

Effect of Tacticity of Poly(methyl methacrylate) on the Miscibility with Poly(styrene-*co*-acrylonitrile)

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Received 13 October 1998; accepted 16 April 1999

ABSTRACT: Isotactic, atactic, and syndiotactic poly(methyl methacrylates) (PMMA) (designated as iPMMA, aPMMA, and sPMMA) with approximately the same molecular weight were mixed separately with poly(styrene-*co*-acrylonitrile) (abbreviated as PSAN) containing 25 wt % of acrylonitrile in tetrahydrofuran 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 PSAN. The aPMMA/PSAN and sPMMA/PSAN blends were found to be miscible because all the prepared films were transparent and showed composition dependent glass transition temperatures (T_g 's). The glass transition temperatures of the two miscible blends were fitted well by the Fox equation, and no broadening of the glass transition regions was observed. The iPMMA/PSAN blends were found to be immiscible, because most of the cast films were translucent and had two glass transition temperatures. Through the use of a simple binary interaction model, the following comments can be drawn. The isotactic MMA segments seemed to interact differently with styrene and with acrylonitrile segments from atactic or syndiotactic MMA segments. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2894–2899, 1999

Key words: tacticity; poly(methyl methacrylate); poly(styrene-*co*-acrylonitrile); 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 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. Because atactic PMMA is mainly composed of syndiotactic ones, the result of the atactic one is often similar to the syndiotactic one.

Most of the previous studies^{1–8} were concentrated on a few blends such as poly(vinylidene fluoride) (PVDF), poly(ethylene oxide) (PEO), and poly(vinyl chloride) (PVC) with stereoregular PMMA. According to Fowler et al.,⁹ PMMA is miscible with poly(styrene-*co*-acrylonitrile) (PSAN) when the AN content is between the lower and upper limits of miscibility window. The reported lower and upper limits of miscibility window are 6.3–9.5 wt % and 28.0–32.3 wt %, respectively. The experimental glass transition temperature (T_g) of their PMMA is 108°C. The PMMA they

Contract grant sponsor: National Council of Taiwan; contract grant number: NSC-85-2216-E-041-001.

Journal of Applied Polymer Science, Vol. 74, 2894–2899 (1999)

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CCC 0021-8995/99/122894-06

Table I The Glass Transition Temperatures of the Prepared Polymers

	T_{g1} (°C)	T_{g2} (°C)	T_{g2}^a (°C)	T_{g2}^b	ΔT_g (°C)
(1) iPMMA/PSAN					
100/0	71.9	74.6	—	—	20
74.8/25.2	71.3, 114.8	71.8, 110.2	84.0	84.8	15, 13
48.9/51.1	73.7, 105.2	71.0, 111.5	94.2	95.3	8, 14
25.1/74.9	105.7	109.8	104.1	104.9	12
(2) aPMMA/PSAN					
100/0	103.4	102.7	—	—	12
75.0/25.0	78.7, 109.5	109.5	105.7	105.8	13
51.4/48.6	109.8	109.9	108.6	108.7	11
25.0/75.0	110.5	109.8	111.9	112.0	10
(3) sPMMA/PSAN					
100/0	121.4	122.4	—	—	13
74.9/25.1	123.5	122.2	120.5	120.6	13
50.0/50.0	121.0	121.7	118.7	118.8	11
24.8/75.2	117.0	116.6	116.9	116.9	11
0/100	117.2	115.1	—	—	9

^a Estimated from the Fox equation.^b Estimated from weight average.

used can be classified as aPMMA. Suess et al.¹⁰ reported that PMMA is miscible with PSAN when the AN content is between 8.9–9.4 wt % and 34.4–36.9%. The T_g values of their miscible PMMA/PSAN blends were fitted well by the Fox equation and a broadening of the glass transition was observed for blend compositions above 60 wt % PMMA. The T_g of their PMMA is estimated to be 125°C, and can be considered syndiotactic. Therefore, from the literature, PMMA is miscible with PSAN with a specific range of AN content. The driving force for the miscibility observed is believed to be a highly repulsive styrene–acrylonitrile interaction.¹¹ To our knowledge, there have been no reports about tacticity effect of PMMA on the miscibility with poly(styrene-*co*-acrylonitrile). Therefore, a systematic study of the effect of tacticity of PMMA on its miscibility with PSAN was pursued in our laboratory.

In this article, isotactic, atactic, and syndiotactic PMMAs with approximately the same molecular weight were blended with poly(styrene-*co*-acrylonitrile) (PSAN) containing 25 wt % of acrylonitrile in tetrahydrofuran to cast into films. The glass transition temperatures of the polymers were measured. It is believed that there is no or weak interaction existing between PMMA and PSAN. Therefore, Fourier transform infrared spectroscopy or other spectroscopic techniques were not used in this study. In this report, the miscibility of the prepared blends is investigated

based on the data of glass transition temperatures and transparency of the cast films.

EXPERIMENTAL

Materials

Isotactic, atactic, and syndiotactic PMMAs (designated as i, a, and sPMMA in this study) were purchased from Polysciences, Inc, Warrington, PA. According to the supplier information, the molecular weights (M_w s) of iPMMA, aPMMA, and sPMMA are the same at about 100,000. The polydispersities (M_w/M_n) of the three PMMAs were not measured. However, the molecular weight distribution effect is believed to be minimal in the current study when compared with the effect of tacticity. The poly(styrene-*co*-acrylonitrile) (PSAN) copolymer contained 25 wt % of AN units, and was purchased from Aldrich Chemical Company Inc., Milwaukee, WI. The M_w value for PSAN is 165,000. PSAN was mixed with each PMMA individually to form blends in the weight ratios of approximately 1/3, 1/1, and 3/1. The actual compositions will be shown later in Table I. We did not characterize the tacticity of PMMA by NMR. Therefore, a simple estimation of the fractions of meso and racemic diads was resorted. The meso diad fractions of PMMA were computed previously.¹² The meso fractions of iPMMA, aPMMA,

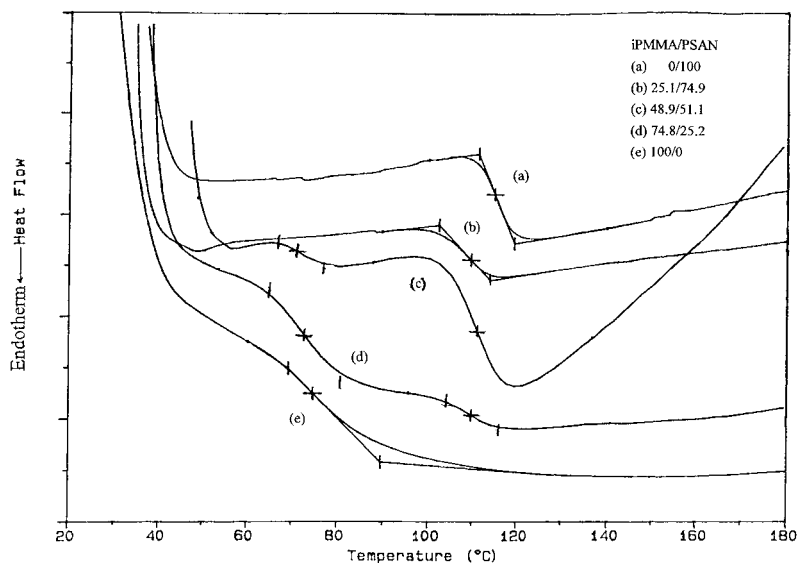


Figure 1 DSC thermograms of iPMMA/PSAN blends.

and sPMMA are $68.7 \pm 8.2\%$, $33.8 \pm 6.4\%$, and $9.3 \pm 5.1\%$, respectively.

Film Preparation

Thin films of individual polymers and their blends were made by solution casting onto glass plates. 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, NJ. The final drying step for all the films took place in a vacuum oven for about 1 day at $92\text{--}125^\circ\text{C}$, which was above the glass transition temperatures of the individual polymers. Then the films were cooled down to room temperature slowly by air cooling. The as-cast films were used for DSC studies.

Differential Scanning Calorimetry (DSC)

The glass transition temperatures (T_g s) of the polymer blends were determined by using a DuPont 2000 thermal analyzer. Experiments were performed in two consecutive scans in an ambient environment of nitrogen gas at a flowing rate of $100\text{--}110\text{ mL/min}$. 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 a second time. A scanning temperature from 30 to 200°C and a heating rate of 20°C/min were used in each scan. The samples were quenched quickly enough to prevent any crystallization detected by DSC. There was also no trace of solvent in the

films detected 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_{g1} and T_{g2} , respectively. Therefore, T_{g1} is the T_g of the as-cast films and T_{g2} is the T_g of the quenched films.

RESULTS AND DISCUSSION

Glass Transition Temperature

The aPMMA/PSAN and sPMMA/PSAN blends after preparation appeared to be transparent, indicating possible miscibility. But for the iPMMA/PSAN blends, most of the prepared films were translucent, indicating possible immiscibility. The second thermal scans from 30 to 180°C of the three polymer blends are presented in Figures 1, 2, and 3, respectively. The T_{g1} and T_{g2} values of the three polymer blends are listed in Table I. There is little difference between most of the T_{g1} and T_{g2} values with few exceptions. For the iPMMA/PSAN ($74.8/25.2$ and $48.9/51.1$) blends, the as-cast and quenched films behaved somehow differently. If the difference of T_g over 4°C is considered to be significant, the following comments can be drawn. For the iPMMA/PSAN ($74.8/25.2$) blend, the as-cast film had two phases. The low T_g phase was composed of iPMMA, and the high T_g one corresponded to PSAN. After quench-

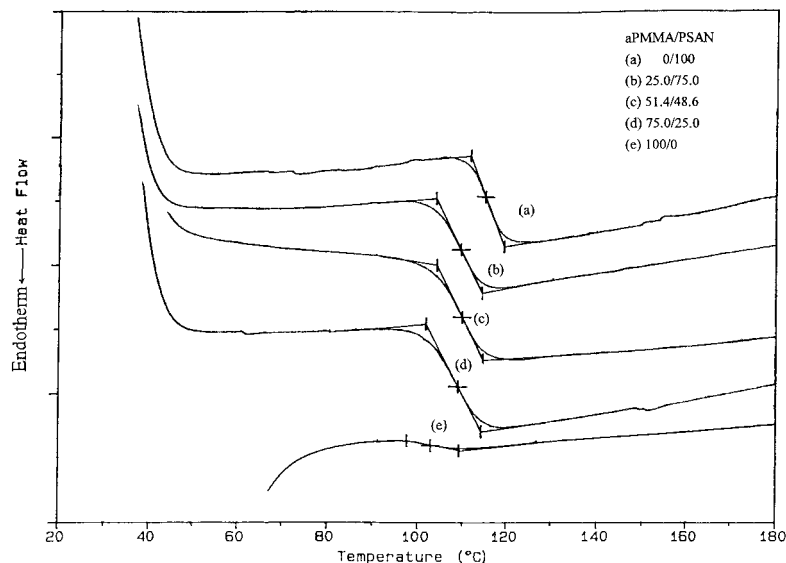


Figure 2 DSC thermograms of aPMMA/PSAN blends.

ing, some of the iPMMA dissolved in PSAN and caused a lowering of the T_g . However, the low T_g phase had practically the same T_g , indicating little or no PSAN solubility in iPMMA. The as-cast iPMMA/PSAN (48.9/51.1) blend also had two phases. The high T_g phase was a mixture of iPMMA and PSAN, and the low T_g one was again iPMMA. Quenching of this sample seemed to cause the high T_g phase to have a higher T_g (i.e., a lower solubility of iPMMA in PSAN). The low T_g phase was again not affected by quenching. The other and obvious exception is the aPMMA/PSAN

(75.0/25.0) blend. The as-cast sample had two T_g s. However, the quenched sample appeared to be miscible with only one T_g . Because the T_{g2} values are considered independent of thermal history, they are used to define miscibility in the following discussion.

The aPMMA/PSAN and sPMMA/PSAN blends are miscible because all the prepared polymers were transparent and exhibited a single T_g . The results of the two miscible blends are the same as the literature findings.^{9,10} The iPMMA/PSAN (74.8/25.2 and 48.9/51.1) blends appeared to be

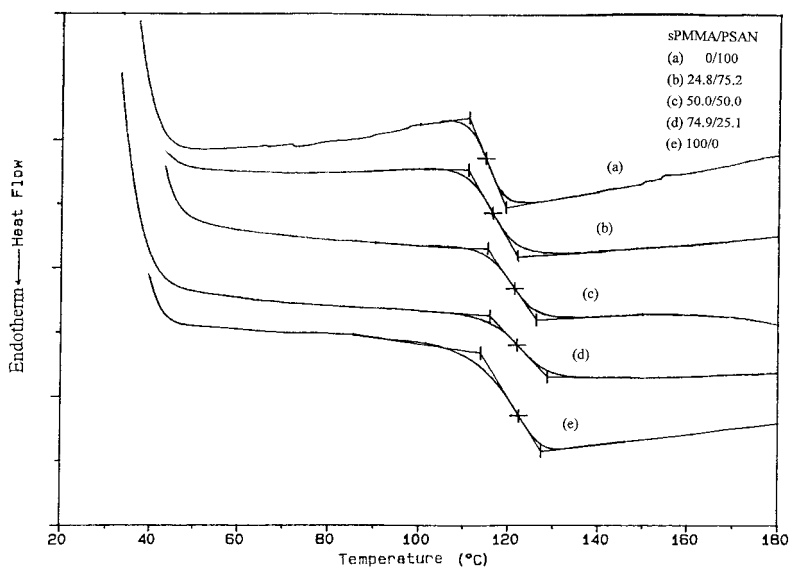


Figure 3 DSC thermograms of sPMMA/PSAN blends.

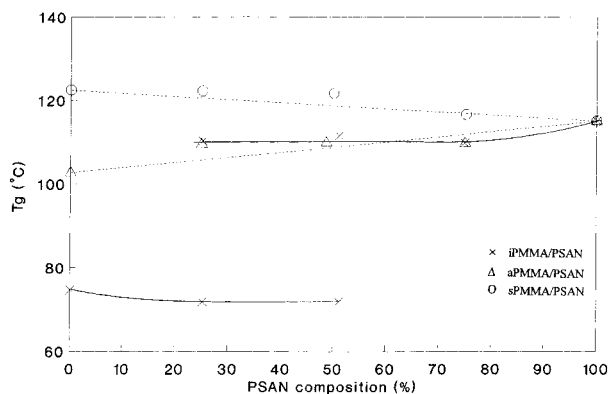


Figure 4 Glass transition temperatures of three polymer blends. estimated according to the Fox eq.

phase separated, and had two T_g s. But the iPMMMA/PSAN (25.1/74.9) blend showed one T_g , and appeared to be miscible. Taking into account the inaccuracy in estimating T_g , the following observations can be made from the T_{g2} data of the iPMMMA/PSAN blends. The iPMMMA/PSAN (74.8/25.2 and 48.9/51.1) blends both seemed to separate into two similar phases. The low T_g phase was composed mainly of iPMMMA. The high T_g phase was a mixture of iPMMMA and PSAN with about 1 to 3 weight ratio. Adding more of the iPMMMA (causing a ratio of iPMMMA to PSAN higher than 1/3) seemed to induce immiscibility. The iPMMMA/PSAN blends are considered to be immiscible according to opacity and two T_g s observed in most of the prepared samples.

All the T_{g2} values of the three polymer blends plotted vs. PSAN composition are shown in Figure 4. For polymer blends with weak or no interaction, the Fox equation¹³ seems to predict the glass transition temperature quite well. The Fox equation is shown below as in eq. (1)

$$1/T_g = w_x/T_{gx} + w_y/T_{gy} \quad (1)$$

where T_g is the glass transition temperature of a blend, w_x is the weight fraction of polymer 1 and w_y is the weight fraction of polymer 2. The weight average equation [$T_g = w_x T_{gx} + w_y T_{gy}$, symbols with the same meanings as in eq. (1)] and the Fox equation were both used to estimate the T_g s of the studied blends. The estimated T_g value from either the Fox or weight average equation is practically the same. For the aPMMA/PSAN and sPMMA/PSAN blends, the T_g values are fitted well by the Fox equation (shown as the dashed

lines in Fig. 4). Because there are two T_g s in most compositions of the iPMMMA/PSAN blends, the estimated T_g values were not plotted in Figure 4.

The glass transition temperature regions (ΔT_g) were calculated as the differences between the onset and the end points of T_{g2} . The calculated results of the three polymer blends are listed in Table I. In Figure 5, only the ΔT_g values of the miscible aPMMA/PSAN and sPMMA/PSAN blends are given. It is interesting to notice that there is no broadening of the glass transition temperature regions. In other words, all the ΔT_g values follow more or less the dotted lines (the weight average values). This can be taken as a sign for the good miscibility that exists in the aPMMA/PSAN and sPMMA/PSAN blends. Suess et al.⁹ observed broadening of T_g in the PMMA/PSAN blend with a PMMA composition above 60 wt %. But the PSAN they used had an AN content of 12.9 wt %, different from the 25.0 wt % in this study.

Conversely, the aPMMA/PSAN and sPMMA/PSAN blends are miscible because all the films are transparent after preparation, and there is a single T_g for each composition of the blends. Because of observed opacity and two glass transition temperatures in most of the compositions of the iPMMMA/PSAN blends, iPMMMA and PSAN are immiscible.

Binary Interaction Model

A simple binary interaction model shown below is often used to explain a blend of homopolymer and copolymer with the so-called "repulsion effect."¹⁴ For a blend of a homopolymer (A) and a random copolymer (B), where A consists of segments of type 1 and B of segments of types 2 and 3, the interaction parameter χ_{AB} can be expressed in

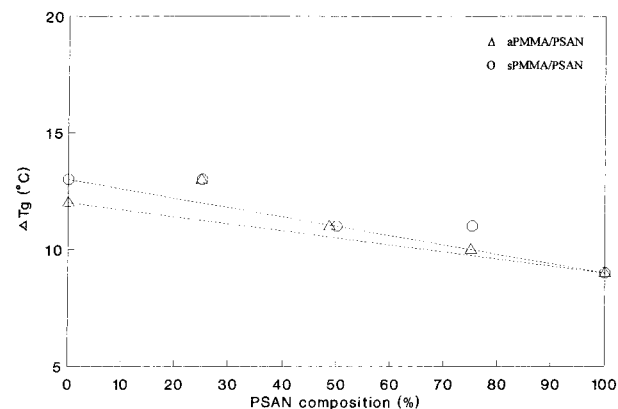


Figure 5 Glass transition temperature regions of three polymer blends. weight average line.

terms of the respective segmental interaction parameters¹⁵:

$$\chi_{AB} = \beta\chi_{12} + (1 - \beta)\chi_{13} - \beta(1 - \beta)\chi_{23} \quad (2)$$

where β represents the mol fraction of component 2 in the random copolymer. Miscibility is only to be expected if $\chi_{AB} < 0$. In the case $0 < \chi_{12} \leq \chi_{13} < \chi_{23}$, the repulsion between the different segments comprising the copolymer is stronger than the repulsions between the homopolymer and copolymer segments. Therefore, the miscibility in a certain range of copolymer composition does not originate from any specific interactions but arises from the special structure of χ_{AB} given by eq. (2).

PMMA is known to be miscible with PSAN because of highly repulsive styrene–acrylonitrile interaction. Therefore, eq. (2) is applicable to PMMA/PSAN blends. Methyl methacrylate (MMA), styrene (S) and acrylonitrile (AN) are designated as segments 1, 2, and 3, respectively. Brannock et al.¹⁶ reported that $0 < \chi_{12} < \chi_{13} < \chi_{23}$ in the aPMMA/PSAN blends. This means that the MMA–S and MMA–AN repulsion interactions are both weaker than the S–AN interaction. The MMA–AN interaction is more repulsive than the MMA–S interaction. According to the results of refs. 9 and 10 and this study, the miscibility of PMMA/PSAN blends increases very likely with the increasing syndiotacticity of PMMA. The interactions of isotactic MMA–S and isotactic MMA–AN are likely to be different from atactic or syndiotactic PMMA interactions with S and AN causing the χ_{AB} value higher than 0. Conversely, the iPMMA/PSAN blends are immiscible. Although a segment repulsion (enthalpic) effect is used here to explain the miscibility behavior, the role of backbone conformation (tacticity) is the primary factor affecting miscibility.

CONCLUSIONS

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

PSAN. The prepared aPMMA/PSAN and sPMMA/PSAN blends are determined to be miscible based on the transparency and a single glass transition temperature for each composition of the films. However, iPMMA is immiscible with PSAN because of observed opacity and two glass transition temperatures for most compositions of the blends.

The support by the National Science Council of Taiwan, R.O.C. Grant NSC-85-2216-E-041-001 is greatly appreciated.

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