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Synthesis and thermal properties of copoly(phenylene sulfide/sulfide ether)s

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Copolymerization of phenylene sulfide and phenylene sulfide ether was carried out with various composition ratios. Their thermal properties were investigated by differential scanning calorimetry and thermogravimetric analysis. As the phenylene sulfide ether composition increased in copolymer, glass transition temperature, cold crystallization temperature, melting temperature and melt crystallization temperature all decreased. These results might be due to the flexibility of oxide group of phenylene sulfide ether. When the compositions of phenylene sulfide ether were between 4 and 20% in the copolymer, it showed maximum heat of fusion and heat of solidification. All of the copolymers exhibited excellent thermal stabilities. ©1997 Elsevier Science Ltd.

(Keywords: copoly(phenylene sulfide/sulfide ether)s; thermal properties; crystallization temperature)

INTRODUCTION

Poly(phenylene sulfide) (PPS) is a semicrystalline polymer which forms orthorhombic crystals[1]. Since it was commercialized by Phillips Petroleum Co. in 1973[2], it has had many potential applications[3-5], such as moulded products, composites, films etc., due to its thermal and mechanical properties which are excellent except for impact resistance. By the Phillips method, it was polymerized by condensation polymerization of *p*-dichlorobenzene and sodium sulfide ($Na_2S \cdot 9H_2O$) in *N*-methyl-2-pyrrolidinone (NMP). But it was very difficult to obtain high molecular weights of PPS because of premature precipitation during the polymerization[6]. Thus, it had low melt viscosity and chain relaxation capability[7-9], which caused difficulty in processing and low impact strength. Besides these troubles, there was one more problem to application of PPS: it had a relatively high melting temperature (T_m) of 280°C, which created difficulties in melt processing. Many researchers tried to solve these problems by using various methods. Nadkarini and coworkers[10,11] attempted to solve these problems by blending PPS with other polymers. Unfortunately, they could not find any blend system which showed good miscibility. On the other hand, Springer and coworkers[12] reported that CO_2 gas absorbed into PPS can act as the plasticizer. But this effect is not enough to solve the problems either.

We have also reported[13-16] many results related to solving these problems. First of all, we tried to solve these problems by syntheses of new PPS derivatives. However, this method was not economical because of the high cost of monomers of those, although it proposed a possibility to improve the weak point of PPS. In the study of PPS/poly(phenylene sulfide ether) (PPSE) blends, we could control glass transition temperature (T_g) and T_m of PPS by varying the amounts of PPSE in the blends. However, these blends showed partial miscibility.

In this study, copoly(phenylene sulfide/sulfide ether)s (PSEs), which had different monomer composition ratios, were synthesized. The thermal and crystallization behaviours of these copolymers were investigated with the monomer composition ratios.

EXPERIMENTAL

Materials

Dibromobenzene (Lancaster Synthesis Ltd), dibromobiphenyl ether (Aldrich Chemical Co.), and sodium sulfide (Aldrich Chemical Co.), 1-chloronaphthalene (Aldrich Co.) and acetone (Duksan Chem. Co.) were used without further purification. NMP solvent was distilled several times before use.

Polymerization

The synthesis scheme for PSEs is as shown in *Scheme 1*.

A mixture of sodium sulfide (0.125 mol) and NMP (150 ml) was placed in a 350 ml bomb-type reactor made of corrosion-resistant alloy. The various molar ratios of dibromobenzene (DBB) and dibromobiphenyl ether (DBPE) were added under Ar gas and stirred for 4 h at 240°C. Monomer feed ratios are listed in *Table 1*.

The product mixture was poured into acetone and the precipitate was filtered. To remove the salt and water-soluble by-products, the polymer was washed several
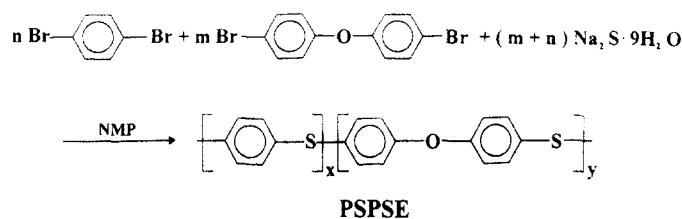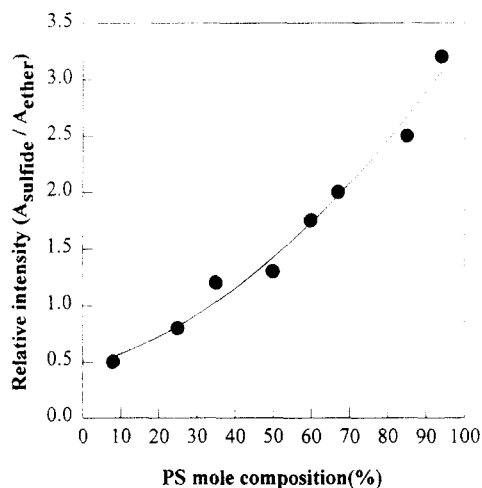

Scheme 1

Table 1 Feed ratios of DBB and DBPE in copolymerization of PSEs

	Feed ratio^a (mol%)	
Code of polymer	DBB	DBPE
PSE1	90	10
PSE2	80	20
PSE3	70	30
PSE4	60	40
PSE5	50	50
PSE6	40	60
PSE7	30	70
PSE8	20	80
PSE9	10	90

^{a} Total 0.125 mol

Figure 1 Calibration curve of PPS–PPSE blend

Table 2 Compositions, intrinsic viscosities and yields of PSEs

Code of polymer	PS (mol% in copolymer)	Yield (%)	Intrinsic viscosity (g dl^{-1})
PSE1	96	73	0.086
PSE2	79	72	0.088
PSE3	64	71	0.062
PSE4	57	71	0.091
PSE5	48	80	0.049
PSE6	32	75	0.058
PSE7	25	76	0.099
PSE8	16	76	0.037
PSE9	9	79	0.056

Figure 2 I.r. spectroscopy of PSEs, PS/PSE. PSE1, 9/1; PSE3, 7/3; PSE5, 5/5; PSE7, 3/7; PSE9, 1/9

times in hot water and acetone with stirring. PPS homopolymer was not dissolved[13] in NMP even though it was heated up to 220°C. On the contrary, PPSE homopolymer showed a good solubility in NMP[13]. By using these results, we could remove PPS and PPSE homopolymers from the product mixture. Then residual PSEs were dried in a vacuum oven at 100°C for 240 h.

Viscosity measurements

Intrinsic viscosities of each copolymer were measured in 1-chloronaphthalene solvent at 210°C by using an Ubbelohode Viscometer.

Composition analysis

The infra-red (i.r.) spectrum, the characteristic peaks of the sulfide group on PPS and the ether group on PPSE could be observed[17] at 800–840 cm^{-1} and at 1280 cm^{-1}, respectively. On the basis of this report, a calibration curve was made from the relative intensity of area ratios of each peak of 800–840 cm^{-1} and 1280 cm^{-1} ($A_{sulfide}/A_{ether}$) on PPS/PPSE blends which had different composition ratios, and this is shown in *Figure 1*.

Compositions of each component in the copolymers obtained were determined by using this calibration curve.

Thermal analysis

Thermal properties of PSEs were investigated with a Du Pont Thermal Analyzer DSC-2000 (d.s.c.) and Thermogravimetric Analyzer TGA-2100 (t.g.a.). Indium was used as a internal standard in the DSC.[18] Heating and cooling rates were 20°C min^{-1}. T_g, cold crystallization temperature (T_{cc}), and T_m were recorded during a second heat. Melt crystallization temperature (T_{mc}) was
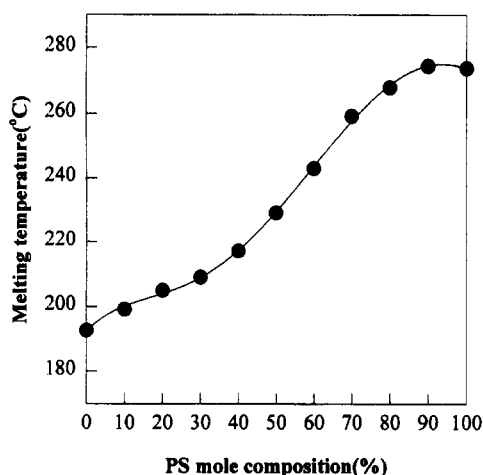
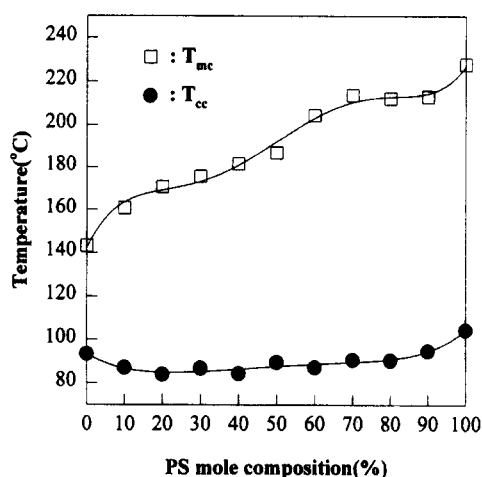**Figure 3** T_m (°C) of PSEs vs PS mole composition (%)

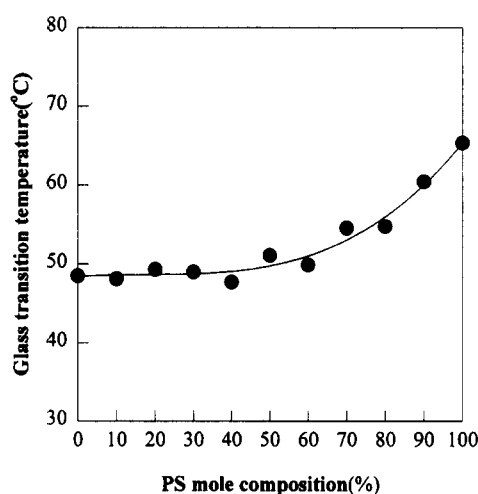**Figure 5** T_{cc} (°C) and T_{mc} (°C) vs PS mole composition (%)

Figure 4 T_g (°C) of PSEs vs PS mole composition (%)
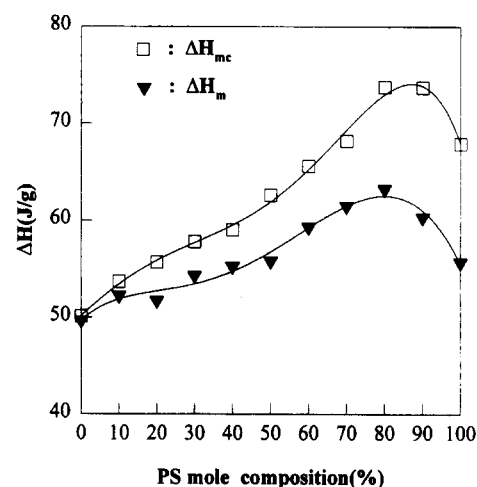

Figure 6 ΔH(J g^{-1}) vs PS mole composition (%)

recorded during a second cooling cycle. Isothermal crystallization experiments were carried out at near T_{cc}. To make the sample for isothermal study, it was heated to above its T_m at a heating rate of 20°C min^{-1}, and held for 5 min at this temperature in order to melt all crystallinities, and then quenched in liquid N_2.

RESULTS AND DISCUSSION

To identify the copolymerization that has taken place, Fourier transform i.r. (*FT*i.r.) spectra are illustrated in *Figure 2*. The absorption bands at 800–840 cm^{-1} and 1280 cm^{-1} are assigned to the sulfide and ether groups in copolymers. From the results of relative intensities of $A_{\text{sulfide}}/A_{\text{ether}}$ in *Figure 2*, the compositions of each monomer in copolymers were evaluated by using the calibration curve of *Figure 1*, and are summarized in *Table 2*.

The polymerization yields and intrinsic viscosities are also summarized in *Table 2*. The mol% of phenylene sulfide (PS) in the copolymer increases along with the increasing contents of PS monomer feed. We observed high polymerization yields in these copolymerizations. The intrinsic viscosities of obtained copolymers have similar values to that of PPS (Suntra 100, supplied by Sunkyung Industry, Korea, the number-average

molecular weights, $M_n \cong 10\,000$) which was 0.93 g dl^{-1}. Therefore, the molecular weights of copolymers are also similar to that of Suntra 100.

T_m and T_g for copolymers with varying compositions are shown in *Figure 3* and *Figure 4*. It shows only one T_m and one T_g in the entire compositions range, demonstrating a random copolymer. As seen in these figures, decreasing T_g and T_m, as the phenylene sulfide ether unit increases, are caused by the flexibility of oxide group in phenylene sulfide ether and imperfect folding during crystallization[19].

In *Figure 5*, T_{mc} and T_{cc} also decrease with increasing content of phenylene sulfide ether unit. This is also due to the flexibility of oxide group.

Figure 6 shows the heat of fusion (ΔH_m) and heat of solidification (ΔH_{mc}) for PSEs with different compositions. In both cases, the maximum values are appeared when the compositions of phenylene sulfide ether are between 4 and 20 mol%. This result shows that an appropriate amount of PS ether unit in PSE give the samples the advantage of formation of a crystalline region over others. Anyway, impact strength of PPS would be improved by 5% addition of phenylene sulfide ether unit in the copolymer. To get more detailed information, mechanical properties and crystallization kinetics are being studied. The results will be reported in the next paper.

Table 3 Degradation temperature and residue of PSEs by t.g.a.

Code of polymer	Starting point (°C)	Maximum point (°C)	Residue at 1000°C (%)
PPS (Suntra 100)	495	570	44
PSE1	495	562	40
PSE2	508	572	41
PSE3	482	563	36
PSE4	479	549	36
PSE5	477	531	36
PSE6	422	528	33
PSE7	469	562	35
PSE8	486	560	38
PSE9	486	555	36
PPSE	482	560	37

In *Table 3*, we listed t.g.a. data for PSEs. As is shown in *Table 3*, all of the PSEs exhibit a degradation starting point and a maximum degradation point between 500 and 600°C. This means that all the copolymers have very good thermal stability, similar to that of each homopolymer[13].

CONCLUSION

The copolymerization of PS and PSE was conducted with relatively high polymerization yields. Each copolymer shows only one T_g in all composition ratios. This result means that all of the copolymers are random copolymers. As the PSE group was introduced to the copolymer, a lower T_g, T_m, T_{cc} and T_{mc} is seen than in homo PPS. In the case of a copolymer containing 5 mol% PSE units, its ΔH_m and ΔH_{mc} are larger than those of PPS. All of the copolymers obtained have still maintained the thermal stabilities of the original homopolymer.

ACKNOWLEDGEMENT

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