# Miscibility of Stereoregular Poly(methyl methacrylates) with Poly(styrene-*co*-*p*-(hexafluoro-2-hydroxy-2-propyl)styrene)

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ABSTRACT: A modified polystyrene, poly(styrene-*co*-*p*-(hexafluoro-2-hydroxy-2-propyl)styrene) (FPS), was blended with syndiotactic or isotactic poly(methyl methacrylate) (PMMA) in toluene. Films were prepared under different conditions to control the self-aggregation of PMMA segments. The formation of hydrogen bonding and the attendant changes in the aggregation or crystallization of PMMA segments were determined in the solid state by means of FTIR and WAXD. The results indicate that the aggregation of the PMMA segments is diminished by hydrogen-bonding interaction in both s-PMMA and i-PMMA blends. However, hydrogen bonding between the hydroxyl and carbonyl groups is slightly favored in the s-PMMA blends.

## Introduction

Stereoregular poly(methyl methacrylates) (PMMAs) have been shown to have widely divergent physical properties and provide a unique example where these differences, e.g., glass transition temperature ($T_g$), can be interpreted in terms of molecular architecture and conformational energies.[1] Extensive studies in the past decade have shown that the stereoregularity of poly(methyl methacrylate) has a strong influence on its miscibility with poly(vinylidene fluoride),[2,3] poly(ethylene oxide),[4–8] poly(vinyl chloride) (PVC),[9–15] and other chlorinated polymers.[16] The poor miscibility of isotactic PMMA (i-PMMA) with PVC in comparison with atactic or syndiotactic PMMA (s-PMMA) has been ascribed by Vorenkamp to the differences in the equation of state parameters.[10] A recent calculation[17] based on the polymer reference interaction site model (PRISM) for the PMMA–PVC pair supports the hypothesis that the differences in miscibility result primarily from the different conformations adopted by syndiotactic and isotactic PMMA chains.

In an earlier investigation, we studied the effect of PMMA tacticity on its miscibility with a styrene copolymer containing 5 mol% vinylphenol units as hydrogen bond donors.[18] Since the copolymer contains only 5 mol % vinylphenol units, the hydrogen-bonding interaction is not overwhelming and the system is balanced among the contributions of physical forces, hydrogen bonding, and equation of state effect. Accordingly, even small perturbation of these contributions caused by tacticity differences may disturb the delicate balance and change the sign (positive or negative) of the net free energy of mixing. Indeed, our results indicate that s-PMMA blends are miscible over the entire range of compositions, according to glass transition temperature and NMR proton spin–lattice relaxation time measurements, while i-PMMA is miscible with the styrene copolymer only if the copolymer content reaches ~70 wt % in the blend.

While the use of a styrene copolymer containing only 5 mol % hydrogen bond donating units serves the purpose of magnifying the miscibility differences of the two tactic PMMAs, it has the drawback of rendering the determination of the fraction of hydrogen-bonded carbonyl groups (a few percent) difficult. Therefore we did not try to determine whether the numbers of OH---O=C bonds were different in the two types of blends. The primary motivation of this study was to use a related styrene copolymer which was miscible with both s-PMMA and i-PMMA and to compare the fractions of bound carbonyl groups, $f_b$(C=O), in the two PMMA blends. The copolymer chosen for the purpose contains 10 mol % of *p*-(hexafluoro-2-hydroxy-2-propyl)styrene units. The hexafluoro-2-phenyl-2-propanol group (HFPP) is a very effective hydrogen bond donor, and the equilibrium constants describing the self-association of the HFPP and the interassociation of HFPP with the ester carbonyl groups have been determined from infrared spectroscopic data.[19] This information allow us to compare the experimental values of $f_b$(C=O) with theoretical predictions based on the formulation of Painter and Coleman.[19,20]

A second unresolved problem in the earlier study[18] concerns the observation of two NMR rotating frame spin–lattice relaxation times in two of the syndiotactic PMMA blends; the two relaxation times are suggestive of the presence of microheterogeneities.[21] Although neither X-ray nor light scattering experiments in that study indicated a measurable amount of crystalline PMMA domains, the possibility of aggregation of PMMA segments on a much smaller scale, for example, involving short sequences of stereoregular segments, nevertheless could not be readily dismissed. Therefore, our initial strategy was to select film preparation conditions so that complications arising from the self-aggregation of PMMA segments could be avoided. It turned out, however, that the aggregation phenomenon was not necessarily a handicap in our blending study because changes in the degree of aggregation of PMMA segments provided equally important clues to the extent of mixing. Accordingly, film preparation conditions which favored PMMA aggregation were also included in this investigation. The results are presented below.

## Experimental Section

Poly(styrene-*co*-*p*-(hexafluoro-2-hydroxy-2-propyl)styrene) (FPS) copolymer with 10 mol % hydroxyl group was synthesized according to a procedure published previously.[22] Stereoregular PMMAs were purchased from Polymer Laboratories Ltd. These polymers were used after precipitation of their methylene chloride solution into a large excess of methanol (twice for s-PMMA) or after fractionation in a chloroform–methanol solvent–nonsolvent system (for i-PMMA). The molecular weights of these polymers were determined by GPC (Waters Chromatography) using polystyrene standards. The triad contents were determined by $^1$H NMR (Table I).

In the preparation of blends, the polymers were first dissolved in toluene (spectroscopic grade, used as purchased from Aldrich

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**Table I. Characteristics of the Polymer Samples**[a]

| | MW | MWD | characteristics |
|---|---|---|---|
| i-PMMA | $1.27 \times 10^4$ | 1.51 | i > 95%, h < 5% |
| s-PMMA | $3.40 \times 10^4$ | 1.25 | s > 85%, h < 15% |
| FPS | $3.03 \times 10^4$ | 1.95 | 10 mol% HFPS |

[a] i = isotactic; s = syndriotactic; h = heterotactic; FPS = styrene copolymer; HFPS = *p*-hexafluoro-2-hydroxyisopropyl–substituted styrene unit.

Chemical Co.) separately at a concentration of 2.0% (w/v), and TKK blends of 25/75, 50/50, and 75/25 PMMA/FPS by weight were prepared by mixing the two solutions. Thin films of the blends were prepared by evaporation of the solvent on KBr crystals for infrared spectroscopic studies. For reasons which will become apparent later in the text, three sets of film preparation conditions were used for s-PMMA and its blends: cast and dried at room temperature in vacuo for 1 week; cast at room temperature and dried at 90 °C in a vacuum oven for 3 days; cast and dried at 90 °C. For i-PMMA and its blends the films were cast at room temperature followed by drying either at room temperature or at 120 °C in a vacuum oven for 8 days. The infrared spectra were recorded on a Digilab FTS-60 Fourier transform infrared spectrometer with 2-cm$^{-1}$ resolution and 256 scans. The fraction of hydrogen-bonded carbonyl groups was calculated by spectral deconvolution and by the use of a conversion factor and to account for the different extinction coefficients of the free and bound species.[20] The uncertainty in the curve-fitting procedure was estimated to be within 10% of the computed value when the bound carbonyl fraction exceeded 0.15; for smaller amounts of bound carbonyls, the error was larger, probably in the range of 20%. In blend films dried at 120 or 90 °C for extended periods of time, the extent of hydrogen bonding probably approached the "equilibrium" value because the temperatures used are near or above the glass transition temperatures of the blends. However, we are less certain of the situation in films dried at room temperature.

Films used for WAXD measurement were made by the same procedure as above except that glass slides were used. WAXD was measured by means of a PW1700 automated powder diffractometer in this study. For each measurement, the $2\theta$ is from 5 to 40° using Cu K$\alpha$ radiation with a step speed of 0.040°/8 s.

Glass transition temperature measurements were carried out by using a Du Pont 9900 thermal analyzer equipped with a Model 910 DSC cell. The heating rate was 20 °C/min, and the scanning range was from 15 to 170 °C in all experiments.

## Results and Discussion

**(1) Self-Aggregation of s-PMMA: Background Information.** Spevacek and co-workers have carried out extensive studies of aggregation of s-PMMA in solutions and in solvent-cast films by a combination of infrared, Raman, and NMR spectroscopy.[23,36] The results of infrared studies are summarized below. In the 800–900-cm$^{-1}$ region, the 843–860-cm$^{-1}$ doublet is sensitive to chain conformation.[29,31,33] The band at 860 cm$^{-1}$ is ascribed to sequences having all *tt* conformations, whereas the band at 843-cm$^{-1}$ can be assigned to diads having a *tg* conformation. The intensities of the 860- and 843-cm$^{-1}$ bands were comparable in nonaggregating solvents such as acetonitrile, but there was a pronounced increase in the relative intensity of the 860-cm$^{-1}$ band in toluene in which aggregation was confirmed by NMR spectroscopy,[25-27] light scattering, and other techniques.[27,30,37] In the carbonyl absorption region, a single peak at 1733 cm$^{-1}$ was seen in acetonitrile but three peaks were seen in toluene at 1742, 1735, and 1727 cm$^{-1}$.[31,32] The peak at 1742 cm$^{-1}$ is associated with ordered sequences, and the peak at 1735 cm$^{-1}$ with disordered structures. Peak splitting is due to transition dipole coupling of the carbonyl group in ordered sequences.[32] (We take note of the different assignments by O'Reilly and Mosher.[38])

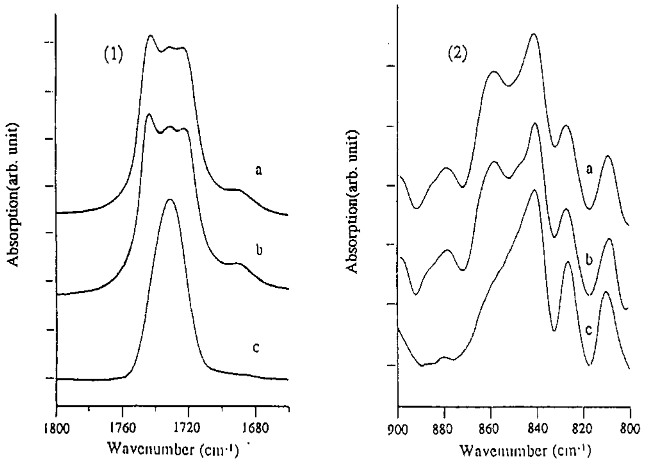

**Figure 1.** Two regions in the IR spectra of s-PMMA cast from toluene solution: (a) cast and dried at room temperature; (b) cast at room temperature and dried at 90 °C; (c) cast and dried at 90 °C.

The infrared spectra of solvent-cast films retain the characteristics of the respective solution spectra. For example, peaks at 1742, 1731, and 1727 cm$^{-1}$ can be seen in the carbonyl absorption region of toluene-cast films.[31,32] However, the temperature dependency of the degree of aggregation in films is totally different from that in solution. While the dissociation of aggregates begins at 35 °C in toluene and is complete at 60 °C,[25-27] aggregation persists in toluene-cast films to ca. 150 °C.[31]

In consideration of the above information, we have chosen the following conditions for film preparation from toluene solution: (a) cast and dried at 25 °C; (b) cast at 25 °C and dried at 90 °C; (c) cast and dried at 90 °C. Self-aggregation of s-PMMA segments was favored under conditions a and b; however, even under these conditions, the extent of aggregation was changed by blending, as will be seen later. When films were cast at 90 °C, at which s-PMMA aggregates had dissociated completely, the blends were expected to be free of microheterogeneities caused by the aggregation of s-PMMA sequences having *tt* conformation. This was indeed the case.

**(2) Aggregation of s-PMMA in Blends.** The infrared spectra of s-PMMA films cast from toluene solutions are shown in Figure 1. The spectra of films a and b are similar to those described by Spevacek.[31,32] The absorption band at 860 cm$^{-1}$ is readily distinguished from the 843-cm$^{-1}$ peak, and three peaks in the carbonyl stretching region, at 1742, 1733, and 1727 cm$^{-1}$, respectively, are easily recognized. On the other hand, only a very small shoulder at 860 cm$^{-1}$ and a single peak at 1733 cm$^{-1}$ are seen in the spectra of the film cast at 90 °C; the spectral characteristics correspond to s-PMMA in nonaggregating solvents.

When s-PMMA was blended with the copolymer, the degree of aggregation decreased drastically even when the films were cast and dried at 25 °C. In the 75 wt % s-PMMA blend, only the middle peak at 1733 cm$^{-1}$ which is associated with disordered structures is prominent in the carbonyl stretching region (Figure 2); the 1742-cm$^{-1}$ band appears as a shoulder. The 860-cm$^{-1}$ band, though still present, has decreased sharply in intensity in relation to the 843-cm$^{-1}$ band. The spectra for the 50 wt % blend again shows the 1733-cm$^{-1}$ band with a weak shoulder at 1742 cm$^{-1}$; the 860-cm$^{-1}$ absorption now becomes a shoulder. For the 25 wt % s-PMMA blend, the 860-cm$^{-1}$ absorption is barely identifiable. The carbonyl band at 1733 cm$^{-1}$ seems to have a shoulder at 1727 cm$^{-1}$; however,

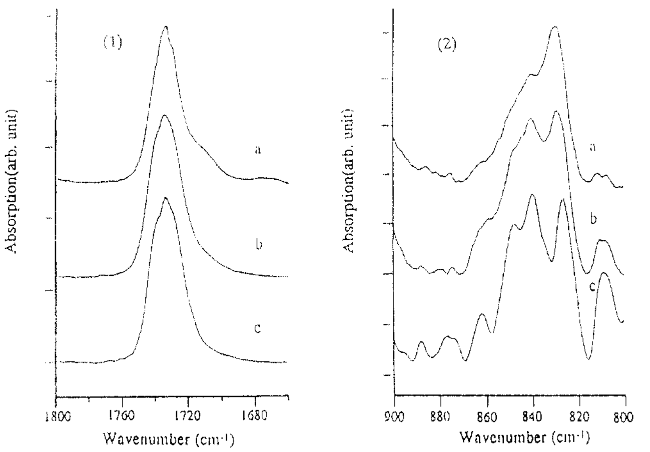

**Figure 2.** Two regions in the IR spectra of s-PMMA/FPS blends cast and dried at room temperature. Weight percent of s-PMMA: (a) 25; (b) 50; (c) 75.

it is broadened to include additional absorption around 1711 cm$^{-1}$ which, according to earlier investigations,[19,22] can be assigned to bound carbonyl, (C=O)$_b$, that is, hydrogen-bonded carbonyl groups. The spectra of films cast at 25 °C and dried at 90 °C are omitted from Figure 2 because they essentially duplicate the curves already shown. These spectroscopic data provide clear evidence that for s-PMMA segments there is competition between self-aggregation and hydrogen-bonding interactions, even under conditions which normally favor self-aggregation. In a sense, the results are perhaps not surprising because the enthalpy of melting of s-PMMA gel in *o*-xylene is only ca. 0.5 kcal/mol[39] while the enthalpy of hydrogen-bonding formation between atactic PMMA and hexafluoro-2-propanol is ca. −5.9 kcal/mol.[40] Certainly, the hydrogen-bonding interaction has the competitive advantage. It stands to reason that the aggregation of *tt* sequences is disrupted by hydrogen-bonding interactions and decreases as the amount of hydrogen-bond donor in the blend increases. The large decrease in the intensity of the 860-cm$^{-1}$ band may imply that there are conformational changes as well.

To confirm the conclusions drawn from the infrared results about the state of s-PMMA aggregation, we carried out WAXD measurements. The X-ray diffraction data of s-PMMA and 75 and 50 wt % blends, all cast and dried at 25 °C, are shown in Figure 3. There are at least three diffraction peaks in the s-PMMA film at $2\theta$ equal to 10.9, 13.2, and 17.4°, respectively. The shape of the curve and the locations of the peaks are the same as those reported by Spevacek.[31] For the blend containing 75 wt % s-PMMA, the 17.4° peak has disappeared and the other two peaks have greatly reduced in intensity. None of the three peaks is detectable in the 50 wt % blend; i.e., the film is essentially amorphous. Thus the results of the X-ray measurements fully support the conclusions of the IR studies.

**(3) s-PMMA Blends Prepared under Nonaggregating Conditions.** In the infrared spectra of blends both cast and dried at 90 °C, the 860-cm$^{-1}$ absorption appears only as a shoulder in each spectrum (Figure 4). For the 25 wt % s-PMMA blend, the 1733-cm$^{-1}$ band is accompanied by bonded carbonyl absorption at ca. 1711 cm$^{-1}$. The latter absorption is weak in the 50 and 75 wt % blends, but its presence can be seen after deconvolution of the carbonyl peak. The fraction of the bound carbonyl group in each blend was calculated from the peak area by using a factor of 1.6 to account for the extinction coefficient difference of the free and bonded species,[20] and the values are listed in Table II.

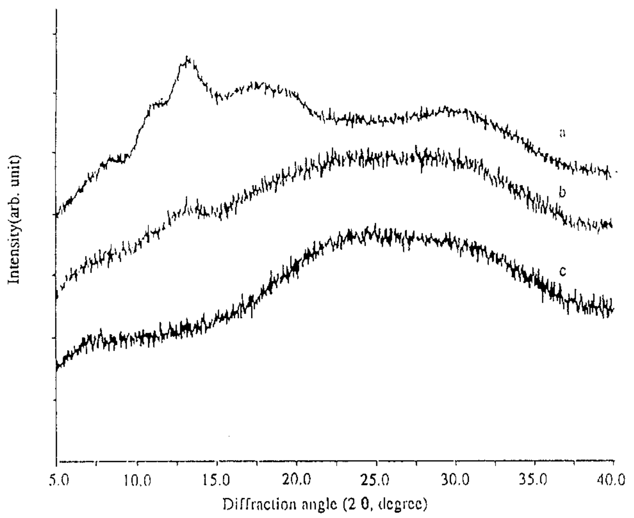

**Figure 3.** X-ray diffraction spectra of s-PMMA and its blends cast and dried at room temperature. Weight percent of s-PMMA: (a) 100; (b) 75; (c) 50.

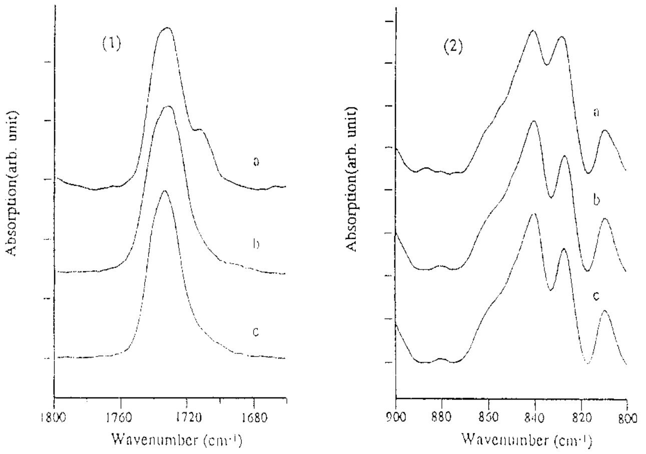

**Figure 4.** Two regions in the IR spectra of s-PMMA/FPS blends cast and dried at 90 °C. Weight percent of s-PMMA: (a) 25; (b) 50; (c) 75.

**Table II. Fraction of H-Bonded Carbonyl in Amorphous PMMA Blends**

| wt % PMMA | $f_b$(C=O)$^a$ s-PMMA | i-PMMA | calcd |
|---|---|---|---|
| 25 | 0.21 (0.23) | 0.18 (0.18) | 0.25 |
| 50 | 0.07 (0.06) | 0.06 (0.06) | 0.09 |
| 75 | 0.03 (0.04) | 0.03 (0.04) | 0.03 |

[a] Calculation based on the formulation of refs 19 and 20. Values in parentheses are obtained by using Lorentzian and Gaussian functions (program: Jandel Scientific Peakfit, Version 3.11B).

Each of the three amorphous blends prepared under nonaggregating conditions shows a single glass transition temperature ($T_g$) in the DSC thermogram. The $T_g$ values are shown in Figure 5a as a function of blend compositions. (The line connecting the data points is drawn only for the purpose of aiding visual inspection.) Although we have $T_g$ data for only three blend compositions, the trend of $T_g$ change is the same as that reported earlier for atactic PMMA[22] and a styrene copolymer containing nearly the same amount of HFPP groups. Therefore the trend is believed to be valid. For the 75 wt % s-PMMA blend, the $T_g$ is ca. 1 °C higher than the weight-average value of the component polymers. The 50 wt % blend has a $T_g$ about 2.5 °C higher than the weight-average value, and for the 25 wt % blend, the difference is 6.5 °C. The magnitude of the $T_g$ in excess of the weight-average value, that is, $T_g - (w_1T_{g_1} + w_2T_{g_2})$, where $w$ is the weight fraction, increases

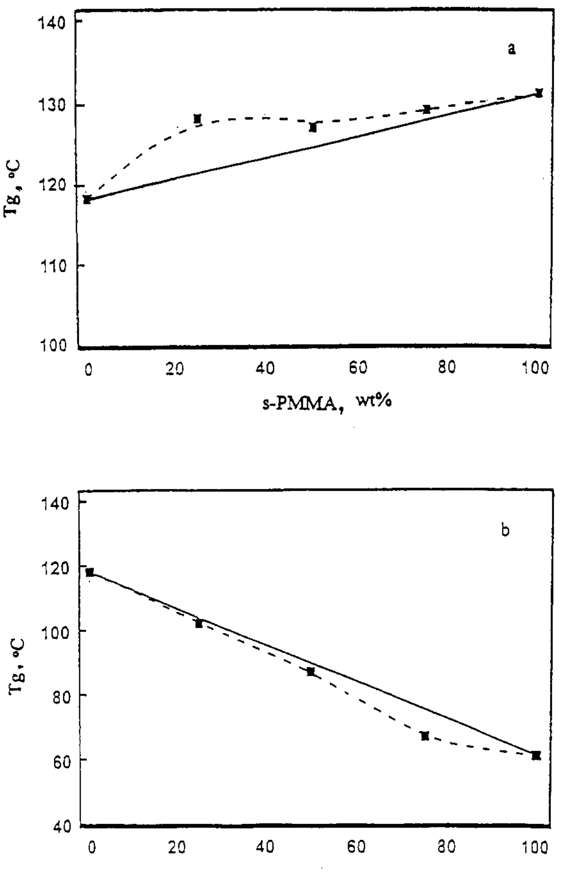

**Figure 5.** Glass transition temperatures of amorphous s-PMMA/FPS and i-PMMA/FPS blends.

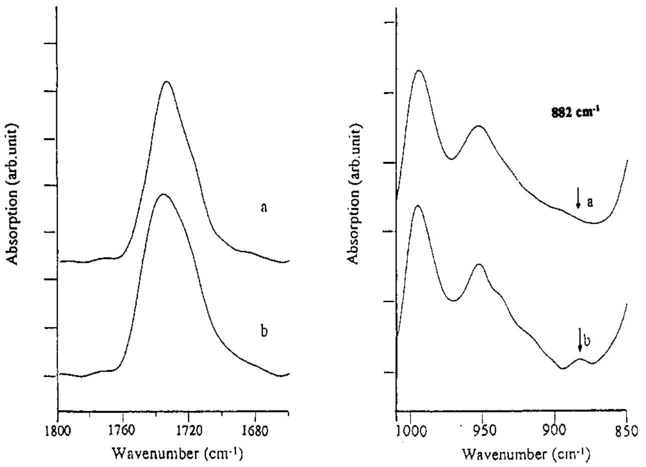

**Figure 6.** Two regions in the IR spectra of i-PMMA cast from toluene solution: (a) cast and dried at room temperature; (b) cast at room temperature and dried at 120 °C.

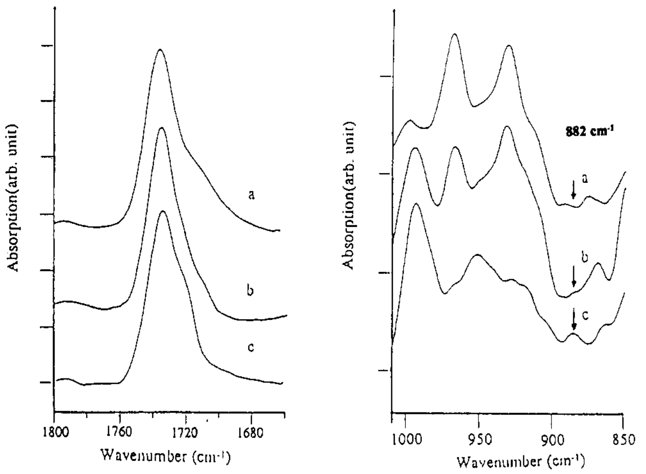

**Figure 7.** Two regions in the IR spectra of i-PMMA/FPS blends cast at room temperature and dried at 120 °C. Weight percent of i-PMMA: (a) 25; (b) 50; (c) 75.

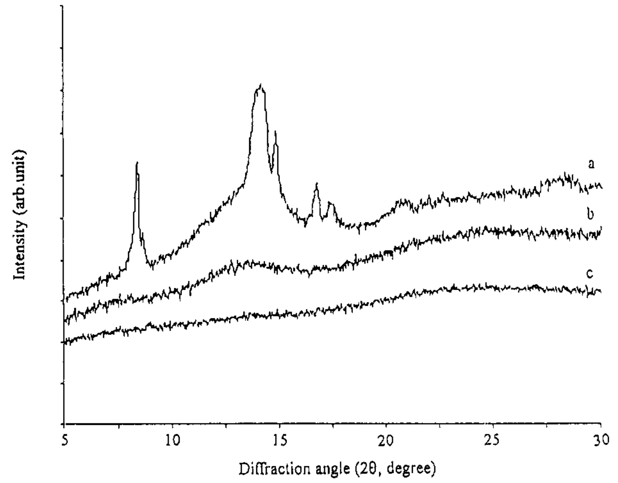

**Figure 8.** X-ray diffraction spectra of i-PMMA and its blends dried at 120 °C. Weight percent of i-PMMA: (a) 100; (b) 75; (c) 50.

with the fraction of the bonded carbonyl in accordance with the predictions of empirical[41] and theoretical equations[42-45] which describe the effect of strong interaction on the glass transition temperatures of polymer blends.

**(4) Annealed i-PMMA Blends.** Without being annealed at an elevated temperature, i-PMMA is usually amorphous. According to the literature, annealing at 120 °C was one of the optimum conditions for crystallization.[46,47] We have therefore chosen two sets of conditions for film preparation. Films were cast from toluene at room temperature and dried either at room temperature or at 120 °C in vacuo for 8 days. The infrared spectra of the two films are qualitatively similar in the carbonyl stretching region (Figure 6). In addition to the main peak at 1733–1735 cm$^{-1}$, there appears to be a shoulder at lower wavenumber in each spectrum. However, the fingerprint regions are different. For the annealed film, there is a small band at 882 cm$^{-1}$ which is an indicator of the crystalline structure.[48,49] This band is absent in the film dried at room temperature.

The spectra of the annealed blend films are shown in Figure 7. The 882-cm$^{-1}$ band remains in the 75 wt % i-PMMA blend, is visible as a shoulder in the 50 wt % blend, and disappears in the 25 wt % blend. Clearly, the presence of the hydrogen bond donating copolymer suppresses the development of the crystalline structure of i-PMMA in the annealed blends. The conclusion is again supported by X-ray measurements. In Figure 8, there are several diffraction peaks for the annealed i-PMMA specimen, but only one peak is seen in the 75 wt % blend and none in the 50 wt % blend.

Returning to the infrared spectra in Figure 7, we notice that the carbonyl band of the 75 wt % i-PMMA blend has the same shape as that of the amorphous i-PMMA (Figure 6a). The two curves are almost superimposable. This is consistent with the low crystallinity of the 75 wt % blend deduced from X-ray measurements (Figure 8). The carbonyl bands of the 50 and 25 wt % blends have shoulders which are different from the one in the 75 wt % blend. There are at least two peaks in that region. Although we did not attempt to resolve the bands into component peaks, the low-wavenumber shoulder in curve a located close to 1711 cm$^{-1}$ may suggest carbonyl–hydroxyl interactions in

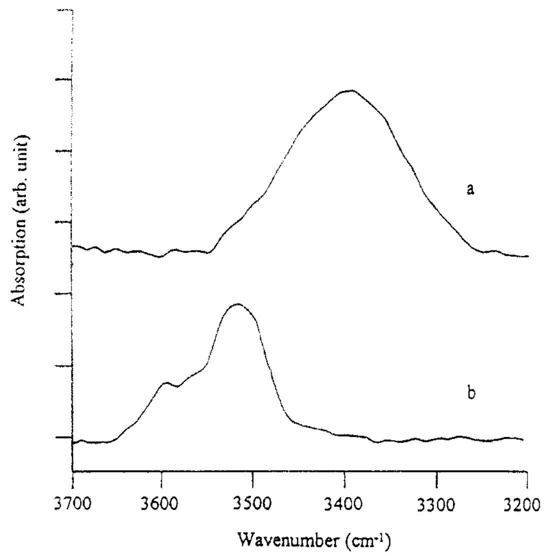

**Figure 9.** Hydroxyl stretching region in the IR of FPS and its blend. (a) 25 wt % i-PMMA; (b) FPS.

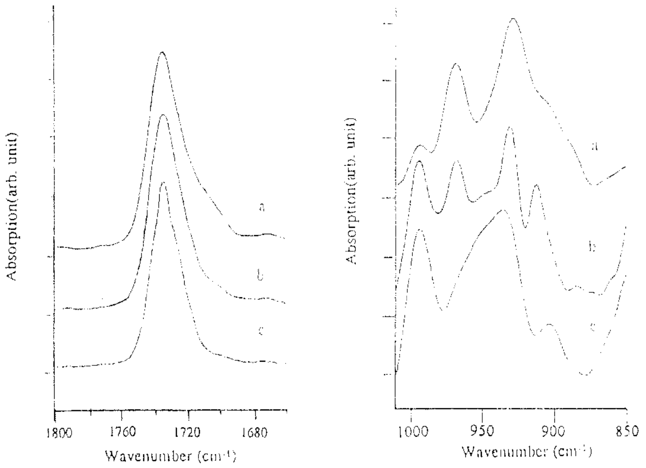

**Figure 10.** Two regions in the IR spectra of i-PMMA/FPS blends cast and dried at room temperature. Weight percent of i-PMMA: (a) 25; (b) 50; (c) 75.

the blend. Indeed, evidence for carbonyl–hydroxyl interaction was found readily in the hydroxyl stretching region of the spectra (Figure 9); the bands due to the free and self-associated hydroxyl groups diminished in intensities and the OH---O=C species was responsible for the new absorption at ca. 3400 $cm^{-1}$.

**(5) Amorphous i-PMMA Blends.** The 882-$cm^{-1}$ bands in the three amorphous blends dried at room temperature are either weak or barely visible as shoulders (Figure 10). Each blend exhibits a single $T_g$ which is lower than the weight-average value; the $T_g$ values are plotted as a function of blend composition in Figure 5b.

The carbonyl band of the amorphous i-PMMA consists of a major peak at 1733–1735 cm-1 and a shoulder at ca. 1720 $cm^{-1}$ (Figure 6a). (The latter absorption is associated with the *tt* conformation.[38]) However, this shoulder is no longer seen in the blend spectra. Instead, the blend can be resolved satisfactorily into free and hydrogen-bonded (1710 ± 2 $cm^{-1}$) components, and the bound fractions are listed in Table II.

We now compare the fraction of hydrogen-bonded carbonyl groups ($f_b$(C=O)) in the amorphous s-PMMA and i-PMMA blends. For the purpose of discussion, we have included in Table II the calculated bound fractions using the equilibrium constants determined by Painter and Coleman.[19] (Although we make no claim that the casting films are at equilibrium states, comparison with theory is nevertheless believed to be instructive.) It is seen that the experimental fractions are the same as the calculated values when the carbonyl groups are present in large excess. In the 75 wt % blends, the number of hydroxyl groups engaged in hydrogen bonding is stoichiometric for both PMMAs. The bound fraction in the 50 wt % s-PMMA blend is 0.07, while the value for the corresponding i-PMMA blend is 0.06; both are close to the calculated value of 0.09. The fraction in the 25 wt % s-PMMA blend is 0.21, and for the corresponding i-PMMA blend, the fraction is 0.18. These values are to be compared with the calculated result of 0.25. To confirm that the small difference between 0.21 and 0.18 is not due to a certain arbitrariness in curve fitting, we tried another deconvolution program. The corresponding values are 0.23 and 0.18. In the context of the Coleman–Painter model of self-association versus interassociation of hydroxyl groups,[20] the difference, if real, suggests a smaller equilibrium constant for interassociation between the OH and C=O groups in the i-PMMA blends compared to the s-PMMA blend. It follows from the above that the free energy of breaking a PMMA–PMMA contact must be larger for the isotactic than for the syndiotactic chains. This is consistent with Vorenkamp's assertion[10] that the miscibility difference can be attributed to differences in the equation of state parameters[50] which, in turn, are influenced by chain conformation.

## Conclusions

We have shown that the aggregation of s-PMMA or i-PMMA segments is diminished when the two stereoregular polymers are blended with a styrene copolymer containing hydrogen bond donating groups. Amorphous blend films are homogeneous according to the single-$T_g$ criterion. The fraction of hydrogen-bonded carbonyl groups is slightly smaller in the 25 wt % i-PMMA blend than in the corresponding s-PMMA blend. The smaller equilibrium constant in the i-PMMA blend for the association of the OH and C=O groups implied by this finding is consistent with the explanation that the difference in the miscibility behaviors of the two tactic PMMAs in attributable to the difference in equation of state parameters.

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