ELSEVIER

Thermochimica Acta 285 (1996) 141–154

thermochimica acta

Miscibility and phase separation study of blends of random copolymers of poly[*ortho*(*para*)-fluorostyrene-co-*ortho*(*para*)-bromostyrene] with phenylsulphonylated poly(2,6-dimethyl-1,4-phenylene oxide) copolymers by thermal methods

R. Vuković[a,*], G. Bogdanić[a], A. Erceg[a], D. Fleš[a], F.E. Karasz[b], W.J. MacKnight[b]

[a] *INA-Industrija nafte, Research and Development, Zagreb, Savska 41/X, Croatia*

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

Received 27 July 1995; accepted 12 January 1996

Abstract

The miscibility and phase separation behaviour of random copolymer blends of poly [*ortho*(*para*)-fluorostyrene-co-*ortho*(*para*)bromostyrene] (poly[o(p)FSt-co-o(p)BrSt]) with partially sulphonylated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) copolymers has been studied by differential scanning calorimetry (DSC) at temperatures up to 573 K. It was found that these systems exhibited miscibility–immiscibility behaviour which was dependent on the halogen atom, its position on the benzene ring and predominantly on the degree of sulphonylation. Copolymers of oFSt and pFSt with pBrSt exhibited miscibility with SPPO with higher degree of sulphonylation than copolymers containing oBrSt. The miscibility behaviour was analysed on the basis of the mean-field theory in terms of the individual segmental interaction parameters.

Keywords: Copolymer; DSC; Mean-field theory; Miscibility; Partially sulphonylated poly(2,6-dimethyl-1,4-phenylene oxide); Phase separation; Poly[*ortho*(*para*)-fluorostyrene-co-*ortho* (*para*)bromostyrene]

---

[*] Corresponding author.

PII: S0040-6031(96)02858-4

1. Introduction

In recent papers we have described the miscibility and phase behaviour of blends of partially sulphonylated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) copolymers with poly(oFSt-co-pFSt) [1], poly(oClSt-co-pClSt) [2], poly(oBrSt-co-pBrSt) [3], poly[oFSt-co-o(p)ClSt] [4] and poly[pFSt-co-o(p)ClSt]) [5]. A comparison of the miscibility of SPPO with three halogenated styrene copolymers [1–3] showed that the results for the brominated and chlorinated systems were qualitatively similar and highly asymmetric relative to the isomer contents of the respective copolymers. *Ortho* substitution is a strong inhibitor of miscibility. In the case of fluoro substitution the free isomeric effect was considerably smaller, and the miscibility domain was more accurately described by a band parallel to the abscissa the width of which was primarily a result of the repulsion between the substituted and unsubstituted phenylene oxide moieties. Continuing our studies of the miscibility of random copolymers of halogenated styrene derivatives, we also studied the miscibility–immiscibility behaviour of blends of SPPO with poly[oFSt-co-o(p)ClSt] [4] and with poly[pFSt-co-o(p)ClSt] [5]. It was found that these systems exhibit miscibility–immiscibility behaviour which depends on the halogen atom and his position in benzene ring and predominantly on the degree of sulphonylation. Copolymers of oFSt with pClSt exhibited miscibility with SPPO with a higher degree of sulphonylation than copolymers containing oClSt [4]. Copolymers of pFSt with pClSt also showed miscibility with SPPO with a higher degree of sulphonylation than copolymers containing oClSt. In this system the miscibility window is very wide and similar for all copolymer compositions [5]. Taking into consideration the result obtained for the miscibility with SPPO in the previously discussed blends, we now present the results obtained for the miscibility–immiscibility behaviour of blends of SPPO copolymers with poly[o(p)FSt-co-o(p)BrSt]. The experimental results will be discussed in the context of the mean-field treatment [6].

2. Experimental

2.1. Materials

High molecular weight copolymers of *ortho*(*para*)-fluorostyrene with *ortho*(*para*)-bromostyrene with a range of copolymer composition (Table 1) were prepared by free radical polymerization in toluene solution at 60°C using azobis(isobutyronitrile) (AIBN) as initiator. The polymerization was stopped when conversion was between 10 and 35% in order to minimize copolymer composition drift. The precipitated dried powders were characterized and used in blend studies.

SPPO copolymers with different levels of phenylsulphonylation, from 3.5 to 91 mol% were prepared by Friedel–Crafts sulphonylation of PPO [7, 8]. The molecular weights $\bar{M}_w$, $\bar{M}_n$ and the ratio $\bar{M}_w/\bar{M}_n$ are also given in Table 1.

Polymer blends were prepared by coprecipitation from chloroform solution, which contained a total of 5 wt% of polymer, with methanol. The dried samples were used in DSC experiments.

Table 1
Molecular weights of poly[*ortho*(*para*)fluorostyrene-co-*ortho*(*para*)bromostyrene] of different copolymer compositions and phenylsulphonylated poly(2,6-dimethyl-1,4-phenylene oxide) copolymers of different degrees of sulphonylation

Sample	Mol. wt. × 10^{-5}		
	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
Poly(oFSt-co-oBrSt)[a]			
7.7	2.60	1.30	2.00
25.4	2.23	1.00	2.23
32.6	2.00	0.97	2.06
48.4	1.90	0.98	1.94
58.2	1.72	1.02	1.69
65.4	1.54	0.91	1.69
74.9	1.42	0.80	1.78
83.8	1.33	0.79	1.68
90.1	1.20	0.66	1.82
92.9	1.15	0.66	1.74
Poly(oFSt-co-pBrSt)[a]			
10.3	2.63	1.26	2.09
23.6	2.00	1.12	1.79
32.8	1.90	1.10	1.73
42.7	1.75	0.94	1.86
57.6	1.62	0.89	1.82
68.0	1.50	0.87	1.72
75.0	1.62	0.88	1.84
84.5	1.30	0.73	1.78
89.0	1.34	0.71	1.89
93.5	1.24	0.70	1.77
Poly(pFSt-co-oBrSt)[b]			
10.0	2.35	1.24	1.90
17.0	1.94	1.15	1.69
24.0	1.78	1.04	1.71
34.7	1.71	0.94	1.82
43.6	1.57	0.96	1.64
55.2	1.47	0.86	1.71
65.2	1.43	0.84	1.70
76.9	1.34	0.79	1.70
86.9	1.30	0.81	1.60
Poly(pFSt-co-pBrSt)[b]			
8.3	2.12	1.06	2.00
11.4	1.71	0.95	1.80
20.5	1.60	0.94	1.72
31.8	1.55	0.90	1.67
53.0	1.57	0.94	1.65

Table 1 (*Continued*)

Sample	Mol. wt. $\times 10^{-5}$		
	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
60.8	1.58	0.96	1.76
69.2	1.44	0.82	1.66
81.3	1.33	0.80	1.54
90.3	1.23	0.80	1.70
SPPO copolymers[c]			
3.5	0.393	0.147	2.67
8.6	0.430	0.172	2.50
11.5	0.438	0.160	2.74
15.5	0.445	0.167	2.67
19.9	0.481	0.178	2.70
25.4	0.500	0.180	2.78
29.0	0.520	0.173	3.01
36.7	0.610	0.210	2.90
45.0	0.580	0.200	2.90
49.3	0.590	0.200	2.95
55.0	0.593	0.190	3.12
60.7	0.615	0.220	2.80
68.0	0.710	0.248	2.86
75.0	0.730	0.245	2.98
84.0	0.730	0.230	3.17
87.0	0.720	0.210	3.43
91.0	0.780	0.230	3.39

[a] oFSt content in mol%.
[b] pFSt content in mol%.
[c] Degree of sulphonylation of SPPO in mol%.

2.2. Measurements

Copolymer compositions were determined by fluorine [9] and bromine [10] elemental analysis.

Polystyrene equivalent molecular weights were determined by GPC in tetrahydrofuran at 25°C. The GPC (Varian 8500) was calibrated using monodisperse polystyrene samples of known molecular weight.

The stabilities of the blends were investigated by thermogravimetric analysis with a Perkin–Elmer TGS-2 under a N_2 atmosphere.

The glass transition temperatures, T_g, were measured using a Perkin–Elmer DSC-2. The T_g was taken as the temperature at which the heat capacity reached one half of the total heat capacity change as observed on the thermogram. The annealing experiments were also performed in the DSC. The procedure consisted in heating a homogeneous sample to the selected temperature and holding it at that temperature for 15 min. The quenched samples were reheated at 20°C min^{-1} to determine whether one or two phases were present.

3. Results and discussion

The thermal stability of the blends at temperatures up to 573 K was determined by measuring the weight loss in TGA experiments. The maximum weight loss in all cases was below 1 wt%. Thus it was concluded that thermal degradation was not an important factor in this study.

The miscibility of the blends was determined by the usual criterion of a single glass transition in DSC measurements (second scan). Blends that were found to exhibit miscibility using samples precipitated as described ("as-precipitated" blends) were investigated further at annealing temperatures of 473, 523 and 573 K.

3.1. *Poly(oFSt-co-oBrSt)–SPPO blends*

As previously shown, homopolymers of oFSt [11], pBrSt and oBrSt [12] are immiscible with PPO. The same was also found for the blends of poly(oFSt-co-oBrSt) with PPO [13]. Recently, we have found that homopolymer blends of oFSt exhibit miscibility with SPPO of the degree of sulphonylation from 4 to 17 mol% at 473 K. The boundary between the one and two phase diagram was temperature-dependent [14]. Poly(oBrSt)–SPPO blends are immiscible in all proportions [14]. For the poly(pBrSt)–SPPO blends, miscibility was found for the samples containing SPPO with the degree of sulphonylation higher than 12 mol%. In this system no change in miscibility could be observed after heating the samples to higher temperatures [14].

Poly(oFSt-co-oBrSt)–SPPO blends, as-precipitated and annealed at 473 K showed the same behaviour. It was found that styrene copolymers with oFSt from 65.4 to 92.9 mol% content exhibited miscibility in blends with SPPO with a degree of sulphonylation from 3.5 to 19.4 mol%. The copolymer with 58 mol% oFSt was miscible with SPPO with a degree of sulphonylation from 8.6 to 15.5 mol%. Other copolymers with an oFSt content of 48.2 mol% or less, were immiscible with SPPO copolymers of all degrees of sulphonylation. These results are shown in Fig. 1. The dashed line represents miscibility–immiscibility boundaries calculated on the basis of the first-order mean-field theory of phase behaviour in the copolymer blends [6] and will be discussed in the next section. In Fig. 1, the left and right ordinates represent, respectively, data obtained for the blends of homopolymers of oBrSt and oFSt with SPPO copolymers. We also examined the temperature behaviour of the miscible blends. At the temperatures of 523 and 573 K, respectively, small changes in the miscibility–immiscibility boundaries were observed, as can be seen in Fig. 2. The area of the miscibility regime became smaller at 523 K for the SPPO with a degree of sulphonylation of 3.5 and 19.4 mol% for all copolymers with oFSt content from 58.2 to 92.8 mol%. At 573 K copolymers with oFSt of 58.2 mol% became immiscible with SPPO with all degrees of sulphonylation.

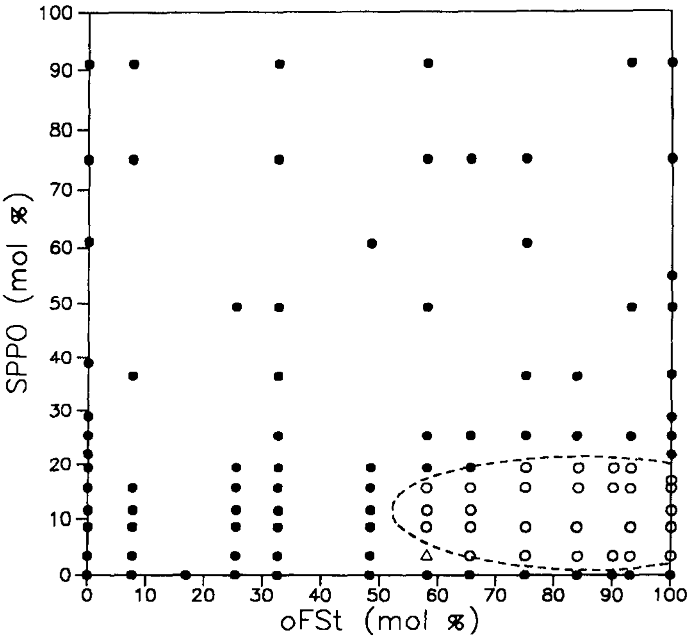

Fig. 1. Miscibility of 50/50 wt% blends of poly(oFSt-co-oBrSt) and SPPO copolymers, annealed at 473 K. (○) one phase; (●) two phases; (△) intermediate situation.

3.2. Poly(oFSt-co-pBrSt)–SPPO Blends

Fig. 3 shows experimental miscibility–immiscibility boundaries at 473 K for the SPPO–poly(oFSt-co-pBrSt) copolymers. First we noted that the boundaries exhibited no change after annealing of the blends at 473 K, compared to those of the as-precipitated blends. As can be seen in Fig. 3, miscibility for these blends lay in a band between the two ordinates, with a distinct narrowing as the oFSt content in the styrene copolymers increased. The bottom left-hand corner of the miscibility map corresponds to a blend of pure poly(pBrSt) and PPO while the bottom right-hand corner corresponds to a blend of pure poly(oFSt) and PPO. In both cases, the blends were immiscible, as previously determined. At 473 K, however, PPO was miscible with a range of poly(oFSt-co-pBrSt) copolymers which contained 27 to 89 mol% oFSt [13]. The dashed lines represent the calculated miscibility–immiscibility boundaries. This is discussed below. Annealing the miscible blends at elevated temperatures led to phase separation at 523 K only for the blend containing 33 mol% oFSt and SPPO with a degree of sulphonylation of 3.5 mol%. At 573 K just two small changes in the miscibility were observed. The copolymer blend of 13 mol% oFSt and SPPO with a degree of sulphonylation of 91 mol% showed partial miscibility. The blend of the copolymer with 93.5 mol% oFSt with SPPO with a degree of sulphonylation of 19.4 mol% was separated. These results are shown in Fig. 4. It can be concluded that miscibility in this system does not change as the equilibrium temperature increases.

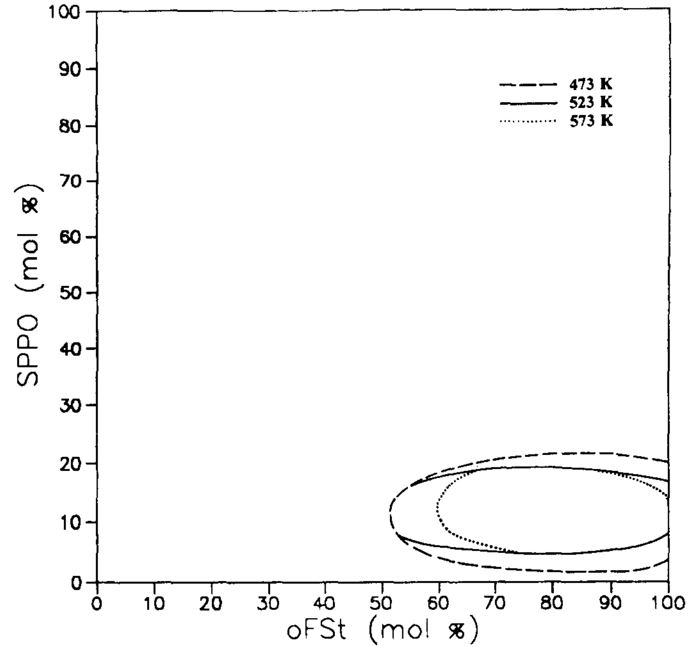

Fig. 2. Miscibility of 50/50 wt% blends of poly(oFSt-co-oBrSt) and SPPO copolymers annealed at 473, 523 and 573 K. Data have been omitted for clarity. The boundaries in the same section of the diagram overlap significantly.

3.3. *Poly(pFSt-co-oBrSt)–SPPO blends*

In previous papers we have described the behaviour of blends of pFSt and oBrSt homopolymers with PPO [11,12]. It was found that both homopolymers were immiscible with PPO. Immiscibility was also observed for poly(pFSt-co-oBrSt)–PPO [13]. At 473 K poly(pFSt) exhibited miscibility with SPPO with a degree of sulphonylation from 17 to 66 mol%. The only change during the annealing of the miscible blends was observed for blends containing SPPO with a degree of sulphonylation of 17 and 66 mol%, which were found to be immiscible at 573 K [14]. For the poly(oBrSt)–SPPO blends, immiscibility was found to be independent of the degree of sulphonylation of SPPO copolymers [14]. A quantitative explanation of these results was obtained by calculating the segmental interaction parameters according to the mean-field theory of copolymer phase behaviour.

The results obtained for the miscibility–immiscibility behaviour of poly(pFSt-co-oBrSt)–SPPO blend systems after annealing at 473 K are presented in Fig. 5. We found no difference between as-precipitated blends, and those annealed at 473 K. As is evident, the miscibility window depends on the degree of sulphonylation and copolymer composition. Immiscibility was found for all copolymers containing 17 mol% or less pFSt, independent of the SPPO copolymer degree of sulphonylation. The copolymer samples with pFSt from 24 to 87 mol% showed miscibility with SPPO of

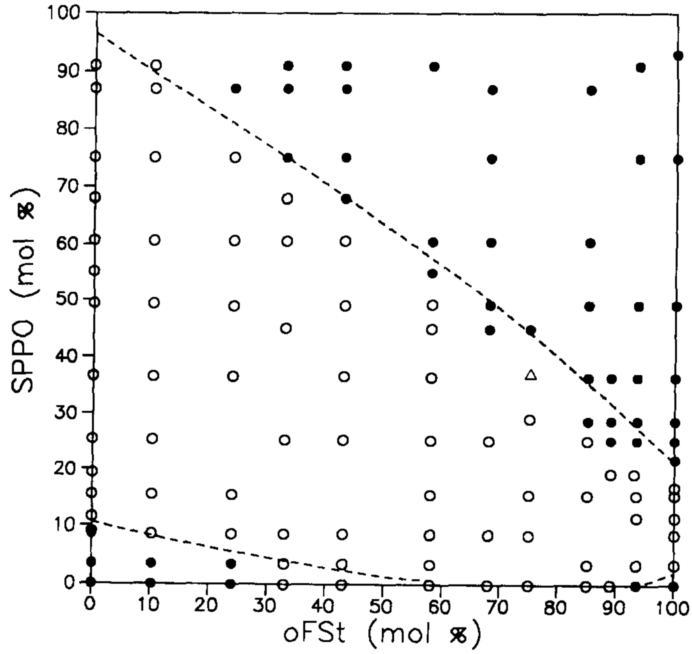

Fig. 3. Miscibility of 50/50 wt% blends of poly(oFSt-co-pBrSt) and SPPO copolymers, annealed at 473 K. (○) one phase; (●) two phases; (△) intermediate situation.

some degree of sulphonylation. The miscibility window was quite narrow for samples containing copolymers with low mol% pFSt and became wider as the pFSt content of the copolymer was increased. The miscibility–immiscibility boundaries calculated on the basis of a first order mean-field theory of phase behaviour in copolymer–copolymer blends, represented by dashed lines, will be discussed in the next section. The miscible blends were further analysed by annealing at temperature of 523 and 573 K. The blends exhibited very good stability at these temperatures. Thus, at 523 K the only changes were observed in the system which contained 17 mol% pFSt and SPPO with a degree of sulphonylation of 8.6 mol%, as well as for the system with 77 mol% pFSt and SPPO with a degree of sulphonylation of 8.6 mol%, which became immiscible at 573 K.

3.4. Poly(pFSt-co-pBrSt)–SPPO Blends

The copolymers of pFSt with pBrSt were immiscible with PPO in all copolymer compositions [13]. Immiscibility was also found for the poly(pBrSt)–PPO homopolymer blends [11,12]. The miscibility of poly(pBrSt)–SPPO copolymers was found for the blends containing SPPO with a degree of sulphonylation from 11.5 to 92 mol%. In these systems no changes in miscibility could be observed after heating the samples to higher temperatures, up to 573 K. The miscibility window in the poly(pFSt-co-BrSt)–SPPO blends was very wide for all mixtures with copolymers containing

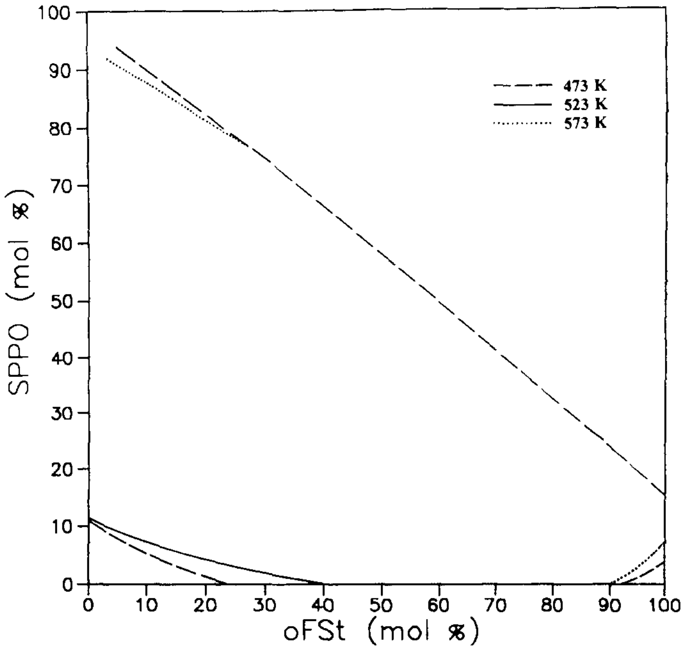

Fig. 4. Miscibility of 50/50 wt% blends of poly(oFSt-co-pBrSt) and SPPO copolymers annealed at 473, 523 and 573 K. Data have been omitted for clarity. The boundaries in the same section of the diagram overlap significantly.

pFSt from 8 to 81.3 mol% independent of the degree of sulphonylation of SPPO, and changed very little on raising the pFSt content to 91 mol% (Fig. 6). This figure represents miscibility–immiscibility behaviour at 473 K. The same results were also obtained for the as-precipitated blends. The only exception was the blend containing copolymer with 91 mol% pFSt and SPPO with a degree of sulphonylation of 11.5 mol%, which exhibited miscibility as for as-precipitated blends. The calculated miscibility–immiscibility boundaries obtained by using segmental interaction parameters at 473 K, are marked with dashed lines and conform very well to the experimental data. This is discussed in the next section. These blends also show very good stability by annealing at temperatures up to 573 K. At 523 K we observed only one change, i.e. the polymer blend with a pFSt content of 91 mol% in the copolymer and SPPO copolymer with a degree of sulphonylation of 84 mol% showed immiscibility. By raising temperature up to 573 K the sample containing pFSt of 8.3 mol% and SPPO with a degree of sulphonylation of 91 mol% showed partial phase separation.

4. Segmental interaction parameters

By utilizing the mean-field approach [6], the experimental phase behaviour of random copolymer blends of SPPO with poly(oFSt-co-oBrSt), poly(oFSt-co-pBrSt),

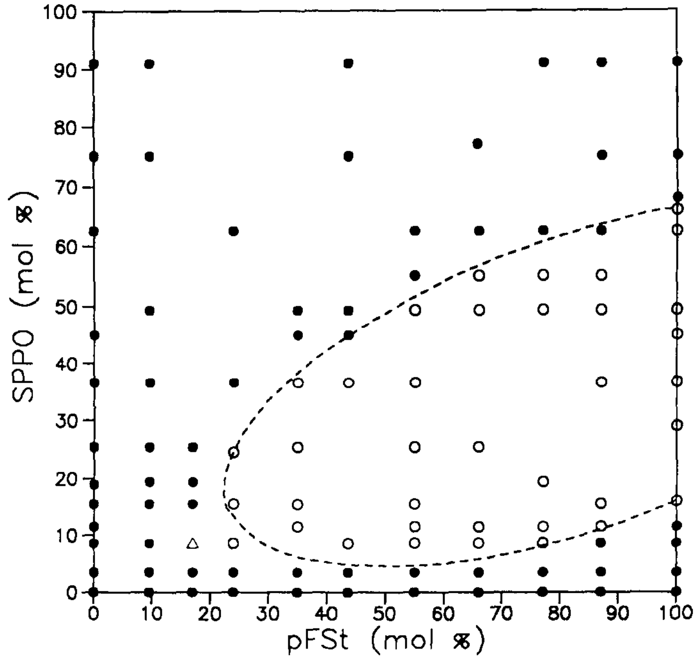

Fig. 5. Miscibility of 50/50 wt% blends of poly(pFSt-co-oBrSt) and SPPO copolymers, annealed at 473 K. (○) one phase; (●) two phases; (△) intermediate situation.

poly(pFSt-co-oBrSt) and poly(pFSt-co-pBrSt) will be analyzed here. The overall interaction parameter, χ_{blend}, for copolymer–copolymer blend systems of the type $(A_{1-x}B_x)_{n1}/(C_{1-y}D_y)_{n2}$ can be expressed as a linear combination of the segmental interaction parameters:

$$\chi_{\mathrm{blend}} = (1-x)(1-y)\chi_{AC} + (1-x)y\chi_{AD} + x(1-y)\chi_{BC} + xy\chi_{BD} - x(1-x)\chi_{AB} - y(1-y)\chi_{CD} \qquad (1)$$

where x and y denote the copolymer composition. For the blend systems from this study A represents oFSt or pFSt, B represent oBrSt or pBrSt, and C and D represent PPO and SPPO units, respectively. The first four terms on the right-hand side of Eq. (1) define additive interactions between the non-bonded component monomers of the mixture of two copolymers, weighted according to the copolymer compositions, whereas the remaining two terms define the intramolecular forces between the two different monomers comprising each of the copolymers.

The quantitative determination of χ_{ij}s requires the experimental observation of miscibility–immiscibility boundaries as a function of copolymer composition to obtain the fit to the mean-field equation by minimizing the adequate objective function [4]. For the mentioned polymeric systems five of the χ_{ij} parameters required by Eq. (1) were already available from earlier investigations [14]. The sixth χ_{ij} parameter, χ_{AB}, was

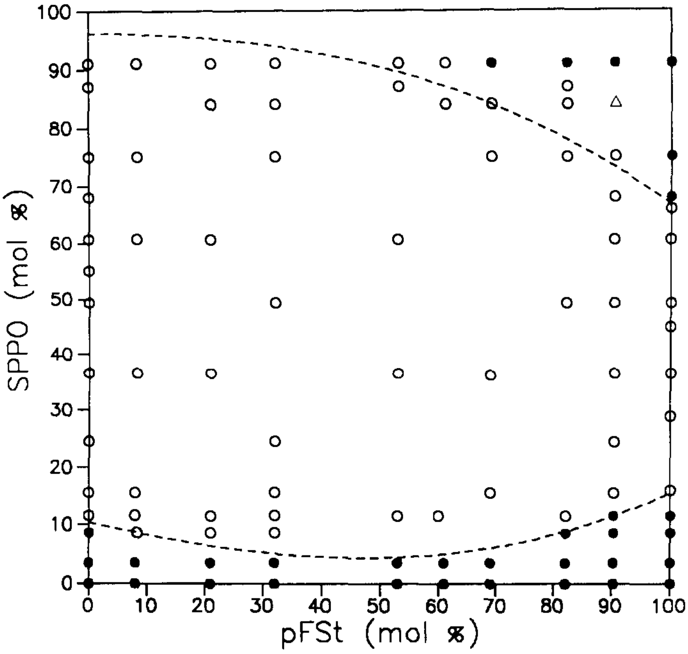

Fig. 6. Miscibility of 50/50 wt% blends of poly(pFSt-co-PBrSt) and SPPO copolymers, annealed at 473 K. (○) one phase; (●) two phases; (△) intermediate situation.

treated as an adjustable parameter and was calculated by fitting the experimental miscibility–immiscibility boundary to the mean–field equation.

The conformation molecular-weight-related entropy term, $\chi^{\text{crit}}_{\text{blend}}$, was calculated from the degree of polymerization of the respective blend components through the critical condition:

$$\chi^{\text{crit}}_{\text{blend}} = \frac{1}{2}\left[\frac{1}{\sqrt{n_1}} + \frac{1}{\sqrt{n_2}}\right]^2 \tag{2}$$

For all systems considered in this study, the value of 0.004 was used for $\chi^{\text{crit}}_{\text{blend}}$, corresponding to $n_1 = 1000$ and $n_2 = 300$. The data were calculated from Table 1. From the experimentally determined phase boundary for poly(oFSt-co-oBrSt)/SPPO, poly(pFSt-co-oBrSt)/SPPO and poly(pFSt-co-PBrSt)/SPPO, respectively, and previously determined χ_{ij} parameters [14], the remaining parameters $\chi_{\text{oFSt,oBrSt}}$, $\chi_{\text{pFSt,oBrSt}}$ and $\chi_{\text{pFSt,pBrSt}}$ at 473 K were calculated. The value of the segmental interaction parameter $\chi_{\text{oFSt,pBrSt}}$ has been fitted on the basis of experimental data for poly(oFSt-co-pBrSt)/SPPO obtained in this study and previously published experimental results for poly(oFSt-co-pBrSt)/PPO [13]. The value of the segmental interaction parameters for all binary combinations of SPPO with poly(oFSt-co-oBrSt), poly(oFSt-co-pBrSt), poly(pFSt-co-oBrSt) and poly(pFSt-co-pBrSt) derived in this way, together with the results from earlier studies are listed in Table 2.

Table 2
Segmental interaction parameters, χ_{ij}, at 473 K

Segment pair	χ_{ij}
PPO, oFSt	0.005[a]
SPPO, oFSt	0.252[a]
PPO, pFSt	0.037[a]
SPPO, pFSt	0.093[a]
PPO, oBrSt	0.029[a]
SPPO, oBrSt	0.270[a]
PPO, pBrSt	0.035[a]
SPPO, pBrSt	0.013[a]
PPO, SPPO	0.318[a]
oFSt, oBrSt	0.033
oFSt, pBrSt	0.057
pFSt, oBrSt	0.091
pFSt, pBrSt	0.082

[a] From Ref. [14].

The boundary between miscibility and immiscibility, where $\chi_{\text{blend}} = \chi_{\text{blend}}^{\text{crit}}$ can be described by a function expressed in terms of x and y, such that:

$$f(x, y) = \chi_{\text{blend}} - \chi_{\text{blend}}^{\text{crit}} = 0 \tag{3}$$

Eq. (1) can equivalently be written as:

$$x^2\chi_{\text{AB}} + y^2\chi_{\text{CD}} + (\chi_{\text{AC}} - \chi_{\text{AD}} - \chi_{\text{BC}} + \chi_{\text{BD}})xy + (\chi_{\text{BC}} - \chi_{\text{AB}} - \chi_{\text{AC}})x$$
$$+ (\chi_{\text{AD}} - \chi_{\text{AC}} - \chi_{\text{CD}})y + (\chi_{\text{AC}} - \chi_{\text{crit}}) = 0 \tag{4}$$

or in general quadratic form:

$$ax^2 + by^2 + cxy + dx + ey + f = 0 \tag{5}$$

from which solutions can be readily obtained in the xy plane. Hence all the constants of the quadratic generalized equation are directly related to the χ_{ij} parameters — the geometry of $f(x, y)$ is dependent on the sign and magnitude of the χ_{ij} parameters that appear in the appropriate χ_{blend} expression. Because the critical value of χ_{blend} for the mixture of two copolymers is extremely small, miscibility in these copolymeric systems is a consequence of specific binary interactions. The fact that in this study all binary χ_{ij} parameters are positive for all binary combinations leads to the possibility of obtaining miscibility through a "repulsion" effect between the units of a copolymer. The shapes of the miscibility boundary curves are determined by the difference in interaction strength between different copolymer segments. It can be seen from Figs. 1, 3, 5 and 6 that the dashed line, which represents the calculated miscibility–immiscibility boundary at 473 K, is elliptical in shape as required by mean-field theory, i.e. the condition for the miscibility boundary [15]:

$$c^2 - 4ab < 0 \tag{6}$$

Table 3
Condition: $c^2 - 4ab = [\chi_{AC} - \chi_{AD} - \chi_{BC} + \chi_{BD}]^2 - 4\chi_{AB}\chi_{CD}$ for the blend systems studied

System	$c^2 - 4ab$	c^2
Poly(oFSt-co-oBrSt)–SPPO	-4.19×10^{-2}	3.60×10^{-5}
Poly(oFSt-co-pBrSt)–SPPO	-1.43×10^{-4}	7.24×10^{-2}
Poly(pFSt-co-oBrSt)–SPPO	-8.15×10^{-2}	3.42×10^{-2}
Poly(pFSt-co-pBrSt)–SPPO	-9.82×10^{-2}	6.08×10^{-2}

is fulfilled for all mentioned systems (see Table 3). The analysis of the c^2 term value, which represents the contribution of segmental dissimilarity, shows that the poly(oFSt-co-pBrSt)–SPPO system should exhibit a wider miscibility region than the poly(oFSt-co-oBrSt)–SPPO blend systems and also that the poly(pFSt-co-pBrSt)–SPPO system should exhibit a wider miscibility region than the poly(pFSt-co-oBrSt)–SPPO blend systems; this is in agreement with experimental results, as can be seen from Figs. 1, 3, 5 and 6.

In summarizing the results of our studies on the miscibility of blends of SPPO with poly(oFSt-co-oBrSt), poly(oFSt-co-pBrSt), poly(pFSt-co-oBrSt) and poly(pFSt-co-pBrSt) it is evident that a remarkable agreement exists between the miscibility–immiscibility boundaries obtained experimentally and by using the simple mean-field approach. It is also evident that the interaction parameters derived previously [14] are sufficiently quantitative to be of predictive value in all copolymer systems studied in this work.

The results show that the degree of sulphonylation of SPPO is the predominant factor in determining miscibility and this again demonstrates the influence of relatively small structural changes on miscibility in copolymer blends.

Acknowledgement

This work was supported by the National Science Foundation of the United States of America and the Ministry of Science of the Republic of Croatia.

References

[1] R. Vuković, G. Bogdanić, V. Kurešević, N. Šegudović F.E. Karasz and W.J. MacKnight, Polymer, 35 (1994) 3055.

[2] R. Vuković, G. Bogdanić, V. Kurešević, M. Tomašković, F.E. Karasz and W.J. MacKnight, Polym. Sci., Polym. Phys. Ed., 32 (1994) 1079.

[3] R. Vuković, G. Bogdanić, V. Kurešević, V. Srića, F.E. Karasz and W.J. MacKnight, J. Appl. Polym. Sci., 52 (1994) 1499.

[4] R. Vuković, G. Bogdanić, N. Šegudović, D. Fleš, F.E. Karasz and W.J. MacKnight, Thermochim. Acta, 264 (1995) 125.

[5] R. Vuković, G. Bogdanić, A. Erceg, D. Fleš, F.E. Karasz and W.J. MacKnight, Thermochim. Acta, in press.

[6] G.Ten Brinke, F.E. Karasz and W.J. MacKnight, Macromolecules, 16 (1983) 1827.

[7] H.S. Kang, W.J. MacKnight and F.E. Karasz, Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem., 27 (1986) 65.

[8] R. Vuković, V. Kurešević, G. Bogdanić and D. Fleš, Thermochim. Acta, 195 (1992) 351.

[9] T.S. Light and R.F. Mannian, Anal. Chem., 41 (1969) 107.

[10] T.S. Ma and R.C. Rittner, Modern Organic Elemental Analysis, Marcel Dekker, New York (1979), pp. 178–181.

[11] R. Vuković, F.E. Karasz and W.J. MacKnight, J. Appl. Polym. Sci., 28 (1983) 219.

[12] C.L. Ryan, Ph.D. Dissertation, University of Massachusetts, Amherst MA (1979).

[13] R. Vuković, G. Bogdanić, V. Kuresević, F.E. Karasz and W.J. MacKnight, Eur. Polym. J., 24 (1988) 123.

[14] R. Vuković, M. Žuanić, G. Bogdanić, V. Kurešević, F.E. Karasz and W.J. MacKnight, Polymer, 34 (1993) 1449.

[15] H. Ueda and F.E. Karasz, Polymer J., 24 (1992) 1363.