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Phase behaviour in copolymer blends of phenylsulphonylated poly(2,6-dimethyl-1,4-phenylene oxide) and poly(*o*-fluorostyrene-co-*p*(*o*)-chlorostyrene)

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Abstract

Miscibility and phase behaviour in copolymer blends of partially phenylsulphonylated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) with poly(*o*-fluorostyrene-co-*p*(*o*)-chlorostyrene) have been studied by differential scanning calorimetry at temperatures up to 573 K. It was found that miscibility depends on the copolymer compositions and the degree of sulphonylation of the SPPO copolymers and on temperature. The width of the miscibility window in the blends containing copolymers with various p-chlorostyrene (pClSt) content and SPPO is much wider than in the corresponding blends containing copolymers with *o*-chlorostyrene (oClSt) and SPPO. It was also found that sulphonylated segments of SPPO copolymers enhanced miscibility in comparison with blends with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). A qualitative account of these results was obtained by using the segmental interaction parameters according to the mean-field theory of phase behaviour.

Keywords: Blends copolymer; DSC; Partially phenylsulphonylated poly(2,6-dimethyl-1,4-phenylene oxide (SPPO); Phase behavior poly(*o*-fluorostyrene-co-p(*o*)-chlorostyrene

1. Introduction

In several recent publications were reported the miscibility and phase separation behaviour of blends of styrenic halogen-substituted random copolymers and partially

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sulphonlyated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) copolymers [1–3]. It was shown that miscibility depends on both the degree of sulphonylation of the SPPO copolymers and copolymer composition. It has been also established that the miscibility window in these systems differs from the corresponding PPO blends. All these results can be explained on the basis of the mean-field treatment [4].

In the continuation of our studies of the miscibility of random copolymers of halogenated styrene derivatives we have investigated the miscibility of blends of SPPO with poly(*o*-fluorostyrene-co-*o*-chlorostyrene) [poly(oFSt-co-oClSt)] and with poly(*o*-fluorostyrene-co-*p*-chlorostyrene) [poly(oFSt-co-pClSt)] random copolymers. As previously published, these copolymers in blends with PPO exhibited miscibility for some, but different copolymer compositions [5]. On the basis of previous results, we would expect that sulphonylated segments of SPPO copolymers will enhance miscibility in the blends. Again, the miscibility behaviour was analyzed on the basis of the mean-field theory in terms of the individual segmental interaction parameters.

2. Experimental

2.1. Materials

Poly(oFSt-co-oClSt) and poly(oFSt-co-pClSt) of high molecular weight with polydispersity index 1.5 and 2 and different copolymer composition were prepared by free radical polymerization in toluene as previously described [5].

The composition of copolymers was determined from the halogen content [5]. Molecular weights were determined by osmometry, light scattering and GPC methods [5–7]. The copolymers used in this study are essentially identical to those employed in studies reported in Refs. [5–7].

A series of random SPPO copolymers containing systematically varying levels of phenylsulphonylation (mol% : 3.5, 8.6, 12, 15.5, 19.4, 25.4, 27, 29, 36.7, 45, 47, 49, 55, 61, 66, 75, 87 and 91) were prepared by a Friedel–Crafts sulphylation of PPO [8,9].

Polymer blends (50/50 wt%) were prepared by dissolving equal quantities of the pure components in chloroform and coprecipitating them into a large excess of methanol. The resulting precipitates were filtered and dried at 80°C in vacuum for 60 h. The dried mixtures were then used in DSC experiments.

2.2. Measurements

Thermogravimetric measurements (to investigate stability of the blends) were carried out using a Perkin-Elmer TGS-2 thermobalance at a heating rate of 10°C min^{-1} with nitrogen purge.

Glass transition temperatures (T_g) of polymer blends were performed by using a Perkin-Elmer DSC-2 at a heating rate of 20°C min^{-1} under nitrogen. The T_g was taken as the inflection point in the heat capacity discontinuity in the second scan. The annealing experiments were also performed in the DSC. The typical procedure consisted of heating a homogeneous sample to the selected temperatures at the fastest available rate, 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 [10].

3. Results and discussion

All investigated polymer blends are stable in nitrogen up to 573 K, as shown by measuring weight loss thermogravimetrically. At the highest test temperature (573 K) maximum weight losses were less than 1% after annealing the samples for 15 min. For example, for the blend of SPPO (3.5 mol%) and poly(oFSt-co-oClSt) with 14 mol% oFSt weight loss at 573 K was 0.99%. For SPPO (91 mol%) and copolymer with 73 mol% oFSt, weight loss obtained at 573 K was 0.98%. Similar behaviour was observed for the copolymers with pClSt. Blend of SPPO (8.6 mol%) and copolymer containing 10 mol% oFSt exhibited 0.98% weight loss. For sulphonylated PPO (SPPO 91 mol%) in the blend with copolymer containing 85% oFSt weight loss of 0.97% was found. From these data, it was concluded that thermal degradation was not significant in this study.

The miscibility–immiscibility behaviour of the blends was determined by the usual criterion of a single glass transition in the DSC experiments. In both systems the miscibility was first studied for the "as-precipitated" blends that were obtained by coprecipitation of an equal amount of each component from chloroform solution by methanol. Blends that were found to exhibit miscibility using as-precipitated samples, were investigated further at annealing temperatures of 473, 523 and 573 K.

3.1. *Miscibility of blends of poly*(oFSt-co-pClSt) *with* SPPO *copolymers*

As previously shown, homopolymers poly(oFSt) and poly(pClSt) are immiscible with PPO [11, 12]. In the mixture with SPPO miscibility was found for a range of sulphonylation for both poly(oFSt) and poly(pClSt) homopolymers, although the compositions at which miscibility occurred were different [13].

Table 1 summarizes the results of the miscibility–immiscibility behaviour of 50/50 wt% blends, annealed at 473, 523 and 573 K. All miscible as-precipitated blends were found to be also miscible at 473 K. From Table 1 it is evident that the miscibility window is significantly influenced by the degree of sulphonylation of the SPPO. For example miscibility was found in blends containing copolymers with SPPO content equivalent to the degree of sulphonylation of 8.6 to 87 mol% and styrene copolymer with an oFSt content of 10 mol%. At higher oFSt content of the poly(oFSt-co-pClST) copolymers, the window of miscibility became progressively narrower. Thus, for example, for blends of the copolymer containing 85 mol% oFSt, miscibility was observed with SPPO copolymer ranging from 3.5 to 19.4 mol% substitution. In Fig. 1 are represented data obtained for the 50/50 wt% blends of poly(oFSt-co-pClSt)/SPPO copolymers annealed at 473 K. The dashed line is the calculated miscibility–immiscibility boundary. The bottom left-hand corner in the diagram corresponds to a blend of pure poly(pClSt) and PPO, and the bottom right-hand corner corresponds to a blend

Table 1
Influence of the degree of sulphonylation of SPPO copolymers on the miscibility in the blends with poly(oFSt-co-pClSt)

SPPO content in mol% (T_g in K)	Temperature in K	oFSt content in mol% (T_g in K)								
		10 (405)	18 (400)	26 (397)	38 (394)	45 (392)	60 (388)	65 (383)	75 (380)	85 (377)
3.5 (495)	473	440	440	438	438	436	434	430	428	424
	523	435	439	438	437	434	433	432	426	421
	573	415, 490	438	436	436	435	432	432	425	422
8.6 (502)	473	448	440		439		430	428		425
	523	448	440		438		432	428		425
	573	449	440		439		432	428		427
15.5 (514)	473	445		443		440		433	432	430
	523	445		443		440		434	432	430
	573	445		440		440		435	432	430
25.4 (526)	473	447		446			443			433
	525	448		445			440			430
	573	450		447			441			400, 520
29 (495)	473		448		446		440		427	405, 528
	523		448		446		438		415, 530	–
	573		449		445		438		–	–
36.7 (536)	473	458				442		435	378, 533	378, 533
	523	558				443		435	–	–
	573	458				443		390, 530	–	–
45 (541)	473			443			440			
	523			443			440			
	573			442			405, 535			

49 (542)	473		440			442		386, 535	395, 540	
	523		439			442		–	–	
	573		441			440		–	–	
55 (544)	473	455			452	440				390, 540
	523	457			450	440				–
	573	457			450	406, 537				–
61 (552)	473	460	458		453	393, 535		385, 535	380, 543	
	523	460	457		453	–		–	–	
	573	460	457		400, 550	–		–	–	
66 (557)	473	463			400, 550					380, 550
	523	462			–					–
	573	463			–					–
75 (565)	473	465	455	405, 560		400, 562		400, 560		
	523	465	455	–		–		–		
	573	465	455	–		–		–		
87 (574)	473	460	410, 565	400, 565			390, 568		386, 568	381, 567
	523	460	–	–			–		–	–
	573	462	–	–			–		–	–
91 (579)	473	415, 525	405, 575			388, 575		382, 575		377, 576
	523	–	–			–		–		–
	573	–	–			–		–		–

Values given are T_g in K for samples heated to the temperatures indicated.

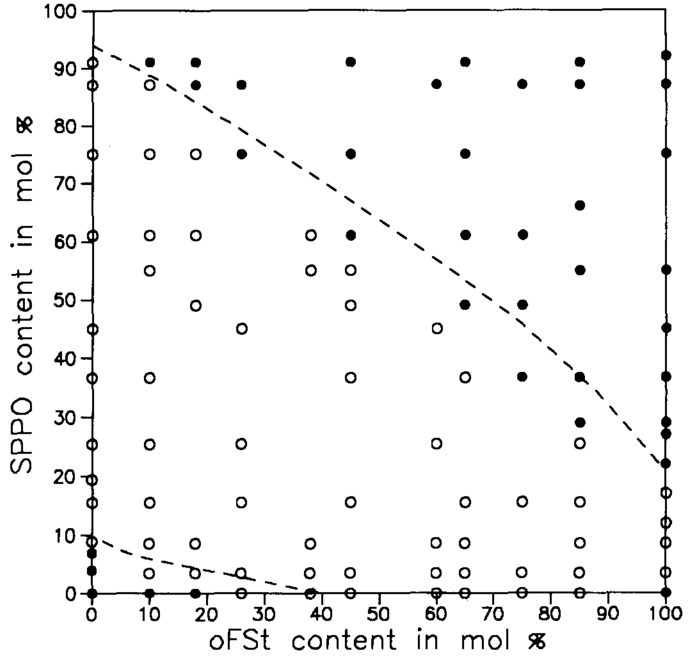

Fig. 1. Miscibility of 50/50 wt% blends of poly(oFSt-co-pClSt)/SPPO copolymers: (○) one phase; (●) two phases. The dashed curve represents the theoretical boundary calculated on the basis of segmental interaction parameters at 473 K.

of pure poly(oFSt) and PPO. These blends are immiscible. In our previous studies it was shown that blends of PPO with poly(oFSt-co-pClSt) which contains 26 to 85 mol% of oFSt are miscible [5]. The "as-precipitated" miscible blends were also further analysed by annealing at 523 and 573 K. As can be seen from Table 1, at the higher annealing temperatures the miscibility window does not change significantly. Phase separation occurred only in blends close to miscibility–immiscibility boundary as shown in Fig. 1.

3.2. *Miscibility of blends of poly*(oFSt-co-oClSt)/SPPO *copolymers*

It was shown that blends of poly(oClSt) and PPO are immiscible at all blend compositions [12]. Blends of poly(oClSt)/SPPO exhibited also two T_gs for all SPPO samples containing from 3.5 to 92 mol% SPPO [13]. PPO is, however, miscible with poly(oFSt-co-oClSt) copolymers with oFSt content from 64 to 85 mol%. The results obtained for these copolymers in blends with SPPO are presented in Table 2 and in Fig. 2. It is evident that the miscibility window in this system is relatively narrow and does not show a significant influence of the degree of sulphonylation on miscibility, in comparison with the corresponding oFSt-ClSt copolymers. For example, at 473 K the copolymer of 50/50 wt% containing 21 mol% of oFSt shows miscibility with SPPO

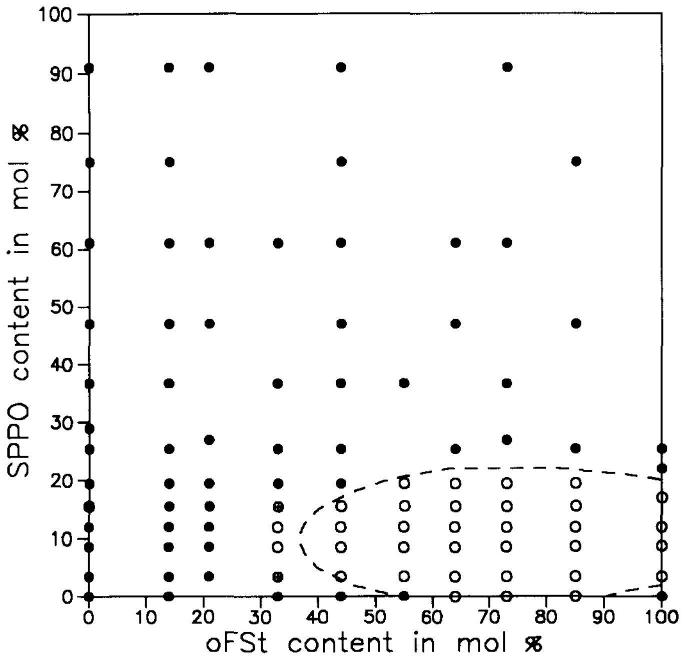

Fig. 2. Miscibility of 50/50 wt% blends of poly(oFSt-co-oClSt)/SPPO copolymers: (○) one phase; (●) two phases; (⊕) intermediate situation. The dashed curve represents the theoretical boundary calculated on the basis of segmental interaction parameters at 473 K.

copolymers with a degree of sulphonylation from 3.5 to 15.5 mol%. Practically the same behaviour is observed for the sample with 85 mol% oFSt content. In this system the results at 473 K are also indistinguishable from those for the as-precipitated blends.

Regarding the behaviour of initially miscible polymer blends on annealing at higher temperatures, i.e. up to 573 K (Table 2), some changes in the miscibility–immiscibility boundary were also observed. The fact that miscibility diminshes as the equilibrium temperature increases, implies lower crytical solution temperature (LCST) behaviour. Fig. 2 represents the data obtained for 50/50 wt% blends for these copolymers annealed at 473 K. The dashed curve is the theoretical boundary between miscible and immiscible blends calculated on the basis of segmental interaction parameters at 473 K. The bottom left-hand corner corresponds to a blend of pure poly(oClSt) and PPO. The bottom right-hand corner represents a blend of pure poly(oFSt) and PPO as in the previous system.

3.3. Segmental interaction parameters

In this section the results of the application of the thermodynamic criteria to the study of phase equilibria in the mentioned polymeric systems is presented. These calculations are based on a first-order mean-field theory of phase behaviour in polymer

Table 2
Influence of the degree of sulphonylation of SPPO copolymers on the miscibility in the blends with poly(oFSt-co-oClSt)

SPPO content in mol% (T_g in K)	Temperauture in K	oFSt content in mol% (T_g in K)							
		14 (405)	21 (401)	33 (369)	44 (391)	55 (387)	64 (383)	73 (377)	85 (373)
3.5 (495)	473	410, 495	415, 495	427[a]	430	430	428	425	422
	523	405, 495	403, 495	405, 490	428	430	428	425	422
	573	–	—	–	412, 492	410, 495	409, 496	400, 495	490
8.6 (502)	473	420, 495	420, 490	430	440	437	435	430	425
	523	415, 495	415, 495	430[a]	440	436	435	430	425
	573	410, 500	412, 495	415, 500	440	436	433	430	425
12 (509)	473	415, 507	415, 495	430	440	439	432	425	423
	523	405, 505	405, 506	430[a]	440	438	432	425	423
	573	–	–	415, 510	440	435	430	425	420
15.5 (514)	473	412, 500	415, 510	430[a]	430	430	424	418	419
	523	400, 505	405, 512	405, 510	430	430	425	417	418
	573	–	–	–	430	426	423	405, 505	505, 515
19.4 (520)	473	410, 518	405, 520	415, 520	410, 510	430	420	418	418
	523	–	–	408, 518	–	430	420	400, 515	395, 510
	573	–	–	–	–	393, 515	395, 518	–	–
25.4 (526)	473	410, 522		410, 520	415, 520		400, 523		390, 520
	523	–		–	–		–		–
	573	–		–	–		–		–
27 (527)	473	408, 520	405, 518	410, 520	415, 525		395, 525	393, 520	395, 515
	523	–	–	–	–		–	–	–
	573	–	–	–	–		–	–	–

36.7 (536)	473	405, 525		400, 530	405, 530	395, 530		382, 527	
	523	–		–	–	–		–	
	573	–		–	–	–		–	
47 (541)	473	405, 535	403, 535		400, 535		395, 540		390, 540
	523	–	–		–		–		–
	573	–	–		–		–		–
61 (552)	473	405, 553	400, 550	398, 552	405, 550		385, 550	378, 550	
	523	–	–	–	–		–	–	
	573	–	–	–	–		–	–	
75 (565)	473	405, 560			390, 560	386, 562			380, 565
	523	–			–	–			–
	573	–			–	–			–
91 (578)	473	405, 560	402, 570		406, 570			397, 570	
	523	–	–		–			–	
	573	–	–		–			–	

Values given are T_g in K for samples heated to the temperatures indicated.

[a] Partially miscible blends.

blends [4]. Both systems constitute a blend of type $(A_{1-x}B_x)_{n1}/(C_{1-y}D_y)_{n2}$, i.e. blends of two random copolymers.

We commence our discussion by restating the expression for the overall interaction parameter, χ_{blend}, related to the six segmental interaction parameters representing the non-identical binary interactions of the monomeric units and the copolymer compositions, by:

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

where A, B, C and D represent *o*-fluorostyrene (oFSt), *p*-chlorostyrene (pClSt) [in poly(oFSt-co-pClSt) system] or *o*-chlorostyrene (oClSt) [in poly(oFSt-co-oClSt) system], 2,6-dimethyl-1,4-phenylene oxide (PPO) and the sulphonylated phenylene oxide (SPPO) units, respectively.

Five of the χ parameters (at 473 K) required in Eq. (1) for both systems are already available [13]. The sixth χ parameter, χ_{AB}, representing interaction between oFSt and pClSt in the poly(oFSt-co-pClSt)/SPPO system and ineraction between oFSt and oClSt in the poly(oFSt-co-oClSt)/SPPO system, was treated as an adjustable parameter. $\chi_{\text{oFSt,pClSt}}$ was estimated using the experimental data for poly(oFSt-co-pClSt)/SPPO system obtained in this study and also from the earlier published results for the poly(oFSt-co-pClSt)/PPO system [14]. Similarly, $\chi_{\text{oFSt,oClSt}}$ was estimated using the experimental data for the poly(oFSt-co-oClSt)/SPPO system presented in this study and from the earlier results for the poly(oFSt-co-oClSt)/PPO system [14]. The value of the molecular-weight-related, conformational entropic term $\chi^{\text{crit}}_{\text{blend}} = 0.004$, was calculated from the degree of polymerization of the respective blend components and from the conventional conditions that the boundary is represented by $\chi_{\text{blend}} = \chi^{\text{crit}}$. The objective functions for parameter estimation may be defined in many ways. We have tried different functions, and the objective function minimized in this study was:

$$F_{\text{min}} = \sum_j \sum_i \left[\frac{Y^{\text{exp}}_{ji} - Y^{\text{cal}}_{ji}}{Y^{\text{exp}}_{ji}} \right]^2 \tag{2}$$

where Y is an experimental and calculated, i is summed over the number of measured variables in a data point, and j is summed over the total number of data points. The optimization algorithm used in the parameter estimation program is the Levenberg–Marquard algorithm [15]. Based on the experimental isothermal data, using previously determined χ parameters, the remaining parameters $\chi_{\text{oFSt,pClSt}}$ and $\chi_{\text{oFSt,oClSt}}$ at 473 K were estimated to be 0.068 and 0.032, respectively. The values of the segmental interaction parameters for all binary combinations of poly(oFSt-co-pClSt) and poly(oFSt-co-oClSt) with SPPO estimated in this paper, together with the results obtained from earlier studies, are collected in Table 3.

In summarizing the results of our studies on the miscibility of blends of poly(oFSt-co-pClSt) and poly(oFSt-co-oClSt) with SPPO, it is evident that remarkable agreement exists between the miscibility–immiscibility boundaries obtained experimentally and by using the simple mean-field approach (Fig. 1 and Fig. 2). It is also evident that the interaction parameters derived previously [13] are sufficiently quantitative to be of predictive value in both copolymer systems studied in this work.

Table 3
Segmental interaction parameters at 473 K

Segment pair	χ_{ij}
PO, oFSt	0.005[a]
SPO, oFSt	0.252[a]
PO, pClSt	0.03[a]
SPO, pClSt	0.017[a]
PO, oClSt	0.02[a]
SPO, oClSt	0.28[a]
oFSt, pClSt	0.068
oFSt, oClSt	0.032
PO, SPO	0.318[a]

[a] From Ref. [14].

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