Blending studies of styrene and α-methyl styrene copolymers: a guide to the segmental interaction parameter

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Blends of both polystyrene and of poly(α-methylstyrene) with poly(styrene-*stat*-α-methyl styrene) samples of varying composition have been studied using differential scanning calorimetry to determine the limits of miscibility with respect to composition and molecular weight. From an analysis of the results a value for the styrene–α-methylstyrene segmental interaction energy density, $B_{\text{S–MS}}$, was determined and compared with other estimates of this quantity. Discrepancies with the results of other workers are discussed in terms of possible solvent effects derived from the blend preparation. Compared to the molecular weight limited miscibility of polystyrene blended with poly(α-methylstyrene), enhanced miscibility of both polystyrene and poly(α-methylstyrene) with the copolymers is demonstrated.

(Keywords: polystyrene; blends; copolymers)

INTRODUCTION

The phase behaviour of polystyrene (PS) and poly(α-methyl styrene) (PAMS) blends has attracted the attention of a number of investigators[1–9]. The system is one in which there is no potential for specific interactions, but there is a close similarity of chemical structures. 'Conditional' compatibility was predicted[3] on the basis of solubility parameters, and indeed the two polymers are found[5] to be miscible up to a molecular weight limit of $70 \times 10^3\ \text{g mol}^{-1}$ for toluene-cast blends, although this is decreased somewhat to $50 \times 10^3\ \text{g mol}^{-1}$ when propylene oxide is employed as the casting agent.

The temperature-induced phase separation of PS–PAMS blends occurs via an upper critical solution demixing process, although investigators[6,8,9] disagree on the precise temperature. These phase boundaries can only be located by extrapolation of the cloud points of ternary mixtures of the two polymers and a solvent, and this may exert an effect on the exact position of the boundary. The influence of the solvent has been discussed by Saeki *et al.*[5] in terms of the so-called $\Delta\chi$ effect.

On a simplistic argument of predicting an increase in miscibility with closer values of the solubility parameters for each component, it is expected that copolymers of styrene with α-methyl styrene (SMS copolymers) should show enhanced miscibility with either PS or PAMS, and this should be evidenced by higher molecular weight limits of miscibility. Such a possibility is explored in this paper. Additionally, focusing on blends of copolymers introduces a means of deriving the segmental interaction parameters B_{ij} which describe the thermodynamic state of the blend. In the general case of two copolymers $A_xB_{1-x} + C_yD_{1-y}$, these are embodied in the expression[10–12]:

$$B_{\text{blend}} = xyB_{\text{AC}} + (1-x)yB_{\text{BC}} + x(1-y)B_{\text{AD}} + (1-x)(1-y)B_{\text{BD}} - x(1-x)B_{\text{AB}} - y(1-y)B_{\text{CD}} \qquad (1)$$

where x and y define volume fraction compositions and B_{blend} is the interaction energy density in the Flory–Huggins sense[13]. The particular system we investigate here is that of a homopolymer plus a copolymer with a common segment, $A + A_yB_{1-y}$, where, more simply:

$$B_{\text{blend}} = (y-1)^2B_{\text{AB}} \qquad (2)$$

At any phase boundary B_{blend} attains its critical value which is given in terms of the molar volumes (V_i) of the blend components 1 and 2 by:

$$B_{\text{crit}} = 0.5RT(V_1^{-0.5} + V_2^{-0.5})^2 \qquad (3)$$

From the experimentally observed phase behaviour of binary blends of PS or PAMS with SMS copolymers, determined as a function of either molecular weight (i.e. molar volume) or copolymer composition (y), it is possible to deduce a value for the styrene–α-methyl styrene segmental interaction parameter $B_{\text{S–MS}}$.

EXPERIMENTAL

Monodisperse standard polystyrenes were obtained from Polysciences and Dow Chemical Co. One polydisperse PS sample was obtained from BDH. Two monodisperse PAMS standards from Polysciences and one polydisperse PAMS sample from Aldrich were used. The polydisperse samples were reprecipitated prior to measurements. Homopolymer details are in *Table 1*.

Commercial styrene (S) and α-methyl styrene (MS) monomers were freed from inhibitor and distilled under

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Table 1 Homopolymer sample molecular weights, molar volumes and glass transition temperatures

Sample	Origin[a]	10^3M_n (g mol^{-1})	10^3M_w (g mol^{-1})	10^3V (cm^3 mol^{-1})	T_g (K)
PS61	a	59	61	52	376
PS79	a	75	79	65	377
PS113	b	114	216	99	376
PS267	c	247	267	216	378
PS400	a	377	400	330	377
PS575	a	542	575	474	379
PS900	a	818	900	716	377
PAMS49	d	–	113	104[b]	441
PAMS400	a	381	400	352	444
PAMS700	a	636	700	588	435

[a] a, Polysciences; b, BDH Chemicals; c, Dow Chemical Co; d, Aldrich
[b] From M_w

Table 2 Copolymer sample molecular weights, compositions, molar volumes and glass transition temperatures

Sample	10^3M_n (g mol^{-1})	10^3V (cm^3 mol^{-1})	Composition mol% MS	Composition vol% MS	M_w/M_n	T_g (K)
SMS3	13	11	3	4	1.9	380
SMS16	62	55	15	17	2.2	388
SMS20	91	80	18	21	2.1	390
SMS25	62	55	23	26	2.1	392
SMS32	59	53	30	34	2.1	403
SMS33	78	70	31	35	2.1	400
SMS36	60	53	34	38	2.1	403
SMS44	21	19	41	45	1.8	409
SMS48	44	39	45	50	1.9	413
SMS51	35	31	48	53	2.1	421
SMS60	56	51	57	61	2.0	413
SMS65	17	15	63	67	–	–
SMS67	115	104	64	68	2.2	434
SMS71	50	46	69	73	2.9	433
SMS97	146	135	97	97	2.1	437

a reduced pressure of nitrogen. Methylene dichloride was distilled from calcium hydride and then from triisobutylaluminium under nitrogen. SMS copolymer samples were prepared by cationic polymerization in methylene dichloride using boron trifluoride–diethyl ether complex as catalyst at 198–233 K under nitrogen. Copolymer compositions were determined using *FT*i.r. spectroscopy based on a calibration curve drawn up from homopolymer blends. The bands at 1238 cm^{-1} and 907 cm^{-1}, due to PS and PAMS respectively, were used. Molecular weights, in terms of polystyrene equivalents, were measured using size exclusion chromatography, employing tetrahydrofuran as solvent. Sample designations, compositions and glass transitions (T_g) are listed in *Table 2*. The molar volumes shown are obtained from the number average molecular weights via copolymer densities estimated from group additivity[14].

Blends of PS and of PAMS with SMS samples were obtained by codissolving the components in toluene followed by precipitation into methanol. The precipitated blends were dried at 333 K under vacuum for at least 24 h. A Perkin Elmer DSC-2 differential scanning calorimeter was used to determine the glass transition behaviour of the blends. Samples were scanned at 20 K min^{-1} between 303 K and 463 K until reproducible behaviour was obtained; typically three or four cycles were required to achieve this constant response. The appearance of a single T_g was taken as the criterion for blend miscibility. Further annealing of the samples at the upper temperature limit caused no further changes in phase behaviour.

DISCUSSION

Experimental results

The blends are examined in two groups: polystyrene plus SMS copolymers with greater than 50% MS, and poly(α-methylstyrene) plus SMS copolymers with less than 50% MS. *Figures 1* and *2* show the results for the former, and *Figures 3* and *4* the results for the latter. As noted above, blends of PS and PAMS are expected to be two-phase when the molecular weights of the components exceed 70 × 10^{-3} g mol^{-1}, but with PS113 (113 × 10^3 g mol^{-1}) and SMS67 (115 × 10^3 g mol^{-1}) this limit is increased and single-phase behaviour is found over the entire composition range (*Figure 1*). Further increasing the molecular weight of the PS component to

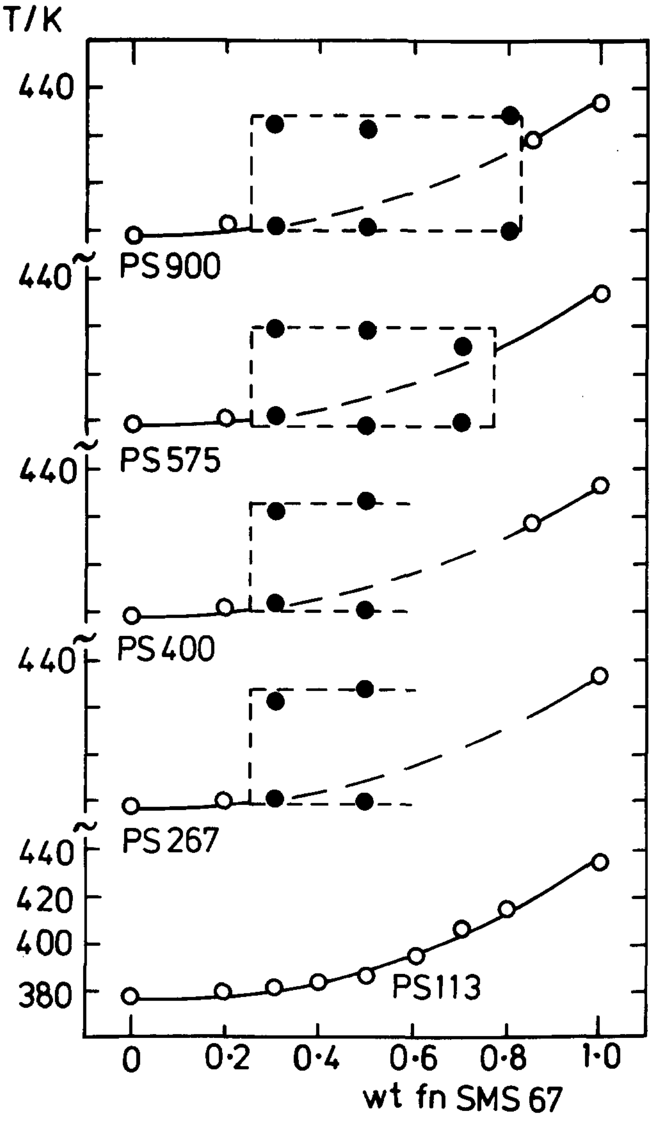

Figure 1 The glass transition values for SMS67–PS blends as a function of blend composition. PS codes are indicated on the figure and the temperature scale is displaced for each blend. Broken lines outline the two-phase composition regions

267×10^3 g mol^{-1}, and greater, results in phase-separated blends.

Figure 2 represents the effect of PS molecular weight and the MS copolymer composition at a blend ratio of 50% by weight of each component. Quite a number of phase boundaries are contained in this figure and each may be subjected to the analysis outlined in the introduction. Again it illustrates the enhanced miscibility of SMS copolymers and PS. For example, SMS71 will form a single-T_g blend with molecular weights up to 400×10^3 g mol^{-1}, and SMS60 appears to represent the composition at which miscibility is unlimited, at least up to the highest PS molecular weight sample available in this study.

The data for SMS25 in *Figure 3* indicate restricted miscibility with PAMS400; however, the PAMS113 sample does show single T_g behaviour over the whole composition range. Parallel behaviour is exhibited in *Figure 4*, at the fixed blend combination of 50 wt%, with the SMS16, SMS20 and SMS33 samples. SMS36 locates the composition limit for unrestricted miscibility with the PAMS samples here.

The extraction of a value for a segmental interaction using such data assumes the phase boundary to lie between the limits defined by an adjacent miscible and immiscible pair. Averaged values of the molecular weight and composition would then be appropriately inserted into equations (2) and (3). Given closely defined data (usually involving a large degree of luck or a large number of samples!) this is quite satisfactory. Although our data do contain several such satisfactory points, we have chosen to adopt a slightly different approach.

Data analysis

Any pair of adjacent one-T_g and two-T_g points in *Figures 2* and *4* represents blends where the values of B_{blend} are respectively below and above the critical value B_{crit} for phase separation. The adjacent points may vary

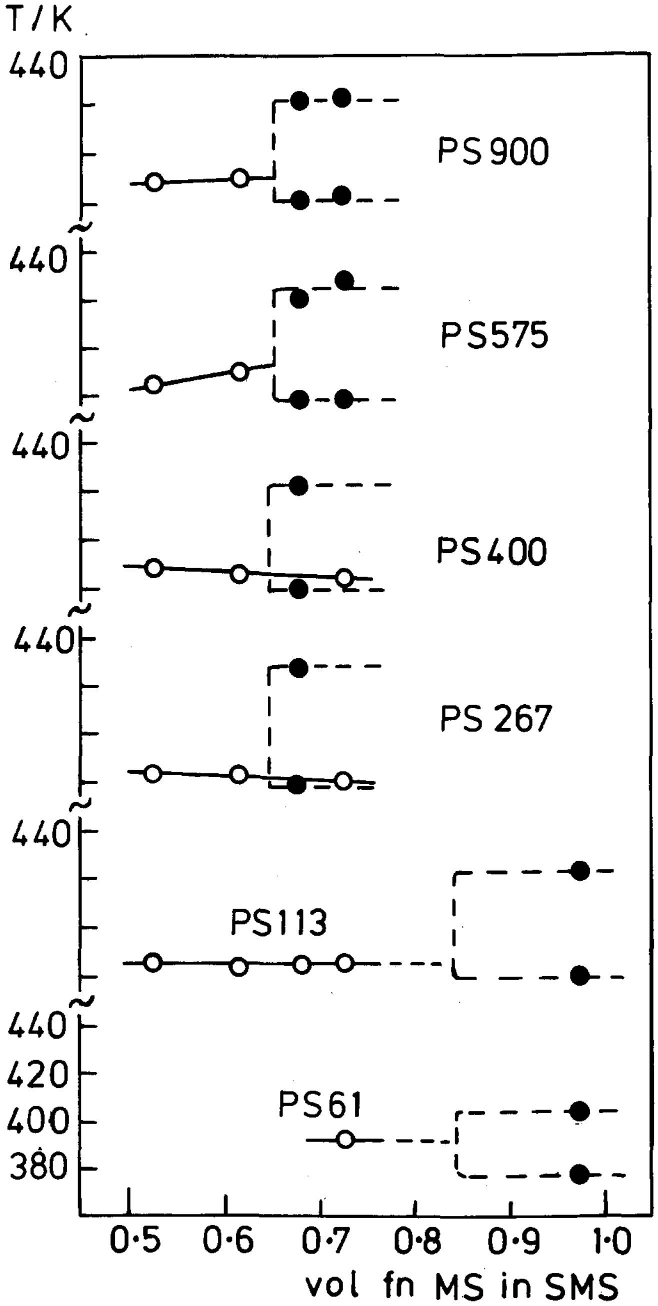

Figure 2 The glass transition values for SMS–PS blends at a fixed 50/50 weight composition. PS codes are indicated on the figure and the temperature scale is displaced for each PS sample used. The broken lines indicate two-T_g behaviour, full lines the single-T_g behaviour

in SMS composition at constant PS molecular weight (*Figure 2*), or constant PAMS molecular weight (*Figure 4*). Alternatively they may be the same SMS sample but blended with two different PS (or two different PAMS) samples. In the former case change in composition, and in the latter, change in molecular weight, has brought about the change from miscibility to immiscibility. In either instance equation (3), evaluated for such pairs of samples, gives the possible maximum and the possible minimum value for the B_{crit} operating in this situation. Equating these limits of B_{crit} with B_{blend}, and evaluating the segmental interaction energy density via equation (2) with the appropriate composition values, yields an estimate of the range within which B_{S-MS} lies.

As an example, *Figure 2* shows SMS71 miscible with PS400 but immiscible with PS575. If phase separation occurred close to the molecular weight of PS400 then $B_{crit} \sim 0.051$ J cm^{-3}; alternatively, if the phase boundary is located close to the molecular weight of PS575, then $B_{crit} \sim 0.045$ J cm^{-3}. For SMS71, $(1-y) = 0.73$ and, applying equation (2), B_{S-MS} lies in the range 0.096–0.084 J cm^{-3}.

In total, ten phase boundaries are located in *Figure 2* and ten in *Figure 4*. By no means all are as closely defined as the example selected and this may be seen from *Figure 5*, which displays all the B_{S-MS} ranges obtained. As argued above, B_{S-MS} should lie commonly within each of these ranges and it is indeed the case that all encompass the values shown by the hatched band in the figure. This band is also gratifyingly coincident with the best defined of the data and allows us to conclude a value for the

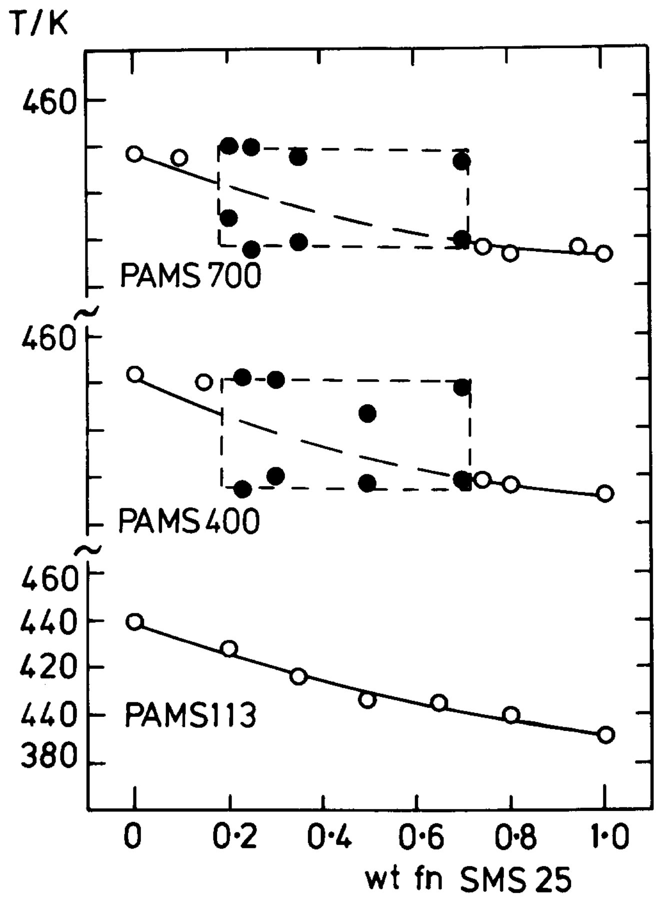

Figure 3 The glass transition values for SMS25–PAMS blends as a function of blend composition. PAMS codes are indicated on the figure and the temperature scale is displaced for each blend. Broken lines outline the two-phase composition regions

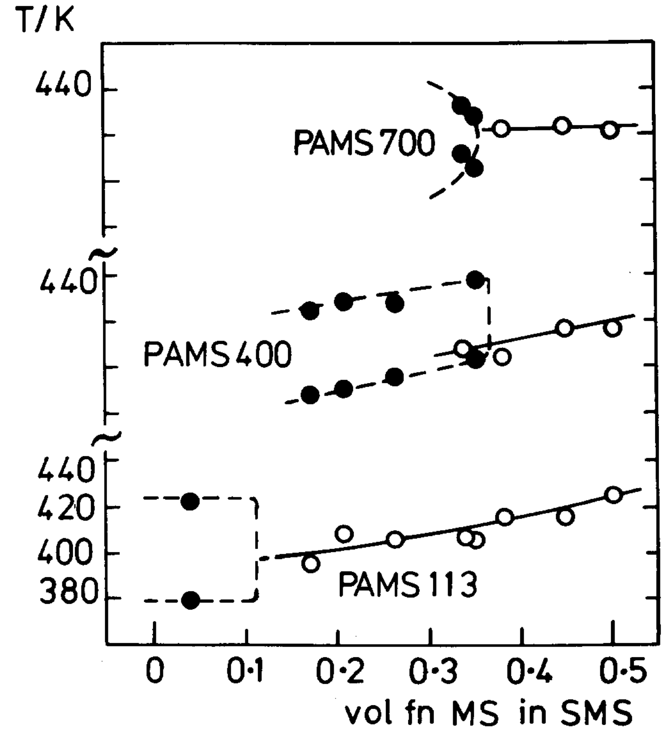

Figure 4 The glass transition values for SMS–PAMS blends at a fixed 50/50 weight composition. PAMS codes are indicated on the figure and the temperature scale is displaced for each PAMS sample used. The broken lines indicate two-T_g behaviour, full lines the single-T_g behaviour

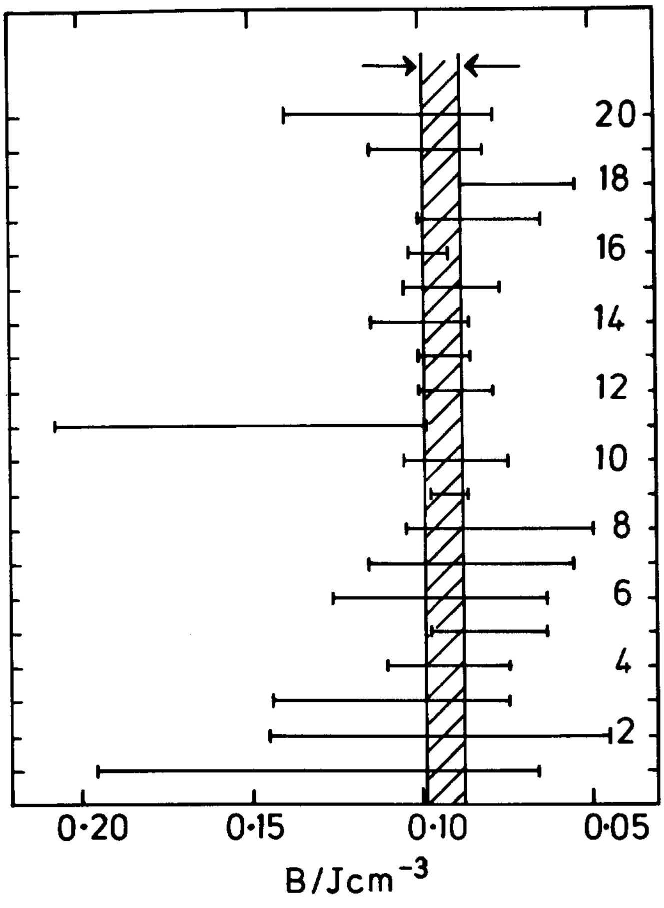

Figure 5 The ranges of the B_{S-MS} values calculated as described in the text for each of the phase boundaries in *Figures 2* and *4*. These may be identified by the numbers on the figure and the key given in *Table 3*

Table 3 Key to the blend pairs from which the B_{S-MS} values shown in *Figure 5* are derived

Number	Miscible blend	Immiscible blend
1	PS61 + SMS71	PS61 + SMS97
2	PS113 + SMS71	PS113 + SMS97
3	PS267 + SMS60	PS267 + SMS67
4	PS267 + SMS71	PS267 + SMS67
5	PS400 + SMS71	PS400 + SMS67
6	PS400 + SMS60	PS400 + SMS67
7	PS575 + SMS60	PS575 + SMS67
8	PS900 + SMS60	PS900 + SMS67
9	SMS71 + PS400	SMS71 + PS575
10	SMS67 + PS113	SMS67 + PS267
11	PAMS113 + SMS16	PAMS113 + SMS3
12	PAMS400 + SMS32	PAMS400 + SMS25
13	PAMS400 + SMS32	PAMS400 + SMS33
14	PAMS400 + SMS36	PAMS400 + SMS33
15	PAMS700 + SMS33	PAMS700 + SMS36
16	SMS32 + PAMS400	SMS32 + PAMS700
17	SMS16 + PAMS113	SMS16 + PAMS400
18	SMA20 + PAMS113	SMS20 + PAMS400
19	SMS25 + PAMS113	SMS25 + PAMS400
20	SMS33 + PAMS113	SMS33 + PAMS400

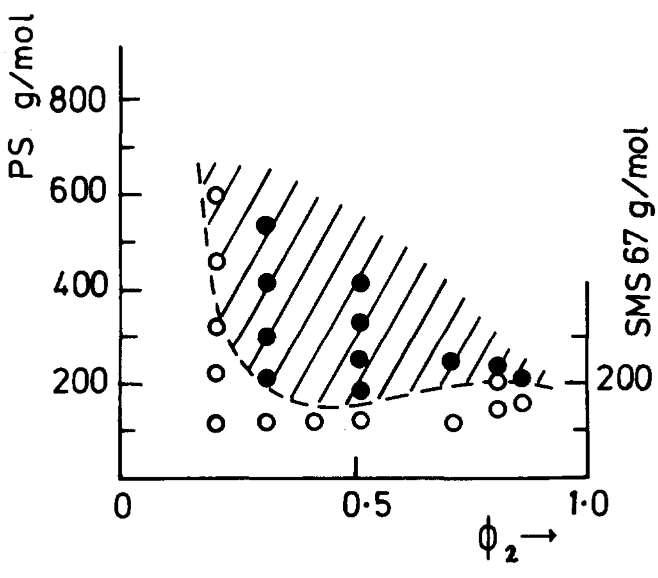

Figure 6 Phase diagram as a function of volume fraction SMS67 (ϕ_2) and SMS67/PS molecular weights for SMS67–PS blends: (○) one-phase blend; (●) two-phase blend. Binodal (------) calculated with $B_{S-MS} = (0.093–0.043\phi_2)$ J cm^{-3} as described in text

segmental interaction B_{S-MS} of 0.087–0.098 J cm^{-3} on the basis of these phase studies.

Figures 6 and *7* show blend behaviour, as a function of molecular weight and composition, drawn from the data in *Figures 1* and *3* where the two-phase regions have been delineated along 'tie-lines' between the sample molecular weights as described previously[5]. Using the familiar expression[13]:

$$\Delta\mu_i = RT\{\ln \phi_i + \phi_j(1 - V_i/V_j)\} + V_i\phi_j^2 B_{ij} \quad (4)$$

for the change in the chemical potential $\Delta\mu_i = (i = 1, 2; j = 2, 1)$, and applying the usual condition of equality of chemical potential in each phase at equilibrium, phase boundaries as a function of blend composition (ϕ_2) and molecular weight may be determined by standard non-linear methods. In the present case $B_{ij} = B_{\text{blend}}$ as given by equation (2). We found it impossible adequately to reproduce the data using a composition independent B_{S-MS}; the two-phase regions calculated as shown in *Figures 6* and *7* were obtained using an empirical linear composition dependent $B_{\text{blend}} = B_0 + B_1\phi_2$ and replacing the second term on the right-hand side of equation (4) with $V_i\phi_j^2(B_{ij} - \phi_i \partial B_{ij}/\partial\phi_j)$.

The range of B_{S-MS} required to fit the data (see captions to the figures) is somewhat greater than the estimate from *Figure 5* and this hints at a limitation inherent in adopting the framework of the lattice theory. Neutron scattering studies well illustrate that the interaction parameter is more properly formulated as a function of composition and temperature, and possibly molecular weight also[15]. Strictly then, the analysis presented here gives a value appropriate to the annealing temperature of the blends and for 50/50 compositions. However, as pointed out by ourselves[16] and others[17], the general approach adopted here has the double virtue of simplicity with utility, since the data are segment-based and not polymer-specific. With an appropriate data base of B_{ij} values, equation (1) (which in itself embodies the single liquid approximation of Scott[18]) can usefully describe the blending behaviour to be expected from a copolymer pair.

Free volume approach

The value obtained above compares sensibly with $B_{S-MS} \sim 0.08$ J cm^{-3} estimated from solubility parameters[6,19] via:

$$B_{ij} = (\delta_i - \delta_j)^2 \quad (4)$$

An alternative estimate is based on the experimental phase boundaries for PS–PAMS homopolymer blends already determined[5]. Application of the Flory free volume approach[20,21] to these data yielded[6] values for the characteristic contact interaction parameter X_{12} and the interaction entropy parameter Q_{12}. The relevant equation of state data are available from our previous publication[6] and the reduced residual chemical potential of the mixture is identified with the interaction energy density through equation (5)[22]:

$$\begin{aligned} B_{12} = {} & (p_1^*/\phi_2^2)\{3T \ln[(v_1^{1/3} - 1)/(v^{1/3} - 1)] \\ & + (1/v_1 - 1/v)\} + (X_{12}\theta_2^2)/(v\phi_2^2) \\ & + (TQ_{12}\theta_2^2)/(\phi_2^2) \end{aligned} \quad (5)$$

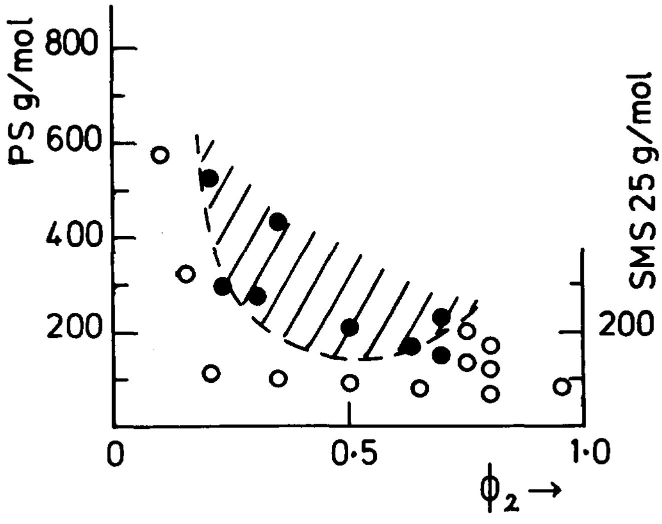

Figure 7 Phase diagram as a function of volume fraction SMS25 (ϕ_2) and SMS25/PAMS molecular weights for SMS25–PAMS blends: (○) one-phase blend; (●) two-phase blend. Binodal (------) calculated with $B_{S-MS} = (0.128–0.069\phi_2)$ J cm^{-3} as described in text

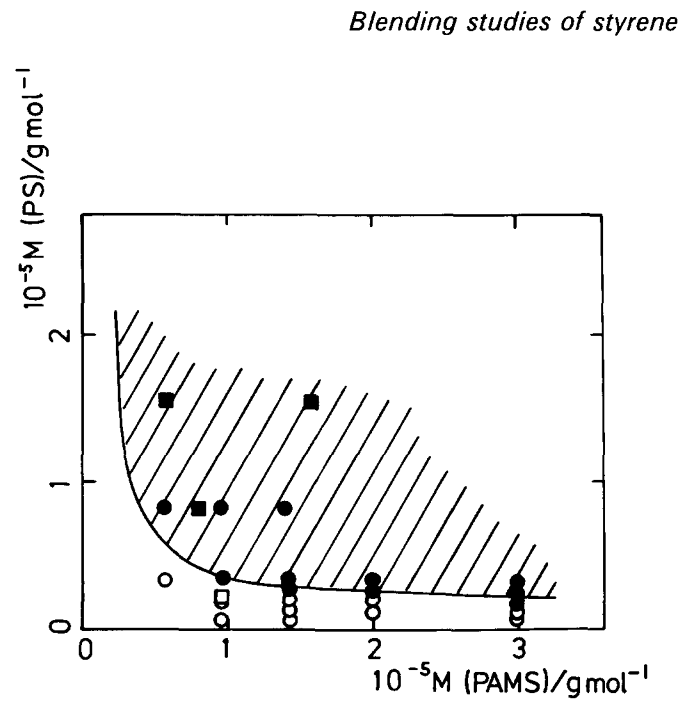

Figure 8 Phase diagram as a function of PS and PAMS molecular weight for 50/50 PS–PAMS homopolymer blends: (○), (●) one-phase and two-phase blends respectively from ref. 7; (□), (■) one-phase and two-phase blends from ref. 5. Full line calculated with $B_{\text{S–MS}} = 0.094$ J cm^{-3}

where p_1^* is the pressure reduction parameter and v_1 is the reduced volume for species 1 (PS); v is the reduced volume of the mixture with ϕ_2 and θ_2 respectively volume and segment fractions of species 2 (PAMS). Evaluating (5) with $v_1 = 1.153$, and with ϕ_2 set to 0.5, gives $B_{\text{S–MS}} = 0.090$ J cm^{-3}. This is in good agreement with the present estimate and satisfactorily ties together our formerly determined PS–PAMS phase behaviour with those described here.

Comparison with other data

Widmaier and Mignard[7] suggest that low molecular weight PS is miscible with PAMS over a wider range of molecular weights than predicted by the lattice theory. These authors also conclude that their data is somewhat at variance with our earlier phase boundaries[5]. However, we believe that they have misinterpreted these since they are not directly comparable with their form of presentation. *Figure 8* reproduces their tabulated data (which puzzlingly excludes points given on their phase diagram), along with our own PS–PAMS data. The phase boundary is given by equation (3) with $B_{\text{crit}} = 0.094$ J cm^{-3} and is a quite reasonable description of all the data points. Admittedly the low PS–high PAMS region would be better delineated with $B_{\text{S–MS}} \sim 0.13$ J cm^{-3}, somewhat higher than our estimate.

Lin and Roe[8] have employed an empirical temperature and composition dependence of the PS–PAMS interaction energy density in order to fit binodal data extrapolated from dibutyl phthalate solutions of the two polymers. Their data suggest a value of $B_{\text{S–MS}} \sim 0.045$ J cm^{-3} is appropriate in this case. It is tempting to propose the reason for the obvious discrepancy with the value determined here may lie in the solvent employed; the present, previous[5,6] and Widmaier and Mignard's[7] studies are based on toluene- or benzene-cast blends and are certainly more comparable on this basis. However in a second publication[9] these authors apply essentially the same dependence to binodal curves determined for melt-blended samples by interpretation of detailed changes in the blend thermograms, as a function of annealing time and temperature, in terms of progressive demixing.

This forces us to address the eternal question accompanying the use of the d.s.c. technique to determine phase behaviour. The state of the glass is undoubtedly revealed, but does this represent the blend 'as prepared' or the blend as quenched from a temperature above T_g? We have examined the effect of annealing PS–PAMS toluene-prepared samples in our own laboratory and have failed to observe any changes in the thermal responses that would indicate demixing. On the contrary, for miscible combinations, annealing appears to narrow the glass transition region, pointing to more intimate mixing.

We conclude that the state of mixing of toluene-cast blends of styrene and α-methyl styrene homopolymers and copolymers is determined by molecular weight and copolymer composition. The value of the segmental interaction energy density, $B_{\text{S–MS}}$, is estimated as 0.087–0.098 J cm^{-3}.

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