

Ring-opening polymerization study of cyclic (aromatic disulfide) oligomers derived from 4,4'-isopropylidene bithiophenol

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The ring-opening polymerization of cyclic (aromatic disulfide) oligomers derived from 4,4'-isopropylidene bithiophenol was studied both in diphenyl ether solution and in the melt. The polymers formed were soluble in solvents such as chloroform, tetrahydrofuran, DMF, NMP and characterized by n.m.r., g.p.c., d.s.c. and t.g.a. techniques. The ring-opening polymerization began at about 150°C in solution, but did not begin until around 200°C in the melt, as determined by the melting point of the cyclic oligomers. A ¹³C-n.m.r. study indicated that structurally regular polydisulfides were formed below 250°C, however, structural irregularity occurred above this temperature. There were no cross-linking reactions observed below 300°C for short times, although cross-linking was very serious above 300°C. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Poly(aliphatic disulfide)s have long been commercialized and have found many applications. The Thiokol Company in the USA marketed the first synthetic polysulfide rubber in 1929 and it remains the main producer today. Cured polydisulfides have high resistance to environmental degradation, good low-temperature properties, low water-vapour transmission, good adhesion to wood, metal, glass and concrete and have excellent resistance to solvents, water, acids and bases. Due to their importance in industry and academia, there are several reviews devoted to this class of polymers^{1–4}. Contrary to the extensive studies of poly(aliphatic disulfide)s, little information is available about poly(aromatic disulfide)s, which can be mainly attributed to their insolubility. Ghafoor *et al.* synthesized a polyquinazolone containing a disulfide group which showed increased ductility and decreased hardness upon curing due to the presence of the flexible disulfide linkage⁵. 4,4'-Dihydroxydiphenylsulfone treated with S₂Cl₂ forms an hydroxy functionalized polyaryldisulfide⁶. Several poly(aromatic disulfide)s, including polybiphenyldisulfide, have been synthesized from difunctional sulfonyl chlorides and dithiols. N.m.r. and molecular weight data are not available for these materials because they are not soluble in common solvents⁷. DMSO was used as the oxidation agent to prepare poly(*m*-phenylene disulfide) from dithioresorcinol. The number average molecular weight of the polymer obtained was 880 (DP *ca.* 6) and intrinsic viscosity in NMP at 30°C was 0.11 dl g⁻¹. The oligomers were further chemically modified by chlorosulfonic acid and showed a conductivity of 1 × 10⁻⁵ S cm⁻¹⁸. Using oxidative coupling with

oxygen catalysed by copper salts and an amine, Hay was able to prepare a series of polyarylene disulfides which were not soluble in common organic solvents, and which were not fully characterized⁹.

Recent research has been carried out to prepare high performance polymers from cyclic oligomers to solve processing problems such as low solvent solubility and high melt viscosities^{10–15}. Although it is routine to prepare poly(aliphatic disulfide)s by ring-opening polymerization of cyclic (aliphatic disulfide)s¹⁶, little attention has been given to the ring-opening polymerization study of cyclic (aromatic disulfide)s¹⁷. In a previous paper, we reported the synthesis and characterization of a series of cyclic (aromatic disulfide) oligomers¹⁸. Herein we describe in detail the study of the ring-opening polymerization reaction for the cyclic disulfide oligomer (**II**) derived from 4,4'-isopropylidene bithiophenol (**I**). Cyclic **II** was chosen here because it provides a poly(aromatic disulfide) which is readily soluble in common organic solvents such as chloroform and tetrahydrofuran.

EXPERIMENTAL

Materials

Cyclic (aromatic disulfide) **II** was synthesized by a copper (**I**) and amine catalysed oxidation reaction with oxygen. Reagent grade diphenyl ether and DMAc were purchased from Aldrich. Cuprous chloride was purchased from J. T. Baker, and *N,N,N',N'*-tetramethylethylenediamine was purchased from Lancaster.

Analytical procedure

G.p.c. analyses were performed on a Waters 510 HPLC equipped with 5 μ phenogel columns (linear, 3 × 500 Å) arranged in series with chloroform as solvent

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and a u.v. detector at 254 nm. The apparent molecular weight data were reported with polystyrenes as standards. D.s.c. scans were obtained using a Seiko 220 d.s.c. instrument at a heating rate of $20^{\circ}\text{C min}^{-1}$ in N_2 (160 ml min^{-1}). The weight loss data were obtained from a Seiko 220 TG/TGA instrument at a heating rate of $20^{\circ}\text{C min}^{-1}$ in nitrogen. ^1H n.m.r. data (TMS reference) and ^{13}C n.m.r. data (solvent reference) were recorded at 500 MHz and 125 MHz respectively on a Varian UNITY500 n.m.r. machine with CDCl_3 as solvent.

General procedure for ring-opening polymerization in solution

A Pyrex test tube (1.5 × 15 cm) equipped with a nitrogen inlet and a mini magnetic stirring bar was charged with 200 mg of cyclics and 1 ml of diphenyl ether and immersed in a preheated salt bath to a depth of about 2 cm to cover the contents inside. From time to time, aliquots for g.p.c. analysis were made with a pipette and quenched with chloroform.

General procedure for ring-opening polymerization in the melt

The cyclic sample (~10 mg) was placed on a d.s.c. aluminium pan and was heated under nitrogen atmosphere with a flow rate of 200 ml min^{-1} on a Seiko 220 TGA/DTA instrument. After cooling, the resulting material was subjected to either n.m.r. or g.p.c. analysis.

The ring-opening polymerization was also carried out

on 200 mg of cyclic samples in test tubes under nitrogen atmospheres.

Synthesis of poly(aromatic disulfide) III by direct oxidation

A 25 ml three neck round bottom flask equipped with an oxygen inlet, a condenser, a thermometer and a magnetic stirrer was charged with 5 ml of DMAc, 0.20 g (2.0 mmol) of CuCl , and 0.38 g (3.3 mmol) of N,N,N',N' -tetramethylethylenediamine (TMEDA). The reaction mixture was vigorously stirred for 5 min while oxygen was bubbled in. Then, 1.0 g (3.8 mmol) of 4,4'-isopropylidene bithiophenol in 2 ml of DMAc was added in one portion. After stirring for another 2 h, the reaction mixture was poured into 100 ml of diluted HCl solution to precipitate out polymer. The solid was filtered and redissolved in 20 ml of chloroform. The chloroform solution was filtered through a thin layer of alumina, concentrated, and coagulated in methanol. The fibrous polymer was recovered by filtration and dried under vacuum at 100°C for 24 h.

RESULTS AND DISCUSSION

Cyclic (aromatic disulfide) oligomers

Cyclic(aromatic disulfide) oligomer II was synthesized from 4,4'-isopropylidene bithiophenol (Figure 1)¹⁸. The cyclic oligomers contain 26% of dimer, 22% of trimer, 14% of tetramer, 11% of pentamer, and other higher oligomers as measured by gradient h.p.l.c. ^1H n.m.r.

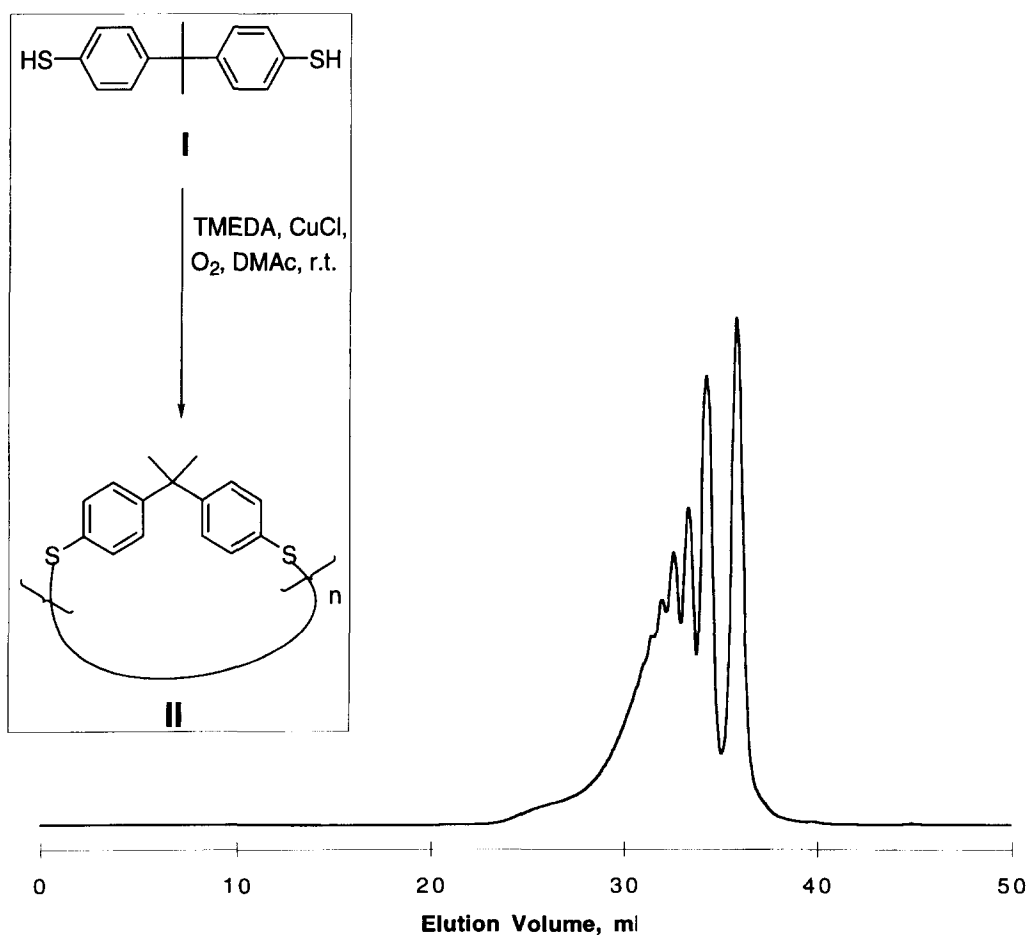
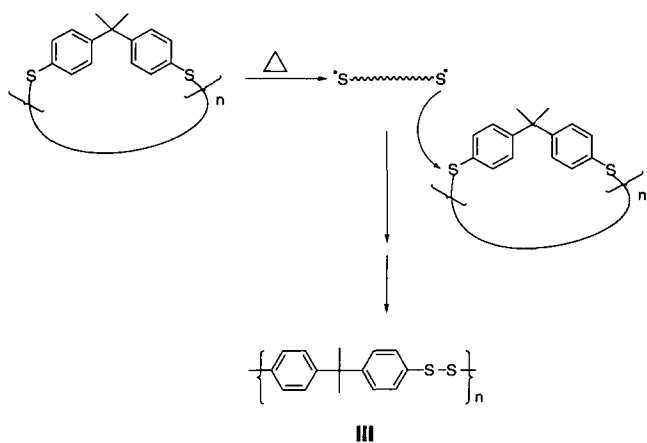


Figure 1 G.p.c. trace of typical cyclic (aromatic disulfide) (II) oligomers

spectra indicated that the cyclic oligomers do not contain any detectable SH end groups. The g.p.c. trace of this cyclic oligomer is shown in *Figure 1*. Differential scanning calorimetry (d.s.c.) of the cyclic mixtures shows a T_g of 81°C and a melting point 219°C (range 195–223°C).

Ring-opening polymerization of cyclic (aromatic disulfide) oligomers in solution

The ring-opening polymerization was first conducted in diphenyl ether solution without adding any catalyst. The reaction was monitored by g.p.c. There are numerous reports of ring-opening polymerization of cyclic(aliphatic disulfide)s catalysed by base or acids³. However, there are only a few reports of ring-opening polymerization of cyclic sulfides without any catalyst. In 1972, Hiatt found some cyclic bis(arylene tetrasulfide)s undergo instant ring-opening polymerization upon heating¹⁹. A 1,2,3-trithiane was reported to form a high molecular weight polymer upon standing in a closed flask at room temperature over 12h²⁰. We found that cyclic disulfides underwent ring-opening polymerization in the absence of a catalyst. It is well known that the disulfide bond ruptures to form radicals at elevated temperatures²¹. This property has been utilized to prepare poly(*p*-phenylene sulfide) and to initiate ring-opening polymerization of cyclic oligomers containing thio-ether linkages^{13,22}. Therefore, one can conclude that **II** forms radical species upon heating which initiate the ring-opening polymerization reaction (*Scheme 1*).



Scheme 1

The g.p.c. traces of products from the ring-opening polymerizations of **II** at 150°C for different times are shown in *Figure 2*. This chart indicates that the ring-opening polymerization was very slow at this temperature. The conversion to polymers increased at longer reaction times. High molecular weight polymers formed in spite of the low conversion, which is a characteristic of a typical chain growth free radical polymerization reaction. When the polymerization temperature was raised to 200°C, high molecular weight polydisulfide formed almost instantly with less than 20% of cyclic remaining. Examining *Table 1*, we can see that the molecular weights of poly(aromatic disulfide)s from the ring-opening polymerization reaction are independent of reaction time, however, they depend on the reaction temperatures.

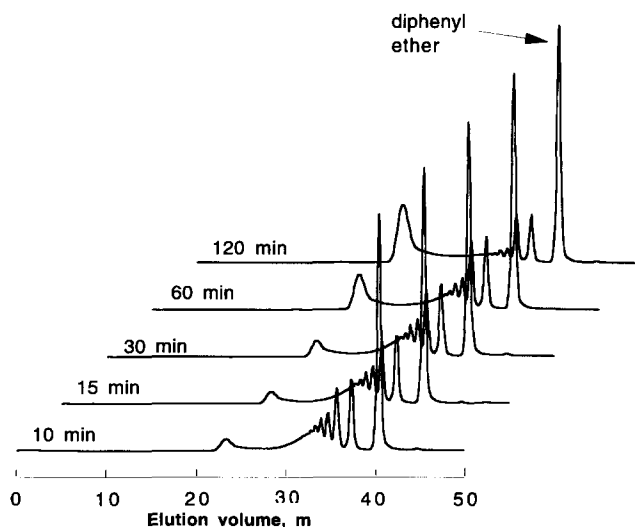


Figure 2 G.p.c. charts for ring-opening polymerization of **II** at 150°C in diphenyl ether solution

Table 1 G.p.c. results of ring-opening polymerization in diphenyl ether solution

Temperature (°C)	Time (min)	M_n (g mol ⁻¹)	M_w (g mol ⁻¹)	Conversion of cyclics (%)
150	10	47 000	80 000	6
	15	43 000	75 000	7
	30	41 000	70 000	12
	60	49 000	90 000	24
	120	53 000	106 000	60
200	10	64 000	123 000	82
	120	62 000	125 000	83
250	10	27 000	51 000	98
	120	26 000	60 000	97
300	10	27 000	54 000	98
	120	25 000	64 000	98 ^a

^a Soluble portion

Table 2 G.p.c. results of ring-opening polymerization in the melt

Temperature (°C)	Time (min)	M_n (g mol ⁻¹)	M_w (g mol ⁻¹)	Cyclics remaining (%)
150	15	1 000	1 700	100
	120	1 000	1 700	100
200	15	88 000	189 000	1.6
	120	88 000	211 000	1.4
250	15	30 000	97 000	1.5
	30	30 000	111 000	1.6
	120	39 000	282 000	1.5
300	15	4 400	14 500	Soluble portion
	30	1 900	10 000	Soluble portion
	120	1 200	4 300	Soluble portion

Under the examined conditions, the highest molecular weight polymers were formed at 200°C. Above this temperature, the higher the temperature, the lower the molecular weights of polymers formed by ring-opening polymerization. For example, the weight average molecular weight of polymer **III** formed at 200°C in a 15 min reaction was 108 000. However, the molecular weights were 62 000 and 52 000, respectively, at 250°C and 300°C under the same conditions (*Table 1*). A cross-linking

reaction with the formation of insoluble products became very serious above 300°C.

Ring-opening polymerization of cyclic(aromatic disulfide) oligomers in the melt

Encouraged by the results from solution ring-opening polymerization, we carried out the ring-opening polymerization in the melt. Soluble polydisulfides were obtained below 300°C. No polymerization was observed

at 150°C, even for 2 h, as detected by g.p.c. Ring-opening polymerization took place almost instantly around 200°C (Table 2). The typical cyclic oligomers start to melt around 195°C as detected by d.s.c. The results indicate that ring-opening polymerization of cyclic oligomers does not take place below the melting point. However, the movements of cyclic molecules are assisted by solvents, hence in solution the ring-opening polymerizations can take place well below the melting points.

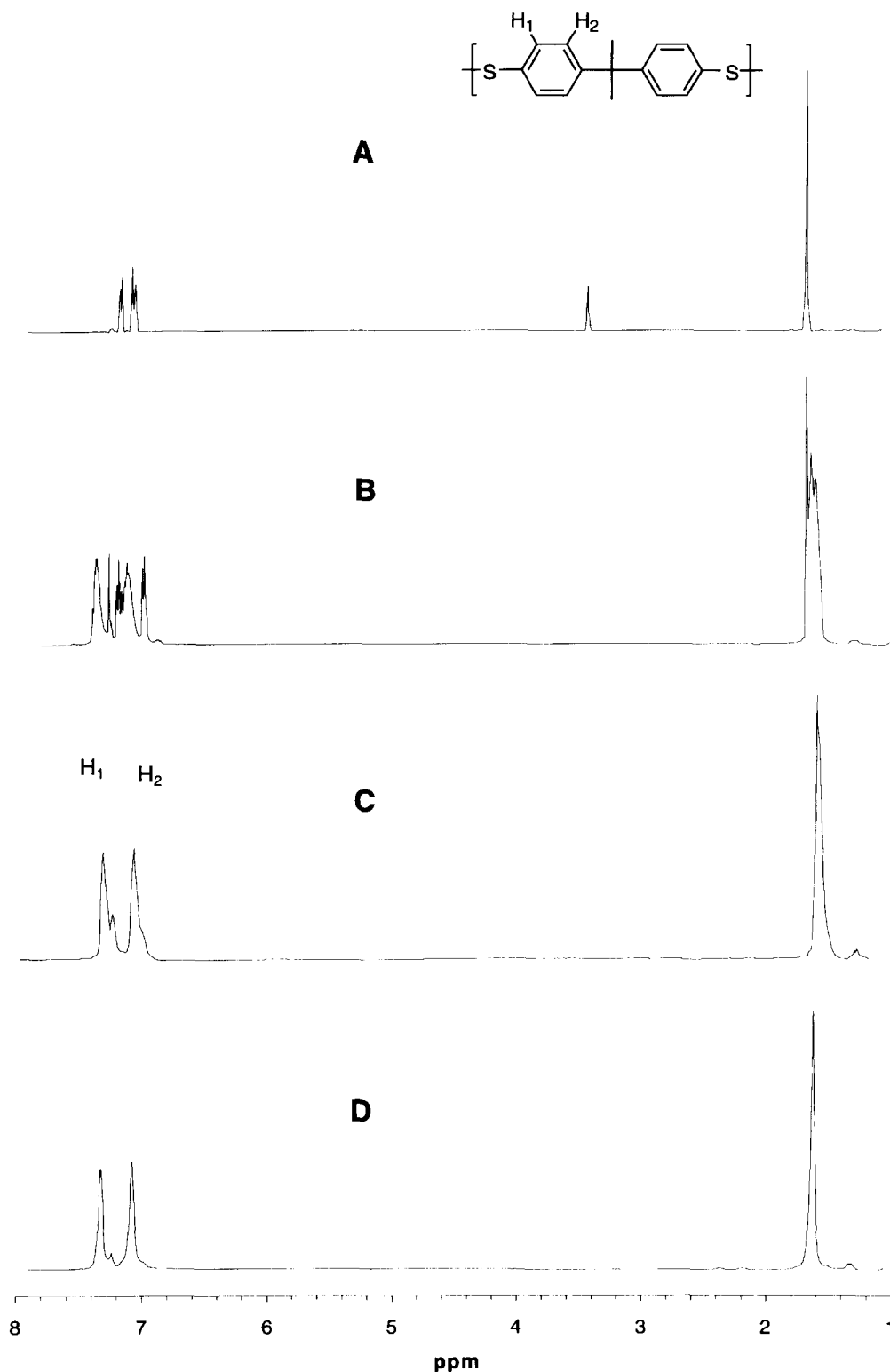


Figure 3 ¹H n.m.r. spectra. (A) 4,4'-Isopropylidene bithiophenol; (B) cyclic disulfide oligomers **II**; (C) poly(aromatic disulfide) **III** from melt ring-opening polymerization at 200 °C for 15 min; (D) poly(aromatic disulfide) **III** from direct oxidative polymerization

High molecular weight polymers were formed in melt ring-opening polymerization reactions at 200°C with only trace amounts of cyclic oligomers remaining. Again, we found that molecular weights of the polymers formed from ring-opening polymerization reaction are independent of the reaction time, however they depend on the reaction temperatures. The highest molecular weight polymers were obtained by reaction at 200°C. Increase of the reaction temperature resulted in the decrease of the molecular weights of polymers. Presumably, this is due to the decomposition of disulfide bonds in the polymer chain at higher temperatures. Branching also occurred at

higher temperatures and much longer reaction times, which resulted in polymers with high polydispersities at 250°C. At the same reaction temperatures, the molecular weights were higher for polymers obtained in the melt than for polymers obtained from solution, which could be due to the ring-chain equilibration in solution.

A cross-linking reaction became very serious at temperatures above 300°C and insoluble black products were obtained in all cases. Below 300°C, soluble polyaromatic disulfide **II** can be obtained. There is no reaction between the thiyl radical and methyl group even for 2 h reaction below 250°C. Below 300°C the thiyl

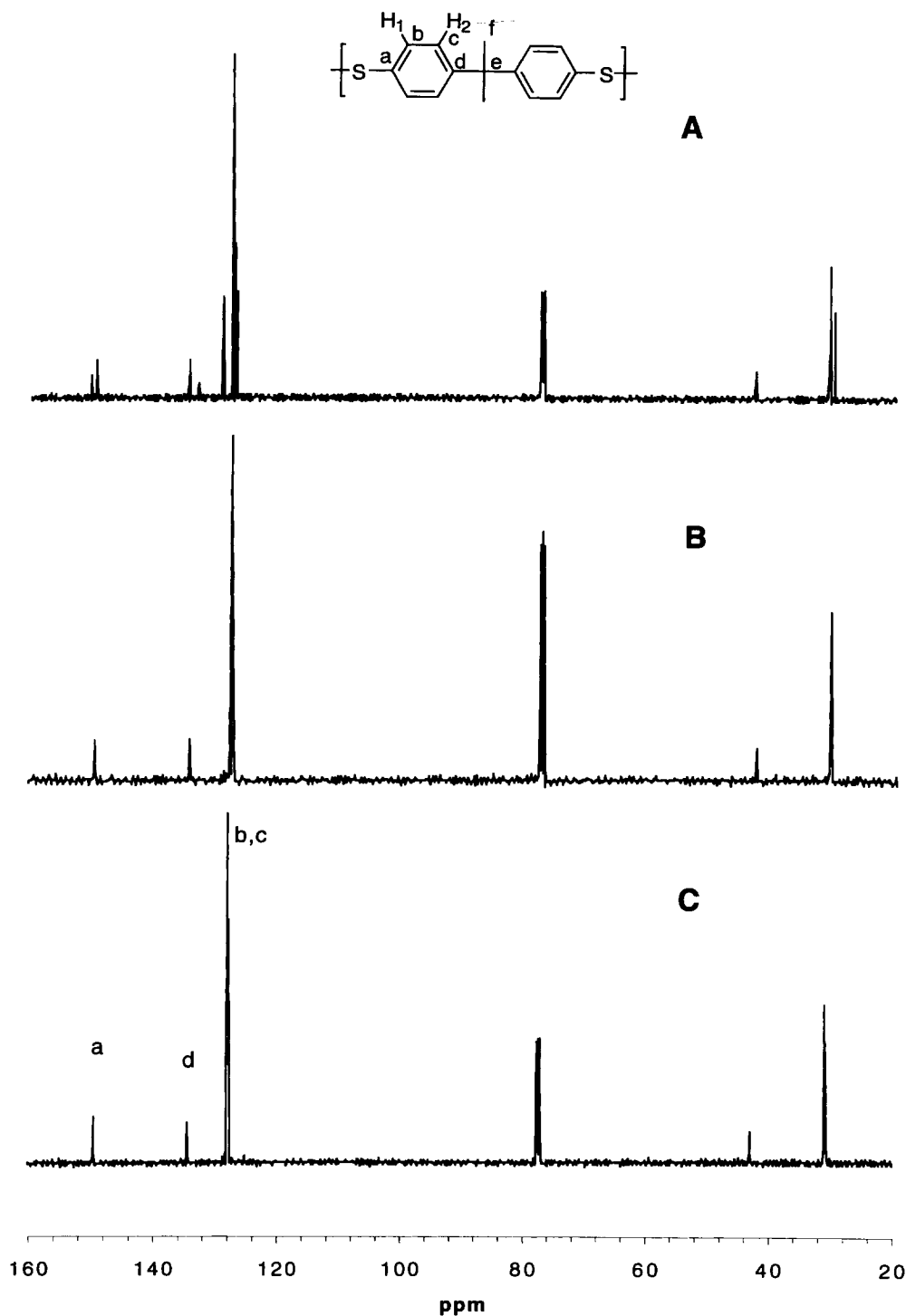


Figure 4 ¹³C n.m.r. spectra. (A) Cyclic disulfide oligomers **II**; (B) poly(aromatic disulfide) **III** from melt ring-opening polymerization at 200°C for 15 min; (C) poly(aromatic disulfide) **III** from direct oxidative polymerization

radical reacts with disulfide group first to form polymers. In previous studies, we also found that the thiyl radical *ipso*-substitutes iodine to form an aromatic sulfide by reacting with *p*-iodotoluene at 280°C^{23,24}.

The thermal properties of a typical polymer were measured by d.s.c. and t.g.a. at a heating rate of 20°C min⁻¹ under an atmosphere of nitrogen. This polymer was obtained by ring-opening polymerization at 200°C for 15 min. It had a T_g of 126°C. The 5% weight loss temperature of this polymer was 369°C.

The structure of the poly(aromatic disulfide)

To study the structures of the polydisulfides from ring-opening polymerization, an authentic polydisulfide polymer was prepared by oxidative polymerization of the corresponding dithiol compound⁹. A white fibrous high molecular weight polymer was obtained after a 2 h polymerization reaction. The polymer is readily soluble in common organic solvents. The apparent number average molecular weight was 90 000 and weight average molecular weight was 131 000 as determined by g.p.c. using polystyrenes as standards. The polymer is virtually identical to the polymers obtained from cyclic oligomers at 200°C by ring-opening polymerization.

¹H n.m.r. spectra for dithiol compound **I**, cyclic oligomers, polydisulfide **III** from ring-opening polymerization at 200°C for 15 min and **III** from direct oxidation reaction were taken in CDCl₃ solution and are shown in Figure 3. Aromatic proton signals became much more complex because of the formation of cyclics (Figure 3B). However, the signals after the ring-opening polymerization became simpler (Figure 3C) and were the same as that of authentic polydisulfide (Figure 3D). The proton signals of H₁ for cyclic oligomers and polydisulfides are downfield compared to dithiol compound **I**, because the disulfide group is at a higher oxidation state than the thiol group.

¹³C n.m.r. spectra of cyclic disulfide oligomers, polydisulfide **II** from ring-opening polymerization at 200°C for 15 min and that from direct oxidation are shown in Figure 4. Again, we observed the complex carbon signals of cyclic oligomers became simpler after ring-opening polymerization reaction. Polydisulfide from ring-opening polymerization showed exactly the same ¹³C signals as that of authentic polydisulfide. Therefore, we can conclude that polydisulfide **II** obtained by ring-opening polymerization at 200°C is a structurally regular polydisulfide.

However, the structural regularity decreased as the ring-opening polymerization temperature increases as evidenced by ¹³C n.m.r. spectra. Several extra peaks appeared for **II** when the polymerization was carried out at 250°C, presumably because of the formation of trisulfide bonds and/or thioether bonds. It is well documented that thermolysis of diphenyl disulfide at high temperatures (*ca.* 250°C) produces diphenyl sulfide and elemental sulfur²⁵. Diphenyl disulfide or diphenyltrisulfide can also be formed by reaction of diphenyl sulfide or diphenyldisulfide with sulfur. The higher the

reaction temperature, the more complex the polymer structures.

CONCLUSIONS

The ring-opening polymerization reaction of the oligomeric cyclic disulfide **II** was conducted both in diphenyl ether solution and in the melt. The reaction took place at 150°C in solution, however, it only took place at 200°C or above in the melt. The ring-opening polymerization reaction was very rapid above *ca.* 150°C. The highest molecular weight polymers were formed at 200°C. Structurally regular polydisulfides were obtained below 250°C, however, structural irregularities were introduced above 250°C.

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