Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Ding, Yong and Hay, Allan S.(1997) 'Synthesis and Characterization of Amorphous Aromatic Poly(Thioether Ketone)s and Poly(Thioether Phenyl Phosphine Oxide)s', Journal of Macromolecular Science, Part A, 34: 3, 405 — 415

To link to this Article: DOI: 10.1080/10601329708014968

URL: http://dx.doi.org/10.1080/10601329708014968

J.M.S.—PURE APPL. CHEM., A34(3), pp. 405–415 (1997)

SYNTHESIS AND CHARACTERIZATION OF AMORPHOUS AROMATIC POLY(THIOETHER KETONE)S AND POLY(THIOETHER PHENYL PHOSPHINE OXIDE)S

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ABSTRACT

A series of aromatic poly(thioether ketone)s were synthesized from 4,4′-dimercaptodiphenyl ether (I) and 4,4′-dimercaptodiphenyl thioether (II), by reaction with a series of ketone-activated aromatic fluoro compounds (IIIa–e) in DMF in the presence of anhydrous K_2CO_3. Two poly(thioether phenyl phosphine oxide)s were also prepared from bis(4-fluorophenyl)phenyl phosphine oxide (IV). The aromatic polythioethers had inherent viscosities of 0.3–0.88 dL/g. All polymers were amorphous and soluble in such solvents as $CHCl_3$, DMF, DMAc, NMP, and DMSO. The glass transition temperatures of these aromatic polythioethers were in the 154–251°C range, and the 5% weight loss temperatures in TGA were in the 420–541°C range in N_2 and the 503–527°C range in air. Wide-angle x-ray diffraction data on selected polymers showed that the polymers were amorphous.

INTRODUCTION

Due to their application in the aerospace, electronic, automotive, and related markets, high performance polymers are currently receiving considerable attention. Much research has been carried out in recent years toward the development of new or improved thermoplastic resins. In this area, aromatic poly(ether ketone)s have been given special attention because of their chemical resistance and excellent mechanical and thermal properties.

Only a few reports have been published on poly(thioether ketone)s, although conceptually their synthesis is similar to that of poly(ether ketone)s. In 1989, researchers at Dow Chemical reported the preparation of poly(thioether ketone)s from ketone-activated aromatic fluoro compounds by reaction with anhydrous sodium sulfide in *N*-cyclohexyl-2-pyrrolidinone (CHP) [1]. Senn studied the synthesis and characterization of *ran*-copoly(*p*-phenylene sulfide sulfone/ketone)s from sodium hydrosulfide [2]. Ueda et al. synthesized a series of poly(thioether ketone)s by the direct polycondensation of aromatic dicarboxylic acids with aryl compounds containing sulfide structures using phosphorous pentoxide/methanesulfonic acid (PPMA) as the condensing agent and solvent [3]. Poly(thioether ketone)s have also been prepared from masked bisthiophenols in the presence of potassium bicarbonate [4].

A major effort in our laboratory has been the synthesis of amorphous high performance materials. Over the years, a series of ketone-containing monomers have been developed, and the properties of the poly(arylether ketone)s derived from them with a variety of bisphenols have been evaluated [5–7]. More recently, we reported on a facile free-radical ring-opening polymerization of cyclic oligomers containing thioether [8]. In addition, we have prepared novel oligomeric cyclic disulfides by oxidative coupling of several dimercapto-substituted compounds [9]. Reaction of these cyclic disulfides with diiodo compounds yields high molecular weight poly(thioether)s. Herein, we describe the synthesis and characterization of poly(thioether ketone)s prepared by reaction of ketone-containing monomers with 4,4′-dimercaptodiphenyl ether and 4,4′-dimercaptodiphenyl thioether which were used in the previous studies. Poly(thioether phenyl phosphine oxide)s were also prepared from **I** and **II** by reaction with bis(4-fluorophenyl)phenyl phosphine oxide (**IV**). Poly(arylether)s from **IV** have been extensively studied because of their high temperature stability, flame resistance, and resistance to oxygen plasma [10–12].

EXPERIMENTAL

Materials

The required 4,4′-dimercaptodiphenyl thioether was purchased from Aldrich Chemical Inc. and recrystallized from absolute ethanol. **IIIa**, **IIIb**, and **IIIc** were prepared according to the previously published method [5]. The syntheses of **IIId** and **IIIe** have been published elsewhere [6, 7]. **V** was synthesized by a Grignard technique [11]. DMF was purchased from Aldrich Chemical Inc. and used directly without further purification.

Synthesis of 4,4′-Di(chlorosulfonyl)diphenyl Ether

A three-neck round-bottom flask was charged with 100 mL of chlorosulfonic acid and cooled to 0°C. To this cooled solution, 40.0 g (0.235 mol) of diphenyl ether was added dropwise over a 3-hour period through a dropping funnel, and the resulting mixture was allowed to stir at room temperature for another 8 hours. The mixture was then carefully poured into 1 kg of ice, and the resulting white solid was filtered. Recrystallization from hexane yielded 61.6 g of the desired product: mp 126-127°C (Lit. [13], 128-129°C)

Synthesis of 4,4′-Dimercaptodiphenyl Ether [14]

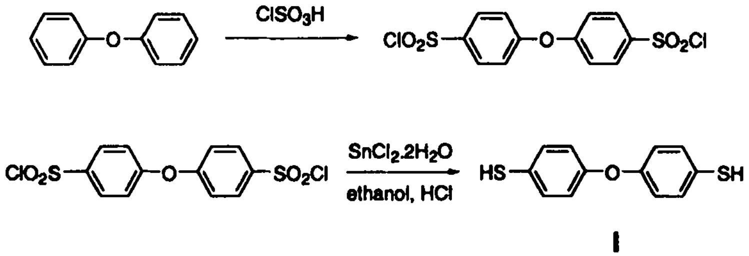
A 1000-mL three-neck round-bottom flask equipped with a magnetic stirrer, a thermometer, and a reflux condenser was charged with 38.0 g of 4,4′-di(chlorosulfonyl)diphenyl ether (0.104 mol), 250 g (1.1 mol) of stannous chloride dihydrate, and 300 mL each of anhydrous ethanol and concentrated hydrochloric acid. The mixture was heated to reflux for 8 hours, cooled to room temperature, poured into 500 mL of concentrated hydrochloric acid, and filtered. The crude product was dissolved in 500 mL of 5% NaOH and precipitated out by adding concentrated hydrochloric acid to the filtrate. **I** (17.7 g) was obtained by recrystallization from ethanol. Yield, 73%: mp 103-104°C (Lit. [15], 103-104°C).

Polymerization

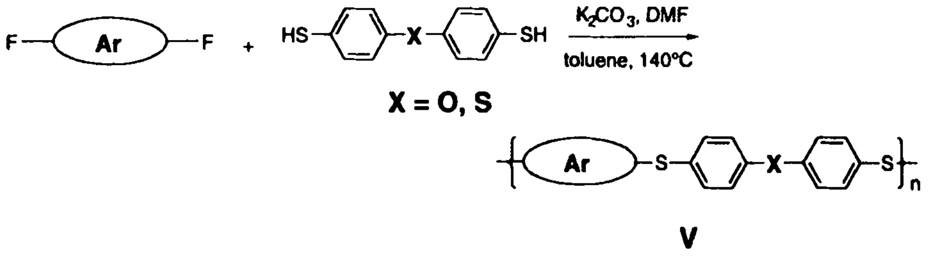
Polymerization reactions were conducted in a 50-mL three-neck flask equipped with a gas inlet, a thermometer, a Dean-Stark trap, and a reflux condenser. A typical example is given below. A flask was charged with 1.2520 g (2.0 mmol) of **IIIc**, 0.5008 g (2.0 mmol) of **II**, 0.54 g (3.9 mmol) of anhydrous K_2CO_3, 6.0 mL of DMF, and 5 mL of toluene. The reaction mixture was blanketed with nitrogen and placed in a preheated oil bath. Toluene was gradually removed, and the reaction mixture was raised to 140-145°C and kept at that temperature until the viscosity increased dramatically. The reaction mixture was cooled and diluted with 8 mL DMF, and several drops of acetic acid were added to neutralize the thiophenoxide end groups. The polymer solution was then poured into vigorously stirred methanol (100 mL), filtered, redissolved in chloroform, and filtered through a thin layer of Celite. The chloroform solution was concentrated and then coagulated in methanol. The fibrous polymer was recovered by filtration and dried under vacuum at 120°C for 24 hours.

Characterization

^{1}H-NMR spectra were recorded on a Varian UNITY-500 spectrometer using chloroform-*d* as solvent. Gel permeation chromatography (GPC) was performed on a Waters 510 HPLC equipped with 5μ phenogel columns (linear, 3 × 500 Å) arranged in series and a UV detector at 254 nm. Chloroform was used as eluent with polystyrene standards. Glass transition temperatures were determined on a Seiko 220 DSC instrument at a heating rate of 20°C/min under a nitrogen atmosphere. Thermogravimetric analysis (TGA) data were obtained using a Seiko TG/DTA instrument at a heating rate of 20°C/min in nitrogen or air atmosphere. Inherent viscosities were measured using chloroform solution at a concentration of 0.5 g/dL in a Ubbelohde viscometer. Wide-angle x-ray diffraction (WAXD) measurements were performed on a Philips PW1710-based x-ray diffractometer using CuKα radiation with the films cast from chloroform solution. The intensity of 1 second counts was taken every 0.02° (2Θ).



SCHEME 1.



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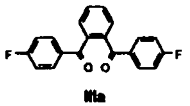
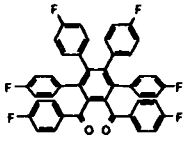
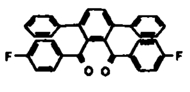
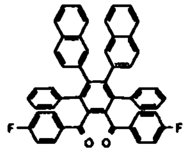
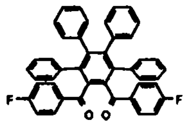
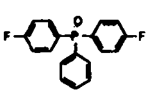
 IIIa	O	Va	 IIId	O	Vg
	S	Vb		S	Vh
 IIIb	O	Vc	 IIIe	O	Vi
	S	Vd		S	Vj
 IIIc	O	Ve	 IV	O	Vk
	S	Vf		S	Vl

SCHEME 2.

RESULTS AND DISCUSSION

Monomer Synthesis

The synthesis of monomer **I** is outlined in Scheme 1. 4,4′-di(chlorosulfonyl)-diphenyl ether was selectively formed in the presence of an excess of sulfonyl chloride. The disulfonyl chloride was subjected to reduction with stannous chloride by Baron's modified method [14], and **I** was obtained in 73% yield.

Polymer Synthesis and Characterization

The monomers **I** and **II** were polymerized with a series of ketone-activated difluoro compounds **IIIa–e**, which were previously synthesized in this laboratory, and bis(4-fluorophenyl)phenyl phosphine oxide (**IV**) in DMF (Scheme 2). This polymerization procedure was first described by Baron and Blank to synthesize poly(thioether sulfone) from bis(4-chlorophenyl)sulfone [14]. The thiophenoxide anions are stronger nucleophiles than phenoxide, therefore it is understandable that a lower temperature is necessary for the condensation reaction of thiophenoxide with fluoro compounds. High molecular weight poly(thioether ketone)s and poly(thioether phenyl phosphine oxide)s were generally obtained after 4–8 hours of reaction times. All the polymers are amorphous and soluble in common organic solvents, such as chloroform, toluene, DMF, DMAc, and NMP.

The polymers were characterized by ^{1}H-NMR. The ID ^{1}H-NMR and 2D COSY spectra in $CDCl_3$ of polymer **Vf** are shown in Figs. 1(a) and 1(b), respectively. The H_1 signal shifted to 7.47 ppm from 7.60 ppm [5] following polymerization due to the replacement of fluoro atoms by sulfur atom, while the H_2 signal shifted downfield from ~6.9 ppm to 7.01 ppm.

The apparent molecular weights of the polymers were obtained by GPC and are given in Table 1. Polymers **Vk** and **Vl** appear to interact with the column using chloroform as eluent, and hence their apparent molecular weights are not available. The monomer **IIIa** gave rise to polymers with very broad distributions as suggested by GPC results. This indicates that some crosslinking or branching reaction occurred during the polymerization process. The formation of narrow distribution polymers **Vg** and **Vh** shows that the four fluorine atoms on the four pendant phenyl rings were not replaced by a sulfur atom. As indicated by ^{19}F-NMR and HMO calculations, the ketone-activated fluoro atom has considerably higher reactivity than a fluoro atom without activation. However, suitable low temperature conditions have to be maintained to avoid branching [6].

Inherent viscosities were taken at a concentration of 0.5 g/dL chloroform solution, and the results are listed in Table 2. The inherent viscosities of these polymers vary from 0.30 to 0.88.

The glass transition temperatures (T_gs) of polymers **V** were measured by differential scanning calorimetry at a heating rate of 20°C/min under an atmosphere of nitrogen (Table 2). The T_gs of these polymers range from 154 to 251°C. As observed previously [5], the increasing number of pendant phenyl groups going from monomer **IIIa** to monomer **IIIc** resulted in the T_gs of the resultant polymers increasing from around 150 to 230°C. Changing the **X** group of the dithiol compounds from oxygen to sulfur led to a decrease in the T_gs. For example, polymers **Ve** and **Vk** have T_gs of 237 and 195°C, respectively; however, their sulfur counterparts **Vf** and **Vl**

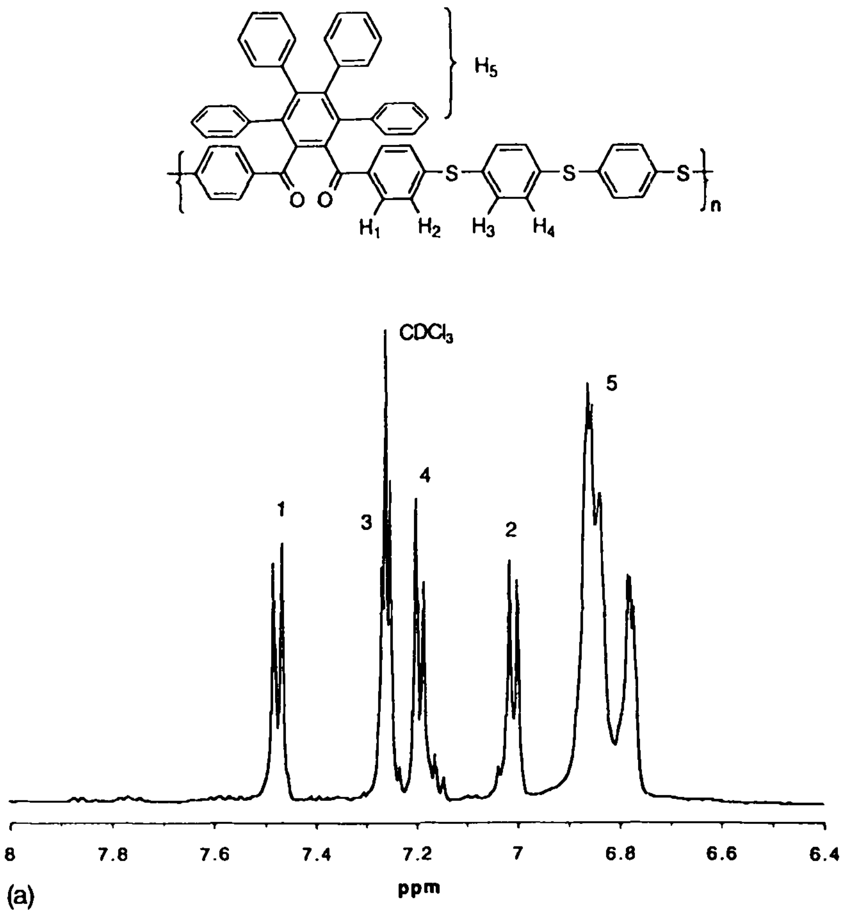


FIG. 1. NMR spectra of polymer **Vf**. (a) 1D-^{1}H NMR spectrum; (b) 2D-COSY spectrum.

have lower T_gs of 227 and 182°C. This is understandable since the C—S bond is more flexible than the C—O bond. In terms of glass transition temperature, monomer **IV** is equivalent to monomer **IIIb**.

All polymers showed excellent stability according to their thermogravimetric analysis in nitrogen and air atmospheres (Table 2). Polymer **Vb** showed the poorest thermal stability in a nitrogen atmosphere based on the 5% weight loss temperature. The 5% weight losses are above 500°C for all the polymers tested under air atmosphere, and generally they are higher than those obtained under nitrogen atmosphere. We speculate this results from oxidation of the sulfide groups in air which would result in an increase in weight. This apparent thermal stability, which is higher in air than in nitrogen, has also been noticed by other researchers in other polymer systems [16]. It is interesting to notice that again polymers **Vc** and **Vd** showed almost the same thermal stabilities as those of polymers prepared from

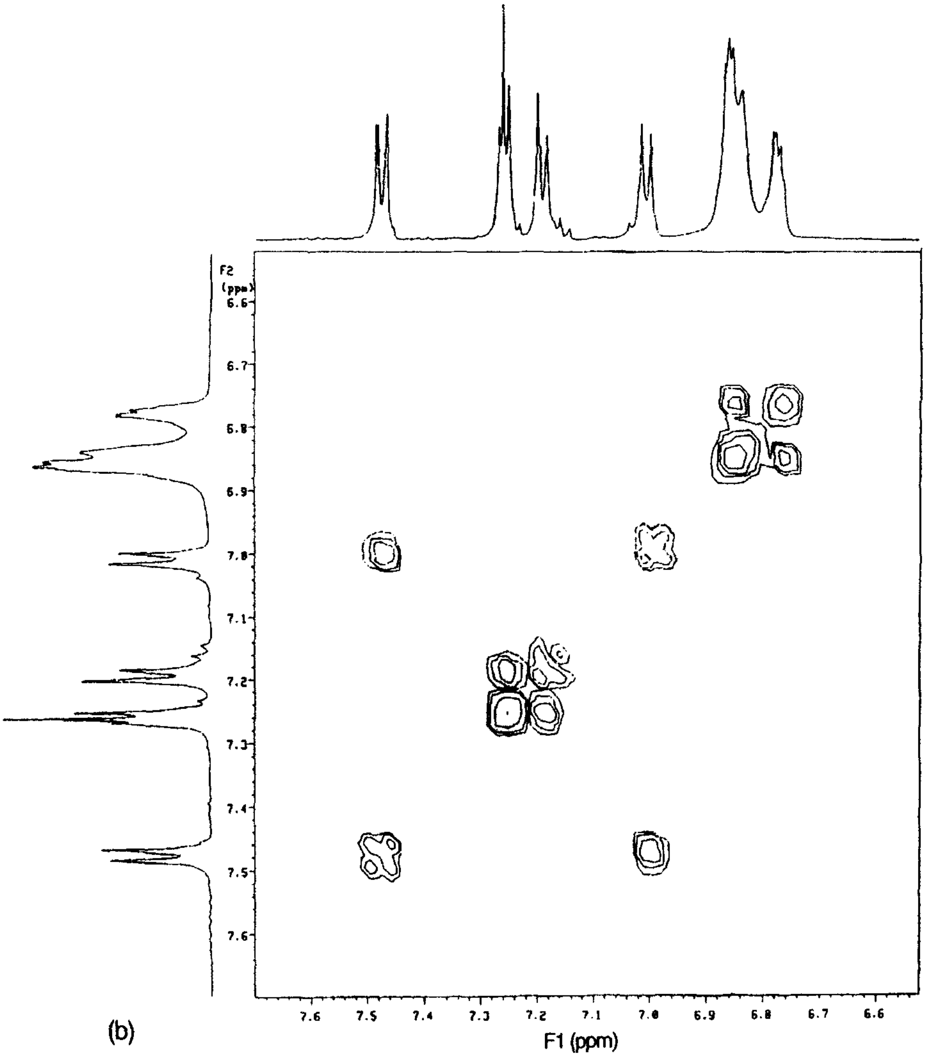


FIG. 1. Continued.

monomer **IV**, although polymers **Vk**, and **VI** had a slightly lower thermal stability in air than that in nitrogen. In terms of char weight remaining after 500°C, polymers **Va–I** were more stable in nitrogen atmosphere than in air atmosphere. TGA charts in Fig. 2 indicate that the weight losses of polymers **Vi** and **VI** were faster in air than in nitrogen above the 5% weight loss temperatures.

WAXD measurements were made for the film samples of polymers **Vh** and **Vi** (Figure 3). The WAXD curves indicated the polymers were amorphous. It is well known that poly(*p*-phenylene sulfide) (PPS) is a highly crystalline polymer. The

TABLE 1. GPC Data for Polymers **Va**–**Vj**

Polymer	M_n, g/mol	M_w, g/mol	Polydispersity
Va	68,000	534,000	7.9
Vb	55,000	801,000	14.6
Vc	68,000	156,000	2.3
Vd	90,000	155,000	1.7
Ve	69,000	107,000	1.6
Vf	62,000	102,000	1.6
Vg	88,000	124,000	1.4
Vh	92,000	126,000	1.4
Vi	100,000	162,000	1.6
Vj	65,000	102,000	1.6

TABLE 2. Properties of Polymers **Va**–**Vl**

Polymer	Inherent viscosity[a]	T_g, °C[b]	TGA, °C[c] (5% weight loss)	
			N_2	Air
Va	0.88	161	462	503
Vb	0.40	154	420	502
Vc	0.50	203	496	510
Vd	0.43	192	499	522
Ve	0.30	237	517	518
Vf	0.36	227	537	527
Vg	0.46	228	541	520
Vh	0.35	232	520	518
Vi	0.42	251	515	527
Vj	0.31	225	514	514
Vk	0.37	195	511	508
Vl	0.32	182	506	503

[a] 0.5 g/dL in chloroform at 25°C.

[b] Heating rate was 20°C/min under nitrogen atmosphere.

[c] Heating rate was 20°C/min.

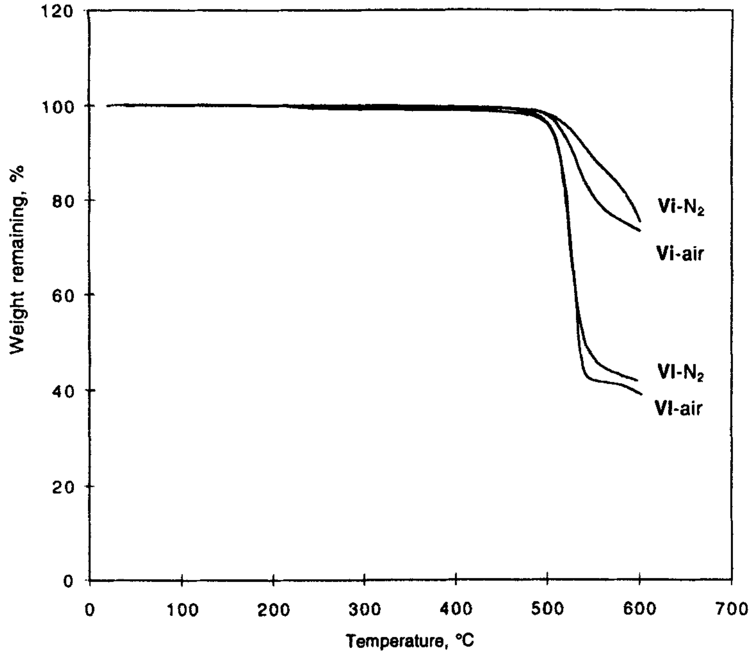


FIG. 2. TGA curves of polymers **Vi** and **VI** in nitrogen and air atmospheres.

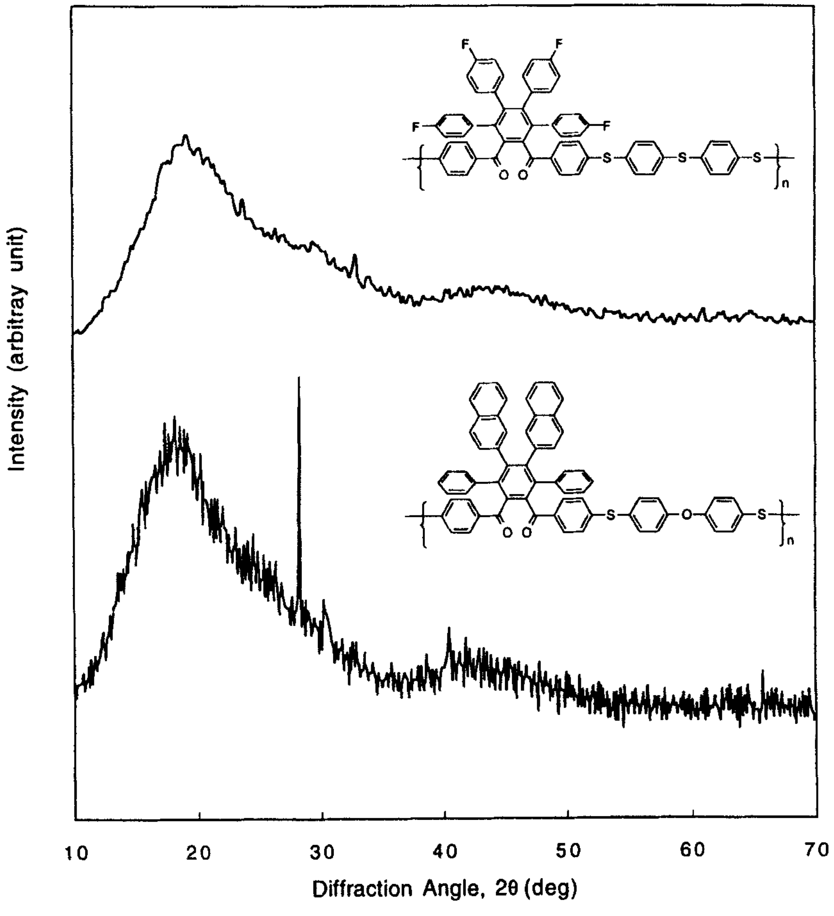


FIG. 3. WAXD curves of polymers **Vh** and **Vi**.

WAXD result showed that a PPS chain with three repeating units is not sufficient to form any crystallinity.

CONCLUSIONS

Series of poly(thioether ketone)s and poly(thioether phenyl phosphine oxide)s were successfully prepared from dithiol compound **I** and **II** by reaction with a series of ketone-activated aromatic difluoro compounds **IIIa–e** and **IV** in DMF in the presence of anhydrous potassium carbonate. The polymers formed were amorphous as evidenced by WAXD measurements, and soluble in normal organic solvents. They had inherent viscosities of 0.3–0.88 g/dL in chloroform at 25°C. The glass transition temperatures of these polythioethers were in the range of 154 to 251°C. The 5% weight loss temperatures by TGA were in the range of 420 to 541°C in N_2 and 503 to 527°C in air.

ACKNOWLEDGMENTS

This work was supported by the Natural Sciences and Engineering Research council of Canada. Y.D. thanks Drs. E. Elce and C. Herbert for providing some fluoro compounds.

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Received April 12, 1996
Revision received June 15, 1996