

# Synthesis and Characterization of Poly(phenylene Sulfide), Poly(2-methylphenylene Sulfide), and Poly(2,6-Dimethylphenylene Sulfide)

A. B. PORT\* and R. H. STILL, *Department of Polymer and Fibre Science, UMIST, Manchester, England*

## Synopsis

A facile synthesis of poly(phenylene sulfide) (PPS), poly(2-methylphenylene sulfide) (PMPS), and poly(2,6-dimethylphenylene sulfide) (PDMPS) from the respective copper (I) bromothiophenoxides is described. Polymerization was effected in a 10:1 quinoline:pyridine mixture at atmospheric pressure and conditions optimized for the preparation of high-molecular-weight materials. The preparation of PPS in pyridine under pressure at 250°C has been investigated for comparative purposes. Yields and the properties of materials produced by solution polymerization are comparable to or better than those produced in the autoclave reaction. Properties have been investigated as a function of reaction time and molecular weight, and the deficiencies of the molecular-weight assessment methods are discussed. PMPS and PDMPS have been similarly studied and their properties evaluated. The use of heat of crystallization determinations for molecular-weight studies on PPS are described and critically evaluated.

## INTRODUCTION

Poly(arylene sulfides), in particular poly(phenylene sulfide) (PPS), have recently been commercially produced from *p*-dichlorobenzene and sodium sulfide and marketed under the trade name of Ryton.<sup>1</sup> This class of materials was first reported as the by-product of various electrophilic reactions<sup>2-7</sup> and described as amorphous, insoluble powders "melting" at 300°C or higher. Such polymers probably had branched or cross-linked structures and varying proportions of polysulfide links.

Although some linear poly(arylene sulfides) and polysulfones can be prepared by electrophilic reactions,<sup>8-11</sup> PPS precipitates from the reaction medium before high molecular weights are attained.<sup>12</sup>

The first synthesis of PPS was reported by Macallum<sup>13-15</sup> from *p*-dichlorobenzene, sulfur, and sodium carbonate, but the forcing conditions employed rendered the reaction and its product irreproducible. Lenz, Smith, and co-workers<sup>16-18</sup> and Hortling and Lindberg<sup>19</sup> investigated this reaction, and Lenz developed a more reliable synthesis based on the self-condensation of metal-*p*-halogenothiophenoxides.<sup>18,20-22</sup>

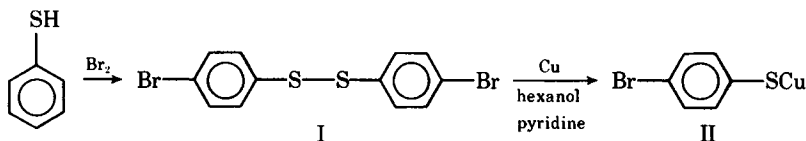
In this study the reactions of copper (I) bromothiophenoxides under less drastic conditions than those reported by Lenz and Smith have been assessed as routes to PPS, poly(2-methylphenylene sulfide) (PMPS), and poly(2,6-dimethylphenylene sulfide) (PDMPS).

\* Present address: M.O.D.(PE), A.W.R.E., Aldermaston, Berkshire, England.

## EXPERIMENTAL

## Materials

Copper (I)-4-bromothiophenoxide (II), the precursor to PPS, was synthesized from benzene thiol by the following route:



Bis(*p*-bromophenyl) disulfide (I) was prepared by the method of Bourgeois<sup>23</sup> as modified by Handlovits,<sup>22</sup> yielding pale yellow plates in 65% yield mp 94–94.5°C, lit<sup>23</sup> 94°C.

ANAL: Found: C, 38.2%; H, 1.9%; Br, 42.8%; S, 17.3%.  $\text{C}_{12}\text{H}_8\text{Br}_2\text{S}_2$  requires: C, 38.30%; H, 2.13%; Br, 42.55%; S, 17.02%.

Copper (I)-4-bromothiophenoxide was prepared from I by the method of Handlovits<sup>22</sup> and was obtained as yellow needles in 88% yield, mp 270–275°C lit<sup>22</sup> 260–275°C. The monomer was observed to melt and to then rapidly resolidify by hot-stage microscopy. Studies by differential scanning calorimetry (DSC) at a heating rate of 20°C/min showed a single sharp exotherm with peak maximum at 275°C.

ANAL: Found: C, 27.8%; H, 1.6%; Br, 30.1%; S, 11.7%; Ash, 26.5%.  $\text{C}_6\text{H}_4\text{BrSCu}$  requires: C, 28.64%; H, 1.59%; Br, 31.80%; S, 12.72%.

The copper-metal impurity in the sample was determined by atomic absorption spectroscopy and EDTA titrimetry as 2–3% after digestion of the salt in hot concentrated nitric acid. Copper(I)-4-bromo-2-methylthiophenoxide, the precursor to PMPS, was synthesized by two routes. First, 4-bromo-2-methyl aniline was converted to 4-bromo-2-methylbenzene thiol via the Leuckart reaction as modified by Campaigne and Osborne.<sup>24</sup> The thiol was oxidized to the disulfide with excess dimethylsulfoxide.<sup>25</sup> Recrystallization of the product from acetone gave white crystals in 21% yield, mp 89–90°C, lit<sup>26</sup> 86°C.

ANAL: Found: C, 41.3%; H, 3.0%; Br, 39.6%; S, 15.5%.  $\text{C}_{14}\text{H}_{12}\text{Br}_2\text{S}_2$  requires: C, 41.58%; H, 2.97%; Br, 39.61%; S, 15.84%.

In the second route, bis(4-bromo-2-methylphenyl) disulfide was prepared by bromination of *o*-toluene thiol. Thus *o*-toluene thiol (Eastman Kodak) (50 g) was reacted with bromine (62.5 ml, 100% excess) and yielded a product 61.6g, 76% yield of mp 89–90°C. It gave a mixed mp of 89–90°C with the product from the Leuckart reaction and an identical IR spectrum.

Bis(4-bromo-2-methyl phenyl) disulfide was converted into copper(I)-4-bromo-2-methyl thiophenoxide using the method reported for II with the reaction time increased to 16 hr. The bright yellow copper salt was obtained in 86% yield (based on copper). It had a mp 286–288°C and was observed to melt and then rapidly resolidify on hot-stage microscopy. When examined by DSC, it gave a sharp exotherm with peak temperature of 285°C.

ANAL: Found: C, 31.3%, H, 2.2%; Br, 29.8%; S, 12.6%.  $\text{C}_7\text{H}_6\text{S Cu}$  requires: C, 31.62%, H, 2.26%; Br, 30.12%; S, 12.05%.

Copper impurity was estimated by titration with EDTA as 0.5%.

Copper(I)-4-bromo-2,6-dimethyl thiophenoxide, the precursor to PDMPS, was prepared from dimethylaniline or dimethylphenol by the following methods.

1. 2,6-Dimethylaniline (Ralph Emmanuel) was purified by distillation (bp 175°C at 4.5 mm Hg) and brominated in acetic acid at 30°C<sup>27</sup> to yield 4-bromo-2,6-dimethylaniline from ligroin in 60% yield, mp 49.5–50°C lit.<sup>27</sup> 50°C or more easily purified as the hydrochloride, mp 175–200°C (sublimed) lit.<sup>28</sup> 203–204°C.

ANAL: Found: C, 40.7%; H, 4.9%; N, 6.2%; Halogens 48.2% (by difference). C<sub>8</sub>H<sub>11</sub>BrClN requires: C, 40.63%; H, 4.69%; N, 5.92%; halogens 48.77%.

2. 4-Bromo-2,6-dimethylaniline-hydrochloride was treated in a similar manner to that described for 4-bromo-2-methylaniline to yield bis(4-bromo-2,6-dimethylphenyl) disulfide as pale yellow crystals in 20% yield, mp 129–130°C, lit.<sup>26</sup> 129–130°C.

ANAL: Found: C, 44.7%; H, 4.0%; Br, 36.5%; S, 14.5%. C<sub>16</sub>H<sub>16</sub>Br<sub>2</sub>S<sub>2</sub> requires: C, 44.44%; H, 3.70% Br, 37.04%; S, 14.81%.

Attempts were also made to prepare 2,6-dimethylbenzene thiol by the Newman-Kwart reaction.<sup>29</sup> 2,6-Dimethylphenol (BDH) was purified by recrystallization from hexane, mp 49°C, lit.<sup>30</sup> 49°C. Dimethylthiocarbamyl chloride (Aldrich Chemical Co.) was used as received. Tetrahydrofuran was dried over anhydrous potassium carbonate and distilled under nitrogen prior to use. 2,6-Dimethylphenol (18.33 g) was dissolved in aqueous potassium hydroxide [8.41 g in water (100 ml)] and treated with dimethylthiocarbamyl chloride (25 g) in tetrahydrofuran (40 ml) as described by Newman and Hetzel.<sup>29</sup> A yellow compound (10 g) was isolated and had mp 143–147°C.

ANAL: Found: C, 56.4%; H, 6.5%; N, 9.3%; S, 21.1%; O, 6.7% (by difference). The expected product *O*-(2,6-dimethylphenyl) dimethylthiocarbamate, C<sub>9</sub>H<sub>15</sub>NOS requires: C, 63.16%; H, 7.18%; N, 6.70%; O, 7.66%; S, 15.31%.

The NMR spectrum showed the following absorptions on the  $\delta$  scale, a singlet at 2.20 intensity 6, two methyl groups attached to an aromatic nucleus, doublets at 3.28, 3.38, and 3.44, 3.56, intensity 12, methyl groupings attached to nitrogen; a complex multiplet at 6.7–7.3 intensity 2, aromatic protons. The IR spectrum showed major absorptions at 880 cm<sup>-1</sup> (1,2,3,5-tetra-substituted phenyl ring) and 1150 cm<sup>-1</sup> (C=S stretching in RCSN—).

Bis(4-bromo-2,6-dimethylphenyl) disulfide was converted into copper (I)-4-bromo-2,6-dimethylthiophenoxide using the method reported for copper(I)-4-bromothiophenoxide with the reaction time extended to 18 hr. The yellowish green copper salt was obtained in 69% yield and had mp 270–275°C. On the hot-stage microscope it was observed to melt and then resolidify. On DSC it exhibited complex behavior (Fig. 1). The elemental copper impurity level was estimated as 5.0% by EDTA titration.

### Polymerization of Copper (I)-4-Bromothiophenoxides

Copper (I)-4-bromothiophenoxide was polymerized in pyridine at 250°C under pressure for 16 hr using the method reported by Smith and Handlovits.<sup>21</sup> In

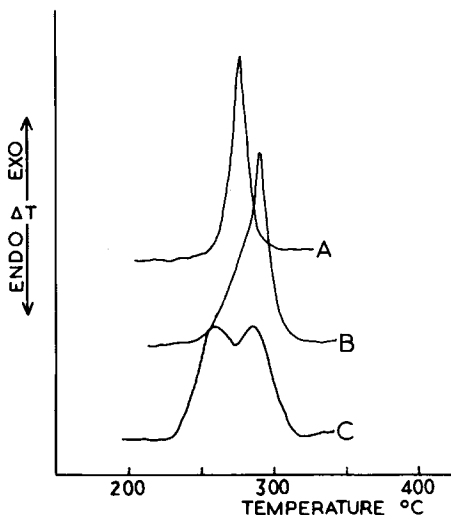


Fig. 1. DSC behavior of the monomers: A, copper (I)-4-bromothiophenoxide; B, copper (I)-4-bromo-2-methylthiophenoxide; and C, copper (I)-4-bromo-2,6-dimethylthiophenoxide.

the laboratory it was polymerized in a boiling 10:1 quinoline:pyridine mixture. Copper (I)-4-bromothiophenoxide (25 g) was polymerized in a quinoline-pyridine mixture (91/9 ml) by boiling under reflux for 2 days under a nitrogen atmosphere. The monomer dissolved yielding a deep red solution after 30 min. The boiling point of the solvent gradually rose from 198–235°C over the reaction period. At the completion of the heating period, the reactants were poured into 50% aqueous methanol and PPS was isolated and the copper (I) thiophenoxide end groups and copper (I) bromide removed by suspending the polymer for 1 hr in concentrated hydrochloric acid as recommended by Smith and Handlovits.<sup>21</sup> The procedure was repeated twice and the polymer washed with water until free from chloride ion, followed by acetone and diethyl ether prior to fractionation. Low-molecular-weight materials were extracted with boiling toluene and isolated by precipitation into acidified methanol after concentration of the toluene solution. This toluene-soluble (TS) fraction was filtered, washed with methanol, and dried at 60°C/1 Torr to constant weight. The toluene-insoluble (TI) residue was heated to boiling in diphenyl ether and filtered hot. The filtrate was reheated to boiling and added cautiously to stirred acidic methanol. The precipitated solid was filtered, washed with methanol and dried at 120°C/1 Torr to constant weight, yielding the diphenyl ether-soluble fraction (DPES). The insoluble residue (DPEI) was similarly washed and dried, and the yields, combustion analyses, and melting points of the various fractions are presented and compared with those from the autoclave reaction in Table I.

After the initial study above, which showed the viability of the quinoline-pyridine method, an investigation was made to optimize reaction conditions. In a series of reactions, aliquots were removed from solution initially 1M in monomer at times from 0.5 to 54 hr. Isolation of the polymer was effected as previously, with 1-chloronaphthalene (CN) replacing diphenyl ether, which eliminated the hazardous precipitation. Solutions of PPS in CN were allowed to cool, which caused the polymer to precipitate. Addition of methanol to the

TABLE I  
Comparison of Solution Polymerization Methods for Copper (I)-4-Bromothiophenoxide

Solvent	Time, hr	Temp., °C	Yield %	Polymer fraction				
				TS		DPES		DPEI,
				%	$T_m$ , °C	%	$T_m$ , °C	%
Pyridine	16	250 <sup>a</sup>	85	20	120–125	75	270–275	5
Quinoline: pyridine	48	198 <sup>b</sup> –235	87	6	97–100	90	271–275	4

<sup>a</sup> Under pressure in an autoclave.

<sup>b</sup> Reflux temperature at atmospheric pressure.

suspension greatly aided filtration and the polymer could be washed free from CN with methanol and dried to constant weight at 120°C/1 Torr. Assessment of the chloronaphthalene-soluble (CNS) fraction was made as shown in Table II.

Only trace amounts of CNI polymers were formed up to 54 hr, and these were not further investigated. Low-molecular-weight (TS) fractions were obtained in 10%–17% yield of  $T_m$  112–120°C and all had the following

ANAL: Found: C, 67.1%; H, 4.1%; Br, 0.23%; S, 27.4%; Ash 1.4%. Calc.  $(C_6H_4S)_n$ : C, 66.63%; H, 3.73%; S, 29.64%.

### Solution Polymerization of Copper (I)-4-Bromo-2-Methylthiophenoxide

Polymerization of solutions of the copper salt (initially 0.5M) was effected as previously and aliquots removed at reaction times between 0.5 and 70 hr. The polymers were obtained as for PPS and then subjected to three 1-hr washings

TABLE II  
Polymerization of Copper (I)-4-bromothiophenoxide in Quinoline:Pyridine—CNS Fractions

Run No.	Time, hr	Overall yield, %	CNS, %	$T_m$ , °C <sup>a</sup>	Combustion analysis, %				
					C	H	Br	S	Ash
1	0.5	77	87	267–277	65.2	3.9	3.73	28.8	0.5
	1.5	84	89	274–283	66.0	3.9	1.15	29.1	1.2
	3.5	78	86	275–285	67.1	4.1	0.51	29.4	0.8
	5.0	77	93	278–285	66.7	3.8	0.31	29.1	1.2
2	6.0	80	85	279–283	66.0	3.9	0.40	27.3	0
	22.0	82	84	282–285	66.4	3.9	0.08	28.5	1.0
	27.0	80	84	282–284	66.4	3.8	0.04	28.3	1.9
	31.0	84	85	280–284	65.3	3.5	0.08	27.9	2.2
	46.0	77	84	275–280	66.8	3.8	0.10	28.5	0.6
	54.0	77	84	275–280	67.3	3.9	0.16	27.2	1.9
3	12.0	83	80 <sup>b</sup>	280–285	65.0	4.0	0.14	27.3	5.2
	17.0	67	83	279–284	66.8	4.0	0.16	28.5	1.6
	41.0	64	83	280–282	66.7	3.7	0.12	28.3	0.7
Calculated for $(C_6H_4S)_n$					66.63	3.73	—	29.64	—

<sup>a</sup> Hot-stage microscope.

<sup>b</sup> DPES fraction.

in concentrated hydrochloric acid and then washed with water until free from chloride ion, followed by methanol and diethyl ether. No methanol-soluble fraction was obtained at any reaction time. Soxhlet extraction with toluene resulted in almost complete polymer solution. The solutions were concentrated and precipitated into acidified methanol. PMPS samples obtained after filtration and washing were redissolved in toluene or chloroform and precipitated into methanol, filtered, washed, and dried at 60°C/1 Torr, to constant weight, yielding white or pale grey powders. Yields, melting ranges, and combustion analyses of samples obtained at different reaction times are shown in Table III.

PMPS was also prepared on a larger scale by refluxing the copper salt (50 g) in quinoline (320 ml) and pyridine (32 ml) under a nitrogen atmosphere at 190–194°C for 9 hr. After precipitation, fractionation, and washing, a white powder (20.5 g) was obtained in 89% yield. It softened and melted at 120–130°C and had the following

ANAL: Found: C, 67.2%; H, 4.7%; Br, 0.86%; S, 26.1%; Ash, 2.6%. Calc.  $(C_7H_6S)_n$ : C, 68.80%; H, 4.95%; S, 26.25%.

### Solution Polymerization of Copper (I)-2,6-Dimethylthiophenoxide

Copper salt (7.68 g) was boiled under reflux in quinoline (50 ml) and pyridine (5 ml) for 9 hr under nitrogen, and the polymer obtained after a similar work-up procedure to that used for PMPS. A pale grey powder (2.15 g) was obtained in 57% yield, which softened at 185–200°C and melted at 215–220°C.

ANAL: Found: C, 70.1%; H, 5.8%; Br, 0.12%; S, 24.0%; Ash, 0.4%.  $(C_8H_6S)_n$  requires: C, 70.54%; H, 5.92%; S, 23.54%.

TABLE III  
Solution Polymerization of Copper (I)-2-Methyl-4-Bromothiophenoxide in Quinoline:Pyridine—  
TS Fractions

Run No.	Time, hr	Overall yield, %	Melting <sup>a</sup> range, °C	Combustion analysis, %				
				C	H	Br	S	Ash
1	0.5	56	105–110	64.6	4.6	5.36	24.4	0
	1.5	75	140–144	67.9	4.7	0.97	25.2	1.3
	3.5	78	140–145	68.3	4.5	0.20	25.7	0.7
	5.0	75	138–155	69.6	4.6	0.28	25.1	3.7
	7.0	68	148–155	68.7	5.2	0.37	25.7	5.5
	9.0	76	145–152	68.5	5.2	0.10	25.2	0
	11.0	72	143–150	68.7	5.0	0.32	26.0	0.3
2	15.5	70	138–140	68.7	4.5	0.72	26.6	0.6
	24.0	79	140–146	69.5	4.4	0.43	26.4	2.2
	39.5	75	130–143	68.3	4.7	0.22	26.5	0.5
	48.0	70	130–142	67.6	4.9	0.27	25.7	2.0
	63.5	76	128–140	67.1	5.0	0.13	24.3	1.6
	70.0	75	128–140	69.0	5.1	0.02	25.8	1.9
3	6.0	—	120–130	67.7	5.3	1.36	24.3	2.8
	13.5	—	131–140	68.1	5.3	1.07	24.4	3.6
	24.5	—	120–140	68.2	5.1	0.78	24.5	1.3
Calculated for $(C_7H_6S)_n$				68.80	4.95	—	26.25	—

<sup>a</sup> Hot-stage microscope.

## Characterization Procedures

### *Melting-Point Determination*

Melting points were determined on a Reichert hot-stage polarizing microscope at a heating rate of 2°C/min. Melting ranges of polymers are the temperatures at which melting was first observed and those at which birefringence finally disappeared for samples which had been melted, pressed flat between glass slides, cooled, and reheated.

### *Spectroscopic Studies*

The IR spectra were recorded on a Unicam SP200 IR spectrophotometer using a 2%–4% suspension in potassium bromide for solids and thin films between sodium chloride plates for liquid samples and low-melting solids.

The NMR spectra were recorded on a Perkin-Elmer Hitachi R20 (60-MHz) or R32 (90-MHz) instruments using saturated solutions in deuteriochloroform with tetramethylsilane as internal standard.

### *Thermal Analysis Studies*

Thermal analytical studies were made on a DuPont 900 thermal analyzer with facilities for DSC. Samples (5–10 mg) of PPS were heated at 20°C/min in crimped aluminum pans in a static air atmosphere.

Glass transition temperatures ( $T_g$ ) were measured in the following manner. Samples of powdered polymer (8–10 mg) were weighed into an aluminum pan, which was then placed on the heated platen of the hot-stage microscope at 310°C. After 15 sec the pan was dropped into liquid nitrogen for a similar period before crimping. Several determinations could be made on the same sample providing the temperature of cold crystallization was not exceeded. Five samples of each polymer were employed, giving a reproducibility of  $\pm 1^\circ\text{C}$ . The  $T_g$  was obtained from the DSC curve by drawing tangents to the base line prior to the step and to the steepest part of the base-line step. PMPS and PDMPS were prepared and analyzed in a similar way by shock-cooling from temperatures 20°C above the melting ranges.

### *Heat of Crystallization Studies*

Heats of crystallization ( $\Delta H_c$ ) were measured using a Perkin-Elmer model DSC 2 differential scanning calorimeter. Samples of polymer ( $7\text{--}10 \pm 0.005$  mg) were heated rapidly in the calorimeter to 305°C under an argon atmosphere. After 30 sec, a cooling rate of 20°C/min was applied and the crystallization exotherm recorded five times for two separate samples. The peaks were cut from the paper and weighed ( $\pm 0.05$  mg) after correction for the base-line shift after crystallization using the method due to Wilburn.<sup>31</sup> A calibration curve for indium enabled  $\Delta H_c$  to be calculated.

*Determination of Reduced Viscosities*

The reduced viscosity of high-molecular-weight PPS samples was determined in 1-chloroanaphthalene at  $209.7 \pm 0.3^\circ\text{C}$  in a U-tube viscometer (M1 bore). Reduced viscosities of PMPS, PDMPS, and TS PPS fractions were measured as 0.4% solutions in toluene at  $25 \pm 0.01^\circ\text{C}$  in a Sofica automatic viscometer.

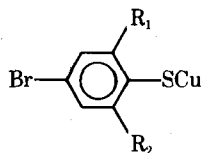
*Gel-Permeation Chromatography*

Poly(arylene sulfides) soluble in toluene were investigated by GPC analysis. 0.05% solutions of polymer in tetrahydrofuran (2 ml) were injected at room temperature onto five Styragel columns of pore sizes 100, 150–300, 700–2000, 5000–15,000, and 50,000–150,000 Å. A flow rate of 1 ml/min was used and the eluates monitored by a differential refractometer. Calibration was effected using narrow distribution polystyrene standards and the chromatograms analyzed by computer program.

The data obtained using these characterization methods is presented in Tables IV and V below.

**RESULTS AND DISCUSSION****Monomer Synthesis**

The monomers prepared in this study are of general formula III:



III

where  $R_1 = R_2 = \text{Me}$ ,  $R_1 = R_2 = \text{H}$ ,  $R_1 = \text{H}$ , and  $R_2 = \text{Me}$ .

These monomers were prepared by the reductive cleavage of the corresponding bis(4-bromoaryl)disulfide. The most direct route to these disulfides is via the oxidation of the corresponding 4-bromoaryl thiol, which was obtained either by the Leuckart reaction<sup>32</sup> or by bromination of the aryl thiol prepared by the Leuckart reaction or via the Newman-Kwart reaction.<sup>29,33,34</sup> The bromination of aryl thiols with vacant para positions to yield bis(4-bromoaryl) disulfides has been used to advantage in this work.

The preparation of copper (I)-4-bromothiophenoxide gave a material of purity at least as high as that reported by Smith.<sup>20</sup>

The preparation of 4-bromo-2-methylbenzene thiol via the Leuckart reaction and its oxidation to bis(4-bromo-2-methyl phenyl) disulfide was accomplished in overall yields of 20%. The route via the bromination of *o*-toluene thiol has not been previously reported, and it gave the desired product in a cleaner, quicker, and less hazardous reaction in significantly greater yield. The copper (I)-4-bromo-2-methylthiophenoxide prepared had a purity greater than 99%.

The preparation of bis(4-bromo-2,6-dimethylphenyl) disulfide from 4-



TABLE IV  
 Characterization of PPS Fractions from Solution Polymerization in Quinoline:Pyridine

Reaction no., fraction	Time, hr	DP (Br)	DP (S)	$MW_{Br}$ , <sup>d</sup> $\times 10^{-3}$	$MW_S$ , <sup>d</sup> $\times 10^{-3}$	$\Delta H_c$ , cal/g	$\eta_{sp}/c$ , <sup>b</sup> dl/g
1, CNS	0.5	19	26.0	2.14	2.89	12.73	0.06
	1.5	64	41.2	6.96	4.53	12.40	0.07
	3.5	145	96.0	15.7	10.5	10.54	0.18
	5.0	240	41.2	25.8	4.53	10.46	0.20
2, CNS	6.0	185	8.7	20.0	1.12	8.47	0.21
	22.0	925	8.7	100.0	1.12	7.75	0.27
	27.0	1850	15.7	200.0	1.78	7.60	0.24
	31.0	925	11.9	100.0	1.37	8.40	0.24
	46.0	740	18.5	80.0	2.08	—	0.23
	54.0	460	8.3	50.0	0.98	7.65	0.23
3, CNS	12.0	530	8.7	57.1	1.12	6.82	0.27
	17.0	40	18.5	50.0	2.08	8.14	0.25
	41.0	620	15.7	66.6	1.57	8.97	0.22
1-3, TS	0.5-54	320	9.1	34.7	1.06	—	—
	2 days	73	20.4	8.0	2.28	—	0.16
Ryton, DPES <sup>a</sup>	—	6.4 <sup>c</sup>	10.18	0.724	1.14	11.41	0.15

<sup>a</sup> Ryton, Phillips Petroleum, TS fraction removed, DPEI removed.

<sup>b</sup> 0.4% solution in 1-chloronaphthalene at  $209.7 \pm 0.3^\circ\text{C}$ .

<sup>c</sup> Structure assumed to be  $\text{Cl}-\left[\text{C}_6\text{H}_4-\text{S}\right]_n-\text{H}$ .

<sup>d</sup> Molecular weights determined from bromine and sulfur contents.

bromo-2,6-dimethylaniline via the Leuckart reaction and subsequent oxidation again gave low yields. The preparation of the copper salt was effected in a similar manner to the other salts, with an extended reaction time in anticipation of enhanced steric hindrance due to four *o*-methyl groups. The preparation proved to be more difficult than the two previous monomers and resulted in lower yields and purity. Longer reaction times resulted in production of oligomeric poly(2,6-dimethylphenylene sulfide).

The DSC curve (Fig. 1) of this copper salt differed markedly from that obtained from copper (I)-4-bromothiophenoxide and copper (I)-2-methyl-4-bromothiophenoxide, which gave single sharp exotherms whose peak temperature corresponded closely to the melting temperatures observed by hot-stage microscopy. Copper (I)-4-bromothiophenoxide is known to polymerize slowly below its melting point, yielding a linear polymer, whereas in the melt rapid, highly exothermic polymerization takes place, yielding cross-linked PPS.<sup>20</sup> This behavior is confirmed by the DSC exotherm and the observation that the monomer melts and rapidly resolidifies. In the case of copper (I)-2,6-dimethylthiophenoxide, the visual melting point appeared to correspond with an endothermic minimum superimposed on a polymerization exotherm. This suggests that the polymerization exotherm is reduced in this case, such that the heat of fusion of the salt becomes significant. It appears that the reactivity of this copper salt is lower than the other two monomers, as would be expected from steric considerations.

In view of the low yields obtained by the Leuckart reaction an alternative route to the thiol via the Newman-Kwart reaction<sup>29,33,34</sup> on phenols was investigated.

TABLE V  
Characterization of PMPS and PDMPs TS Fractions

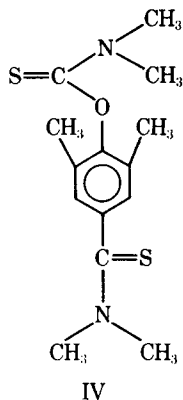
Polymer reaction No.	Time, hr	MW <sub>Br</sub> , <sup>b</sup> × 10 <sup>-3</sup>	MW <sub>S</sub> , <sup>b</sup> × 10 <sup>-3</sup>	T <sub>m</sub> , °C <sup>a</sup>	T <sub>g</sub> , °C	η <sub>sp</sub> /c, dl/g	M <sub>w</sub> <sup>c</sup>	M <sub>n</sub> <sup>c</sup>	M <sub>w</sub> /M <sub>n</sub> <sup>c</sup>
PMPS 1	0.5	1.49	1.16	111	62.0	0.045	1980	1250	1.59
	1.5	8.25	2.06	133	74.0	0.079	5110	1100	4.64
	3.5	40.0	4.01	143	95.5	0.085	8250	1410	5.84
	5.0	28.6	1.88	146	95.5	0.093	9770	1360	7.20
	7.0	21.6	4.01	146	96.0	0.108	9620	1510	6.38
	9.0	80.0	2.06	152	95.5	0.117	10,800	1310	8.24
PMPS 2	11.0	25.0	8.71	145	98.0	0.106	12,100	1430	8.46
	15.5	11.1	—	143	98.5	0.077	7020	1540	4.55
	24.0	18.6	—	149	98.0	0.070	7150	1440	4.97
	39.5	36.4	—	140	97.0	0.079	6390	1400	4.57
	48.0	29.6	3.90	150	95.5	0.068	6890	1490	4.63
	63.5	61.5	1.09	142	96.5	0.072	6950	1470	4.71
PMPS 3	70.0	>400	4.78	140	93.0	0.074	5870	1320	4.46
	6.0	5.88	1.09	130	86.0	0.079	6330	1670	3.78
	13.5	7.47	1.15	135	82.0	0.085	7830	2020	3.87
PMPS 4	24.5	10.20	1.22	140	88.0	0.070	6480	1500	4.56
	9.0	9.29	14.76	160	93.0	—	5440	1470	3.70
PDMPs	9.0	66.6	—	218	180	0.14	8270	1120	7.35

<sup>a</sup> Peak minimum as determined by DSC.

<sup>b</sup> Molecular weights derived from S and Br analyses.

<sup>c</sup> Molecular weights from GPC.

Using the method described by Newman and Hetzel,<sup>29</sup> 2,6-dimethylphenol did not yield the expected product. The material obtained was identified by NMR and IR spectroscopy and combustion analysis as O-(4-*N,N*-dimethylthioamide-2,6-dimethylphenyl)*N,N*-dimethylthiocarbamate (IV):



Further work (R.H. Still et al., unpublished observations) on the preparation of methoxy thiols has also shown that the thioamido-substituted compound is formed when the Newman and Hetzel method is employed.<sup>29</sup> The desired product is, however, obtained when the Newman-Karnes<sup>33</sup> method is employed, and after a suitable work-up procedure, the thiols can be converted after bromination and reduction of the disulfide with copper into the copper salt in yields which compare very favorably with the Leuckart synthesis.

### Polymerization Studies

The polymerization of copper (I)-4-bromothiophenoxide has been extensively studied by Smith and coworkers<sup>20,22</sup> using solutions in pyridine under pressure and in the solid state. Optimum reaction conditions reported in their studies were used for comparison of the autoclave polymerization in pyridine at 250°C and solution polymerization in a 10:1 quinoline:pyridine mixture at the reflux temperature at atmospheric pressure.

Such studies were prompted by the excellent yields reported for the preparation of diaryl sulfides from unactivated aryl halides and copper (I)-thiophenoxides using this reaction medium at atmospheric pressure.<sup>35</sup>

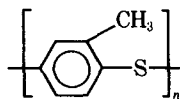
The initial results (Table I) showed that polymerization could be effected in this medium, in simple apparatus, giving comparable yields and molecular weights to the autoclave reaction in pyridine. The procedure was simple and could be readily controlled, and samples could be easily removed at various times, allowing the ready optimization of reaction conditions and the preparation of a range of samples of differing molecular weights, as shown in Table II. Reaction is rapid, leading to good yields of high polymer after 30 min, and the method is a viable alternative to the autoclave reactions described by Smith and coworkers.<sup>20-22</sup>

The experimental yields and melting points (Table II) show an initial increase with reaction time before reaching a virtually constant value. The bromine

analysis remains virtually constant after 12–20 hr and has been used as a measure of end-group concentration, as described below. Combustion analyses are in close agreement with theory, although the sulfur figures are occasionally low, which is thought to arise from problems associated with combustion rather than differences in chemical structure. The IR spectra of the polymers prepared by solution polymerization in this study were similar to Ryton (Fig. 2).

The solution polymerization of copper(I)-2-methylthiophenoxide to yield PMPS has not been reported before. Tsunawaki and Price<sup>26</sup> have reported the synthesis of low-molecular-weight PMPS after polymerization of sodium and lithium thiophenoxides in dimethylformamide at the reflux point for 1–7 days. Yields of 80%–90% are reported, which consisted of methanol-soluble materials (10%–50%) of molecular weight 300–900 and 40%–80% benzene-soluble material of molecular weight 500–1500 that had a melting range 50–120°C.

In this study, PMPS was obtained in 60%–90% yield, and only trace amounts were methanol soluble. Melting ranges (Table III) of 110–150°C were higher than those previously reported and bromine contents significantly lower, indicating polymers of higher molecular weight had been prepared after shorter reaction periods. Combustion analyses were in good agreement with theory (Table III), and IR spectra (Fig. 3) were consistent with the structure



The synthesis of PDMPS from copper (I)-2,6-dimethylthiophenoxide has not been reported previously. Polymers of melting range 100–180°C, which were benzene soluble and had molecular weights up to 4000, have been prepared by Tsunawaki and Price<sup>26</sup> by methods similar to those used for PMPS. The yield of polymer and its melting range obtained at an arbitrary reaction time of 9 hr

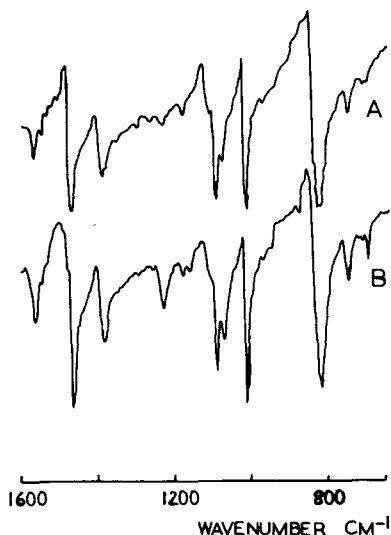


Fig. 2. The IR spectra of PPS: (A) Ryton and (B) PPS prepared in quinoline:pyridine solution, DPES fraction.

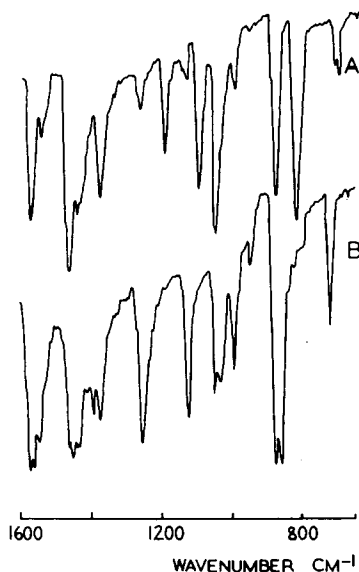
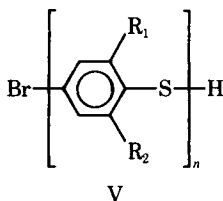


Fig. 3. The IR spectra of the substituted phenylene sulfide polymers: (A) PMPS and (B) PDMPS.

in this study were superior to those reported.<sup>26</sup> The IR spectrum (Fig. 3) and combustion analysis results are in close agreement with theory, and it is significant that the bromine content of the polymer was lower than the large-scale 9-hr PMPS sample and comparable to that for PPS of similar reaction times. This suggests that the nucleophilic reactivity of this salt is not significantly lower than the two previous monomers. The steric hindrance to substitution by the methyl groups is possibly balanced by their electron donation, thereby producing a more powerful nucleophile.

### Polymer Characterization

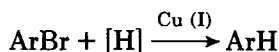
The molecular weights of PPS, PMPS, and PDMPS (Tables IV and V) have been computed from bromine and sulfur analyses on the assumption that the polymers have the structure V:



where  $R_1 = R_2 = \text{H}$  for PPS;  $R_1 = \text{H}$ ,  $R_2 = \text{CH}_3$  for PMPS; and  $R_1 = R_2 = \text{CH}_3$  for PDMPS.

Bromine analyses were performed to an accuracy of  $\pm 0.03\%$ , but the data is not considered to be reliable at long reaction times because the fraction of end-groups becomes too small to be measured with precision, especially with high-temperature-resistant polymers.

In our studies there is a large discrepancy between molecular weights calculated from bromine and sulfur (accuracy  $\pm 0.3\%$ ) contents. This was also observed previously by Smith and Handlovits<sup>20</sup> and Tsunawaki and Price<sup>26</sup> and ascribed to the presence of polymers having no bromine end groups. Since that work, Bacon and coworkers (Refs. 36–40 and private communication) have described copper-catalyzed reductive dehalogenation of aryl bromides in competition with nucleophilic substitution. In the presence of hydrogen donors, dehalogenation can be the predominant reaction, and it has been shown to occur when the only source of hydrogen was an aromatic nucleus<sup>38</sup>:



Bacon (private communication) has suggested that quinoline:pyridine or pyridine alone, as in the autoclave reaction, would provide a suitable solvent medium and hydrogen source for this reaction. Benzene was confirmed as a reaction product when bromobenzene and copper (I) chloride were boiled in a 10:1 quinoline:pyridine mixture. No biphenyl was detected, however, suggesting that Ullmann coupling, which could also account for the low bromine analyses, is absent, although such coupling has been reported for unactivated aryl halides and copper (I) salts.<sup>39</sup>

The bromine-derived molecular weights ( $MW_{\text{Br}}$ ) at long reaction times are unrealistically high in view of the evidence for dehalogenation, and such molecular weights are not expected for a step-growth polymerization. Since debromination appears to be slower than polymerization, values up to 12 hr are likely to be reasonably accurate and yield  $M_n$  values of  $1\text{--}2 \times 10^4$ .

The TS PPS fraction, which was assumed to be of low molecular weight, gave anomalously high  $MW_{\text{Br}}$  values of  $3.5 \times 10^4$ . The molecular weight appears to be in error, since step-growth polymerization theory<sup>41</sup> predicts a finite fraction of low polymer even when the extent of reaction approaches unity, and thus bromine-substituted oligomers should be present throughout the reaction. Macrocyclic oligomers<sup>42,43</sup> have been prepared from copper (I)-3-bromothiophenoxide, and hence the TS PPS fractions may contain both the oligomers and cyclic compounds. GPC analysis appears to support such a hypothesis, since several low-molecular-weight species are present in the TS fraction.

The data presented in Table V for PMPS fractions again points to the occurrence of reductive dehalogenation, with molecular weights assessed by bromine analysis steadily increasing with reaction time, while viscosity results and GPC analysis suggest that molecular weights reach a maximum at 10–20 hr, followed by a slow decrease. Poor reproducibility between experiments, as seen in this case, is not uncommon<sup>42,44</sup> in copper-catalyzed nucleophilic substitution reactions.

Viscosity measurements for PPS provide a useful relative assessment of molecular size, although the experimental procedure proved to be difficult and hazardous. For PMPS the variation of viscosity with molecular weight (Fig. 4) is given by

$$\eta_{\text{sp}}/c = 11.7 \times 10^{-4} \bar{M}_w^{0.48}$$

where  $\bar{M}_w$  is the weight-average molecular weight from GPC analysis. No such relationship could be derived for PPS, since the high-molecular-weight fractions

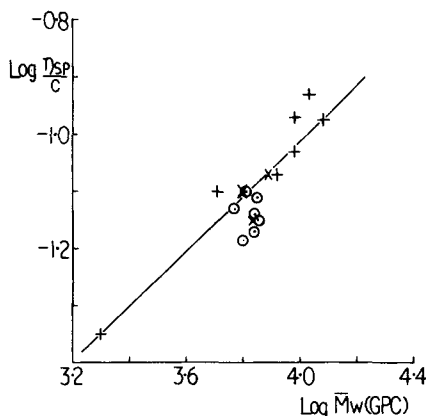


Fig. 4. Variation of viscosity with molecular weight for PMPS: (+) reaction 1, (o) reaction 2, and (x) reaction 3.

could not be assessed by GPC due to their relative insolubility. However, when  $\log(\eta_{sp}/c)$  is plotted against  $\log MW_{Br}$  as in Fig. 5, the following relationship is obtained:

$$\eta_{sp}/c = 9.8 \times 10^{-4} MW_{Br}^{0.54}$$

which compares well with the relationship derived in a similar manner by Smith and Lenz<sup>20</sup> for PPS in diphenyl ether at 250°C:

$$\eta_{sp}/c = 2.5 \times 10^{-4} MW_{Br}^{0.54}$$

The values of reduced viscosity reported in Table IV for PPS (0.1–0.3 dl/g) fall within the range reported by Smith and compare favorably with those quoted for Ryton<sup>1</sup> (0.01–0.2 for 0.4% solutions in chloronaphthalene at 206°C).

Figure 6 shows that the viscosity of PPS increases to a maximum between 12–24 hr and confirms the trend observed for  $MW_{Br}$ ,  $T_m$ ,  $T_g$ , and  $\Delta H_c$  as reported in Table IV, suggesting an optimum time for this reaction as 15–20 hr.

The variation of the  $T_g$  and  $\Delta H_c$  with reaction time for PPS is shown in Figs. 7 and 8. The variation of  $T_g$  with molecular weight may be represented by the relationship<sup>45,46</sup>

$$T_g = T_{g\infty} - KM^{-1}$$

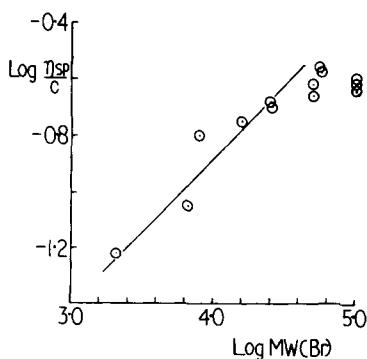


Fig. 5. Variation of viscosity with molecular weight for PPS, CNS fractions.

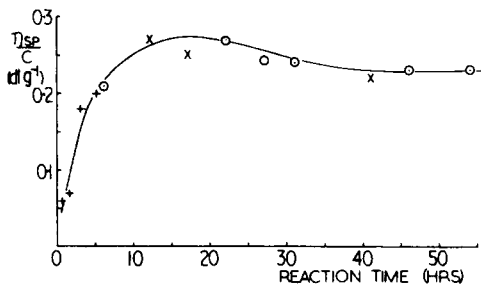


Fig. 6. Variation of viscosity with reaction time for PPS, CNS fractions: (+) reaction 1, (o) reaction 2, and (x) reaction 3.

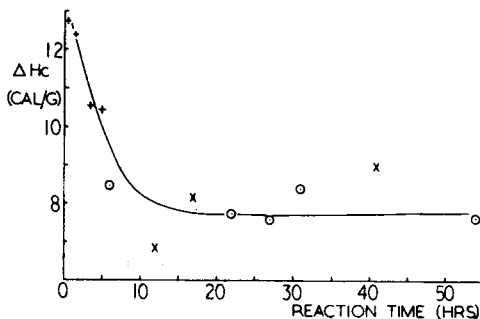


Fig. 7. Variation of  $\Delta H_c$  with reaction time for PPS, CNS fractions: (+) reaction 1, (o) reaction 2, and (x) reaction 3.

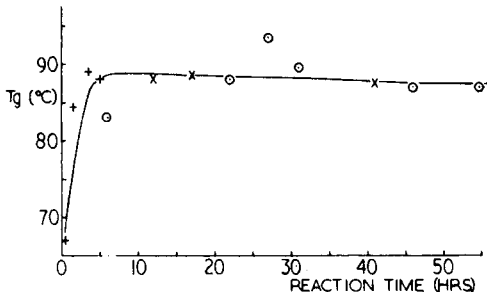


Fig. 8. Variation of the  $T_g$  of PPS with reaction time: (+) reaction 1, (o) reaction 2, and (x) reaction 3.

where the  $T_g$  of a polymer of molecular weight  $M$  reaches an asymptotic value  $T_{g\infty}$  which is independent of chain length. For PPS a plot of  $T_g$  against  $(MW_{Br})^{-1}$  [Fig. 9(A)] is linear, giving a  $T_{g\infty}$  of  $90^\circ\text{C}$  by a least-squares procedure. The  $T_g$  results for PMPS [Fig. 9(B)] yield a  $T_{g\infty}$  value of  $111^\circ\text{C}$ . From the previous discussion, it is likely that  $MW_{Br}$  values are too high and the actual range is smaller than indicated. The  $T_{g\infty}$  for PPS is consistent with the experimental results, while for PMPS, the  $T_{g\infty}$  is some  $11^\circ\text{C}$  higher than the maximum value obtained. This suggests that debromination occurs to a greater extent for PMPS and that molecular weights where the  $T_g$  is independent of chain length are not achieved. A virtually identical plot was obtained when  $\bar{M}_w$ , GPC was substituted for  $MW_{Br}$ .

Cowie<sup>47</sup> has recently investigated the  $T_g$ -molecular weight relationships for



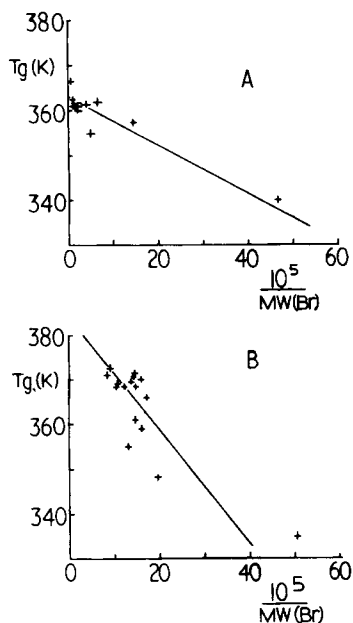


Fig. 9. (A) The  $T_g$ -molecular weight relationship for PPS. (B) The  $T_g$ -molecular weight relationship for PMPS.

oligomers and amorphous polymers. Plots of  $T_g$  against  $x$ , where  $x$  was the number of chain segments, revealed three distinct regions defined as follows: I, the region where the asymptotic value of  $T_g$  had been reached; II, where the  $T_g$  became chain length dependent; and III, where for oligomers  $T_g$  was even more dependent on chain length Fig. (Fig. 10).

Figure 11 shows the  $T_g$ -molecular weight relationships for PPS and PMPS. Two regions are observed for PPS plots, which together with the  $T_g$ - $MW_{Br}$  graph [Fig. (9A)] suggests that the asymptotic value of  $T_g$  has been reached. A third region for oligomeric PPS is not observed, as expected for CNS fractions. The results for PMPS show more scatter but suggest that the asymptotic value has not been reached.

The higher  $T_g$  of PMPS relative to PPS indicates that rotation about the phenylene-sulfur bond is hindered by the 2-methyl group and rotation is even

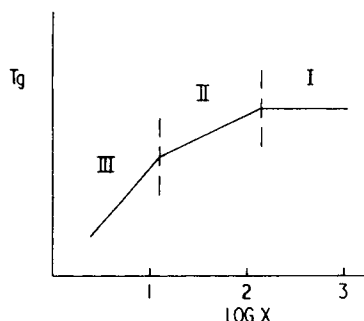


Fig. 10. Cowie's representation (Ref. 47) of the  $T_g$ -molecular weight relationship for amorphous polymers ( $x$  is the degree of polymerization).

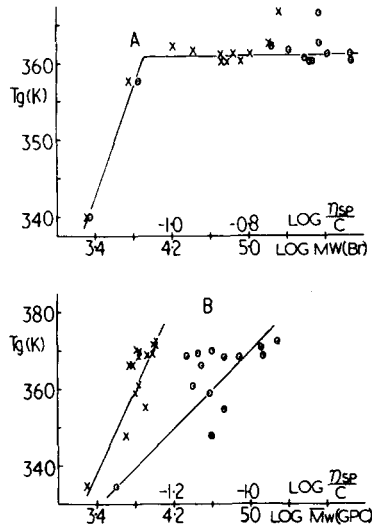


Fig. 11. (A) The  $T_g$ -molecular weight relationships for PPS: (x) molecular weight from bromine analysis and (o) reduced viscosity. (B)  $T_g$ -molecular weight relationships for PMPS: (x)  $\bar{M}_w$  from GPC and (o) reduced viscosity.

further restricted in PDMPS, where the  $T_g$  is raised to 180°C. In comparison, poly(2,6-dimethylphenylene oxide) has a  $T_g$  of 220°C,<sup>48</sup> whereas that of poly(phenylene oxide) is 82°C, which suggest PDMPS is of moderate molecular weight.

Recently, Suwa<sup>49</sup> reported that the molecular weight of poly(tetrafluoroethylene) could be rapidly and accurately determined by the assessment of  $\Delta H_c$ . A calibration curve of  $\log \bar{M}_n$  against  $\log \Delta H_c$  was linear and unaffected by the cooling rate for this system. In view of the difficulties associated with the assessment of molecular weight for PPS, the method reported for poly(tetrafluoro-

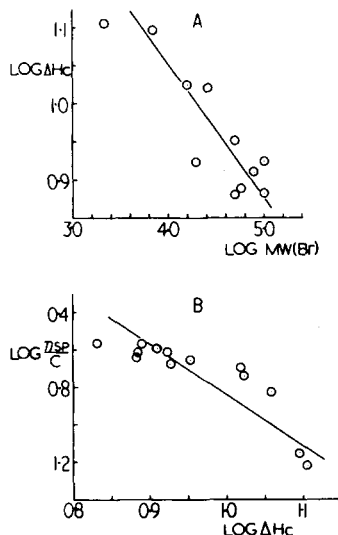


Fig. 12. Relationships between molecular weight and  $\Delta H_c$  for PPS, CNS fractions: (A)  $\Delta H_c$  vs molecular weight from bromine analysis and (B)  $\Delta H_c$  vs reduced viscosity.

roethylene) is of considerable interest for these systems. Accordingly, studies were made on the variation of  $\Delta H_c$  with reaction time (Fig. 7 and Table IV). A rapid decrease in  $\Delta H_c$  with molecular weight increase is seen up to 12–24 hr, followed by a steady or slowly increasing value at longer reaction time. The possible application of  $\Delta H_c$  measurements for molecular-weight assessment is illustrated in Fig. 12, which leads to the relationship

$$\log \Delta H_c = 1.795 - 0.186 \log MW_{Br}$$

or

$$\bar{M}_n = 0.44 \times 10^{10} \Delta H_c^{-5.4}$$

where  $\Delta H_c$  is in cal/g. However, to be of absolute value the above method requires calibration with polymers of known molecular weights, since the molecular-weights calculated from bromine analyses are subject to the difficulties discussed in detail earlier in this paper.

One of the authors (A.B.P.) thanks the University of Manchester, Institute of Science and Technology, for a Research Grant.

### References

1. Ryton PPS, Phillips Petroleum Co., Technical Information, 1974.
2. C. Friedel and J. M. Crafts, *Ann. Chim. Phys.*, **14**, 433 (1888).
3. P. Genvresse, *Bull. Soc. Chim. Fr.*, **17**, 599 (1897).
4. T. Hilditch, *J. Chem. Soc.*, **97**, 2579 (1910).
5. J. J. B. Deuss, *Rec. Trav. Chim. Pays-Bas*, **28**, 136 (1909).
6. H. S. Tasker and H. O. Jones, *Proc. Chem. Soc.*, **25**, 24 (1909).
7. H. B. Glass and E. E. Reid, *J. Am. Chem. Soc.*, **51**, 3428 (1928).
8. Z. Binfield and A. F. Damanski, *Bull. Soc. Chim. Fr.*, 679 (1961).
9. T. Fujisawa and M. Kakutami, *J. Polym. Sci., Part B*, **8**, 19 (1970).
10. T. Fujisawa and M. Kakutami, *J. Polym. Sci., Polymer Lett.*, **8**, 511 (1970).
11. J. Dewing, Br. Pat. 927,822 (1963).
12. Sagami Chem. Res. Centre, Br. Pat. 1,213,678 (1968).
13. A. D. Macallum, *J. Org. Chem.*, **13**, 154 (1948).
14. A. D. Macallum, U.S. Pat. 2,513,188 (1950).
15. A. D. Macallum, U.S. Pat. 2,538,941 (1951).
16. R. W. Lenz, C. E. Handlovits, and W. K. Carrington, *J. Polym. Sci.*, **43**, 333 (1959).
17. R. W. Lenz, and W. K. Carrington, *J. Polym. Sci.*, **43**, 167 (1960).
18. R. W. Lenz, C. E. Handlovits, and H. A. Smith, *J. Polym. Sci.*, **58**, 351 (1962).
19. B. Hortling and J. J. Lindberg, *Chem. Scr.*, **2**, 179 (1972).
20. H. A. Smith and C. E. Handlovits, "Phenylene Sulphide Polymers," ASD-TDR-62-322, Parts I, II (1962).
21. H. A. Smith and C. E. Handlovits, ASD-TDR-62-372 (1962).
22. C. E. Handlovits, *Macromol. Synth.*, **3**, 132 (1968).
23. E. Bourgeois, *Rec. Trav. Chim.*, **18**, 447 (1899).
24. E. Campaigne and S. W. Osborne, *J. Org. Chem.*, **22**, 561 (1957).
25. C. N. Yiannos and J. V. Karabinos, *J. Org. Chem.*, **28**, 3246 (1963).
26. S. Tsunawaki and C. C. Price, *J. Polym. Sci., Part A*, **2**, 1511 (1964).
27. H. E. Dadsell and J. Kenner, *J. Chem. Soc.*, 1102 (1927).
28. H. Hyeds, K. P. Hansen, and B. Jerslev, *Acta Chem. Scand.*, **19**, 2166 (1965).
29. M. S. Newman and F. W. Hetzel, *Org. Synth.*, **51**, 139 (1971).
30. A. I. Vogel, *Textbook of Practical Organic Chemistry*, Longmans, London, 1957.
31. F. W. Willburn, R. McIntosh, and A. Turnock, *Trans Br. Ceram. Soc.*, **73**, 117 (1974).
32. R. Leuckart, *J. Prakt. Chem.*, **41**, (2), 206 (1890).
33. M. S. Newman and H. A. Karnes, *J. Org. Chem.*, **31**, 3980 (1966).
34. H. Kwart and E. R. Evans, *J. Org. Chem.*, **31**, 410 (1966).
35. R. Adams, W. Reifschneider, and M. D. Nair, *Croat. Chem. Acta*, **29**, 277 (1957).

36. R. G. R. Bacon, *Q. Rev. Chem. Soc.*, **19**, 95 (1965).
37. R. G. R. Bacon and H. A. O. Hill, *J. Chem. Soc.*, 1112 (1964).
38. R. G. R. Bacon and O. J. Stewart, *J. Chem. Soc., C*, 301 (1969).
39. R. G. R. Bacon and H. A. O. Hill, *J. Chem. Soc.*, 1108 (1964).
40. R. G. R. Bacon and H. A. O. Hill, *J. Chem. Soc.*, 1097 (1964).
41. P. J. Flory, *Chem. Rev.*, **39**, 1 (1946).
42. G. P. Brown and A. Goldman, *Am. Chem. Soc., Div. Polym. Chem. Prepr.*, **5**, 195 (1964).
43. C. W. Bird and M. Singh, *Chem. Ind.*, **18**, 749 (1974).
44. R. G. R. Bacon and S. C. Rennison, *J. Chem. Soc., C*, 308 (1969).
45. T. G. Fox and P. J. Flory, *J. Appl. Phys.*, **21** 581 (1950).
46. T. G. Fox and S. Loshaek, *J. Polym. Sci.*, **15**, 371 (1955).
47. J. M. G. Cowie, *Eur. Polym. J.*, **11**, 297 (1975).
48. F. E. Karasz and J. M. O'Reilly, *J. Polym. Sci., Part B*, **3**, 561 (1965).
49. T. Suwa, M. Takehisa, and S. Machi, *J. Appl. Polym. Sci.*, **17**, 3253 (1973).

Received July 29, 1978

Corrected proof received 22 June 1979