2	9
50.1/49.9	106.6	7
24.7/75.3	105.8	11
12.5/87.5	118.3	16
3. sPMMA/PVP1		
100/0	122.4	13
87.1/12.9	128.5	13
75.3/24.7	127.8	13
49.9/50.1	128.8	13
25.5/75.5	126.8	14
0/100	128.7	22

that these two blends are miscible based on a single T_g criterion. Although T_g values of aPMMA, sPMMA, and PVP1 are at most 16°C apart, based on their T_g behavior (see Figs. 2, 3), their miscibility is certain. However, two T_g values were observed in the iPMMMA/PVP1 blends. Therefore, the iPMMMA/PVP1 blends are determined to be partially miscible because of phase separation and also due to the fact that T_g values are located between those of the component polymers. Table III presents the result of PMMA/PVP2 blends; the data bear out a similar conclusion to that in Table II. The aPMMA/PVP2 and sPMMA/PVP2 blends are miscible; however, immiscibility was found mostly between iPMMMA and PVP2. For a high PVP2 composition (75.1%), the blend showed partial miscibility because of the observation of low T_g higher than iPMMMA values of T_g and high T_g even higher than that of PVP2. The T_g regions (ΔT_g) were calculated as differences between the onset and end points of T_g . All the ΔT_g values of the blends are listed in Tables II and III for reference. For miscible aPMMA/PVP1 (or 2) and sPMMA/PVP1 (or 2) blends no or little broadening of the T_g was detected.

Table III Glass-Transition Temperatures of Chloroform-Cast PMMA/PVP2 Blends

	T_g (°C)	ΔT_g (°C)
1. iPMMA/PVP2		
100/0	74.6	20
75.1/24.9	77.0, 116.1	17, 15
49.8/50.2	81.7, 120.3	15, 15
24.9/75.1	91.7, 125.2	15, 8
2. aPMMA/PVP2		
100/0	102.7	12
74.6/25.4	106.2	6
50.4/49.6	104.7	11
24.9/75.1	108.1	17
3. sPMMA/PVP2		
100/0	122.4	13
74.9/25.1	128.9	14
49.8/50.2	129.2	13
25.0/75.0	126.7	16
0/100	118.3	18

Data taken from Tables II and III are plotted in Figures 1–3 to show the effect of using different PVP. In Figure 1, the T_g values of iPMMA with PVP1 or PVP2 are presented. Two T_g values were observed for all the blend compositions, indicating the presence of iPMMA-rich phase and PVP-rich phase. For the iPMMA-rich phase of these two blends in Figure 1, T_g increases slightly with increasing PVP concentration. For PVP1-rich phase, T_g decreases with the increase of iPMMA concentration. However, T_g of PVP2-rich phase exhibits complex concentration dependence. Ac-

**Figure 1** Glass-transition temperatures of isotactic poly(methyl methacrylate) (iPMMA) with poly(vinyl pyrrolidone) (PVP1 or PVP2) (chloroform-cast). ×, PVP1; □, PVP2.**Figure 2** Glass-transition temperatures of atactic poly(methyl methacrylate) (aPMMA) with poly(vinyl pyrrolidone) (PVP1 or PVP2) (chloroform-cast). ○, PVP1; △, PVP2; . . ., weight average; —, Gordon-Taylor equation.

cording to experimental observation, the high T_g of iPMMA/PVP2 (24.9/75.1) is even higher than PVP2. For this blend, domains with distinct mobilities were detected, and the reason for the high T_g is antiplasticization or some favorable interaction occurred between iPMMA and PVP2. Although PVP2 has a lower T_g than PVP1, it is interesting to see T_g of iPMMA/PVP2 blends corresponds well to that of iPMMA/PVP1 blends with the same PVP composition (25–75 wt %).

The T_g values of aPMMA with PVP1 or PVP2 are given in Figure 2. The T_g values of these two blends are mostly below weight average. The Gordon-Taylor equation,¹⁷ as follows, was used to fit the experimental T_g values:

$$T_g = (w_1 T_{g1} + k w_2 T_{g2}) / (w_1 + k w_2) \quad (1)$$

where T_g is the glass-transition temperature of a blend, w_i and T_{gi} are the weight fraction and the T_g of polymer i (1 or 2) and k is used as a fitting parameter. T_{g1} is designated as the low T_g one. For aPMMA/PVP1 and aPMMA/PVP2 blends, k values of 0.223 and 0.284 were found to describe the T_g data qualitatively, except at one composition of aPMMA/PVP1 blends. The low k value often indicates weak interaction between two polymers. Also observed in aPMMA/PVP1 and aPMMA/PVP2 blends, the T_g values of these two blends are very close to each other for the compositions studied, regardless of which PVP was used.

Figure 3 presents the T_g data of sPMMA with PVP1 or PVP2. No matter which kind of PVP was

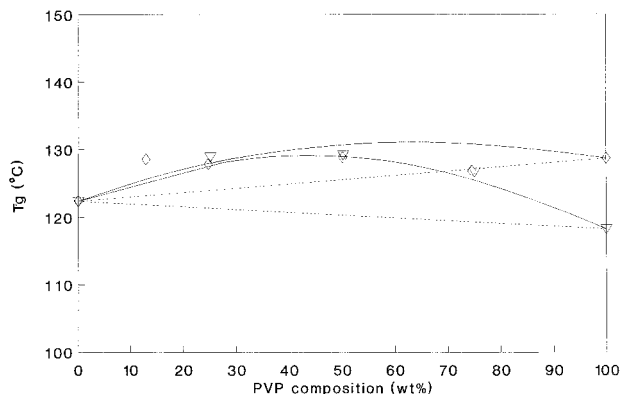


Figure 3 Glass-transition temperatures of syndiotactic poly(methyl methacrylate) (sPMMA) with poly(vinyl pyrrolidone) (PVP1 or PVP2) (chloroform-cast). \diamond , PVP1; ∇ , PVP2; \dots , weight average; —, simplified Kwei equation.

used, most T_g values were found to be higher than for the weight average. The simplified Kwei equation¹⁸ as follows was used to describe the experimental T_g value:

$$T_g = w_1 T_{g1} + w_2 T_{g2} + q w_1 w_2 \quad (2)$$

where T_g , T_{g1} , T_{g2} , w_1 , and w_2 have the same meanings as in eq. (1). q is a parameter corresponding to the strength of interaction between polymers 1 and 2. q values of 22.6 and 38.3 were found to fit the T_g data of the sPMMA/PVP1 and sPMMA/PVP2 reasonably well, except for the sPMMA/PVP1 (25.5/74.5) blend. It is again interesting to note that although PVP2 has a lower T_g than PVP1, the sPMMA/PVP blends exhibit almost exactly the same T_g value whether PVP1 or PVP2 was used for blending. Based on higher k or q values of PVP2 with aPMMA (or sPMMA) than PVP1, it is concluded that stronger interaction occurred between PVP2 and aPMMA (or sPMMA) than PVP1.

If the deviation of T_g values from weight average is taken as an indicator of interaction between two polymers. Since sPMMA/PVP blends show mostly positive T_g deviation from weight average, however, negative deviation was often found in the aPMMA/PVP blends. Therefore, sPMMA interacts more favorably with PVP in blending than does aPMMA. The interaction between iPMMA and PVP is the least favorable among the three PMMA, as immiscibility was observed. Therefore, the order of interaction be-

Table IV Glass-Transition Temperatures of THF-Cast aPMMA/PVP1 Blends

	T_g (°C)	ΔT_g (°C)
aPMMA/PVP1		
100/0	102.7	12
75.2/24.8	106.6	9
50.0/50.0	104.6	8
25.1/74.9	116.8	18
0/100	117.7	11

tween tactic PMMA and PVP should be as follows: sPMMA > aPMMA > iPMMA.

aPMMA and PVP1 were blended in a different solvent (THF); their T_g values are reported in Table IV. Again, a single T_g was detected in each blend composition. ΔT_g (also listed in Table IV) has the same meaning as aforementioned in Tables II and III. A broadening of T_g was observed in the THF-cast aPMMA/PVP1 (25.1/74.9) blend. It is interesting to note that THF-cast PVP1 exhibits a lower T_g than the same polymer when cast from chloroform. The reason is likely due to strong interaction between solvent and polymer thus making a more ordered film and a lower free volume after solvent removal. To indicate the solvent effect, the T_g values of aPMMA/PVP1 blends, cast from either chloroform or THF, are presented in Figure 4. Using THF as solvent, a complex dependence of T_g on PVP1 concentration was observed. If the data are taken literally, the T_g values of the three blend compositions in the THF-cast aPMMA/PVP1 blends are equal to,

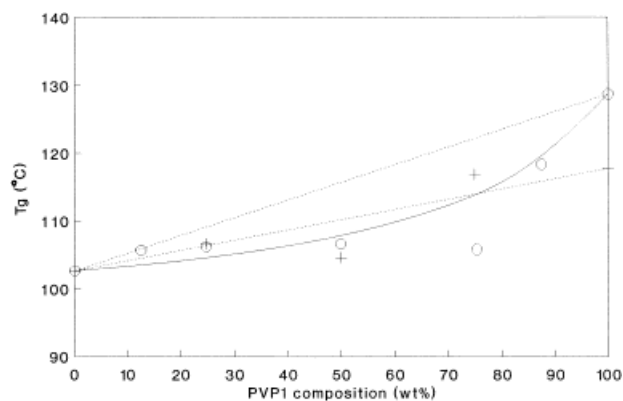


Figure 4 Glass-transition temperatures of atactic poly(methyl methacrylate)/poly(vinyl pyrrolidone) (aPMMA/PVP1) [chloroform-cast and tetrahydrofuran (THF)-cast]. \circ , chloroform; +, THF.

Table V Phase Compositions of iPMMMA/PVP1 Blends

iPMMMA/PVP1 $W_{1T}(\%)/W_{2T}(\%)$	iPMMMA-Rich Phase $w'_1(\%)[W'(\%)]$	PVP1-Rich Phase $w''_1(\%)[W''(\%)]$
87.7/12.3	93.2 (93.4)	10.2 (6.6)
74.5/25.5	85.3 (83.4)	16.4 (15.7)
50.3/49.7	95.9 (46.4)	10.9 (53.6)
24.9/75.1	52.7 (41.2)	5.4 (58.8)

lower than and slightly higher than weight average.

Phase Compositions of iPMMMA/PVP1 Blends

Although two T_g values were detected in the iPMMMA/PVP2 blends, their phase compositions were not estimated because of the observed complex T_g behavior. Because two T_g values were found in the iPMMMA/PVP1 blends, iPMMMA-rich and PVP1-rich phases were assumed. Estimations of the compositions of these two phases were attempted and are illustrated as follows. If T_g is located between iPMMMA and PVP1, its composition was computed from the Fox equation¹⁹:

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \quad (3)$$

where $T_g, T_{g1}, T_{g2}, w_1,$ and w_2 have the same meaning as before. The Fox equation was derived, and is often used for, miscible blends. These attempts made represented a qualitative estimation. Equation (3) can be rearranged as

$$w'_1 = T_{g1}(T_{g1,b} - T_{g2})/[T_{g1,b}(T_{g1} - T_{g2})] \quad (4)$$

where w'_1 is the apparent weight fraction of iPMMMA in the iPMMMA-rich phase, $T_{g1,b}$ is the observed T_g of iPMMMA-rich phase. Similarly, eq. (1) can also be rearranged to

$$w''_1 = T_{g1}(T_{g2,b} - T_{g2})/[T_{g2,b}(T_{g1} - T_{g2})] \quad (5)$$

where w''_1 is the apparent weight fraction of iPMMMA in the PVP1-rich phase, $T_{g2,b}$ is the observed T_g of the PVP1-rich phase.

Applying eqs. (4) and (5) to the T_g values of iPMMMA/PVP1 blends, the apparent weight fraction of iPMMMA in the iPMMMA-rich phase (w'_1) and in the PVP1-rich phase (w''_1) were calculated. The results are presented in Table V. Estimation of

the phase compositions of the iPMMMA/PVP1 (12.4/87.6) blend failed and thus is not included because unreasonable values were obtained. This may be because the T_g of the blend does not follow the Fox prediction at this composition. A qualitative trend can be observed from Table V. For the blends with PVP1 compositions ranging within 12.3–49.7%, the blends behave similarly and phase separate into an iPMMMA-rich phase, with iPMMMA compositions of 85.3–95.9%, and a PVP1-rich phase with iPMMMA compositions of 10.2–16.4%. However, for the iPMMMA/PVP1 blends with a high PVP1 concentration (75.1%), markedly different phase composition was observed. iPMMMA compositions of iPMMMA-rich and PVP1-rich phase were estimated to be 52.7% and 5.4%, respectively.

The overall weight fraction of iPMMMA-rich phase (W') and PVP1-rich phase (W'') is calculated by the following material balance equations:

$$W_{1T} = w'_1W' + w''_1W'' \quad (6)$$

$$W_{2T} = w'_2W' + w''_2W'' \quad (7)$$

where W_{1T} and W_{2T} are the overall weight fraction of iPMMMA and PVP1 for blending, respectively, and w'_1 and w'_2 are obtained from eqs. (6) and (7), respectively. The W' and W'' values were calculated and are also listed in Table V. Lower W' value (iPMMMA-rich phase) and higher W'' value (PVP1-rich phase) with increasing PVP1 concentration were observed. This behavior corresponds well to the general trend.

Comparison With PMMA/PSAN Blends

One of our previous publications²⁰ investigated the tacticity effect of PMMA on its miscibility with poly(styrene-co-acrylonitrile). The AN units content and M_w of PSAN are 25 wt % and 165,000 g/mol, according to supplier information. Similar conclusions to the results of PMMA/PVP blends were drawn. aPMMA and sPMMA were found to be miscible with PSAN, based on the transparency and a single T_g for each composition of the films. The T_g of the two miscible blends were fitted well either by the Fox equation or by the weight average; no broadening of the glass-transition region was observed. However, iPMMMA is immiscible with PSAN because of observed opacity and two T_g for most compositions of the blends. Judging from the T_g deviation from

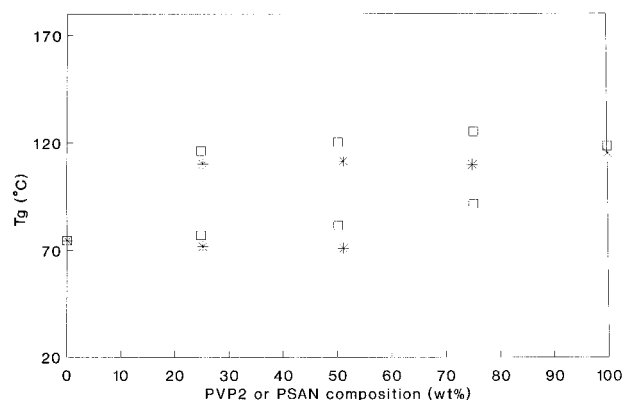


Figure 5 Glass-transition temperatures of isotactic poly(methyl methacrylate)/poly(vinyl pyrrolidone) (iPMMA/PVP2) vs. iPMMA/PSAN. □, PVP2; *, PSAN.

weight average, the order of interaction between PMMA and PSAN is as follows: sPMMA \approx aPMMA > iPMMA.

Because the M_w of PVP1 (or PVP2) is different from that of PSAN, for comparison, PVP2 was chosen because of the proximity of its T_g to PSAN (115.1°C). T_g values of all the PMMA/PVP2 and PMMA/PSAN blends are presented in Figures 5, 6, and 7 in the order iPMMA, aPMMA, and sPMMA, respectively. In Figure 5, iPMMA and PVP2 show partial miscibility with each other. However, iPMMA and PSAN are almost completely immiscible for the two blends (i.e., iPMMA/PSAN (74.8/25.2 and 48.9/51.1). For these two compositions, the blends are composed of an almost pure iPMMA phase and a PSAN-rich phase. It is interesting to note that iPMMA and PSAN were found to be miscible for the iPMMA/

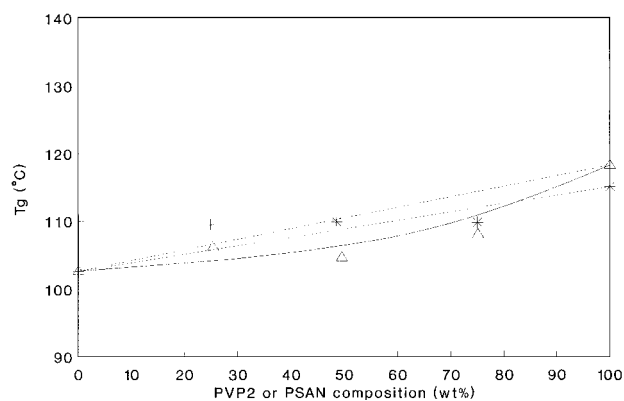


Figure 6 Glass-transition temperatures of atactic poly(methyl methacrylate)/poly(vinyl pyrrolidone) (aPMMA/PVP2) vs. aPMMA/PSAN. Δ, PVP2; *, PSAN; . . . , weight average; —, Gordon–Taylor equation.

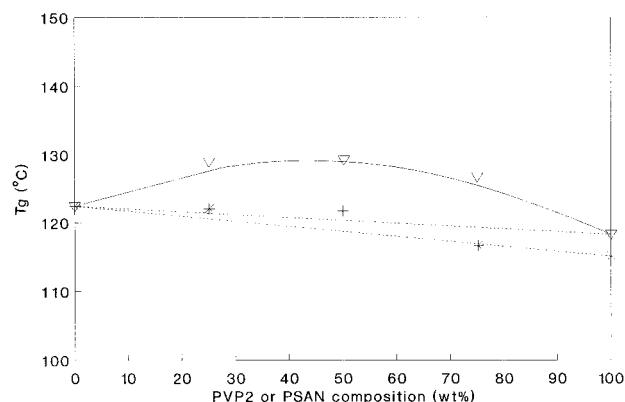


Figure 7 Glass-transition temperatures of syndiotactic poly(methyl methacrylate)/poly(vinyl pyrrolidone) (sPMMA/PVP2) vs. sPMMA/PSAN. ▽, PVP2; *, PSAN; . . . , weight average; —, simplified Kwei equation.

PSAN (25.1/74.9) blend. As shown in Figure 6, most T_g values of aPMMA/PVP2 are lower than weight average and those of aPMMA/PSAN blends are close to weight average. Based on observation, it is likely that aPMMA interacts more favorably with PSAN than does PVP2. In Figure 7, it is obvious that sPMMA/PVP2 blends show a much larger positive T_g deviation from weight average than sPMMA/PSAN blends. Therefore, the interaction between sPMMA and PVP2 is stronger than that between sPMMA and PSAN.

The driving force for the miscibility observed in PMMA/PSAN blends is believed to be a highly repulsive styrene-acrylonitrile interaction.²¹ According to our experimental observation, isotacticity of PMMA has an adverse effect on its miscibility with PSAN. This may be because isotactic MMA segments interact differently with styrene and acrylonitrile segments from atactic or syndiotactic MMA segments.²⁰ On the other hand, the driving force for the miscibility observed in PMMA/PVP blends is believed to be the interaction process of blend components.⁹ The interaction seems to be involved in the carbonyl groups from component polymers. Syndiotacticity of PMMA seems to have a favorable effect on its miscibility with PVP likely due to stronger interaction between syndiotactic MMA segments with PVP units than atactic or isotactic MMA segments.

CONCLUSIONS

The results show that the backbone conformation of PMMA plays a major role in its miscibility with

PVP. The prepared aPMMA/PVP1 (or PVP2) and sPMMA/PVP1 (PVP2) blends are determined to be miscible based on a single glass-transition temperature for each composition of the films. The T_g values of aPMMA/PVP1 (or PVP2) blends can be qualitatively described by the Gordon–Taylor equation with a k value of 0.223 (or 0.284). For the sPMMA/PVP1 (or PVP2) blends, the T_g values can be fitted by the simplified Kwei equation with a q value of 22.6 (or 38.3). Higher k and q values of PVP2 than those of PVP1 indicate that a stronger interaction occurred between aPMMA or sPMMA with PVP2 than PVP1. Conversely, iPMMA is immiscible or partially miscible with PVP1 (or PVP2) because of the observation of two T_g in all the blends studied. Based on the observation of T_g deviation from weight average, it is concluded that the order of interaction between tactic PMMA and PVP is as follows: sPMMA > aPMMA > iPMMA.

REFERENCES

1. Roerdink, E.; Challa, G. *Polymer* 1978, 19, 173.
2. Roerdink, E.; Challa, G. *Polymer* 1980, 21, 509.
3. Eijkelenboom, A. P. A. M.; Mass, W. E. J. R.; Vee-man, W. S.; Buning, G. H. W.; Vankan, J. M. J. *Macromolecules* 1992, 25, 4511.
4. Rao, G. R.; Castiglioni, C.; Gussoni, M.; Zeroi, G.; Martuscelli, E. *Polymer* 1985, 26, 811.
5. John, E.; Ree, T. *J Polym Sci Polym Chem Ed* 1990, 28, 385.
6. Silvestre, C.; Cimmino, S.; Martuscelli, E.; Karasz, F. E.; MacKnight, W. J. *Polymer* 1987, 28, 1190.
7. Schurer, J. W.; de Boer, A.; Challa, G. *Polymer* 1975, 16, 201.
8. Vorenkamp, E. J.; ten Brinke, G.; Meijer, J. G.; Jager, H.; Challa, G. *Polymer* 1985, 26, 1725.
9. da Silva, E. P.; Tavares, M. I. B. *Polym Bull* 1998, 41, 307.
10. Guo, Q. *Makromol Chem Rapid Commun* 1990, 11, 279.
11. Galin, M. *Makromol Chem* 1987, 188, 1391.
12. Goh, S. H.; Siow, K. S. *Polym Bull* 1990, 23, 205.
13. Equizabal, J. I.; Iruin, J. J.; Cortazar, M.; Guzman, G. M. *Makromol Chem* 1984, 185, 1761.
14. Moscala, E. J.; Varnell, D. F.; Coleman, M. M. *Polymer* 1985, 26, 228.
15. Hsu, W. P.; Yeh, C. F. *J Appl Polym Sci* 1999, 73, 431.
16. Li, D.; Brisson, J. *Macromolecules* 1996, 29, 868.
17. Gordon, M.; Taylor, J. S. *J Appl Chem* 1952, 2, 493.
18. Kwei, T. K. *J Polym Sci Polym Lett Ed* 1984, 22, 307.
19. Fox, T. G. *J Appl Bull Am Phys Soc* 1956, 1, 123.
20. Hsu, W. P. *J Appl Polym Sci* 1999, 74, 2894.
21. Cowie, J. M. G.; Lath, D. *Polym Commun* 1987, 28, 300.