

# Compatibility Studies of Polystyrene–Polybutadiene Blends by Thermal Analysis

WOO-NYON KIM and CHARLES M. BURNS, *Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1*

## Synopsis

In order to examine the behavior of incompatible blends of polystyrene and polybutadiene, the glass transition temperature, the melting point, and the specific heat increment at the glass transition temperature for atactic polystyrene (*a*-PS), isotactic polystyrene (*i*-PS), polybutadiene (PBD), and blends of *a*-PS/PBD and *i*-PS/PBD were determined by use of a differential scanning calorimeter. Blends were prepared by solution casting, freeze-drying, and milling. Weight fractions of polystyrene in the blends ranged from 0.95 to 0.05. The glass transition temperature of polystyrene changed with weight fraction in the blends, and with blending preparation methods; the glass transition temperature of polybutadiene remained essentially unchanged. The specific heat increment at the glass transition temperature of PBD decreases linearly with increasing proportions of PS in the PS/PBD blend for the broad and narrow molecular weight distribution polybutadiene polymers, whereas the specific heat increment for PS did not decrease with increasing proportions of PBD in the PS/PBD blend. These results suggest that the polybutadiene dissolves more in the polystyrene phase than does the polystyrene in the polybutadiene phase.

## INTRODUCTION

Thermal analysis was used to study the incompatible blends of polystyrene and polybutadiene. The glass transition temperature ( $T_g$ ), the melting point ( $T_m$ ), the crystallization temperature ( $T_c$ ), and the specific heat increment ( $\Delta C_p$ ) at  $T_g$  of the homopolymers and the blends were determined by differential scanning calorimetry (DSC). This method was found to be useful for determining the extent of the miscibility of one polymer in another.

A miscible polymer blend will exhibit a single glass transition between the  $T_g$ s of the components.<sup>1–3</sup> Recently, some investigators<sup>4–6</sup> have used the specific heat increment ( $\Delta C_p$ ) at  $T_g$  to investigate the polymer–polymer compatibility by DSC.

It is well known that incompatibility exists for blends of polystyrene (PS) and polybutadiene (PBD).<sup>7</sup> Many authors have found phase separation in many solvents<sup>8–11</sup> or two  $T_g$ s<sup>12–14</sup> for these mixtures. Brostrom et al.<sup>13</sup> have used DSC to report the two  $T_g$ s of PS/PBD solution-cast blends (50/50, w/w) with different thermal pretreatments. Turley<sup>14</sup> studied the  $T_g$  behavior of PS/PBD blends by a dynamic mechanical method, and reported two  $T_g$ s. Some investigators<sup>15–17</sup> have studied the viscosity–composition and elastic modulus–composition relations for mill blended PS and PBD. Narasimhan et al.<sup>18</sup> reported experimental values of the polymer–polymer interaction parameter  $\chi_{23}$  in ternary solution with tetrahydrofuran. Muniz<sup>19</sup> deter-

mined the interaction parameter ( $\chi_{23}$ ) of polystyrene with polybutadiene in chloroform.

The interaction between component polymers in a compatible blend where one of the constituents is crystalline has been studied using the experimentally determined melting point depression.<sup>20-33</sup> An equation for evaluation of the polymer-polymer interaction parameter ( $\chi_{12}$ ) for polymer-polymer blends in which one component is crystalline was treated by Scott<sup>34</sup> using the Flory-Huggins approximation.<sup>35</sup> Nishi and Wang<sup>20</sup> applied a simplified form to mixtures of polymers.

In our present study we are examining the compatibility of blends of polystyrene and polybutadiene by determining experimentally the glass transition temperature and the specific heat increment ( $\Delta C_p$ ) at  $T_g$  of the polymer blends, as well as determining these quantities for the homopolymers.

## EXPERIMENTAL

### Polymers

The characteristics and sources of the polystyrene (PS) and polybutadiene (PBD) samples used in this study are shown in Tables I and II. 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 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 vacuum for 7 days at

TABLE I  
Characteristics of Polystyrene Samples

Sample	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	$T_g$ (K) <sup>a</sup>	$\Delta C_p$ (J g <sup>-1</sup> K <sup>-1</sup> ) <sup>a</sup>
PS 237,770 <sup>b</sup>	237,700 <sup>c</sup>	98,600	2.41	374.0	0.282
PS 116,000 <sup>d</sup>	116,000	110,500	< 1.05	375.9	0.284
PS 35,000 <sup>e</sup>	35,000	33,300	< 1.05	371.0	0.284
<i>i</i> -PS 851,000 <sup>f</sup>	851,000	143,500	5.93	368.4	—

<sup>a</sup> Measured in our laboratory by differential scanning calorimetry.

<sup>b</sup> Supplied by Polysciences, Inc.

<sup>c</sup> Measured in our laboratory by gel permeation chromatography using the Chang-Huang correction method (Ref. 36).

<sup>d</sup> Supplied by Pressure Chemical Co.

<sup>e</sup> Supplied by Polymer Laboratory, Ltd.

<sup>f</sup> Isotactic polystyrene, supplied by Polysciences, Inc.

TABLE II  
 Characteristics of Polybutadiene Samples

Sample	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	$T_g$ (K) <sup>a</sup>	$T_m$ (K) <sup>a</sup>	$\Delta C_p$ (J g <sup>-1</sup> K <sup>-1</sup> ) <sup>a</sup>
PBD 270,000 <sup>b</sup>	270,000 <sup>c</sup>	51,900	5.2	164.3	257.9	0.545
PBD 128,000 <sup>d</sup>	128,000	121,000	1.07	176.5	—	0.488
PBD 17,000 <sup>e</sup>	17,000	16,000	1.06	176.5	—	0.485

<sup>a</sup> Measured in our laboratory by differential scanning calorimetry.

<sup>b</sup> Taktene 1202, 98.0% *cis*-1,4, supplied by Polysar Corp.

<sup>c</sup> Measured in our laboratory by gel permeation chromatography using the Chang-Huang correction method (Ref. 36).

<sup>d</sup> 38% *cis*, 53.0% *trans*, 9.0% vinyl, 0.3% antioxidant, supplied by Phillips Petroleum Co.

<sup>e</sup> 43.5% *cis*, 49.1% *trans*, 7.4% vinyl, 0.05% antioxidant, supplied by Phillips Petroleum Co.

room temperature. Cast film thickness was  $10 \pm 2$   $\mu\text{m}$ . 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 1 mm Hg vacuum for 5 h. The freeze-dried polymer was dried under vacuum for 7 days at room temperature. The solution cast films and low bulk density freeze-dried powders were compacted at room temperature by using a Perkin-Elmer Quick Press<sup>37</sup> before use. Mill blends were prepared using the laboratory mill which has been described elsewhere.<sup>38</sup> The rotation speed was 14 and 7 rpm for front and back rolls, respectively. Polymer blending was accomplished by adding polystyrene resin to a polybutadiene 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 has been found that the polystyrene did not melt. In each run, 3 g of 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<sup>-1</sup>, 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 polybutadiene, and a range of 303–423 K using air cooling for polystyrene. The sample was surrounded by a helium atmosphere. The samples were then reheated at the heating rate of 20 K min<sup>-1</sup> a certain number of times under the same thermal regime followed by 135 K min<sup>-1</sup> programmed cooling immediately between heats. Samples containing isotactic polystyrene were initially heated from 303 to 438 K at 20 K min<sup>-1</sup>, held at 438 K for 30 min and cooled at 60 K min<sup>-1</sup> to 333 K. They were

then reheated at  $20 \text{ K min}^{-1}$  to  $533 \text{ K}$ . 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 this midpoint method.<sup>5</sup> From our experiment, we have found that the choice of tangent placements allows approximately  $\pm 0.5 \text{ K}$  uncertainty in  $T_g$  and approximately  $\pm 0.02 \text{ J g}^{-1} \text{ deg}^{-1}$  uncertainty in  $\Delta C_p$  of the blended polymers.

## RESULTS AND DISCUSSION

### $T_g$ and $\Delta C_p$ of PS and PBD

Many investigators have reported the  $T_g$  and  $\Delta C_p$  of polystyrene<sup>5,39-44</sup> and polybutadiene.<sup>40,45,46</sup> In our study, the experimental value of  $T_g$  of polystyrene  $\overline{M}_w = 237,700$  is found to be  $374 \text{ K}$  (cf. Table I). For  $\Delta C_p$ , the value  $0.282 \text{ J g}^{-1} \text{ K}^{-1}$  found for polystyrene  $\overline{M}_w = 237,700$  is similar to the values found by Shultz and Young,<sup>5</sup> Bair,<sup>40</sup> and Fried et al.<sup>41</sup> A typical DSC thermogram of high (98.0%) *cis*-1,4-polybutadiene is shown in Figure 1. The high *cis*-1,4-polybutadiene is known to crystallize about 30% at low temperatures (at  $273 \text{ K}$ ) because of its regularity.<sup>47,48</sup> From this figure the  $T_g$  and  $T_m$  do not change significantly after annealing the samples from  $123$  to  $273 \text{ K}$ . But in the case of the crystallization temperature ( $T_c$ ), we have found a significant depression by about  $15 \text{ K}$ . We have found the  $T_g$  of polybutadiene to be  $164.3$  and  $176.5 \text{ K}$  for samples having  $98.0$  and  $38.0\%$  *cis*-1,4 content, respectively (cf. Table I). The  $T_g$  of polybutadiene has been reported by other investigators to be  $171$ ,<sup>45</sup>  $178$ ,<sup>46</sup> and  $188 \text{ K}$ .<sup>40</sup> The  $\Delta C_p$  values of  $0.545$  and  $0.485 \text{ J g}^{-1} \text{ K}^{-1}$  found from our experimental data for  $98.0$  and  $38.0\%$  *cis*-1,4 contents, respectively, are somewhat higher than those found by Bair ( $0.385 \text{ J g}^{-1} \text{ K}^{-1}$ ).<sup>40</sup> The  $\Delta C_p$  values are consistent with

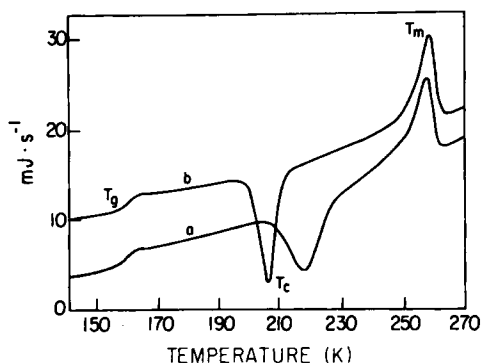


Fig. 1. Thermograms showing the glass transition temperature  $T_g$ , the crystallization temperature  $T_c$ , and the melting point  $T_m$  of 98% *cis*-1,4-polybutadiene 270,000 (a) before annealing and (b) after annealing at  $273 \text{ K}$ , followed by  $135 \text{ K/min}$  cooling immediately to  $123 \text{ K}$ . Sample size =  $11.0 \text{ mg}$ . Heating rate =  $20 \text{ K/min}$  (Table II). The ordinate (heat input rate) is not absolute.

the equation proposed by Boyer<sup>49</sup>:

$$\Delta C_p T_g = 15 + 4 \times 10^{-2} T_g \quad (1)$$

The  $T_m$  of solution cast 98.0% *cis*-1,4-polybutadiene  $\overline{M}_w = 270,000$  was found to be  $257.9 \pm 0.2$  K (cf. Table II). The equilibrium melting temperature ( $T_m^\circ = 274.15$  K) and heat of fusion ( $\Delta H_f^\circ = 9,200$  J mol<sup>-1</sup>) had been measured earlier by Natta and Moraglio<sup>50</sup> for 98.5% *cis*-1,4-polybutadiene polymer.

### Dependence of $T_g$ and $\Delta C_p$ on Concentration

The effect of solution concentration [% (w/v)] in benzene on the  $T_g$  and  $\Delta C_p$  for the freeze-dried blend PS 237,700/PBD 270,000 0.95 weight fraction of PS is shown in Figure 2. At concentrations lower than 4.0% (w/v), significant depressions of  $T_g$  and  $\Delta C_p$  were observed. The  $T_g$  at 4.0% (w/v) was found to be 374 K which is the same value as that of the pure polystyrene sample. Also, in the study of Kuleznev et al.,<sup>15</sup> the concentration at which polystyrene and polybutadiene began to separate in benzene solution was 4.2%. This result suggests that phase separation of PS/PBD blends in the solution state in benzene occurs at concentrations above 4.0% (w/v). At 5.0% (w/v) concentration, we have observed that polystyrene and polybutadiene solutions are very turbid.

### $T_g$ of PS/PBD Blends

Polystyrene (PS) and polybutadiene (PBD) are known to be incompatible and two glass transition regions are observed,  $T_g(\text{PS})$ , associated with PS-rich regions, and  $T_g(\text{PBD})$ , associated with PBD-rich regions. In Figure 3,

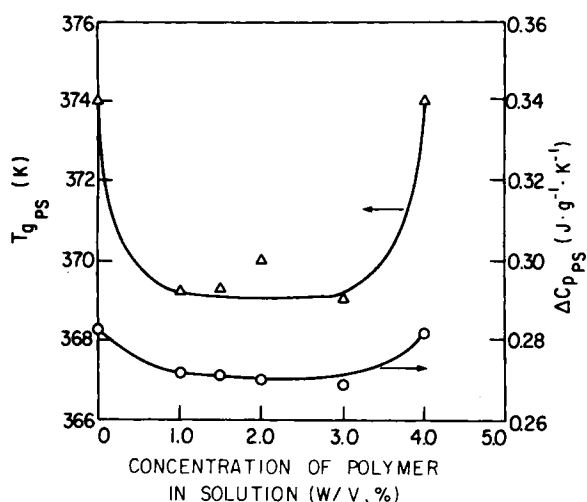


Fig. 2. Effect of solution concentration before freeze-drying on the glass transition temperature  $T_g$  and specific heat increment  $\Delta C_p$  at  $T_g$  of polystyrene for PS 237,700/PBD 270,000 (0.95 weight fraction PS) blends freeze-dried from benzene solution: (Δ) for  $T_g$ ; (○) for  $\Delta C_p$ .

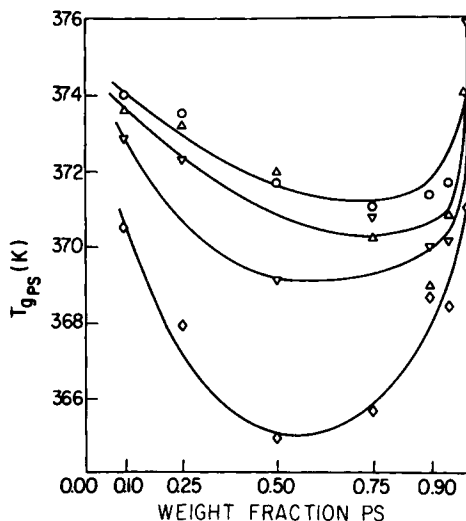


Fig. 3. Effect of blend composition on the  $T_g(\text{PS})$  for PS 237,700/PBD 270,000 ( $\Delta$ ), PS 237,700/PBD 128,000 ( $\circ$ ), PS 116,000/PBD 270,000 ( $\nabla$ ), and PS 35,000/PBD 17,000 ( $\diamond$ ). Blends solution cast from 1.0 % (w/v) benzene solution.

the  $T_g$  of polystyrene as a function of composition for the PS/PBD solution cast blends is presented. In this figure, the  $T_g$ s decrease for the blends of 0.75, 0.50, and 0.25 weight fraction of PS compositions by about 2–7 K. The  $T_g(\text{PS})$  of PS 116,000/PBD 270,000 and PS 35,000/PBD 17,000 blends decreases more than that of PS 237,700/PBD 270,000 and PS 237,000/PBD 128,000 blends. This result suggests that low molecular weight polystyrene is more compatible with polybutadiene than is high molecular weight polystyrene, and compatibility increases in the intermediate regions of PS blend compositions.

The effect of milling time on  $T_g$  of polystyrene as a function of blend composition is presented in Figure 4. Three different milling times were investigated, 10, 15, and 20 min, at a mill surface temperature of 140°C. When a roll surface temperature of 130°C was employed, the polystyrene polymer did not melt. From this figure the  $T_g$ s decrease for the 20 min milling time curve by about 2 K for blends of 0.75 weight fraction PS and about 5 K for blends of 0.50 and 0.25 weight fraction. From the milling curve at 15 min, the  $T_g$ s decrease by about 2 K for blends of 0.75 and 0.25 weight fraction and 3 K for blends of 0.50 weight fraction PS. From the above milling data, we can conclude that the compatibility increases in the intermediate regions of PS compositions with the increase of milling time. We could speculate that a phase inversion may be occurring at intermediate compositions, but further research would be needed to confirm whether such a condition exists.

The  $T_g$ s of polystyrene as a function of composition and molecular weight for the PS/PBD freeze-dried blends are shown in Figure 5. In this figure, the  $T_g$ s decrease by about 5 K in the region of 0.95 weight fraction of PS composition for PS 237,700/PBD 270,000, and PS 237,700/PBD 128,000, and by about 2 K for PS 116,000/PBD 270,000 blends. Further annealing did not cause the curves for  $T_g$  of freeze-dried PS to approach those of solution cast and mill blended polystyrene.

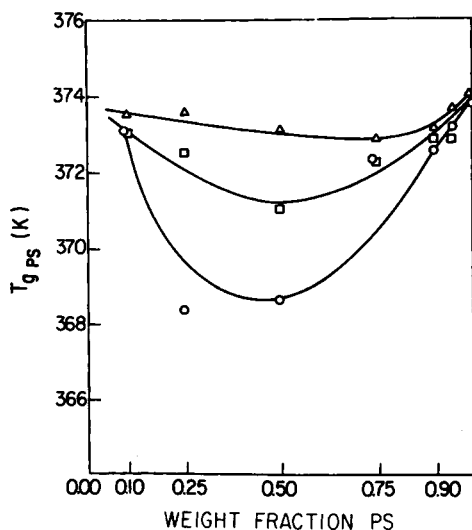


Fig. 4. Effect of milling time on the  $T_g(\text{PS})$  for PS 237,700/PBD 270,000 mill blends at 413 K (140°C) mill surface temperature with different milling times: ( $\Delta$ ) 10 min; ( $\square$ ) 15 min; ( $\circ$ ) 20 min.

The  $T_g$  of polybutadiene for the PS/PBD mill blending samples is shown in Figure 6. In this figure, the  $T_g$ s increase more at 20 min milling than at 10 and 15 min milling, although in no case is the change in  $T_g$  very large. This  $T_g$  elevation behavior is complementary to the  $T_g$  depression behavior of polystyrene for the PS/PBD mill blending samples (cf. Fig. 4). The  $T_g$ s of polybutadiene for the PS/PBD solution casting and freeze-drying blends are shown in Figure 7. From this figure we can see that the  $T_g$ s do not change appreciably with compositions for the PS/PBD solution cast and freeze-dried blends.

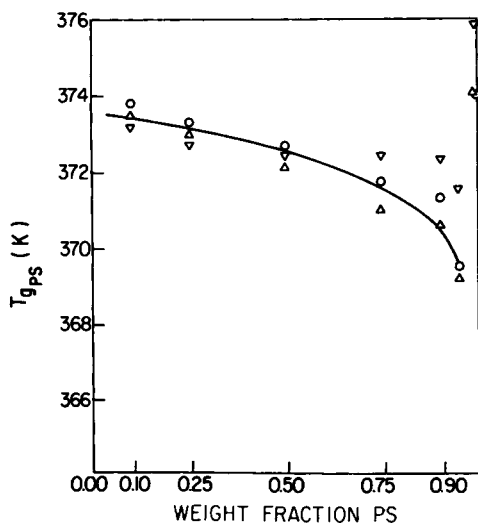


Fig. 5. Effect of freeze-dried blend composition on the  $T_g(\text{PS})$  for PS 237,700/PBD 270,000 ( $\Delta$ ), PS 237,700/PBD 128,000 ( $\circ$ ), and PS 116,000/PBD 270,000 ( $\nabla$ ). Blends freeze-dried from 1.0% (w/v) benzene solution.

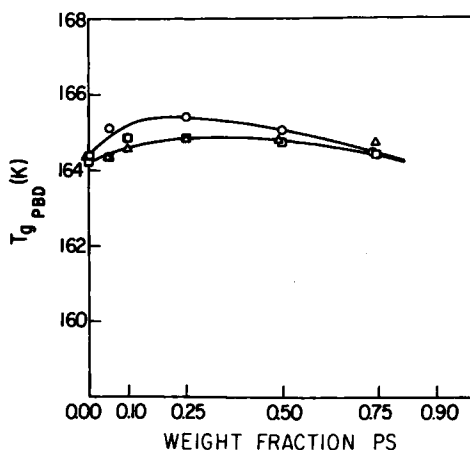


Fig. 6. Effect of milling time on the  $T_g$ (PBD) for PS 237,700/PBD 270,000 mill blends at 413 K (140°C) mill surface temperature. Differential milling times: ( $\Delta$ ) 10 min; ( $\square$ ) 15 min; ( $\circ$ ) 20 min.

### $\Delta C_p$ of PS/PBD Blends

The values of  $\Delta C_p$  for polystyrene in blends prepared by solution casting, freeze-drying, and milling are presented in Figure 8. From this figure, the  $\Delta C_p$  of polystyrene in the PS/PBD blends does not appear to change significantly with composition. These small changes are within the range of experimental error.

From Figures 9–12, the  $\Delta C_p$  of polybutadiene is seen to decrease linearly with composition of PS/PBD blends for both broad and narrow molecular weight distribution polybutadiene polymers. Since in a perfectly miscible system the  $T_g$ s would coalesce at an intermediate value, the  $\Delta C_p$  value at the original  $T_g$  of polybutadiene would be zero. These results suggest, then, that the polybutadiene is dissolving in the polystyrene phase, while the polystyrene (cf. Fig. 8) does not appear to be dissolving in the polybutadiene

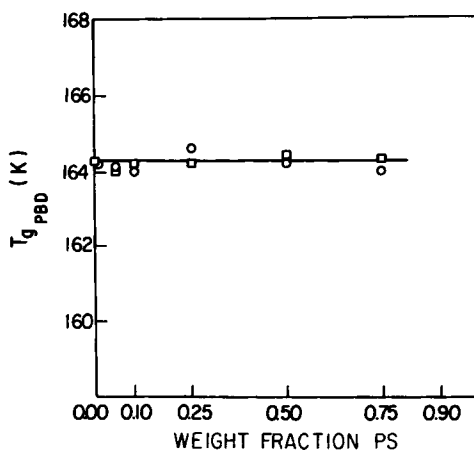


Fig. 7. Effect of blend composition on the  $T_g$ (PBD) for the PS 237,700/PBD 270,000 blend: ( $\square$ ) solution casting; ( $\circ$ ) freeze-drying. Blends from 1.0% (w/v) benzene solution.



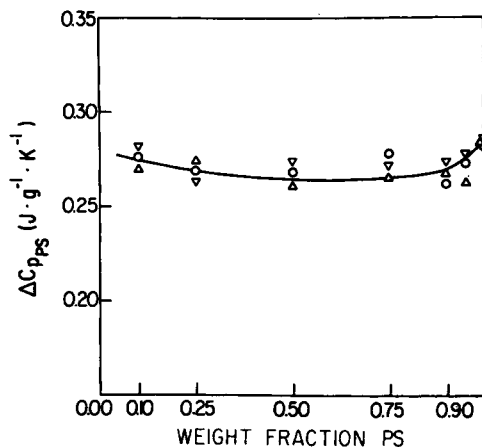


Fig. 8. Specific heat increment  $\Delta C_p$  at the  $T_g$  of polystyrene for PS 237,700/PBD 270,000 blends from 1.0% (w/v) benzene solution: ( $\Delta$ ) solution casting; ( $\circ$ ) freeze-drying; ( $\nabla$ ) milling (20 min).

phase. This interpretation is consistent with the earlier observation that the  $T_g$  of polystyrene decreases with increasing PBD concentration, while the  $T_g$  of PBD remains essentially unchanged with increasing PS concentration.

In Figures 9 and 10 are presented the  $\Delta C_p$  values of polybutadiene for the PS 237,700/PBD 270,000 and PS 116,000/PBD 270,000 blends, respectively. In these figures the  $\Delta C_p$  of polybutadiene decreases more significantly with composition for the PS 116,000/PBD 270,000 blends. This result suggests that the PBD 270,000 dissolves more in the PS 116,000 than it does in the PS 237,700 phase. We have already seen in Figure 3 that the  $T_g$  of PS is reduced more when the PS has a lower molecular weight. From

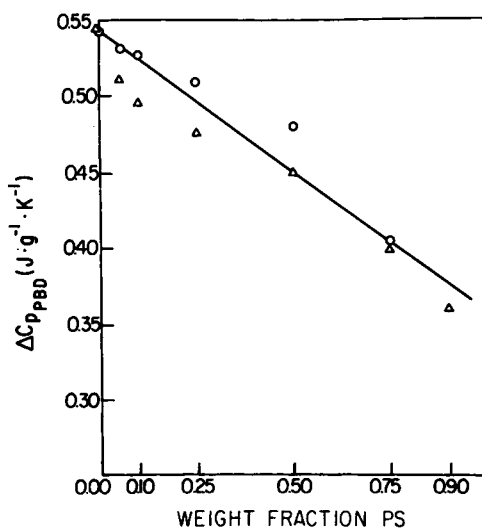


Fig. 9. Specific heat increment  $\Delta C_p$  at the  $T_g$  of polybutadiene for PS 237,700/PBD 270,000 blends from 1.0% (w/v) benzene solution: ( $\Delta$ ) solution casting; ( $\circ$ ) freeze-drying.

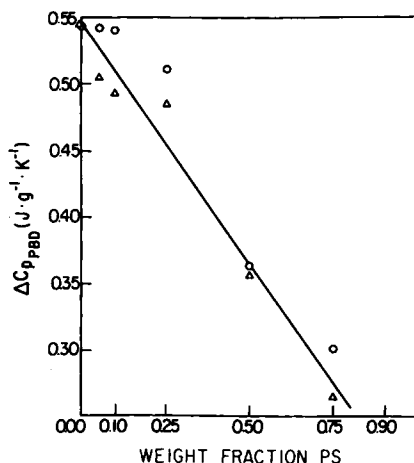


Fig. 10. Specific heat increment  $\Delta C_p$  at the  $T_g$  of polybutadiene for PS 116,000/PBD 270,000 blends from 1.0% (w/v) benzene solution: ( $\Delta$ ) solution casting; ( $\circ$ ) freeze-drying.

Figures 3, 9, and 10 we have concluded that PS 116,000 is more compatible with PBD 270,000 than PS 237,700. The relative contributions of molecular weight and molecular weight distribution will require further investigation.

In Figures 11 and 12 are presented the  $\Delta C_p$  values of polybutadiene for the PS 116,000/PBD 128,000 and PS 237,700/PBD 128,000 blends, respectively. In these figures the  $\Delta C_p$  of polybutadiene decreases linearly with composition of the PS/PBD blends, but there is not much difference in the  $\Delta C_p$  behavior between PS 116,000/PBD 128,000 and PS 237,700/PBD 128,000 blends.

The effect of milling time on  $\Delta C_p$  of polybutadiene for the PS 237,700/PBD 270,000 blends is presented in Figure 13. In this figure the  $\Delta C_p$  of

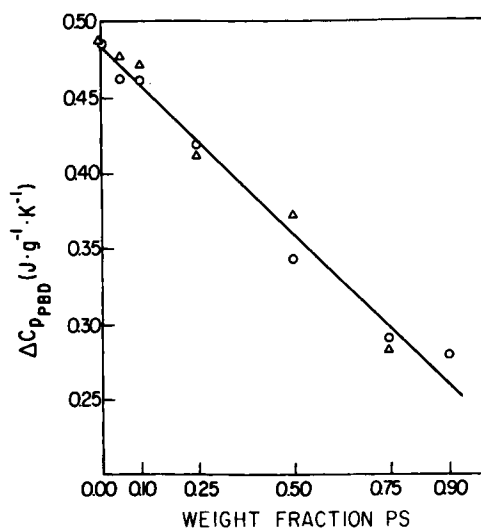


Fig. 11. Specific heat increment  $\Delta C_p$  at the  $T_g$  of polybutadiene for PS 116,000/PBD 128,000 blends from 1.0% (w/v) benzene solution: ( $\Delta$ ) solution casting; ( $\circ$ ) freeze-drying.

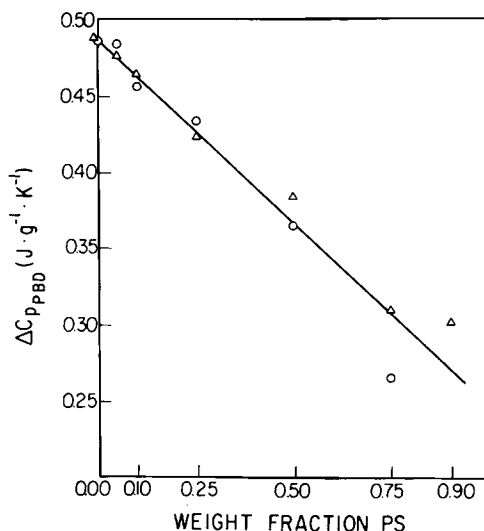


Fig. 12. Specific heat increment  $\Delta C_p$  at the  $T_g$  of polybutadiene for PS 237,700/PBD 128,000 blends of 1.0% (w/v) benzene solution: ( $\Delta$ ) solution casting; ( $\circ$ ) freeze-drying.

polybutadiene decreases more significantly with composition for the 15- and 20-min milling curves than it does for the 10-min milling curve. From the experimental data of  $T_g$  and  $\Delta C_p$  (cf. Fig. 4, 6, and 13), and furthermore from the  $T_m$  depressions with milling time (cf. Fig. 14) for the PS/PBD mill blends, we can conclude that the compatibility increases with an increase of milling action. From Figures 9 and 14, we can see that the degree of decrease of  $\Delta C_p$ (PBD) for milled blends is larger than for solution cast and freeze-dried PS 237,700/PBD 270,000 blends. The shearing involved in mill

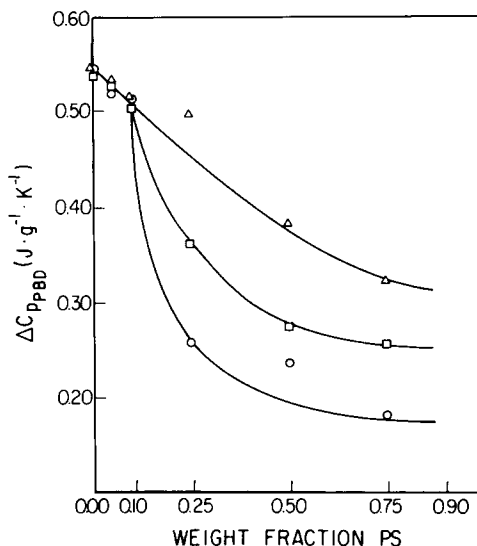


Fig. 13. Specific heat increment  $\Delta C_p$  at the  $T_g$  of polybutadiene for PS 237,700/PBD 270,000 mill blends at 413 K (140°C) mill surface temperature with different milling times: ( $\Delta$ ) 10 min; ( $\square$ ) 15 min; ( $\circ$ ) 20 min.

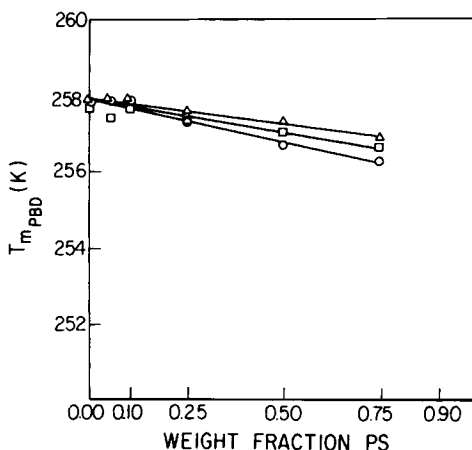


Fig. 14. Melting temperatures of polybutadiene in PS 237,700/PBD 270,000 milled blends at 413 K (140°C) mill surface temperature with different milling times: (Δ) 10 min; (□) 15 min; (○) 20 min.

blending may result in a distribution of polymers in the blend which is more dispersed than can be obtained by the other methods.

### Melting Point Depression of Polybutadiene

The melting point ( $T_m$ ) depression of 98.0% *cis*-1,4-polybutadiene  $\overline{M}_w = 270,000$  is presented in Figure 14 as a function of composition for the PS 237,700/PBD 270,000 milled blends. Three different curves show the  $T_m$  depression with different mill times of 10, 15, and 20 min at 140°C. The 20-min milling time curve shows a larger  $T_m$  depression than the 10- and 15-min milling time curves. The maximum  $T_m$  depression is observed at the 0.75 weight fraction of PS composition for the 10-, 15-, and 20-min milling time curves, and has values of 1.0, 1.2, and 1.7 K, respectively. The  $T_m$  depression of PBD 270,000 is presented in Figure 15 for the PS 237,700/PBD 270,000 solution cast and freeze-dried blends. The maximum depression of melting point is observed at the 0.75 weight fraction of PS composition for the freeze-dried and solution cast blends and has values of 1.3 and 1.1 K, respectively. The  $T_m$  depression of freeze-dried, solution-cast and mill-blended samples having 0.75 weight fraction of PS composition has been found to be in the range of 1.1–1.7 K.

### Melting Point Depression of Isotactic Polystyrene

The melting behavior of isotactic polystyrene (*i*-PS) of  $\overline{M}_w = 851,000$  is shown in Figure 16. The sample was freeze-dried and analyzed before annealing and after annealing at 438 K (165°C) for 30 min. This dual melting behavior of *i*-PS after annealing has been reported earlier.<sup>22,26,51</sup> In the first heating of the *i*-PS, we see that only one melting peak ( $T_{m_2} = 490.4$  K) (Table III) has been measured. In the second heating curve after the sample has been annealed at 438 K (165°C), two melting peaks are observed ( $T_{m_1} = 473.0$  K and  $T_{m_2} = 490.7 \pm 0.2$  K). The higher melting point ( $T_{m_2}$ ) is slightly increased by 0.3 K, after annealing the single *i*-PS freeze-dried sample (Table III).

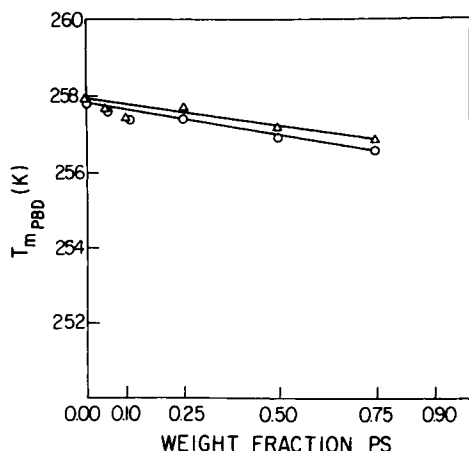


Fig. 15. Melting temperature of polybutadiene in PS 237,700/PBD 270,000 solution cast ( $\Delta$ ) and freeze-dried ( $\circ$ ) blends from 1.0% (w/v) benzene solution.

The complex melting behavior of *i*-PS depends on the crystallization temperature and the thermal treatment after crystallization.<sup>51</sup> The occurrence of a double melting endotherm is ascribed to a fast reorganization during heating of crystallites formed at the crystallization temperature ( $T_c$ ), resulting in an increase of the melting point  $T_m$ .<sup>22</sup> Although the mechanism of the reorganization is not yet completely understood,<sup>22</sup> it is supposed to involve cooperative diffusion of chain segments in amorphous and crystalline regions. This reorganization occurs only when the polymer is heated in its original melting domain, where the chains possess a high degree of mobility. Consequently, any change in the chemical structure of the amorphous phase surrounding the lamellas will change the melting behavior and eventually suppress any reorganization.<sup>52</sup>

There are two possible explanations of this multiple melting peaks phenomenon. One is that the multiple peaks reflect the presence of different crystal structures, and the other is that the peaks are a consequence of reorganization occurring during the heating process, perhaps lamellar

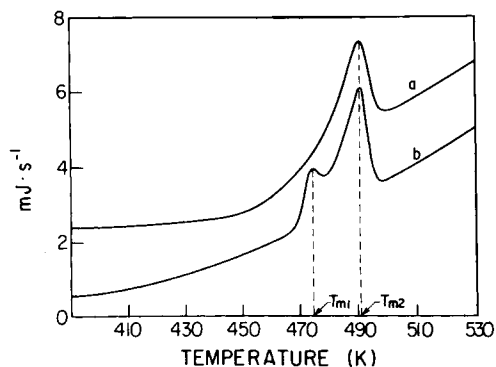


Fig. 16. Thermograms showing the melting behavior of isotactic PS 851,000 freeze-dried from 1.0% (w/v) benzene solution: (a) before annealing and (b) after annealing at 438 K for 30 min. The ordinate (heat input rate) is not absolute.

TABLE III  
Melting Points ( $T_m$ ) and Glass Transition Temperatures ( $T_g$ ) of the Isotactic PS 851,000/  
PBD 128,000 Blends

Blend <sup>a</sup>	First heating <sup>b</sup>		Second heating <sup>c</sup>				
	$T_{m2}$ (K)	$\Delta T_{m2}$	$T_g$ (K)	$T_{m1}$ (K)	$\Delta T_{m1}$	$T_{m2}$ (K)	$\Delta T_{m2}$
1.00	490.4	—	368.4	473.0	—	490.7	—
0.95	489.7	0.7	367.0	472.5	0.5	489.9	0.8
0.90	490.1	0.3	368.4	472.4	0.6	490.4	0.3
0.75	489.9	0.5	368.1	472.5	0.5	490.1	0.6

<sup>a</sup> Blend composition given as weight fraction *i*-PS in the *i*-PS/PBD blend.

<sup>b</sup> 20 K/min heating from 333 to 533 K.

<sup>c</sup> 20 K/min heating from 333 to 438 K, annealed at 438 K (165°C) for 0.5 h followed by 60 K/min cooling to 333 K, rescanned at 20 K/min heating from 333 to 533 K.

thickening. The low angle X-ray data are consistent with the reorganization hypothesis since the lamellar thickness increases with increasing  $T_c$ .<sup>2</sup>

In our experiments with *i*-PS/PBD blends, the melting point depression of *i*-PS 851,000 is shown in Table III as a function of composition for the *i*-PS 851,000/PBD 116,000 freeze-dried blend. Both the first heating curve and the second heating curve after annealing show the same melting point depression behavior with composition. The maximum melting point depression is observed at the 0.95 weight fraction *i*-PS composition for the first heating curve and the second heating curve, and has values of 0.7 K and 0.8 K, respectively. In the study by Runt<sup>26</sup> on polymer blends containing isotactic polystyrene, the polymer blend was prepared by embedding *i*-PS single crystals in a polybutadiene polymer matrix, and no significant depression in  $T_m$  was found. These melting point depression data may be used to calculate the polymer-polymer interaction parameters.

## CONCLUSIONS

Values of glass transition temperature ( $T_g$ ), melting point ( $T_m$ ), and specific heat increment ( $\Delta C_p$ ) at  $T_g$  for atactic polystyrene, isotactic polystyrene, polybutadiene, and blends of PS/PBD have been determined by differential scanning calorimetry. In the study of the effect of solution concentration in benzene on the  $T_g$  and  $\Delta C_p$ , phase separation of PS/PBD blends in the solution state occurs above 4.0% (w/v). In the solution-cast and mill-blend samples, the  $T_g$  of polystyrene decreases by about 2–7 K, in the regions of 0.75, 0.50, and 0.25 weight fraction PS compositions between the two  $T_g$ s of the two component polymers. In the case of freeze-dried blends, the  $T_g$  of polystyrene decreases by about 2–5 K in the region of 0.95, 0.90, and 0.75 weight fraction PS compositions from the  $T_g$  of pure PS. The  $T_g$ (PS) of PS 116,000/PBD 270,000 and PS 35,000/PBD 17,000 blends decreases more than that of PS 237,700/PBD 270,000, and PS 237,700/PBD 128,000 blends. From these experimental data it can be concluded that lower molecular weight polystyrene is more compatible with polybutadiene than higher molecular weight polystyrene.

In the study of  $\Delta C_p$ (PBD) with various blend compositions, the  $\Delta C_p$  of polybutadiene decreases linearly with increasing proportions of PS in the

PS/PBD blend for the broad and narrow molecular weight distribution polybutadiene polymers, whereas the  $\Delta C_p(\text{PS})$  did not decrease with increasing proportions of PBD in the PS/PBD blend. These results suggest that the polybutadiene dissolves more in the polystyrene phase than does the polystyrene in the polybutadiene phase. This conclusion is consistent with the  $T_g$  of PS decreasing with increasing concentrations of PBD while the  $T_g$  of PBD does not change with increasing concentration of PS.

In the case of mill blending, the  $\Delta C_p$  of polybutadiene with composition decreases significantly with increasing milling time. From the  $T_g(\text{PS})$  and  $\Delta C_p(\text{PBD})$  experimental data of the PS/PBD blends, it can be concluded that the compatibility increases with increase of milling action.

In the study of melting point ( $T_m$ ) depressions of polybutadiene polymer in the 0.75 weight fraction PS blends, the  $T_m$  depressions of freeze-dried, solution-cast, and mill-blend samples have been found to be in the range of 1.0–1.7 K. For the isotactic polystyrene (*i*-PS)/PBD freeze-dried blends, the  $T_m$  depressions with various compositions are observed to be in the range of 0.3–0.8 K.

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