

## Poly(Phenylene Sulfide)의 고분자량화 및 Sulfone 유도체와의 중합 반응

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### Polymerization and Copolymerization of Poly(p-phenylene sulfide) and Poly(p-phenylene sulfide/sulfone)

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**요 약 :** Poly(phenylene sulfide), PPS의 고분자량화를 위하여 공중합법 및 상전이 촉매 효과를 조사하였다. 먼저 sodium sulfide( $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ )를 p-dichlorobenzene(DCB)와 중합시켜 PPS를 그리고 4-chlorophenylsulfone(CPS)와 중합시켜 poly(phenylene sulfide/sulfone), PPSS를 얻는 단독중합 조건에 대해 조사하였다. 소량의 CPS를 DCB와 직접 공중합하기 보다 coupling 반응을 통하여 PPS의 분자량을 증가시킬 수 있음을 알았다. 또 crown ether들을 상전이 촉매로 사용할 때 PPS의 분자량이 증가함을 확인하였으나 그 효과는 lithium acetate 첨가제를 NMP 용매에 투입할 때 보다 크지 않음을 알 수 있었다.

**Abstract :** For the improvement of molecular weight of poly(phenylene sulfide), PPS, copolymerization method and phase transfer catalyst as additive were investigated. As a preliminary experiment the optimum homopolymerization conditions of PPS from p-dichlorobenzene(DCB) and  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  and poly(phenylene sulfide/sulfone), PPSS from 4-chlorophenylsulfone(CPS) and  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  were examined. The use of minor amount of CPS comonomer with DCB in a coupling type reaction was found to give higher molecular weight polymer than direct copolymerization or homopolymerization of PPS. The addition of 1/50 amount of phase transfer catalysts such as 15-crown-5, 18-crown-6, dibenzo 18-crown-6, dicyclohexano 18-crown-6 based on sodium sulfide also improved the molecular weight of PPS. The effect, however, was not so great as that of lithium acetate added equimolar amount of  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  into NMP solvent.

## INTRODUCTION

Poly(p-phenylene sulfide), PPS is a semi-crystalline thermoplastic polymer which possesses good thermal, mechanical, and chemical properties in addition to self-extinguishing.<sup>1-4</sup> Although PPS has a long history in the chemical literature, recent research on PPS was begun by A. D. Macallum in 1948.<sup>5</sup> R. W. Lenz and coworkers reported the synthesis of PPS by a self-condensation of copper(I) p-bromobenzenethiolate.<sup>6</sup> This method, however, has a problem of removing copper(I) bromide by-product due to its low solubility in water. Edmonds and Hill at Phillips Petroleum Company<sup>7</sup> introduced a new route to PPS utilizing p-dichlorobenzene and sodium sulfide in N-methyl-2-pyrrolidone(NMP) at elevated temperature. This method is currently used in the commercial production of PPS.<sup>8</sup>

On the mechanism of PPS polymerization, Koch and Heitz reported a reactive intermediate polycondensation involving radical cations generated by single electron transfer(SET). Fahey and Ash<sup>9</sup> recently showed that PPS was synthesized through an aromatic nucleophilic substitution( $S_NAr$ ) mechanism from the model compound study. According to them, the unusual growth of high molecular weight PPS at low conversion could be explained in terms of increasing reaction rates of  $S_NAr$  reactions as oligomers are formed. Tsuchida et. al.<sup>10</sup> reported that they could also synthesize PPS from diphenyl disulfides as monomers. Their method, however, is based on oxidative cationic polymerization, and out of the scope of this work.

One of the problems of PPS and related polymers is inherently low molecular weight of virgin polymers made by polycondensation reaction routes.

In this work increasing the molecular weight of PPS was attempted in two ways. The first approach was direct copolymerization of CPS with p-DCB/ $Na_2S$  system or coupling reaction of PPS polymer with CPS monomer. The second was to study the effect of additive like crown ethers on the molecular weight of PPS homopolymer.

## EXPERIMENTAL

### Materials

Sodium sulfide( $Na_2S \cdot 9H_2O$ ), p-dichlorobenzene, 4-chlorophenyl sulfone were obtained from Aldrich Chemical and used as received. NMP solvent was distilled under reduced pressure in the presence of  $CaH_2$ . 1-chloronaphthalene used for the measurement of viscosity of PPS was obtained from Aldrich Chemical and used without further purification.

### Polymerization

For the polymerization of PPS, 0.125 mole of  $Na_2S \cdot 9H_2O$  was dissolved in 150 ml of NMP in a three necked flask equipped with Ar gas inlet-outlet adapter, thermometer, and Dean-Stark trap, and then the solution was heated to 200°C. The amount of water collected was close to sodium sulfide crystal water. Dehydrated sodium sulfide/NMP solution was placed in a 350 ml stainless bomb type reactor. To this solution 0.125 mole of p-dichlorobenzene dissolved in 100 ml of NMP was added under Ar gas atmosphere. The reactor was capped and the mixture was reacted at 250°C with stirring for 3 to 6 hours. For homopolymerization of PPSS in which dehydration of  $Na_2S \cdot 9H_2O$  was not conducted, 4-chlorophenyl sulfone and  $Na_2S \cdot 9H_2O$  were directly dissolved in NMP and then reacted.

For the copolymerization of PPS and PPSS,  $Na_2S \cdot 9H_2O$ -NMP solution was dehydrated first and the mixture solution of p-dichlorobenzene and 4-chlorophenyl sulfone in NMP was added to the bomb type reactor, and reaction mixture was then reacted at 250°C. For the coupling type copolymerization, polymerization reaction was conducted in two stage. In the first stage,  $Na_2S \cdot 9H_2O$ (5 to 20 mole % excess) and p-dichlorobenzene was polymerized at 220°C for 3 hours by the same way as the PPS homopolymerization. The reactor cap was opened and a small amount of NaOH and 4-chlorophenyl sulfone (5 to 20 mole %) was added and the reaction mixture was reacted at a given temperature for 3 hours.

After the polymerization reaction, reaction mixture was poured into 5 times amount of acetone.

The precipitate was filtered and washed with water at 80°C under stirring for 3 hours. After another wash with water and final wash with acetone, the polymer was dried in vacuo at 60°C for 6 hours, and then conversion was determined.

**Characterization**

The viscosity of PPS homopolymer and copolymer was measured with Ostwald viscometer in 1-chloronaphthalene solvent at 208°C. Intrinsic viscosity was calculated by single point relative viscosity method, equation (1) proposed by Solomon and Ciuta.<sup>11</sup>

$$[\eta] = (1/C) \sqrt{2(\eta_{sp} - \ln \eta_r)} \quad (1)$$

Viscosity average molecular weight of PPS was calculated from the Mark-Houwink-Sakurada equation (2) using K and a values reported by Stacy.<sup>12</sup>

$$[\eta] = K \bar{M}_v^a \quad (2)$$

$K = 8.91 \times 10^{-5}, a = 0.747$

IR spectra were obtained from Midac FT-IR spectrophotometer and thermal property was checked with Du Pont 2000 thermal analyzer.

**RESULTS and DISCUSSION**

**Homopolymerization of PPS and PPSS**

From the previous research on PPS<sup>13</sup> the optimum reaction condition ( $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ /p-dichlorobenzene ratio of 1 : 1, 250°C reaction temperature, about 4 hour reaction time, and complete dehydration of  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  crystal water) was used to synthesize PPS. The synthesis of poly(p-phenylene sulfide/sulfone), PPSS, from  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  and p-chlorophenyl sulfone(CPS) required quite different reaction conditions from those of PPS. The effect of reaction temperature on PPSS synthesis is shown in Table 1. The optimum polymerization temperature of 200°C for PPSS is about 50°C lower than that of PPS.

In Table 2 is shown the effect of added amount of water in the NMP reaction medium on the polymerization of PPSS. The highest yield of PPSS was

**Table 1.** The Effect of Reaction Temperature on PPSS Synthesis

Sample No.	AS-4	AS-5	AS-3	AS-6	AS-7
Reaction temp.(°C)	160	180	200	220	240
Polymer conv.(%)	40.4	60.4	64.4	52.7	49.3

Reaction condition : Water(contains only  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  crystal water), Monomer conc.(0.125mole/l), NaOH (none), Reaction time(4hr.)

obtained with 150% excess of water added into NMP solvent in addition to  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  crystal water(sample AS-23) with sodium sulfide and CPS mole ratio of 1 : 1 and reaction temperature at 200 °C. In the polymerization of PPS<sup>13</sup> the complete dehydration of sodium sulfide crystal water was required in order to have high conversion to polymer. From Table 2 it is noted that complete removal of sodium sulfide crystal water could not give any conversion to PPSS polymer.

This may be due to the drastic difference of reactivity of DCB and CPS substrate toward thiolate anion. According to Fahey and Ash, PPS is synthesized by the stepwise aromatic nucleophilic substitution reactions. Since reactivity of CPS monomer toward the sodium thiolate anion of growing oligomer is much higher than that of DCB toward it, the presence of water may not interfere with polycondensation reactions in case of PPSS simply changing the solvent property of the reaction medium. In case of PPS for which the reactivity of DCB is low and reaction temperature is high, the presence of water may lead to undesirable side reactions to a higher degree than PPSS, which results in the disturbance of the stoichiometric balance of monomers required in the polycondensation reactions.

**Copolymerization of PPS and PPSS**

Assuming the low molecular weight of virgin PPS polymer may be due to premature precipitation of stiff PPS chains in the reaction medium, copolymerization of a minor amount of p-chlorophenyl sulfone(CPS) in addition to DCB with so-

**Table 2.** The Effect of Water Content in the NMP Reaction Medium on the PPSS Polymerization

Sample No.	AS-12	AS-13	AS-14	AS-8	AS-15	AS-16	AS-23	AS-28	AS-29
Water content (g/200 g NMP)	0	4.1	6.2	8.2	12.3	16.4	20.5	24.6	41.0
(x as Na <sub>2</sub> S · xH <sub>2</sub> O)	0	4.5	6.8	9.0	13.5	18.0	22.5	27.0	45.0
Polymer conv. (%)	0	0	5.0	72.8	80.9	80.3	86.2	74.1	75.9
Viscosity(η <sub>r</sub> ) (NMP, 30°C)	—	—	—	1.55	1.64	1.68	1.80	1.58	1.57

Reaction condition : Reaction temp.(200°C), Reaction time(4hr.), CPS/Na<sub>2</sub>S = 1/1, Monomer conc.(0.25 mole/l)

**Table 3.** Copolymerization of CPS & p-DCB with Na<sub>2</sub>S

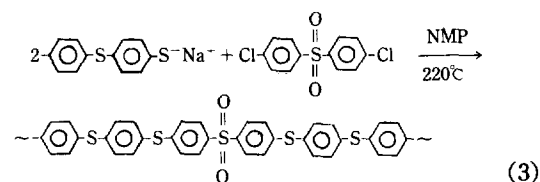
Sample No.	mole ratio (CPS/DCB)	conversion (%)	η <sub>r</sub>	Mv (×10 <sup>3</sup> )
PSC-4	0/100	63.70	1.25	5.75
PSC-6	5/95	64.82	1.21	4.66
PSC-5	10/90	48.02	1.16	3.32
PSC-8	20/80	20.65	1.11	2.10
PSC-9	30/70	5.44	—	—

Reaction condition : Dehydration of Na<sub>2</sub>S · 9H<sub>2</sub>O conducted, 1st step(220°C, 3hr.), 2nd step(250°C, 3hr.), Monomer conc.(0.5 mole/l NMP)

dium sulfide was investigated in two ways. The first one was direct copolymerization of PPS and PPSS for which reaction conditions are shown in Table 3. The copolymerization was run with the complete dehydration of sodium sulfide crystal water, since CPS was used as minor comonomer compared to DCB. The polymerization was conducted in two stages at reaction temperature of 220 and 250°C in order to take account of the different reaction temperature of PPSS and PPS. The results were both the very low conversion to polymer and low viscosity of the resulting polymer with the increasing amount of CPS.

Since direct copolymerization did not give high polymer yield, another method i. e. coupling type reaction was studied. In this method the complete dehydration of sodium sulfide was employed and polymerization was run in two stages. In the first stage, 5, 10, 15% excess of sodium sulfide was

reacted with DCB at 220°C for 3 hours and then 5, 10, 15% of CPS was added and finally the mixture was reacted at 220°C for another 3 hours. This was done assuming highly reactive CPS could couple the preformed polymer chains as shown in eq. (3)



The result of coupling type reaction is shown in Table 4. The polymer by coupling method gave higher yield and viscosity compared to direct copolymerization method. The IR spectra of direct and coupling type copolymerization product are shown in Fig. 1. The polymer by coupling method exhibited sulfone stretching peaks at 1,324 and 1,158cm<sup>-1</sup>, but the direct copolymerization did not.

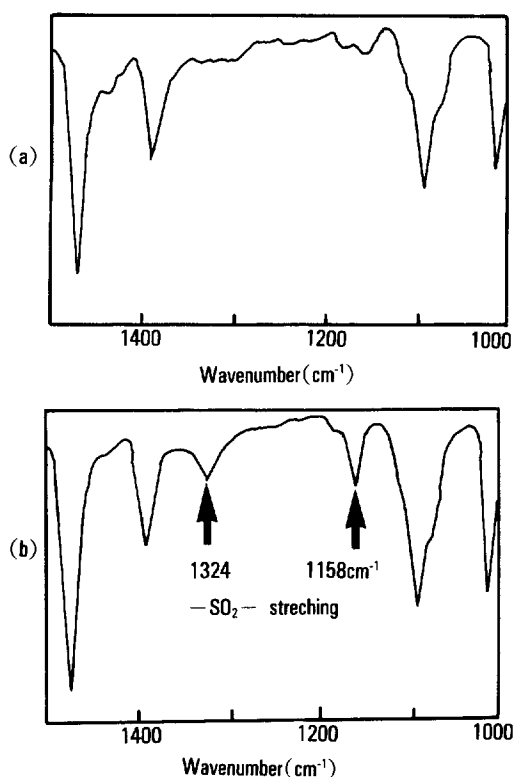
#### Effect of Phase Transfer Catalyst on PPS

In the previous paper<sup>13</sup> it was reported that lithium acetate as additive in NMP solvent improved the molecular weight of PPS. Since polymerization of PPS involves nucleophilic attack of sodium thiolate anions, the effect of adding crown ethers on PPS polymerization were studied. The crown ethers used were 15-crown-5, 18-crown-6, dicyclohexano 18-crown-6, and dibenzo 18-crown-6. Polymerization data are shown in Table 5. The polymerization reactions were conducted at three different temperature of 210, 230 and 250°C. The

**Table 4.** PPS Polymerization by Two-Stage Coupling Method

Sample No.	2nd st. excess mole ratio (CPS/DCB)	conversion (%)	$\eta_r$	Mv ( $\times 10^3$ )
PSC-4	0.000/0.1	63.70	1.25	5.75
PSC-7	0.005/0.1	70.74	1.30	7.37
PSC-10	0.010/0.1	63.74	1.24	5.57
PSC-11	0.015/0.1	57.01	1.23	5.31

Reaction condition : Dehydration of  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  was conducted, 1st step(220°C, 3hr.), 2nd step(220°C, 3 hr.), Monomer conc.(0.5 mole/l)

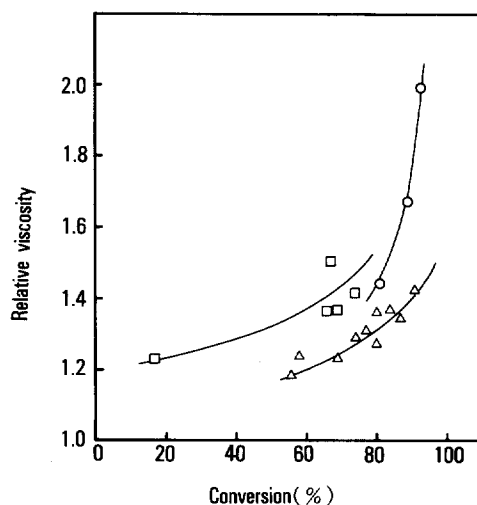


**Fig. 1.** IR spectra of PPS/PPSS copolymer samples of (a) direct copolymerization and (b) coupling type copolymerization.

molecular weight and conversion of PPS were higher at 230°C compared to 210 or 250°C. This may be due to better chelating efficiency of crown ethers at 230°C than high temperature of 250°C. At

**Table 5.** The Effect of Phase Transfer Catalyst(PTC) on the PPS Polymerization

PTC	Temp. (°C)	Time (hr.)	Conv. (%)	$\eta_r$	Mv ( $\times 10^3$ )	
15-Crown-5	210	6	69.0	1.36	9.13	
	230	6	73.7	1.41	10.69	
	250	6	69.6	1.31	7.61	
18-Crown-6	210	6	66.7	1.33	8.22	
	230	6	75.9	1.41	10.69	
Dicyclohexano	210	6	68.7	1.34	8.52	
	230	6	75.6	1.37	9.45	
18-Crown-6	250	6	77.6	1.35	8.82	
	Dibenzo	210	6	69.3	1.27	6.41
		230	6	74.3	1.34	8.52
18-Crown-6	250	6	70.9	1.29	7.01	



**Fig. 2.** Relative viscosity of PPS samples as a function of conversion with different additives :  $\Delta$  : Sodium Sulfide + DCB + None,  $\circ$  : Sodium Sulfide + DCB + LiAc,  $\square$  : Sodium Sulfide + DCB + 15-Crown-5.

210°C the conversion and thus molecular weight of PPS became low since the optimum temperature of PPS polymerization was about 250°C. It was also noted that 15-crown-5 and 18-crown-6 are better than dibenzo or dicyclohexano 18-crown-6, suggesting the steric hindrance of the latter compounds.

The relative effectiveness of lithium acetate (added the same mole as sodium sulfide) and crown

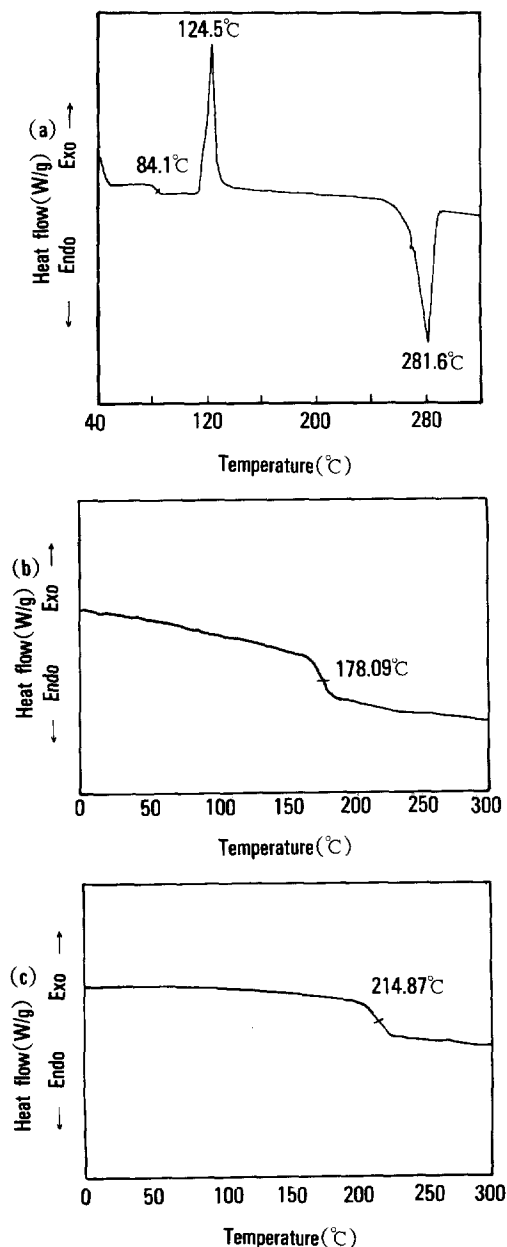


Fig. 3. DSC thermograms of (a) PPS sample, (b) PPSS sample, and (c) PPSS sample after heat curing.

ether(added 1/50 mole of sodium sulfide) were compared in Fig. 2. From Fig. 2 crown ethers did improve the molecular weight of PPS compared to uncatalyzed PPS, but their effect was not so great as that of lithium acetate.

#### Thermal Properties of PPS and PPSS

The thermal properties of PPS and PPSS were compared in Fig. 3. PPS showed both  $T_g$  (ca. 84°C) and  $T_m$  (ca. 282°C), but PPSS exhibited only  $T_g$  at 178°C. The heat curing of PPSS for 30 min. at 235°C improved the thermal stability as evidenced by increased  $T_g$  at 215°C. This kind of behavior was similar to that of known thermal crosslinking of PPS.

#### REFERENCE

1. J. M. Margolis, "Engineering Thermoplastics", Marcel Dekker (1985).
2. H. W. Hill, Jr. and D. G. Brady, *Chem. Tech.*, **49**, 33 (1977).
3. D. G. Brady, *J. Appl. Polym. Sci.*, **20**, 2541 (1976).
4. J. N. Short and H. W. Hill, Jr., *Chem. Tech.*, **2**, 481 (1972).
5. S. R. Sandler and Wolf Karo, "Polymer Syntheses", **3**, 81, Academic Press (1980).
6. Encyclopedia of Chemical Technology, 3rd Ed., **18**, 793 (1982).
7. P. A. Lovell and R. H. Still, *Makromol. Chem.*, **188**, 111 (1987).
8. J. T. Edmonds, Jr. and H. W. Hill, Jr., U. S. Pat. 3,354,129 (1967), U. S. Pat. 3,524,835 (1970).
9. Darryl R. Fahey and Carlton E. Ash, *Macromolecules*, **24**, 4242 (1991).
10. Eishun Tsuchida et al., *Macromolecules*, **23**, 930, (1990).
11. O. F. Solomon and I. Z. Ciuta, *J. Appl. Polym. Sci.*, **6**, 683 (1962).
12. C. T. Stacy, *J. Appl. Polym. Sci.*, **32**, 3959 (1986).
13. L. S. Park, K. H. Seo, J. G. Chang, Y. H. Kwon, S. K. Han and I. H. Cha, *Polymer(Korea)*, **13**, 866 (1989).