

Miscibility and Thermal Properties of Blends of Polystyrene with Poly(5-benzoyl-2,6-dimethyl-1,4-phenylene oxide) or Poly(5-acetyl-2,6-dimethyl-1,4-phenylene oxide)

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ABSTRACT: Miscibility and thermal properties of blends of polystyrene (PS) with poly(5-benzoyl-2,6-dimethyl-1,4-phenylene oxide) (BPPO) or poly(5-acetyl-2,6-dimethyl-1,4-phenylene oxide) (APPO) were investigated using light scattering, FTIR spectroscopy, and thermogravimetric analysis. The optical clarity and light-scattering behavior showed that both BPPO/PS blends and APPO/PS blends cast from chloroform were miscible over the entire composition ranges in part because of the van der Waals interaction between the

component polymers. The light-scattering studies showed that the miscibility of the APPO/PS blend is better than that of the BPPO/PS blend. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1071–1076, 2002

Key words: polystyrene; poly(5-benzoyl-2,6-dimethyl-1,4-phenylene oxide); poly(5-acetyl-2,6-dimethyl-1,4-phenylene oxide); miscibility; blends; thermal properties

INTRODUCTION

Polymer blends are one of the most investigated categories in the polymer sciences, from both theoretical and practical points of view, because of the technical advantages of obtaining a specified portfolio of physical properties, without the need to synthesize specialized polymer systems.^{1–4}

Most pairs of polymers are immiscible with each other because of their small entropy gain on mixing. However, some polymer blends show miscible behavior when there is a specific interaction between the components in the mixture. In most polymer mixtures that are known to be truly miscible, the degree of miscibility decreases with increasing temperature, and the phenomenon of lower critical solution temperature (LCST) is exhibited. Such mixtures usually owe their miscibility to the presence of some specific favorable interactions that decrease in strength on increasing the temperature, whereas the unfavorable effect attributed to the free-volume change on mixing increases, thus eventually leading to phase separation

above the LCST. A number of works of calorimetric, spectroscopic, light or neutron scattering, and other experimental techniques have been reported to investigate the miscibility of polymer blends.^{5,6}

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), with relatively high glass-transition temperature ($T_g = 208^\circ\text{C}$), has a high softening point, good chemical resistance, electrical insulation, and dimensional stability and has been used in a number of electrical applications and gas separation membrane and water pump applications.^{7,8} Recently, modified PPOs with enhanced properties also attracted much interest in our laboratory. They include poly(5-benzoyl-2,6-dimethyl-1,4-phenylene oxide) (BPPO; $T_g = 255^\circ\text{C}$) and poly(5-acetyl-2,6-dimethyl-1,4-phenylene oxide) (APPO; $T_g = 244^\circ\text{C}$). The modified PPOs were developed for application as a gas separation membrane by incorporating bulky benzoyl or acetyl groups in PPO to induce a larger free volume.⁹ However, their relatively high production cost and high processing temperature have led us to blend with polystyrene (PS) for more versatile applications, as for the well-known miscible PPO/PS blends.^{10–12}

The objective of the present work, therefore, was to investigate the miscibility of both BPPO/PS blends and APPO/PS blends by light-scattering and FTIR spectroscopy, and to measure the thermal properties of the blends.

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TABLE I
Characteristics of the Polymers Used in This Work

Polymer	Abbreviation	Molecular weight	Density	Source
Poly(5-benzoyl-2,6-dimethyl-1,4-phenylene oxide)	BPPO	$M_n = 44,290$ $M_w = 77,030$	1.26	Synthesized
Poly(5-acetyl-2,6-dimethyl-1,4-phenylene oxide)	APPO	$M_n = 14,810$ $M_w = 27,900$	1.24	Synthesized
Polystyrene	PS	$M_n = 32,000$ $M_w = 45,000$	1.06	Aldrich

EXPERIMENTAL

Materials

Table I lists the polymers used in this study with their abbreviations, the sources from which they were obtained, molecular weight information, and density. PS (Aldrich Chemicals, Milwaukee, WI) was used as received without further purification; poly(5-benzoyl-2,6-dimethyl-1,4-phenylene oxide) (BPPO) and poly(5-acetyl-2,6-dimethyl-1,4-phenylene oxide) (APPO) were kindly supplied by Prof. S. K. Kwon (Gyeongsang National University, Chinju, Korea). BPPO and APPO were used as received. Figure 1 illustrates the chemical structures of BPPO and APPO. Details of the synthesis of APPO and BPPO are described elsewhere.⁹ For a typical synthesis, BPPO was obtained by reacting 0.02 mol of benzoyl chloride with PPO at the reflux temperature in 100 mL of carbon disulfide for 24 h. After the reaction, 4N HCl (60 mL) was poured into the reaction mixture. The carbon disulfide was evaporated and then circulated for 2 h in 100 mL methanol. The resultant polymer was filtered from this process and recrystallized from methanol. The APPO was prepared by a method similar to that for BPPO. The degree of substitution of the modifications to the PPO units was found to be 100 and 64% for BPPO and

APPO, respectively, by FTIR and ¹H-NMR spectroscopies. The degrees of substitution were found to be quite high compared to those of other modified PPOs, which had previously been prepared in nitrobenzene instead of CS₂ by Percec.¹³ The molecular weight of the polymers was measured by GPC (Waters 244; Waters Associates, Milford, MA) with Ultrastaygel 500-Å linear columns. The measurement was conducted using an RI detector in chloroform at a flow rate of 1.0 mL/min at 28°C. PS was used as the standard for calibration. The density was measured by the dilatometric method.

Preparation of blends

Films of BPPO/PS blends and APPO/PS blends with various concentrations were prepared by casting from 5 wt % chloroform solutions of the blend. The films were dried slowly in a petri dish at room temperature and then kept under a vacuum until they reached constant weight. The films were used for the optical clarity test and thermal analysis. For the light scattering, films were prepared by spin coating from 5 wt % chloroform solutions of the blends onto a slide glass at 500 rpm for 30 s. For the FTIR analysis, samples were prepared separately.

Measurements

Light scattering

The temperature at which phase separation occurred on heating (cloud point) for blends was obtained by a homemade light-scattering apparatus.¹⁴ A small piece of film was sandwiched between two glass slides and placed on a hot plate device. A He-Ne laser source of 632.8 nm wavelength was applied vertically to the film specimen. The scattered light measured at 90° was focused onto the slit of a photomultiplier detector (Hamamatsu Photonics, Hamamatsu, Japan). The temperature was cycled repeatedly from about 50°C below the cloud point to about 30°C above it at constant heating and cooling rates. All measurements were performed at 3°C/min. Experiments were carried out in a nitrogen atmosphere.

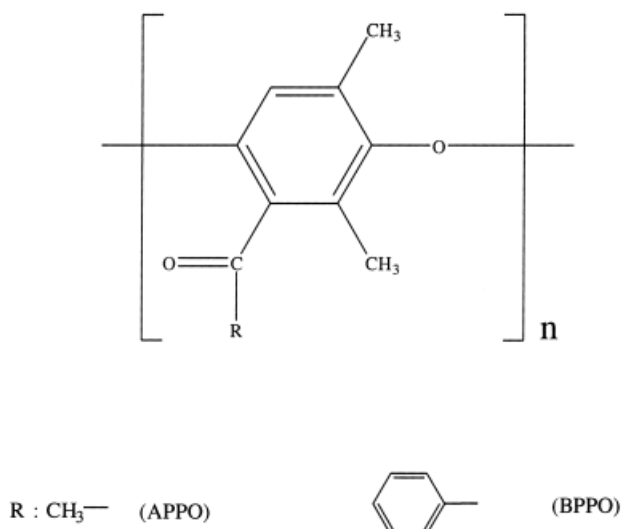


Figure 1 Chemical structures of APPO and BPPO.

TABLE II
Optical Clarity and Glass-Transition Temperatures for
BPPO/PS Blends and APPO/PS Blends

Blend (wt %)	Optical clarity	T_g (K)	Miscibility
BPPO/PS			
100/0	Clear	528.35	M
80/20	Clear	489.78	M
75/25	Clear	473.20	M
60/40	Clear	441.50	M
50/50	Clear	430.20	M
40/60	Clear	417.23	M
25/75	Clear	392.20	M
20/80	Clear	382.30	M
0/100	Clear	379.00	M
APPO/PS			
100/0	Clear	517.19	M
80/20	Clear	470.23	M
75/25	Clear	458.20	M
60/40	Clear	432.55	M
50/50	Clear	426.63	M
40/60	Clear	412.30	M
25/75	Clear	389.36	M
20/80	Clear	380.32	M
0/100	Clear	379.00	M

Infrared spectroscopy

The samples used for FTIR studies were prepared by compression molding with KBr powder and then annealed in a vacuum oven at 50°C for more than 48 h. Infrared spectra were taken using a Polaris/FTIR spectrometer (Shimadzu Co., Kyoto, Japan). Thirty-two scans at a resolution of 2 cm⁻¹ were signal-averaged.

Thermal analysis

Glass-transition temperatures (T_g 's) were measured using a differential scanning calorimeter (Perkin-Elmer DSC-7500; Perkin Elmer Cetus Instruments, Norwalk, CT) calibrated with pure indium as a standard. Experiments were carried out in a nitrogen atmosphere. To avoid the thermal history from the samples packed in the aluminum pan and to eliminate any small traces of solvent, samples were heated to 620 K at a heating rate of 10°C/min, annealed at 620 K for 5 min, and then quenched with liquid nitrogen. The thermal scan was then repeated for the quenched sample. All the glass-transition temperatures were taken as the half-height point of the heat capacity increase in the second scan. Thermal stability of blends was also studied by thermogravimetric analysis (TGA-50; Shimadzu, Kyoto, Japan) under nitrogen atmosphere. The heating rate was 10°C/min.

RESULTS AND DISCUSSION

The optical clarity and the T_g 's of the BPPO/PS blends and the APPO/PS blends are summarized in Table II.

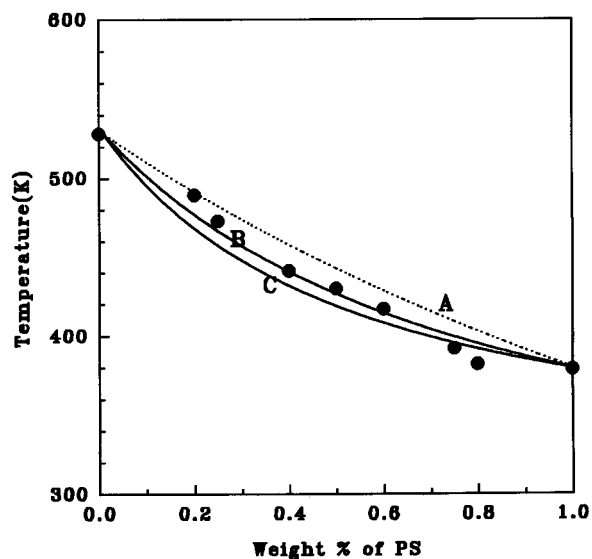


Figure 2 Glass-transition temperatures of BPPO/PS blends as a function of PS concentration: ●, experimental values; (A) Fox equation; (B) Gordon-Taylor equation, $k = 0.45$; (C) Gordon-Taylor equation, $k = 0.35$.

In this table, the criteria for miscibility are the existence of a single T_g on the DSC thermogram and optical clarity of the blend films. BPPO/PS blends and APPO/PS blends cast from chloroform were miscible over the entire range of blend compositions.

If the T_g 's are plotted as functions of composition, as given in Figures 2 and 3, the resulting curves show a composition dependency. Further analysis of the results obtained was carried out by comparing the blend T_g values with those calculated from the Fox equation,¹⁵

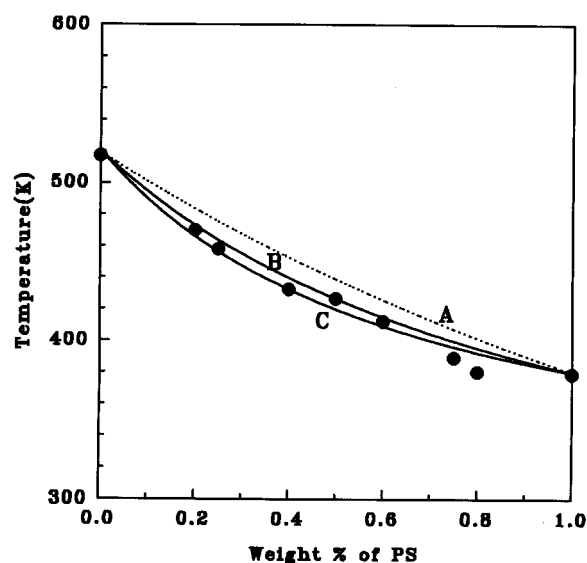


Figure 3 Glass-transition temperatures of APPO/PS blends as a function of PS concentration: ●, experimental values; (A) Fox equation; (B) Gordon-Taylor equation, $k = 0.45$; (C) Gordon-Taylor equation, $k = 0.35$.

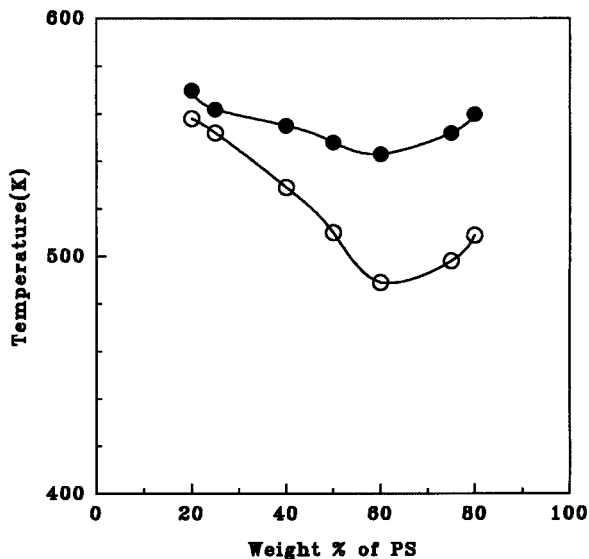


Figure 4 Cloud points of BPPO/PS blends (○) and APPO/PS blends (●). The solid lines are just to the visual guides.

$$\frac{1}{T_g} = \frac{W_A}{T_{gA}} + \frac{W_B}{T_{gB}} \quad (1)$$

and the Gordon–Taylor equation,¹⁶

$$T_g = \frac{kW_B T_{gB} + W_A T_A}{W_A + kW_B} \quad (2)$$

where W_A , W_B , T_{gA} , and T_{gB} are, respectively, the weight fractions and the glass transitions corresponding to polymers A and B; T_g is the glass transition of a blend; and k is a constant. Figures 2 and 3 show the deviation of the experimental T_g values from the Fox equation and the Gordon–Taylor equation, respectively. By varying the constant k , however, the Gordon–Taylor equation can be adjusted to give the best fit at $k = 0.45$ for BPPO/PS blends and at $k = 0.40$ for APPO/PS blends.

The observed cloud points of BPPO/PS blends and APPO/PS blends are plotted in Figure 4. Because cloud point values depend on the rate at which phase separation in the sample responds to the temperature changes, as a rule, the lower the heating rate, the lower the cloud point value. Therefore, the cloud point values should be measured with various heating rates to get an equilibrium phase diagram. In general, extrapolating the heating rate to zero may then be used to obtain a value close to the true cloud point. It should be noted, however, that the cloud points reported here were measured at only one heating rate (3°C/min) because of the instrumental limitation in this laboratory.

Figure 4 shows that the LCST of the APPO/PS blend is higher than that of the BPPO/PS blend, mean-

ing that BPPO/PS blends are less miscible than APPO/PS blends. The result is ascribed to the presence of the bulkier benzoyl group compared to the less bulky acetyl group in the modified PPOs.

It has been reported that the miscibility of PPO/PS blends could be accounted for by a strong van der Waals interaction between the phenyl rings of the PPO and PS.¹⁰ Thus, we investigated the band of phenyl ring and carbonyl group of BPPO and APPO by FTIR spectra. BPPO has an intensity band at 849 cm^{-1} , which was suspected of being the C—H out-of-plane vibration of the penta-substituted phenylene ring.^{11,12} Figure 5 shows the spectra of C—H out-of-plane vibration of BPPO in BPPO/PS blends of different compositions. As the PS content in the blend increases, the C—H out-of-plane vibration frequency increases. Similarly, APPO has an intensity band at 853 cm^{-1} , attributed to the C—H out-of-plane vibration of the penta-substituted phenylene ring.^{11,12} Figure 6 shows the spectra of the C—H out-of-plane vibration of APPO in APPO/PS blends of different compositions. As the PS content in the blend increases, the C—H out-of-plane vibration frequency increases. Table III shows the C—H out-of-plane vibration of the penta-substituted phenylene ring and C=O stretching frequencies of BPPO/PS blends and APPO/PS blends, which exhibit almost no changes, depending on their blend compositions. Therefore, there seem to be no specific interactions between the carbonyl groups of BPPO, APPO, and the phenyl ring of PS. The increases in the C—H out-of-plane vibration frequency, with increasing PS contents in the blends, could be accounted for by a van der Waals interaction between the phenyl rings of the BPPO, APPO, and PS. The miscibility of BPPO/PS

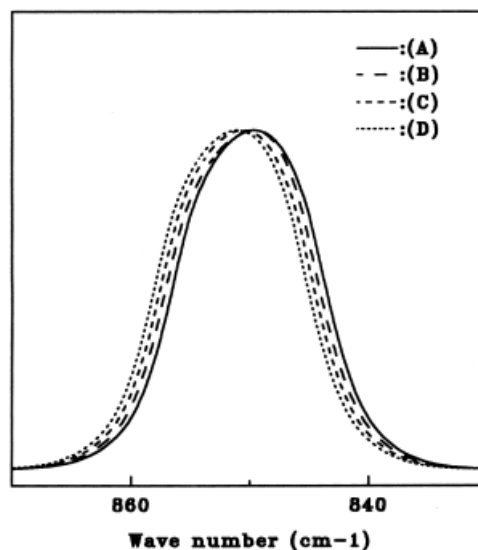


Figure 5 FTIR spectra of C—H out-of-plane vibration of BPPO in different BPPO/PS blend compositions: (A) 0 wt % of PS; (B) 25 wt % of PS; (C) 50 wt % of PS; (D) 75 wt % of PS.

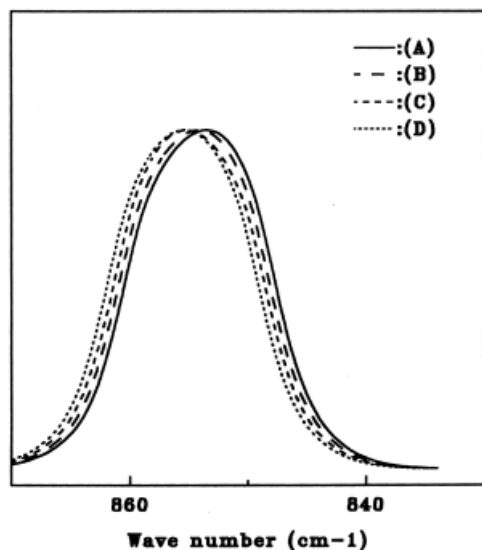


Figure 6 FTIR spectra of C—H out-of-plane vibration of APPO in different APPO/PS blend compositions: (A) 0 wt % of PS; (B) 25 wt % of PS; (C) 50 wt % of PS; (D) 75 wt % of PS.

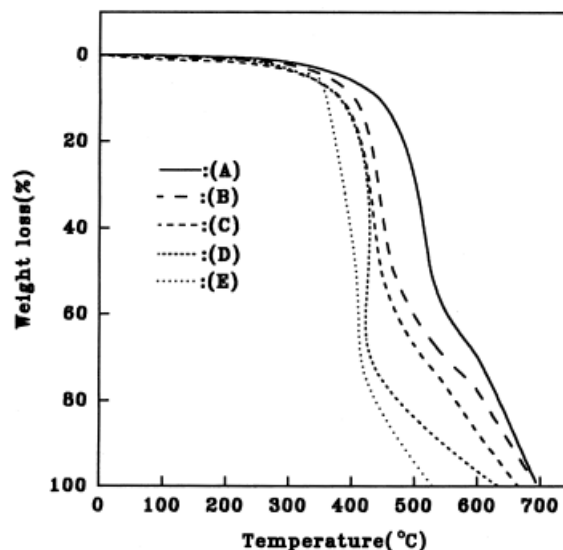


Figure 7 TGA curves of BPPO/PS blends under nitrogen (flow rate 10 cm³/min; heating rate 10°C/min): (A) BPPO; (B) BPPO/PS (75/25 wt %); (C) BPPO/PS (50/50); (D) BPPO/PS (25/75); (E) PS.

blends and APPO/PS blends is thus likely to be the consequence of this interaction.

Figures 7 and 8 show the TGA curves of BPPO/PS blends and APPO/PS blends, respectively. Table IV shows the TGA data of BPPO/PS blends and APPO/PS blends. The thermal stabilities for both blends are comparable to each other, although BPPO blends possess slightly higher thermal stability and higher glass-transition temperature than those of APPO blends because of the bulkier benzoyl group. Both blends showed thermal stabilities between those of the component polymers, as expected.

CONCLUSIONS

The miscibility of BPPO/PS blends and APPO/PS blends was investigated by thermal analysis, light

scattering, and FTIR spectra. BPPO/PS blends and APPO/PS blends cast from chloroform were miscible over the entire range of compositions. The criteria for miscibility were the existence of a single T_g on the DSC thermogram and optical clarity of the blend films. The light-scattering studies showed that the miscibility of the APPO/PS blend is better than that of the BPPO/PS blend. FTIR studies showed that the C=O stretching frequencies of both BPPO/PS blends and APPO/PS blends showed no changes, meaning there were no specific interactions between the carbonyl group of

TABLE III

C—H Out-of-Plane Vibration of the Penta-Substituted Phenylene Ring and C=O Stretching Frequencies of BPPO/PS Blends and APPO/PS Blends

Blend (wt %)	C—H out-of-plane vibration (cm ⁻¹)	C=O stretching (cm ⁻¹)
BPPO/PS		
100/0	849.59	1676.04
75/25	849.68	1676.04
50/50	850.56	1676.04
25/75	851.03	1676.04
APPO/PS		
100/0	853.45	1701.12
75/25	854.12	1701.12
50/50	855.23	1701.12
25/75	855.38	1701.12

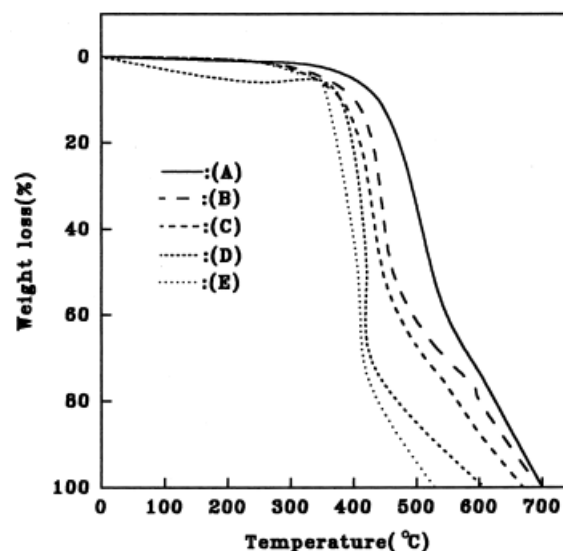


Figure 8 TGA curves of APPO/PS blends under nitrogen (flow rate 10 cm³/min; heating rate 10°C/min): (A) APPO; (B) APPO/PS (75/25 wt %); (C) APPO/PS (50/50); (D) APPO/PS (25/75); (E) PS.

TABLE IV
TGA Data of BPPO/PS Blends and APPO/PS Blends
Under Nitrogen^a

Blend (wt %)	Temperature (°C)			Weight Loss at 600°C (%)
	at 10% weight loss	at 50% weight loss	at 75% weight loss	
BPPO/PS				
100/0	442.5	526.3	617.8	69.8
75/25	403.8	466.9	585.6	77.65
50/50	382.3	447.2	542.1	87.33
25/75	380.0	426.6	448.2	96.45
0/100	358.8	407.0	423.8	100.0
APPO/PS				
100/0	439.8	525.6	613.5	73.25
75/25	402.1	462.5	582.4	79.96
50/50	381.3	446.65	541.3	87.58
25/75	379.5	421.5	444.1	98.93
0/100	358.8	358.8	423.8	100.0

^a Flow rate 10 cm³/min; heating rate 10°C/min.

either BPPO or APPO and the phenyl ring of PS. On increasing the PS content in the blend, however, the C—H out-of-plane vibration frequency increased slightly. The frequency change could be accounted for by a van der Waals interaction between the phenyl rings of either BPPO or APPO and PS. The miscibility of BPPO/PS blends and APPO/PS blends is, therefore, likely to be a consequence of this interaction. Finally, the thermal stabilities of both blends are comparable to each other, although BPPO blends possess slightly higher thermal stability and higher glass-transi-

sition temperature than those of APPO blends because of the bulkier benzoyl group.

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