Effect of the Tacticity of Poly(Methyl Methacrylate) on the Phase Diagram of Its Ternary Blends

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ABSTRACT: Previously, isotactic and atactic poly(methyl methacrylates) (PMMAs) were found to be miscible with poly(vinyl phenol) (PVPh) and poly(hydroxy ether of bisphenol-A) (phenoxy) because all the prepared films were transparent and showed composition-dependent glass transition temperatures (T_g's). However, syndiotactic PMMA was immiscible with PVPh because most of the cast films had two T_g's. On the contrary, syndiotactic PMMA was still miscible with phenoxy. According to our preliminary results, PVPh and phenoxy are not miscible. Also to our knowledge, nobody has reported any results concerning the effect of the tacticity of PMMA on its ternary blend containing PVPh and phenoxy. The miscibility of a ternary blend consisting of PVPh, phenoxy, and tactic PMMA was thus investigated and reported in this article. Calorimetry was used as the principal tool to study miscibility. An approximate phase diagram of the ternary blends containing different tactic PMMA was established, probably for the first time, based on differential scanning calorimetry data. Immiscibility was found in most of the studied ternaries but a slight difference due to the effect of tacticity of PMMA was definitely observed. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 2720–2726, 2002

Key words: tacticity; poly(methyl methacrylate); ternary blends

INTRODUCTION

Ternary blends have been gaining importance in the field of polymers throughout the years. The first systematic study on ternary blends was reported by Kwei et al.[1] in 1977. In their study, the addition of poly(vinylidene fluoride) (PVDF) to the immiscible pair, poly(methyl methacrylate)(PMMA)/ poly(ethyl methacrylate) (PEMA), was studied and found to be miscible. The list of ternaries investigated has been considerably enlarged since then.[2–8] In nearly all these blends, a third component, either a homopolymer or a copolymer, is added to homogenize an immiscible pair. Miscibility is often achieved in cases where this third component is miscible with other polymers.

Recently, Bicakci and Cakmak[9] investigated the phase behavior of binary and ternary blends of poly-(ethylene naphthalate) (PEN), poly(ether imide) (PEI), and poly (ether ether ketone) (PEEK) by using differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMTA) techniques. PEN/PEI and PEI/PEEK binary blends exhibit single glass transition temperatures T_g's over the full composition range and PEN and PEEK were found to be immiscible, particularly at midconcentrations. When PEI is added to the immiscible PEN/PEEK system, first the blends form two separated PEN-rich and PEEK-rich phases below about 40% PEI concentration, and above this concentration, the three homopolymers form a miscible phase in the amorphous state exhibiting a single T_g. An approximate ternary phase diagram was established by them based on the DSC and DMTA results.

In previous studies,[10–12] isotactic, atactic, and syndiotactic PMMAs (designated as i-, a-, and sPMMAs) with approximately the same molecular weight were blended with poly(vinyl phenol) (PVPh) and phenoxy in 2-butanone to cast into films. The T_g's of the polymers were measured calorimetrically. iPMMA and aPMMA were found to be miscible with PVPh and phenoxy because all the prepared films were transparent and had a single composition-dependent T_g. However, sPMMA is not miscible with PVPh because most of the cast films had two T_g's. Conversely, sPMMA is still miscible with phenoxy. PVPh is not miscible with phenoxy, according to the preliminary results. Also to our knowledge, no one has reported any article concerning the effect of the tacticity of PMMA on its ternary blend. Therefore, an investigation of the miscibility of ternary blends composed of PVPh, phenoxy, and tactic PMMA was considered worthwhile and pursued in this laboratory. Because iPMMA and aPMMA are both miscible with PVPh and phenoxy, iPMMA or aPMMA is acting as a cosolvent between PVPh and phenoxy in this study. Strictly speaking, the study of sPMMA ternaries is for comparative pur-

TABLE I
Glass Transition Temperatures of
aPMMA/Phenoxy/PVPh Blends

aPMMA/phenoxy/PVPh	T_g (°C)	ΔT_g (°C)
1. (75.0/12.5/12.5)	112.1	13
2. (62.2/12.7/25.1)	123.4	13
3. (37.2/12.9/49.9)	116.5, 153.9	15, 17
4. (12.4/12.6/75.0)	115.6, 153.8	13, 15
5. (12.5/43.7/43.8)	103.3, 149.4	9, 13
6. (12.5/74.9/12.6)	103.6, 148.5	5, 15
7. (37.6/49.9/12.5)	112.6, 146.5	19, 13
8. (62.6/25.0/12.4)	102.1, 149.1	6, 12
9. (50.1/24.7/25.2)	126.4	18
10. (25.0/25.2/49.8)	106.1, 163.5	12, 17
11. (24.9/37.2/37.9)	101.1, 161.0	13, 18
12. (24.9/50.0/25.1)	104.1, 142.5	5, 9

TABLE III
Glass Transition Temperatures of
sPMMA/Phenoxy/PVPh Blends

sPMMA/phenoxy/PVPh	T_g (°C)	ΔT_g (°C)
1. (75.0/12.5/12.5)	117.3, 138.6	13, 14
2. (62.5/12.5/25.0)	109.5, 147.5	10, 16
3. (37.6/12.5/50.0)	115.4	12
4. (12.5/12.5/75.0)	113.8	17
5. (12.5/43.7/43.8)	102.2, 148.5	5, 14
6. (12.5/75.0/12.5)	101.3, 149.1	5, 16
7. (37.4/50.2/12.4)	104.3, 144.4	6, 17
8. (62.5/24.9/12.6)	103.9, 135.8	11, 14
9. (50.0/25.0/25.0)	106.7, 148.7	12, 16
10. (24.9/25.0/50.1)	104.1, 169.6	7, 20
11. (24.9/37.4/37.7)	103.6, 171.7	4, 16
12. (24.9/50.0/25.1)	102.6, 159.0	7, 17

poses because sPMMA is not a cosolvent for PVPh and phenoxy.

In this article, probably for the first time, ternary blends containing PVPh, phenoxy, and tactic PMMA were prepared in several weight ratios. The T_g's of the ternary mixtures were determined calorimetrically. An approximate phase diagram of the ternary blends was established based on calorimetry data and a single T_g was used as the criterion for determining miscibility. The results indicated that the ternary blends were not miscible for most of the studied compositions. The effect of tacticity of PMMA on its ternaries was examined and included in the discussion.

EXPERIMENTAL

Materials

Isotactic, atactic, and syndiotactic PMMAs (designated as i-, a-, and sPMMAs in this study) and PVPh were purchased from Polysciences, Inc., Warrington, PA. According to supplier information, the molecular weights (M_w's) of iPMMA, aPMMA, and sPMMA are the same, $\sim$ 100,000 g/mol. The estimation of meso

TABLE II
Glass Transition Temperatures of
iPMMA/Phenoxy/PVPh Blends

iPMMA/phenoxy/PVPh	T_g (°C)	ΔT_g (°C)
1. (75.0/12.5/12.5)	103.6	14
2. (62.5/12.5/25.0)	105.1, 135.8	15, 13
3. (37.5/12.5/50.0)	104.6	13
4. (12.5/12.5/75.0)	103.6, 133.9	14, 14
5. (12.5/43.75/43.75)	102.7, 136.3	11, 12
6. (12.5/75.0/12.5)	102.0, 135.0	9, 13
7. (37.5/49.9/12.6)	101.6, 135.6	8, 17
8. (62.5/25.0/12.5)	137.2	10
9. (50.1/25.0/24.9)	102.1, 127.0	11, 15
10. (25.1/25.0/49.9)	104.1, 138.5	12, 15
11. (24.9/37.5/37.6)	103.2, 139.0	10, 12
12. (25.0/50.0/25.0)	104.4, 145.9	6, 14

(m) and racemic (r) fractions was reported previously.[12] The calculated m and r fractions of iPMMA, aPMMA, and sPMMA are 68.7 and 31.3%, 33.8 and 66.2%, and 9.3 and 90.7%, respectively. The error is $\sim$ 5–8%. The molecular weight of PVPh is $\sim$ 30,000 g/mol. The poly(hydroxy ether of bisphenol-A) (phenoxy) used for this study was obtained from Scientific Polymer Products, Inc., Ontario, NY. The M_w value for phenoxy is 70,000 g/mol.

Film preparation

Thin films of ternary blends of PVPh, phenoxy, and tactic PMMA in different weight ratios were made by solution casting onto glass plates. The actual compositions of the ternary blends are shown in the order of aPMMA, iPMMA, and sPMMA in Tables I, II, and III, respectively. 2-Butanone was used as solvent for all the blend compositions. 2-Butanone is an American Chemical Society reagent purchased from Aldrich Chemical Company, Inc., Milwaukee, WI. The final drying step for all the films took place in a vacuum oven at 157–160°C for 15–23 h. Then, the films were slowly cooled to room temperature by air to make as-cast samples. The as-cast samples were used for DSC studies.

Differential scanning calorimetry

T_g's of the polymer blends were determined by a DuPont 2000 thermal analyzer coupled with a mechanical cooling system. The scanning range for temperature was from 30 to 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 100–110 ml/min. In the first thermal scan, the samples remained at 200°C for 1 min. Then, the samples were quenched to 30°C by using a cooling rate of 20°C/min. The inflection point of the specific heat
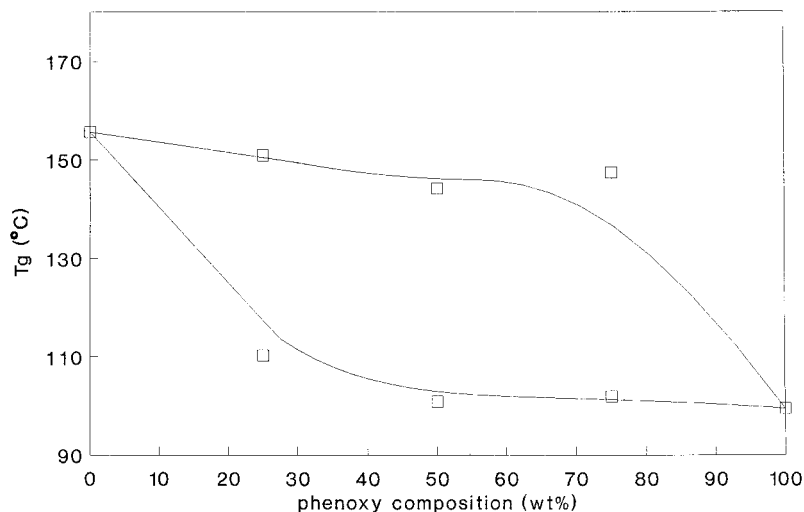
Figure 1 Glass transition temperatures of PVPh/phenoxy blends.

jump of a second thermal scan was taken as the T_g. The cooling rate was proven to be fast enough to produce virtually the same results as quenching.

RESULTS AND DISCUSSION

Glass transition temperatures

For the sake of brevity, the DSC thermal scans of the binary and ternary blends are omitted. Figure 1 presents the T_g's of phenoxy/PVPh blends. It is obvious that phenoxy and PVPh are not miscible because of the observation of two T_g's. These two T_g's can be assigned to the T_g of PVPh-rich and phenoxy-rich phases. Both phenoxy and PVPh can be considered as polymers with strong self-associating tendency. They show broad hydroxyl absorption at around 3418–3422 cm^{-1}, indicating extensive intrahydrogen bonding among hydroxyl groups.[10–12] Therefore, it is natural for them not to be miscible. Through careful inspection of Figure 1, the solubility of phenoxy in PVPh in general seems to be better than that of PVPh in phenoxy. This minute difference turns out to be important in the exposition of the results of the ternary phase diagram and will be discussed later.

For the ternary blends of PMMA, phenoxy, and PVPh, 12 compositions were studied. Four compositions with phenoxy to PVPh in weight ratio 1:1 and various concentrations of PMMA were used to investigate the effect of PMMA concentration on the ternaries. The T_g's of the three ternary blends in the order of aPMMA, iPMMA, and sPMMA are tabulated in Tables I, II, and III, respectively. Obviously, the majority of the ternary blends showed two T_g's and therefore is not miscible. For the 12 studied compositions, a single T_g was observed in three compositions of both aPMMA and iPMMA ternary blends. Despite general immiscibility between sPMMA and PVPh,[10–11] there

are still two ternary compositions showing single T_g and indicating miscibility. The results are not totally unexpected and comments on them are as follows: Although both aPMMA and iPMMA form miscible blends with phenoxy (or PVPh), the interaction between aPMMA (or iPMMA) and PVPh is stronger than that between aPMMA (or iPMMA) and phenoxy. This viewpoint can be substantiated by the IR observation of the shift in the carbonyl absorption region. No or little shift was observed in PMMA/phenoxy blends[12] in comparison with a 17-cm^{-1} shift in PMMA/PVPh blends.[11] The strong interhydrogen bonding between PMMA and PVPh likely causes phenoxy to be mostly excluded; thus, phase separation was observed. Coleman and Painter[13] studied another similar carbonyl containing polymer, poly(ε-caprolactone) (PCL). They found PCL was miscible with both phenoxy and PVPh. A comparison of shifts of the PCL carbonyl stretching mode in blends with phenoxy and PVPh ($\sim$ 13 and 26 cm^{-1}, respectively) suggests that the relative strength of the intermolecular interactions, in the case of the phenoxy blend, is roughly half that of the analogous PVPh blend. Therefore PCL (similar to PMMA) forms stronger hydrogen bonds with PVPh than with phenoxy. Regardless of the tacticity of PMMA, the blends of PMMA/phenoxy/PVPh with compositions of Nos. 5–7 and Nos. 10–11 all showed immiscibility. The immiscibility occurs in the blends with PMMA content < 50% and PVPh concentration $\geq$ 50%. The above observation is in agreement with the lower solubility of phenoxy in phenoxy/PVPh blends when phenoxy concentration is high or blend phase separation because of low cosolvent (PMMA) concentration. The ΔT_g regions (shown as the last column in Tables I, II, and III) were calculated as differences between the onset and end points of T_g and are included for reference.
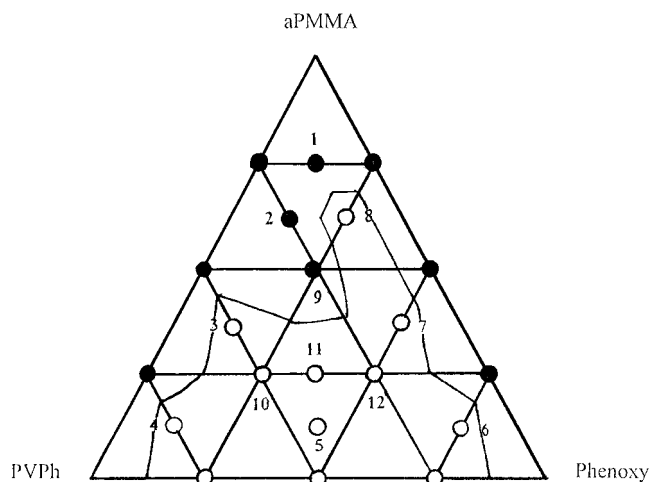
Figure 2 Phase diagram of aPMMA/phenoxy/PVPh blends. ●: miscible; ○: immiscible; - - -: estimated immiscible region. Numbers in the figure indicate the same compositions as in Table I.

Phase diagram of the ternary blends

Using the single T_g as the criterion for the miscibility, the phase diagrams of the ternary blends composed of PMMA, phenoxy, and PVPh are shown in Figures 2,3, and 4 in the order of aPMMA, iPMMA, and sPMMA, respectively. For aPMMA and iPMMA ternary blends (as shown in Figs. 2 and 3), their phase diagrams are similar but not exactly the same. The majority of the miscible region of aPMMA ternary blends has a characteristic of high concentration PMMA (at least >50%) and low concentration of phenoxy or PVPh (<25%). For iPMMA ternary blends, the miscible region occurs in blends with a low concentration of phenoxy or PVPh (<25%) and an even higher PMMA concentra-
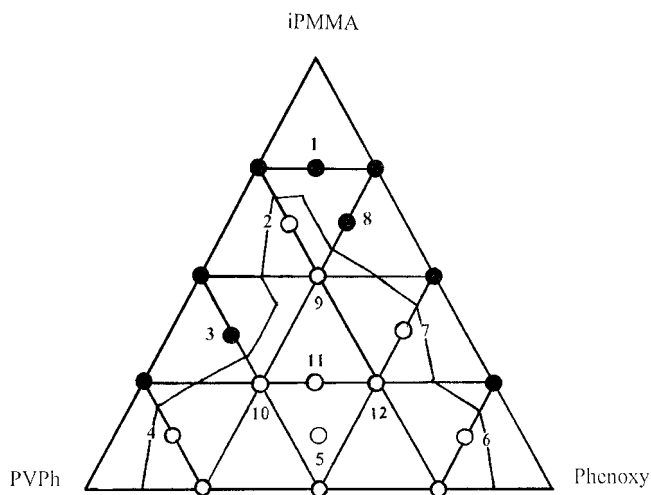

Figure 3 Phase diagram of iPMMA/phenoxy/PVPh blends. ●: miscible; ○: immiscible; - - -: estimated immiscible region. Numbers in the figure indicate the same compositions as in Table II.
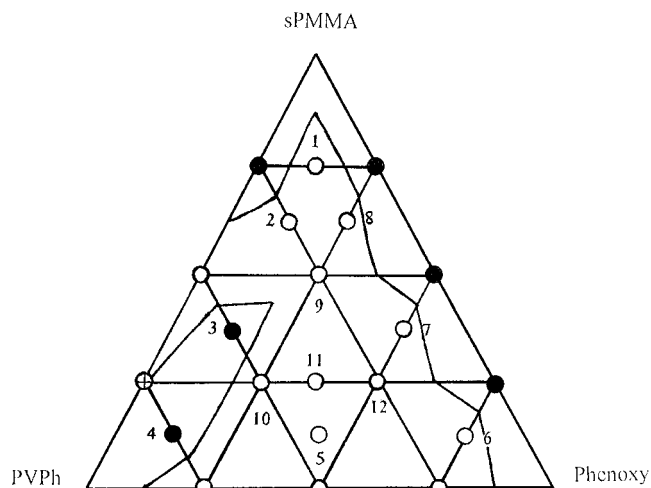

Figure 4 Phase diagram of sPMMA/phenoxy/PVPh blends. ●: miscible; ○: immiscible; - - -: estimated immiscible region. Numbers in the figure indicate the same compositions as in Table III.

tion (>75%). In the sPMMA/phenoxy/PVPh blends, only one binary (i.e., sPMMA and phenoxy) is miscible and the other two are not. Therefore, the immiscible region is larger than the aforementioned two ternaries. However, it is still observed that the blends with a high PVPh concentration and low phenoxy content can be miscible. The data point with the symbol of a cross in a circle (Fig. 4) is considered to be borderline miscible because at this composition the blends are miscible when cast from tetrahydrofuran[10] and immiscible when cast from 2-butanone.[11] Postulated phase boundaries (shown as solid lines in Fig. 2–4) were established for reference by connecting through middle points between miscibility and immiscibility data or borderline miscible data point.

The often-observed asymmetric immiscible region is not detected in aPMMA or iPMMA ternaries. The asymmetric immiscibility often occurs when the interaction of one miscible binary is much stronger than that of another. In our system, aPMMA (or iPMMA) forms stronger interactions with PVPh than with phenoxy. If asymmetry is observed, then the region in the phase diagram close to the PMMA/PVPh side should always be immiscible. However, this is not the case here. Su and Fried[14] used the Flory–Huggins lattice theory to predict the phase behavior of ternary polymer blends. The curve k of Figure 2 in ref (13) has a similar feature as shown in Figure 4 (the sPMMA ternaries). The χ values they used to produce the diagram are $\chi_{12} = 0.0025$, $\chi_{23} = 0.003$, and $\chi_{13} = 0$. For simplification, they assumed equal chain length (degree of polymerization = 1000) and the critical χ_{ij} value was calculated to be 0.002. In our figure, 1 corresponds to phenoxy, 2 corresponds to PVPh, and 3 represents sPMMA. The following comments can be made through comparison with Su's results. Polymer
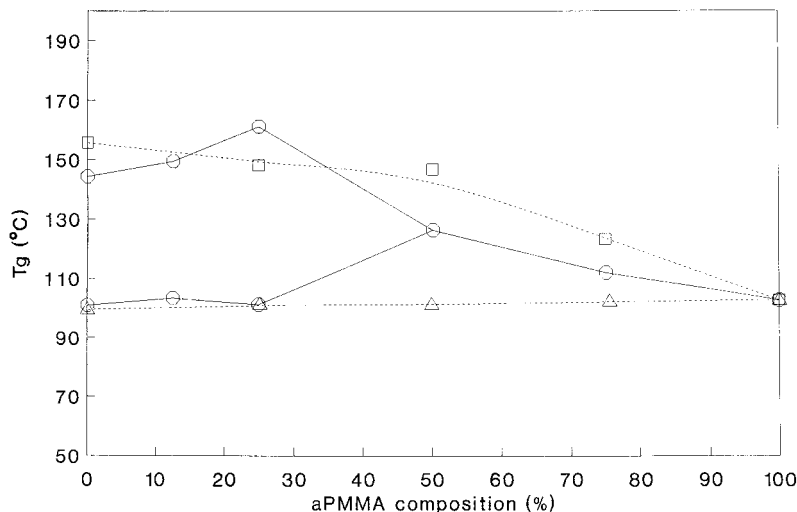
Figure 5 Change of T_g of the ternary blends with aPMMA composition (phenoxy/PVPh weight ratio = 1). ○: data point; Δ: T_g of PVPh/aPMMA blend (curve drawn for viewing); □: T_g of phenoxy/aPMMA blend (curve drawn for viewing).

1 (phenoxy) and polymer 2 (PVPh) are immiscible; therefore χ_{12} > critical χ value. Polymer 1 (phenoxy) and polymer 3 (sPMMA) are miscible (i.e., χ_{13} < critical χ value). Polymer 2 (PVPh) and polymer 3 (sPMMA) behave similarly to immiscible polymers 1 and 2.

Cosolvent effect of PMMA

For the purpose of illustrating the cosolvent effect of PMMA, the T_g values of the ternary blends with phenoxy/PVPh weight ratio ∼ 1 are plotted in Figures 5, 6, and 7 in the order of aPMMA, iPMMA, and sPMMA, respectively. Strictly speaking, sPMMA is not a cosolvent between phenoxy and PVPh. Here, sPMMA is used for comparison with other tactic PMMAs. Previous results[10-12] of the corresponding bina-

ries (phenoxy/PMMA and PVPh/PMMA blends) are also presented in Figures 5–7 for comparison. Because the T_g difference between phenoxy/PMMA and PVPh/PMMA blends with the same PMMA composition is always >30°C, the single T_g criterion for miscibility seems to be justified in our ternary system. The following comments can be drawn from Figure 5. First, the ternary T_g values are mostly located between those of the two binaries with the same aPMMA concentration except at one concentration. Addition of 12.5 or 25.0 wt % of aPMMA to the phenoxy/PVPh binaries did not produce miscible ternaries. In these two situations, aPMMA seemed to be distributed more or less evenly between phenoxy and PVPh, judging from the trend of T_g data. Second, the addition of at least 50 wt % aPMMA into the phenoxy/PVPh mixture is sufficient to cause miscibility. The explana-
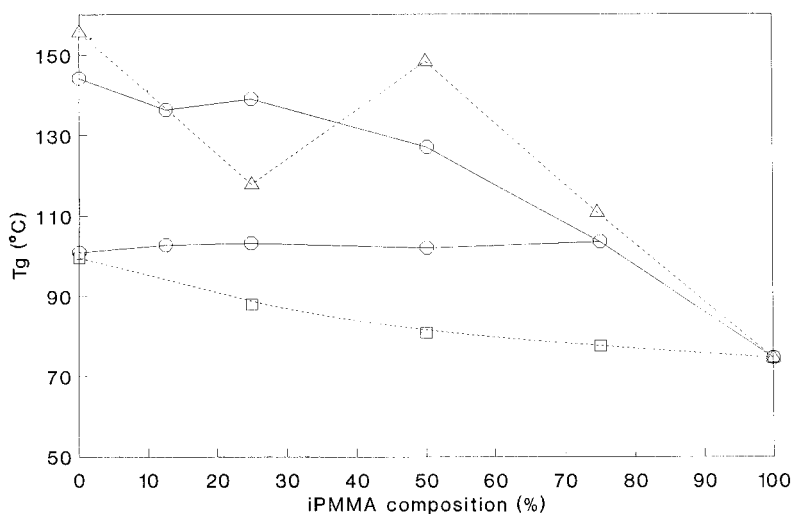

Figure 6 Change of T_g of the ternary blends with iPMMA composition (phenoxy/PVPh weight ratio = 1). ○: data point; Δ: T_g of PVPh/iPMMA blend (curve drawn for viewing); □: T_g of phenoxy/iPMMA blend (curve drawn for viewing).
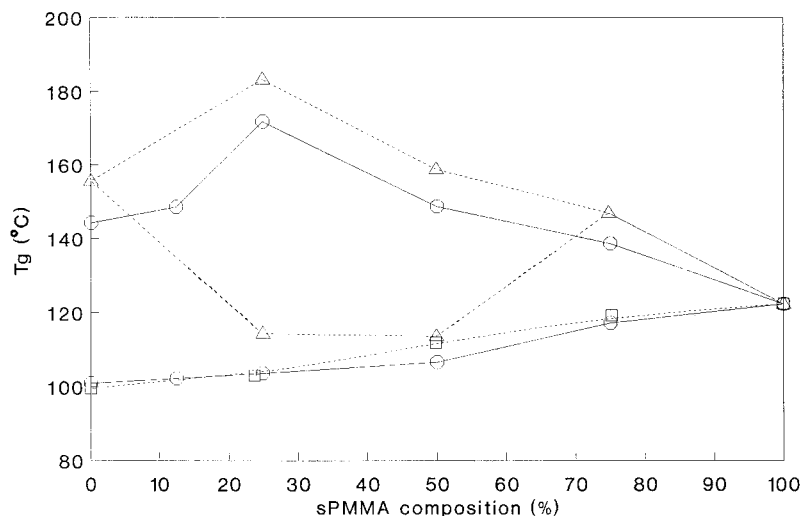
Figure 7 Change of T_g of the ternary blends with iPMMA composition (phenoxy/PVPh weight ratio = 1). $\bigcirc$: data point; Δ: T_g of PVPh/iPMMA blend (curve drawn for viewing); $\square$: T_g of phenoxy/iPMMA blend (curve drawn for viewing).

tion for the iPMMA ternary blends as shown in Figure 6 is complicated by the T_g values of PVPh/iPMMA blends, owing to different degrees of hydrogen bonding in the blends after sample preparation. Despite this situation, the ternary T_g values are still located mostly between those of the two binaries with the same iPMMA composition. When iPMMA concentration reaches 50.0 wt % in the ternaries, the T_g values of phenoxy-rich and PVPh-rich phases are getting closer than those ternaries with 12.5 or 25.0 wt % of iPMMA. This situation can be considered as partial miscibility. However, a higher iPMMA concentration (75%) than previous aPMMA blends is needed to produce miscible ternary blends. It is expected, as observed in Figure 7, that no miscible blends were obtained because sPMMA is not acting as a cosolvent. However, judging from the similarity of the ternary T_g values with

those of the two binaries with the same sPMMA composition, it can be concluded that sPMMA is distributed approximately evenly between phenoxy and PVPh.

To show the effect of tacticity of PMMA on the ternaries with an equal amount of phenoxy and PVPh, the ternary data from Figures 5–7 were taken and combined together to produce Figure 8. Recall that the T_g values of aPMMA, iPMMA, and sPMMA are 102.7, 74.6, and 122.4°C, respectively.[10] So the T_g difference between iPMMA and aPMMA is larger than between sPMMA and aPMMA. For the ternary blends with 12.5% of PMMA as shown in Figure 8, the situation is quite similar regardless of the tacticity of PMMA. One thing that stands out is that the T_g of the high T_g phase of the iPMMA ternary blends is lower. The situation for the ternary blends with 25% PMMA is quite sim-
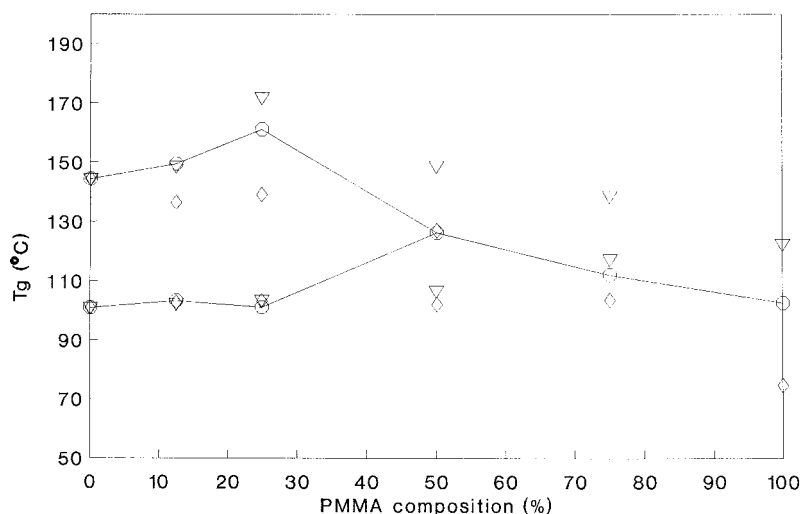

Figure 8 Change of T_g of the ternary blends with PMMA composition (phenoxy/PVPh weight ratio = 1). $\bigcirc$: aPMMA; $\lozenge$: iPMMA; $\triangledown$: sPMMA.

ilar to the 12.5% PMMA ternary blend. The only difference is due to a higher content of PMMA, and T_g of the high T_g phase of the ternaries increases exactly in the T_g ascension order of iPMMA, aPMMA, and sPMMA. For the ternary blends with 50% of PMMA, a miscible blend is obtained by using aPMMA; however, immiscibility is still detected when iPMMA and sPMMA are used. The situation for the 75% PMMA ternaries is summarized as follows: miscibility is found in the blends with iPMMA or aPMMA. Because sPMMA is not a cosolvent of phenoxy and PVPh, the blends are still not miscible. It is concluded therefore that aPMMA is the best candidate for cosolubilizing equal amount of phenoxy and PVPh.

CONCLUSIONS

Phenoxy is not miscible with PVPh based on the observation of two T_g's in all the studied composition. aPMMA and iPMMA are both miscible with phenoxy (or PVPh) according to previous results. However, sPMMA is not miscible with PVPh but still miscible with phenoxy. The effect of tacticity of PMMA on its ternary blends with phenoxy and PVPh is examined and discussed probably for the first time with the help of calorimetry data and ternary phase diagrams. Although immiscibility is mostly encountered, the reason is probably due to the stronger interaction between PMMA and PVPh than that between PMMA and phenoxy. The miscible region in the ternary phase diagram of the blends containing aPMMA or iPMMA is naturally larger than that with sPMMA. Strictly

speaking, sPMMA is not acting as a cosolvent between phenoxy and PVPh because of the immiscibility observed between sPMMA and PVPh. The T_g values of the ternary blends with phenoxy/PVPh (weight ratio = 1) are used to evaluate the role of the tacticity of PMMA on the miscibility of its ternary blends. At least 50% aPMMA or 75% iPMMA is needed to cause the corresponding ternaries to be miscible. According to this fact, aPMMA is a better candidate than iPMMA or sPMMA in cosolubilizing an equal amount of phenoxy and PVPh.

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