

Phase Behavior of Binary and Ternary Blends of Poly(styrene-*co*-methacrylic acid), Poly(styrene-*co*-4-vinylpyridine), and Poly(2,6-dimethyl-1,4-phenylene oxide)

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ABSTRACT: Poly(styrene-*co*-methacrylic acid) (PSMA) and poly(styrene-*co*-4-vinylpyridine) (PS4VP) of different compositions were prepared and characterized. The phase behavior of these copolymers as binary PSMA/PS4VP mixtures or with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) as PPO/PSMA or PPO/PS4VP and PPO/PSMA/PS4VP ternary blends was investigated by differential scanning calorimetry (DSC). This study showed that PPO was miscible with PS4VP containing up to 15 mol % 4-vinylpyridine (4VP) but immiscible with PS4VP-30 (where the number following the hyphen refers to the percentage 4VP in the polymer) and PSMA-20 (where the number following the hyphen refers to the percentage methacrylic acid in the polymer) over the entire composition range. To examine the morphology of the immiscible blends, scanning electron microscopy was used. Because of the hydrogen-bonding specific interactions that occurred between the carboxylic groups of PSMA and the pyridine groups of PS4VP,

chloroform solutions of PSMA-20 and PS4VP-15 formed interpolymer complexes. The obtained glass-transition temperatures (T_g 's) of the PSMA-20/PS4VP-15 complexes were found to be higher than those calculated from the additivity rule. Although, depending on the content of 4VP, the shape of the T_g of the PPO/PS4VP blends changed from concave to S-shaped in the case of the miscible blends, two T_g were observed with each PPO/PS4VP-30 and PPO/PS4VP-40 blend. The thermal stability of the PSMA-20/PS4VP-15 interpolymer complexes was studied by thermogravimetry. On the basis of the obtained results, the phase behavior of the ternary PPO/PSMA-20/PS4VP-15 blends was investigated by DSC. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 220–227, 2008

Key words: differential scanning calorimetry (DSC); glass transition; miscibility; phase behavior; thermogravimetric analysis (TGA)

INTRODUCTION

Polymer blending is an economical way to elaborate new polymeric materials with tailored properties at a relatively low cost. Because the physical properties of the blends depend on the mixing scale, it is, therefore, of great interest to investigate the miscibility and phase behavior of polymer blends. It is now well established that two dissimilar polymers possessing complementary functional groups can form miscible blends if sufficient favorable interpolymer interactions act between them.^{1–4} It has also been reported that blends of a homopolymer and a random copolymer can be miscible even in the absence of specific interactions, provided that strong intramolecular repulsions exist between the comonomers.

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)/polystyrene (PS) mixtures are one of the best known miscible blends in the whole composition range.^{5–7} Several studies have been carried out to elucidate the origin of the interactions responsible for the miscibility of these blends. It has been concluded^{8–10} that specific interactions occur between PPO and PS chains through the formation of π -cation complexes between the methyl groups of PPO and the aromatic rings of PS. Kuo et al.¹¹ showed that similar and stronger specific interactions occurred with PPO-*b*-PS copolymers. Because of the presence of stronger specific polymer–polymer interactions evidenced within miscible polymer blends and complexes, these latter have higher glass-transition temperatures (T_g 's) than those predicted by the additivity rule. In any case, the T_g -composition of PS/PPO is predicted by the Fox rule.

Several authors have reported that the miscibility of PPO with styrene copolymers depends not only on the nature of the second comonomer but also on

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the composition of the copolymer.^{12–16} Styrene-*ran-t*-butyl acrylate copolymers containing less than 23 mol % *t*-butyl acrylate were found to be miscible with PPO in the whole composition range, whereas PPO is miscible with potassium salts of poly(styrene-*ran*-acrylic acid) containing less than 3% ionic content.¹⁷

In previous studies,^{18,19} we reported that PPO is totally miscible with poly(styrene-*co*-methacrylic acid) (PSMA) containing 7.8 mol % methacrylic acid (PSMA-7.8, where the number following the hyphen refers to the percentage methacrylic acid in the polymer) and with blends of PSMA-12 containing less than 67 wt % PPO. As we have also confirmed qualitatively and quantitatively by Fourier transform infrared (FTIR) spectroscopy,²⁰ the miscibility of PSMA-12/poly(styrene-*co*-4-vinylpyridine) (PS4VP) containing 22% 4-vinylpyridine (PS4VP-22, where the number following the hyphen refers to the percentage 4VP in the polymer) is due to the presence of hydrogen-bonding interactions.

By continuing our studies on miscibility enhancement by specific interactions in binary or ternary polymer blends, in the first part of this contribution, we report the results of the effect of introducing increasing amounts of specific groups, such as 4VP or methacrylic acid, in styrene copolymers on its miscibility with PPO and on the T_g -composition relationships of these blend systems. Moreover, the thermal stability of the PSMA-15/PS4VP-20 complexes was determined by thermogravimetric analysis (TGA), and the morphology of the PPO/PSMA-20 blends was examined by scanning electron microscopy (SEM). On the basis of the results obtained with the binary mixtures, the phase behavior of the ternary PPO/PS4VP-15/PSMA-20 blends was then investigated by differential scanning calorimetry (DSC).

EXPERIMENTAL

Materials

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) purchased from Aldrich (France) was purified by solution in chloroform and precipitation in methanol. The viscosimetry-average molecular weight of PPO was determined after purification and was 20,000 g/mol. PS4VP containing 5, 15, 30, and 40 mol % 4VP (PS4VP-05, PS4VP-15, PS4VP-30, and PS4VP-40, respectively) and PSMA containing 15 and 20 mol % methacrylic acid (PSMA-15 and PSMA-20, respectively) were prepared by solution free-radical polymerization at 60°C with chloroform as the solvent and azobisisobutyronitrile as the initiator. These copolymers were purified by repeated solution/precipitation from chloroform into heptane and were dried *in vacuo* at 60°C for several days.

Material characterization

The styrene and 4VP contents in the PSMA and PS4VP copolymers were determined by elemental analysis and UV and ¹H-NMR spectroscopy. The molecular weights of these copolymers were determined by gel permeation chromatography relative to a PS standard. The polydispersities were in the range 1.6–1.8. Before DSC analysis, TGA measurements were carried out under nitrogen from 50 to 600°C on a TGA-Q500 instrument (New Castle, DE) at a heating rate of 10°C/min. The T_g values of the pure polymers and their binary or ternary blends were measured with a PerkinElmer DSC PYRIS 1 instrument (Waltham, MA) equipped with an intracooler. All T_g measurements were carried out at a heating rate of 20°C/min under nitrogen, and the T_g value was taken as the midpoint of the transition. The 30/70, 50/50, and 70/30 PPO/PSMA blends were fractured cryogenically, and their scanning electron micrograms were taken with a Hitachi S2700 scanning electron microscope (Tokyo, Japan). The main characteristics of the polymers are given in Table I.

RESULTS AND DISCUSSION

As shown in Figure 1, the TGA analysis (TGA) and derivative thermogravimetry (DTG) curves of the different polymers confirmed their relative stability in the temperature range; this permitted the determination of their T_g values before the degradation step took place. In these curves, two stages were observed. The first-stage weight loss of these copolymers was less than 3% that which occurred in the 100–180°C temperature range; this was attributed to the release of water adsorbed by the hydrophilic groups of these copolymers. On the other hand, it is interesting to note that the percentage mass loss of the PS4VP copolymers increased slightly with increasing 4VP in the copolymer. Moreover, the main degradation of these polymers occurred in a second stage with temperatures of maximum weight loss between 380 and 430°C (see Table II).

TABLE I
Characteristics of the Polymers

Polymer	M_w	M_w/M_n	T_g (°C)
PS4VP-05	103,000	1.80	105
PS4VP-15	134,000	1.60	109.5
PS4VP-30	98,500	1.54	114
PS4VP-40	143,000	1.77	116.5
PSMA-15	112,000	1.73	132.5
PSMA-20	150,000	1.84	135.8

M_w = weight-average molecular weight; M_n = number-average molecular weight.

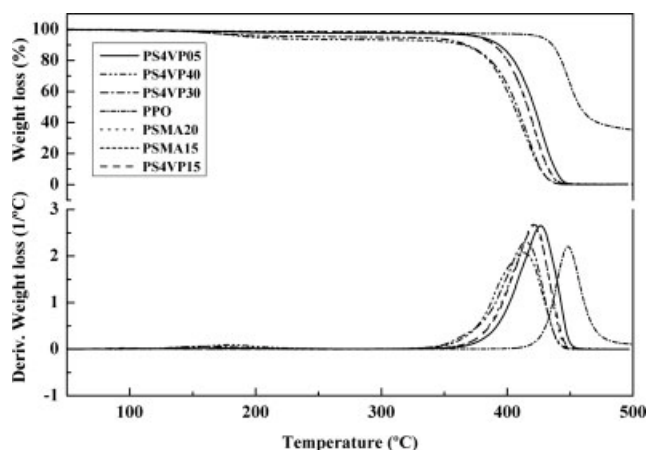


Figure 1 TGA and DTG curves for PS4VP-05, PS4VP-15, PS4VP-30, PS4VP-40, PSMA-15, PSMA-20, and PPO.

PPO/PS4VP blends

The thermograms corresponding to PPO, PS4VP-05, and their blends of different compositions are displayed in Figure 2. The single T_g observed with each blend, as shown in Figure 3, which illustrates the T_g -composition, is an indication of the miscibility. As shown in this figure, a change in the shape of these curves was glimpsed with an increase in 4VP within PS4VP. It was reported¹¹ that the T_g -composition of PPO/PS was predicted by the Fox equation. In that study, the authors also showed an increase in T_g in PPO-*b*-PS copolymers compared to their corresponding PPO/PS blends. Their T_g -composition analysis with the well-known Kwei equation²¹ revealed, from the positive value of the Kwei q constant, the presence of stronger specific interactions in PPO-*b*-PS copolymers. In our case, at low 4VP contents, as with PS4VP-05, the PPO/PS4VP-05 blends containing an excess of PPO had lower T_g values than those calculated from the additivity rule. Furthermore, slightly higher T_g values than those calculated from the weight-average line were observed with blends containing an excess of PS4VP-05. As the 4VP content increased in the copolymer, a differ-

TABLE II
TGA Parameters of PSMA-20, PS4VP-15, and Their Blends

Sample	Stage I		Stage II	
	T_1 (°C)	% weight loss	T_2	% weight loss
PSMA-20/PS4VP-15				
PSMA-20	98	1.25	420	60
80/20	136	2.13	417	65
50/50	134	3.08	413	66.37
20/80	124	2.34	403	58.56
PS4VP-15	138	2.26	409	61.75

T_1 , temperature of maximum degradation of first stage; T_2 , temperature of maximum degradation of second stage.

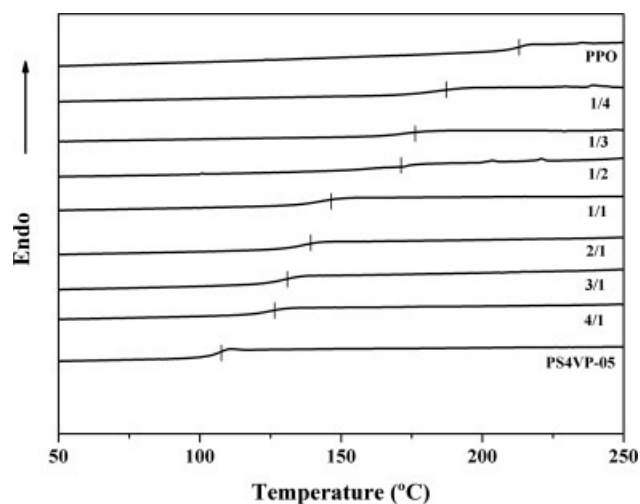


Figure 2 DSC thermograms of the PS4VP-05, PPO, and PPO/PS4VP-05 blends with different ratios.

ent behavior in the T_g -composition was observed. Thereby, in the PPO/PS4VP-15 blends containing an excess of the PS4VP-15, even though a single T_g was obtained with all the blends, broader transitions were observed, particularly with the 1 : 1 and 1 : 2 PS4VP-15/PPO blends. These results indicate that the blends were miscible on different molecular scales. The T_g width-composition for these blends is shown in Figure 4. An increase in the 4VP content within PS4VP led to immiscible blends, as shown with PPO/PS4VP-30 illustrated in Figure 5. Two T_g 's were obtained with each blend. However, the analysis of the change in specific heat (ΔC_p) versus the weight fraction of PPO, as displayed in Figure 6, showed two phases. The first one decreased with increasing PPO in the blends, whereas the second phase increased with decreasing PS4VP-30 in blends. On the basis of these results, we can state that the first phase contained mostly PS4VP, whereas the

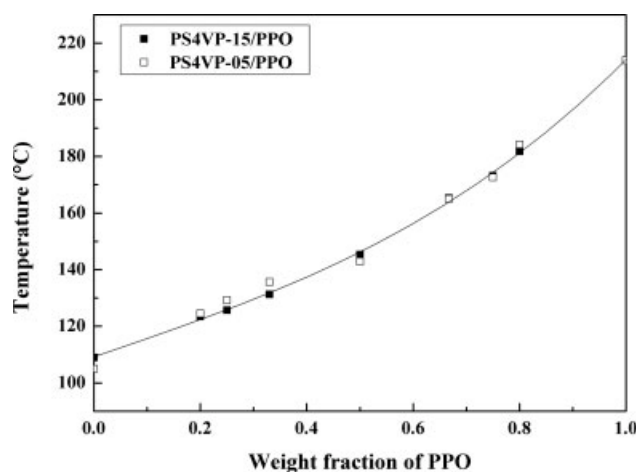


Figure 3 T_g -composition variation versus the PPO weight fraction of PS4VP-05/PPO and PS4VP-15/PPO.

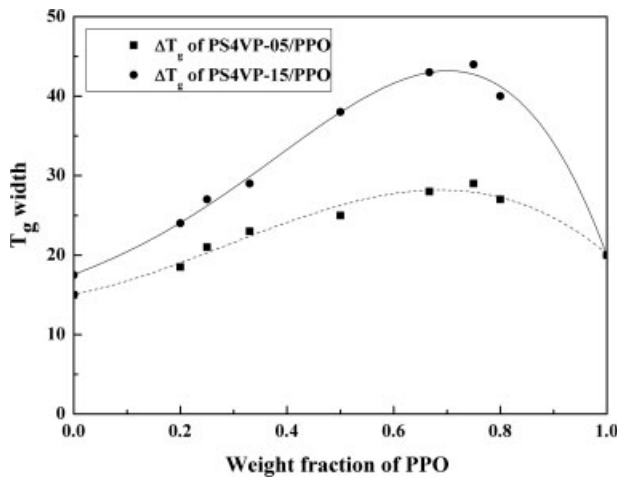


Figure 4 T_g width-composition variation versus the PPO weight fraction of PS4VP-05/PPO and PS4VP-15/PPO.

second was a PPO-rich phase. In addition, equilibrium between the two phases was achieved at a blend composition of approximately 1 : 1. On the other hand, it is interesting to note the similar behavior that was also observed with the PS4VP-40/PPO blends.

To measure interaction intensities between the different comonomers in PS4VP/PPO blends, we applied the mean-field theory. Here, we are interested in the case of a random copolymer $P(S_x-co-4VP_{1-x})$ with a homopolymer PPO. The Gibbs free energy of mixing per segment (ΔG_m), with monodisperse polymers assumed, is given by the following equation:²²

$$\frac{\Delta G_m}{kT} = \frac{\phi}{N_1} \ln \phi + \frac{(1-\phi)}{N_2} \ln(1-\phi) + \chi_{eff} \phi(1-\phi) \quad (1)$$

where k is the Boltzmann constant, T is the temperature, N_1 and N_2 are the chain lengths of the copoly-

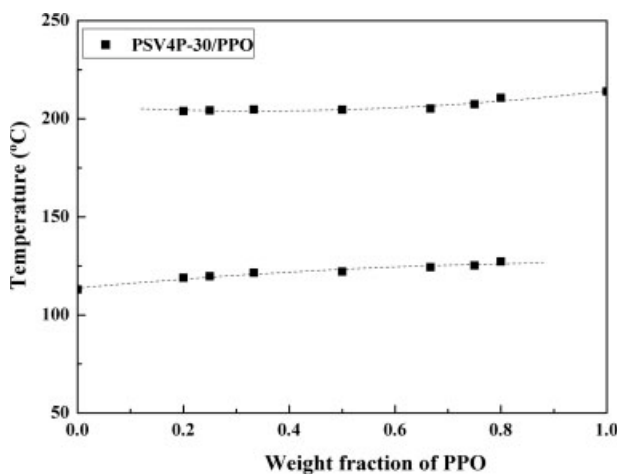


Figure 5 T_g -composition variation versus the PPO weight fraction of PS4VP-30/PPO.

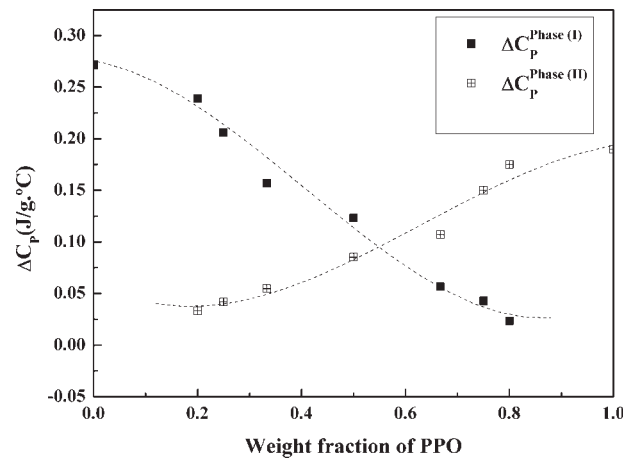


Figure 6 ΔC_p variation of the two phases versus the PPO weight fraction of the PS4VP-30/PPO blends.

mer (PS4VP) and the homopolymer PPO, respectively; ϕ is the volume fraction of PS4VP; and χ_{eff} is the net interaction parameter. The net interaction parameter for the PPO/PS4VP blend is given in the mean-field approximation by the following equation:

$$\begin{aligned} \chi_{eff} &\equiv \chi_{PPO/PS4VP} \\ &= x\chi_{PPO/S} + (1-x)\chi_{PPO/4VP} - x(1-x)\chi_{S/4VP} \quad (2) \end{aligned}$$

where x is the copolymer composition (in volume fraction of the 4VP segments), S is the styrene and χ_{ij} represents the respective segmental interaction parameters.

ten Brinke et al.²² reported that the interaction between PS and P4VP ($\chi_{S/4VP}$) was on the order of 0.3–0.35. On the basis of this value and an interaction parameter ($\chi_{PPO/S}$)¹⁷ of -0.52 , the deduced $\chi_{PPO/4VP}$ was greater than 0.55. This value was in agreement with the results of ten Brinke et al.,²³ in a very recent study, they concluded that the interaction between PS4VP and PPO was more unfavorable than that between PS and PS4VP.

PPO/PSMA blends

Figure 7 shows the thermograms corresponding to PPO, PSMA-20, and PPO/PSMA-20 blends at different ratios. As reported in the Introduction, the miscibility of PPO with PSMA decreased progressively as the content of methacrylic acid within the PS matrix increased.

A single T_g was observed with PSMA-15/PPO blends up to 33% PPO, whereas two T_g 's were shown with the other compositions. As we previously reported,¹⁹ the PSMA-15 copolymer achieved its PPO saturation concentration below 33%. Katime et al.²⁴ reported that poly(vinyl phenyl ketone hydrogenated) was miscible with PPO in the whole

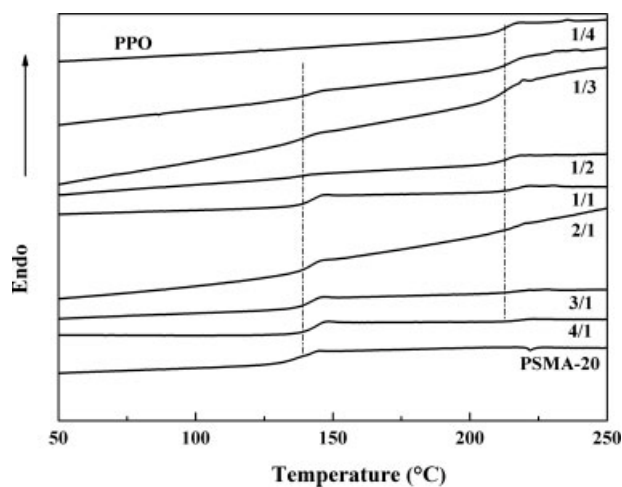


Figure 7 DSC thermograms of PSMA-20, PPO, and their blends with different ratios.

range of composition with the exception of the 50 wt % PPO.

Two T_g 's, each characterizing one phase, were, however, observed when the carboxylic group content increased to 20 mol %, as with the PSMA-20/PPO blends. The lower T_g values of these blends were relatively higher than that of PSMA-20, which indicated the presence of a small fraction of PPO in the acidic, copolymer-rich phase. The T_g values of the second phases, practically similar to that of PPO, confirmed that these phases contained essentially pure PPO. This study showed that 20 mol % methacrylic acid introduced within the PS matrix induced its immiscibility with PPO.

According to the mean-field approximation given by eq. (2), because of the styrene/methacrylic acid repulsive interactions and the specific hydrogen-bonding interactions that may occur between the carboxylic groups of PSMA and the ether groups of PPO, these blends were expected to be miscible. The results obtained by DSC show, however, that these last blends were immiscible as the density of carboxylic groups in the PSMA copolymer increased. In previous studies, we confirmed by FTIR the presence of acid–acid dimers, and we calculated self-association constants for styrene/methacrylic acid²⁰ and styrene/acrylic acid²⁵ copolymers containing increasing amounts of carboxylic groups. From a qualitative point of view, the PPO/PSMA blends were miscible only when the self-association contribution was relatively low (due to the high PS dilution), which was overcome by the styrene/methacrylic acid repulsive interactions within the PSMA copolymers.

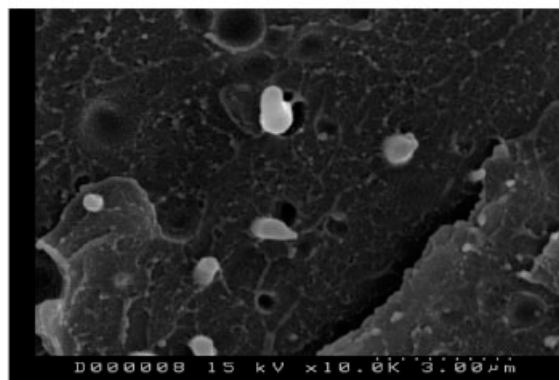
The morphology of the three PPO/PSMA-20 blends (75/25, 50/50, and 25/75) was examined by SEM. In agreement with the DSC results presented earlier, the scanning electron micrographs of the fractured surfaces shown in Figure 8 confirmed the

immiscibility of these blends. An improved PPO dissolution in the PSMA-20 phase was, however, observed when this one was in excess.

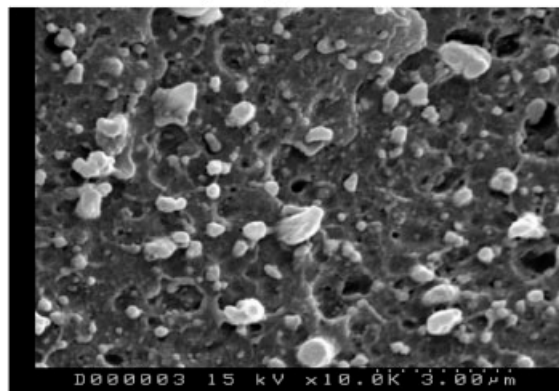
PSVP-15/PSMA-20 blends

Separate solutions of the copolymers were prepared in chloroform and mixed by dropwise addition of the PS4VP-15 solution to the PSMA-20 solution with stirring. The blends were recovered by precipitation

PSMA-20/PPO (75/25)



PSMA-20/PPO (50/50)



PSMA-20/PPO (25/75)

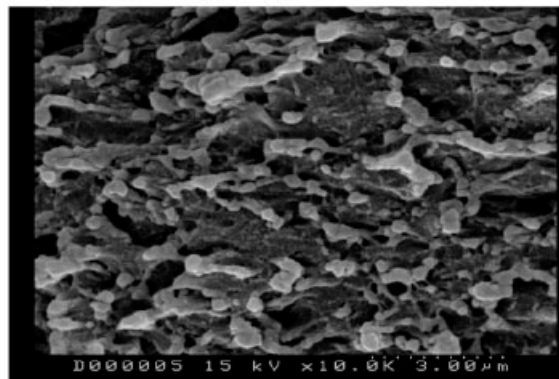


Figure 8 SEM photomicrographs of the PSMA-20/PPO blends with three different ratios (75/25, 50/50, and 25/75).

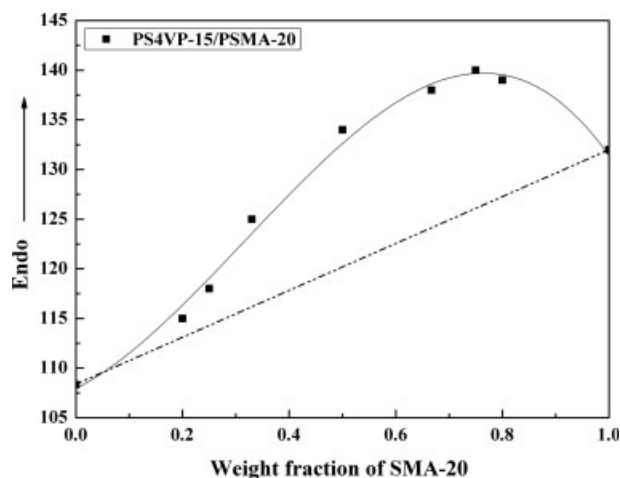


Figure 9 T_g -composition variation versus the PSMA-20 weight fraction of PS4VP-15/PSMA-20.

in heptane. Precipitates that occurred with mixtures containing an excess of PSMA-20 were isolated. All of the samples were dried to constant weight in a vacuum oven at 60°C for several days. These blends, miscible in the whole composition range, as evidenced from the single T_g observed with each blend, had higher T_g values than those calculated from the weight-average values of the pure copolymers. The T_g -composition curve of this system, as displayed in Figure 9, could be described by the Kwei equation:²¹

$$T_{g,\text{blend}} = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} + q w_1 w_2 \quad (3)$$

where $T_{g,\text{blend}}$ is the glass transition temperature on the blend, w_1 , w_2 , T_{g1} , and T_{g2} are the weight fractions and glass-transition temperatures, respectively, of the corresponding constituents. The q constant measures the extent of the specific interactions that occur between the two copolymers. A previous FTIR spectroscopy study²⁰ in similar systems confirmed that hydrogen-bonding-type interactions occurred between the carboxylic groups of PSMA and the pyridine groups of PS4VP. Moreover, the positive deviation of the T_g 's from the weight-average values was an indication of intermolecular interactions. The obtained q value of 71 indicated that these interactions were certainly strong.

Figure 10 shows the TGA and DTG curves of PSMA-20, PS4VP-15, and their blends at different ratios. The copolymers and their blends degraded in a two-stage process. The first step of degradation, with a very small weight-loss amount in the 100–150°C temperature range, was attributed to a loss of adsorbed water from the hydrophilic groups of the copolymers. The second step of degradation corresponded to the main degradation of the polymers. Table II summarizes the TGA parameters of the

studied copolymers and their blends at different ratios. The thermal stability improvement noticed with the resulting miscible blends containing an excess of the acidic copolymer PSMA-20 was ascribed to the hydrogen-bonding interactions that occurred between these two copolymers, which acted as physical crosslinks. The onset temperature and T_{max} of the first degradation stage, observed with all of these blends, shifted toward a higher temperature compared to that of the copolymers. However, when PS4VP-15 was in excess, the thermal stability improvement was not observed.

PPO/PS4VP-15/PSMA-20 blends

On the basis of the results presented earlier, PS4VP-15 was found to be miscible over the entire composition range with both PPO and PSMA-20, whereas these two were immiscible with each other. In addition and due to the strong specific interactions that occurred between the carboxyl and pyridine groups incorporated within the PS matrix, interpolymer complexes were formed when PSMA-20 and PS4VP-15 were mixed together. We, therefore, expected that PS4VP-15 may have acted as a compatibilizer and enhanced the miscibility of the ternary PSMA/PPO/PS4VP blends. Several ternary blends with different compositions of PPO/PSMA-20/PS4VP-15 were prepared, and their phase behavior was analyzed by DSC. Some thermograms of these blends are displayed in Figure 11.

For the ternary PSMA-20/PPO/PS4VP-15 system, in the first part, we studied blends containing the same amounts of PPO and PSMA-20 with an increasing proportion of PS4VP-15 (47/47/6, 45/45/10, 40/40/20, 35/35/30, 30/30/40, and 25/25/50). Two T_g 's characterizing two phases were observed with the first three blends; see the data correspond-

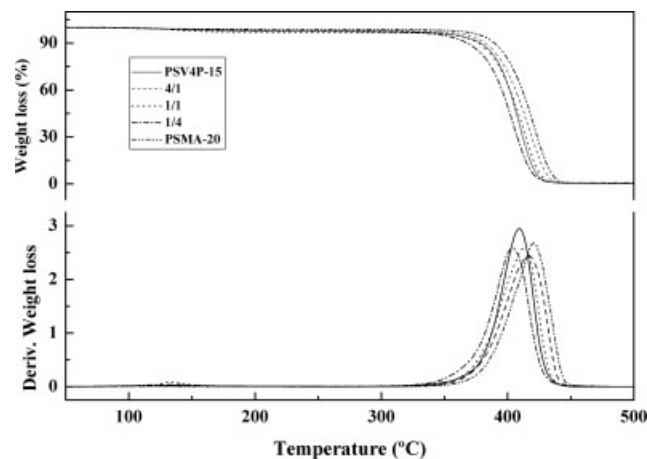


Figure 10 TGA and DTG curves for PS4VP-15, PSMA-15, and their blends with different ratios.

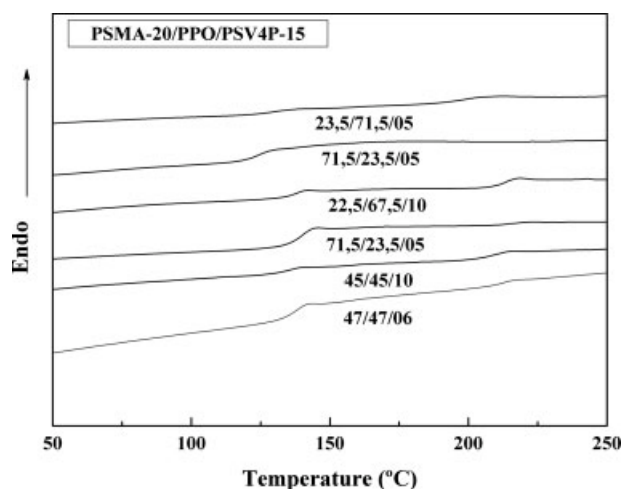


Figure 11 DSC thermograms of some PSMA-20/PPO/PS4VP-15 ternary blends.

ing to series A in Table III. The T_g of the lowest transition (136°C) seemed to correspond to a phase containing the PSMA-20/PS4VP-15 (1 : 1 ratio) pair as an interpolymer complex, whereas the T_g of the highest transition (212°C) was characteristic of a phase that mainly contained PPO. In such mixtures, the preferential interpolymer interactions between the two complementary copolymers formed complexes of compact structures. On the other hand, when the acidic PSMA-20 was in excess, the PPO dissolution in the ternary phases was considerably affected by the preferential interaction between PSMA-20 and PS4VP-15, respectively. This was confirmed by the earlier results that showed that, indeed, the 1 : 1 ratio PSMA-20/PPO blend separated into two phases with a T_g of a lower phase of 141°C, which was characteristic of a better PPO dissolution in the PSMA-20 matrix. As the fraction of PS4VP-15 increased within the ternary blend (the last three blends), a main transition (with a greater ΔC_p) that decreased slightly was observed around 132°C. In addition, two very small transitions were also depicted at 156 and 202°C with the 35/35/30 and 30/30/40 blends. Such observations indicated a progressive dissolution of PPO within the main phase as the fraction of PS4VP-15 increased in the mixture. A single phase characterized by a T_g of 134°C was, however, observed with the 25/25/50 blend.

In the second part of this series, ternary blends containing an excess of PS4VP-15 at a constant 3 : 1 PS4VP-15/PPO ratio were considered (PS4VP-15/PPO/PSMA-20 = 60/20/20, 67.5/22.5/10, and 71.5/23.5/5). A major phase with a T_g of 123°C and a very small transition around 155°C were observed with these ternary blends. When PS4VP-15 was in excess compared to the other components in these ternary mixtures, the interactions between PSMA-20 and PS4VP-15 were not as intense as before and did

not form compact interpolymer complexes that would exclude the PPO in its own domain. A better dispersion of the three components was expected in such mixtures. On the contrary, ternary PSMA-20/PPO/PS4VP-15 blends (71.5/23.5/5, 67.5/22.5/10, 60/20/20, 23.5/71.5/5, and 22.5/67.5/10) showed two T_g 's that varied from blend to blend and that indicated that the polymers were immiscible at these compositions where the PPO was in excess compared to both PSMA-20 and PS4VP-15. When the PSMA-20 was in excess compared to PS4VP-15, a similar behavior as presented earlier was observed, the tendency toward complexation acted in favor of the PPO exclusion in its own phase. Ternary blends containing an excess of PSMA-20 (23.5/71.5/5, 22.5/67.5/10, and 20/60/20) behaved similarly. The obtained T_g 's for the ternary blends considered are summarized in Table III.

CONCLUSIONS

The phase behavior of binary PSMA/PS4VP, PPO/PSMA, and PPO/PS4VP blends and ternary PPO/PSMA/PS4VP blends was investigated by DSC. This study showed that PPO was miscible with PS4VP containing up to 15 mol % 4VP but immiscible with PS4VP-30 and PSMA-20 over the entire composition range. Because of specific hydrogen-bonding type interactions that occurred between the carboxylic groups of PSMA and the pyridine groups of PS4VP, interpolymer complexes were formed. The thermal stability of these interpolymer complexes was studied by TGA and confirmed from the values of their

TABLE III
Summarized DSC Data of Some
PSMA-20/PPO/PS4VP-15 Blends

Designation		T_g
A	PSMA-20/PPO/PS4VP-15	
1	47/47/06	136.7–212.4
2	45/45/10	135.1–209.4
3	40/40/20	138.7–214
4	35/35/30	136.1–207.4
5	30/30/40	134.1–203.1
6	25/25/50	136
B	PS4VP-15/PPO/PSMA-20	
13 (3/1)	71.5/23.5/05	123.7–163.7
14 (3/1)	67.5/22.5/10	123.7–160.7
15 (3/1)	60/20/20	123.7–166.4
16 (1/3)	23.5/71.5/05	130.4–199.4
17 (1/3)	22.5/67.5/10	130.4–199.7
C	PSMA-20/PPO/PS4VP-15	
7 (3/1)	71.5/23.5/05	139.4–214
8 (3/1)	67.5/22.5/10	138.7–214
9 (3/1)	60/20/20	136.1–210.7
10 (1/3)	23.5/71.5/05	139.4–212.1
11 (1/3)	22.5/67.5/10	137.1–213.1
12 (1/3)	20/60/20	136.1–214

T_g 's, which were higher than those calculated from the additivity rule. On the basis of the miscibility of PS4VP-15 over the entire composition range with both PPO and PSMA-20, several ternary PPO/PSMA-20/PS4VP-15 blends were studied by DSC. The preferential interpolymer interactions between the two complementary PSMA-20 and PS4VP-15 copolymers formed complexes of compact structures. Moreover, when the acidic PSMA-20 was in excess, the dissolution of PPO in the ternary phases was considerably affected.

When PS4VP-15 was in excess compared to the other components in these ternary mixtures, the interactions between PSMA-20 and PS4VP-15 were not dense, and compact interpolymer complexes that excluded the PPO in their own domains were not formed. A better dispersion of the three components resulted. A single phase characterized by a T_g of 134°C was, however, observed with the 25/25/50 blend.

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