

Determination of the Flory–Huggins Interaction Parameter of Polystyrene–Polybutadiene Blends by Thermal Analysis

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ABSTRACT: Blends of polystyrene (PS) and polybutadiene (PBD) were investigated by differential scanning calorimetry. From the phase composition diagram of the blends, it appears that PBD dissolves more in the PS-rich phase than does PS in the PBD-rich phase. This result is consistent with the behavior of the specific heat increment at the glass transition temperature of PBD in the PS–PBD blends. From the measured glass transition temperature and apparent weight fractions of PS and PBD dissolved in each phase, values of the Flory–Huggins polymer–polymer interaction parameter (χ_{12}) were determined to be 0.0040–0.0102 depending on the composition and molecular weights of the PS and the PBD. No significant difference in χ_{12} was observed among the blending methods. The composition-dependent value of the Flory–Huggins polymer–polymer interaction parameter was found to be similar to the value of χ_{12} . The polymer–polymer interaction parameter appears to depend on the degree of polymerization of the polymers as well as on the apparent volume fraction of the polymers dissolved in each phase. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1301–1308, 1997

Key words: polymer–polymer interaction parameter; thermal analysis; polystyrene–polybutadiene blends; phase composition diagrams

INTRODUCTION

Polystyrene (PS) and polybutadiene (PBD) are known to be incompatible.^{1–17} However, incompatible blends also have utility. Impact PS is an example of a useful incompatible system, although impact resistance is improved when the incompatible rubber is partially grafted to the rigid PS matrix.^{2,3} In partially miscible blends, phase separation occurs, but at the same time, a certain number of molecules of polymer A penetrate the polymer B-rich phase and vice versa. The interface between the two phases becomes diffuse and good mechanical properties may re-

sult.⁴ In our earlier studies of blends of PS and PBD, it was suggested that PBD dissolves more in the PS phase than does PS in the PBD phase.¹

In recent years, many investigators have studied the blends of PS and PBD by thermal analysis,¹ ternary solution methods,^{5–8} some light-scattering methods,^{9–13} NMR,¹⁴ electron microscopy,^{15–17} and rheometry.^{17,18} Several techniques have been used to determine the thermodynamic polymer–polymer interaction parameter (χ_{12}).^{5–9}

In our present study, we examined the Flory–Huggins interaction parameter, χ_{12} , of blends of PS and PBD by determining experimentally the glass transition temperature (T_g) of the blends by thermal analysis. We used a method which was developed in our earlier studies to determine the χ_{12} of the blends of polycarbonate with partially miscible polymers.^{19–23} An equation for determining the polymer–polymer interaction parameter (χ_{12}) from phase compositions of incompatible

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Table I Characteristics of Polymer Samples Used in PS–PBD Blends^a

Sample	M_w	M_n	M_w/M_n	T_g (K)	ΔC_p (J g ⁻¹ K ⁻¹)
PS 237,700 ^b	237,700	98,600	2.41	374.0	0.282
PS 116,000 ^c	116,000	110,500	1.05	375.9	0.282
PBD 270,000 ^d	270,000	45,000	6.00	164.4	0.545
PBD 128,000 ^e	128,000	121,000	1.07	176.5	0.488

^a Data from Kim and Burns.¹

^b Supplied by Polysciences, Inc.

^c Supplied by Pressure Chemical Co.

^d Taktene 1202, 98% *cis*-1,4, supplied by Polysar Corp.

^e 38% *cis*, 53% *trans*, 9% vinyl, 0.3% antioxidant, supplied by Phillips Petroleum Co.

polymer–polymer blends is based on Flory–Huggins theory.^{24–26}

EXPERIMENTAL

Polymers

The characteristics and sources of the polystyrene (PS) and polybutadiene (PBD) samples used in this study are shown in Table I. Molecular weights for the broad distribution polymers were measured by gel permeation chromatography at 25°C in tetrahydrofuran. Benzene (“Baker-analyzed” reagent grade, supplied by J. T. Baker Chemical Co.) was used as a solvent in the preparation of film-cast samples and freeze-dried samples.

Blend Preparations

Blends were prepared by solution casting, freeze-drying, and milling. For solution casting, a total of 0.2 g of PS–PBD mixtures in weight ratios of 100/0, 95/5, 90/10, 75/25, 50/50, 25/75, 10/90, 5/95, and 0/100 was dissolved in 20 mL of benzene solvent for at least 1 day at room temperature (1.0% [w/v] solution). These solutions were stirred for 2 h. Blends were cast on glass plates and all film samples were dried under a vacuum for 7 days at room temperature. The cast film thickness was 10 ± 2 μm . To prepare freeze-dried blends, 20 mL of solution (1.0% [w/v]) was stirred for 2 h. The polymer solution was then transferred to a round-bottom flask and immersed in liquid nitrogen. The benzene was sublimed in an ice-water bath under a 1 mmHg vacuum for 5 h. The freeze-dried polymer was dried under a vacuum for 7 days at room temperature. Mill blends were prepared using a laboratory mill. The rotation speed was 14 and 7 rpm for front and back rolls, respectively. Polymer blending was accomplished

by adding PS resin to a PBD band on the mill and milling for about 10, 15, and 20 min at a roll surface temperature of 140°C. The roll surface temperature was measured with a surface thermometer. At a 130°C roll surface temperature, it was found that the PS did not melt. In each run, 3 g of the total polymer was supplied to the mill.

Differential Scanning Calorimetry Measurements

The thermal properties of all samples were measured calorimetrically using a Perkin-Elmer differential scanning calorimeter, Model DSC-4, with a Perkin-Elmer thermal analysis data station, Model TADS-101. Temperature calibration was performed using *n*-heptane ($T_m = -90.56^\circ\text{C}$), *n*-dodecane ($T_m = -9.65^\circ\text{C}$), and indium ($T_m = 156.60^\circ\text{C}$) as standards. Differential power was calibrated by the heat of fusion of *n*-heptane ($\Delta H_f = 140.2$ J/g), *n*-dodecane ($\Delta H_f = 216.8$ J/g), and indium ($\Delta H_f = 28.5$ J/g). Two heating cycles were conducted at a heating rate of 20 K min⁻¹, with a sample size between 10 and 17 mg with standard aluminum sample pans. A temperature range of 123–273 K using liquid nitrogen cooling was used for PBD, and a range of 303–423 K using air cooling, for PS: The sample was surrounded by a helium atmosphere. The samples were then reheated at the heating rate of 20 K min⁻¹ a certain number of times under the same thermal regime followed by 135 K min⁻¹ programmed cooling immediately between heats. Samples containing atactic PS were initially heated from 303 to 438 K at 20 K min⁻¹, held at 438 K for 30 min, and cooled at 60 K min⁻¹ to 333 K. They were then reheated at 20 K min⁻¹ to 533 K. Following the convention used in other thermal analysis studies, the T_g was taken as the temperature at which the heat capacity reached one-half of the entire step change as observed on the thermogram. All glass transition temperatures were measured by

Table II Apparent Weight Fraction (W) and Apparent Volume Fraction (ϕ) of PS and PBD Components in the PS-rich Phase and the PBD-rich Phase and the Polymer–Polymer Interaction Parameter of PS 237,000–PBD 270,000 Mill Blends

Blend ^a	$T_{g1.b}$ ^b	$T_{g2.b}$ ^b	$W_1^{\prime c}$	$W_1^{\prime\prime c}$	ϕ_1'	ϕ_1''	g_0	g_1	g_{12}^d	χ_{12}^e
0.90	372.6	164.5	0.9933	0.0010	0.9918	0.0008	0.0096	−0.0012	0.0095	0.0086
0.75	372.3	164.5	0.9919	0.0010	0.9894	0.0008	0.0082	0.0002	0.0083	0.0083
0.50	370.0	164.6	0.9809	0.0014	0.9777	0.0017	0.0069	0.0008	0.0073	0.0073
0.25	369.7	165.4	0.9795	0.0052	0.9765	0.0048	0.0068	−0.0003	0.0066	0.0067

^a Blend composition given as overall weight fraction PS in the PS–PBD blend.

^b Data from Kim and Burns.¹ Subscript 1 denotes PS component. T_g 's are in K.

^c Single prime denotes PS-rich phase; double prime denotes PBD-rich phase. w_1' is calculated from eq. (2).

^d All g_{12} 's are calculated from eqs. (6) and (7).

^e All χ_{12} 's are calculated from eq. (5).

this midpoint method.²⁷ From our experiment, we found that the choice of tangent placements allows approximately ± 0.5 K uncertainty in T_g and approximately ± 0.02 J g^{−1} deg^{−1} uncertainty in ΔC_p of the blended polymers.

RESULTS AND DISCUSSION

T_g of PS–PBD Blends

PS and PBD are known to be incompatible and two glass transition regions are observed, which we designate T_g (PS), associated with the PS-rich phase, and T_g (PBD), associated with the PBD-rich phase. The T_g 's of PS and PBD of the PS–PBD mill blend are presented in Table II, which was determined previously by DSC.¹ From the T_g of PS and PBD in PS–PBD blends, we can estimate the apparent weight fractions of PS and PBD dissolved in the PS-rich phase and the PBD-rich phase.²⁰ The apparent weight fractions of PS are determined in the PS-rich phase and PBD-rich phase by the following Fox²⁸ and Couchman equations.²⁹ The Fox equation is

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \quad (1)$$

Equation (1) may be rearranged to²⁰

$$W_1' = \frac{T_{g1}(T_{g1.b} - T_{g2})}{T_{g1.b}(T_{g1} - T_{g2})} \quad (2)$$

where W_1' is the apparent weight fraction of polymer 1 in the polymer 1-rich phase and $T_{g1.b}$ is the observed T_g of the polymer 1-rich phase in the blend.

The Couchman relation which yields T_g 's for

miscible polymer–polymer blends from values of T_g and ΔC_p at T_g for the unblended polymer components is given by the equation

$$\ln T_g = \frac{W_1 \Delta C_{p1} \ln T_{g1} + W_2 \Delta C_{p2} \ln T_{g2}}{W_1 \Delta C_{p1} + W_2 \Delta C_{p2}} \quad (3)$$

where $\Delta C_p = C_p^l(T_g) - C_p^s(T_g) =$ difference in specific heat at T_g , $C_p^l(T_g)$ is the specific heat of the liquid at T_g , and $C_p^s(T_g)$ is the specific heat of the solid at T_g .

Equation (3) may be rearranged to²⁰

$$W_1' = \frac{\Delta C_{p2}(\ln T_{g1.b} - \ln T_{g2})}{\Delta C_{p1}(\ln T_{g1} - \ln T_{g1.b}) + \Delta C_{p2}(\ln T_{g1.b} - \ln T_{g2})} \quad (4)$$

where W_1' is the apparent weight fraction of polymer 1 in the polymer 1-rich phase and $T_{g1.b}$ is the observed T_g of the polymer 1-rich phase in the blend.

Applying eq. (2) to the DSC results of T_g 's in the blends, we calculated the apparent weight fraction of PS in the PS-rich phase (W_1') and the apparent weight fraction of PS in the PBD-rich phase (W_1''), which are shown in Table II. Using the apparent weight fractions which we have calculated from the glass transition temperatures of the blends, we can then estimate the Flory–Huggins polymer–polymer interaction parameter (χ_{12}), provided that the system is at equilibrium or nearly so.

Phase Behavior of the Blends

In our previous work,¹ we saw that the specific heat increment at T_g (ΔC_p) of PBD decreases linearly with increasing proportions of PS in the PS–

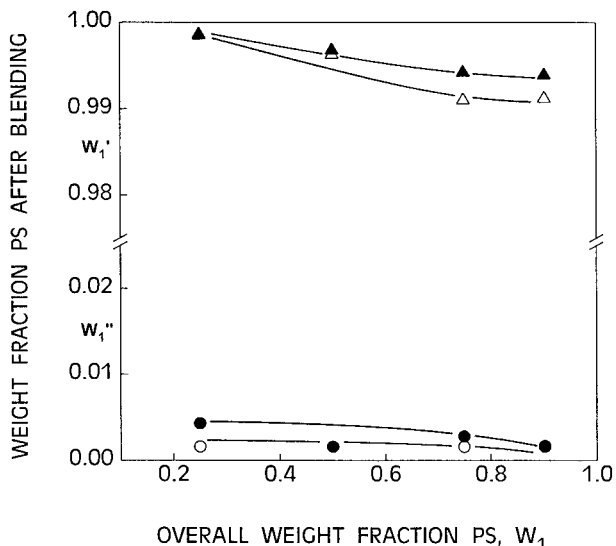


Figure 1 Phase composition diagram of PS 237,700–PBD 270,000 blends from (Δ , \circ) solution casting and (\blacktriangle , \bullet) freeze-drying: (Δ , \blacktriangle) weight fraction of PS in the PS-rich phase; (\circ , \bullet) weight fraction of PS in the PBD-rich phase.

PBD blends, whereas the specific heat increment for PS did not decrease with increasing proportions of PBD in the PS–PBD blend. Therefore, it was previously suggested that the PBD dissolves more in the PS phase than does the PS in the PBD phase.

In the present study, this behavior is explained quantitatively²² in Figures 1–4 in which are pre-

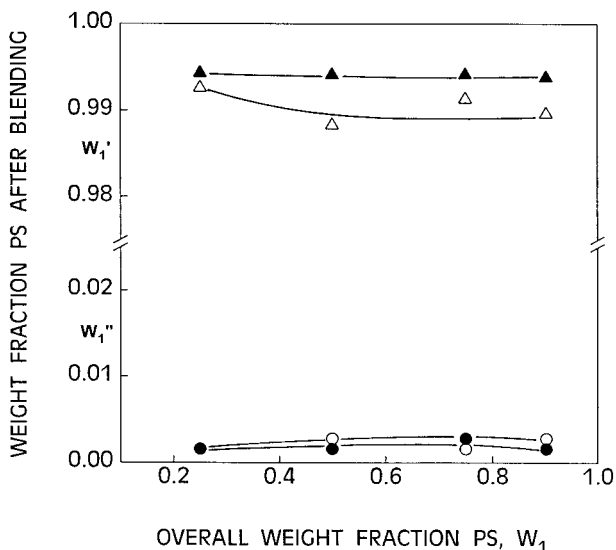


Figure 2 Phase composition diagram of PS 116,000–PBD 270,000 blends from (Δ , \circ) solution casting and (\blacktriangle , \bullet) freeze-drying: (Δ , \blacktriangle) weight fraction of PS in the PS-rich phase; (\circ , \bullet) weight fraction of PS in the PBD-rich phase.

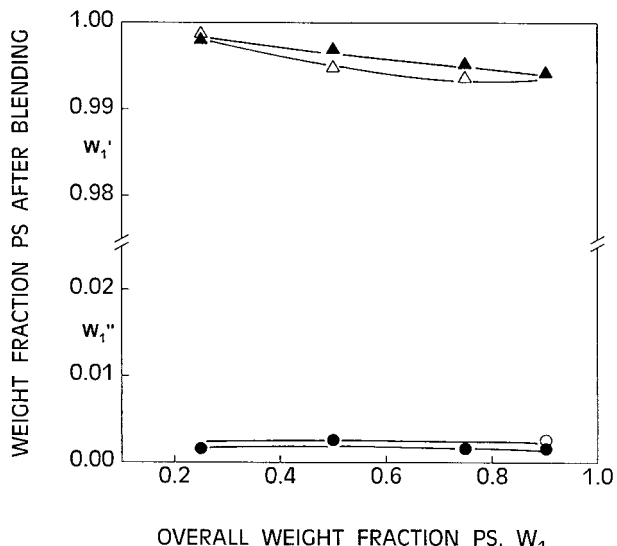


Figure 3 Phase composition diagram of PS 237,700–PBD 128,000 blends from (Δ , \circ) solution casting and (\blacktriangle , \bullet) freeze-drying: (Δ , \blacktriangle) weight fraction of PS in the PS-rich phase; (\circ , \bullet) weight fraction of PS in the PBD-rich phase.

sented phase composition diagrams of solution-cast and freeze-dried PS 237,700–PBD 270,000, PS 116,000–PBD 270,000, PS 237,700–PBD 128,000, and PS 116,000–PBD 128,000 blends, respectively. From Figures 1–4, we can see that the amount of PS dissolved in the PBD-rich phase (W_1'') is less than the amount of PBD dissolved in

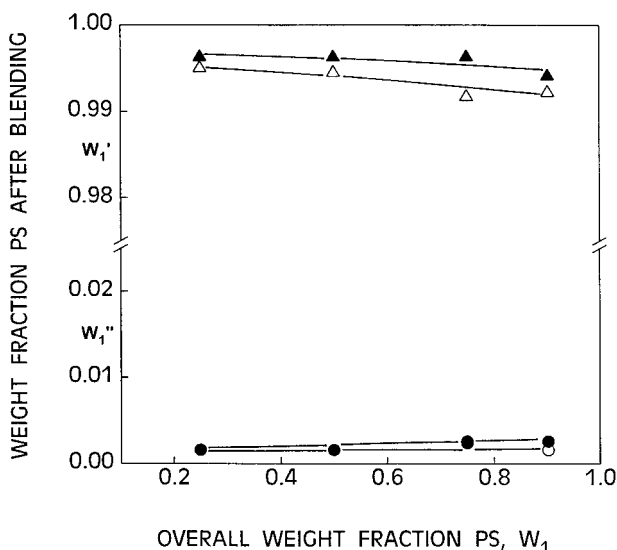


Figure 4 Phase composition diagram of PS 116,000–PBD 128,000 blends from (Δ , \circ) solution casting and (\blacktriangle , \bullet) freeze-drying: (Δ , \blacktriangle) weight fraction of PS in the PS-rich phase; (\circ , \bullet) weight fraction of PS in the PBD-rich phase.

the PS-rich phase ($1 - W'_1$). Therefore, the overall weight fraction of the PS-rich phase after blending is slightly greater than is the overall weight fraction of the PBD-rich phase after blending. The magnitude of the amounts of PS and PBD dissolved in the PBD-rich and the PS-rich phases, respectively, is similar between the solution-cast blends and the freeze-dried blends. The weight fraction of PS dissolved in the PS-rich phase (W'_1) was calculated from eq. (4).

From Figures 1–4, we can see that similar phase behavior is observed among the PS–PBD blends. From these results, it appears that PBD dissolves more in the PS-rich phase than does the PS in the PBD-rich phase. This result is consistent with the behavior of the specific heat increment at $T_g(\Delta C_p)$ of the PBD which is obtained from our previous work for PS–PBD blends.¹

From Figures 1–4, we can also see that the magnitude of the amounts of PBD dissolved in the PS-rich phase (W'_2) is greater in the PS 116,000–PBD 270,000 blend than in the other blends. This result is consistent with the result that the decrease of ΔC_p of PBD is observed to be greater with the PS 116,000–PBD 270,000 blend than with the other blends.

Polymer–Polymer Interaction Parameter

The Flory–Huggins polymer–polymer interaction parameter (χ_{12}) of the mixture can be determined by using eq. (4)²⁰:

$$\chi_{12} = \frac{\{(\phi_1'^2 - \phi_1''^2)[m_2 \ln(\phi_1''/\phi_1')] + (m_1 - m_2)(\phi_2' - \phi_2'') + (\phi_2'^2 - \phi_2''^2) \times [m_1 \ln(\phi_2''/\phi_2')] + (m_2 - m_1)(\phi_1' - \phi_1'')\}}{2m_1m_2(\phi_1'^2 - \phi_1''^2)(\phi_2'^2 - \phi_2''^2)} \quad (5)$$

where ϕ_1' is the apparent volume fraction of PS dissolved in the PS-rich phase, ϕ_1'' is the apparent volume fraction of PS dissolved in the PBD-rich phase, and m_1 and m_2 are essentially the number-average degree of polymerization of PS and PBD components, respectively.

Several assumptions are made in the theory discussed above. The most important assumptions are that the χ_{12} is taken to be constant and that both components of the blends are considered to be monodisperse. For polydisperse polymers, it has been found⁶ that number-average molecular weights can be used in place of monodisperse molecular weights in the modified Flory–Huggins

equation with very little qualitative effect on the consequent value of χ .

In this treatment, the fractionation of polymer molecular weights between the phases has been ignored. To apply the Flory–Huggins equation in the PS–PBD blend system, two criteria of equilibrium were tested.³⁰ To test the criterion of constancy of properties with time, we redissolved and recast the first cast film of the 0.50 weight fraction PS in toluene. The T_g of PS was found to be 372.5 K for the redissolved cast film which is very close to the T_g of the first solution-cast film (372.7 K) for the PS 237,700–PBD 270,000 blend. To test for reversibility, the blend compositions were obtained by blending pure components first with each other and second with previously blended components to the same final composition. The T_g of PS for the 0.75 weight fraction PS was found to be 370.4 K, which is very close to the T_g of the first solution-cast film (370.2 K) for the PS 237,700–PBD 270,000 blend. From these results, it appears that the PS–PBD blend system using solution casting is close to an equilibrium condition. For these cases, then, eq. (5) can be used to determine the polymer–polymer interaction parameter of the mixture without solvent in partially miscible blends.

Equation (5) was proposed in our earlier studies²⁰ based on the Flory–Huggins theory^{24–26} to determine the χ_{12} in partially miscible blend systems. Using eq. (4), the χ_{12} from the measured volume fractions for the PS–PBD blend system were calculated (Table II). The volume fraction was obtained from the weight fraction divided by the density of each polymer. The values of $m_1 = 947.2$ and 1061.5 were used for PS 237,700 and PS 116,000, respectively, and $m_2 = 508.9$ and 1368.3 were used for PBD 270,000 and PBD 128,000, respectively. A repeat unit of PS was chosen as a lattice site volume.

To examine χ_{12} as a function of composition, eqs. (6) and (7) were proposed in our earlier studies as follows^{21–23}:

$$\ln(\phi_1'/\phi_1'') + (1 - m_1/m_2)(\phi_2' - \phi_2'') + m_1g_0(\phi_2'^2 - \phi_2''^2) + m_1g_1 \times [(1 - 2\phi_1')\phi_2'^2 - (1 - 2\phi_1'')\phi_2''^2] = 0 \quad (6)$$

$$\ln(\phi_2'/\phi_2'') + (1 - m_2/m_1)(\phi_1' - \phi_1'') + m_2g_0(\phi_1'^2 - \phi_1''^2) + 2m_2g_1(\phi_1'^2\phi_2' - \phi_1''^2\phi_2'') = 0 \quad (7)$$

Table III Comparison of the Polymer–Polymer Interaction Parameters, χ_{12} and g_{12} , from Different Values of Apparent Volume Fraction (ϕ_1) of PS by the Fox and Couchman Relations for PS 237,000–PBD 270,000 Mill Blends

Blend ^a	Fox		Couchman	
	g_{12}^b	χ_{12}^c	g_{12}^b	χ_{12}^c
0.90	0.0095	0.0086	0.0102	0.0090
0.75	0.0083	0.0083	0.0095	0.0088
0.50	0.0073	0.0073	0.0078	0.0078
0.25	0.0066	0.0067	0.0062	0.0071

^a Blend composition given as overall weight fraction PS in the PS–PBD blend.

^b All g_{12} 's are calculated from eqs. (6) and (7).

^c All χ_{12} 's are calculated from eq. (5).

Using eqs. (6) and (7), we can get g_0 and g_1 so that the composition-dependent polymer–polymer interaction parameter, $g_{12} = g_0 + g_1\phi_2$, is determined.^{31,32} Here, ϕ_2 is defined as the overall volume fraction of polymer 2 in the blends. From eqs. (6) and (7), we calculated the g_{12} of the PS 237,700–PBD 270,000 mill blends (Table II). In Table II, the values of χ_{12} and g_{12} are compared with compositions. The values of χ_{12} and g_{12} are shown to be very similar. However, the g_{12} decreases with decrease of ϕ_1' , which means that the g_{12} decreases with increase of the apparent volume fraction of PBD dissolved in the PS-rich phase (ϕ_2'). In Table III, the values of χ_{12} are compared with different ways of treatment of the apparent weight fraction of PS and PBD components by the Fox and Couchman relations, and similar values of χ_{12} and g_{12} are observed between the two different ways of treatment of the apparent weight fraction.

In Tables IV and V, the values of χ_{12} and g_{12}

are compared for different blending methods and for different molecular weight averages of PS and PBD. The values of χ_{12} and g_{12} are very similar between the solution-cast and freeze-dried blends. However, the values of χ_{12} and g_{12} decrease with increase of m of PS and PBD. Here, it is noted that the m is related to the number-average molecular weight of each polymer. In Table IV, it is shown that the g_{12} of PS 116,000 ($m_1 = 1,061.5$) and PBD 128,000 ($m_2 = 1,368.3$) blend varies in the range 0.0040 to 0.0057 with composition. The g_{12} of PS 237,000 ($m_1 = 947.2$) and PBD 270,000 ($m_2 = 508.9$) is in the range 0.0083–0.0089.

The χ_{12} values from the solid state which are shown in Tables II–V can then be compared with the values from solution studies.^{5–8} They are found to be in reasonable agreement with the χ_{23} values (cf. Table VI) which were published by Narasimhan et al.⁶ Also, Roe and Zin⁹ reported χ values ranging from 0.07 to 0.09 at 150°C, and Tseng et al.⁸ reported χ values from 0.009 to 0.012 in a ternary solution at room temperature for PS 92,000–PBD 93,000 blends.

We can also determine the critical value of χ_{12} , $(\chi_{12})_c$, by eq. (8)²⁵:

$$(\chi_{12})_c = \frac{1}{2}(m_1^{-1/2} + m_2^{-1/2})^2 \quad (8)$$

Using eq. (8), the $(\chi_{12})_c$ was found to be 0.0030, 0.0028, 0.0018, and 0.0017 for blends of PS 237,700–PBD 270,000, PS 116,000–PBD 270,000, PS 237,700–PBD 128,000, and PS 116,000–PBD 128,000, respectively. It can be surmised that if $\chi_{12} < (\chi_{12})_c$ is observed then the polymers are compatible with each other and there will be no phase separation. If $\chi_{12} > (\chi_{12})_c$ is observed in the blends, phase separation will occur.³³ The values of χ_{12} which are shown in Tables II–V are

Table IV Comparison of the Polymer–Polymer Interaction Parameter, χ_{12} and g_{12} , for the Different Molecular Weights of PS and PBD in PS–PBD Solution-cast Blends

Blend ^a	PS 237,700–PBD 270,000		PS 116,000–PBD 270,000		PS 237,700–PBD 128,000		PS 116,000–PBD 128,000	
	χ_{12}^b	g_{12}^c	χ_{12}	g_{12}	χ_{12}	g_{12}	χ_{12}	g_{12}
0.90	0.0081	0.0083	0.0073	0.0077	0.0051	0.0043	0.0050	0.0040
0.75	0.0081	0.0083	0.0078	0.0080	0.0054	0.0047	0.0046	0.0042
0.50	0.0090	0.0089	0.0072	0.0071	0.0052	0.0052	0.0051	0.0052
0.25	0.0099	0.0089	0.0081	0.0077	0.0061	0.0065	0.0051	0.0057

^a Blend composition given as overall weight fraction PS in the PS–PBD blend. All apparent weight fractions are calculated from eq. (4).

^b All χ_{12} 's are calculated from eq. (5).

^c All g_{12} 's are calculated from eqs. (6) and (7).

Table V Comparison of the Polymer-Polymer Interaction Parameter, χ_{12} and g_{12} , for the Different Molecular Weights of PS and PBD in PS-PBD Freeze-dried Blends

Blend ^a	PS 237,700-PBD 270,000		PS 116,000-PBD 270,000		PS 237,700-PBD 128,000		PS 116,000-PBD 128,000	
	χ_{12} ^b	g_{12} ^c	χ_{12}	g_{12}	χ_{12}	g_{12}	χ_{12}	g_{12}
0.90	0.0085	0.0089	0.0081	0.0087	0.0055	0.0043	0.0047	0.0040
0.75	0.0083	0.0087	0.0078	0.0083	0.0055	0.0049	0.0049	0.0046
0.50	0.0092	0.0091	0.0081	0.0081	0.0053	0.0054	0.0052	0.0053
0.25	0.0091	0.0079	0.0082	0.0077	0.0058	0.0064	0.0052	0.0058

^a Blend composition given as overall weight fraction PS in the PS-PBD blend. All apparent weight fractions are calculated from eq. (4).

^b All χ_{12} 's are calculated from eq. (5).

^c All g_{12} 's are calculated from eqs. (6) and (7).

greater than are the values of $(\chi_{12})_c$, which indicates that the PS-PBD blends are immiscible for all blend compositions.

A model calculation of g_{12} using eqs. (6) and (7) is shown in Figure 5. In Figure 5, the degrees of polymerization of component 1 (m_1) and component 2 (m_2) are set equal, and the apparent volume fraction of component 1 in the component 1-rich phase (ϕ_1') is set equal to the apparent volume fraction of component 2 in the component 2-rich phase (ϕ_2''). From Figure 5, we can see that the value of g_{12} is decreasing with decrease of ϕ_1' at a certain degree of polymerization. Also, the value of g_{12} decreases with increase of m_i at a certain apparent volume fraction (ϕ_1'). This phenomenon is consistent with the g_{12} values shown in Tables IV and V. From these results, we can say that the values of the polymer-polymer interaction parameter depend on the degree of polymerization (m_i) as well as on the apparent volume fraction (ϕ_i) dissolved in each phase.

CONCLUSIONS

From the experimental T_g 's of PS and PBD, we determined the apparent weight fractions of PS

Table VI Interaction Parameters for PS 233,000-PBD 270,000-Toluene^a

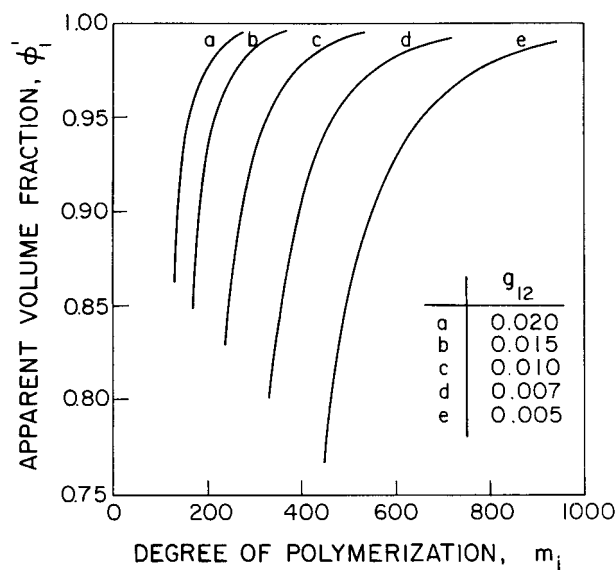
Blend ^b	Wt % Solvent	χ_{15}	χ_{13}	χ_{23}
0.50	81.56	0.403	0.448	0.004
0.45	81.55	0.402	0.439	0.005
0.50	84.51	0.404	0.430	0.008

^a Data from Narasimhan et al.⁶

^b Blend composition given as overall weight fraction PS in the PS-PBD blend.

and PBD components dissolved in the PS-rich phase and in the PBD-rich phase. From the results of the T_g 's and the phase composition diagrams of the blends, it can be concluded that PBD dissolves more in the PS-rich phase than does PS in the PBD-rich phase, which is consistent with the behavior of the ΔC_p of PBD in the PS-PBD blends.

Using the apparent volume fractions of the PS-rich phase and the PBD-rich phase, the polymer-polymer interaction parameter of PS-PBD blends with various compositions was determined based on the Flory-Huggins theory. The polymer-polymer interaction parameter of PS-PBD blends was calculated and found to vary from 0.0040 to 0.0102

**Figure 5** Model calculation of polymer-polymer interaction parameter (g_{12}) with degree of polymerization (m_i) and apparent volume fraction (ϕ_i).²²

with composition and molecular weights of PS and PBD.

We have been able to compare the values of χ obtained by two different methods: the glass transition temperature method and ternary solution method. The two methods are in good agreement for χ values of PS–PBD blends. There was no significant difference in the value of χ_{12} obtained for the different blending methods. The composition-dependent value of the Flory–Huggins interaction parameter (g_{12}) was found to be similar to the value of χ_{12} . From the observed polymer–polymer interaction parameter and from the model calculation, it is suggested that the polymer–polymer interaction parameter depends on the degree of polymerization (m_i) as well as on the apparent volume fraction (ϕ_i) dissolved in each phase.

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