Thermochimica Acta, 195 (1992) 351–364
Elsevier Science Publishers B.V., Amsterdam

Miscibility study of the alternating copolymers of α-methylstyrene with maleimides in blends with PS, PPO or sulphonylated PPO

R. Vuković, V. Kurešević, G. Bogdanić and D. Fleš

INA-Industrija nafte, Research and Development, Proleterskih brigada 78, Zagreb, Croatia (Yugoslavia)

(Received 7 June 1991)

Abstract

The miscibility of alternating copolymers of α-methylstyrene (αMeS) and maleimides (RMI; R=H, Me, Ph) in the blends with polystyrene (PS), with poly(2,6 dimethyl-1,4-phenylene oxide) (PPO) and with sulphonylated PPO (SPPO) copolymers of different degrees of sulphonylation was studied by differential scanning calorimetry (DSC) and by visual observation of film clarity. It was found that miscibility in these systems depends on the chemical structure of the blend components. Immiscibility was found for all alternating copolymer blends with PS and with PPO. The miscibility/immiscibility behaviour in the blends of SPPO with alternating copolymers depends on the degree of sulphonylation of SPPO copolymers as well as on the chemical structure of αMeS–RMI copolymers. High-temperature phase separation in the miscible blends is a function of the degree of sulphonylation of SPPO and blend composition. The results can be explained on the basis of the mean field theory of phase behaviour for copolymer-copolymer systems.

INTRODUCTION

In recent years the study of polymer blends has led to the discovery of a number of miscible polymer pairs. In a series of publications the miscibility and phase separation behaviour of blends of homopolymers and random copolymers of halogen- and methyl-substituted styrene derivatives with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) [1–14], with sulphonylated poly(2,6-dimethyl-1,4 phenylene oxide) (SPPO) [13,15,16] and with polystyrene (PS) [13,17–20] has been studied extensively. It was found that relatively small changes in the chemical structure of any blend component has significant influence on the miscibility behaviour. It was also found that specific interactions are not always necessary for miscibility. These phenomena can be explained by a mean field treatment [10,11].

Recently the miscibility behaviour in blends of two random copolymers with four distinct repeat units was also studied [15,16]. However, as far as we know, no studies on blends of random copolymers with alternating copolymers have been reported. The present paper reports our results on the miscibility and phase behaviour in blends of one alternating and one random copolymer, i.e. α-methylstyrene (αMS) and maleimides (RMI; R=H, Me, Ph), with sulphonylated PPO copolymers of different degrees of sulphonylation and the miscibility of alternating copolymers with PS and with PPO. The behaviour of the initially miscible blends has also been examined at higher temperatures. The miscibility and phase separation phenomena in the present work are based on differential scanning calorimetry (DSC) measurements and visual observation of film clarity.

EXPERIMENTAL

Materials

Alternating copolymers of αMeS with RMI (R = H, Me, Ph) of high molecular weights were prepared by solution polymerization using, 2,2′-azobis(isobutyronitrile) (AIBN) as initiator. Copolymerization was performed in vacuum-sealed 10 ml glass vials which are thoroughly degassed, filled with purified nitrogen before sealing and placed in an oil bath thermostated to 60 ° C . The polymerization was performed in chloroform or toluene in 1 :1 monomer : monomer ratio. After the required reaction time, the vial was removed from the bath and cooled down; the viscous solution was diluted with chloroform and precipitated with methanol, yielding a white powdery product. The precipitated polymer was filtered off and dried in vacuum at 70 ° C overnight.

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), General Electric Co. ($\overline{M}_w$, 35 000; $\overline{M}_n$, 17 000) was purified before use by precipitation in excess methanol from a dilute toluene solution, and was dried under vacuum at 80 ° C for 60 h.

Polystyrene (PS), Monsanto Co. ($\overline{M}_w$, 280 000; $\overline{M}_n$ 120 000) was purified before use in the same manner as PPO.

Sulphonylated PPO copolymers of different degrees of sulphonylation were prepared by Fiedel–Crafts sulphonylation of PPO. The electrophilic substitution reactions were carried out in nitrobenzne solution in the presence of $AlCl_3$, under nitrogen at temperatures ranging from 45 to 80 ° C [21,22]. After the required reaction time, the $AlCl_3$ complex was destroyed by adding the reaction mixture to methanol acidified with HCl. The precipitated polymer was filtered off, washed with additional acidified methanol and water, and then vacuum dried to constant weight. The degree of sulphonylation was determined by elemental analysis and from the data of NMR spectra. The thermal behaviour of the polymers was analysed by DSC and TGS methods.

Polymer blends were prepared by dissolving appropriate quantities of the pure components in toluene, chloroform or dimethylformamide, and

TABLE 1

Characterization of alternating copolymers of αMeS with maleimides and sulphonylated PPO copolymers

Sample [a]	T_g (K)	Mol.wt. × 10^{-4}		
		$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
Poly(αMeS-co-MI)	574	2.97	1.82	1.6
Poly(αMeS-co-MeMI)	523	11.7	6.26	1.9
Poly(αMeS-co-PhMI)	543	14.2	7.85	1.8
SPPO 4	495	3.93	1.47	2.67
SPPO 7	497	4.35	2.1	2.07
SPPO 11	509	4.40	1.40	3.14
SPPO 19	520	4.81	1.78	2.70
SPPO 27	527	5.20	1.60	3.25
SPPO 39	537	6.10	2.10	2.90
SPPO 47	541	5.78	2.0	2.89
SPPO 55	544	5.93	1.90	3.12
SPPO 64	554	6.20	2.50	2.48
SPPO 68	558	7.10	2.48	2.86
SPPO 75	565	7.30	2.45	2.97
SPPO 87	574	7.20	2.10	3.43
SPPO 92	579	7.85	2.30	3.41

[a] Numbers with SPPO indicate mol.% of sulphonylated PPO in copolymer.

precipitating the solution into a large excess of methanol. Blends were dried at 100 °C in vacuum for 60 h. The dried blends were used in DSC experiments. For visual observation of film clarity, thin films were prepared by casting the polymer solutions onto a cover glass and evaporating the solvent.

Physicochemical measurements

The copolymer composition was determined by NMR spectroscopy on a Varian EM 390 spectrometer.

Glass transition temperature (T_g) measurements of polymers and polymer blends were carried out using a Perkin–Elmer DSC-2 at a heating rate of 20 °C min^{-1} in nitrogen. T_g was taken as the inflection point of the ΔC_p.

Thermogravimetric measurements were made on a Perkin–Elmer TGS-2 thermobalance at a heating rate of 10 °C min^{-1} with nitrogen purge.

Molecular weights were determined by GPC on a Waters instrument using a μ-Styrogel column and Varian 8500 pump with THF as solvent at 25 °C with PS reference.

T_g and molecular weight values of the copolymers are listed in Table 1.

RESULTS AND DISCUSSION

Thermal stability of polymers and polymer blends

Blends of PS, PPO and SPPO with alternating copolymers of αMeS with maleimides (RMI;R = H, Me, Ph) are thermostable polymers with T_g values up to 580 K. Initially miscible polymer blends were annealed at temperatures up to 583 K, and the thermal stability of pure components and polymer blends was evaluated by TGA. The samples were pre-dried at 473 K for 5 min in the TGA furnace in order to remove traces of absorbed water, and the experiments were then performed in two steps. Pure components and copolymer blends were first heated from 323 to 590 K and the sample weight loss was determined; in the second experiment the initially miscible blends were annealed at 553, 568 and 583 K respectively for 15 min.

In the first step it was found that the observed weight loss of the pure components was nearly independent of the type of copolymer. For the alternating copolymers of αMeS with RMI, the weight loss was less than 0.2% at 553 K and between 0.2% and 0.4% at 583 K. The thermal stability of PPO was practically independent of the degree of sulphonylation, in agreement with the observation made by Kang [15]. The obtained weight loss at 553 K was less than 0.2% and between 0.2% and 0.4% at 583 K when the degree of sulphonylation of PO was changed from 4 to 92 mol.%. Alternating copolymers RMI/SPPO blends of different degrees of sulphonylation were found to experience a loss of less than 0.3% at 553 K, and between 0.4% and 0.6% at 583 K. In another series of experiments it was found that the weight loss of initially miscible poly(αMeS–co–PhMI)/SPPO blends (Table 2) was between 0.4% and 0.5% at 553 K, between 0.5% and 0.8% at 568 K and less than 1% at 583 K.

Miscibility of alternating copolymers with PS and with PPO

Alternating poly(αMeS–co–RMI) (R = H, Me, Ph) / PS blends

Figure 1 shows the DSC thermograms of 50/50 wt.% poly(αMeS–co–MI)/PS, poly(αMeS–co–MeMI)/PS and poly(αMeS–co–PhMI)/PS blends. It can be seen that all of these polymer blends exhibit two T_g values which are close to those of the pure components and are, therefore, considered immiscible.

Alternating poly(αMeS–co–RMI) (R = H, Me, Ph) / PPO blends

Poly(αMeS–RMI) copolymers in the blends with PPO also show two T_g values in the DSC thermograms, as can be seen in Fig. 2.

TABLE 2

Influence of the degree of sulphonylation of SPPO copolymers on the miscibility behaviour in the blends with α-methylstyrene–maleimides copolymers

Alternating copolymers	SPPO copolymers [a] T_g (K)		Polymer blends, T_g (K)			
			As precipitated		Annealed 15 min at	
			1st run	2nd run	553 K	583 K
Poly(αMeS–co–MI)	SPPO 4	459	502,574	498,574		
$T_g = 574$ K	SPPO 11	509	508,575	508,575		
	SPPO 19	520	523,574	521,574		
	SPPO 27	527	527,574	527,574		
	SPPO 39	537	536,575	536,575		
	SPPO 47	541	542,575	543,575		
	SPPO 55	544	545,547	545,547		
	SPPO 64	554	555,574	554,574		
	SPPO 68	558	558,574	558,574		
	SPPO 75	565	565 [b]	565 [b]		
	SPPO 87	574	573 [b]	573 [b]		
	SPPO 92	579	575 [b]	575 [b]		
Poly(αMeS–co–MeMI)	SPPO 4	495	501,515	495,519		
T_g·523 K	SPPO 7	497	505,517	500,519		
	SPPO 11	509	513,521	519,520		
	SPPO 19	520	520 [b]	520	520	
	SPPO 27	526	527 [b]	527	527	
	SPPO 39	537	533	523,538		
	SPPO 47	541	535	523,541		
	SPPO 55	544	536	523,544		
	SPPO 64	554	537	523,553		
	SPPO 68	558	537	523,557		
	SPPO 75	565	538	523,565		
	SPPO 87	574	539	523,570		
	SPPO 92	579	540	523,574		
Poly(αMeS–co–PhMI)	SPPO 4	495	500,540	495,543		
$T_g = 543$ K	SPPO 11	509	512,543	508,543		
	SPPO 19	520	535	523,543		
	SPPO 27	527	536	536	536	536
	SPPO 39	537	541	541	541	541
	SPPO 47	541	541	541	541	541
	SPPO 55	544	544	544	544	544
	SPPO 64	554	549	550	550	550
	SPPO 68	558	551	551	551	551
	SPPO 75	565	553	553	553	553
	SPPO 87	574	556	556	556	556
	SPPO 92	579	560	560	560	560

---

[a] Numbers with SPPO indicate mol.% of sulphonylated PPO in copolymer.

[b] Owing to the small difference between the T_gs of the copolymers, two separated T_g were not obtained for immiscible blends.

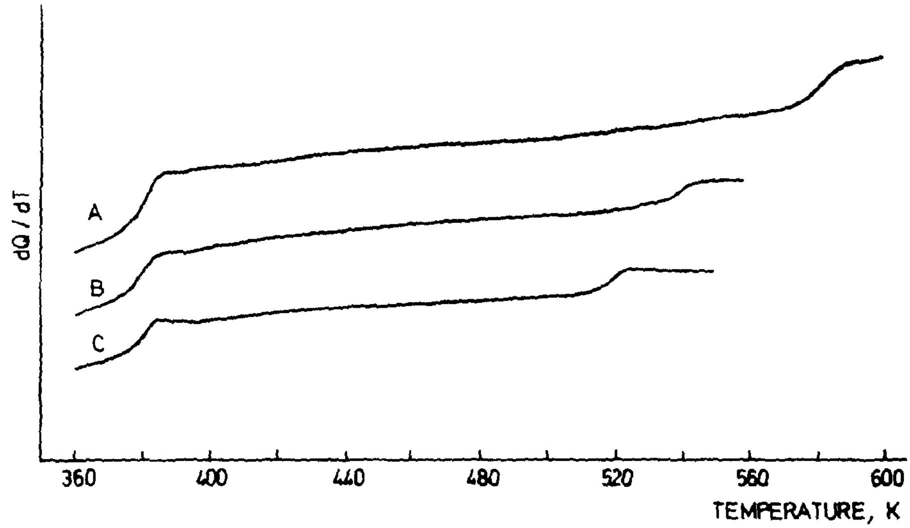

Fig. 1. DSC thermograms of 50/50 wt.% of alternating poly(αMeS–co–RMI) (R = H, Me, Ph)/PS blends: A, MI; B, PhMI; C, MeMI.

Miscibility of alternating poly(αMeS–co–RMI) (R=H, Me, Ph) / SPPO blends

The miscibility of alternating αMeS–RMI copolymers with SPPO was also studied. It was found that miscibility depends on the alternating copolymer structure as well as on the degree of sulphonylation of the SPPO copolymers which varied from 4 to 92 mol.%.

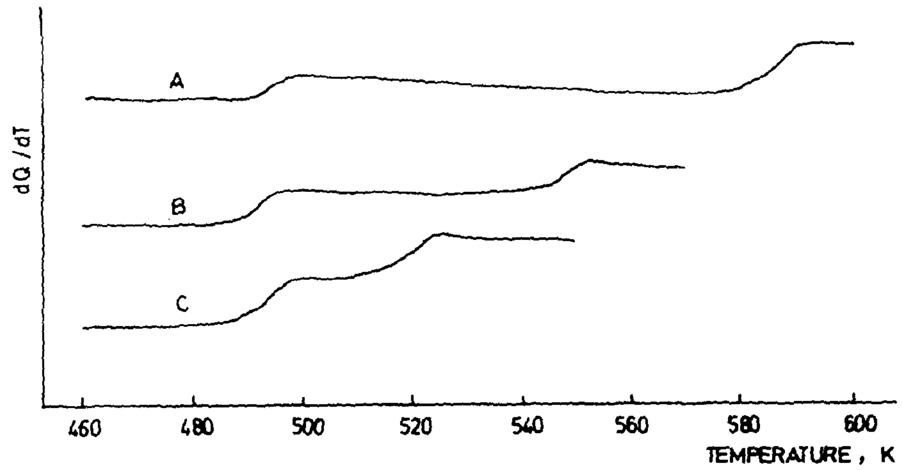

Fig. 2. DSC thermograms of 50/50 wt.% of alternating poly(αMeS–co–RMI) (R = H, Me, Ph)/PPO blends: A, MI; B, PhMI; C, MeMI.

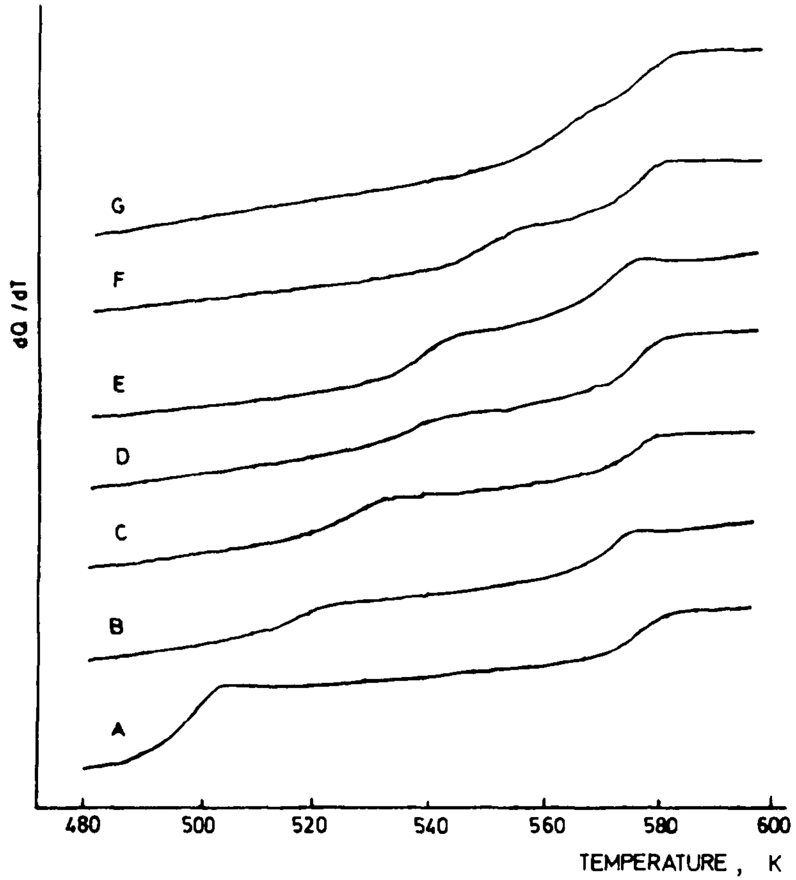

Fig. 3. DSC thermograms of 50/50 wt.% of alternating poly(αMeS–co–MI)/SPPO blends: A, SPPO 4; B, SPPO 19; C, SPPO 27; D, SPPO 39; E, SPPO 47; F, SPPO 55; G, SPPO 68. Numbers with SPPO indicate mol.% of sulphonylated PPO in copolymer.

Poly(αMeS-co-MI) / SPPO blends

The glass transition temperatures are summarized in Table 2. The T_g values of the first and second heats are reported. It is evident that all the samples have two T_g values at essentially the same temperatures as those of the constituents; therefore the blends are considered immiscible. Typical DSC tracings for several polymer pairs are shown in Fig. 3.

Poly(αMeS-co-MeMI) / SPPO blends

These blends behave somewhat differently from the maleimide copolymers. For these copolymers, one T_g value was obtained after the first DSC run for samples containing SPPO with sulphonylation degrees from 39 to 92 mol.%. After the second run, two T_gs appeared, close in value to those of the pure blend components, as is shown in Table 2. It was concluded that these blends are partly miscible. For the samples containing SPPO

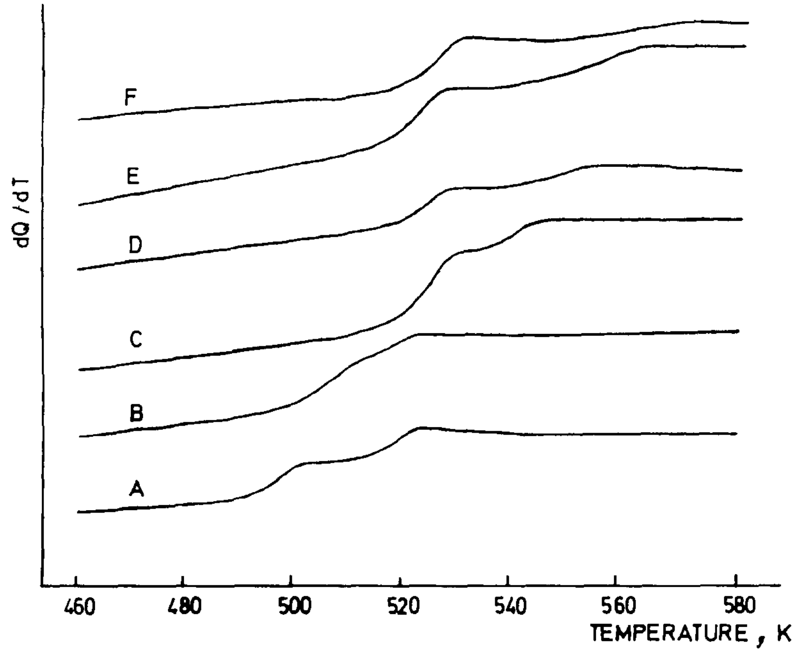

Fig. 4. DSC thermograms of 50/50 wt.% of alternating poly(αMeS–co–MeMI)/SPPO blends: A, SPPO 4; B, SPPO 11; C, SPPO 39; D, SPPO 55; E, SPPO 68; F, SPPO 75. Numbers with SPPO indicate mole.% of sulphonylated PPO in copolymer.

with a degree of sulphonylation below 19 mol.%, two T_gs were found after the first run, thus showing immiscibility. Figure 4 illustrates DSC thermograms for several blend samples.

Poly(αMeS–PhMI) / SPPO blends

In this system, miscibility was found for samples containing SPPO with a degree of sulphonylation from 27 to 92 mol.% (Table 2). The polymer blend with SPPO copolymer of 19 mol.% sulphonylation exhibits one T_g after the first DSC run (T_g, 535 K) and two after the second (T_g, 523 and 543 K). This indicates that this sample is on the miscibility–immiscibility boundary. Immiscibility was found for the blends containing SPPO 4, SPPO 7 and SPPO 11. For the blends containing SPPO 39, SPPO 47, SPPO 55 and SPPO 64, due to the small difference between the T_gs of the copolymers (Table 2), the conclusion that they are miscible is based on the film clarity. As an example, DSC thermograms representing some poly(αMeS–co–PhMI)/SPPO blends are shown in Fig. 5.

In continutation of this study, initially miscible poly(αMeS–co–PhMI)/SPPO blends (as precipitated) were further analysed by annealing at elevated temperatures. It is known that polymer blends with an observed miscibility at low temperatures often exhibit phase separation at higher temperatures. This behaviour was demonstrated experimentally for many

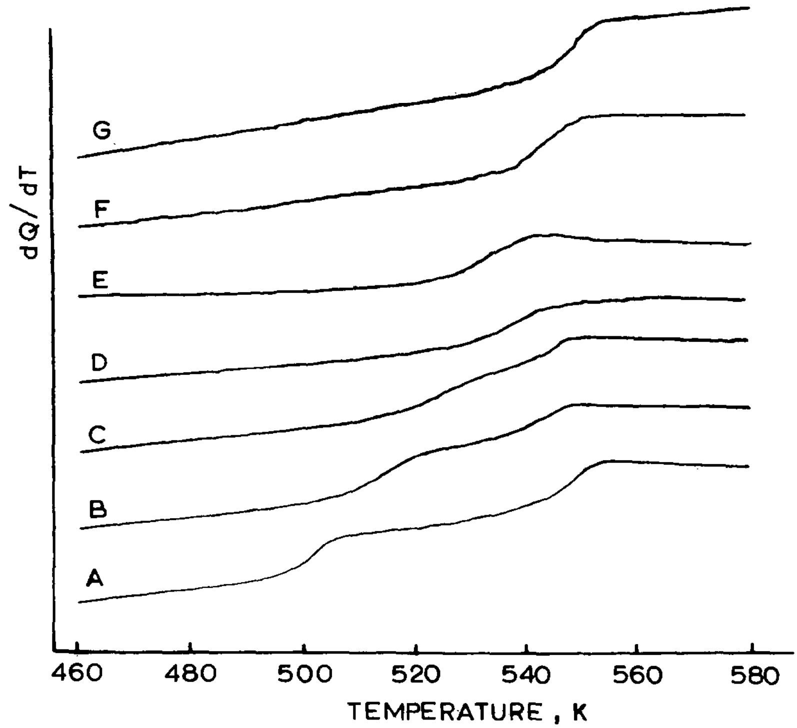

Fig. 5. DSC thermograms of 50/50 wt.% of alternating poly(αMeS-co-PhMI)/SPPO blends: A, SPPO 4; B, SPPO 11; C, SPPO 19; D, SPPO 27; E, SPPO 39; F, SPPO 66; G, SPPO 75. Numbers indicate mol.% of sulphonylated PPO in copolymer.

combinations of PPO with halogen-substituted styrene derivatives [11]. It was therefore of interest to analyse the miscible SPPO/poly(αMeS-co-PhMI) blends annealed at temperatures up to 583 K. The experiments were carried out in the DSC cell and consisted of heating a sample known to be homogeneous to the selected annealing temperature and holding it at that temperature for 15 min [11]. Samples were then quenched to ambient temperature and T_g values were determined.

For the SPPO/poly(αMeS-co-PhMI) blends containing SPPO of sulphonylation degrees from 64 to 92 mol.% annealed at 583 K, no changes in miscibility were observed, as shown by the presence of a single T_g. Moreover, the glass transition widths were unchanged indicating an intimate level of mixing in such blends. For the blend with SPPO 27, phase separation was observed by annealing at 568 K. At 553 K this blend shows broad transition width.

Further insight into the thermal behaviour of poly(αMeS-co-PhMI)/SPPO blends can be gained by preparing samples of different blend composition. The blends of different composition containing SPPO

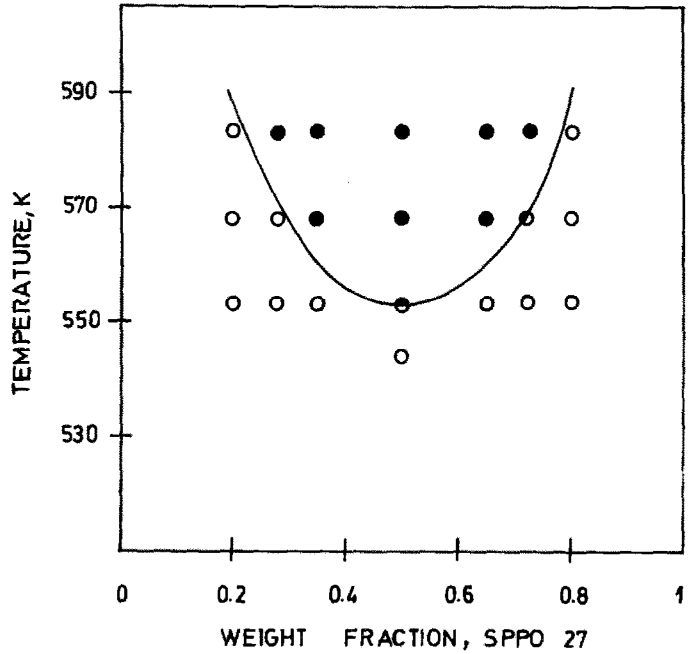

Fig. 6. Miscibility of blends of poly(αMeS–co–PhMI) and SPPO, containing 27 mol.% of sulphonylated PPO copolymers, as a function of blend composition: (o) one phase; (o) intermediate situation; (●) two phases.

copolymer of sulphonylation degrees 19, 27, 66 and 87 mol.%, respectively, were prepared. Figure 6 shows the phase diagram for the blend containing SPPO copolymer with 27 mol.% sulphonylation as a function of blend composition. All blends are miscible at 543 K. At 553 K, for the blend containing 50/50 wt.% of each component, a relatively broad transition width was observed and this blend is therefore considered to be partially miscible. At 568 K, for blends of 50/50, 35/65 and 65/35 wt.% SPPO, phase separation can be seen. For the blend compositions 20/80 and 80/20 wt.% SPPO, one T_g was observed even at 583 K. It should be noted that for these blends it is difficult to determine phase behaviour using DSC because of the relatively small amount of the second component.

Because copolymer containing SPPO 19 is on the miscibility–immiscibility boundary, the behaviour of this blend with different blend compositions was also investigated. For a blend composition of 50/50 wt.%, the sample (as precipitated) is immiscible and two T_gs were observed after the second run in the DSC instrument. Under the same conditions for blend compositions 80/20, 65/35, 35/65 and 20/80 wt.% SPPO, one T_g value was observed. For the blends 65/35 and 35/65 wt.% SPPO, phase separation occurred by annealing at 553 K, and at 583 K for the blends 80/20 and 20/80 wt.% SPPO.

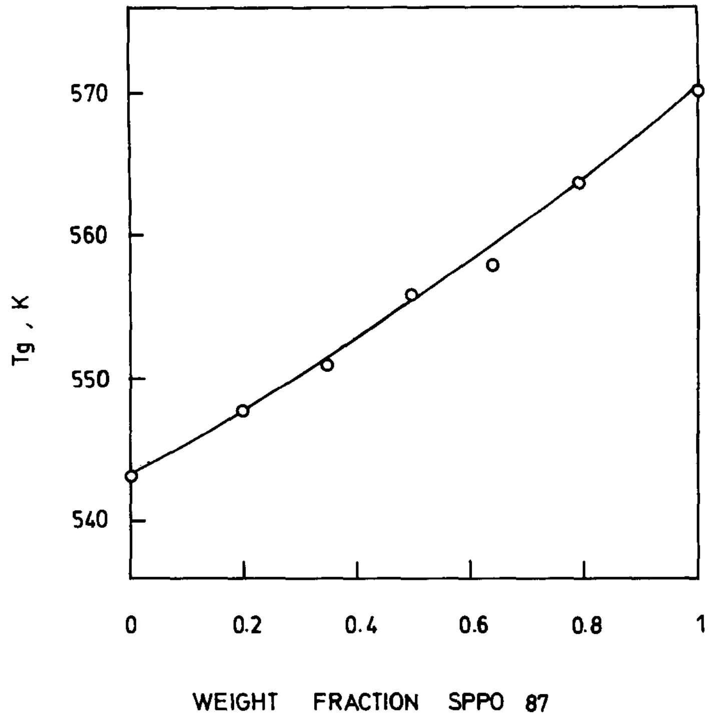

Fig. 7. Glass transition temperature dependence on the blend composition for blends of poly(αMeS-co-PhMI) with SPPO containing 87 mol.% of sulphonylated PPO.

As previously mentioned the best miscibility in the SPPO/poly(αMeS-co-PhMI) blends occurs in samples with SPPO content from 64 to 92 mol.%. The influence of the blend composition was studied for the samples containing SPPO 66 and SPPO 87. It was found that all blends show one T_g at temperatures up to 583 K.

The T_g-composition curves of the compatible blend systems containing SPPO 27, SPPO 66 and SPPO 87 with different blend composition can be fitted into the Gordon–Taylor equation [23]

$$T_g = (w_1 T_{g1} + k w_2 T_{g2})/(w_1 + k w_2) \quad (1)$$

where T_g is the glass transition temperature of the blend and T_{g1} and T_{g2} are glass transition temperatures of components 1 and 2, w_1 and w_2 are corresponding weight fractions and k is an adjusting parameter related to the degree of curvature of the T_g-composition diagram. The k values are 0.66, 0.81 and 0.85 for blends containing SPPO 27, SPPO 66 and SPPO 87, respectively. Figure 7 shows the composition dependence of the glass transition temperatures of poly(αMeS-co-PhMI)/SPPO 87 blends. The k value increases with increasing SPPO content in the blend, thus indicating a more intensive interaction in such blends. This is in good agreement with the experimental results. Similarly, the T_g-composition curves of various blends can be adequately derived by the Gordon–Taylor equation [24,25].

Segmental interaction parameters

Poly(αMeS-co-PhMI) / SPPO blends

The calculation of segmental interaction parameters is based on the first-order mean field treatment [10,11]. Poly(αMeS–co–RMI) (R=H, Me, Ph)/SPPO copolymers represent blends of the type $(A_{1-x}B_x)_{n1}/(C_{1-y}D_y)_{n2}$ in which A, B, C and D represent αMeS, RMI, PPO and SPPO units, respectively. The segmental interaction parameter χ_{blend} for blends of copolymers αMeS with NPhMI and SPPO copolymers is given by the quadratic equation derived by ten Brinke et al. [10]

$$\begin{aligned}\chi_{\text{blend}} = {} & \chi_{\alpha\text{MeS,PhMI}} X^2 + (\chi_{\text{PO},\alpha\text{MeS}} - \chi_{\text{PO,PhMI}} - \chi_{\text{SPO},\alpha\text{MeS}} + \chi_{\text{SPO,PhMI}})XY \\ & + \chi_{\text{PO,SPO}} Y^2 + (\chi_{\text{PO,PhMI}} - \chi_{\text{PO},\alpha\text{MeS}} - \chi_{\alpha\text{MeS,PhMI}})X \\ & + (\chi_{\text{SPO},\alpha\text{MeS}} - \chi_{\text{PO},\alpha\text{MeS}} - \chi_{\text{PO,SPO}})Y + \chi_{\text{PO},\alpha\text{MeS}} \qquad (2)\end{aligned}$$

where segmental interaction parameters between different monomer units are indicated by their subscripts. The function $f(x, y)$ is defined as

$$f(x, y) = \chi_{\text{blend}} - \chi_{\text{blend}}^{\text{crit}} \qquad (3)$$

It is evident that six segmental interaction parameter are involved in these blends. Segmental interaction parameter $\chi_{\text{PO,SPO}} = 0.15$ was previously determined [16]. By employing a mean field treatment and using experimental results published by Kressler et al. [25] for poly(S–co–αMeS)/PPO blends, $\chi_{\text{PO},\alpha\text{MeS}}$ is determined to be 0.024. In this calculation $\chi_{\text{PO,S}} = -0.043$ [18] and $\chi_{\text{S},\alpha\text{MeS}} = 0.032$ [26] were used. Furthermore, the value of χ_{crit} was estimated to be 0.0045. This value was obtained for a degree of polymerization of 490 for poly(αMeS–co–PhMI) and of 420 for SPPO. The functional dependance of $\chi_{\text{PO,PhMI}}$ on $\chi_{\text{SPO,PhMI}}$ was determined from the critical degree of sulphonylation of SPPO copolymers on the miscibility in the blends with poly(αMeS–co–PhMI) which is obtained experimentally

TABLE 3

Segmental interaction parameters for poly(αMeS–co–PhMI)/SPPO blends

Segment pair	χ_{ij}
αMeS, PhMI	0.04
PO,SPO	0.15
PO,αMeS	0.024
SPO,αMeS	0.015
PO,PhMI	0.038
SPO,PhMI	0.006

(Table 3). From these data, employing the mean field approach, the four remaining segmental interaction parameters, αMeS,PhMI; αMeS,SPO; PO,PhMI and SPO,PhMI, respectively were adjusted to the best fit with experimental data. The results are shown in Table 3. Because the annealing temperatures were in the range 543–583 K, the calculated segmental interaction parameters can be regarded as corresponding to this temperature range. By introducing corresponding values into the above equation, the boundary line is predicted at 17.3% of sulphonylated PPO. This prediction based on the mean field treatment is in reasonable agreement with the experimental findings of 19 mol.%.

PPO / poly(αMeS–co–PhMI) and PS / poly(αMeS–co–PhMI) blends

For these systems, immiscibility over the entire copolymer composition range was found. The expression for χ_{blend} for the respective systems is given by

PPO/poly(αMeS–co–PhMI):

$$\chi_{\mathrm{blend}} = Y\chi_{\mathrm{PO},\alpha\mathrm{MeS}} + (1-Y)\chi_{\mathrm{PO,PhMI}} - \mathrm{Y}(1-\mathrm{Y})\chi_{\alpha\mathrm{MeS,PhMI}} \tag{4}$$

PS/poly(αMeS–co–PhMI)

$$\chi_{\mathrm{blend}} = Y\chi_{\mathrm{S},\alpha\mathrm{MeS}} + (1-Y)\chi_{\mathrm{S,PhMI}} - Y(1-Y)\chi_{\alpha\mathrm{MeS,PhMI}} \tag{5}$$

From the calculated values of segmental interaction parameters for the system SPPO/poly(αMeS–co–PhMI) (Table 3) it can be seen that

$$\chi_{\alpha\mathrm{MeS,PhMI}} > \chi_{\mathrm{PO,PhMI}} > \chi_{\mathrm{PO},\alpha\mathrm{MeS}}$$

but that $\chi_{\alpha\mathrm{MeS,PhMI}} \approx \chi_{\mathrm{PO,PhMI}}$, which indicates that "repulsion" between αMeS and PhMI is too small to compensate the values of $\chi_{\mathrm{PO},\alpha\mathrm{MeS}}$ and $\chi_{\mathrm{PO,PhMI}}$, and immiscibility occurs over the whole range of composition.

As found experimentally, miscibility in the PS/poly(αMeS–co–PhMI) blend also occurs over the whole composition range. It is possible to obtain information on the sign and magnitude of $\chi_{\mathrm{S,PhMI}}$ from the available data for $\chi_{\mathrm{S},\alpha\mathrm{MeS}}$ and $\chi_{\alpha\mathrm{MeS,PhMI}}$ interaction parameters. From $\chi_{\mathrm{S},\alpha\mathrm{MeS}} = 0.032$ and $\chi_{\alpha\mathrm{MeS,PhMI}} = 0.04$, it follows that $\chi_{\mathrm{S,PhMI}}$ is positive and is close to or exceeds the magnitudes of both $\chi_{\mathrm{S},\alpha\mathrm{MeS}}$ and $\chi_{\alpha\mathrm{MeS,PhMI}}$, thus indicating that the lack of miscibility can be explained in the same manner as for PPO/poly(αMeS–co–PhMI).

ACKNOWLEDGMENT

This work was supported by the National Science Foundation of the United States through funds made available to the US–Yugoslav Joint Board of Scientific and Technical Cooperation.

REFERENCES

1 A.R. Shultz and B.M. Beach, Macromolecules, 7 (1974) 902.
2 J.R. Fried, F.E. Karasz and W.J. MacKnight, Macromolecules, 11 (1978) 150.
3 P.R. Alexandrovich, F.E. Karasz and W.J. MacKnight, Polymer, 18 (1977) 1022.
4 C.L. Ryan, Ph.D. Thesis, University of Massachusetts, Amherst, MA, 1979.
5 R. Vuković, F.E. Karasz and W.J. MacKnight, Hem. Ind., 35 (1981) 361.
6 R. Vuković, V. Kurešević, F.E. Karasz and W.J. MacKnight, Thermochim. Acta, 54 (1982) 349.
7 P.T. Russell and R.S. Stein, J. Polym. Sci. Polym. Phys. Ed., 20 (1982) 1593.
8 R. Vuković, V. Kurešević, N. Šegudović, F.E. Karasz and W.J. MacKnight, J. Appl. Polym. Sci., 28 (1983) 1379.
9 R. Vuković, F.E. Karasz and W.J. MacKnight, J. Appl. Polym. Sci., 28 (1983) 219.
10 G. ten Brinke, F.E. Karasz and W.J. MacKnight, Macromolecules, 16 (1983) 2827.
11 R.P. Kambour, J.T. Bendler and R.C. Bopp, Macromolecules, 16 (1983) 753.
12 R. Vuković, V. Kurešević, F.E. Karasz and W.J. MacKnight, J. Appl. Polym. Sci., 30 (1985) 317.
13 R. Vuković, V. Kurešević and M. Zuanić, Polimeri, 10 (1989) 148.
14 S.H. Goh and S.Y. Lee, Eur. Polym. J., 25 (1989) 997.
15 H.S. Kang, Ph.D. Thesis, University of Massachusetts, Amherst, MA, 1987.
16 H.S. Kang, W.J. MacKnight and F.E. Karasz, Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem., 28 (1987) 134.
17 R. Vuković, F.E. Karasz and W.J. MacKnight, Polymer, 24 (1983) 529.
18 G. ten Brinke, E. Rubinstein, F.E. Karasz, W.J. MacKnight and R. Vuković, J. Appl. Phys., 56 (1984) 2440.
19 R. Vuković, V. Kurešević, C.L. Rynan, F.E. Karasz and W.J. MacKnight, Thermochim. Acta, 85 (1985) 383.
20 R. Vuković, V. Kurešević, F.E. Karasz and W.J. MacKnight, 31st IUPAC Macromolecular Symposium, Merseburg, June, 1987, Abstracts, p. 66.
21 H.S. Kang, W.J. MacKnight and F.E. Karasz, Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem., 27 (1986) 65.
22 S. Percec, J. Appl. Polym. Sci., 33 (1987) 191.
23 M. Gordon and J.S. Taylor, J. Appl. Chem., 2 (1952) 495.
24 S.H. Goh and S.Y. Lee, Makromol. Chem., 191 (1990) 3081.
25 J. Kressler, H.W. Krammer, K. Herzos and H. Heyde, Acta Polym., 41 (1990) 1.
26 J.M.G. Cowie and I.J. McEven, Polymer, 26 (1985) 1662.