Studies of polystyrene–polybutadiene blend system by inverse gas chromatography

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(Received 13 June 1991; revised 7 February 1992; accepted 26 March 1992)

Inverse gas chromatography (i.g.c.) has been used to calculate thermodynamic interaction parameters of polystyrene (PS) and polybutadiene (PBD) with 15 different probes of varying polarities at 155, 165, 175 and 185°C. Polymer–polymer interaction parameters were also evaluated at five different compositions of PS–PBD blends and were found to show marked probe dependence. Using various approaches such as those given by Horta *et al.*, by Sanchez and by Chee, the experimental data have been analysed to provide probe-independent interaction parameters. It is shown that rearrangement of an equation due to Su and Patterson explains the $\Delta\chi$ effect and gives probe-independent interaction parameters by a more simplified method.

(Keywords: inverse gas chromatography; polymer–polymer interaction parameter; polymer–probe interaction parameter; polymer blends; contact interaction parameter; equation-of-state parameter)

INTRODUCTION

The use of inverse gas chromatography (i.g.c.) in characterizing polymer systems has been widely recognized[1,2]. The technique involves using the solid material of interest as a stationary phase on a column. The stationary phase may be a thin polymeric coating on an inert substrate, a finely divided solid, or a thin polymeric coating on the column wall. A volatile probe of known characteristics is passed through the column by an inert mobile phase and the output is monitored. The residence time of the probe and the shape of the chromatogram indicate the characteristics of the stationary phase and its interaction with the probe. The word 'inverse' indicates that the component of interest is the stationary polymer phase, rather than the injected volatile probe. Added advantages of this technique are simplicity, accuracy, precision and rapid data collection. I.g.c. has been used for the determination of the probe–polymer and polymer–polymer interaction parameters of many polymer systems[3].

Deshpande *et al.* were the first to suggest the use of i.g.c. for studying polymer blends[4]. Starting from the Flory–Huggins expression for the change of free enthalpy in mixing, which was extended to three-component systems, they proposed a method of analysis of i.g.c. measurements on polymer blends which yielded the polymer–polymer interaction parameter χ'_{23}. One of the major problems with the i.g.c.-determined interaction parameter is that its value varies with the probe used. It was suggested that such a variation arises from the differences between χ_{12} and χ_{13} and was described as the $\Delta\chi$ effect[5]. Accordingly, one must select probes that give $\chi_{12}=\chi_{13}$ for studying the blend. This is not always feasible. Moreover, we should attempt to understand the reason behind the probe dependence of polymer–polymer interaction and try to develop a method to evaluate probe-independent interaction.

In order to obtain a solution to this problem, Horta *et al.*[6], Sanchez[7] and Chee[8] have independently proposed different methods to get probe-independent interaction parameters. The first two methods allow us to evaluate the polymer–polymer interaction parameter for each of the probes used, whereas Chee's method provides a single interaction parameter for the whole set of probes used.

The present study is aimed at analysing the specific retention volume measurements made on polystyrene (PS), polybutadiene (PBD) and PS–PBD blends at five different compositions in view of the above approaches and to calculate the probe-independent interaction parameter and compare the results of these methods. The pair PS + PBD is chosen because it is the constituent of block copolymers most often studied. Moreover, they are non-polar hydrocarbon polymers for which theories of polymer liquids and mixtures are likely to apply more quantitatively.

EXPERIMENTAL

Materials

PS was supplied by Polychem Ltd, Bombay ($\bar{M}_n = 1.02\times10^4$, $\bar{M}_w = 1.01\times10^5$ and $\bar{M}_v = 7.29\times10^4$). It was purified by dissolving it in tetrahydrofuran (THF) and reprecipitating with methanol. PBD was obtained from IPCL, Baroda (Cisamer, $\bar{M}_n = 8.95\times10^4$, $\bar{M}_w = 4.68\times10^5$, 96% *cis*). It was purified by precipitation from a solution in chloroform after adding an excess amount of methanol. The chromatographic support was 60–80 mesh Chromosorb W, acid-washed and treated with dimethyldichlorosilane (AW-DMCS). Packed columns were prepared from 150 cm long annealed copper tubing of 0.635 cm outer diameter. Tubes were

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rinsed with acetone, followed by petroleum ether, and were then dried by passing dry nitrogen gas. The 15 different probes of varying polarities used were of analytical grade (*Table 1*).

Columns

Weighed amounts of the polymer samples were dissolved in about 50 ml of THF. The support (Chromosorb W, AW-DMCS, 60–80 mesh), which was kept under vacuum for 6 h, was coated using the soaking method of Al-Saigh *et al.*[9]. The percentage coating of the polymer over the support was determined by calcination of the coated support in duplicate. A correction was made for the loss of volatile matter from the uncoated support. It was found that the amount determined by calcination matched closely with the amount of polymer taken up. The column characteristics are given in *Table 2*. Prior to any retention measurements, each new column was conditioned in the chromatograph at 185°C for 8 h, for attainment of equilibrium at the experimental temperature.

Data acquisition

Retention times were measured using a dual-column gas chromatograph fabricated by us with thermal conductivity detector. Iolar grade hydrogen was used as a carrier gas. The gas flow rate was measured using a soap-bubble flow meter. The inlet pressure was measured using a U-tube mercury manometer and outlet pressure by a barometer. Less than 0.1 μl of probes (together with marker, air) were injected manually with a 10 μl Hamilton syringe in order to approach the infinite dilution condition for the probe. The retention time was taken as the difference of retention time of the probe and the air peak, which was measured using a Hewlett–Packard integrator (HP 3396A). For each probe the average of triplicate readings of retention time was taken for a given flow rate of the carrier gas. Measurements were made at two different flow rates for each column at each temperature. There was no evidence for the flow-rate dependence of the retention volume (V_g^0). The V_g^0 data for each probe were found to agree within 2% for each measurement.

THEORY

Data reduction

The standard specific retention volumes (V_g^0) were calculated in the usual manner[10], using the equation:

$$V_g^0 = \frac{t_r}{W_L}\left(F\frac{p_0 - p_w}{p_0}\frac{273.15}{T_\alpha}\right)\frac{3}{2}\left(\frac{[p_i/p_0]^2 - 1}{[p_i/p_0]^3 - 1}\right) \quad (1)$$

where t_r is the retention time for the probe, W_L is the weight of the stationary phase, F is the carrier-gas flow rate measured at room temperature T_α, p_0 is atmospheric pressure, p_i is the inlet pressure and p_w is the water vapour pressure at temperature T_α.

The polymer–solvent interaction parameters χ_{1i} were calculated from the relation[11] applicable for polymers having high molecular weight:

$$\chi_{1i} = \ln\left(\frac{273.15Rv_i}{P_1^0 V_g^0 V_1}\right) - \frac{P_1^0}{RT}(B_{11} - V_1) - 1 \quad (2)$$

The standard specific retention volumes of the probes obtained with a column containing a blend of the two polymers (V_{g23}^0) were used together with the following relation to determine the interaction parameter χ'_{23} between the two polymers[4]:

$$\chi_{1(23)} = \ln\left(\frac{273.15R(w_2v_2 + w_3v_3)}{P_1^0 V_{g23}^0 V_1}\right) - \frac{P_1^0}{RT}(B_{11} - V_1) - 1$$

$$= \left[\left(\frac{\chi_{12}}{V_1}\right)\phi_2 + \left(\frac{\chi_{13}}{V_1}\right)\phi_3 - \left(\frac{\chi_{23}}{V_2}\right)\phi_2\phi_3\right]V_1 \quad (3)$$

and

$$\chi'_{23} = [V_1/V_2]\chi_{23} \quad (4)$$

where subscript 1 refers to the probe and subscripts 2 and 3 refer to the respective polymers. V_i, ϕ_i and w_i represent respectively the molar volume, volume fraction and weight fraction of the components. B_{11} and P_1^0 are second virial coefficient and vapour pressure respectively of the probes. Values of these parameters were obtained or calculated from various sources[12,13].

The corresponding equation-of-state parameter, $\chi^{*\prime}_{23}$, can be obtained easily by replacing in equations (2) and (3) the specific volume by core specific volume and volume fraction by segment fraction ϕ_i^* defined as:

$$\phi_i^* = \frac{w_i v_i^*}{\Sigma w_i v_i^*} \quad (5)$$

where v_i^* is the core specific volume. The energy density parameter can be obtained by using the relation[14]:

$$B_{23} = \chi'_{23} RTV_1 \quad (6)$$

and its corresponding equation-of-state energy parameter by:

$$B^*_{23} = \chi^{*\prime}_{23} RTV_1^* \quad (7)$$

Table 1 List of the probes used and their corresponding numbers

Probe no.	Probe name
1	n-Octane
2	n-Nonane
3	n-Decane
4	Methylcyclohexane
5	*trans*-Decalin
6	*cis*-Decalin
7	Toluene
8	*p*-Xylene
9	*o*-Xylene
10	Chlorobenzene
11	n-Butyl acetate
12	Isoamyl acetate
13	Isobutyl methyl ketone
14	Cyclohexanone
15	*p*-Dioxane

Table 2 Summary of chromatographic column characteristics

Stationary phase	Loading (% w/w)	Weight of polymer in column (g)
Polystyrene (PS)	9.99	0.7411
Polybutadiene (PBD)	9.96	0.8644
PS + PBD (10:90)	9.36	0.6819
PS + PBD (23:77)	9.48	0.6858
PS + PBD (50:50)	7.45	0.5240
PS + PBD (77:23)	9.34	0.6954
PS + PBD (90:10)	9.56	0.6957

Table 3 Equation-of-state parameters of the probes and polymers at 20°C

Probe no.	V^* (cm^3 mol^{-1})	P^* (cal cm^{-3})	T^* (K)
1	127.74	104.60	4825
2	142.01	104.68	5003
3	156.16	104.59	5134
4	100.96	113.58	4929
5	130.93	120.72	5683
6	127.30	129.81	5739
7	84.58	134.00	4941
8	99.10	127.00	5112
9	97.59	130.30	5313
10	82.62	140.39	5550
11	104.13	128.88	4901
12	116.51	132.20	4734
13	98.13	119.91	4795
14	84.46	149.33	5444
15	71.02	80.05	5730
PS	0.8068 cm^3 g^{-1}	129.93	7420
PBD	0.9508 cm^3 g^{-1}	119.86	6758

The Flory–Prigogine exchange interaction parameter X_{1i} was calculated using the following relationship[15]:

$$RT\chi_{1i}^* = \frac{V_1^* X_{1i}}{\tilde{V}_i} + P_1^* V_1^* \left[\frac{1}{\tilde{V}_1} - \frac{1}{\tilde{V}_2} + 3\tilde{T}_1 \ln\left(\frac{\tilde{V}_1^{1/3} - 1}{\tilde{V}_2^{1/3} - 1} \right) \right] \tag{8}$$

where the first term is the interaction term and the second is the free-volume term. P_1^* and V_1^* are the pressure and volume reduction parameters (*Table 3*) and :

$$\tilde{V} = V/V^* \tag{9}$$

$$\tilde{T} = T/T^* = (\tilde{V}^{1/3} - 1)/\tilde{V}^{4/3} \tag{10}$$

$$\tilde{V}^{1/3} = 1 + \frac{\alpha T}{3(1+\alpha T)} \tag{11}$$

where α is the thermal expansion coefficient.

X_{23} was obtained using the equation for a ternary system with a mixed stationary phase by the iteration method[3]:

$$RT\chi_{1(23)} = \frac{s_1 V_1^*}{\tilde{V}_0} \left[\left(\frac{X_{12}}{s_1} \right)\theta_2 + \left(\frac{X_{13}}{s_1} \right)\theta_3 - \left(\frac{X_{23}}{s_2} \right)\theta_2\theta_3 \right] + P_1^* V_1^* \left[\frac{1}{\tilde{V}_1} - \frac{1}{\tilde{V}_0} + 3\tilde{T}_1 \ln\left(\frac{\tilde{V}_1^{1/3} - 1}{\tilde{V}_0^{1/3} - 1} \right) \right] \tag{12}$$

where $\tilde{V}_0$ is the reduced volume of the mixed stationary phase, s_i is the molecular surface-to-volume ratio, and θ_i is the surface fraction defined by:

$$\theta_i^* = \frac{w_i v_i^* s_i}{\Sigma w_i v_i^* s_i} \tag{13}$$

Horta's method

A modified equation that enables us to calculate the probe-independent interaction parameter χ_{23}^{*T} has been developed by Horta *et al.*[6]. This equation is a modified form of Flory's equation, which takes account of the equation-of-state parameters. This equation enables us to calculate the χ_{23}^{*T} from the i.g.c.-determined $\chi_{23}^{*'}$. The i.g.c.-determined $\chi_{23}^{*'}$, which is estimated at infinite dilution of the probe, is related to the χ_{23}^{*T} by the following equation:

$$\chi_{23}^{*'} = \chi_{23}^{*T} \frac{V_1^* s_1}{V_2^* s_3} + (\chi_{12}^* - \chi_{13}^*) \frac{s_3 - s_2}{\phi_2 s_2 + \phi_3 s_3} - K \tag{14}$$

where subscripts 1, 2 and 3 stand for the probe, the first polymer and the second polymer respectively. V_i^*, s_i and ϕ_i are the molar hard-core volume, surface-to-volume ratio and segmental fraction respectively. χ_{12}^* and χ_{13}^* are the probe–polymer interaction parameters of the respective polymers determined by i.g.c. K is given by:

$$K = \frac{\Gamma}{\phi_2\phi_3} + \chi_{12}^* \left[\frac{\tilde{V}_2}{\tilde{V}_{23}} - 1 \right] \left(\frac{1}{\phi_3} + \frac{s_2 - s_3}{\phi_2 s_2 + \phi_3 s_3} \right) + \chi_{13}^* \left[\frac{\tilde{V}_3}{\tilde{V}_{23}} - 1 \right] \left(\frac{1}{\phi_2} - \frac{s_2 - s_3}{\phi_2 s_2 + \phi_3 s_3} \right) \tag{15}$$

where $\tilde{V}_i$ is the reduced volume and $\tilde{V}_{23}$ is the mixed reduced volume of the polymer blend, which can be calculated by iteration using the method of Mandal *et al.*[3]. Γ is a free-volume term and is given by:

$$\Gamma = \frac{P_1^* V_1^*}{RT} \left(\Gamma_{1(23)} - \frac{\tilde{V}_2}{\tilde{V}_{23}} \theta_2 \Gamma_{12} - \frac{\tilde{V}_3}{\tilde{V}_{23}} \theta_3 \Gamma_{13} \right) + \frac{P_2^* V_1^* s_1 \theta_2}{RT s_2 \theta_3} \Gamma_{23} \tag{16}$$

where

$$\Gamma_{ij} = \frac{1}{\tilde{V}_i} - \frac{1}{\tilde{V}_{ij}} - 3\tilde{T}_i \ln\left(\frac{\tilde{V}_{ij}^{1/3} - 1}{\tilde{V}_i^{1/3} - 1} \right) \tag{17}$$

Here P_i^* and θ_i are the pressure reduction parameter and surface fraction respectively. Since the probe is at infinite dilution, the mixed reduced volume containing the probe term becomes the reduced volume of the other component only, i.e. $\tilde{V}_{ij} = \tilde{V}_j$ when $i = 1$.

Sanchez's method

This method is based on the lattice-fluid theory developed by Sanchez *et al.*[16,17]. According to this theory the polymer–probe interaction parameter χ_{1i}^S is given by:

$$\chi_{1i}^S = \frac{\bar{P}_1^*}{RT} - \frac{\bar{\rho}_1^*}{M_1 \tilde{\rho}_i} \left[\ln\left(\frac{H_{1i} RT \rho_i}{M_1} \right) + r_1 \left(1 + \frac{1 - \tilde{\rho}_i}{\tilde{\rho}_i} \ln(1 - \tilde{\rho}_i) \right) \right] \tag{18}$$

and the polymer–polymer interaction parameter χ_{23}^S is given by:

$$\chi_{23}^S = \frac{1}{\phi_2\phi_3} \left\{ \frac{\bar{\rho}_1^*}{M_1 \tilde{\rho}_b} \left[\ln\left(\frac{H_{1(23)} RT \rho_b}{M_1} \right) + r_1 \left(1 + \frac{1 - \tilde{\rho}_b}{\tilde{\rho}_b} \ln(1 - \tilde{\rho}_b) \right) \right] - \frac{\bar{P}_1^*}{RT} + \phi_2 \chi_{12}^S + \phi_3 \chi_{13}^S \right\} \tag{19}$$

Here the Henry's law constant H_{1i} is given by:

$$H_{1i} = \frac{V_{g1i}^0 M_1 \rho_i}{273.15R} \tag{20}$$

where the subscripts 1, 2 and 3 stand for the probe and the two polymers respectively. $\bar{P}_i^*$, $\bar{\rho}_i^*$ and $\bar{T}_i^*$ are the equation-of-state parameters of Sanchez for pressure, mass density and temperature respectively (*Table 4*). The quantities with tildes are the corresponding reduced quantities. V_{g1i}^0 is the specific retention volume. r_1 is a

Table 4 Sanchez's equation-of-state parameters of the probes and polymers

Probe no.	$\tilde{\rho}^*$ (g cm^{-3})	$\bar{P}^*$ (cal cm^{-3})	$\bar{T}^*$ (K)
1	0.815	73.67	502
2	0.828	73.43	517
3	0.837	72.70	530
5	0.935	75.37	621
6	0.960	79.73	631
7	0.966	96.21	543
8	0.949	91.12	561
9	0.965	94.27	571
10	1.206	104.45	585
11	1.003	94.27	498
15	1.163	128.23	519
PS	1.105	85.55	735
PBD	0.961	112.45	606

dimensionless size parameter proportional to the molecular weight, M_1:

$$r_1 = \frac{M_1 \bar{P}_1^*}{R \bar{T}_1^* \tilde{\rho}_1^*} \tag{21}$$

The volume fraction ϕ_i is defined by:

$$\phi_i = \frac{w_i/\tilde{\rho}_i^*}{\Sigma w_i/\tilde{\rho}_i^*} \tag{22}$$

The ρ_b is the mass density of the blend and $\tilde{\rho}_b$ is the reduced mass density, which can be obtained by iteration from the following equations:

$$\tilde{\rho}_b = 1 - \exp\left[-\frac{\tilde{\rho}_b^2 \bar{T}_b^*}{T} - \tilde{\rho}_b\right] \tag{23}$$

where $\bar{T}_b^*$ is given by:

$$\bar{T}_b^* = \frac{\phi_2 \bar{P}_2^* + \phi_3 \bar{P}_3^* - \phi_2 \phi_3 RT \chi_{23}^S}{\phi_2 \bar{P}_2^*/\bar{T}_2^* - \phi_3 \bar{P}_3^*/\bar{T}_3^*} \tag{24}$$

T is the temperature of the experiment.

Chee's method

This method is based on the equation developed by Guillet *et al.*[18] for the calculation of the solubility parameter of a polymer as given by:

$$\frac{\delta_1^2}{RT} - \frac{\chi_{1i}}{V_1} = \frac{2\delta_i}{RT}\delta_1 - \left[\frac{\delta_i^2}{RT} + \frac{\gamma_{1i}}{V_1}\right] \tag{25}$$

where subscript 1 stands for the probe and i stands for the polymers or the blends. δ_i is the solubility parameter of the probe calculated using the method by Uriarte *et al.*[19], χ_{1i} is the i.g.c.-determined interaction parameter and V_1 is the molar volume of the probe at the experimental temperature T. By using this equation we can calculate the polymer (or blend) solubility parameter δ_i and the entropy contribution to the interaction parameter $\bar{\gamma}_{1i}$, i.e. γ_{1i}/V_1, from the slope and the intercept respectively. The entropy components of polymers and blend are related by the following equation:

$$\bar{\gamma}_{1(23)} = \phi_2 \bar{\gamma}_{12} + \phi_3 \bar{\gamma}_{13} - \phi_2 \phi_3 \left[\frac{\partial \phi_3 \bar{\gamma}_{23}}{\partial \phi_3}\right] \tag{26}$$

where ϕ_i is the volume fraction of the polymer. Here the entropy component of the blend is considered to be composition-dependent, so that by plotting $\partial \phi_3 \bar{\gamma}_{23}/\partial \phi_3$ against the volume fraction of one of the polymers, i.e. ϕ_3, we can get an equation as a function of ϕ_3. In the present analysis we set:

$$f(\phi_3) = \partial \phi_3 \bar{\gamma}_{23}/\partial \phi_3 \tag{27}$$

which is a polynomial.

We can calculate the polymer–polymer interaction parameter $\bar{\chi}_{23}^C$ from the following relationship:

$$\bar{\chi}_{23}^C = \frac{\chi_{23}^C}{V_2} = \frac{(\delta_2 - \delta_3)^2}{RT} + \frac{1}{\phi_3}\int_0^{\phi_3} f(\phi_3)\, d\phi_3 \tag{28}$$

The polymer energy density parameter B_{23}^C is defined by

$$B_{23}^C = RT\bar{\chi}_{23}^C \tag{29}$$

The present method

We propose another method, which reduces the detailed steps of the other methods by using the following equation, which is a rearranged form of equation (3):

$$\frac{\chi_{1(23)} - \chi_{13}}{V_1} = \phi_2\left[\frac{\chi_{12} - \chi_{13}}{V_1}\right] - \left[\frac{\chi_{23}}{V_2}\right]\phi_2\phi_3 \tag{30}$$

Here, by plotting the l.h.s. of the equation against $(\chi_{12} - \chi_{13})/V_1$, we get the interaction parameter of the blend, χ_{23}/V_2, from the intercept and consequently the energy density parameter B_{23}^P is obtained by the following relationship:

$$B_{23}^P = [\chi_{23}/V_2]RT \tag{31}$$

RESULTS AND DISCUSSION

Polymer–probe interaction

The weight fraction activity coefficient Ω_1^∞ calculated for PS with some of the probes was found to be slightly lower than that of DiPaola-Baranyi *et al.*[20] and Newman *et al.*[21] and higher than that of Schuster *et al.*[22] and Covitz *et al.*[23]. But it was very close to that of Su *et al.*[24] (*Table 5*). No i.g.c. data on PBD are available for the temperature range of the present study. The interaction parameters (χ_{1i}, χ_{1i}^* and X_{1i}) calculated for both the polymers at 155°C are listed in *Table 6*. For both PS and PBD the χ_{1i} values for most of the probes show a linear dependence on the temperature. In the case of PS, χ_{12} decreases with increase in temperature for both polar and non-polar sets of probes (*Figure 1*); whereas, in the

Table 5 Comparison of weight fraction activity coefficient Ω_1^∞ of polystyrene at 175°C

Probe no.	Ω_1^∞	
	Present work	Literature values
1	10.51	8.99[b]
2	10.64	8.89[b]
3[a]	10.40	12.23[c]
5[a]	5.54	5.94
6[a]	5.14	5.47[c]
7	4.75	4.98[b], 5.29[d], 4.24[e], 4.88[f]
7[a]	4.72	4.98[c]
8	4.87	4.44[e]
9	4.62	4.15[e]
10	3.58	3.85[d], 3.11[e]
14	5.21	6.14[d]
15	4.63	5.41[d], 4.15[e]

[a] At 185°C; [b] ref. 22 (support, Chromosorb A); [c] ref. 20 (Chromosorb G, AW-DMCS); [d] ref. 21 (Fluoropak); [e] ref. 23 (Chromosorb P); [f] ref. 24 (Chromosorb P, AW-DMCS)

Table 6 The χ, χ^* and X parameters of PS and PBD at 155°C

Probe no.	PS			PBD		
	χ_{12}	χ^*_{12}	X_{12} (cal cm^{-3})	χ_{13}	χ^*_{13}	X_{13} (cal cm^{-3})
1	0.89	1.10	4.32	0.42	0.60	1.72
2	0.92	1.11	4.29	0.41	0.57	1.69
3	0.95	1.12	4.18	0.43	0.57	1.75
4	0.63	0.83	4.04	0.24	0.41	1.17
5	0.52	0.63	3.13	0.12	0.20	0.62
6	0.51	0.61	3.16	0.08	0.15	0.31
7	0.26	0.44	1.32	0.19	0.34	1.57
8	0.30	0.45	0.66	0.18	0.30	0.61
9	0.28	0.42	1.21	0.16	0.28	1.01
10	0.25	0.39	4.96	0.20	0.31	4.11
11	0.52	0.73	1.91	0.50	0.68	3.26
12	0.66	0.86	1.20	0.64	0.81	2.79
13	0.67	0.88	3.73	0.62	0.80	4.76
14	0.49	0.62	4.46	0.61	0.71	7.25
15	0.40	0.54	6.94	0.52	0.62	9.12

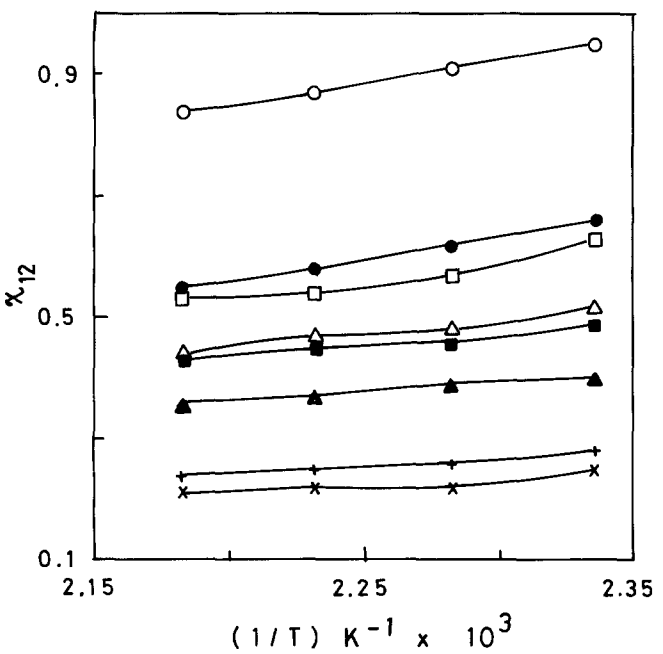

Figure 1 Variation of χ_{12} of PS with temperature for probes 3 (○), 4 (□), 5 (△), 9 (+), 10 (×), 12 (●), 14 (■) and 15 (▲)

case of PBD, the variation with temperature was very small for the non-polar set of probes and decreases with increase in temperature for polar probes (*Figure 2*). The χ^*_{1i} and X_{1i} of both polymers show a similar trend to that of χ_{1i}. From the value of the interaction parameters, it can be concluded that, in the case of PS, except for a few probes such as toluene, *p*-xylene, *o*-xylene, chlorobenzene and *p*-dioxane, the others are poor solvents, whereas for PBD all are good solvents except isoamyl acetate, isobutyl methyl ketone and cyclohexanone. Even though χ_{12} and χ_{13} of chlorobenzene show very small values, its contact energy term shows a higher value.

Blend

From the V_g^0 values of the homopolymer and blends it is observed that the V_g^0 values of blends are only slightly higher than the weight-average V_g^0 of individual homopolymers, especially at higher PBD content (*Figure 3*). The deviation, which is about 2.5%, can be neglected on the basis of the 2% experimental variation in V_g^0 values. This is the case for both the non-polar and polar probes used, except in the case of cyclohexanone where at 23% of PS an unusually low V_g^0 is observed. These observations are quite in agreement with those of Klein *et al.*[25], who reported that V^0_{g23} of the blend was found to be the weight-average V_g^0 of individual homopolymers.

The polymer–polymer interaction parameter χ'_{23}, the equation-of-state interaction parameter $\chi^{*\prime}_{23}$, their corresponding energy density terms B_{23} and B^*_{23} and the contact interaction parameter X_{23} of all the five compositions at 155°C are given in *Tables 7–9*. From the tables it is quite clear that all the interaction parameters exhibit a marked dependence on the probes, which is a

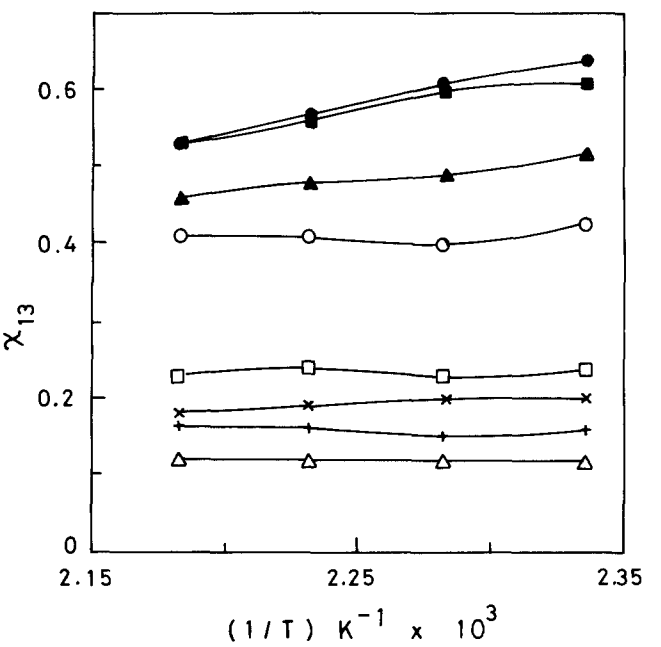

Figure 2 Variation of χ_{13} of PBD with temperature for probes 3 (○), 4 (□), 5 (△), 9 (+), 10 (×), 12 (●), 14 (■) and 15 (▲)

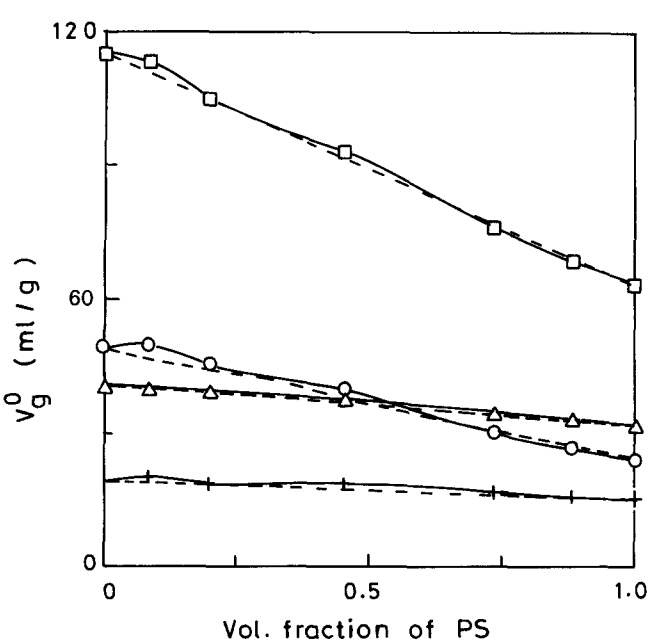

Figure 3 Composition dependence of V_g^0 of PS–PBD blend at 155°C for probes 3 (○), 5 (□), 10 (△) and 11 (+); the broken curves indicate the weight-average V_g^0 of individual homopolymers

Table 7 PS–PBD blend at 155°C; dependence of χ'_{23} and $\chi^{*\prime}_{23}$ on the probe and composition of the blend, shown as PS (wt%) above column entries

Probe no.	χ'_{23}					$\chi^{*\prime}_{23}$				
	10	23	50	77	90	10	23	50	77	90
1	0.75	0.34	0.41	0.26	0.26	0.75	0.35	0.42	0.28	0.28
2	0.58	0.29	0.37	0.17	0.02	0.58	0.30	0.38	0.18	0.04
3	0.92	0.41	0.46	0.21	0.16	0.91	0.42	0.47	0.23	0.18
4	0.54	0.39	0.37	0.27	0.32	0.54	0.40	0.38	0.28	0.34
5	0.48	0.19	0.25	0.15	0.15	0.48	0.20	0.26	0.17	0.16
6	0.15	0.19	0.27	0.25	0.30	0.16	0.20	0.28	0.27	0.32
7	0.25	0.18	0.13	0.14	0.02	0.25	0.18	0.13	0.15	0.02
8	0.32	0.20	0.18	0.14	0.06	0.31	0.20	0.18	0.15	0.07
9	0.34	0.14	0.15	0.12	0.12	0.34	0.14	0.15	0.12	0.13
10	0.10	0.10	0.12	0.10	0.11	0.10	0.10	0.12	0.10	0.11
11	0.68	0.07	0.29	0.19	−0.04	0.67	0.07	0.29	0.20	−0.04
12	0.58	0.05	0.26	0.17	−0.12	0.56	0.05	0.26	0.18	−0.12
13	0.34	0.02	0.23	0.13	0.26	0.34	0.02	0.23	0.14	0.27
14	0.01	−0.13	0.23	0.06	0.21	0.07	−0.13	0.23	0.05	0.21
15	0.27	0.05	0.20	0.14	0.02	0.26	0.05	0.20	0.14	0.00

Table 8 PS–PBD blend at 155°C; dependence of B_{23} (cal cm^{-3}) and B^*_{23} (cal cm^{-3}) on the probe and composition of the blend, PS (wt%)

Probe no.	B_{23} (cal cm^{-3})					B^*_{23} (cal cm^{-3})				
	10	23	50	77	90	10	23	50	77	90
1	3.27	1.49	1.78	1.13	1.11	5.00	2.33	2.82	1.85	1.83
2	2.32	1.16	1.46	0.66	0.09	3.48	1.80	2.27	1.10	0.22
3	3.40	1.53	1.68	0.79	0.60	4.98	2.30	2.56	1.27	0.98
4	3.01	2.18	2.04	1.48	1.81	4.54	3.34	3.18	2.37	2.90
5	2.25	0.91	1.18	0.73	0.70	3.10	1.30	1.70	1.10	1.07
6	0.74	0.93	1.33	1.23	1.45	1.08	1.33	1.90	1.80	2.12
7	1.69	1.19	0.86	0.97	0.13	2.49	1.77	1.30	1.49	0.23
8	1.87	1.19	1.05	0.86	0.38	2.69	1.73	1.55	1.29	0.60
9	2.07	0.84	0.89	0.71	0.72	2.93	1.22	1.31	1.06	1.09
10	0.70	0.73	0.84	0.70	0.77	0.99	1.04	1.22	1.04	1.14
11	3.64	0.37	1.56	1.03	−0.23	5.45	0.57	2.39	1.61	−0.35
12	2.77	0.25	1.26	0.18	−0.59	4.11	0.39	1.92	1.29	−0.90
13	1.95	0.09	1.32	0.14	1.48	2.93	0.16	2.03	1.20	2.34
14	0.07	−0.93	1.65	0.05	1.47	0.07	−1.32	2.29	0.54	2.09
15	2.28	0.42	1.71	0.14	0.02	3.15	0.55	2.40	1.71	−0.01

Table 9 PS–PBD blend at 155°C; dependence of X_{23} (cal cm^{-3}) on the probe and composition of the blend

Probe no.	PS (wt%) in blend				
	10	23	50	77	90
1	−0.10	−0.36	0.88	−0.47	−2.02
2	−1.16	−0.66	0.51	−0.99	−3.13
3	0.87	0.06	0.92	−0.70	−2.25
4	−0.65	0.65	1.22	−0.08	−1.25
5	0.02	−0.61	0.47	−0.71	−2.11
6	−2.71	−0.61	0.59	0.01	−0.98
7	−3.37	−1.00	−0.47	−0.76	−3.75
8	−2.26	−0.67	−0.01	−0.71	−2.96
9	−1.43	−1.01	−0.14	−0.80	−2.24
10	0.63	0.96	1.19	0.86	0.79
11	−0.10	−2.03	0.63	−0.51	−3.72
12	−2.13	−2.50	0.03	−0.97	−4.53
13	−2.83	−2.54	0.25	−0.92	−1.65
14	−4.69	−3.49	0.96	−1.06	−1.20
15	0.96	−0.57	1.98	0.90	−1.70

major problem encountered with the i.g.c. technique. It can be noticed that the values of χ'_{23} and $\chi^{*\prime}_{23}$ are almost the same for all the compositions at all the temperatures of the experiment. But the energy density term B_{23} is found to be lower than that of B^*_{23}.

The χ'_{23} are found to be very close to zero for the blend containing 90% w/w PS and even negative values are found for some of the probes. As the amount of PS decreases in the blend it can be seen that the χ'_{23} becomes more positive and it is maximum at 10% PS content (*Figure 4*). There is an exception to this trend, in that 23% PS shows a lower value than that of 50% PS. This trend is found to be true for all the probes used. The 23% PS blend shows a different trend from the rest of the compositions for almost all the calculated parameters. We can conclude from the trend in χ'_{23} that in the PS-rich region the polymers are more compatible, which is in good agreement with the d.s.c. studies done by Kim *et*

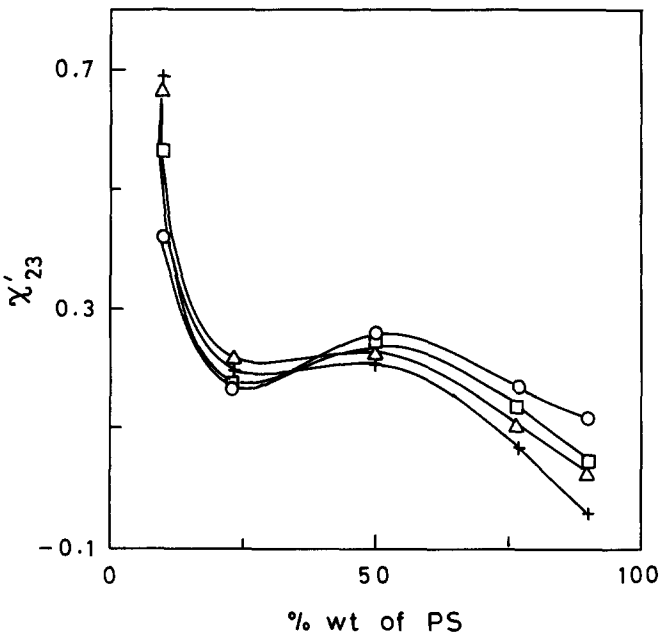

Figure 4 Composition dependence of χ'_{23} (average value of all probes) of PS–PBD blend at 155°C (○), 165°C (□), 175°C (△) and 185°C (+)

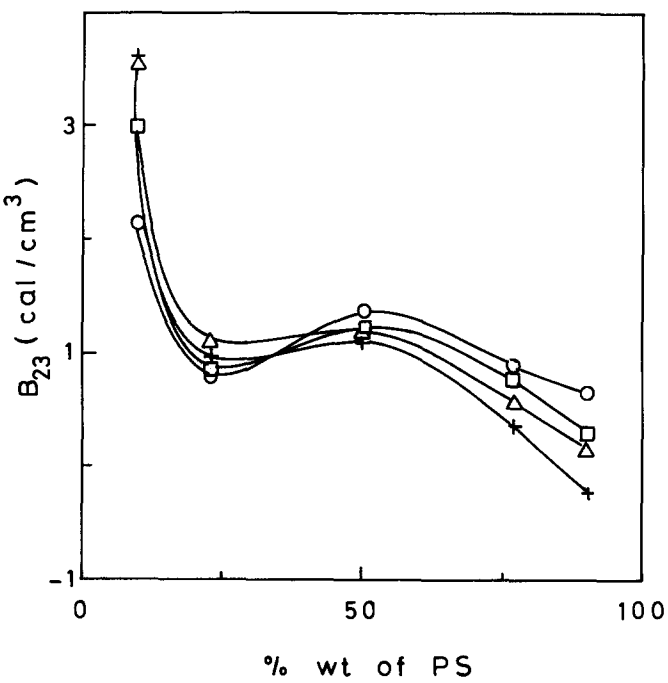

Figure 5 Composition dependence of B_{23} (average value of all probes) of PS–PBD blend at 155°C (○), 165°C (□), 175°C (△) and 185°C (+)

al.[26]. At all compositions, χ'_{23} obtained using methylcyclohexane as the probe was found to be maximum. The B_{23} and B^*_{23} were also found to show a similar trend (*Figures 5* and *6*). Using the cloud-point method, Roe and Zin[27] have reported the polymer–polymer interaction parameter Λ (which is equivalent to B_{23}) for blends using low-molecular-weight samples of PS and PBD. At 150°C, Λ was found to be in the range of 0.74–0.79 cal cm^{-3}. This is comparable to B_{23} values (average of all the probes used) reported by us at 155°C, which are in the range of 0.66–2.14 cal cm^{-3} depending on the blend composition.

Another interesting observation is that in the PS-rich region χ'_{23} is found to decrease with increase in temperature, i.e. a negative slope in the plot of χ'_{23} vs. temperature. As the amount of PS decreases in the blend, the slope decreases, and at 50% PS, it becomes almost zero. At higher composition the slope becomes positive, i.e. χ'_{23} increases with increase in temperature (*Figure 7*). This is predominant at 10% PS. These trends are found to be true for most of the probes. B_{23} and B^*_{23} also show a similar trend (*Figures 8* and *9*). Since there is no specific interaction in a system such as PS–PBD, the contact interaction parameter X_{23} should be positive. According to Patterson *et al.*[28], when X_{23} is positive, the variation of interaction parameter (χ'_{23}/V_1) with temperature will have a U-shaped curve (*Figure 10*), i.e. the interaction

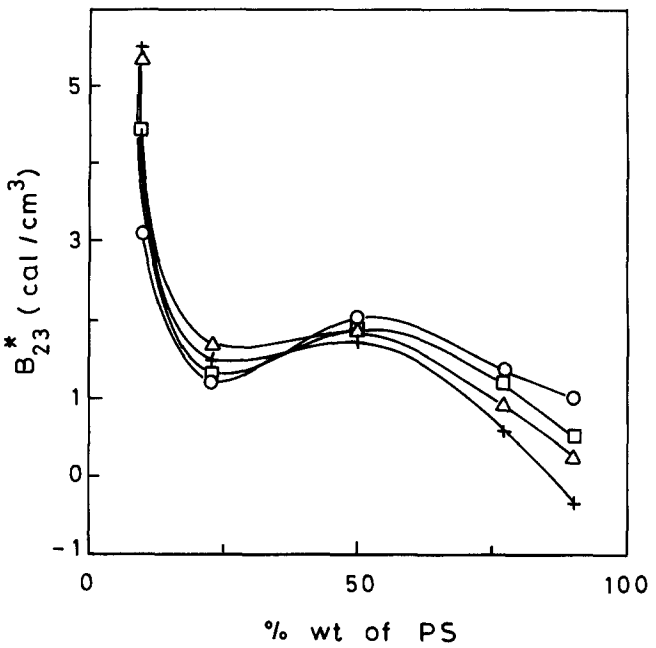

Figure 6 Composition dependence of B^*_{23} (average value of all probes) of PS–PBD blend at 155°C (○), 165°C (□), 175°C (△) and 185°C (+)

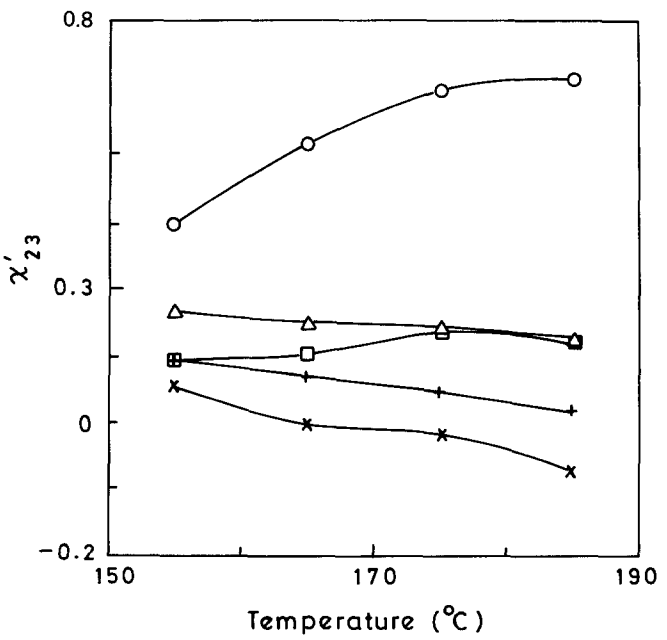

Figure 7 Temperature dependence of χ'_{23} (average value of all probes) of PS–PBD blend at 10% (○), 23% (□), 50% (△), 77% (+) and 90% (×) of PS

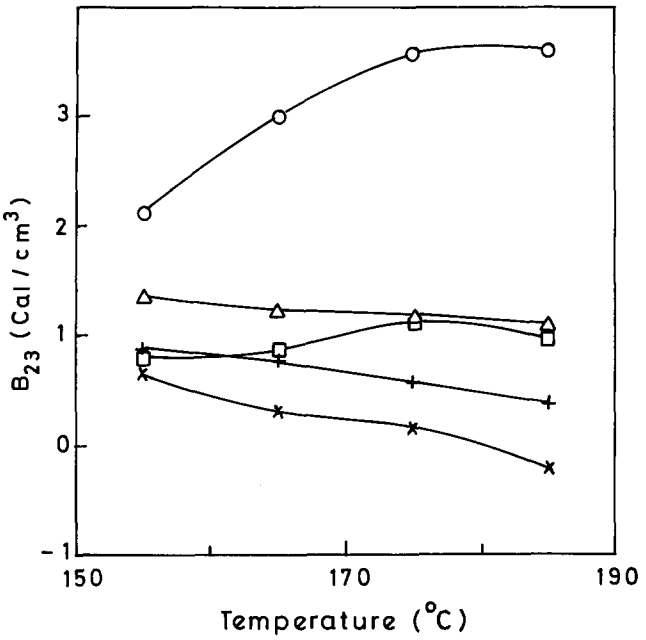

Figure 8 Temperature dependence of B_{23} (average value of all probes) of PS–PBD blend at 10% (○), 23% (□), 50% (△), 77% (+) and 90% (×) of PS

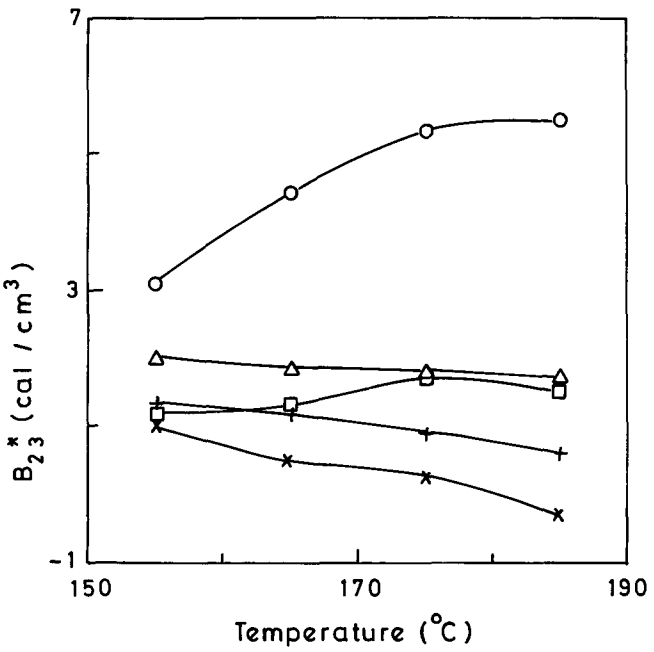

Figure 9 Temperature dependence of B_{23}^* (average value of all probes) of PS–PBD blend at 10% (○), 23% (□), 50% (△), 77% (+) and 90% (×) of PS

parameter initially decreases with temperature, reaches a minimum and then increases with increase in temperature. So it can be explained that for the present experimental temperature of 155–185°C each composition is in a different region of the U-shaped curve. Hence we observe different trends of the temperature dependence of the interaction parameter at different compositions, i.e. 90% PS could be in the left part of the curve, and as the PS content decreases it moves towards the right of the curve, and at 50% PS it must be in the flat minimum region and as PS content decreases still further to 10% then it must be on the right part of the curve where the interaction parameter increases with increase in temperature. The critical value of χ'_{23}/V_1 for miscibility can be estimated as:

$$\chi'_{23}/V_1(\text{critical}) = \frac{1}{2}\left(\frac{1}{(M_2v_2)^{1/2}} + \frac{1}{(M_3v_3)^{1/2}}\right)^2 \quad (32)$$

For the present blend system of PS–PBD its value was found to be 8.3×10^{-5}. Thus the χ'_{23}/V_1 values obtained here are well above the critical value of interaction parameter, so we should not expect any miscible blend throughout the entire composition.

The contact interaction parameter X_{23} is found to be negative for most of the probes. Even at 10% PS, many probes show negative X_{23}. This cannot be explained for

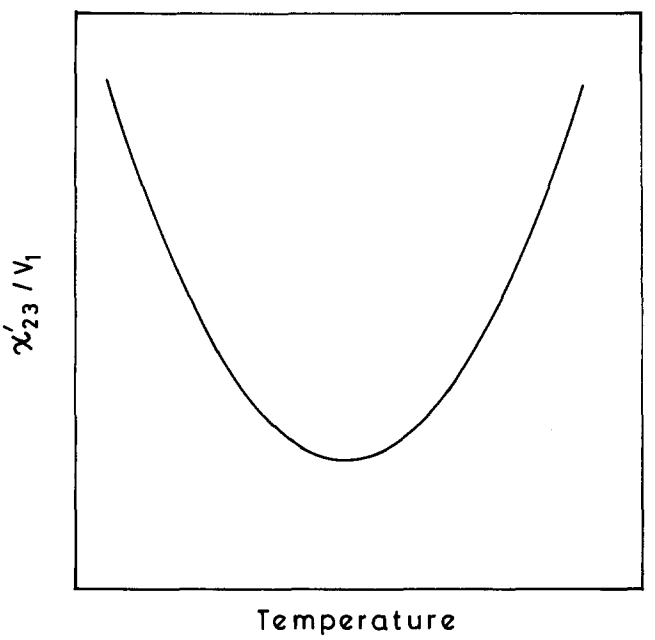

Figure 10 Variation of interaction parameter with temperature as proposed by Patterson *et al.*[28] for a blend system having positive contact interaction parameter, X_{23}

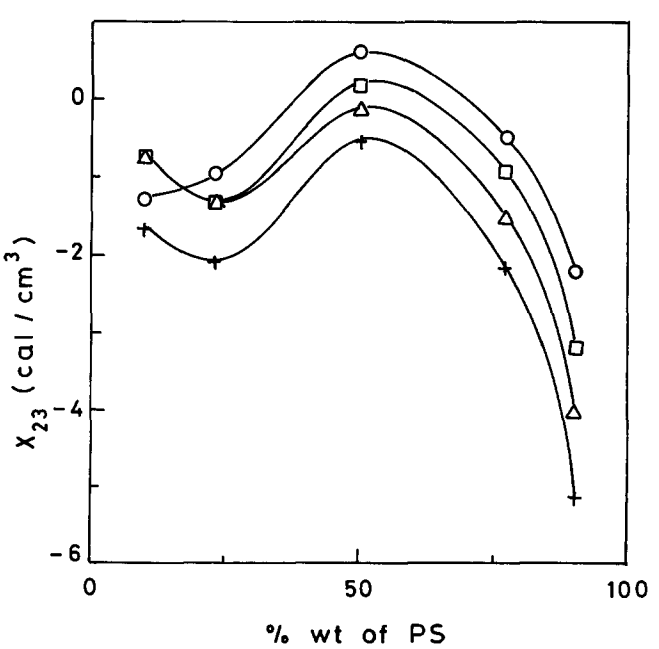

Figure 11 Composition dependence of X_{23} (cal cm^{-3}) (average value of all probes) of PS–PBD blend at 155°C (○), 165°C (□), 175°C (△) and 185°C (+)

the present system since there is no specific interaction between PS and PBD. Another interesting feature is that the average value of X_{23} increases from 90% PS to 50% PS, after which it decreases as we go to 10% PS blend (*Figure 11*). Here chlorobenzene shows an exception, as it gives a small positive value, which does not vary much with composition (*Table 9*). This should be expected for the PS–PBD blend system. Also X_{23} decreases with increase in temperature at all the compositions of the blend, except for a few probes at 10% PS blend (*Figure 12*). This is different from the trend we observed with other interaction parameters.

Horta's method

The i.g.c.-determined $\chi_{23}^{*\prime}$ values were used to calculate the χ_{23}^{*T}/V_2^* for the blend system at all the compositions. The values at 155°C are given in *Table 10*, and are found to be probe-dependent. It also shows negative values for most of the probes at all compositions. The negative values cannot be explained for the present system. It is also found that χ_{23}^{*T}/V_2^* increases smoothly as the amount of PS decreases (except at 23% PS) (*Figure 13*). Also χ_{23}^{*T}/V_2^* decreases with increase in temperature for 90% PS up to 23% PS blend, whereas at 10% PS content it increases with increase in temperature (*Figure 14*). This is the same trend as that of the contact interaction parameter X_{23} and even the different behaviour of chlorobenzene is observed here. This suggests that χ_{23}^{*T}/V_2^* is the direct consequence of X_{23} and the method in no way shows any improvement for obtaining a probe-independent interaction parameter and the sign obtained is also different for this blend system.

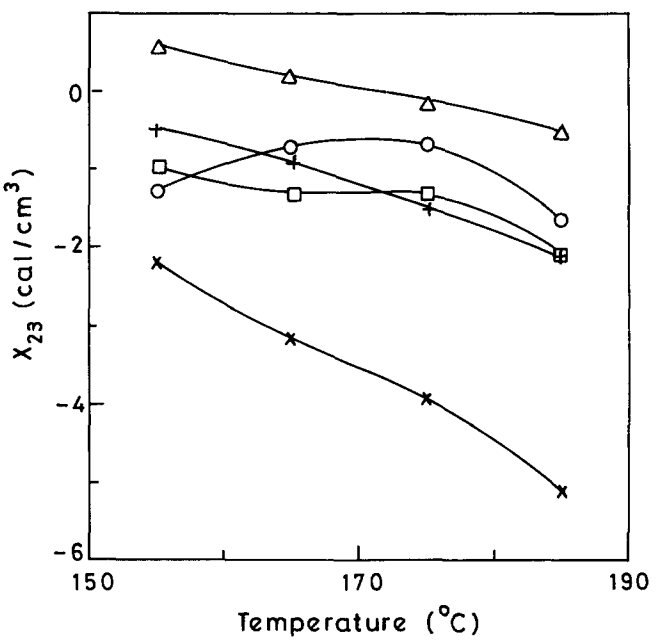

Figure 12 Temperature dependence of X_{23} (cal cm^{-3}) (average value of all probes) of PS–PBD blend at 10% (○), 23% (□), 50% (△), 77% (+) and 90% (×) of PS

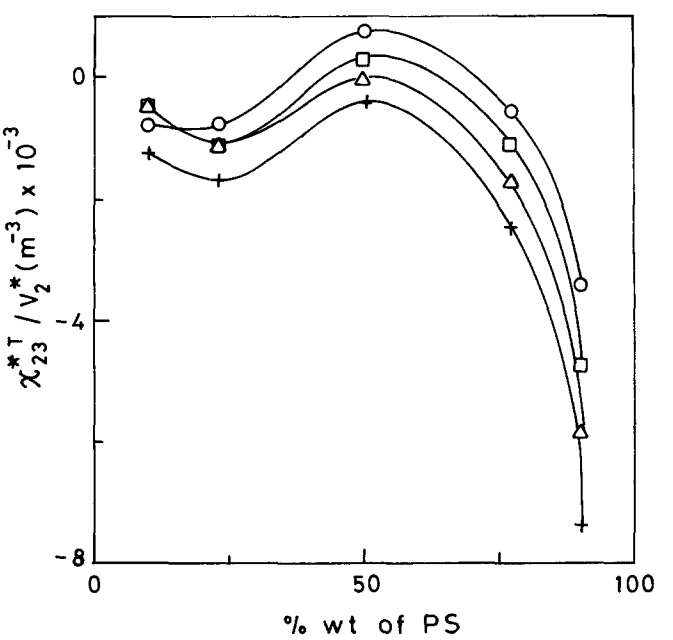

Figure 13 Composition dependence of χ_{23}^{*T}/V_2^* (m^{-3}) (average value of all probes) of PS–PBD blend calculated using Horta's method at 155°C (○), 165°C (□), 175°C (△) and 185°C (+)

Table 10 The χ_{23}^{*T}/V_2^* parameter of PS–PBD blend at 155°C calculated by Horta's method

Probe no.	PS (wt%) in blend				
	10	23	50	77	90
1	70.46	−195.99	1034.35	−573.35	−3188.66
2	−922.55	−487.07	655.52	−1155.06	−4540.73
3	967.00	212.46	1083.66	−828.16	−3472.80
4	−445.73	793.04	1396.26	−119.20	−2292.81
5	175.69	−444.63	611.83	−843.95	−3300.18
6	−2372.44	−440.06	738.66	−15.75	−1964.20
7	−2992.39	−817.67	−368.16	−889.45	−5251.09
8	−1947.53	−496.31	111.58	−841.69	−4300.76
9	−1178.55	−833.78	−20.56	−934.49	−3469.77
10	750.43	1079.67	1357.97	944.42	122.29
11	67.23	−1825.99	776.91	−605.03	−5209.07
12	−1828.32	−2267.50	154.44	−1138.33	−6197.50
13	−2476.52	−2333.18	377.15	−1071.49	−2757.84
14	−422.79	−3240.53	1128.29	−1231.90	−2231.57
15	1056.17	−408.81	2182.64	988.51	−2825.00

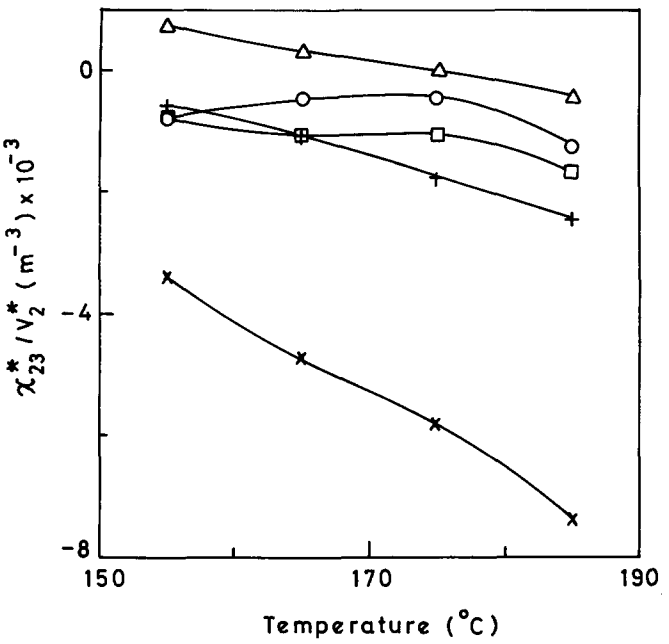

Figure 14 Temperature dependence of χ_{23}^{*T}/V_2^{*} (m^{-3}) (average value of all probes) of PS–PBD blend calculated using Horta's method at 10% (○), 23% (□), 50% (△), 77% (+) and 90% (×) of PS

Sanchez's method

Using Sanchez's approach, we have calculated the probe–polymer, χ_{1i}^{S} (*Table 11*), and the polymer–polymer, χ_{23}^{S} (*Table 12*), interaction parameters for the 11 probes for which the equation-of-state parameters are available. It has been observed that in the case of both homopolymers the interaction parameters (χ_{12}^{S} and χ_{13}^{S}) were found to decrease with increase in temperature (*Figures 15* and *16*). It shows a similar trend to that of χ_{1i} parameters except for polar probes, where it gives a higher value for PBD and a lower one for PS.

The χ_{23}^{S} of all the blend compositions show a decrease in value with increase in temperature (*Figure 17*). This is different from χ'_{23}, but similar to that of contact energy parameter X_{23}. It has also been found that *cis*- and *trans*-decalin have a maximum value for χ_{23}^{S}, whereas *p*-dioxane and butyl acetate have minimum values at almost all compositions and temperatures. In most of the cases the χ_{23}^{S} values were found to be negative, and it has been observed that at 90% PS it shows a minimum value and as the PS content decreases, χ_{23}^{S} increases till 50% PS. Below that, χ_{23}^{S} starts decreasing again as PS content decreases in the blend (*Figure 18*). This result is different from that obtained for χ'_{23}, where it increased continuously from 90% to 10% PS content blend. But

Table 11 Sanchez's interaction parameters of PS and PBD

Probe no.	χ_{12}^{S} (m^{-3}) (PS)				χ_{13}^{S} (m^{-3}) (PBD)			
	155°C	165°C	175°C	185°C	155°C	165°C	175°C	185°C
1	4589.9	3703.8	3034.4	2290.2	2459.1	2202.2	1848.5	1515.8
2	4658.0	4031.8	3448.3	2848.2	2465.0	2250.6	1984.5	1756.3
3	4605.2	4075.2	3484.1	2956.6	2520.8	2131.3	1939.9	1672.6
5	3528.9	3038.2	2728.8	2274.5	970.1	834.2	761.0	653.0
6	3610.4	2974.5	2513.7	2143.2	666.2	735.2	694.2	538.2
7	382.9	−142.8	−744.2	−1342.4	934.3	495.8	143.9	−165.8
8	1392.6	920.4	417.1	5.7	1381.1	1008.1	753.3	397.1
9	1429.0	889.0	404.1	6.1	1346.9	1016.7	812.7	540.4
10	1820.2	1190.5	745.8	220.7	2358.0	2053.6	1704.6	1277.0
11	1400.6	646.7	62.3	−548.6	3331.9	2785.8	2240.7	1613.6
15	1816.5	924.8	49.4	−891.3	6108.8	5165.8	4411.0	3487.1

Table 12 The χ_{23}^{S} (m^{-3}) parameter of PS–PBD blend at 155°C calculated by Sanchez's method

Probe no.	PS (wt%) in blend				
	10	23	50	77	90
1	−679.29	−723.07	920.84	−69.40	−430.05
2	−1662.63	−973.73	527.71	−728.96	−2007.03
3	718.67	−88.51	1044.68	−389.18	−1009.65
5	1315.82	58.09	779.72	−3.35	−276.18
6	−805.76	187.73	1039.53	790.48	894.07
7	−3290.77	−1271.13	−747.04	−476.13	−2154.97
8	−1944.21	−770.94	−159.49	−422.41	−1485.90
9	−1378.11	−1229.49	−369.60	−638.18	−919.55
10	−3758.76	−1522.39	−547.56	−734.73	−951.09
11	−1919.37	−3444.69	−34.34	−716.33	−3131.51
15	−6064.36	−4297.81	−511.14	−1070.18	−3326.71

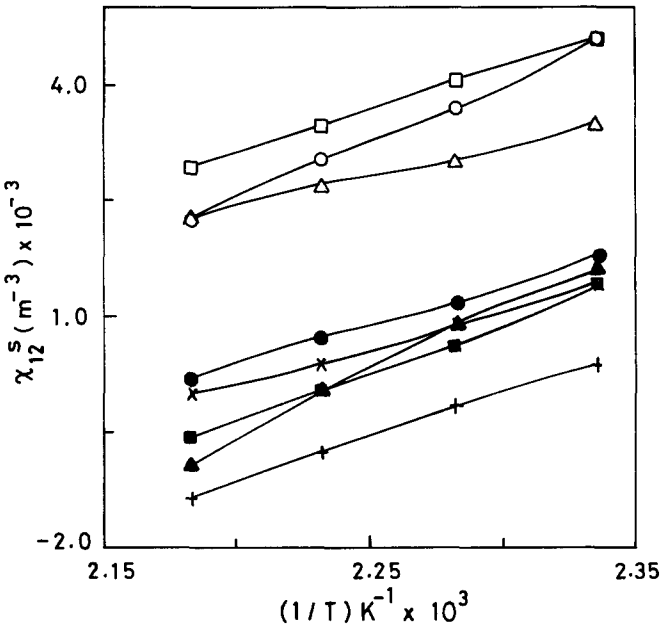

Figure 15 Variation of χ_{12}^{S} of PS calculated using Sanchez's method with temperature for probes 1 (○), 3 (□), 5 (△), 7 (+), 9 (×), 10 (●), 11 (■) and 15 (▲)

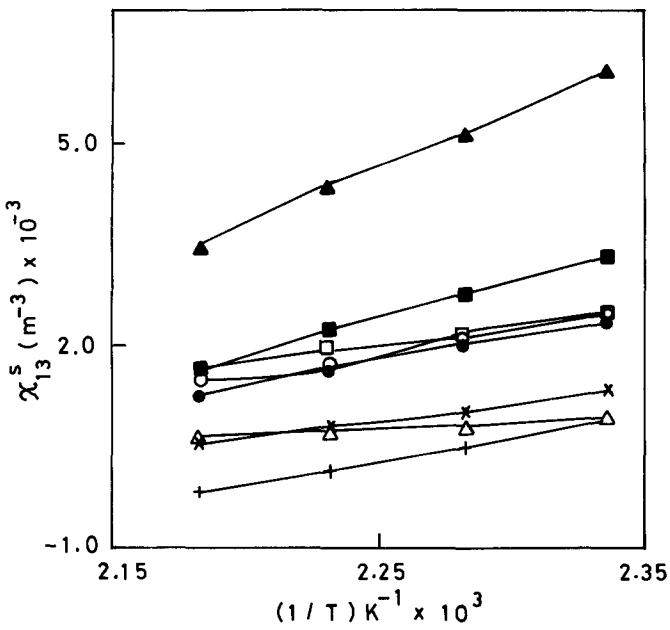

Figure 16 Variation of χ_{13}^{S} of PBD calculated using Sanchez's method with temperature for probes 1 (○), 3 (□), 5 (△), 7 (+), 9 (×), 10 (●), 11 (■) and 15 (▲)

it shows some similarity to that of the contact interaction parameter X_{23}. Thus, Sanchez's method also does not offer a probe-independent interaction parameter for this system.

Chee's method

The equation (27) giving $f(\phi_3)$ can be adequately expressed by the following quadratic functions:

at 155°C:

$$f(\phi_3)(\text{mol cm}^{-3}) = 0.000\,235 + 0.000\,862\phi_3 + 0.001\,615\phi_3^2 \quad (33)$$

at 165°C:

$$f(\phi_3)(\text{mol cm}^{-3}) = -0.000\,123 + 0.000\,634\phi_3 + 0.003\,244\phi_3^2 \quad (34)$$

at 175°C:

$$f(\phi_3)(\text{mol cm}^{-3}) = 0.000\,0529 - 0.001\,255\phi_3 + 0.005\,962\phi_3^2 \quad (35)$$

at 185°C:

$$f(\phi_3)(\text{mol cm}^{-3}) = 0.000\,44 - 0.002\,484\phi_3 + 0.007\,132\phi_3^2 \quad (36)$$

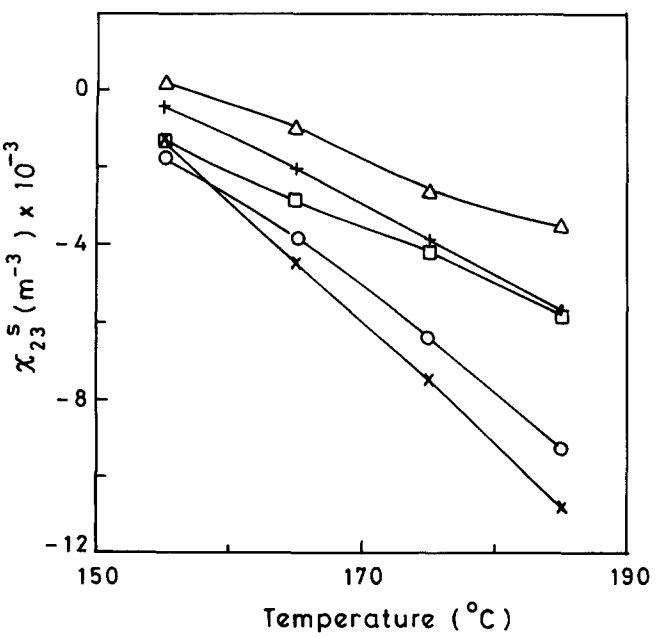

Figure 17 Temperature dependence of χ_{23}^{S} (m^{-3}) (average value of all probes) of PS–PBD blend calculated using Sanchez's method at 10% (○), 23% (□), 50% (△), 77% (+) and 90% (×) of PS

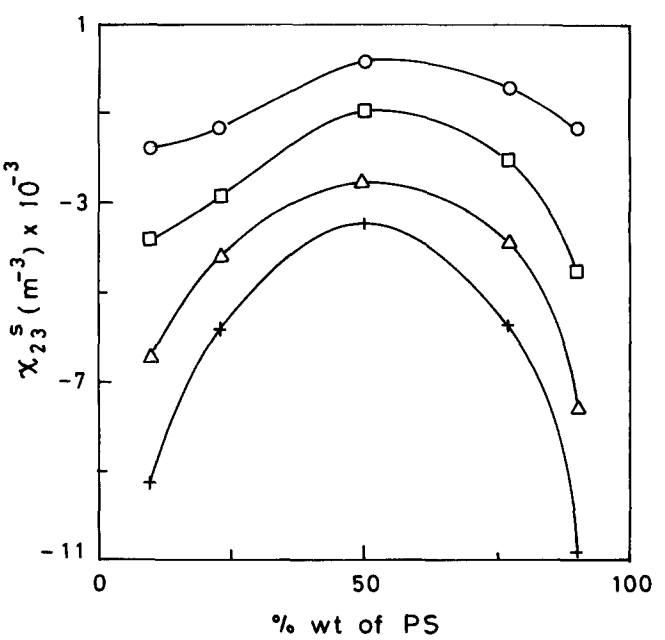

Figure 18 Composition dependence of χ_{23}^{S} (m^{-3}) (average value of all probes) of PS–PBD blend calculated using Sanchez's method at 155°C (○), 165°C (□), 175°C (△) and 185°C (+)

Consequently the interaction energy density parameter B_{23}^C at the corresponding temperatures is expressed by the following equations:

at 155°C:

$$B_{23}^C(\text{cal cm}^{-3}) = 0.64 + 0.367\phi_3 + 0.458\phi_3^2 \quad (37)$$

at 165°C:

$$B_{23}^C(\text{cal cm}^{-3}) = 0.267 + 0.276\phi_3 + 0.942\phi_3^2 \quad (38)$$

at 175°C:

$$B_{23}^C(\text{cal cm}^{-3}) = 0.373 - 0.559\phi_3 + 1.771\phi_3^2 \quad (39)$$

at 185°C:

$$B_{23}^C(\text{cal cm}^{-3}) = 0.687 - 1.132\phi_3 + 2.166\phi_3^2 \quad (40)$$

Figure 19 gives curves corresponding to the equations (37)–(40), which are the variation of B_{23}^C with volume fraction of PBD, i.e. ϕ_3, at four temperatures. It has been observed that B_{23}^C is positive for all the compositions and at the temperature of the experiments. This is understandable for a non-polar system like PS–PBD blend. Another interesting observation is that B_{23}^C increases as the amount of PS decreases from 90% to 10% in the blend, which is in conformity with the behaviour of χ'_{23} and also the concept of greater compatibility in the PS-rich region. The B_{23}^C values calculated using Chee's method have a single value for the whole set of probes used at the given temperature and composition (*Table 13*). It is also revealed that B_{23}^C decreases with increase in temperature at all compositions, except at 10% PS content blend where it increases with increase in temperature (*Figure 20*).

Following Munk *et al.*[14], the B_{23} calculated for each probe was plotted against the probe solubility parameter δ_1 and, from the resulting best-fit plot, the B_{23} corresponding to the value of δ_1 that is equal to the solubility parameter of the blend δ_{23} is taken as the true B_{23}^M of the blend. The blend solubility parameter δ_{23} was calculated by using the method given by Guillet *et al.*[20]. The B_{23}^M calculated for different compositions and temperatures are given in *Table 13*. It is quite interesting to note that B_{23}^M is almost equal to the average value of B_{23} for all the probes. This was quite evident at 50, 77 and 90% PS content (*Table 14*), whereas at 10 and 23% PS content a small difference is observed.

In our method using equations (30) and (31), it has been found that B_{23}^P thus estimated (*Table 14*) are slightly lower than those calculated by Munk's method except at 50% PS content of the blend, but the variations with volume fraction and temperature are found to be similar (*Figures 21–24*). This method is extremely simple and provides a probe-independent interaction energy density parameter of the polymer blend.

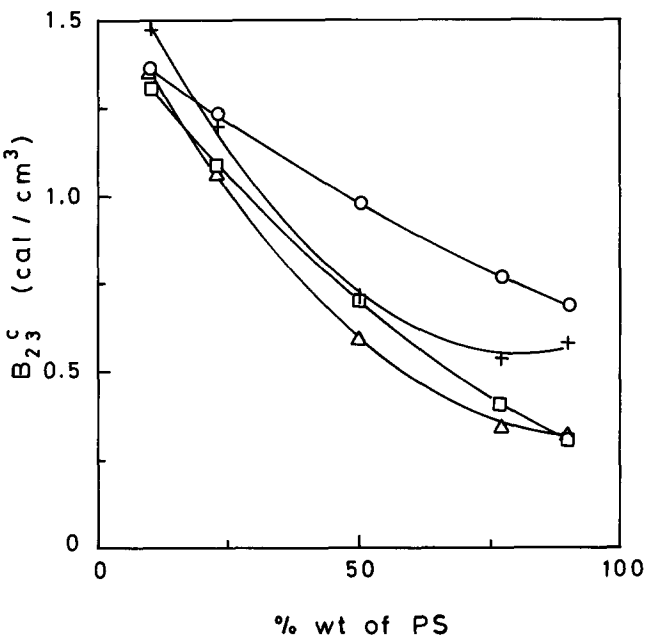

Figure 19 Composition dependence of B_{23}^C (cal cm^{-3}) of PS–PBD blend calculated using Chee's method at 155°C (○), 165°C (□), 175°C (△) and 185°C (+)

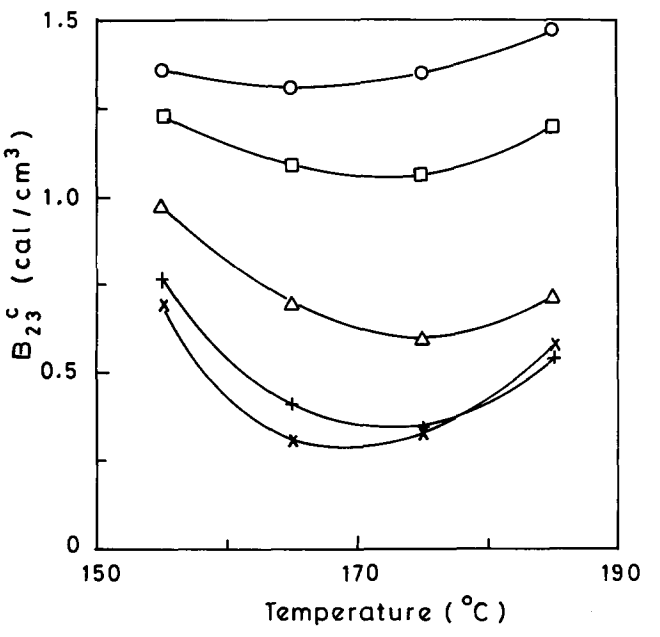

Figure 20 Temperature dependence of B_{23}^C (cal cm^{-3}) of PS–PBD blend calculated using Chee's method at 10% (○), 23% (□), 50% (△), 77% (+) and 90% (×) of PS

Table 13 B_{23}^C (cal cm^{-3}) and B_{23}^M (cal cm^{-3}) parameters of PS–PBD blend calculated by Chee's and Munk's method respectively

	B_{23}^C (cal cm^{-3})				B_{23}^M (cal cm^{-3})			
PS (wt%)	155°C	165°C	175°C	185°C	155°C	165°C	175°C	185°C
10	1.36	1.31	1.35	1.47	2.43	3.13	3.77	3.92
23	1.23	1.09	1.06	1.2	0.97	1.01	1.25	1.15
50	0.98	0.7	0.6	0.72	1.38	1.25	1.21	1.12
77	0.77	0.41	0.35	0.54	0.88	0.76	0.57	0.34
90	0.69	0.31	0.33	0.58	0.66	0.37	0.17	−0.22

Table 14 The average value of B_{23} (cal cm^{-3}) and the B_{23}^{P} (cal cm^{-3}) obtained by plotting method of PS–PBD blend

	Avg. B_{23} (cal cm^{-3})				B_{23}^{P} (cal cm^{-3})			
PS (wt%)	155°C	165°C	175°C	185°C	155°C	165°C	175°C	185°C
10	2.14	3.01	3.58	3.61	1.86	2.99	3.37	3.36
23	0.82	0.88	1.13	0.97	0.35	0.44	0.71	0.47
50	1.37	1.24	1.20	1.11	1.32	1.15	1.05	0.99
77	0.90	0.77	0.59	0.38	0.82	0.72	0.54	0.33
90	0.66	0.32	0.17	−0.21	0.46	0.30	0.05	−0.33

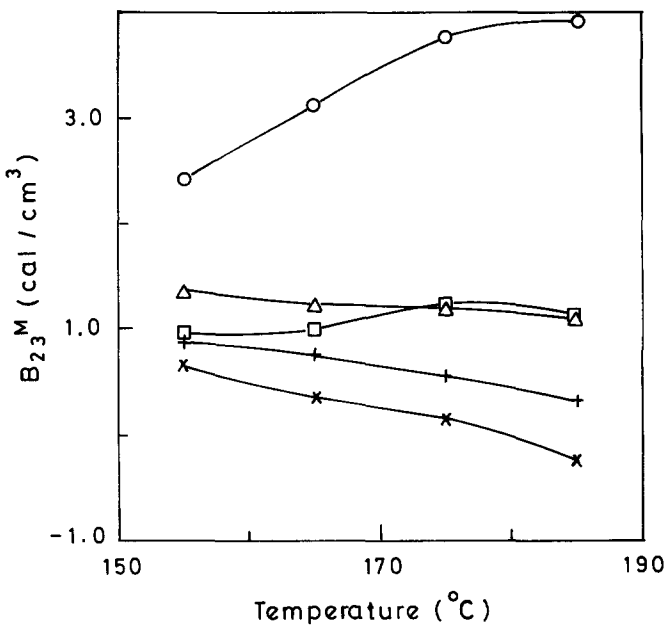

Figure 21 Temperature dependence of B_{23}^{P} (cal cm^{-3}) of PS–PBD blend calculated using equations (30) and (31) at 10% (○), 23% (□), 50% (△), 77% (+) and 90% (×) of PS

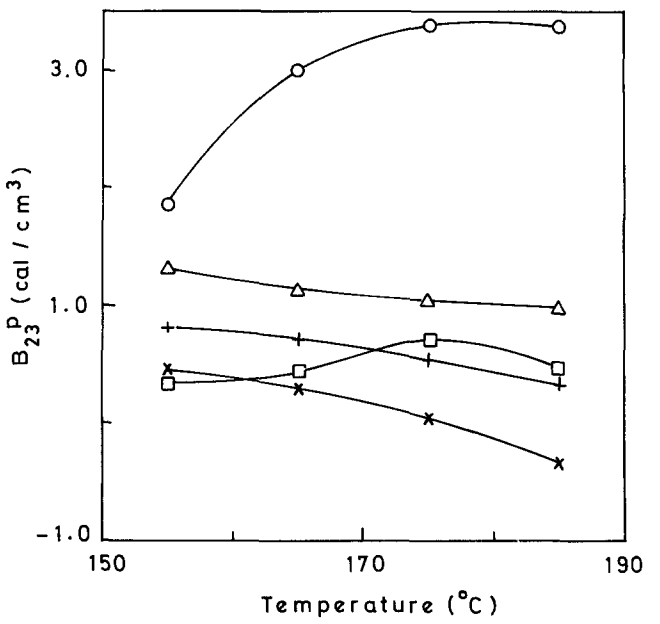

Figure 23 Temperature dependence of B_{23}^{M} (cal cm^{-3}) of PS–PBD blend calculated using Munk's method at 10% (○), 23% (□), 50% (△), 77% (+) and 90% (×) of PS

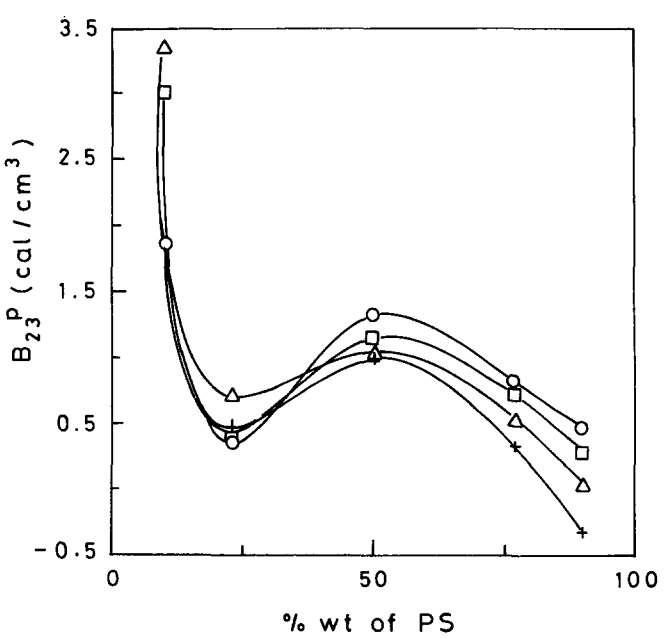

Figure 22 Composition dependence of B_{23}^{P} (cal cm^{-3}) of PS–PBD blend calculated using equations (30) and (31) at 155°C (○), 165°C (□), 175°C (△) and 185°C (+)

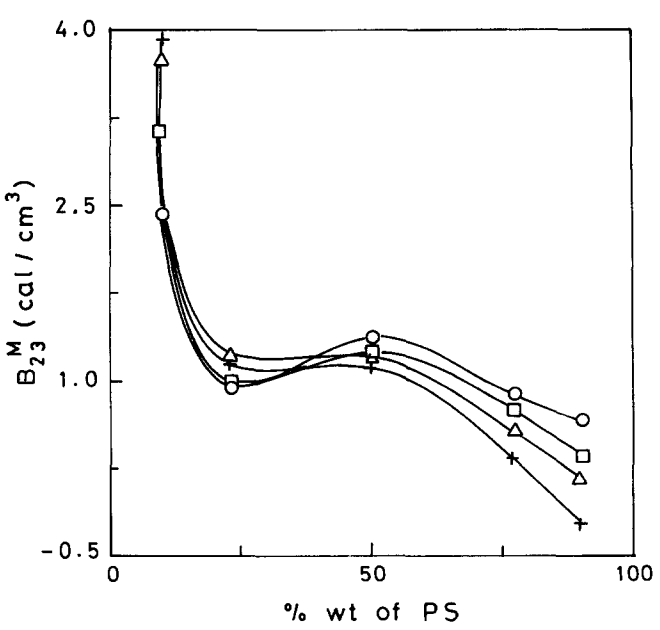

Figure 24 Composition dependence of B_{23}^{M} (cal cm^{-3}) of PS–PBD blend calculated using Munk's method at 155°C (○), 165°C (□), 175°C (△) and 185°C (+)

CONCLUSIONS

From the analysis of all the methods mentioned it has been quite clear that most of the methods except Chee's method show similar trends in the variation of interaction parameters with temperature and composition for the blend containing 50% and more of PS. The blend system that contains less than 50% of PS shows different trends with different methods. This could be due to the completely phase-separated nature of the blend below 50% PS, which is evident from high positive interaction parameter values observed by various methods. The contact interaction parameter and Horta's method gave negative values of interaction parameter for most of the compositions and temperatures, which cannot be explained for a system like PS–PBD, where there is no specific interaction. Sanchez's method also gave negative values for almost all compositions and temperatures. Also the values of interaction parameters for blends containing less than 50% PS were found to be extremely low, which cannot be explained at all.

In contrast to these two methods, Chee's method gave positive values of interaction parameters for all the temperatures studied, and also the variation of interaction parameter with composition was in excellent agreement with experimental values, where it was found that the blend with higher PS content is more compatible than the one with low PS content from the d.s.c. studies[26]. Thus Chee's method provides a better approach to get the probe-independent interaction parameter. However, it needs to be confirmed by comparison with the values measured by other methods that give direct polymer–polymer interaction parameters, such as small-angle neutron scattering or melting-point depression. Another drawback that should be seriously taken into account is that, according to his definition, the enthalpy part of the interaction parameter, i.e. χ_H, will always be positive, and that is counter to the basic definition of Flory, where we should be able to get negative χ_H also. Here we can get negative interaction parameter only when the entropic part χ_s is negative and higher than χ_H.

The method proposed by Munk *et al.* seems to give the average value of B_{23} determined using each probe. The method proposed by us (equations (30) and (31)) is simple, shows the effect of $\Delta\chi$, and the results are closely similar to those of other methods that give a single interaction parameter for a whole set of probes. It needs to be tested for a greater number of systems.

ACKNOWLEDGEMENT

One of us (AMF) wishes to acknowledge CSIR (India) for the award of a Senior Research fellowship.

REFERENCES

1 Lipson, J. E. G. and Guillet, J. E. 'Developments in Polymer Characterization–3' (Ed. J. V. Dawkins), Applied Science, London, 1982, pp. 33–74
2 Aspler, J. S. 'Pyrolysis and GC in Polymer Analysis' (Eds. S. A. Liebman and E. J. Levy), Chromatographic Science Series, Vol. 29, Dekker, New York, 1985, Ch. IX
3 Mandal, B. M., Bhattacharya, C. and Bhattacharya, S. N. *J. Macromol. Sci.–Chem (A)* 1989, **26**, 175
4 Deshpande, D. D., Patterson, D., Schreiber, H. P. and Su, C. S. *Macromolecules* 1974, **7**, 530
5 Su, C. S. and Patterson, D. *Macromolecules* 1977, **10**, 708
6 Prolongo, M. G., Masegosa, R. M. and Horta, A. *Macromolecules* 1989, **22**, 4346
7 Sanchez, I. C. *Polymer* 1989, **30**, 471
8 Chee, K. K. *Polymer* 1990, **31**, 1711
9 Al-Saigh, Z. Y. and Munk, P. *Macromolecules* 1984, **17**, 803
10 Littlewood, A. B., Phillips, C. S. G. and Price, D. T. *J. Chem. Soc.* 1955, 1480
11 Guillet, J. E. and Braun, J. M. *Adv. Polym. Sci.* 1976, **21**, 107
12 Smith, B. D. and Srivastava 'Thermodynamic Data for Pure Components', Physical Science Data 25, Parts A and B, Elsevier, Amsterdam, 1986
13 Reid, R. C., Sherwood, T. K., Prausunitz, J. M. and Poling, B. E. 'Properties of Gases and Liquids', McGraw-Hill, New York, 1987
14 El-Hibri, M. J., Cheng, W. and Munk, P. *Macromolecules* 1988, **21**, 3458
15 Patterson, D. *Pure Appl. Chem.* 1972, **31**, 133
16 Sanchez, I. C. and Lacombe, R. H. *J. Phys. Chem.* 1976, **80**, 2352, 2568
17 Sanchez, I. C. and Lacombe, R. H. *Macromolecules* 1978, **11**, 1145
18 Lipson, J. E. G. and Guillet, J. E. *J. Polym. Sci., Polym. Phys. Edn.* 1981, **19**, 1199
19 Uriarte, C., Fdes-Berridi, M. J., Elorsa, J. M., Iruin, J. J. and Kleintjens, L. *Polymer* 1989, **30**, 1493
20 DiPaola-Baranyi, G. and Guillet, J. E. *Macromolecules* 1978, **11**, 228
21 Newman, R. D. and Prausunitz, J. M. *J. Phys. Chem.* 1972, **76**, 1492
22 Schuster, R. H., Gräter, R. and Cantow, H. J. *Macromolecules* 1984, **17**, 619
23 Covitz, F. H. and King, J. W. *J. Polym. Sci. (A-1)* 1972, **10**, 689
24 Su, A. C. and Fried, J. R. *Adv. Chem. Ser.* 1986, **59**, 211
25 Klein, J., Widdecke, H. and Wolter, G. *J. Polym. Sci., Polym. Symp.* 1981, **68**, 221
26 Kin, W. N. and Burns, C. H. *J. Appl. Polym. Sci.* 1986, **32**, 2989
27 Roe, R. J. and Zin, W. C. *Macromolecules* 1980, **13**, 1221
28 Patterson, D. and Robard, A. *Macromolecules* 1978, **11**, 690