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Synthesis and thermal properties of random-copoly(*p*-phenylene/biphenylene sulfide)s

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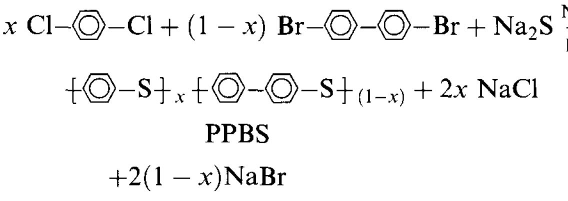
Copoly(*p*-phenylene/biphenylene sulfide)s (PPBS) were synthesized from sodium sulfide and *p*-dichlorobenzene (DCB)/4,4′-dibromobiphenyl (DBB) comonomers in *N*-methyl-2-pyrrolidinone (NMP) solvent under high temperature (270°C) and pressure. The copolymer composition and molecular weight of PPBS were determined by elemental (C,H,S) analysis and high temperature (210°C) g.p.c. with 1-chloronaphthalene as eluent, respectively. The reactivity of DBB monomer was found to be higher than that of DCB toward the thiolate anion from the copolymer composition analysis. The molecular weight of PPBS copolymer showed maximum value ($M_w = 23.9\text{–}24.1 \times 10^3$) at DCB/DBB feed ratio of 70/30–60/40 mol%. The T_gs of copolymer were in good agreement with Fox's equation. The PPBS samples exhibited T_ms over all copolymer compositions by d.s.c. measurement. The eutectic point appeared to be at about 30 mol% of DBB repeat unit in the copolymer. Copyright © Elsevier Science Ltd.

(Keywords: copoly(*p*-phenylene/biphenylene sulfide); poly(*p*-phenylene sulfide); poly(arylene sulfide))

INTRODUCTION

Poly(*p*-phenylene sulfide) (PPS) has found numerous applications owing to its excellent combination of chemical resistance and thermal properties[1]. Several synthetic methods of PPS have been reported. These include self polycondensation of *p*-halothiophenoxy copper salt, by Lenz *et al.*[2] and Still *et al.*[3,4], and oxidative polymerization method by Tsuchida *et al.*[5,6]. PPS is obtained commercially by polycondensation of *p*-dichlorobenzene and sodium sulfide in NMP solvent at high temperature and pressure[7]. This process has some anomalous features in the polymerization kinetics and has evoked a variety of mechanistic interpretations[8–10]. It has been recently shown that PPS growth step is proceeded by ionic S_NAr (aromatic nucleophilic substitution) reactions[11,12]. Synthesis of poly(arylene sulfide)s and PPS copolymers have also been reported[13,14]. This paper describes the effects of polymerization conditions on the structure of random-copoly(*p*-phenylene/biphenylene sulfide)s [PPBS, equation (1)] and its thermal properties.



(1)

EXPERIMENTAL

Materials

Sodium sulfide trihydrate ($Na_2S \cdot 3H_2O$), a gift from Sunkyong Industries, was used as received. *N*-Methyl-2-pyrrolidinone (NMP) was distilled under reduced pressure before use. *p*-Dichlorobenzene (DCB) and 4,4′-dibromobiphenyl (DBB) were reagent grade from Aldrich Chemical Co. and used as received.

*Preparation of random-copoly(*p*-phenylene/biphenylene sulfide)s*

Polymerizations were conducted in a 600 ml autoclave (Parr Instrument Co., model 4843) equipped with mechanical stirrer, temperature and pressure indicator. A typical procedure was as follows. Autoclave was charged with 200 ml of NMP, 0.1 mol of $Na_2S \cdot 3H_2O$ (13.20 g), 0.07 mol of DCB (10.29 g), 0.03 mol of DBB (9.36 g) and 0.6 mol of H_2O (total 0.9 mol H_2O per 0.1 mol Na_2S) in sequence. The autoclave was closed, flushed with argon gas, and then heated to 270°C over 1.5-h period with stirring to dissolve sodium sulfide[11]. The reaction mixture was maintained at 270°C for 5 h. The pressure inside the reactor varied between 164 and 208 psi depending on polymerization conditions. The reaction was stopped by quenching the reactor in ice water and the product was poured into 1 litre of methanol with stirring and filtered. The resulting polymer was washed three times in about 80°C deionized water and finally in THF and then filtered. The polymer sample was dried in a vacuum oven at 100°C over 2 days and then subjected to yield determination and thermal analysis.

Characterization and measurement

The molecular weights of PPBS copolymers were obtained with a high-temperature gel permeation chromatograph (Senshu Scientific Co. Ltd, SSC VHT-7000) with 1-chloronaphthalene as eluent at 210°C. Shodex g.p.c. columns (AT-80M/S) and u.v. detector were employed and polystyrene standards were used for calibration. Copolymer compositions of PPBS were determined from the elemental (C,H,S) analysis (Carlo Erba model 1106) with 0.5–1.5 mg of copolymer samples at combustion temperature of *ca* 1200°C. The thermal properties of copolymer were checked with differential scanning calorimeter (DSC, Du Pont 2000 thermal analyzer). Thermograms were obtained on second run at a scan rate of 20°C min^{-1}. Copolymer samples were melted at 340°C for 2 min to destroy thermal history and then quenched in liquid nitrogen.

RESULTS AND DISCUSSION

Virgin PPS made from *p*-dichlorobenzene and sodium sulfide in NMP solvent exhibits low molecular weight, requiring a so-called curing process. Linear high molecular weight PPS was reported to be prepared by conducting a similar polymerization reaction in the presence of alkali metal carboxylate, especially lithium acetate[10,15]. It was of interest to know whether copolymerization of sodium sulfide with DCB/DBB comonomers in NMP solvent could give high molecular weight polymer comparable to PPS homopolymer prepared with carboxylate salt additives. The effect of presence of DBB repeat unit in the PPBS copolymer on the thermal properties (T_g and T_m) was also investigated.

Effect of DCB/DBB comonomer ratio on M_w *of PPBS*

DCB/DBB feed ratio was varied from 10/90 to 90/10 mol% while keeping the following reaction conditions constant: $Na_2S/(DCB + DBB)$ monomer ratio 1:1; monomer concentration 0.5 mol l^{-1}, total H_2O as additive/Na_2S ratio 9:1, reaction time 5 h and reaction temperature 270°C. Polymer yield and molecular weight of the resulting PPBS are summarized in *Table 1*. The yield did not change much, but the molecular weights of copolymer exhibited a sharp maximum at DCB/DBB feed ratio in the range from 70/30 to 60/40 mol% (sample CO-10 and CO-13) as shown in *Figure 1*.

The high M_w of CO-10 and CO-13 sample may be due to increased solubility of growing copolymer chain in the reaction medium by random nature of copolymer chain compared to the PPS homopolymer. Premature precipitation of growing PPS chain has been cited as one of the reasons for the low molecular weight of PPS homopolymer[3]. M_w of PPBS copolymer decreased sharply above 40 mol% of DBB in the feed. This seemed to be due to higher reactivity of DBB than that of DCB comonomer, as discussed in the copolymer composition. While PPS homopolymer was soluble in 1-chloronaphthalene at 210°C, poly(*p*-biphenylene sulfide) (PBS) homopolymer prepared by the same reaction as PPS homopolymer was not soluble in 1-chloronaphthalene at the same temperature. The copolymer made with DCB/DBB = 20/80 mol% in the feed could not be solublized in 1-chloronaphthalene at 210°C, suggesting the structure of the resulting copolymer was close to that of PBS homopolymer.

Table 1 Effect of DCB/DBB comonomer feed ratio on the yield and molecular weight of PPBS copolymers[a]

Sample no.	Feed ratio (mol%) DCB/DBB	Yield (%)	M_w[d] ($\times 10^{-3}$)	*MWD*[d]
T-1[b]	100/00	—	23.0	4.69
HO-PPS[c]	100/00	76.4	5.8	5.90
CO-11	90/10	67.4	8.8	3.34
CO-12	80/20	79.1	12.9	4.22
CO-10	70/30	81.6	24.1	6.30
CO-13	60/40	82.3	23.9	7.72
CO-14	50/50	78.7	8.3	3.67
CO-15	40/60	77.8	4.6	2.93
CO-16	30/70	77.6	2.9	2.53

[a] Reaction conditions: total water content in the medium (H_2O/Na_2S = 9/1 mol ratio); monomer concentration (0.5 mol l^{-1} NMP); reaction temperature (270°C)

[b] Tohpren® (Japan) virgin PPS (uncured)

[c] Reaction temperature (250°C)

[d] Obtained with high temperature g.p.c.

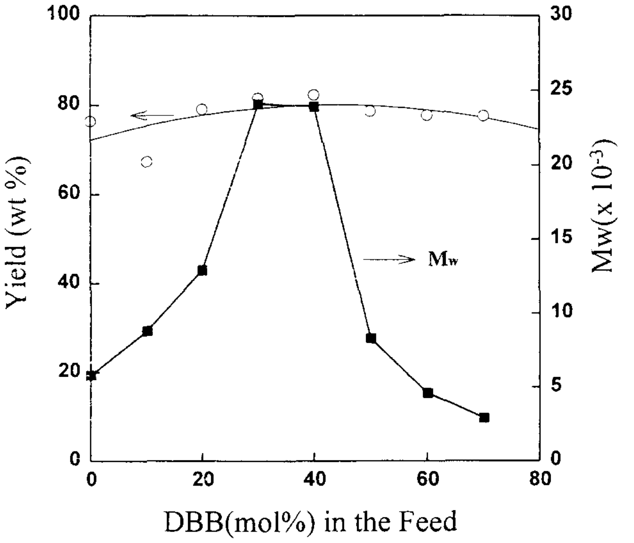
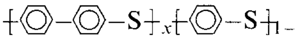


Figure 1 Change of yield (○) and molecular weight (■) of PPBS copolymers with mol% of DBB in the feed

Copolymer composition

From the structure of PPBS and mass ratio of C to S, equation (2) was set up:



$$\frac{W_c}{W_s} = \frac{[12.00 \times 12 \times X] + [12.00 \times 6 \times (1 - X)]}{[32.07 \times 1 \times X] + [32.07 \times 1 \times (1 - X)]} = \frac{72X + 72}{32.07} \qquad (2)$$

Here W_c and W_s represent mass % of C and S in the copolymer and X the mole fraction of DBB unit in the copolymer. The elemental analysis and copolymer composition data of PPBS samples are summarized in *Table 2*. From *Figure 2*, it could be seen that DBB had higher reactivity than DCB comonomer toward thiolate anion in the copolymerization reaction.

Thermal properties of PPBS copolymer

A typical d.s.c. thermogram is shown in *Figure 3* for copolymer CO-10 of which copolymer composition was DCB/DBB = 54/46 mol% and molecular weight was 24.1 × 10^3 g mol^{-1} (M_w). The T_g and T_m of PPS homopolymer (sample HO-PPS) prepared under similar reaction conditions except polymerization temperature (250°C) were 83.0 and 283.2°C, respectively (*Table 3*). These values were in good agreement with the PPS

Table 2 Elemental analysis and copolymer composition data of PPBS copolymers

Sample no.	Feed ratio (DCB/DBB mol%)	Experimental analysis (wt%) C	H	S	Copolymer composition (DCB/DBB mol%)
HO-PPS[a]	100/00	66.7	3.7	29.6	100/00
CO-11	90/10	70.2	3.8	26.8	84/16
CO-12	80/20	70.2	4.0	23.8	69/31
CO-10	70/30	73.5	4.0	22.4	54/46
CO-13	60/40	74.9	4.0	21.1	42/58
CO-14	50/50	73.9	4.2	19.5	32/68
CO-15	40/60	72.9	4.1	17.9	19/81
CO-16	70/30	—	—	—	na[b]
HO-PBS[a]	00/100	78.3	4.3	17.4	00/100

[a] Theoretical values
[b] Not applicable

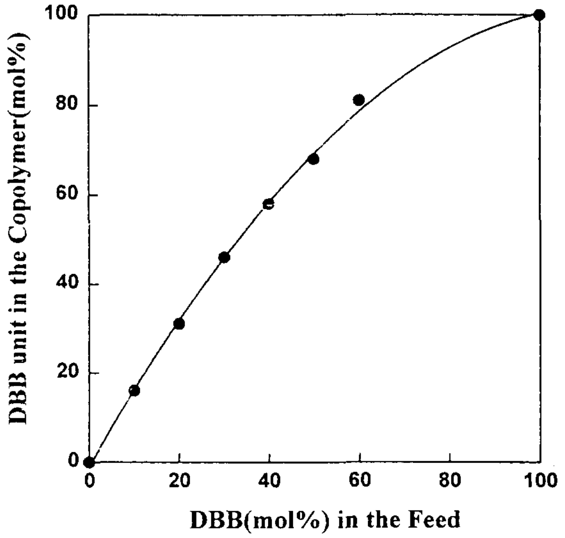


Figure 2 Relationship between copolymer composition and DBB (mol%) in the DCB/DBB feed

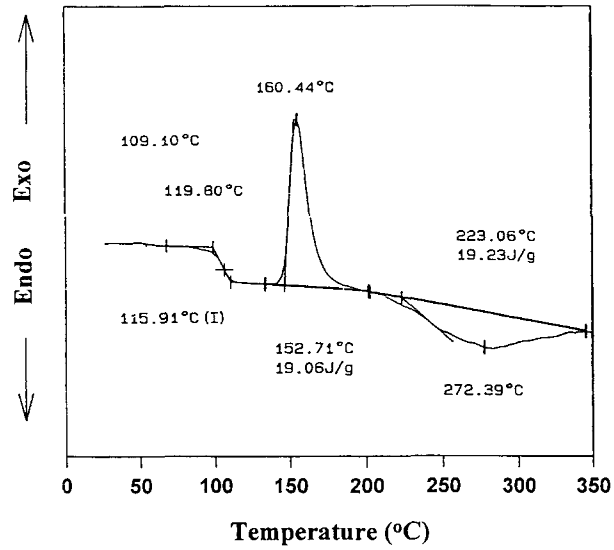


Figure 3 D.s.c. thermogram of CO-10 PPBS copolymer

homopolymer sample ($T_g = 85°C$ and $T_m = 285°C$) reported by Chung and Cebe[16]. The formation of PPBS copolymer was confirmed from the inward shift of both T_g (115.9°C) and T_m (272.4°C) of CO-10 copolymer from the PPS ($T_g = 83.0°C$, $T_m = 283.2°C$) and PBS ($T_g = 150.4°C$, $T_m = 386.5°C$) homopolymer, respectively. The effect of copolymer composition on the thermal transition temperatures of other PPBS copolymers are summarized in *Table 3*.

The T_g and T_m values of PBS homopolymer prepared under similar conditions to PPBS copolymer could not be measured by d.s.c. experiment. Therefore the group contribution method by Van Krevelen was used to calculate T_g and T_m of the PBS homopolymer[17]. The equation and necessary constants are shown in Table 4. The calculated T_g and T_m of PBS homopolymer were 150.4 and 386.5°C, respectively.

The variation of T_gs with copolymer composition was analysed by using Fox's equation (3):

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \tag{3}$$

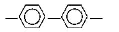
Here T_g is the glass transition temperature of copolymer, T_{g1} and T_{g2} are that of homo-PPS and homo-PBS, respectively. W_1 and W_2 represent mass fractions of DCB and DBB repeat units in the PPBS copolymer. The T_g values of PPBS copolymers using

Table 3 Effect of copolymer composition on the thermal properties of PPBS copolymers[a]

Sample no.	Copolymer composition (DCB/DBB mol%)	M_w ($\times 10^{-3}$)	Thermal transitions (°C) T_g	T_c^c	T_m
HO-PPS[b]	100/00	5.8	83.0	111.7	283.2
CO-11	84/16	8.8	88.6	143.6	239.8
CO-12	69/31	12.9	102.2	159.4	217.9
CO-10	54/46	24.1	115.9	160.4	272.4
CO-13	42/58	23.9	125.6	165.5	295.9
CO-14	32/68	8.3	131.5	165.9	304.4
CO-15	19/81	4.6	—	—	331.0

[a] Reaction conditions (same as *Table 1*)
[b] Reaction temperature (250°C)
[c] Cold crystallization temperature

Table 4 Calculation of T_g and T_m of the PBS homopolymer by the Van Krevelen equation

Group	Y_{gi} (gK mol^{-1} × 10^{-3})	Y_{mi} (gK mol^{-1} × 10^{-3})	M_i (g mol^{-1})
	70	99	152.18
–S–	8	22.5	32.06

$$\sum Y_{gi} = 78 \qquad \sum Y_{mi} = 121.5 \qquad M = 184.24$$

$$T_g = \frac{\sum Y_{gi}}{M} = \frac{78 \times 1000}{184.24} = 423.36\,\text{K} = 150.36^\circ\text{C}$$

$$T_m = \frac{\sum Y_{mi}}{M} = \frac{121.5 \times 1000}{184.24} = 659.47\,\text{K} = 386.47^\circ\text{C}$$

Table 5 Comparison of measured and calculated T_g of PPBS copolymers

Sample no.	W_1	W_2	T_g (°C), Fox equation	T_g (°C), Measured
HO-PPS	1	0		83.0
CO-11	0.755	0.245	93.2	88.6
CO-12	0.567	0.434	103.0	102.2
CO-10	0.408	0.592	113.0	115.9
CO-13	0.298	0.702	121.1	125.6
CO-14	0.216	0.784	127.9	131.5
HO-PPS	0	1		150.4[a]

[a] Estimated value from Van Krevelen equation

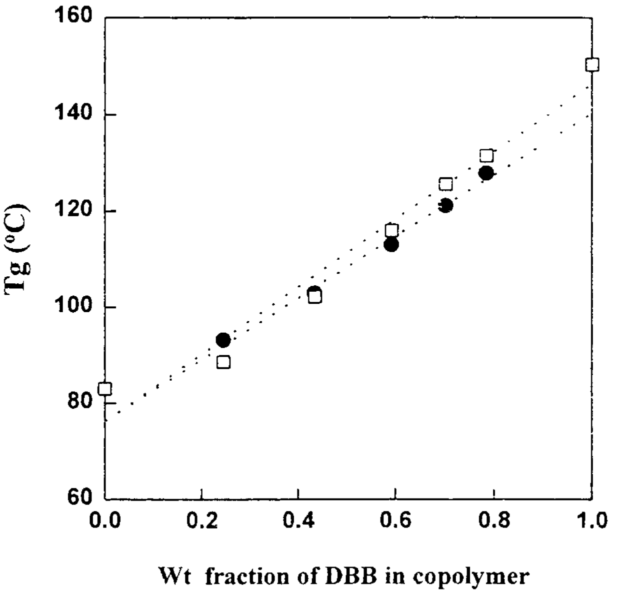


Figure 4 T_g vs DBB wt fraction in PPBS copolymers. (□) T_g calculated from Fox's equation; (●) T_g experimentally determined

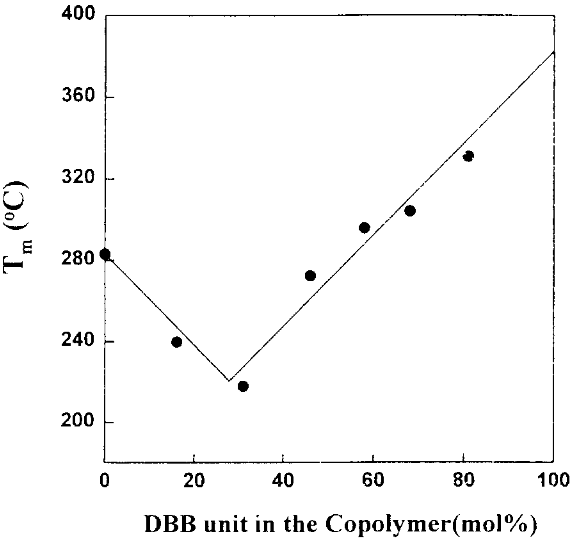


Figure 5 T_m vs DBB content (mol%) in the PPBS copolymers

Table 6 T.g.a. data of PPS, PBS homopolymer and PPBS copolymers

Sample no.	Copolymer composition (DCB/DBB mol%)	IDT[a] (°C)	MDT[b] (°C)	Residue (%) at 850°C
HO-PPS	100/00	495	528	43.9
CO-11	84/16	547.1	597.7	47.8
CO-12	69/31	547.0	596.5	53.7
CO-10	54/46	558.5	597.7	55.0
CO-13	42/58	568.0	608.8	55.4

[a] Initial decomposition temperature
[b] Maximum decomposition temperature (taken as the maximum point in the derivative plot of %mass loss vs temperature)

calculated T_{g2} value were in good agreement with the measured ones, as shown in *Figure 4* and *Table 5*.

The relationship between T_m and content of DBB repeat unit in the copolymer is shown in *Figure 5*. It was of interest to note that the PPBS copolymers exhibited T_ms over all compositions at 20°C min^{-1} scan rate of d.s.c. measurement. The eutectic point appeared to be 217.9°C at 30 mol% DBB unit in the copolymer.

The thermogravimetric analysis data of PPBS copolymer are shown in *Table 6*. The initial decomposition temperature (IDT), maximum decomposition temperature (MDT) and residue at 850°C all increased with the increasing amount of DBB unit in the copolymer.

CONCLUSIONS

Copoly(*p*-phenylene/biphenylene sulfide)s (PPBS) have been shown to be easily prepared from sodium sulfide and DCB/DBB comonomers utilizing NMP as solvent. The reactivity of DBB monomer was found to be higher than that of DCB toward the thiolate anion from the copolymer composition analysis. The molecular weight of PPBS copolymer showed maximum value (M_w = 23.9–24.1 × 10^3) at DCB/DBB feed ratio of 70/30–60/40 mol%. The T_gs of copolymer were in good agreement with Fox's equation. The PPBS copolymers exhibited T_ms over all compositions at 20°C min^{-1} scan rate of d.s.c. measurement. The eutectic point appeared to be 217.9°C at 30 mol% DBB unit in the copolymer.

ACKNOWLEDGEMENTS

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