ELSEVIER

Thermochimica Acta 275 (1996) 259–268

thermochimica
acta

# Copolymer blends of phenylsulphonylated poly(2,6-dimethyl-1,4-phenylene oxide) and poly(*p*-fluorostyrene-co-*p*(*o*)-chlorostyrene)

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

Received 3 January 1995; accepted 31 March 1995

**Abstract**

Miscibility in random copolymers of *p*-fluorostyrene-co-*p*(*o*)-chlorostyrene (poly(*p*-FSt-co-*p*(*o*)-ClSt)) with partially sulphonylated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) has been studied by differential scanning calorimetry (DSC). It was found that miscibility predominantly depends on the degree of sulphonylation of SPPO copolymers. Copolymers of *p*FSt with *p*ClSt exhibit miscibility with SPPO with a higher degree of sulphonylation than the copolymers containing *o*ClSt. Upon annealing to temperatures of 523 and 573 K, only small changes in the miscibility regime were observed. Using the mean-field theory approach, the miscibility behaviour was analysed in terms of the individual segmental interaction parameters.

*Keywords:* Blends; Copolymer; DSC; Sulphonylation

## 1. Introduction

The miscibility of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with poly(*p*-FSt-co-*p*(*o*)-ClSt) has been studied. It was found that these systems exhibited immiscibility independent of blend composition [1]. In addition, the pure homopolymers of *p*FSt, *p*ClSt and *o*ClSt were found to be immiscible with PPO [1–3]. By introducing phenylsulphonyl groups attached to the phenylene oxide, i.e. the SPPO copolymer, in the blends with poly(*p*FSt) and poly(*p*ClSt), miscibility was observed for a range of

---

* Corresponding author.

*SSDI* 0040-6031(94)02398-4

SPPO. Very recently we have found that SPPO/poly(*o*FSt-co-*p*(*o*)ClSt) blends show miscibility for a range of SPPO with different degrees of sulphonylation and copolymer composition [5]. Taking into consideration these results, we now report on the miscibility and phase behaviour of SPPO/poly(*p*FSt-co-*p*(*o*)ClSt) blends that are particulary relevant in the light of the immiscibility of PPO itself with these systems. The experimental results will be discussed in the context of a mean-field treatment [6,7].

## 2. Experimental

### 2.1. Materials

Random copolymers of poly(*p*FSt-co-*p*(*o*)-ClSt) of high molecular weight were prepared by free-radical-initiated polymerization of the respective monomers at 60°C in toluene with 2,2-azobis(isobutyronitrile) (AIBN) following the procedure previously described [1]. Copolymers of poly(*p*FSt-co-*p*-ClSt) with *p*FSt contents of 11, 26, 36, 47, 59, 70 and 82 mol%, and copolymers of poly(*p*FSt-co-*o*-ClSt) with *p*FSt contents of 16, 22, 29, 35, 45, 53, 62, 72 and 81 mol%, were prepared. The properties of the copolymers used in this study were identical to those reported earlier [1,8,9].

The procedure for the preparation of partially sulphonylated PPO copolymers was also described in previous publications [10,11]. SPPO copolymers with degrees of sulphonylation of 3.5, 8.6, 12, 15.5, 19.4, 27, 29, 36.7, 47, 55, 61, 75, 87 and 91 mol%, were used in this study.

Polymer blends were prepared by coprecipitation of chloroform solution, which contained a total of 5 wt% of polymer, with methanol. The desired quantities of the materials to be blended were dissolved in chloroform and precipitated with methanol. The dried samples were used in DSC experiments.

### 2.2. Measurements

The glass transition temperatures ($T_g$) of the 50/50 wt% polymer blends were measured using a Perkin-Elmer DSC-2 at a heating rate of 20°C min$^{-1}$ under nitrogen. The glass transition temperature(s) were the only distinctive features on the DSC thermograms. 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 by the usual procedure which consists of heating the initially miscible samples to the desired temperature and holding the samples at this temperature for 15 min. After that the samples were quenched to room temperature and further analysed [12].

The thermal stability of the blends was evaluated by thermogravimetric analysis (Perkin-Elmer TGS-2) in which samples were heated in nitrogen at a rate of 10°C min$^{-1}$. These samples were predried at 473 K in the DSC furnace to remove traces of absorbed water and then heated from 323 to 573 K to determine weight loss.

## 3. Results and discussion

### 3.1. Calorimetric studies

The miscibility of the blends was determined by the usual criterion of a single glass transition in the DSC measurements (second scan). Blends that were found to exhibit miscibility using samples precipitated as described above ("as-precipitated blends") were investigated further at annealing temperatures of 473, 523 and 573 K. Since these are relatively high temperatures, the thermal stability of the blends was evaluated by using thermogravimetric analysis. It was found that the maximum weight loss for both SPPO/poly(*p*FSt-co-*p*(*o*)-ClSt) systems was less than 1% at 573 K after annealing the samples for 15 min. It was thus concluded that thermal degradation was not an important factor in this study.

### 3.2. *SPPO/poly(*pFSt-co-pClSt*) blends*

Blends of this copolymer were found to be miscible or immiscible depending on the styrenic copolymer composition and, in particular, on the degree of sulphonylation of the SPPO copolymers. First, it was concluded that the behaviour of the as-precipitated blends is the same as that of the blends which were annealed at 473 K. Since the segmental interaction parameters are also calculated at this temperature, the experimentally obtained results (circles) and the theoretical curve obtained from the $\chi_{ij}$ values (dashed lines) are shown for comparison in Fig. 1.

As previously described [1–3], none of the blends of PPO with poly(*p*FSt) or poly(*p*ClSt) were miscible (points at the bottom left-hand and right-hand curves). The immiscibility also occurs in PPO/poly(*p*FSt-co-*p*-ClSt) blends for all copolymer compositions as can be seen on the abscissa of this figure. The miscibility window for SPPO/styrenic copolymer is very wide and is qualitatively similar for all copolymer compositions. For example, for the blends containing 11 and 26 mol% *p*FSt, the miscibility was found for SPPO of sulphonylation degrees from 9 to 91 mol%. For the samples containing 70 and 81 mol% *p*FSt, miscibility was observed for the blends with SPPO of sulphonylation degrees from 12 to 75 and 15.5 to 75 mol%, respectively. It was also found that the boundary between one- and two-phase behaviour is only very slightly temperature-dependent (Table 1). Phase separation occurred only in the blend samples lying on the miscibility–immiscibility boundary shown in Fig. 1.

### 3.3. *SPPO/poly(*oFSt-co-oClSt*) blends*

In this system, the miscibility window is highly asymmetric with respect to the isomer contents (Fig. 2). Fig. 2 summarizes the results for 50/50 wt% blends annealed at 473 K, plotted in terms of copolymer compositions. The as-precipitated blends behave in the same manner as the annealed specimen. As previously shown, the immiscibility was found for PPO blends with poly(*p*FST) and with poly(*o*ClSt) [1–3]. PPO/poly(*p*FSt-co-*o*-ClSt) blends also show immiscibility independent of copolymer and blend compo-

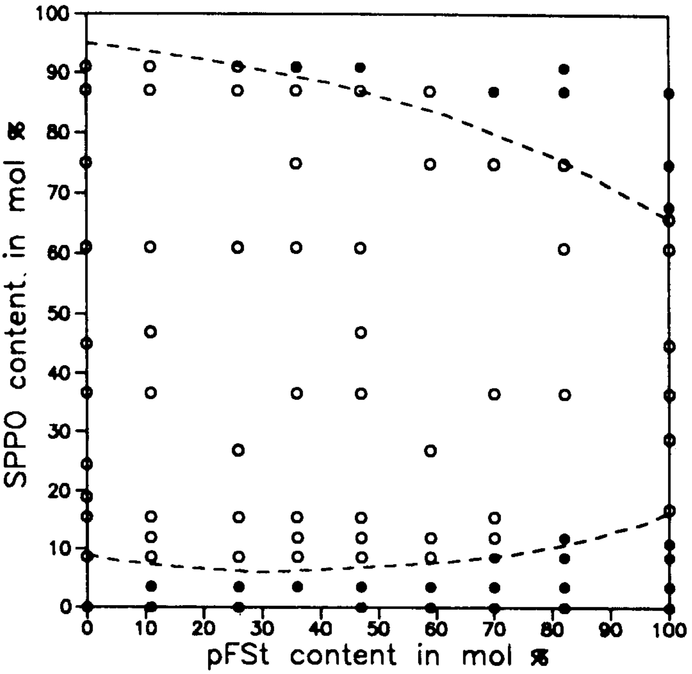

Fig. 1. Miscibility of 50/50 wt% blends of poly(*p*FSt-co-*p*-ClSt)/SPPO copolymers: M, one phase; N, two phases; +, intermediate situation. The broken line represents the theoretical boundary calculated on the basis of segmental interaction parameters at 473 K.

sitions [1]. These properties are presented as solid circles on the abscissa in Fig. 2. The points at the beginning and end of the abscissa represent PPO/poly(*o*ClSt) or PPO/poly(*p*FSt) blends, respectively. In the blends of SPPO/poly(*o*ClSt), immiscibility was also observed for the blends containing SPPO with a degree of sulphonylation from 4 to 92 mol% [5]. In contrast, SPPO/poly(*p*FSt) exhibited miscibility behaviour for SPPO with a degree of sulphonylation from 17 to 66 mol% [5].

The miscibility window in the system under consideration which exists for some degree of SPPO sulphonylation and copolymer compositions, becomes wider with increasing *p*FSt content in the copolymer (Fig. 2). For example, in the blend with copolymer which contains 16 mol% *p*FSt, immiscibility occurs independently of the degree of SPPO sulphonylation. The miscibility was found for the copolymer with 22 mol% *p*FSt in the blends with SPPO of degrees of sulphonylation from 3.5 to 19.4 mol%. The blends containing copolymer with 81 mol% *p*FSt with SPPO of sulphonylation degrees from 12 to 49 mol% exhibited miscibility. Again, the dashed curve represents the calculated miscibility–immiscibility boundaries at 473 K. For this system, miscibility diminishes as the equilibrium temperature increases only for the blends on the miscibility–immiscibility boundary shown in Fig. 2. The results obtained for the miscibility at 473, 523 and 573 K are shown in Table 2.

Table 1
Influence of the degree of sulphonylation of SPPO copolymers on the miscibility in the blends with poly(*p*FSt-co-*p*ClSt)

| SPPO content in mol % ($T_g$/K) | Temperature K | *p*FSt content in mol % ($T_g$/K) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 11 (405) | 26 (405) | 36 (402) | 47 (395) | 59 (395) | 70 (393) | 82 (387) |
| 3.5(495) | 473 | 411,496 | 410,495 | 407,496 | 398,493 | 396,495 | 395,495 | 392.406 |
| | 523 | – | – | – | – | – | – | – |
| | 573 | – | – | – | – | – | – | – |
| 8.6(502) | 473 | 448 | 447 | 443 | 440 | 435 | 395,500 | 393,500 |
| | 523 | 448 | 447 | 443 | 436 | 430* | – | – |
| | 573 | 447 | 446 | 444 | 405,500 | 400,497 | – | – |
| 12(509) | 473 | 452 | | 441 | 443 | 436 | 435 | 395,540 |
| | 523 | 453 | | 442 | 440 | 436 | 435 | 395,507 |
| | 573 | 452 | | 442 | 440 | 435 | 435 | – |
| 15.5(514) | 473 | 446 | 445 | 446 | 442 | | 435 | 430 |
| | 523 | 445 | 445 | 443 | 442 | | 433 | 430 |
| | 573 | 446 | 444 | 443 | 442 | | 435 | 427 |
| 27(527) | 473 | | 450 | | | 452 | | |
| | 523 | | 453 | | | 452 | | |
| | 573 | | 452 | | | 450 | | |
| 36.7(537) | 473 | 456 | | 457 | 453 | | 447 | 444 |
| | 523 | 457 | | 455 | 454 | | 447 | 444 |
| | 573 | 457 | | 455 | 455 | | 446 | 444 |
| 47(541) | 473 | 457 | | | 450 | | | |
| | 523 | 458 | | | 451 | | | |
| | 573 | 458 | | | 450 | | | |
| 61(552 | 473 | 458 | 453 | 455 | 455 | | | 446 |
| | 523 | 459 | 452 | 455 | 455 | | | 435.553 |
| | 573 | 459 | 454 | 456 | 450 | | | 435,553 |
| 75(565) | 473 | | | 445 | | 447 | 446 | 445 |
| | 523 | | | 445 | | 447 | 446 | 440 |
| | 573 | | | 445 | | 447 | 445 | 410,533 |
| 87(574) | 473 | 462 | 462 | 459 | 456 | 445 | 405,565 | 395,570 |
| | 523 | 460 | 460 | 458 | 456 | 445 | – | – |
| | 573 | 457 | 458 | 452 | 455 | 445 | – | |
| 91(597) | 473 | 460 | 460 | 450* | 440,520 | | | 394,575 |
| | 523 | 460 | 460 | 450* | 430,503 | | | – |
| | 573 | 456 | 460 | 450* | 412,575 | | | |

Values given are $T_g$/K for samples heated to the temperatures indicated.
* Partially miscible blend.

### 3.4. Segmental interaction parameters

The behaviour of the blends in this study demonstrates again the effect of relatively small structural changes on miscibility in polymers. A quantitative accounting of these results can be obtained by applying the simple mean-field theory to copolymer phase behaviour. Here we will not review the theory, referring the reader to Refs. [6] and [7].

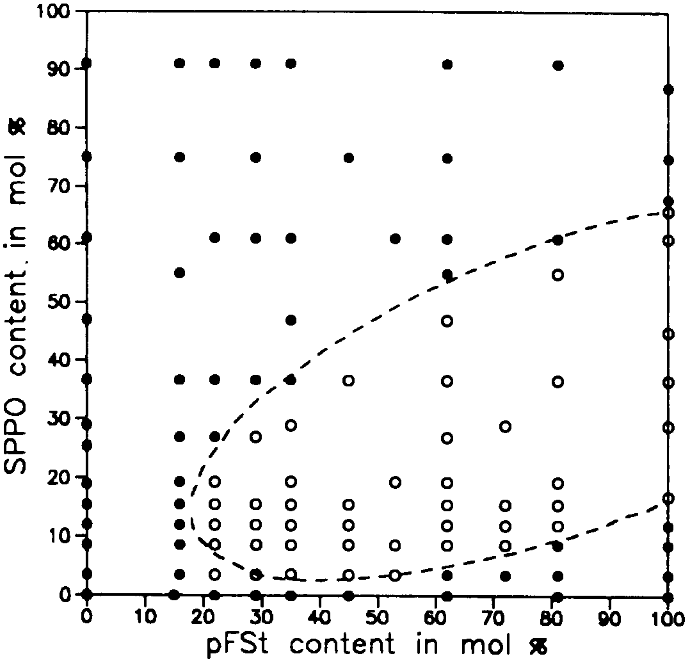

Fig. 2. Miscibility of 50/50 wt% blends of poly(*p*FSt-co-*o*-ClSt)/SPPO copolymers: M, one phase; N, two phases. The broken line represents the theoretical boundary calculated on the basis of segmental interaction parameters at 473 K.

We will, however, demonstrate the applications, verifying again that the mean-field approach may be used for semiquantitative prediction of phase equilibria compositions for mixtures of polymers.

Both systems in this study constitute random copolymer mixtures with four distinct repeating units of the type $(A_{1-x}B_x)_{n1}/(C_{1-y}D_y)_{n2}$. For the general case of two such random copolymers, where $x$ and $y$ denote the copolymer compositions, the $\chi_{\mathrm{blend}}$ expression involves six segmental interaction parameters $\chi_{ij}$ for the comonomer($i$)–comonomer($j$) interactions relevant to the system

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

For the blend systems in this study A, B, C and D represent *p*FSt, *p*ClSt or *o*ClSt (in the poly(*p*FSt-co-*p*-ClSt) or poly(*p*FSt-co-*o*-ClSt) systems), PPO and SPPO units, respectively.

The quantitative determination of $\chi_{ij}$ values using the mean-field theory requires the experimental observation of miscibility–immiscibility boundaries as a function of copolymer composition to obtain the fit as shown in Figs. 1 and 2, by minimizing the adequate objective function [5]. For both the mentioned polymeric systems, five of the $\chi_{ij}$ parameters required in expression (1) are already available from earlier investiga-

Table 2
Influence of the degree of sulphonylation of SPPO copolymers on the miscibility in the blends with poly(*p*FSt-co-*o*ClSt)

| SPPO content in mol % ($T_g$/K) | Temperature K | *p*FSt content in mol % ($T_g$/K) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 16 (404) | 22 (402) | 29 (398) | 35 (397) | 45 (395) | 53 (393) | 62 (390) | 72 (387) | 81 (385) |
| 3.5 (495) | 473 | 423, 495 | 435 | 433 | 434 | 435 | 433 | 400, 490 | 395, 493 | 395, 495 |
| | 523 | 412, 495 | 433 | 432 | 433 | 435 | 433 | – | – | – |
| | 573 | | 429 | 432 | 433 | 435 | 395, 493 | – | – | – |
| 8.6 (502) | 473 | 490, 500 | 440 | 440 | 440 | 440 | 438 | 435 | 438 | 395, 500 |
| | 523 | – | 441 | 440 | 440 | 440 | 436 | 435 | 437 | – |
| | 573 | – | 441 | 440 | 440 | 439 | 437 | 436 | 400, 500 | – |
| 12 (509) | 473 | 405, 505 | 442 | 440 | 440 | 439 | | 436 | 430 | 425 |
| | 523 | – | 442 | 440 | 440 | 438 | | 436 | 430 | 390, 503 |
| | 573 | – | 441 | 440 | 439 | 438 | | 436 | 398, 500 | – |
| 15.5 (526) | 473 | 406, 510 | 442 | 443 | 443 | | 435 | 432 | | 428 |
| | 523 | – | 441 | 443 | 443 | | 435 | 434 | | 426 |
| | 573 | – | 440 | 445 | 443 | | 435 | 433 | | 426 |
| 19.4 (520) | 473 | 405, 518 | 443 | | 441 | | 435 | | | 427 |
| | 523 | – | 442 | | 440 | | 436 | | | 428 |
| | 573 | – | 442 | | 440 | | 433 | | | 425 |
| 27 (527) | 473 | 405, 520 | 428, 475 | 435 | | | | 440 | | |
| | 523 | – | – | 430 | | | | 440 | | |
| | 573 | – | – | 425, 490 | | | | 440 | | |

Table 2 *(Continued)*

| SPPO content in mol % ($T_g$/K) | Temperature K | *p*FSt content in mol % ($T_g$/K) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 16 (404) | 22 (402) | 29 (398) | 35 (397) | 45 (395) | 53 (393) | 62 (390) | 72 (387) | 81 (385) |
| 29 (528) | 473 | | | | 442 | | | | 443 | |
| | 523 | | | | 443 | | | | 442 | |
| | 573 | | | | 442 | | | | 442 | |
| 36.7 (537) | 473 | 405, 535 | 406, 535 | 410, 510 | 407, 515 | 440 | | 442 | | 442 |
| | 523 | – | – | – | – | 440 | | 441 | | 441 |
| | 573 | – | – | – | – | 430* | | 440 | | 441 |
| 47 (541) | 473 | | | | 415, 535 | 413, 540 | | 443 | | |
| | 523 | | | | – | – | | 443 | | |
| | 573 | | | | – | – | | 430* | | |
| 55 (544) | 473 | 405, 540 | | | | | | 404, 542 | | 443 |
| | 523 | – | | | | | | – | | 442 |
| | 573 | – | | | | | | – | | 415, 525 |
| 61 (552) | 473 | | 406, 545 | 410, 552 | 397, 552 | | 395, 550 | 395, 550 | | 410, 550 |
| | 523 | | – | – | – | | – | – | | 400, 551 |
| | 573 | | – | – | – | | – | – | | 395, 550 |
| 75 (562) | 473 | 406, 560 | | 405, 563 | | 397, 560 | | 390, 565 | | |
| | 523 | – | | – | | – | | – | | |
| | 573 | – | | – | | – | | – | | |
| 91 (571) | 473 | 404, 575 | 400, 575 | 400, 575 | 400, 577 | | | 392, 577 | | 390, 575 |
| | 523 | – | – | – | – | | | – | | – |
| | 573 | – | – | – | – | | | – | | – |

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

* Partially miscible blend.

tions [4], using experimental data for miscibility in blends of other homopolymeric/copolymeric combinations of the given segments. The sixth $\chi_{ij}$ parameter, $\chi_{AB}$, was treated as an adjustable parameter. The parameter $\chi_{crit} = 0.004$ for the poly(*p*ClSt-co-*p*-FSt)/SPPO and poly(*o*ClSt-co-*p*-FSt)/SPPO systems, calculated using the known average degrees of polymerization. From the experimentally determined phase boundary and previously determined $\chi_{ij}$ parameters [4], the remaining parameters $\chi_{p\mathrm{FSt},p\mathrm{ClSt}}$ and $\chi_{pFSt,\,oClSt}$ at 473 K were estimated to be 0.052 and 0.083, respectively. The values of the segmental interaction parameters for all binary combinations of poly(*p*FSt-co-*p*-ClSt) and poly(*p*FSt-co-*o*-ClSt) with SPPO estimated in this paper, together with the results obtained from earlier studies, are collected in Table 3. The boundary between miscibility and immiscibility, where $\chi_{blend} = \chi_{crit}$, can be described by a function expressed in terms of $x$ and $y$, such that

$$f(x, y) = \chi_{blend} - \chi_{crit} = 0 \tag{2}$$

Expression (1) can be conveniently rearranged

$$\begin{aligned} &x^2\chi_{AB} + y^2\chi_{CD} + (\chi_{AC} - \chi_{AD} - \chi_{BC} + \chi_{BD})xy + (\chi_{BC} - \chi_{AB} - \chi_{AC})x \\ &\quad + (\chi_{AD} - \chi_{AC} - \chi_{CD})y + (\chi_{AC} - \chi_{crit}) = 0 \end{aligned} \tag{3}$$

to give the generalized quadratic form

$$ax^2 + by + cxy + dx + ey + f = 0 \tag{4}$$

from which solutions can be readily obtained in the $xy$ plane. The geometry of $f(x, y)$ is dependent on the sign and magnitude of the $\chi_{ij}$ parameters that appear in the appropriate $\chi_{blend}$ expression. Examination of the condition for the miscibility boundary, as was shown by Ueda and Karasz [13], demonstrates (see Figs. 1 and 2) that the condition

$$c^2 - 4ab < 0 \tag{5}$$

Table 3
Segmental interaction parameters at 473 K

| Segment pair | $\chi_{ij}$ |
|---|---|
| PPO, *p*FSt | 0.037[a] |
| SPPO, *p*FSt | 0.093[a] |
| PPO, *p*ClSt | 0.03[a] |
| SPPO, *p*ClSt | 0.017[a] |
| PPO, *o*ClSt | 0.02[a] |
| SPPO, *o*ClSt | 0.28[a] |
| pFSt, *p*ClSt | 0.052 |
| pFSt, *o*ClSt | 0.083 |
| PPO, SPPO | 0.318[a] |

[a] From Ref. [4].

is fulfilled for both systems, i.e. $f(x, y)$ is elliptical in shape. The shape of the miscibility boundary curves is shown to be determined by the difference in interaction strength between different copolymer segments. The $c^2$ term in expression (5), which represents the contribution of segmental dissimilarity in the two copolymers, has the value of $4.76 \times 10^{-3}$ for the poly(*p*ClSt-co-*p*-FSt)/SPPO system and $4.16 \times 10^{-2}$ for the poly(*o*ClSt-co-*p*-FSt)/SPPO system, respectively, because the repulsion of the ortho-substituted styrene with SPPO is greater than that of the para-substituted polymer, which is consistent with our earlier investigations of the miscibility of halogenated styrene copolymers with PPO and SPPO [14]. The geometrical analysis shows that the poly(*p*ClSt-co-*p*-FSt)/SPPO blend should exhibit a broader miscibility region than the poly(*o*ClSt-co-*p*-FSt)/SPPO blend system, in agreement with experimental results (Figs. 1 and 2). The wide miscibility window along the para-substituent ordinate is a result of the repulsion between the SPPO and PPO moieties. The total absence along the ortho-substituent ordinate shows that ortho is a strong inhibitor of miscibility. This also implies that the miscibility in these blends is influenced by steric factors.

## Acknowledgments

This work was supported by the National Science Foundation of the United States and the Ministry of Science of the Republic of Croatia as a joint project between INA-Research and Development, Zagreb, and Polymer Science and Engineering, University of Massachusetts, Amherst, MA.

## References

[1] R. Vuković, V. Kurešević, N. Šegudović, F.E. Karasz and W.J. MacKnight, J. Appl. Polym. Sci., 28 (1983) 1379.
[2] J.J. Tkacik, Ph.D. Dissertation, University of Massachusetts, Amherst MA, 1975.
[3] J.R. Fried, Ph.D. Dissertation, University of Massachusetts, Amherst MA, 1976.
[4] R. Vuković, M. Žuanić, G. Bogdanić, V. Kurešević, F.E. Karasz and W.J. MacKnight, Polymer, 34 (1993) 1449.
[5] R. Vuković, G. Bogdanić, N. Sfiegudović, D. Fleš, F.E. Karasz and W.J. MacKnight, Thermochim. Acta, 1994, submitted.
[6] R.P. Kambour, J.T. Bendler and R.C. Bopp, Macromolecules, 16 (1983) 753.
[7] G. ten Brinke, F.E. Karasz and W.J. MacKnight, Macromolecules, 16 (1983) 1827.
[8] N. Šegudović, R. Vuković, V. Kurešević, F.E. Karasz and W.J. MacKnight, Polym. Int., 31 (1993) 197.
[9] N. Šegudović, R. Vuković, V. Kurešević, F.E. Karasz and W.J. MacKnight, Polym. Int., 31 (1993) 207.
[10] H.S. Kang, W.J. MacKnight and F.E. Karasz, Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem., 27 (1986) 65.
[11] R. Vuković, V. Kurešević, G. Bogdanić and D. Fleš, Thermochim. Acta, 195 (1992) 351.
[12] P. Alexandrovich, F.E. Karasz and W.J. MacKnight, Polymer, 18 (1977) 1022.
[13] H. Ueda and F.E. Karasz, Polym. J., 24 (1992) 1363.
[14] R. Vuković, G. Bogdanić, V.Kurešević, M. Tomasković, F.E. Karasz and W.J. MacKnight, J. Polym. Sci., Polym. Phys. Ed., 32 (1994) 1079.