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# DSC study of the miscibility of PPO and sulphonylated PPO in blends with alternating copolymers of β-substituted styrene derivatives with maleic anhydride and with *N*-substituted maleimides

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## Abstract

The miscibility and phase behaviour of alternating copolymers of the type $\{\mathrm{CHPh{-}CHX{-}\overline{CH{-}CO{-}Y{-}CO{-}CH}}\}_n$ (X is Me, OEt, O*sec*-Bu; Y is oxygen, *N*-Me, *N*-Ph) in blends with PPO and sulphonylated PPO (SPPO) have been studied by differential scanning calorimetry, and by visual observation of film clarity. Alternating copolymers of β-methylstyrene with maleic anhydrice (MAn) or with *N*-substituted maleimide (RMI) were found to be immiscible with PPO and SPPO copolymers in all proportions. The same was found for the blends of alternating copolymers of PhCH=CHOR with MAn or with NMeMI in blends with PPO and SPPO copolymers. It was also found that blends of poly(PhCH–CH–OR–alt–NPhMI) (R is Et, *n*-Bu) are miscible with SPPO having a degree of sulphonylation higher than 60 mol%, but they were immiscible with SPPO of a low degree of sulphonylation. The high-temperature phase separation in the miscible blends is a function of the degree of sulphonylation of SPPO and of the blend composition.

## INTRODUCTION

Recently we have studied the miscibility of alternating copolymers of poly(styrene-co-maleic anhydride), and poly(α-methylstyrene-co-maleic anhydride) in blends with random copolymers of sulphonylated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) [1]. The critical degree of sulphonylation for phase separation in these blends was found to be 55 mol% and 66 mol%, respectively. The miscibility of the alternating copolymers of α-methylstyrene (α-MeS) with maleimide (MI) in blends with polystyrene (PS), poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and SPPO copolymers was also studied. It was found that miscibility in these systems depends on the chemical structure of the blend components. Immiscibility was found for the alternating copolymer blends with PS and with PPO. The miscibility and phase separation behaviour in blends with SPPO depend on the degree

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of sulphonylation of the SPPO copolymers as well as on the chemical structure of the $\alpha$-MeS–MI copolymers.

In continuous of our studies on the miscibility in blends of random SPPO copolymers with alternating copolymers, we have systematically investigated the miscibility of pPO or SPPO with the copolymers

poly(CPhX–CHY–alt–$\overline{\text{CH–CO–Z–CO–CH}}$)

| | | | | | | |
|---|---|---|---|---|---|---|
| **I** | X = H | Y = Me | Z = a) | oxygen | b) NMe | c) NPh |
| **II** | X = H | Y = OEt | Z = a) | oxygen | b) NMe | c) NPh |
| **III** | X = H | Y = O*sec*-Bu | Z = a) | oxygen | b) NMe | c) NPh |

It is reasonable to assume that alternating copolymers which consist of different electron donor and electron acceptor monomer units will influence different miscibility/immiscibility behaviour in blends with the very polar phenylsulphonyl group attached to the phenylene oxide, i.e. the SPO unit.

## EXPERIMENTAL

### *Materials*

The alternating high molecular weight copolymers **I**, **II** and **III**, were prepared by free radical initiated copolymerization with AIBN in bulk or in solvent [2–5]. Polymerizations were carried out in vacuum sealed 10-$cm^3$ glass vials which were thoroughly degassed before sealing and placed in a bath thermostated to the desired temperature. The reaction product was dissolved in butanone and precipitated with methanol, separated by filtration, and dried in high vacuum.

All the copolymers were alternating, as proved by elemental analysis and by $^1H$ NMR spectrometry.

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), General Electric Co., ($\bar{M}$w, 35000; $\bar{M}$n, 17000) was precipitated in methanol from a dilute toluene solution, and dried under vacuum at 80°C for 60 h before use.

Sulphonylated PPO copolymers (SPPO) of different degrees of sulphonylation from 7 to 91 mol% were prepared by Friedel–Crafts sulphonylation of PPO [6, 7].

Polymer blends were prepared by co-precipitation of desired quantities of the polymer components from toluene or chloroform solution with methanol. The dried precipitate was used for DSC studies.

### *Physicochemical measurements*

NMR spectra were obtained on a Varian EM 390 spectrometer.

Molecular weights of the samples were determined by GPC on a Waters instrument using a $\mu$ Styragel column and Varian 8500 pump, with THF as a solvent, at 25°C and with PS reference. The copolymers **I**, **II** and **III** were characterized by the following average molecular weights: **Ia**: $\bar{M}$w 52000,

$\bar{M}n$ 28000; **Ib**: $\bar{M}w$ 232000, $\bar{M}n$ 91000; **Ic**: $\bar{M}w$ 199300, $\bar{M}n$ 92300; **IIa**; $\bar{M}w$ 107700, $\bar{M}n$ 40400; **IIb**: $\bar{M}w$ 84700, $\bar{M}n$ 40000; **IIc**: $\bar{M}w$ 116500, $\bar{M}n$ 55000; **IIIa**: $\bar{M}w$ 33600, $\bar{M}n$ 13000; **IIIb**: $\bar{M}w$ 21500, $\bar{M}n$ 10400; **IIIc**: $\bar{M}w$ 23600, $\bar{M}n$ 11000.

Thermogravimetric analysis experiments were carried out on a Perkin-Elmer TGS-2 instrument at a heating rate of 10°C $\text{min}^{-1}$ with a nitrogen atmosphere.

All DSC studies were performed using a Perkin-Elmer DSC-2 at a heating rate of 20°C $\text{min}^{-1}$ in nitrogen.

The glass transition temperature $T_g$ was determined as the temperature at which the heat capacity achieved one half of the entire step change observed.

## RESULTS AND DISCUSSION

Miscibility in the blends was characterized by DSC as described above, at temperatures up to 583 K. The usual single-$T_g$ was criterion was used for assessing miscibility. Blends that were found to exhibit miscibility over a range of copolymer compositions, as precipitated blends, were investigated further at high temperatures. The thermal stabilities of the blends were evaluated by TGA. Representative samples were pre-dried at 473 K in the TGA furnace in order to remove traces of absorbed water, then heated from 330 to 583 K, and the weight loss determined. As previously published, the thermal stability of alternating copolymers of phenylvinyl alkyl ethers with maleic anhydride [8] or N-substituted maleimides [5] is influenced by the steric characteristics of the alkyl substituent in the electron donor moiety of the copolymers. It was found that the weight loss increases from the ethyl substituent to *sec*-butyl. The thermal stability of PPO is practically independent of the degree of sulphonylation [6, 7]. Polymer blends of these constituents show good stability up to 583 K. It was found that the weight loss for each SPPO copolymer-alternating copolymer system studied was less than 1 wt% at the highest temperature of 583 K. β-Methylstyrene copolymers in blends with SPPO show the same behaviour. Therefore, it was concluded that degradation was not an important factor in this investigation.

### *Miscibility of blends of poly(β-methylstyrene-alt-maleic anhydride) (**Ia**) or poly(β-methylstyrene-alt-*N*-methylmaleimide) (**Ib**) or poly(β-methylstyrene-alt-*N*-phenylmaleimide) (**Ic**) with PPO or SPPO copolymers*

The glass transition temperatures for these blends are summarized in Table 1. The $T_g$ values of the second heat are reported. It is evident that all the samples examined have two $T_g$ values and are, therefore, considered immiscible. Immiscibility was also found for all PPO and β-MeS alternating copolymer blends.

### *Miscibility of blends of poly(phenylvinyl ethyl ether-alt-maleic anhydride) (IIa) or poly(phenylvinyl ethyl ether-alt-N-methylmaleimide) (IIb) or poly(phenylvinyl ether ether-alt-N-phenylmaleimide) (IIc) with PPO or SPPO copolymers*

Miscibility in these systems was studied for blends of SPPO copolymers with various degrees of sulphonylation, from 7 to 91 mol% substitution. As can be seen in Table 2, these blends exhibited a somewhat different behaviour from the $\beta$-methyl-styrene copolymers. For the copolymers of **IIa** and **IIb**, immiscibility was found, independent of the degree of sulphonylation of the SPPO copolymers. Copolymers of phenylvinyl ethyl ether with *N*-phenylmaleimide show miscibility in the blends with SPPO of sulphonylation degree from 61 to 91 mol%. For the blend containing SPPO 37, 45 and 55, respectively, one $T_g$ value was also obtained. Due to the small differences between the $T_g$s values of the blend constituents, it is not possible to conclude whether or not they are miscible on the $T_g$ criterion. But these systems exhibited opaque films, thus indicating immiscibility. To observe film clarity, thin films were prepared by casting the polymer solution onto a cover glass and evaporating the solvent. The transition width of the miscible blends is not influenced by the degree of sulphonylation of SPPO.

For illustration, the DSC thermograms of several SPPO/poly(CHPh–CHOEt–alt–*N*–PhMI) blends are shown in Fig. 1.

All alternating copolymers in the blends with PPO exhibited two $T_g$ values and are considered immiscible.

Further insight into the behaviour of the initially (as-precipitated) miscible blends was obtained by annealing to higher temperatures. It is known that some polymer blends with an observed miscibility at low temperature are susceptible to phase separation at elevated temperatures, which indicates the existence of a lower critical solution temperature. Therefore, it is of interest to analyse further the behaviour of the systems which were found to be miscible as precipitated, as a function of the SPPO copolymer composition (different degrees of sulphonylation), blend composition, and annealing temperature. The annealing experiments were carried out in the DSC; a typical experiment consisted of heating a sample known to be homogeneous to the selected annealing temperature and holding it at that temperature for 15 min. Samples were then quenched to ambient temperature, and the $T_g$ behaviour determined by reheating [9].

Annealing the miscible blends at elevated temperature led to phase separation at 473 K for blends containing SPPO with a sulphonylation degree of 91 mol%, and at 553 K for the blend containing SPPO with a sulphonylation degree of 87 mol%. Other polymer blends containing SPPO copolymers of sulphonylation degree between 61 and 75 mol% did not phase-separate even after annealing up to 583 K. These results are shown in

TABLE 1

Miscibility of blends of poly($\beta$-methylstyrene-alt-maleic anhydride) (**Ia**) or poly($\beta$-methylstyrene-alt-*N*-methylmaleimide) (**Ib**) or poly($\beta$-methylstyrene-alt-*N*-phenylmaleimide) (**Ic**) with PPO or SPPO copolymers

| Alternating copolymers | PPO and SPPO copolymers [a] | $T_g$/K | Polymer blends, $T_g$/K, as-precipitated |
|---|---|---|---|
| **Ia**, $T_g$, 555 K | PPO | 490 | 490, 556 |
| | SPPO 7 | 497 | 496, 555 |
| | SPPO 19 | 520 | 517, 555 |
| | SPPO 37 | 536 | 535, 555 |
| | SPPO 45 | 540 | 540, 556 |
| | SPPO 55 | 544 | 540, 555 |
| | SPPO 68 | 558 | 555 [b] |
| | SPPO 75 | 565 | 560 [b] |
| | SPPO 87 | 574 | 555, 570 |
| | SPPO 91 | 578 | 555, 578 |
| **Ib**, $T_g$, 565 K | PPO | 490 | 490, 565 |
| | SPPO 7 | 497 | 505, 565 |
| | SPPO 19 | 520 | 517, 564 |
| | SPPO 37 | 536 | 535, 564 |
| | SPPO 45 | 540 | 540, 565 |
| | SPPO 55 | 544 | 546, 565 |
| | SPPO 68 | 558 | 562 [b] |
| | SPPO 75 | 565 | 565 [b] |
| | SPPO 87 | 574 | 570 [b] |
| | SPPO 91 | 578 | 564, 579 |
| **Ic**, $T_g$, 591 K | PPO | 490 | 491, 591 |
| | SPPO 7 | 497 | 506, 590 |
| | SPPO 19 | 520 | 520, 590 |
| | SPPO 37 | 536 | 536, 591 |
| | SPPO 45 | 540 | 540, 590 |
| | SPPO 55 | 544 | 548, 590 |
| | SPPO 68 | 558 | 563, 589 |
| | SPPO 75 | 565 | 566, 590 |
| | SPPO 87 | 574 | 570, 590 |
| | SPPO 91 | 578 | 577, 590 |

[a] Number with SPPO indicates the mol.% of sulphonylated PPO in the copolymer. [b] Owing to the small difference between $T_g$ values of the copolymers, two separated temperatures $T_g$ were not obtained for immiscible blends.

Fig. 2 for measurements of 50/50 wt% blends. The boundary separating one- and two-phase regimes represents the locus of a series of lower critical solution temperatures (LCSTs) for mixtures of SPPO with the alternating copolymers. The phase diagram for one miscible blend containing SPPO with sulphonylation degree 91 mol% of different compositions is shown in Fig. 3. At 473 K for the blend containing 50/50 wt% of each component,

TABLE 2

Miscibility of blends of poly(phenylvinyl ethyl ether-alt-maleic anhydride) (**IIa**) or poly(phenylvinyl ethyl ether-alt-*N*-methylmaleimide) (**IIb**) or poly(phenylvinyl ethyl ether-alt-*N*-phenylmaleimide) (**IIc**) with PPO or SPPO copolymers

| Alternating copolymers | PPO and SPPO copolymers [a] | $T_g$/K | Polymer blends, $T_g$/K, as-precipitated |
|---|---|---|---|
| **II**a, $T_g$, 506 K | PPO | 490 | 490, 505 |
| | SPPO 7 | 497 | 495, 505 |
| | SPPO 19 | 520 | 507, 517 |
| | SPPO 37 | 536 | 506, 533 |
| | SPPO 45 | 540 | 505, 538 |
| | SPPO 55 | 544 | 505, 542 |
| | SPPO 68 | 558 | 504, 553 |
| | SPPO 75 | 565 | 505, 562 |
| | SPPO 87 | 574 | 506, 570 |
| | SPPO 91 | 578 | 506, 574 |
| **II**b, $T_g$, 508 K | PPO | 490 | 491, 509 |
| | SPPO 7 | 497 | 495, 507 |
| | SPPO 19 | 520 | 506, 518 |
| | SPPO 37 | 536 | 508, 535 |
| | SPPO 45 | 540 | 507, 539 |
| | SPPO 55 | 544 | 515, 538 |
| | SPPO 68 | 558 | 517, 547 |
| | SPPO 75 | 565 | 523, 561 |
| | SPPO 87 | 574 | 523, 567 |
| | SPPO 91 | 578 | 525, 575 |
| **II**c, $T_g$, 531 K | PPO | 490 | 488, 533 |
| | SPPO 7 | 497 | 493, 530 |
| | SPPO 19 | 520 | 517, 532 |
| | SPPO 37 | 536 | 532 [b] |
| | SPPO 45 | 540 | 536 [b] |
| | SPPO 55 | 544 | 538 [b] |
| | SPPO 61 | 554 | 545 |
| | SPPO 68 | 558 | 550 |
| | SPPO 75 | 565 | 555 |
| | SPPO 87 | 574 | 559 |
| | SPPO 91 | 578 | 565 |

[a] The number with SPPO indicates the mol.% of the sulphonylated PPO in the copolymer.

[b] Owing to the small difference between the $T_g$ values of the copolymers, two separate temperatures were not obtained for immiscible blends.

two $T_g$s were observed; all other blends are miscible at this temperature. At 523 K for blends of 50/50 and 35/65 wt% SPPO, phase separation occurred. At 553 K, the blend containing 65/35 wt% SPPO is considered to be partially miscible. At 583 K, all blend compositions except 80/40 wt% SPPO exhibited immiscibility. The influence of the blend

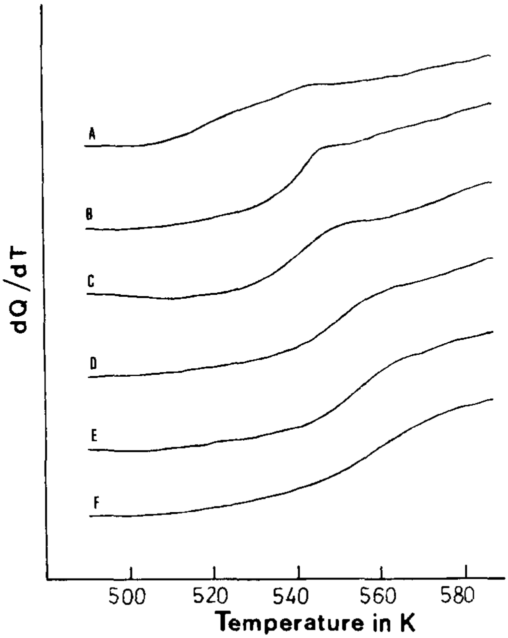

Fig. 1. DSC thermograms of 50/50 wt% of poly(phenylvinyl ethyl ether-alt-*N*-phenylmaleimide) blends: A, SPPO 19; B, SPPO 61; C, SPPO 68; D, SPPO 75; E, SPPO 87; F, SPPO 91. The number with SPPO indicates the mol% of sulphonylated PPO in the copolymers.

composition was also studied for the samples containing SPPO 75; it was found that all blends show miscibility at temperatures up to 583 K.

### *Miscibility of blends of poly(phenylvinyl* sec*-butyl ether-alt-maleic anhydride (IIIa) or poly(phenyl* sec*-butyl ether-alt-*N*-methylmaleimide) (IIIb) or poly(phenylvinyl* sec*-butyl ether)-alt-*N*-phenylmaleimide) (IIIc) with PPO or SPPO copolymers*

The miscibility behaviour of PPO in the blends with these copolymers is the same as those found for the corresponding phenylvinyl ethyl ethers, i.e. immiscibility was found in all systems independent of the copolymer and blend composition.

In blends with SPPO these copolymers show miscibility for SPPO of some degrees of sulphonylation, similar to those found for the corresponding phenylvinyl ethyl ethers. The results are presented in Table 3. It is evident that alternating copolymers with MAn and with *N*-MeMI exhibit two $T_g$s in blends with SPPO. But **IIIc** blends show one $T_g$ for SPPO of sulphonylation degrees 37, 45, 55, 68, 75, and 87 mol%. Polymer pairs containing SPPO of sulphonylation degree 61 and 91 mol%, respectively, were found to be immiscible. The only miscible blends are those with SPPO

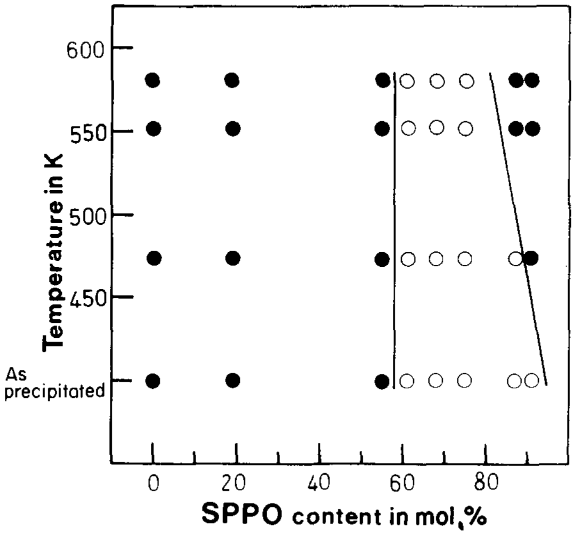

Fig. 2. Miscibility of 50/50 wt% blends of poly(phenylvinyl ethyl ether-alt-*N*-phenylmaleimide) and SPPO: ○, one phase; ●, two phases.

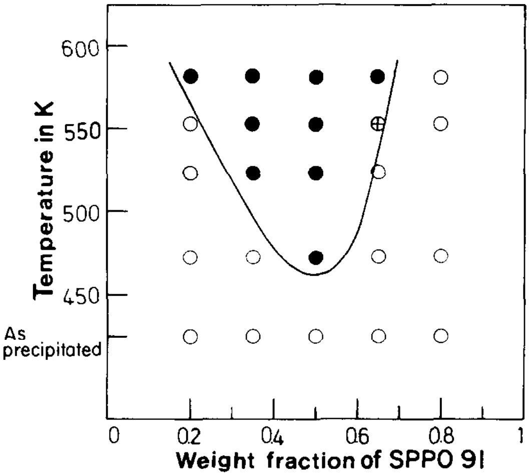

Fig. 3. Miscibility of blends of poly(phenyl ethyl ether-alt-*N*-phenylmaleimide) and SPPO containing 91 mol.% of sulphonylated PPO copolymers, as a function of blend compositions: ○, one phase; ⊕, intermediate situation; ●, two phases.

TABLE 3

Miscibility of blends of poly(phenylvinyl *sec*-butyl ether-alt-maleic anhydride) (**IIIa**) or poly(phenyl *sec*-butyl ether-alt-*N*-methylmaleimide) (**IIIb**) or poly(phenylvinyl *sec*-butyl ether-alt-*N*-phenylmaleimide) (**IIIc**) with PPO or SPPO copolymers

| Alternating copolymers | PPO and SPPO copolymers [a] | $T_g$/K | Polymer blends, $T_g$/K, as-precipitated |
|---|---|---|---|
| **IIIa**, $T_g$, 515 K | PPO | 490 | |
| | SPPO 7 | 497 | 495, 517 |
| | SPPO 19 | 520 | 516 [b] |
| | SPPO 37 | 546 | 513, 533 |
| | SPPO 45 | 540 | 515, 539 |
| | SPPO 55 | 544 | 515, 543 |
| | SPPO 68 | 558 | 517, 555 |
| | SPPO 75 | 565 | 520, 560 |
| | SPPO 87 | 574 | 515, 570 |
| | SPPO 91 | 578 | 518, 575 |
| **IIIb**, $T_g$, 505 K | PPO | 490 | 488, 505 |
| | SPPO 7 | 497 | 598 [b] |
| | SPPO 19 | 520 | 503, 517 |
| | SPPO 37 | 546 | 505, 535 |
| | SPPO 45 | 540 | 505, 538 |
| | SPPO 55 | 544 | 506, 542 |
| | SPPO 68 | 558 | 506, 555 |
| | SPPO 75 | 565 | 505, 565 |
| | SPPO 87 | 574 | 506, 573 |
| | SPPO 91 | 578 | 508, 576 |
| **IIIc**, $T_g$, 535 K | PPO | 490 | 490, 533 |
| | SPPO 7 | 497 | 497, 535 |
| | SPPO 19 | 520 | 517, 537 |
| | SPPO 37 | 536 | 536 [b] |
| | SPPO 45 | 540 | 536 [b] |
| | SPPO 55 | 544 | 538 [b] |
| | SPPO 61 | 554 | 526, 550 |
| | SPPO 68 | 558 | 543 |
| | SPPO 75 | 565 | 553 |
| | SPPO 87 | 574 | 557 |
| | SPPO 91 | 578 | 535, 565 |

[a] The number with SPPO indicates the mol.% of the sulphonylated PPO in the copolymer.
[b] Owing to the small difference between $T_g$ values of the copolymers two separated temperatures were not obtained for immiscible blends.

of sulphonylation degrees 65, 75 and 87 mol%. For blends containing SPPO of sulphonylation degrees 37, 45 and 55 mol%, due to the small difference between the $T_g$ of the blend components, it is not possible to conclude whether or not they are miscible. Immiscibility was proved on the basis of

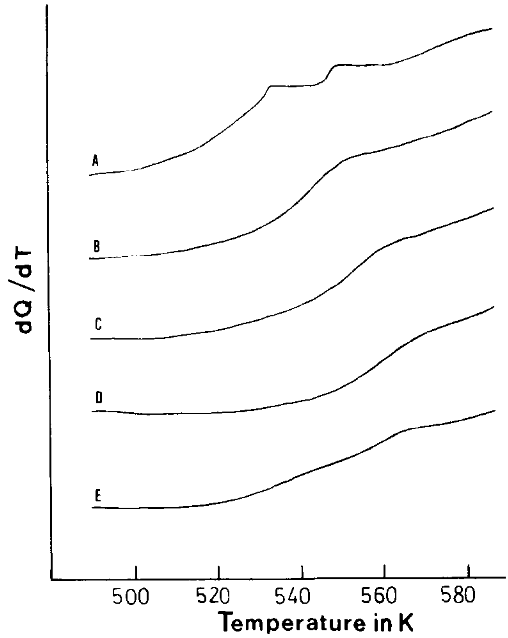

Fig. 4. DSC thermograms of 50/50 wt% of blends of poly(phenylvinyl *sec*-butyl ether-alt-*N*-phenylmaleimide) and SPPO: A, SPPO 61; B, SPPO 68; C, SPPO 75; D, SPPO 87; E, SPPO 91. The number with SPPO indicates the mol% of sulphonylated PPO in the copolymer.

low film clarity of films prepared from chloroform solution. DSC thermograms illustrating this behaviour can be seen in Fig. 4.

For these systems the influence of the annealing temperature and blend composition on the miscibility was also investigated. Annealing the miscible blends at elevated temperature led to phase separation at 553 K only for the blend containing SPPO with a sulphonylation degree of 87 mol%, as evidenced by the observation of two glass transition temperatures. Copolymers containing SPPO 68 and 75 mol%, did not phase-separate, even after annealing up to 583 K. These results are shown in Fig. 5 and represent measurements of 50/50 wt% blends. The influence of the blend composition on the miscibility was checked for the blends containing SPPO of sulphonylation degree 75 mol%. It was found that phase separation did not occur, even after annealing up to 583 K, independent of blend composition.

The behaviour of the blends in this study demonstrates again the effect of structural changes on miscibility in polymers. It was found that the miscibility of alternating copolymers of β-substituted styrene derivatives with maleic anhydride and with *N*-substituted maleimides in blends with SPPO depends on the chemical structure of the alternating copolymers as well on the degree of sulphonylation of SPPO which varied from 7 to 91 mol%.

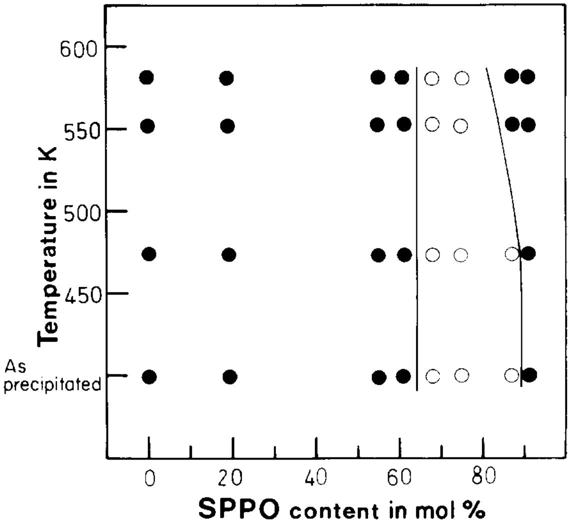

Fig. 5. Miscibility of 50/50 wt% blends of alternating poly(phenylvinyl *sec*-butyl ether-alt-*N*-phenylmaleimide) and SPPO: ○, one phase; ●, two phases.

Alternating $\beta$-methylstyrene–maleic anhydride copolymers were found to be immiscible with SPPO copolymers in all proportions. The same was found for $\beta$-methylstyrene–*N*-substituted maleimide copolymers in blends with SPPO. Alternating copolymers of MAn or N-MeMI with electron donor molecules which contain highly polar ether groups instead of a methyl group in the beta-position of the styrene molecule, also exhibited immiscibility in blends with SPPO.

For some degrees of sulphonylation of the SPPO copolymer, miscibility was found in blends with phenylvinyl alkyl ethers–*N*-phenyl maleimide copolymers. From the data obtained, it is evident that copolymers containing an ethyl group show miscibility over a wider range of sulphonylation degree of the SPPO copolymers than copolymers containing a *sec*-butyl group. This is probably due to the presence of the bulky *sec*-butyl group which can reduce copolymer ability for miscibility with SPPO.

It should also be noted that the best miscibility in both alternating copolymer–SPPO blends was found for SPPO copolymers of sulphonylation degrees 68 and 75 mol%. A very high degree of sulphonylation, 91 mol%, leads to immiscibility in blends with alternating copolymers containing a *sec*-butyl group without annealing, i.e. as-precipitated blends. For polymers containing an ethyl group, immiscibility was obtained after annealing the sample at 473 K.

In further research, it will be interesting to calculate segmental interaction parameters based on the first-order mean-field treatment [10], in order to elucidate this behaviour.

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