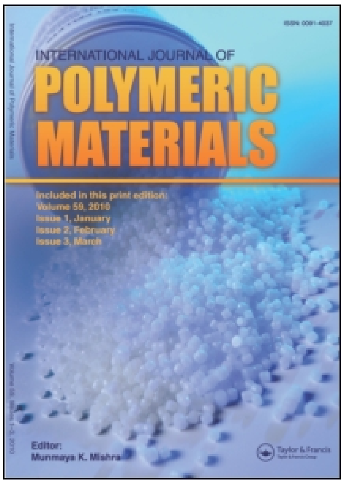

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Structures of Blends of Poly (*p*-Phenylene Sulfide) (PPS) with Poly(*p*-Phenylene Sulfide Ether) (PPSE)

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The blends named in the title were investigated by wide-angle X-ray scattering (WAXS). Given relative chemical similarity of the blend components, formation of a homogeneous blend and co-crystallization were distinct possibilities. The results are compatible with the assumption of orthorhombic structure in PPSE, with the same reflex indices as in PPS. Parameters of the unit cell of PPSE computed on that basis are: $a = 0.837$, $b = 0.559$ and $c = 1.034$ nm. The degree of crystallinity of PPS is approximately 10% lower than that of PPSE. In blends separate crystals of the two components appear to be formed; the crystallinity of a given component seems to be neither enhanced nor diminished by the presence of the other component.

Keywords: Poly(*p*-phenylene sulfide); poly(*p*-phenylene sulfide ether); blends; structure; X-ray diffraction; crystallinity

1. INTRODUCTION AND SCOPE

We have first the studied thermal behavior of poly(*p*-phenylene sulfide) (PPS) and of several its derivatives which were synthesized at the same time [1]. An increasingly popular method of development of new materials is *blending*. Blends often show significant deviations from linear additivity of properties – what can be used to advantage. For instance, ways of reinforcing engineering polymers with polymer liquid crystals (PLCs) have been discussed by one of us [2]. However, there exists a major obstacle to successful blending: blend constituents often show limited miscibility and insufficient compatibility. There exist various-sometimes conflicting-definitions in the literature. We define *miscibility* as the formation of a homogeneous phase while *compatibility* refers to a heterogeneous material which contains numerous small regions of a phase or phases dispersed in a matrix. A miscible system can achieve stable thermodynamic equilibrium. A compatible system is long-living (otherwise it would be useless for practical applications) but not necessarily an equilibrium one.

There exists a fundamental way of achieving miscibility, or at least compatibility: *similarity in molecular structures of the components.* Poly(*p*-phenylene sulfide ether) (PPSE) is a new polymer, synthesized in a reaction of *p*-dichlorophenylene oxide with hydrated sodium sulphate $Na_2S.9H_2O$ [1]. Until now, the crystal structure of PPSE had not been investigated. We know, however, that PPSE has a similar molecular structure to PPS. Thus, *co-crystallization* of PPS and PPSE was a possibility; a partial indication that it might occur was provided by the differential scanning calorimetry (DSC) results obtained for PPS + PPSE and PPS + PPSS blends, where PPSS is poly(phenylene sulfide sulfone) [3].

It is known that the addition of a second component to a polymer might produce unexpected or downright strange results. This happens for instance when low-molecular-mass compounds are added to high polymers [4, 5]. Mixing of polymers can affect the structures of individual components – and this applies also to the main constituent which forms the matrix. Several instances deserve to be mentioned in this context. Isotactic polypropylene (i-PP) produces a new polymorphic structure under the influence of some aromatic compounds [5]. Grebowicz and Pakula [6] investigated melting and crystallization of blends of PP with polyethylene (PE). They have concluded that a blend constituent can *either stimulate or damp* nucleation, growth and morphology of the crystalline phase of the other component. Incidentally, there is no reason why their conclusion should be limited to binary blends. The presence of polycarbonate (PCarb) [7] or of semi-crystalline polyamide-6 [8] in PP results in the formation of the triclinic phase in the iPP matrix. Zhao, Schaper and Ruland [9] studied crystallization kinetics of a thermotropic longitudinal PLC and found heterogeneous crystal nucleation, proceeding from one-dimensional centers of disinclinations and also from two-dimensional domain walls. The extent of mixing can also be a function of *time* if annealing is performed [10]. Needless to say, acquisition of understanding of the reasons why such phenomena occur would lead to improvements in our processing procedures and enhance significantly the structural stability of polymeric materials.

Under these circumstances, we have defined the following questions to be investigated in the present study; are PPS and PPSE indeed isostructural with each other? How does blending of PPS and PPSE affect the total crystallinity of the sample? Are crystallinities of the individual components affected in the blending process?

2. EXPERIMENTAL

2.1. Materials

PPS used was a commercial product manufactured by Sun-Kyung Industries, Republic of Korea, under the name of Suntra-100. PPSE as well as PPS + PPSE blends were prepared at the Taegu location; the synthesis of PPSE was reported in [1] while preparation of the blends from solution was described in [2].

2.2. Structural Investigations

The investigations were performed with the wide-angle X-ray scattering (WAXS) technique using CuKα radiation. Intensity, location as well as width of the refractive lines were investigated. Separation of the diffraction patterns into their components was performed by using the method developed by Hindeleh and Johnson (H-J) [11] and subsequently improved upon and implemented as a computer program by Rabiej [12]. The H-J procedure makes possible separation of a complex XS diagram into crystalline as well as amorphous components. After such separation, the total crystalline contents, crystallinities of individual components and the dimensions of crystalline aggregates were analyzed.

The degrees of crystallinity were evaluated numerically by dividing the integral surface area under the diffraction lines by the areas corresponding to crystalline and amorphous phases. The dimensions of the crystalline aggregates were determined by the standard Scherrer method.

3. STRUCTURES OF PPS AND PPSE

PPS is known to have an orthorhombic structure; for characteristics of crystal lattices see a textbook of materials science and engineering such as [13]. In Figure 1 as well as in Table I we present diffractometric results for both PPS and PPSE; the quasi-isostructural character of both polymers is evident. Given this result, as well as similarities in the respective molecular structures, we have assumed that the crystalline phase of PPSE is orthorhombic while the reflexes from PPSE have the same indices as those for PPS. This made possible an approximate evaluation of parameters of the unit cell of PPSE: $a = 0.837$ nm; $b = 0.559$ nm; and $c = 1.034$ nm. Confirmation of these results by a full structural analysis constitutes the subject of current work.

The results of evaluation of the degrees of crystallinity are reported in Table II. We observe that the crystallinity of pure PPSE is approximately 10% lower than that of PPS.

4. STRUCTURES OF PPS + PPSE BLENDS

The respective WAXS results are shown in Figure 2 a, b and d for several PPS/PPSE ratios. It is not possible on the basis of these results to provide a definitive answer whether the components coexist in a single crystalline phase. To resolve this problem, we have *mechanically* mixed PPS with PPSE in the 1:1 ratio – without melting and dissolution. The resulting diffractogram is shown in Figure 2c. Comparison of the Figures 2b and 2c (the same ratio of the components) indicates that they are quite similar. In other words, operations such as blend melting did *not* affect the diffractometric patterns. We infer that the blends contain *distinct*

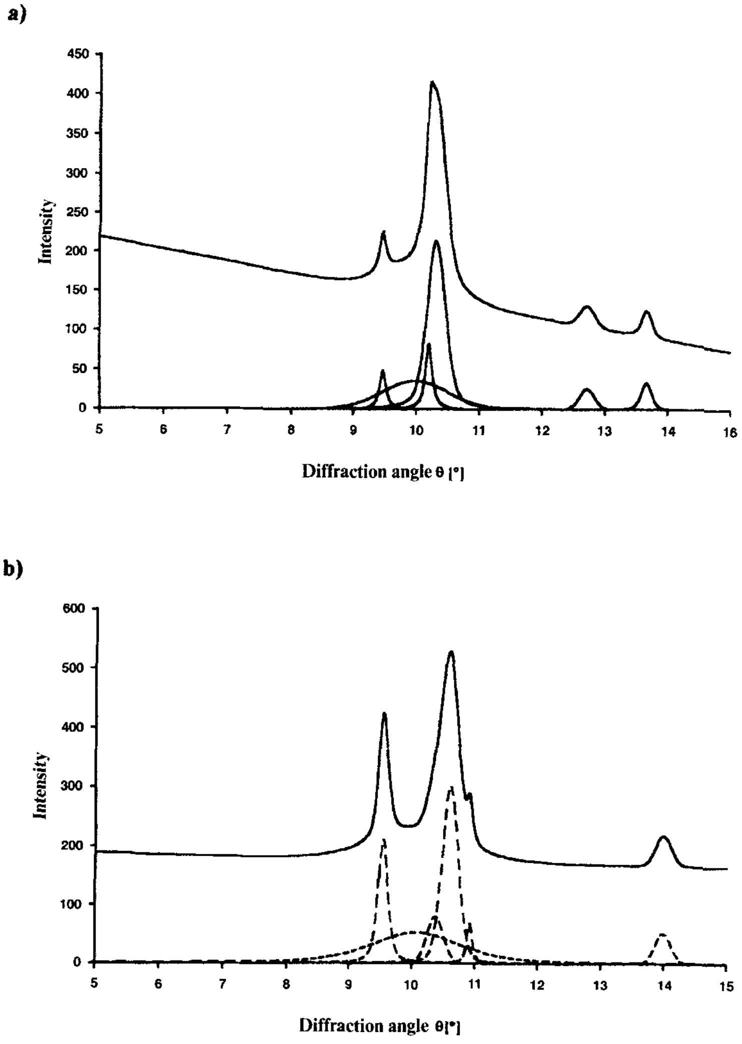

FIGURE 1 Wide-angle X-ray scattering (WAXS) patterns for: a) PPS; and b) PPSE samples. In both a) and b) the top curves represent the total WAXS diagram while the bottom parts show separated diffraction lines.

crystalline phases of PPS and PPSE. The present results are supported by those obtained by DSC, namely by the presence of a peak at ≈ 190°C for the PPPS/PPSE ratios of 5:5 and 7:3 [2]; this corresponds to the melting peak (190°C) of pure PPSE. At the same time, such a peak is not

TABLE I Interplanar distances (**d**) and relative intensities of reflexes (**I**) of PPS and PPSE

PPS		*PPSE*	
d [nm]	*I*	*d [nm]*	*I*
0.4680	10	0.4651	50
0.4349	17	0.4276	22
0.4299	100	0.4188	100
0.3501	9	0.4069	9
0.3264	9	0.3188	15

TABLE II Degree of crystallinity of PPS, PPSE, PPS/PPSE blends (X_c) and degree of crystallinity of PPS in blends (X_{cPPS})

	X_c	X_{cPPS}
PPS	73.7	
PPSE	65.1	
PPS/PPSE(7:3)	73.4	74.3
PPS/PPSE(5:5)	73.8	77.7
PPS/PPSE(3:7)	65.0	64.6

visible for the PPS/PPSE ratios of 7:3 and 6:4, while for the 4:6 ratio it appears only in the form of a shoulder. Overall, the results are indicative of the complexity of crystallization processes; that complexity is augmented by blending and the possibilities of co-crystallization.

Consider now the degrees of crystallinity – as listed in Table II. Starting from pure PPS side, we observe that up to 50 weight percent of PPSE the overall crystallinity hardly changes. The individual crystallinity of PPS is affected only weakly, but shows a slight increase: from 73.7% for pure PPS up to 77.7% for 50% PPSE. When we exceed 50% PPSE, we observe a lowering of the overall crystallinity; this is to be expected, given the difference in the degrees of crystallinity of pure components noted in the preceding Section. Somewhat surprising, however, is the simultaneous *lowering* of the crystallinity of PPS. Thus, PPSE first slightly enhances the capability of PPS to crystallize, but then the *excess* of PPSE adversely affects that capability. The last result can be connected to the DSC diagrams [2]: an increase in the PPSE contents lowers the melting temperature T_m of PPS. For pure PPS we have $T_m = 279°C$ while $T_m = 262°C$ has been found for the blend containing 70% PPSE.

As mentioned in Subsection 2.2, the dimensions of the crystalline aggregates were determined by the Scherrer method; this was done in directions defined by the Miller indices on the basis of the width of the diffraction lines. The results are listed in Table III. We see that the

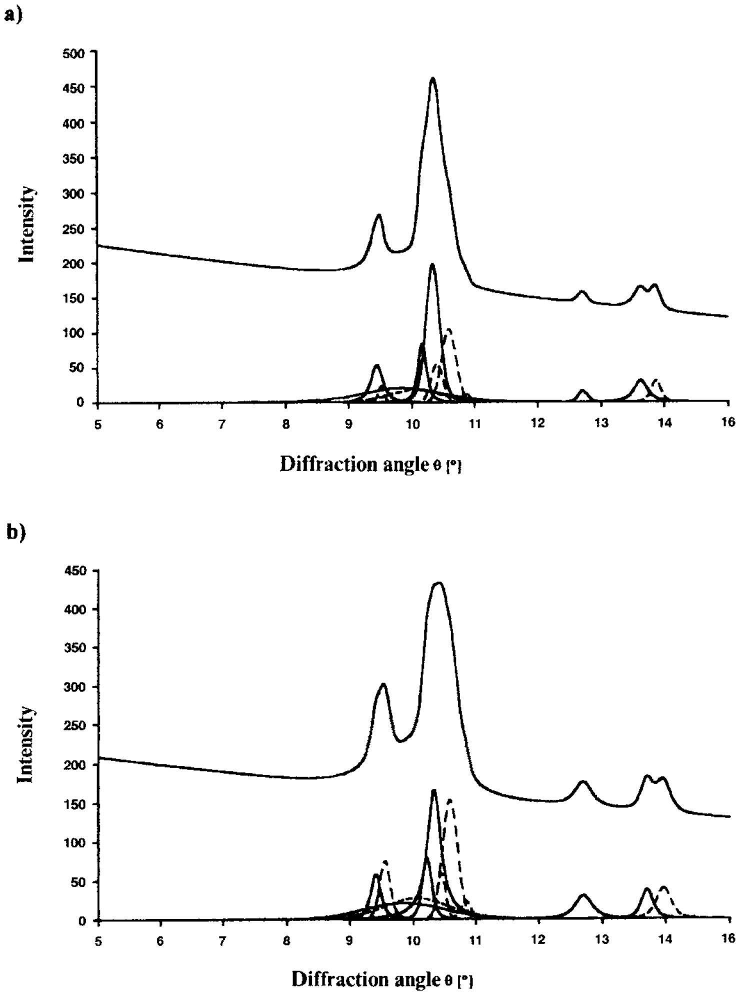

FIGURE 2 WAXS patterns for PPS + PPSE blends for the following ratios of the components: a) 7:3; b) 5:5; c) also 5:5 but mixed only mechanically; d) 3:7. The top and bottom parts to each of the four diagrams contain respectively the same types of information as in Figure 1.

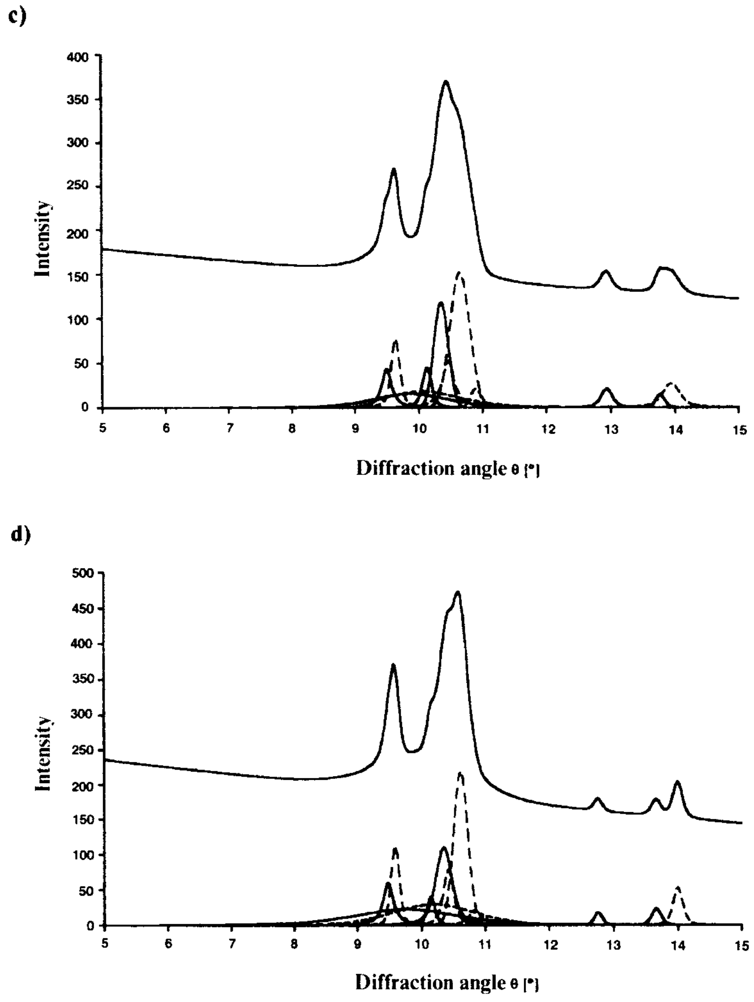

FIGURE 2 (Contd.)

aggregates have dimensions D between 25 and 70 nm. One can follow the changes in the aggregates sizes resulting from blend concentration variation. These changes are evident along the proponderant chain orientation directions as well as perpendicularly to it.

To achieve a better perspicuity in the area of aggregate sizes, we have also calculated from the same diffraction data the so-called relative

TABLE III Dimensions of crystalline aggregates (D[nm]) perpendicular to planes defined by the Miller indices

Planes	*PPS/PPSE*			
	1:0	*7:3*	*5:5*	*3:7*
	D[nm]			
(110)	72.65	38.83	45.84	46.29
(200)	26.10	35.00	43.44	30.13
(112)	31.22	49.32	27.21	59.39
(211)	44.27	34.18	39.94	49.37

TABLE IV Relative changes (RD) of dimensions of PPS crystalline aggregates in PPS + PPSE blends

Planes	*PPS/PPSE*		
	7:3	*5:5*	*3:7*
	RD		
(110)	−0.46	−0.37	−0.36
(200)	0.67	0.34	0.15
(112)	0.58	−0.12	0.90
(211)	−0.23	−0.10	0.11

change parameter RD for the dimensions D; it is defined as

$$RD = (D - D^{\mathrm{PPS-untr}})/D^{\mathrm{PPS-untr}} \tag{1}$$

Here $D^{\mathrm{PPS-untr}}$ pertains to the pure (untreated) PPS material. The resulting RD values are listed in Table IV.

Inspection of Table IV shows that blending results in the *decrease* of the size of crystalline aggregates in the directions perpendicular to the diagonal of the elementary cell. In the direction perpendicular to the main axis of the macromolecules we observe an *increase* in RD; there is no such regularity along the main chain axis.

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