Thermal behaviour of poly(phenylene sulfide) and its derivatives

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Poly(phenylene sulfide) (PPS) and its derivatives, poly(phenylene sulfide-*co*-phenylene ketone) (PPSK), poly(phenylene sulfide-*co*-phenylene ether) (PPSE), poly(biphenylene sulfide) (PBPS) and poly(phenylene sulfide-*co*-phenylene sulfone) (PPSS), were synthesized and their thermal properties were investigated by differential scanning calorimetry and thermogravimetric analysis. PPSK, PBPS and PPS show high crystallinity, in that descending order, while PPSS is totally amorphous. Semi- and non-crystalline PPS/PPSS polymers were melt blended. The blends showed relatively high miscibility and thermal stability. The T_g of PPS/PPSS blends shows 10 and 45°C inward shift; the melt crystallization temperature (T_{mc}) of PPS decreased to 227°C in the PPS/PPSS blend compared to 244°C for the PPS homopolymer, as determined by differential scanning calorimetry in a cooling scan.

(Keywords: poly(phenylene sulfide); crystalline polymers; blends; miscibility; processing)

INTRODUCTION

Poly(phenylene sulfide) (PPS) is a semicrystalline polymer that possesses excellent mechanical, thermal and chemical resistance properties, in addition to the polymer being inherently self-extinguishing. PPS was reported to form rhombic crystals[1] and the crystallization mechanism and kinetics have also been studied[2,3]. Several synthetic routes to PPS were reported before Phillips Petroleum Co. developed a commercial process involving *p*-dichlorobenzene and sodium sulfide equivalent in *N*-methylpyrrolidone (NMP) at 200–280°C[4]. PPS produced by this process is an off-white powder with a linear structure; it contains approximately 150–200 repeat units (M_w = 16000–20000). For this reason, PPS has a rather low melt viscosity; this leads to processing difficulties as well as to low impact strength. High impact strength would require high chain relaxation capability (*CRC*), while low molar mass results in low *CRC*[5–7]. To improve its properties, PPS is heat cured[8] in the presence of air at elevated temperatures and/or filled with aramid, carbon or glass fibres[9–11]. Blending of PPS with polymer liquid crystals was also reported[12,13]. As for curing, the reactions that take place are not well understood because of their complexity[14]. Copolymers of PPS from mixtures of *p*- and *m*-dichlorobenzene and sodium sulfide and poly(arylene sulfide)s employing various dichloroaromatic compounds were also reported to modify the crystallinity and melt viscosity of PPS[14,15]. Moreover, Springer and collaborators[16] have found that CO_2 absorption causes plasticization. The crystallization behaviour of PPS and PPS/PPSS (poly(phenylene sulfide-*co*-phenylene sulfone)) blends is important, since it affects the cycle time during injection moulding and other processing operations. To obtain shorter cycle times, lower cold crystallization temperature (T_c) and higher melt crystallization temperature (T_{mc}) are desirable. It is important to distinguish T_{mc}, determined by differential scanning calorimetry (d.s.c.) in a cooling scan, from the melting temperature T_m, usually determined by d.s.c. in a heating scan.

In this paper, PPS and poly(arylene sulfide)s, including poly(biphenylene sulfide) (PBPS), poly(phenylene sulfide-*co*-phenylene ketone) (PPSK) and poly(phenylene sulfide-*co*-phenylene sulfone) (PPSS), were synthesized. The thermal and crystallization behaviours of the homopolymers and PPS/PPSS melt blends were investigated.

EXPERIMENTAL

Materials

p-Dichlorobenzene, *p*-dichlorobiphenyl, 4,4-dichlorobenzophenone, *p*-chlorophenylsulfone and sodium sulfide ($Na_2S \cdot 9H_2O$) were reagent grade obtained from Aldrich Chemical and used as received. NMP solvent was distilled before reaction. Acetone and methanol used for recovery and purification of PPS were chemical grade.

Polymerization

The synthesis schemes for PPS and its derivatives are as shown in *Scheme 1*. First, $Na_2S \cdot 9H_2O$ (0.125 mol)

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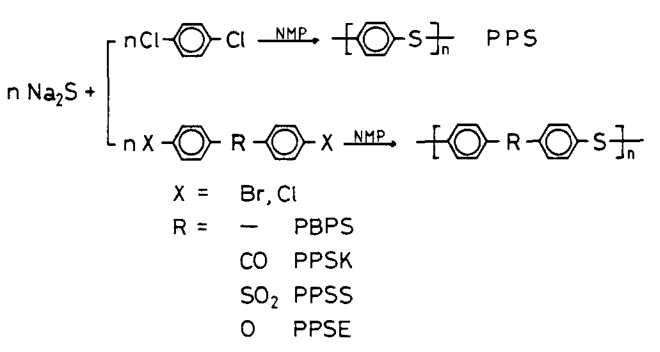

Scheme 1

was added to 150 ml of NMP in a 250 ml three-necked flask equipped with a thermometer, Ar gas inlet/outlet and Dean–Stark trap. The mixture was heated to 200°C under an Ar atmosphere and crystallization water was removed. The dehydrated sodium sulfide/NMP solution was placed in a 350 ml bomb-type reactor made of a corrosion-resistant alloy and cooled to 120°C. *p*-Dichlorobenzene or another appropriate dihaloaromatic compound was added under Ar gas and stirred for 3–6 h at 250–270°C. After reaction, the product mixture was poured into acetone and precipitated polymers were filtered. Washing the polymers in warm water at 60°C with stirring to remove NaCl and other water-soluble by-products and washing with acetone and water was repeated several times. Low-molar-mass PPS and PPS derivatives are soluble in acetone. The PPS resulting from our synthesis is quite similar in its appearance, molar mass and properties to that made by the Phillips Petroleum Co.

For the synthesis of PPSS, *p*-dichlorophenylsulfone and $Na_2S \cdot 9H_2O$, 0.125 mol of each were dissolved in 200 ml of NMP and 15 ml of distilled water and reacted directly either at 200°C for 3 h or at 250°C for 3 h. The resulting polymer was recovered and purified in the same way as PPS. PPSK, PBPS and PPSE (poly(phenylene sulfide-*co*-phenylene ether)) were also synthesized in the same way as PPS. The products were identified by i.r. spectroscopy[17,18].

Blending and thermal analysis

PPS and PPSS were dried in a vacuum desiccator at 80°C overnight and melt blended using a Plasticorder PL 2000 at 295°C for 20 min at 60 rev min^{-1}. Thermal properties of PPS, PBPS, PPSK and PPSS homopolymers and PPS/PPSS blend were investigated with a Du Pont Thermal Analyzer DSC-2000 and also a Du Pont Thermogravimetric Analyzer TGA-2100. Calibration of the d.s.c. apparatus was performed with indium as the standard (T_m = 156.8°C, enthalpy of fusion 28 J g^{-1} (ref. 19)). Heating and cooling rates were 20°C min^{-1}. The d.s.c. thermograms represent second heating runs, after heating each sample to 330°C for 3 min and quenching in liquid N_2.

RESULTS AND DISCUSSION

Polymerization yields of PPS and its derivatives are listed in *Table 1*. As shown in *Table 1*, the yields are relatively high. D.s.c. thermograms for PPS and PPSS are shown in *Figures 1* and *2*, respectively. As seen in these figures, PPS is a semicrystalline polymer with the glass transition temperature T_g = 83°C, melting temperature T_m = 279°C and cold crystallization temperature T_c = 124°C. PPSS

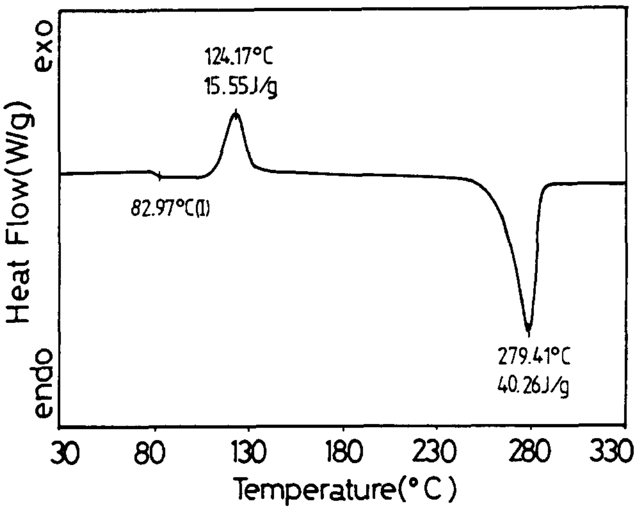

Figure 1 D.s.c. thermogram for PPS

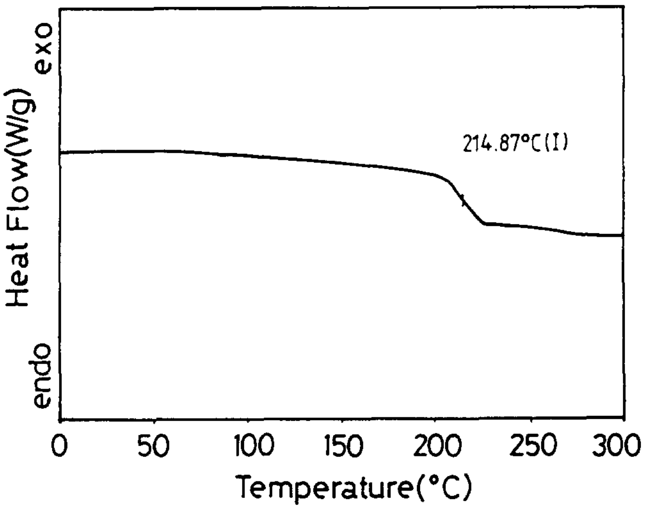

Figure 2 D.s.c. thermogram for PPSS

Table 1 Thermal data and yields for PPS and its derivatives

Samples	T_g (°C)	T_c (°C)	ΔH_c (J g^{-1})	T_{mc} (	ΔH_{mc}	T_m (°C)	ΔH_f (J g^{-1})	Yield (%)
PPS	83.0	124.2	15.6	244.4	45.2	279.4	40.3	85
PPS (cured)				231.3	40.9	289.9	58.3	
PPSK	218.2			297.5	30.8	322.6	42.9	80
PPSS	214.9			none		none		95
PBPS				262.3	45.1	282.3	47.8	80
PPSE	42.7	69.7	6.9	170.2	37.0	185.6	49.1	85

is fully amorphous with $T_g = 215°C$. The d.s.c. data obtained for PPS and its derivatives are summarized in *Table 1*. PPSK has T_m of 322°C and T_g of 218°C. Its thermal properties are similar to those of poly(ether ether ketone)[20], possibly due to high stiffness of the carbonyl group. In the case of PBPS, we expected a higher melting point than that of PPS because it has two aromatic rings per repeat unit: however, we found T_m of 282°C, only insignificantly higher than that of PPS. This result may be explained by low molar masses of PBPS caused by premature precipitation during polymerization: higher mass values should result in an increase of T_m.

In *Table 2*, we list t.g.a. data for PPS and its derivatives. As mentioned above, PPSK exhibits very good thermal stability, similar to that of the poly(ether ether ketone). We infer from *Table 1* that PPS and PPSS have comparable thermal stability. This and other factors led us to the idea of determination of mutual miscibility of these polymers. Therefore, PPS and PPSS were melt blended in the ratio 75:25 wt%. Miscibility was evaluated in terms of T_g shift of d.s.c. in heating scans. The respective d.s.c. thermogram is shown in *Figure 3*.

As can be seen in *Figure 3*, blending has resulted in a shift of the glass transition temperatures of PPS and PPSS towards each other, by approximately 10 and 45°C, respectively. The miscibility we have found can be due to two factors: (i) intermolecular interactions, as is typical for polymer blends; (ii) intramolecular interactions. PPS and PPSS can be cured under an oxygen atmosphere[21,22]. Curing sites usually consist of protons attached to aromatic rings. At high temperatures, oxygen can create radicals. A radical attack on the proton of the aromatic ring of PPS may cause branching as well as crosslinking. If so, crosslinks between protons of aromatic rings of PPS and those of PPSS are also possible.

Table 2 T.g.a. data for PPS and its derivatives

Polymer	Degradation starting temp. (°C)	Maximum degradation temp. (°C)	Percentage of residues at 800°C
PPS	494.5	528.1	43.9
PPSK	520.5	559.5	57.8
PPSS	480.2	516.2	42.2
PBPS	416.5	498.7	27.2
PPSE	412.7	493.4	23.7

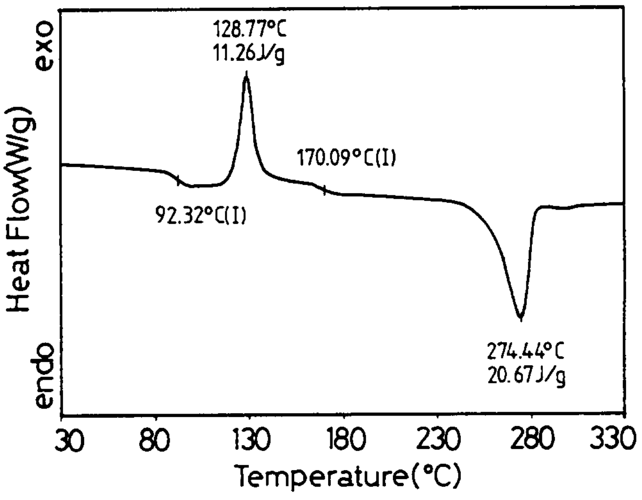

Figure 3 D.s.c. thermogram for PPS–PPSS blend (75:25 wt%)

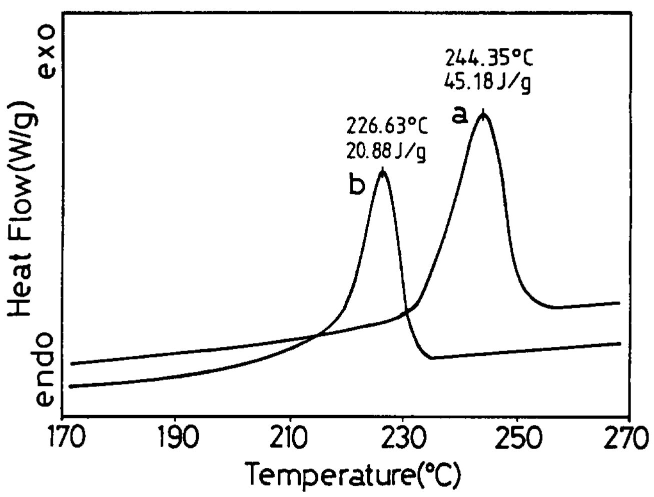

Figure 4 D.s.c. thermograms for PPS and PPS–PPSS blend (75:25 wt%) obtained in cooling scans: (a) PPS, (b) PPSS

Since the polymer processing temperature must be higher than the melt crystallization temperature T_{mc}, processing time and T_{mc} constitute the main factors determining the moulding cycle. Consequently, the same factors determine the economics of the process. Therefore, we have studied T_{mc} of PPS and the blend by d.s.c. under a cooling scan. The results are shown in *Figure 4*. In the case of the PPS homopolymer, the respective thermogram shows $T_{mc} = 244°C$ while the enthalpy of fusion is 45 J g^{-1}. By contrast, for the blend we have $T_{mc} = 227°C$ while the enthalpy of fusion is 21 J g^{-1}. Thus, T_{mc} and the relative crystallinity of the blend are respectively lower by about 20°C and 38% than those of PPS. While the connections between the chemical and physical characteristics of a nucleating agent and its action are not exactly clear[23], we expected instead an enhancement of the degree of crystallinity. When semicrystalline polymers are mixed with amorphous or with other semicrystalline polymers, the misfit of packing because of different chemical structures causes an increase in free volume, and thus favours crystallinity. For instance, polycarbonate crystallizes in the presence of a copolymer of poly(ethylene terephthalate) and *p*-hydroxybenzoic acid, but does not crystallize alone under the same conditions[24]. The decrease of the degree of crystallinity caused by blending in the present case may be explained by a reaction of PPS with PPSS, resulting in a graft copolymer with a higher molar mass. We should note, however, that such an explanation is speculative, albeit a plausible one.

CONCLUSIONS

Aiming at an improvement of the processability of PPS, we investigated first the thermal properties of PPS and its derivatives by d.s.c. PPSK and PBPS have very high thermal stability due to carbonyl groups and aromatic rings. PPSS is an amorphous polymer, with a thermal stability very similar to that of PPS. As already noted, the synthesis of PPSS has a yield exceeding 90% at optimum conditions, and thus is economically viable. The blend system of PPS and PPSS exhibits a significant miscibility of the components, explained by both intermolecular interactions and the propensity to crosslinking between the components. From the point of view of improving the processability and properties of PPS, we have mentioned several options[8–13,15,16]. One more option follows from our results. Therefore, this system can be applied to improve the processing conditions since T_{mc} of the blend is lower than that of PPS. At the same time, blending is expected to improve the impact strength of PPS, since PPSS is an amorphous polymer.

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