Polymer Blends of Stereoregular Poly(methyl methacrylate) and Poly(styrene-*co-p*-hydroxystyrene)

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ABSTRACT: Isotactic, atactic, and syndiotactic poly(methyl methacrylates) (PMMAs) (designated as iPMMA, aPMMA, and sPMMA) were mixed with poly(styrene-co-phydroxystyrene) (abbreviated as PHS) containing 15 mol % of hydroxystyrene separately in 2-butanone to make three polymer blend systems. Differential scanning calorimetry (DSC) and Fourier transform infrared (FTIR) spectroscopy were used to study the miscibility of these blends. The three polymer blends were found to be miscible, because all the prepared films were transparent and there was a single glass transition temperature (T_{g}) for each composition of the polymers. T_{g} elevation (above the additivity rule) is observed in all the three PMMA/PHS blends mainly because of hydrogen bonding. If less effective hydrogen bonding based on the FTIR evidence is assumed to infer less exothermic mixing, sPMMA may not be miscible with PHS over a broader range of conditions as iPMMA and aPMMA. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 431-440, 1999

Key words: polymer blends; stereoregular; PMMA

INTRODUCTION

It has been known for years that the stereoregularity of polymer chains influences polymer-polymer miscibility. Because of its availability in both syndiotactic and isotactic forms, poly(methyl methacrylate) (PMMA) has been used frequently in the investigation of the effect of tacticity on miscibility. Several $\operatorname{articles}^{1-8}$ 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 samples, the results are sometimes inconsistent. Because atactic PMMA is mainly syndiotactic, the results of atactic and syndiotactic are often similar.

The miscibility between dissimilar polymers can be enhanced by favorable intermolecular interactions. Of the various secondary interaction forces commonly encountered, hydrogen bonding has been the subject of many investigations.⁹ It has been demonstrated in several cases that a small amount of interacting groups suffice to pro-duce miscible systems.^{10,11} For example, PMMA is immiscible with polystyrene (PS), but miscible with polyvinylphenol (PVPh).^{12,13} When PS is modified to contain about 4% or more of vinylphenol (or hydroxystyrene) as comonomer units, the free energy change caused by hydrogen bonding interaction between the carbonyl and hydroxyl groups renders the modified PS miscible with PMMA.^{11–14}

In a previous investigation,¹⁵ isotactic, atactic, and syndiotactic PMMAs were blended with PVPh in tetrahydrofuran to make three polymer blend systems. All the films were transparent after preparation. iPMMA was found to be more miscible with PVPh than aPMMA or sPMMA.

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The results are corroborated by the glass transition temperature measurements and Fourier transform infrared (FTIR) spectra. There is a single glass transition temperature for each composition in the blends of iPMMA and PVPh. Therefore, iPMMA forms miscible blends with PVPh. However, there are two glass transition temperatures for one composition of the aPMMA/PVPh or sPMMA/PVPh blends. Thus, partially miscible blends are formed between aPMMA (or sPMMA) and PVPh. Also from FTIR spectra, the degree of hydrogen bonding of iPMMA with PVPh is the highest among these three blends. Similar results are reported by Dong and Ozaki.¹⁶ They investigated the miscibility of aPMMA and PVPh by FTIR and FT-Raman spectroscopy. Although both techniques provide evidence for the formation of hydrogen bonds between the hydroxyl groups of PVPh and the ester groups of aPMMA, the blends show only a limited degree of hydrogen-bonding interactions when cast from tetrahydrofuran solutions. Comparison of the blends with those cast from a ketone solution and changes in the hydrogen-bonded fractions after thermal cycles indicate that the blends are partially miscible mixtures.

The miscibility of poly(styrene-co-hydroxystyrene) containing 5 mol % hydroxystyrene monomer units (MPS-5) with iPMMA or with sPMMA was studied previously by Jong¹⁷ with ¹³C solid state NMR complemented with cloud point measurements and differential scanning calorimetry. sPMMA is more miscible with MPS-5 than iPMMA. The glass transition temperatures $(T_{g}s)$ of the sPMMA/MPS-5 blends are lower than the predictions of the Fox equation or the weight average. This is to be contrasted with the results found for the blends of aPMMA with MPS-5. In the latter blends, the T_g values are higher by 1-4°C than the weight average predictions.¹⁸ Jong also found that two compositions (50 and 70% iPMMA) of the iPMMA/MPS-5 blends showed three transitions, indicative of multiple phases present in the blend. From Jong's results, the following research was prompted. Examining the miscibility of poly(styrene-co-p-hydroxystyrene) with i, a, and sPMMAs from careful sample preparations, T_g measurements, and FTIR spectra (detecting possible hydrogen bonding, which was not measured in ref. 17).

In this article, isotactic, atactic, and syndiotactic PMMAs with almost the same molecular weight were blended with poly(styrene-*co-p*-hydroxystyrene) (PHS) containing 15 mol % (instead of 5 mol %) of hydroxystyrene in 2-butanone to cast into films. The glass transition temperatures

Table IThe Glass Transition Temperatures ofthe Prepared Polymers

	$\underset{(^{\circ}\mathrm{C})}{T_{g1}}$	$\begin{array}{c} T_{g2} \\ (^{\circ}\mathrm{C}) \end{array}$	$\begin{array}{c}{T_{g2}}^{\rm a}\\ (^{\circ}{\rm C})\end{array}$	ΔT_g (°C)
(1) iPMMA/PHS				
100/0	71.9	74.6		20
74.9/25.1	88.5	89.1	89.8	7
50.1/49.9	100.5	102.9	102.9	15
24.9/75.1	114.4	115.0	114.4	11
(2) aPMMA/PHS				
100/0	103.4	102.7		12
75.0/25.0	112.4	111.9	111.2	11
49.9/50.1	117.6	117.0	117.5	10
24.9/75.1	121.8	121.4	121.7	10
(3) sPMMA/PHS				
100/0	121.4	122.4		13
75.0/25.0	128.1	127.3	126.6	11
49.9/50.1	128.5	127.9	128.2	12
24.9/75.1	127.0	126.6	127.3	11
0/100	123.7	123.8		12

^a Estimated from eq. (1).

of the polymers were measured, and FTIR spectra of the polymers were conducted to study the degree of hydrogen bonding between different tactic PMMAs and poly(styrene-*co-p*-hydroxystyrene). In this report, the miscibility of the prepared blends is investigated based on the data of glass transition temperatures and FTIR spectra.

EXPERIMENTAL

Materials

Isotactic, atactic, and syndiotactic PMMAs (designated as i, a, and s-PMMA in this study) were purchased from Polysciences, Inc. (Warrington, PA). According to the supplier information, the molecular weights (M_w) of iPMMA, aPMMA, and sPMMA are the same about 100,000. The poly-(styrene-*co*-p-hydroxystyrene) (PHS) copolymer used for this study contained 15 mol % of HS units and was synthesized by using a procedure described previously.¹⁹ The M_n and M_w/M_n values for PHS are 85,600 and 1.47. PHS was mixed with each PMMA individually to form blends in the weight ratios of about 1/3, 1/1, and 3/1. The actual compositions are shown in Table I.

Film Preparation

Thin films of individual polymers and their blends were made by solution casting onto glass



Figure 1 DSC thermograms of iPMMA/PHS blends.

plates. 2-butanone was used as solvent for most compositions, but for PMMA, toluene was used. 2-butanone and toluene are A.C.S. reagent purchased from Aldrich Chemical Company, Inc. (Milwaukee, WI) and Fisher Scientific (Fair Lawn, NJ), respectively. The final drying step for all the films took place in a vacuum oven for about 1 day at 92–125°C, which was above the glass transition temperatures of the polymers. Then the films were cooled down to room temperature slowly by air cooling. All the films were transparent after air cooling, without any observable phase separation. The as-cast films were used for differential scanning calorimetry (DSC), and FTIR studies.

DSC and FTIR Spectroscopy

The glass transition temperatures $(T_g \mathbf{s})$ of the polymer blends were determined by using a Du-Pont 2000 thermal analyzer. 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 the ambient environment of nitrogen gas at a flowing rate of about 100 ml/min. In the first thermal scan, the samples stayed at 200°C for 1 min. The samples were then quenched to 0°C immediately using an ice-water bath. 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_{g1} and T_{g2} , respectively. Therefore, T_{g1} is the T_g of the as-cast films and T_{g2} is that of the quenched films.



Figure 2 DSC thermograms of aPMMA/PHS blends.

The as-cast polymers were ground with KBr powder to make samples for FTIR studies. Spectra were obtained with 64 scans at a resolution of 4 cm^{-1} . The wavelength range was from 400 to 4000 cm⁻¹.

RESULTS AND DISCUSSION

All the polymers, after preparation, appeared to be transparent, indicating possible miscibility. Most of the polymers were more like powdered solids than films because of the brittleness of the two polymers (sPMMA and PHS).

Glass Transition Temperatures

The second thermal scans, from 30 to 180°C of the three polymer blends, are shown in Figures 1–3. According to these figures, there is a single glass transition temperature for each composition.



Figure 3 DSC thermograms of sPMMA/PHS blends.



Figure 4 The glass transition temperatures of the three polymer blends.

Therefore, all the three polymer blends are miscible based on the transparency of the films and composition-dependent glass transition temperature. The T_{g1} and T_{g2} values of the three polymer blends are listed in Table I. There is only a slight difference between the T_{g1} and T_{g2} values. The T_{g2} values are considered independent of thermal history, so they are used for the following discussion.

All the T_{g2} values of the three polymer blends plotted versus PHS composition are shown in Figure 4. In all the three polymer blends, an elevation of T_g (i.e., above the additivity rule) is observed because of hydrogen bonding between PMMA and PHS. Several empirical equations have been proposed to describe the composition dependence of T_g for miscible blends that involve strong specific interaction. Three publications^{20–22} offer theoretical insights into the underlying reason for the experimental observations. In the limiting case, these equations reduce to a simple expression²³:

$$T_g = W_1 T'_{g1} + W_2 T'_{g2} + q W_1 W_2 \tag{1}$$

where W_1 and W_2 denote the weight fractions of the components 1 and 2, T_g , T'_{g1} , and T'_{g2} are the glass transition temperatures of a blend, polymers 1 and 2, respectively, and q is a parameter that depends on the net polymer–polymer interaction (i.e., hydrogen bonding in this article). The following results were obtained from fitting the T_{g2} values in Figure 4 by using eq. (1). For the iPMMA/PHS, aPMMA/PHS, and sPMMA/PHS blends, the q values were estimated to be 15.0, 17.0, and 20.4, respectively. If the q values are used as an indicator for hydrogen bonding, the degree of hydrogen bonding should be in the following order: sPMMA/PHS > aPMMA/PHS > iPMMA/PHS.

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 are shown in Figure 5 and also listed in Table I. It is interesting to note that there is no broadening of the glass transition temperature regions in all the three polymer blends. In other words, all the ΔT_g values fall below the dotted lines (the weight average values). This can be taken as a sign of the good miscibility that exists in all the three polymer blends.

Tacticity Effects

The mm, mr, and rr fractions of the iPMMA, aPMMA, and sPMMA were not measured. The simple estimation of m (meso) or r (racemic) fractions from T_{g2} was resorted. The molecular weights of the three PMMAs are almost 100,000. Thus, the effect of molecular weight on T_g is negligible. Through the years, several equations describing tacticity dependence of T_g have been proposed:

According to Fernandez-Martin²⁴

$$T_{\sigma} = 41 \ (m) + 126 \ (r) \tag{2}$$

According to Allen²⁵

$$T_{\sigma} = 133.4 - 76.6 \ (m) \tag{3}$$

These two equations assume a linear correlation between T_g and tacticity. m_1 , r_1 , m_2 , and r_2 were calculated from eqs. (2) and (3) separately using the T_{g2} values in Table I. The results are



Figure 5 The glass transition temperature regions of the three polymer blends.

	m_1	r_1	m_2	r_2
iPMMA aPMMA	$0.605 \\ 0.274$	$0.395 \\ 0.726$	$\begin{array}{c} 0.768 \\ 0.401 \end{array}$	$0.232 \\ 0.599$
sPMMA	0.042	0.958	0.144	0.856

Table II Estimated Racemic Fraction of PMMA

listed in Table II. Although there are some differences in the numbers from these two equations, the basic trend is the same. The difference is mainly caused by differing assumptions about the T_g of 100% syndiotactic PMMA. It is obvious that sPMMA has a high degree of syndiotacticity, but iPMMA is not highly isotactic. The estimated q values from eq. (1) seem to increase with the increase of r fractions.

FTIR Studies on the As-Cast Films

The FTIR spectra of iPMMA and sPMMA have a subtle difference (not shown here), and their assignments are well documented.²⁶ Because our focus is on hydrogen-bonding interaction, only the absorption of the carbonyl and hydroxyl groups is reported in the following.

The FTIR spectra of the PMMA/PHS blends in the carbonyl absorption region (from 1650 to 1800 cm^{-1}) are presented in Figures 6–8. For the first two figures (the iPMMA and aPMMA blends), two

peaks are observed. One is the free carbonyl group stretching in 1734 cm^{-1} . The other one in 1717 cm^{-1} can be assigned to the hydrogenbonded carbonyl groups. In these two figures, the increase of hydrogen-bonded fraction from 0 to about 25% PHS composition can be seen. However, further increase of PHS composition does not render much increase of hydrogen-bonded fraction. In Figure 8, aside from free carbonyl absorption, there is only a shoulder observed in the sPMMA/PHS (24.9/75.1) blend. Therefore, the as-cast films of the sPMMA/PHS blends does not seem to have much hydrogen-bonded fraction. In Figure 9, the PMMA/PHS (25/75) blends with different tacticities were replotted for comparison. The hydrogen-bonded fractions for iPMMA and aPMMA are about the same, but the hydrogenbonded fraction of sPMMA is obviously smaller.

The hydroxyl absorption spectra (from 3200 to 3700 cm^{-1}) of the studied blends are shown in Figures 10–12. For PHS (plotted in all the three figs.), there are already two peaks observed attributable to self-association (i.e., OH—OH interaction) of hydroxyl groups. The free hydroxyl groups absorption is in 3535 cm⁻¹, and the self-associated hydroxyl groups absorption in 3445 cm⁻¹. For the iPMMA/PHS and aPMMA/PHS blends (plotted in Figs. 10, 11), adding of PMMA causes free hydroxyl groups almost to disappear, and a new peak (in the same position as OH—OH



Figure 6 FTIR spectra of iPMMA/PHS blends in the $1650-1800 \text{ cm}^{-1}$ region.



Figure 7 FTIR spectra of aPMMA/PHS blends in the $1650-1800 \text{ cm}^{-1}$ region.



Figure 8 FTIR spectra of sPMMA/PHS blends in the $1650-1800 \text{ cm}^{-1}$ region.



Figure 9 FTIR spectra of the PMMA/PHS (25/75) blends in the $1650-1800 \text{ cm}^{-1}$ region.

interaction) emerges because of OH—O—C interaction. Adding more PMMA shows little increase of hydrogen-bonded fractions in Figures 10 and 11. In Figure 12, the spectra of the sPMMA/PHS blends are shown. The peak attributable to the OH—O—C interaction also emerges as the increase of the sPMMA composition. The disappearance of free hydroxyl absorption is not obvious because of higher wave number absorption arising from sPMMA absorption itself. When the spectra of the three PMMA/PHS (75/25) blends were plotted together in Figure 13, there was



Figure 10 FTIR spectra of iPMMA/PHS blends in the $3200-3700 \text{ cm}^{-1}$ region.



Figure 11 FTIR spectra of aPMMA/PHS blends in the 3200-3700 cm⁻¹ region.

little difference in the hydrogen-bonded fractions of the three PMMAs. If the contribution from the high wave number peak is neglected (shown as dashed line) in the sPMMA/PHS blends, it seems that iPMMA and aPMMA have more hydrogenbonded fractions than sPMMA. The hydrogenbonded fractions in the hydroxyl absorption should include contributions from both the OH—OH and OH—O=C interactions. Although the OH—OH and OH—O=C interactions cannot be differentiated in the blends, the influence of OH—OH interaction in the blends is believed to



Figure 12 FTIR spectra of sPMMA/PHS blends in the 3200–3700 cm⁻¹ region.



Figure 13 FTIR spectra of the PMMA/PHS (75/25) blends in the 3200-3700 cm⁻¹ region.

be minimal.^{9,18} From FTIR results of both carbonyl and hydroxyl absorptions, the following comments can be drawn. iPMMA and aPMMA have a higher degree of hydrogen bonding with PHS than sPMMA.

Different conclusions are drawn from the DSC and FTIR results. One reason may be because of different sample states. The DSC results were based on the quenched samples, but the FTIR data were performed on the as-cast samples. The T_{g1} values $(T_g {\rm s} \mbox{ of the as-cast samples})$ were also used to calculate q value, and the q values for iPMMA, aPMMA, and sPMMA were found to be 15.9, 17.8, and 25.5, respectively. The q value of sPMMA is, again, the highest among the three. However, there are some drawbacks in using the q value as a criterion for polymer–polymer interaction. First, the accuracy of $T_{g}\xspace$ value is about $\pm 2^{\circ}$ C, and the T_g elevation is not large (2–5°C) in the studied blends likely not precise. Second, tacticity also influences T_g and was not considered in the derivation of eq. (1). Conversely, a direct measurement of the degree of hydrogen bonding through FTIR is more reliable. Therefore, it is concluded that iPMMA and aPMMA form more hydrogen bonds with PHS than sPMMA. If a lower degree of hydrogen bonding based on the FTIR results is assumed to infer less exothermic mixing, it is likely that sPMMA may not be miscible with PHS over a broader range of conditions as iPMMA and aPMMA.

Another thing worth noting is that the results of aPMMA differ from those of sPMMA. This has seldom been observed in the literature. The reason may be as follows. iPMMA, aPMMA, and sPMMA all have mm (isotactic), mr (heterotactic), and rr (syndiotactic) fractions but in very different degrees. According to Table II and taking into account that part of m and r fractions belong to mr fractions, the following conclusions can be drawn. It is obvious that sPMMA is composed mainly of rr fractions and has very few mm and mr fractions. iPMMA consists of about more than half *mm* fractions, and *mr* and *rr* fractions make up the rest. It is likely that aPMMA has more than 50% rr fractions, and the rest is mmand mr fractions. PHS is a random copolymer with 15 mol % of HS groups. From the experimental results of this study, it is inferred that PHS copolymer forms more hydrogen bonds with mm or mr fractions of PMMA than with rr fractions.

CONCLUSIONS

The three PMMA/PHS blends are all miscible, because all the films are transparent after preparation, and there is a single T_g for each composition of the blends. T_g elevation is observed in all the three PMMA/PHS blends mainly because of hydrogen bonding. However, iPMMA and

aPMMA have a higher degree of hydrogen bonding with PHS than sPMMA. The results are corroborated by the carbonyl and hydroxyl absorptions in the FTIR spectra on the as-cast samples. The FTIR results also infer that PHS forms more hydrogen bonds with mm or mr fractions of PMMA than with rr fractions. If a lower degree of hydrogen bonding based on the FTIR data is assumed to infer less exothermic mixing, it is likely that sPMMA may not be miscible with PHS over a broader range of conditions as iPMMA and aPMMA.

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