ELSEVIER Thermochimica Acta 282/283 (1996) 399–410

thermochimica acta

Blends of poly(isobutyl methacrylate) with poly(styrene-*co*-acrylic acid) and of poly(isobutyl methacrylate-*co*-acrylic acid) with poly(styrene-*co*-*N*,*N*-dimethyl aminoethyl methacrylate)[1]

Said Djadoun[a], Frank E. Karasz *,[a], Assia Siham Hadj Hamou[b]

[a] *Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003, USA*

[a] *Institute of Chemistry, University of Sciences and Technology, Houari Boumediene, BP 32, Elalia, Algiers, Algeria*

Abstract

The miscibility of poly(isobutyl methacrylate) with poly(styrene-*co*-acrylic acid) and of poly(isobutyl methacrylate-*co*-acrylic acid) with poly(styrene-*co*-*N*,*N*-dimethyl aminoethyl methacrylate) was studied by differential scanning calorimetry and inverse gas chromatography. Poly(styrene-*co*-acrylic acid), containing 20 or 32 mol% acrylic acid, and poly(isobutyl methacrylate) were immiscible, as were blends of poly(isobutyl methacrylate-*co*-acrylic acid) containing 10.5 mol% acrylic acid with poly(styrene-*co*-*N*,*N*-dimethyl aminoethyl methacrylate) containing 6 mol% of the basic comonomer. However, as a result of a higher level of favorable specific interactions between moieties in the two copolymers, the same isobutyl methacrylate copolymer or copolymers with a greater content of acrylic acid are miscible with the styrene copolymer containing 12 mol% *N*,*N*-dimethyl aminoethyl methacrylate, as suggested by the negative values of the apparent polymer–polymer interaction parameters.

Keywords: Polymer blends; Styrene–acrylic acid copolymers; Segmental interactions

---

* Corresponding author.

[1] Dedicated to Takeo Ozawa on the Occasion of his 65th Birthday.

SSDI 0040-6031(96)02809-2

1. Introduction

In recent years, extensive research has been carried out in the area of polymer polymer miscibility [1–8]. In previous studies [9–11] we have shown that the introduction of groups capable of providing specific attractive interactions between the two polymers in a blend is a method for increasing the miscibility of polymers. It has also been shown that blends of a random copolymer and a homopolymer can be miscible even in the absence of specific interactions, provided sufficient repulsion between the two comonomers is present [12–15]. It is known that polystyrene is immiscible with poly(isobutyl methacrylate); a recent study [16] showed that poly(styrene-*co*-acrylic acid) containing 8 mol% acrylic acid was miscible with poly(methyl methacrylate), poly(ethyl methacrylate), and poly(*n*-propyl methacrylate), but immiscible with poly(isobutyl methacrylate).

In this contribution, blends of poly(isobutyl methacrylate) with poly(styrene-*co*-acrylic acid) containing 20 or 32 mol% acrylic acid and of poly(isobutyl methacrylate-*co*-acrylic acid) containing 10.5 or 22 mol% acrylic acid with poly(styrene-*co*-*N*,*N*-dimethyl aminoethyl methacrylate) containing 6 or 12 mol% of the basic comonomer were studied by differential scanning calorimetry and by inverse gas chromatography, the latter to measure the apparent polymer–polymer interaction parameters and to interpret the miscibility of the blends. It has been frequently reported that the measured interaction parameter varies with the chemical nature of the probe used [17–20] and several interpretations have been suggested [21–23]. Shi and Schreiber [24] have recently proposed a modified inverse gas chromatography procedure based on the fact that the surface and the bulk compositions differ in polymer blends, a procedure that is said to reduce the probe-to-probe variation. In this study, using this procedure, we have examined both the composition and temperature effects.

2. Experimental

Random copolymers of (1) styrene and acrylic acid (SAA-20 and SAA-32) containing 20 and 32 mol% of acrylic acid, respectively, (2) isobutyl methacrylate and acrylic acid (IBMA-10.5 and IBMA-22) containing 10.5 or 22 mol% acrylic acid, respectively, (3) styrene and *N*,*N*-dimethyl aminoethyl methacrylate (SMAD-6 and SMAD-12) containing 6 and 12 mol% of the basic comonomer, respectively, and (4) the homopolymer poly(isobutyl methacrylate) (PIBMA) were prepared by radical solution polymerization. The degree of conversion was held to below 15%. The styrene contents in the SAA and SMAD copolymers were determined by UV spectroscopy. The acrylic acid content in the IBMA copolymers was determined by standard titration techniques in a mixture of benzene/methanol.

SAA-20/PIBMA, SAA-32/PIBMA, IBMA-10.5/SMAD-6, IBMA-10.5/SMAD-12, and IBMA-22/SMAD-12 blends of different ratios were prepared by coprecipitation from dioxane solution in an excess of either methanol or *n*-hexane. The blends were dried in a vacuum oven at 70°C for 48 h. The glass transition temperatures of the polymers and their blends of different composition ratios were measured using a Perkin-Elmer DSC-7 differential scanning calorimeter at a heating rate of 20 K min^{-1} under a nitrogen atmosphere.

Chromatographic columns, 1.5 or 1 m long, with 9% polymer loading were prepared in the usual way [11], using Chromosorb W AWDMCS 80/100 mesh (Johns Manville) as the solid support. The IGC measurements were carried out on an HP 5730A gas chromatograph equipped with a dual-flame ionization detector using helium as the carrier gas at a flow rate of 10 ml min^{-1} and methane as a noninteracting marker. A small amount (< 0.1 μl) of benzene or *n*-decane, used as the molecular probes, was injected manually, using a Hamilton syringe.

3. Results and discussion

Figs. 1 and 2 show the DSC thermograms for the SAA copolymers for PIBMA, and for SAA-20/PIBMA and SAA-32/PIBMA blends of different ratios. The observation of

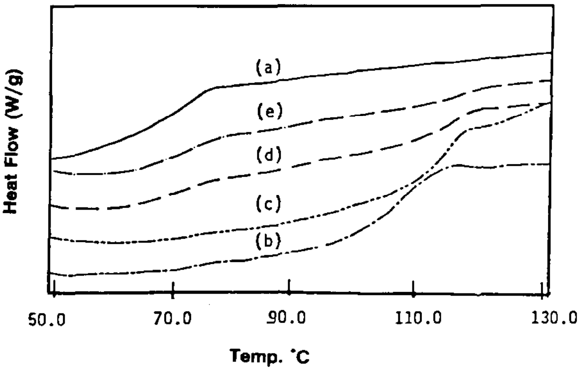

Fig. 1. DSC thermograms of PIBMA (a), SAA-20 (b), and of their blends containing 26% (c), 52% (d), and 75% (e) of PIBMA, respectively.

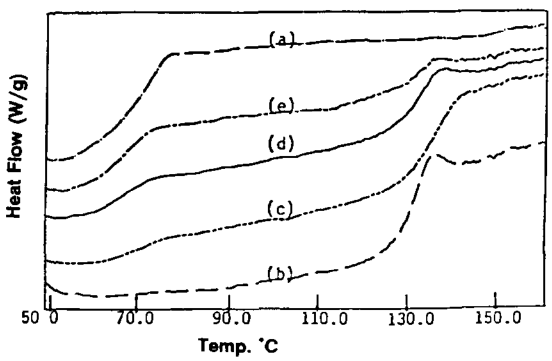

Fig. 2. DSC thermograms of PIBMA (a), SAA-32 (b) and of their blends containing 30% (c), 50% (d), and 71% (e) of PIBMA, respectively.

the two glass transition temperatures, close to the T_gs of the pure polymers, confirms that PIBMA is immiscible with SAA copolymers even at a relatively high content of carboxylic acid groups.

In the mean field approximation, the net interaction parameter for the blend of poly(isobutyl methacrylate) with poly(styrene-*co*-acrylic acid) is given by

$$\chi_{\text{blend}} = (1-x)\chi_{\text{IBMA/S}} + x\,\chi_{\text{IBMA/AA}} - x(1-x)\chi_{\text{S/AA}} \tag{1}$$

where χ_{ij} are the respective segmental interaction parameters and x is the copolymer composition (volume fraction) of acrylic acid segments.

According to Eq. (1), these blends might be expected to be miscible as the amount of acrylic acid in the SAA copolymer increases, because the styrene–acrylic acid interactions are certainly repulsive, and some attractive interactions between the isobutyl methacrylate–acrylic acid segments may also be possible. The results showed that even at 32 mol% acrylic acid content in SAA copolymers, the blends were immiscible.

Qualitatively, in order for these blends to be miscible, the styrene–acrylic acid repulsive interactions within the SAA copolymers, should not only overcome the positive χ associated with the IBMA/S interactions but also the acid–acid self associations that may occur as the acidic density within these copolymers increases. These associations would compete with and reduce the acid–ester interactions.

Fig. 3 shows DSC measurements for the SMAD-6/IBMA-10.5 blends. The blends are also immiscible as evidenced by the observation of two glass transition temperatures, each transition characterizing one of the constituents of the blends.

As the density of the basic groups increased from 6 to 12 mol% within the SMAD copolymer, it was found that the blends of SMAD copolymers with the same acidic copolymer (IBMA-10.5) were miscible in all proportions. The presence of a single T_g for these blends (Fig. 4), intermediate between the T_gs of the constituents, is evidence of their miscibility.

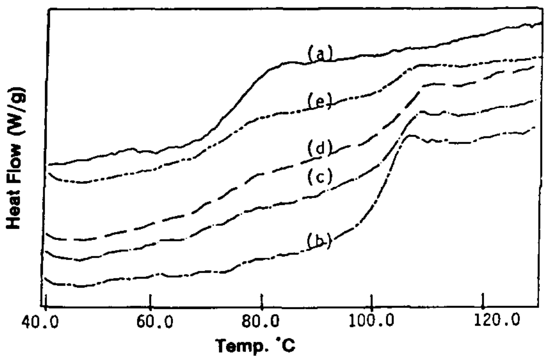

Fig. 3. DSC thermograms of IBMA-10.5 (a), SMAD-6 (b) and of their blends containing 34% (c), 50% (d), and 65% (e) of IBMA-10.5, respectively.

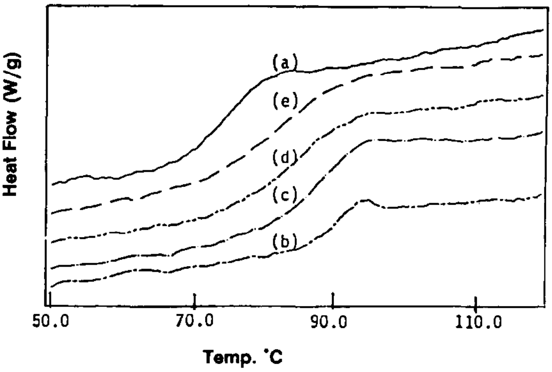

Fig. 4. DSC thermograms of IBMA-10.5 (a), SMAD-12 (b) and of their blends containing 35% (c), 50% (d), and 66% (e) of IBMA-10.5, respectively.

In this case, the χ_{blend} is written as

$$\chi_{\text{blend}} = (1-x)(1-y)\chi_{\text{IBMA/S}} + y(1-x)\chi_{\text{IBMA/MAD}} + x(1-y)\chi_{\text{AA/S}}$$
$$+ xy\,\chi_{\text{AA/MAD}} - x(1-x)\chi_{\text{IBMA/AA}} - y(1-y)\chi_{\text{S/MAD}} \tag{2}$$

where χ has been defined above and y represents the fraction of *N*,*N*-dimethyl aminoethyl methacrylate in the SMAD copolymer. Here the weighted acid–base (AA/MAD), IBMA/AA, and styrene–base (S/MAD) interactions resulted in an overall negative χ_{blend}. Because the number of acid groups within the IBMA-10.5 is relatively low, the acid–acid associations should also be low assuming a random structure; however, the acid–ester intramolecular interactions may not be negligible. Such interactions have to be dissociated in order for the acidic copolymer to develop hydrogen bonding with the basic copolymer. As the amount of acidic groups was increased from 10.5 to 22 mol% within the IBMA copolymer, miscible blends of IBMA-22 and SMAD-12 were also observed.

Glass transition temperatures of the acidic and basic copolymers and of their blends of different ratios were also determined by inverse gas chromatography (IGC) [17]. The retention diagrams of ln V_g, the respective specific retention volumes, versus the reciprocal of the temperature, using benzene as the molecular probe, confirm the immiscibility of the blends of SMAD-6 and IBMA-10.5. Fig. 5 shows an example of these diagrams in which the immiscibility of the SMAD-6/IBMA-10.5 (1:1 ratio) is suggested by the appearance of the two glass transition temperatures of the components of the blend. Figs. 6 and 7 display the retention diagrams of the SMAD-12/IBMA-10.5 and SMAD-12/IBMA-22 blends. The single glass transition temperature observed in each case is evidence of the miscibility of these blends. The results obtained by both techniques are thus in agreement.

A quantification of the miscibility of a polymer blend can be obtained by measuring the specific retention volumes of each binary probe–polymer and of the ternary system (probe–mixed polymeric phase). At temperatures above the glass transition tempera-

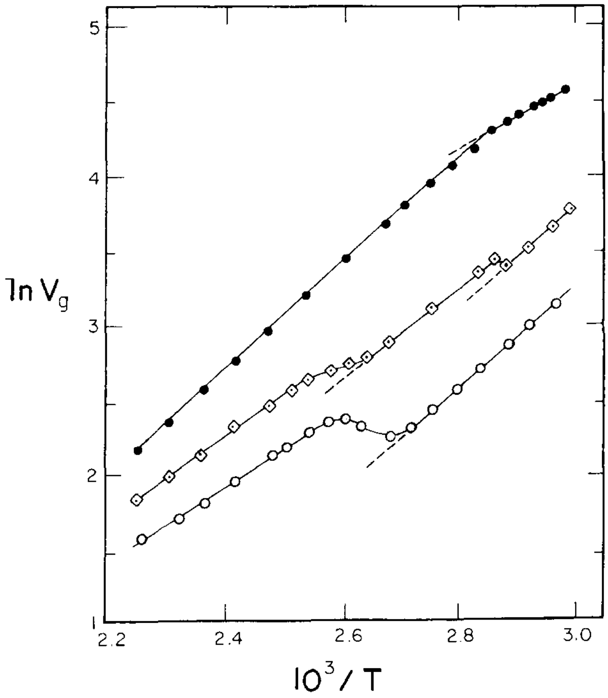

Fig. 5. Retention diagrams of IBMA-10.5 (●), SMAD-6 (○), and IBMA-10.5/SMAD-6 1:1 (◇) using benzene as a probe.

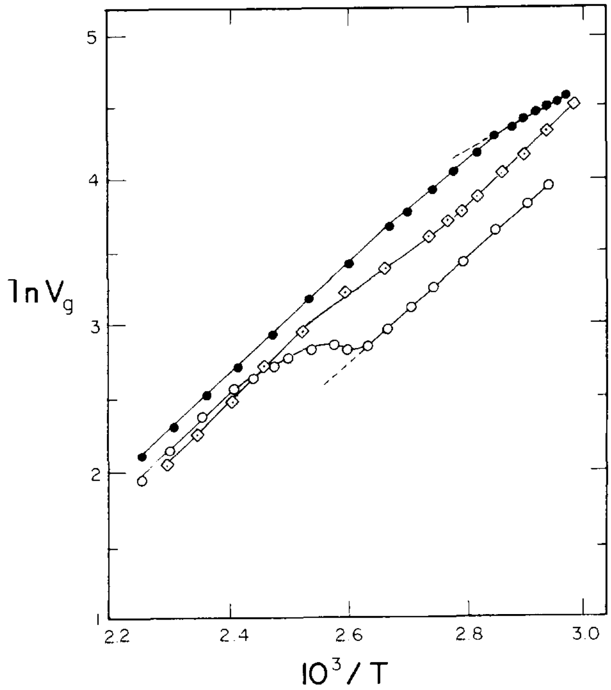

Fig. 6. Retention diagrams of IBMA-10.5 (●) SMAD-12 (○), and IBMA-10.5/SMAD-12 1:1 (◇) using benzene as a probe.

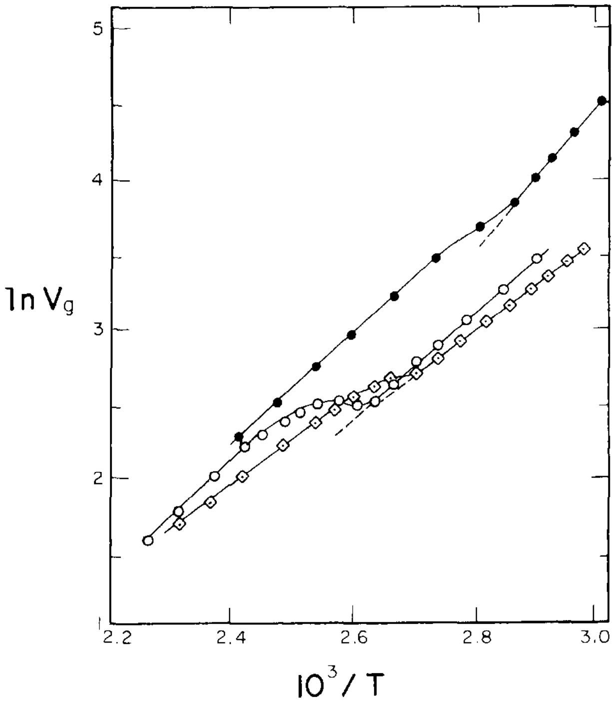

Fig. 7. Retention diagrams of IBMA-22 (●), SMAD-12 (○), and IBMA-22/SMAD-12 1:1 (◇) using benzene as a probe.

tures of the components of the blend, we applied conventional polymer solution theory and determined the apparent χ_{23}(app) values for each SMAD-6/IBMA-10.5, SMAD-12/IBMA-10.5, and SMAD-12/IBMA-22 blends using both benzene and *n*-decane as molecular probes from

$$\chi_{23}(\mathrm{app}) = \frac{1}{\phi_2\phi_3}\left[\ln\left(\frac{V_g(\mathrm{blend})}{W_2v_2 + W_3v_3}\right) - \phi_2\ln\left(\frac{V_{g2}}{v_2}\right) - \phi_3\ln\left(\frac{V_{g3}}{v_3}\right)\right] \tag{3}$$

where v_i and ϕ_i are the specific volume and volume fraction of the polymer *i*, and components 1, 2, and 3 correspond to the probe and the two polymers, respectively.

Tables 1 and 2 summarize the values of these parameters for the SMAD-6/IBMA-10.5 of different ratios. The values of all χ_{23}(app) of SMAD-6/IBMA-10.5 blends, determined in the temperature range of 150–180°C and for the different compositions, using both probes, were positive. This is evidence of the immiscibility of these blends. However, as has often been noted, these values can be a function of the probe. The results obtained also show that the apparent polymer–polymer interaction depends on the composition of the blend. The parameter χ_{23}(app) displays a minimum located around the 1:1 composition ratio for both probes. The decrease of χ_{23}(app) with increasing temperature observed with both molecular probes and for all compositions indicates that miscibility of these blends may be expected at higher temperatures.

Table 1
Measured thermodynamic parameters for SMAD-6, IBMA-10.5, and SMAD-6/IBMA-10.5 of different ratios and benzene at infinite dilution

T/°C		150	160	170	180
SMAD-6	V_g	5.50	5.10	4.60	3.90
IBMA-10-5	V_g	11.50	9.80	8.20	6.40
SMAD-6/IBMA-10.5	V_g	8.50	7.40	6.10	4.90
(2:1)	χ_{23}(app.)	0.954	0.783	0.474	0.343
SMAD-6/IBMA-10.5	V_g	8.30	7.30	6.30	5.10
(1:1)	χ_{23}(app.)	0.233	0.184	0.152	0.124
SMAD-6/IBMA-10.5	V_g	9.70	8.30	7.10	5.60
(1:2)	χ_{23}(app.)	0.381	0.270	0.252	0.172

Table 2
Measured thermodynamic parameters for SMAD-6, IBMA-10.5, and SMAD-6/IBMA-10.5 of different ratios and *n*-decane at infinite dilution

T/°C		150	160	170	180
SMAD-6	V_g	11.50	9.40	7.80	6.40
IBMA-10.5	V_g	36.00	26.80	21.40	17.00
SMAD-6/IBMA-10.5	V_g	23.20	18.20	13.60	11.00
(2:1)	χ_{23}(app.)	1.605	1.550	1.119	1.099
SMAD-6/IBMA-10.5	V_g	21.00	16.00	13.00	10.30
(1:1)	χ_{23}(app.)	0.221	0.120	0.108	0.031
SMAD-6/IBMA-10.5	V_g	26.50	20.30	16.20	12.60
(1:2)	χ_{23}(app.)	0.398	0.382	0.320	0.177

Tables 3 and 4 display the χ_{23}(app) values for the SMAD-12/IBMA-10.5 blends of different ratios. Specific favorable interactions occurring between segments in the two copolymers led to miscible blends as evidenced by the increase of the negative values of the χ_{23}(app), in general, with temperature when benzene is used as the molecular probe. Larger χ_{23}(app) values were observed with *n*-decane, particularly when the acidic copolymer is in excess.

As shown in Table 5, the χ_{23}(app) for SMAD-12/IBMA-22 1:1 ratio confirm the miscibility of this blend. It also appears from these data that the acid–acid associations become more important as the density of acrylic acid within the copolymer increases.

Several reasons have been presented for the probe-to-probe variations in χ_{23}(app), including limitations of the Flory–Huggins theory and the nonrandom partitioning of

Table 3
Measured thermodynamic parameters for SMAD-12, IBMA-10.5, and SMAD-12/IBMA-10.5 of different ratios and benzene at infinite dilution

T/°C		150	160	170	180
SMAD-12	V_g	11.20	8.80	7.20	5.80
IBMA-10.5	V_g	11.50	9.80	8.20	6.40
SMAD-12/IBMA-10.5	V_g	11.00	9.30	7.80	6.50
(1:2)	χ_{23}(app.)	-0.152	-0.063	-0.018	$+0.222$
SMAD-12/IBMA-10.5	V_g	10.00	8.30	6.40	5.70
(1:1)	χ_{23}(app.)	-0.501	-0.438	-0.718	-0.256
SMAD-12/IBMA-10.5	V_g	8.30	7.20	5.40	4.50
(2:1)	χ_{23}(app.)	-1.428	-1.086	-1.524	-1.319

Table 4
Measured thermodynamic parameters for SMAD-12, IBMA-10.5, and SMAD-12/IBMA-10.5 of different ratios and *n*-decane at infinite dilution

T/°C		150	160	170	180
SMAD-12	V_g	22.70	18.40	14.30	11.60
IBMA-10.5	V_g	36.00	26.80	21.40	17.00
SMAD-12/IBMA-10.5	V_g	33.40	25.00	19.80	15.80
(1:2)	χ_{23}(app.)	$+0.378$	$+0.272$	$+0.277$	$+0.265$
SMAD-12/IBMA-10.5	V_g	28.20	21.70	15.80	12.80
(1:1)	χ_{23}(app.)	-0.014	-0.059	-0.372	-0.337
SMAD-12/IBMA-10.5	V_g	20.00	15.80	12.00	9.60
(2:1)	χ_{23}(app.)	-1.256	-1.252	-1.399	-1.431

the molecular probe. Recently, Schreiber and Shi [25] reported that the surface and bulk compositions differ in a polymer blend. Therefore, they determined an effective surface composition corresponding to a given bulk composition. Then they calculated an effective interaction parameter χ_{23}(eff) from the effective surface composition and the apparent specific retention volume of the blend [25]. We have applied this procedure whenever possible; in some cases the specific retention volume of the blend was found to be smaller than that of each constituent of the blend.

Table 6 compares the values of χ_{23}(app) and χ_{23}(eff) of the SMAD-6/IBMA-10.5 blends. Even though the χ_{23}(eff) differed with the nature of the probe, they were positive and decreased with an increase of temperature for both molecular probes and for all compositions of these blends. The results given above show, however, that the χ_{23}(app)

Table 5
Measured thermodynamic parameters for SMAD-12, IBMA-22, and SMAD-12/IBMA-22 (1:1 ratio) and benzene or *n*-decane at infinite dilution

T/°C		V_g(SMAD-12)	V_g(IBMA-22)	V_g(blend) (1:1)	χ_{23}(app.)
150	Benzene	11.20	10.50	9.20	−0.661
	n-Decane	22.70	28.70	25.20	−0.030
160	Benzene	8.80	8.80	7.50	−0.637
	n-Decane	18.40	22.90	20.40	−0.004
170	Benzene	7.20	6.80	6.30	−0.422
	n-Decane	14.30	17.80	16.00	+0.032
180	Benzene	5.80	5.60	5.20	−0.366
	n-Decane	11.60	13.20	12.60	+0.086

Table 6
Apparent and effective polymer–polymer interaction parameters for the SMAD-6/IBMA-10.5 blends
(a) Benzene as the molecular probe

T/°C		150	160	170	180
SMAD-6/IBMA-10.5 (2:1)	χ_{23}(app.)	0.954	0.783	0.474	0.343
	χ_{23}(eff.)	0.325	0.262	0.218	0.168
SMAD-6/IBMA-10.5 (1:1)	χ_{23}(app.)	0.233	0.184	0.152	0.124
	χ_{23}(eff.)	0.335	0.267	0.216	0.164
SMAD-6/IBMA-10.5 (1:2)	χ_{23}(app.)	0.381	0.270	0.252	0.172
	χ_{23}(eff.)	0.294	0.245	0.189	0.152

(b) *n*-Decane as the molecular probe

T/°C		150	160	170	180
SMAD-6/IBMA-10.5 (2:1)	χ_{23}(app.)	1.605	1.550	1.119	1.099
	χ_{23}(eff.)	0.719	0.602	0.582	0.559
SMAD-6/IBMA-10.5 (1:1)	χ_{23}(app.)	0.221	0.120	0.108	0.031
	χ_{23}(eff.)	0.665	0.660	0.629	0.550
SMAD-6/IBMA-10.5 (1:2)	χ_{23}(app.)	0.398	0.382	0.320	0.177
	χ_{23}(eff.)	0.654	0.560	0.525	0.505

Table 7
Apparent and effective polymer–polymer interaction parameters for the SMAD-12/IBMA-10.5 and SMAD-12/IBMA-22 blends with *n*-decane as the probe

T/°C		150	160	170	180
SMAD-12/IBMA-10.5 (1:1)	χ_{23}(app.)	−0.014	−0.059	−0.372	−0.377
	χ_{23}(eff.)	+0.146	+0.105	+0.119	+0.111
SMAD-12/IBMA-10.5 (1:2)	χ_{23}(app.)	+0.378	+0.272	+0.277	+0.265
	χ_{23}(eff.)	+0.128	+0.093	+0.103	+0.072
SMAD-12/IBMA-22 (1:1)	χ_{23}(app.)	−0.030	−0.004	+0.032	+0.086
	χ_{23}(eff.)	+0.048	+0.042	+0.043	+0.020

and χ_{23}(eff) are of the same order of magnitude when benzene is the probe and for IBMA-10.5 compositions in the blend $\geq 50\%$, for which the bulk and the surface compositions were found to be practically the same, while for the same blends, the basic copolymer compositions at the surface were higher than the bulk compositions when *n*-decane is the probe because of the difference in rigidity of the constituents of the blend and their interactions with the probe; the derived χ_{23}(eff) were higher than the χ_{23}(app).

When the basic copolymer is in excess, the acidic copolymer at the surface is dominant with both probes. This led to different values of χ_{23}(app) and χ_{23}(eff). These results agree with the hypotheses of Shi and Schreiber [25].

Table 7 shows the χ_{23}(eff) for the SMAD-12/IBMA-10.5 and SMAD-12IBMA-22 blends when *n*-decane is the molecular probe. The results obtained confirm that the bulk and the surface compositions differ with the chemical nature of the probe. Such important changes may be partially attributed to the specific interactions occurring between the two copolymers.

4. Conclusions

In this contribution, both IGC and DSC techniques confirmed, in the first instance, from the glass transition temperature criterion, the immiscibility of SAA/PIBMA and IBMA-10.5/SMAD-6 blends and the miscibility of IBMA-10.5/SMAD-12 and IBMA-22/SMAD-12 blends. Furthermore, an analysis of the apparent polymer–polymer interaction parameters, χ_{23}(app), as determined by IGC, led to the same conclusions. However, the χ_{23}(app) was found to be dependent on the temperature, the composition of the blend, and the nature of the molecular probe.

Using the Shi and Schreiber procedure [24], the effective interaction parameters showed that the surface and bulk compositions are different and vary with the nature of the probe, mainly as a result of specific interactions between the constituents of the blend.

Acknowledgment

This work was supported by the Air Force Office of Scientific Research Grant No. 95-020.

References

[1] D.R. Paul and S. Newman, Polymer Blends, Academic Press, New York, 1978.
[2] W.H. Jo and H.G. Kim, J. Polym. Sci., Part B, Polym. Phys., 29 (1991) 1579.
[3] J.M.G. Cowie, G. Li, R. Ferguson and I.J.J. McEwen, Polym. Sci., Part B, Polym. Phys., 30 (1992) 1351.
[4] M.K. Neo and S.H. Coh, Polymer, 15 (1992) 3202.
[5] J.M.G. Cowie, M.D. Fernandez, M.J. Fernandez and I.J. McEwen, Polymer, 33 (1992) 2745.
[6] W.H. Jo, C.A. Cruz and D.R. Paul, Polym. Sci., Part B, Polym. Phys., 27 (1989) 1057.
[7] P. Musto, L. Wu, W.J. MacKnight and F.E. Karasz, Polymer, 32 (1991) 3.
[8] M.M. Coleman, J.F. Graf and P.C. Painter, Specific Interactions and the Miscibility of Polymer Blends, Technomic Publishing Co. Inc., Lancaster, PA, 1991.
[9] S. Djadoun, R.N. Goldberg and H. Morawetz, Macromolecules, 10 (1977) 1015.
[10] A. Lassoued and S. Djadoun, Eur. Polym. J., 21 (1985) 669.
[11] D.E. Cherrak and S. Djadoun, Polym. Bull., 27 (1991) 289.
[12] G. ten Brinke, F.E. Karasz and W.J. MacKnight, Macromolecules, 16 (1983) 1827.
[13] J. Kressler, H.W. Kammer, U. Morgenstern, B. Litauszki, W. Berger and F.E. Karasz, Makromol. Chem., 191 (1990) 243.
[14] S. Cimmino, F.E. Karasz and W.J.J. MacKnight, Polym. Sci., Part B, Polym. Phys., 30 (1992) 49.
[15] T. Shiomi, W.J. MacKnight and F.E. Karasz, Macromolecules, 19 (1986) 2274.
[16] G.R. Brannock, J.W. Barlow and D.R. Paul, Polym. Sci., Part B, Polym. Phys., 28 (1990) 871.
[17] D.D. Deshpande, D. Patterson, H.P. Schreiber and C.S. Su, Macromolecules, 7 (1974) 530.
[18] O. Olabisi, Macromolecules, 8 (1975) 316.
[19] Z.Y. Al-Saigh and P. Munk, Macromolecules, 14 (1981) 683.
[20] G. DiPaola-Baranyi, Macromolecules, 14 (1981) 683.
[21] K.K. Chee, Polymer, 31 (1990) 1711.
[22] Z.Y. Al-Saigh and P. Chen, Macromolecules, 24 (1991) 3788.
[23] M.J. El-Hibri, W. Cheng, P. Hattam and P. Munk, ACS Symp. Ser., 391 (1989) 121.
[24] Z.H. Shi and H.P. Schreiber, Macromolecules, 24 (1991) 3522.
[25] Z.H. Shi and H.P. Schreiber, J. Appl. Polym. Sci., 46 (1992) 787.