Miscibility Studies of Binary and Ternary Mixtures of Tactic Poly(Methyl Methacrylates) with Poly(Vinylidene Chloride-Co-Acrylonitrile)

WEN-PING HSU, CHING-FEN YEH

Department of Applied Chemistry, Chia-Nan College of Pharmacy and Science, #60 Sec. 1 Erh-Jen Road, Jen-Te Hsian, Tainan, Taiwan, Republic of China 71710

ABSTRACT: Isotactic, atactic, and syndiotactic poly(methyl methacrylates) (i, a, and s PMMAs) were mixed with poly(vinylidene chloride-co-acrylonitrile) (Saran F) separately in tetrahydrofuran to make three polymer blend systems. Differential scanning calorimetry (DSC) was used mainly to study the miscibility of these blends. iPMMA and aPMMA were found to be miscible with Saran F based on the transparency and a single glass transition temperature (T_g) of the films. However, sPMMA was immiscible with Saran F because of the observation of two T_gs and opacity in most compositions of the blend. aPMMA is known to be miscible with sPMMA. Therefore aPMMA is both miscible with Saran F and sPMMA but Saran F and sPMMA are immiscible. Preliminary results of the effect of adding of aPMMA to immiscible sPMMA and Saran F mixtures were also reported. First, binary mixtures of atactic and syndiotactic PMMAs were also prepared and confirmed to be miscible. Elevation of T_g of the aPMMA/ sPMMA blend above weight average was observed probably due to stereocomplexation occurred between aPMMA and sPMMA. Then ternary blends of atactic and syndiotactic PMMAs and Saran F in the weight ratios of about 3/1/4, 2/2/4, and 1/3/4 were also measured calorimetrically. A single T_g was observed for these three compositions different from two T_gs detected in the sPMMA/Saran F (50.0/50.0, i.e., 4/4) blend. Obviously, the composition of Saran was fixed in the ternary blends. When the other half of the blends was changing from pure sPMMA to sPMMA and aPMMA mixture, the blends became miscible because of the addition of aPMMA. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 1313–1321, 2000

Key words: tacticity; PMMA; Saran F; miscibility

INTRODUCTION

It has been known for years that the stereoregularity of polymer chains influences polymer–polymer miscibility. Due to its availability in both syndiotactic and isotactic forms, poly(methyl methacrylate) (PMMA) has been used frequently in the investigation of the effect of tacticity on miscibility. Several papers[1–8] have shown that the tacticity of PMMA influences blend compatibility, when PMMA is blended with a chemically different polymer. However, because of differences in the molecular weights and the preparation methods of samples, results sometimes are not consistent.

Most of the previous studies were concentrated on few blends such as poly(vinylidene fluoride) (PVDF),[1–3] poly(ethylene oxide) (PEO),[4–6] and poly(vinyl chloride) (PVC)[7,8] with stereoregular PMMA. For the PVDF/PMMA system, isotactic

PMMA was found to be more miscible than syndiotactic one. PVC forms miscible blends with syndiotactic PMMA up to a monomer unit ratio of about 1 : 1, whereas it does not form miscible blends with isotactic PMMA over the entire composition range. For the PEO/PMMA system, the results are not consistent. Because atactic PMMA is mainly syndiotactic, the result of atactic one is often similar to syndiotactic one.

Sarans are random copolymers of vinylidene chloride (VCl_2) and acrylonitrile (Saran F), vinyl chloride (Saran B), or vinyl acetate (Saran C), containing at least 80% VCl_2. Sarans were found to be miscible with polyesters such as polycaprolactone, polyvalerolactone, poly(butylene adipate) and poly(hexamethylene sebacate) because a single glass transition temperature (T_g) was observed at each composition.[9] Tremblay et al.[10] reported Saran B (containing 88% VCl_2) is miscible with atactic poly(methyl, poly(ethyl, poly(n-propyl, poly(n-butyl, poly(n-amyl and poly(n-hexyl methacrylate)s. From Tremblay,[10] Saran B is miscible with atactic PMMA. The reason for Saran B to be miscible with PMMA is likely due to the following two interactions (similar to polycaprolactone/Saran F blend[11]):

1. a hydrogen-bonding interaction between the carbonyl groups of PMMA and the β-hydrogens of the chlorinated polymer,
2. a dipole-dipole interaction between the carbonyl groups of PMMA and the C-Cl groups of Saran.

Because there are no formal and detailed reports of the tacticity effect of PMMA on its miscibility with Saran F, attempts were pursued in this laboratory to clarify this effect. For preparing the PMMA/Saran F blend, thermal stability and history of the sample are very important because Saran F, like PVC, is easy to undergo thermal decomposition mainly via dehydrochlorination. According to Gerrard et al.'s discovery,[12] mass polymerized PVC subjected to annealing treatment between 85 and 140°C under air, nitrogen, vacuum, and hydrogen chloride environment was found to undergo slight decomposition. In our trial runs, we found that Saran F and its blend started to decompose at around 104–116°C under vacuum. Therefore precaution was taken in film preparation to avoid thermal degradation.

In this article, isotactic, atactic, and syndiotactic PMMAs were mixed with Saran F, respectively, to make three polymer blend systems. Miscibility was investigated based on the transparency and glass transition temperatures of the films. After the discovery of immiscibility between syndiotactic PMMA and Saran F and miscibility between isotactic (or atactic) PMMA and Saran F, the study was diverted to determine the miscibility of the ternary blends of atactic and syndiotactic PMMAs and Saran F. The preliminary results indicated that adding of atactic PMMA to immiscible pairs, syndiotactic PMMA and Saran F, caused the ternary blends to be miscible.

EXPERIMENTAL

Materials

Isotactic, atactic, and syndiotactic PMMAs (designated as i, a, and s PMMAs in this study) were purchased from Polysciences, Inc, Warrington, PA. According to the supplier information, the molecular weights (M_ws) of iPMMA, aPMMA, and sPMMA are the same about 100 000. The poly(vinylidene chloride-co-acrylonitrile) (Saran F) used for this study contained 20 wt % of acrylonitrile units was also obtained from Polysciences. The M_w value for Saran F is approximately 260 000. Each tactic PMMA was mixed with Saran F to form a binary blend in the approximate weight ratios of 1/3, 1/1, and 3/1. A blend of aPMMA and sPMMA and ternary mixtures of aPMMA, sPMMA, and Saran F were also prepared. The reason for preparing the aPMMA/sPMMA and ternary blends was already stated in the previous section and thus not mentioned here. The actual compositions of the binary and ternary blends are shown in Tables I and III, respectively.

Film Preparation

Thin films of the binary and ternary blends were made by solution casting onto glass plates. Tetrahydrofuran (THF) was used as solvent for most compositions, but for PMMA toluene was used instead. THF and toluene are A.C.S. reagent purchased from Fisher Scientific, Fair Lawn, New Jersey. Because Saran F and its blend start to decompose at around 104–116°C, therefore the final drying step for all the films took place in a vacuum oven at 75°C for 15–23 h to avoid film degradation. Then the films were cooled down to room temperature slowly by air to make as-cast samples. The as-cast samples were then used for differential scanning calorimetry (DSC) studies.

Table I   The Glass Transition Temperatures of the PMMA/Saran F Blend

	T_{gsc} (°C)	T_{gq} (°C)	ΔT_{gq} (°C)
iPMMA/Saran F			
100/0	72	75	20
75.1/24.9	66, 105	69	14
50.0/50.0	69, 98	71	16
25.1/74.9	68, 99	68	13
aPMMA/Saran F			
100/0	103	103	12
74.7/25.3	92	88	13
50.0/50.0	73, 104	81	15
25.0/75.0	65, 105	77	20
sPMMA/Saran F			
100/0	121	122	13
75.0/25.0	84, 128	103, 124	15, 10
50.0/50.0	—	98, 135	13, 8
25.0/75.0	64, 105	85	10
0/100	57	59	10

DSC

The glass transition temperatures (T_gs) of the polymer blends were determined by using a Du-Pont 2000 thermal analyzer. Saran F had a higher thermal stability in nitrogen environment than in vacuum. In repetitive test runs, we found that Saran F still maintained its thermal stability when the temperature was as high as 200°C. Therefore the experiments were performed in two consecutive scans from 30 to 200°C in the ambient environment of nitrogen gas at a flowing rate of 100–110 mL/min. In the end of the first thermal scan, the samples stayed at 200°C for 1 min. Then the samples were quenched to 0°C immediately using an ice-water bath and were scanned the second time. A heating rate of 20°C/min was used in each scan. The samples were quenched quickly enough to prevent any crystallization as detected by DSC. There was also no trace of solvent in the films detectable by DSC. The inflection point of the specific heat jump of a thermal scan was taken as the glass transition temperature. The glass transition temperatures determined from the first and second thermal scans are designated as T_{gsc} and T_{gq}, respectively. Therefore, T_{gsc} is the T_g of the slowly cooled (as-cast) films and T_{gq} that of the quenched films.

Fourier Transform Infrared Spectroscopy

For detecting possible interactions between PMMA and Saran F, the following experiments were carried out. The polymer blends of PMMA and Saran F were cast on KBr windows using ca. 1 wt % solution (the same solvent as in film preparation). Then the samples were dried in a vacuum oven at 75°C for 21–24 h and stored for Fourier transform infrared spectroscopy (FTIR) studies. Spectra were obtained at room temperature with 64 scans at a resolution of 4 cm^{-1}. The wavelength range was from 400 to 4000 cm^{-1}.

RESULTS AND DISCUSSION

Most of the prepared films, including the PMMA/Saran F, aPMMA/sPMMA, and aPMMA/sPMMA/Saran F blends, appeared to be transparent, indicating possible miscibility.

PMMA/Saran F Blends

The second thermal scans from 30°C to 180°C of the PMMA/Saran F blends are presented in Figures 1–3 in the order of isotactic, atactic, and syndiotactic PMMAs, respectively. The first scans are not shown for brevity. The estimated T_{gsc} and T_{gq} values of the PMMA/Saran F blends are given in Table I. There are differences between most of the T_{gsc} and T_{gq} values except in one composition. Most of the as-cast samples had two T_gs except the aPMMA/Saran F (74.7/25.3) blend had one T_g. Because the T_{gq} values are considered to be free of thermal effects, therefore they are used to determine miscibility. For the iPMMA/Saran F and aPMMA/Saran F blends, each composition of
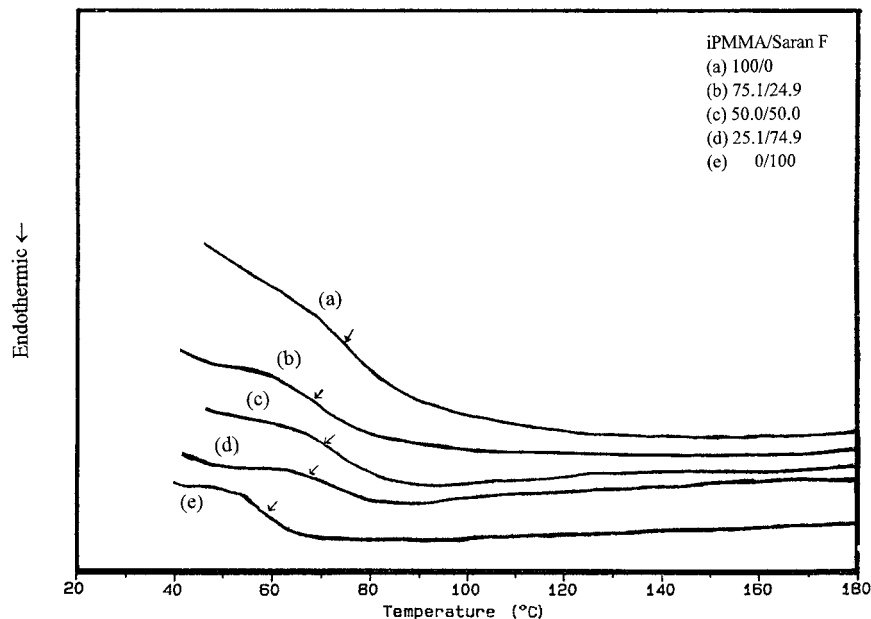
Figure 1 DSC thermograms of the iPMMA/Saran F blend.

the blends showed a single T_g value, so these two blends are determined to be miscible. Observation of two T_gs and opacity in most of the composition of the sPMMA/Saran F blend rendered it immiscible. The T_{gq} values of the PMMA/Saran F blends taken from Table I were plotted in Figure 4. For the miscible iPMMA/Saran F and aPMMA/ Saran F blends, the T_g values are not very far from weight average. However, when these data points are connected by a smooth curve then the curve becomes more like an asymmetric curve for each blend. Recently Woo and Yau[13] observed miscibility and an asymmetric T_g-composition relationship in the binary blends composed of amor-
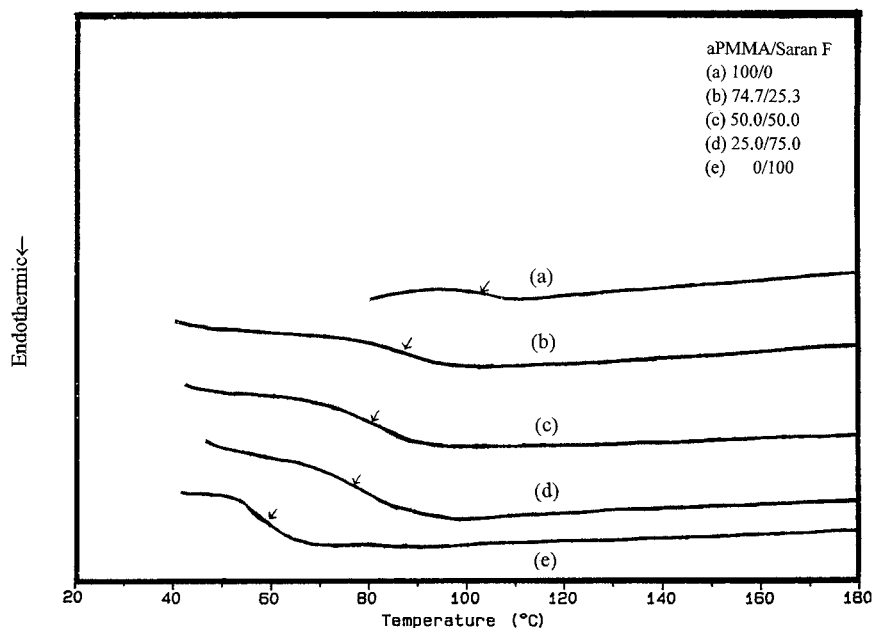

Figure 2 DSC thermograms of the aPMMA/Saran F blend.
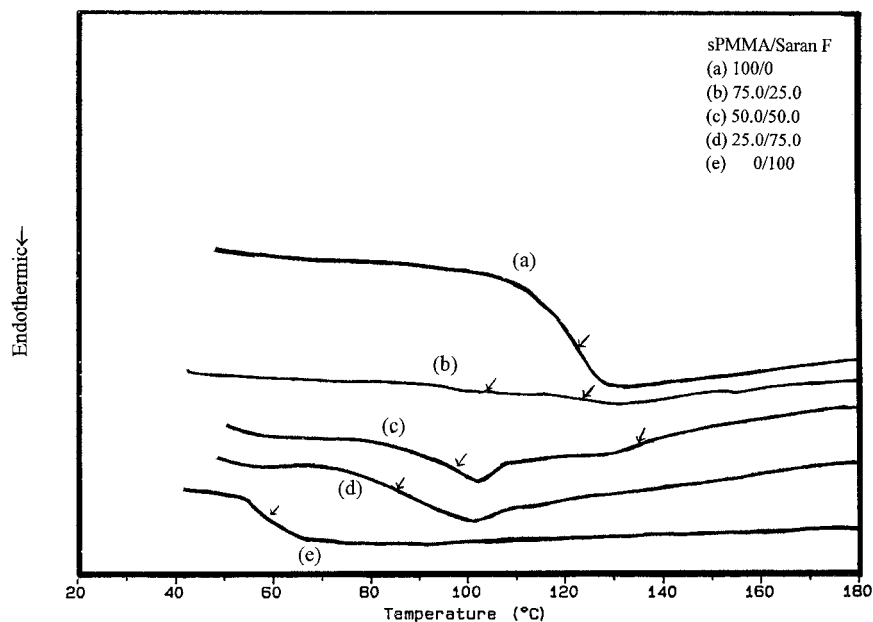
Figure 3 DSC thermograms of the sPMMA/Saran F blend.

phous poly(ether imide) and semicrystalline poly-(butylene terephthalate). In most of the studied blends[13] and a few other miscible systems containing one crystalline polymer,[14,15] the blend T_g values are below weight average. Our case is somehow different because of the closeness of the T_g value to weight average. The T_{gq} values of the sPMMA/Saran F blend are also presented in Figure 4. Only one blend with 75.0% Saran F showed one T_g; the other two compositions had two T_gs. An unusual thing worth noticing is that the high T_g of the blend with 50.0% Saran F is even higher

than that of sPMMA. In the literature Jong et al.[16] found that two of the compositions in the blend of poly(styrene-co-vinylphenol) and iPMMA showed triple transitions. The higher T_g of the three transitions is much higher than that of each component polymer. But they did not give a definite explanation for the observation. Because Hatada et al.[17] reported that the T_g of 100% sPMMA with infinite molecular weight can be as high as 141°C, we conclude that the T_g observation of 134.9°C can be probably assigned to a highly pure sPMMA phase. The glass transition
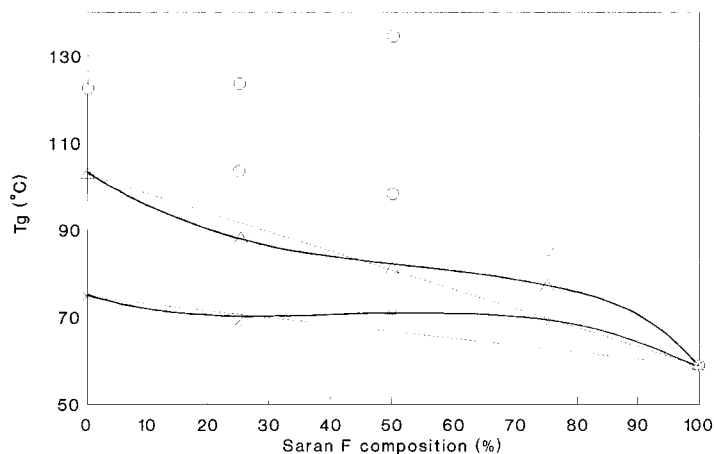

Figure 4 The glass transition temperatures of the PMMA/Saran F blend. ×, iPMMA; △, aPMMA; ○, sPMMA.
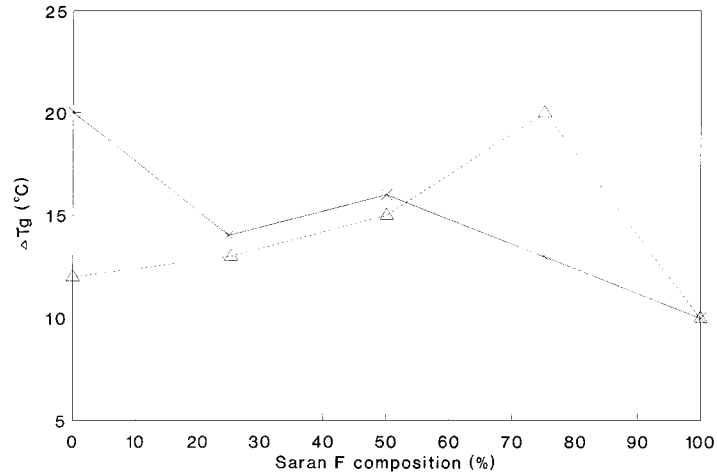
Figure 5   The glass transition regions of the PMMA/Saran F blends. $\times$, iPMMA; $\triangle$, aPMMA.

temperature regions (ΔT_{gq}) were calculated as differences between the onset and the end points of T_{gq} and are also listed in Table I. The ΔT_{gq} values of the two miscible blends were plotted in Figure 5. For the iPMMA/Saran F blend, the ΔT_{gq} are close to and below weight average and this can be taken as a sign of good miscibility observed in this blend. For the aPMMA/Saran blend, a broader glass transition temperature region is

observed with increasing Saran F composition. Because the T_g difference between aPMMA and Saran F is larger, broadening can be caused by the presence of density or composition fluctuation.[18]

FTIR Spectra of the PMMA/Saran F Blends

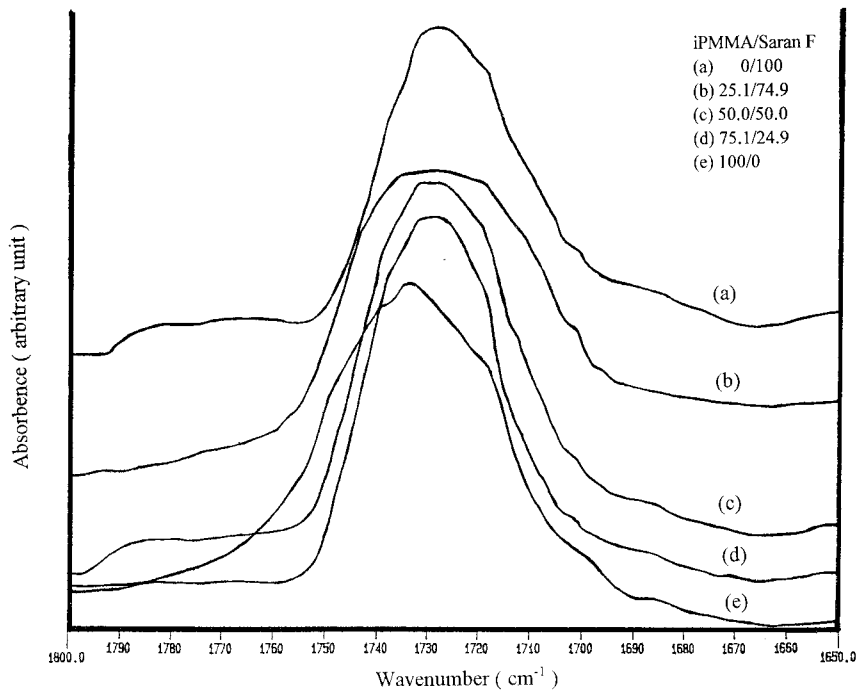The spectra of the PMMA/Saran F blends were experimentally obtained in the region of 400–

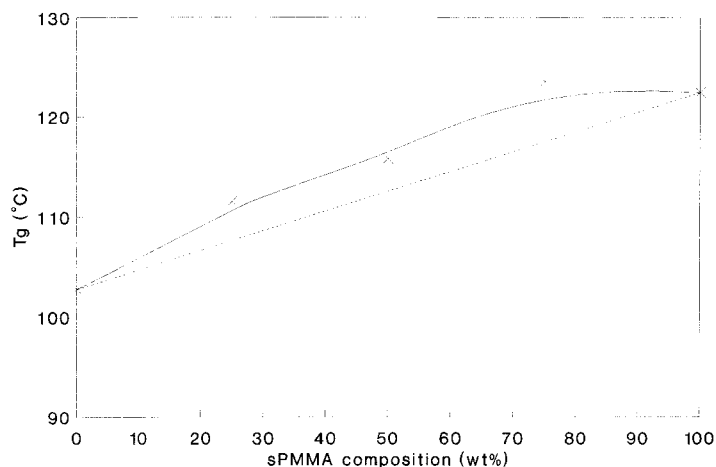**Figure 6**   FTIR spectra of the iPMMA/Saran F blend.

Figure 7 The glass transition temperatures of the aPMMA/sPMMA blends.

4000 cm^{-1}. However, our focus in this study is in the carbonyl absorption region, therefore only the region from 1650 to 1800 cm^{-1} is reported. The spectra of the iPMMA/Saran F blend are given in Figure 6 for representation because the results of the other two blends are similar. The free carbonyl groups of iPMMA absorb at 1733 cm^{-1}. Because the overtone of acrylonitrile has its absorption at 1728 cm^{-1} and the resolution of measurements is 4 cm^{-1}, therefore the seemingly observed peak shift cannot be taken as a definite proof that there are interactions between iPMMA and Saran F. In a similar blend of polycaprolactone and Saran F, Garton et al.[11] observed a peak shift of about 7 cm^{-1} in the carbonyl region between polycaprolactone and a blend with 80% Saran F at 100°C. However, they are still not sure of the nature of the interaction being hydrogen-bonding or dipole-dipole interaction.

aPMMA/sPMMA and Ternary Blends

We have already shown that iPMMA and aPMMA are miscible but sPMMA is immiscible with Saran F. Are ternary mixtures of aPMMA, sPMMA, and Saran F miscible or immiscible? To answer this question, we undertook an investigation on the miscibility of the previously mentioned ternary blends. First, we had to make sure that aPMMA and sPMMA are miscible. The thermal scans of the aPMMA/sPMMA blend are not given for brevity. But the estimated T_{gsc} and T_{gq} values of the same blend are tabulated in Table II. It is obvious that there is essentially no difference between the values of T_{gsc} and T_{gq}. Each composition of the blend had a single T_g indicating miscibility. The

T_{gq} values of the blend were plotted in Figure 7 and found to be higher than those predicted by weight average. The elevation is probably caused by stereocomplexation occurred between aPMMA and sPMMA. The formation of a stereocomplex between iPMMA and sPMMA was known to occur in the bulk or in the dilute solution.[19] But to our knowledge, stereocomplexation between aPMMA and sPMMA has never been reported before. The evidence for stereocomplexation between aPMMA and sPMMA is still thin in the current stage. More works need to be done to clarify this aspect. The ΔT_{gq} values of the aPMMA/sPMMA blend are also listed in Table II. A broadening of the glass transition temperature regions (ΔT_{gq}) was observed in two compositions and can be possibly caused by a distribution of complexed and noncomplexed polymer segments. It is obvious that complexed and noncomplexed polymers do not exhibit the same chain motion thus resulting in slightly different T_gs.

Three compositions of the ternary blends were measured calorimetrically and the second ther-

Table II   The Glass Transition Temperatures of the aPMMA/sPMMA Blend

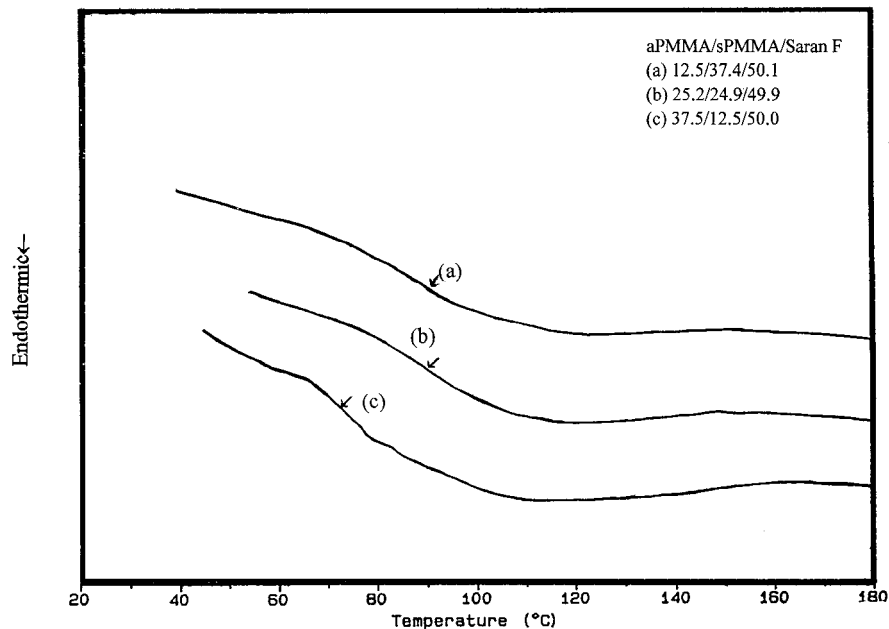|	T_{gsc} (°C)	T_{gq} (°C)	ΔT_{gq} (°C)
aPMMA/sPMMA			
100/0	103	103	12
75.0/25.0	112	112	9
50.0/50.0	116	116	18
25.0/75.0	123	124	17
0/100	121	122	13

Figure 8 DSC thermograms of the aPMMA/sPMMA/Saran F blend.

mal scans of them are shown in Figure 8. The estimated T_{gsc} and T_{gq} values of the ternary blends are tabulated in Table III. All the as-cast samples had two T_gs. However, the quenched samples all had a single T_g. Therefore the ternary blends are determined to be miscible for the studied compositions. The glass transition temperature regions (ΔT_{gq}) (also listed in Table III) of the same blends had broadened when compared with those of component polymers. According to literature, broadening is normal for multicomponent system.

For polymer blends with weak or no interaction, the Fox equation[20] seems to predict the glass transition temperature well. The Fox equation extended for a ternary mixture is shown below as in eq. (1):

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} + w_3/T_{g3} \qquad (1)$$

where T_g is the glass transition temperature of a blend, w_1, w_2, and w_3 are the weight fractions of polymers 1, 2, and 3, respectively. The estimated T_g values from the Fox equation (designated as $T_g{}^a$) are also given in Table III for reference. However, the agreement between the Fox predictions and experimental T_gs is not good.

Kwei et al.[21] reported the results of similar ternary mixtures of PMMA, poly(ethyl metharylate) (PEMA), and PVDF. PMMA and PVDF were found to form miscible mixture through melting point depression and kinetic studies.[22] The binary interaction parameter between PEMA and PVDF was determined to be negative.[23] Therefore PEMA is also miscible with PVDF. However, for PMMA and PEMA mixtures, phase separation has been observed[24] and so they are immiscible. Based on the observation of a single T_g in most of the PMMA/PEMA/PVDF blends, they concluded

Table III   The Glass Transition Temperatures of the Ternary Blends

	T_{gsc} (°C)	T_{gq} (°C)	$T_g{}^a$ (°C)	ΔT_{gq} (°C)
aPMMA/sPMMA/Saran F				
37.5/12.5/50.0	70,94	73	81	24
25.2/24.9/49.9	67,92	90	84	27
12.5/37.4/50.1	71,94	90	86	19

^a Estimated from the Fox equation.

that two immiscible polymers, PMMA and PEMA are brought together by PVDF to form miscible mixtures.[21] The situation in our study is similar but somehow different from Kwei's studies, although Saran F contains vinylidene chloride segments similar to vinylidene fluoride units in PVDF. However aPMMA is the one that is both miscible with the immiscible pair, Saran F and sPMMA. Our results indicate that the ternary blends of aPMMA, sPMMA, and Saran F are miscible for the studied compositions (ca. 3/1/4, 2/2/4, and 1/3/4), but the aPMMA/sPMMA/Saran F (0/4/4) blend is immiscible. Therefore adding aPMMA to a mixture of sPMMA and Saran F by fixing the fraction of Saran F really causes the blends to be miscible. The investigation of the cosolvent effect of aPMMA by keeping the sPMMA/Saran F ratio constant and increasing the aPMMA concentration is currently in progress and will be reported in a forthcoming article.

CONCLUSIONS

iPMMA and aPMMA are determined to be miscible with Saran F. The results are corroborated by observed transparency and a single transition temperature for each composition of the blends. However, immiscibility was found between sPMMA and Saran F because of the observed opacity and double glass transition temperatures in most compositions of the blend. Therefore, it can be concluded that the tacticity of PMMA has an definite impact on its miscibility with Saran F. Although a direct proof of interaction between PMMA and Saran F was not obtained experimentally, the miscibility is still believed to be driven by hydrogen-bonding and/or dipole-dipole interaction. aPMMA and sPMMA are confirmed to be miscible and a T_g elevation is observed in their blends. Although sPMMA is immiscible with Saran F, the ternary blends of aPMMA, sPMMA, and Saran F for the studied compositions are determined to be miscible. Increasing the composition of aPMMA and also decreasing the composition of sPMMA cause the ternary blends to be miscible.

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.; Veeman, 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 Edn 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. Aubin, M.; Bedard, Y.; Morrissette, M.-F.; Prud'homme, R. E. J Polym Sci Polym Phys Edn 1983, 21, 233.
10. Tremblay, C.; Prud'homme, R. E. J Polym Sci Polym Phys Edn 1984, 22, 1857.
11. Garton, A.; Aubin, M.; Prud'homme, R. E. J Polym Sci Polym Letters Edn 1983, 21, 45.
12. Gerrard, D. L.; Maddams, W. F.; Shapiro, J. S. Makromol Chem 1984, 185, 1843.
13. Woo, E. M.; Yau, S. N. Macromolecules 1997, 30, 3626.
14. Siciliano, A.; Seves, A.; Demarco, T.; Cimmino, S.; Martuscelli, E.; Silvestre, C. Macromolecules 1995, 28, 8065.
15. Aubin, M.; Prud'homme, R. E. Macromolecules 1988, 21, 1945.
16. Jong, L.; Pearce, E. M.; Kwei, T. K. Polymer 1993, 34, 48.
17. Hatada, K.; Kitayama, T.; Fujimoto, N.; Nishiura, T. J Macro Sci Pure Appl Chem 1993, A30 (9 & 10), 645.
18. Prud'homme, R. E. Polym Eng Sci 1982, 22, 90.
19. Spevacek, J.; Schneider, B. Adv Coll Interf Sci 1987, 27, 81.
20. Fox, T. G. J Appl Bull Am Phys Soc 1956, 1, 123.
21. Kwei, T. K.; Frisch, H. L.; Radigan, W.; Vogel, S. Macromolecules 1977, 10, 157.
22. Nishi, T.; Wang, T. T. Macromolecules 1975, 8, 909.
23. Kwei, T. K.; Patterson, G. D.; Wang, T. T. Macromolecules 1976, 9, 780.
24. Hughes, L. J.; Britt, G. E. J Appl Polym Sci 1961, 5, 337.