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Sulfur-containing Polymers. XIII.[1] The Synthesis and Properties of Soluble Polydithiocarbamates

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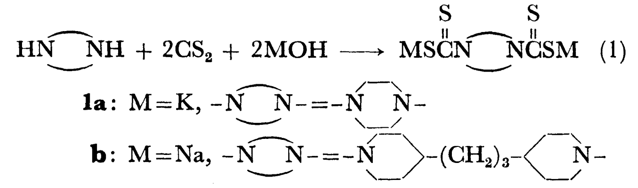
Polydithiocarbamates have been synthesized by the polycondensation of di-K or di-Na bisdithiocarbamates based on secondary diamines with bischloromethylated aromatics in *N,N*-dimethylformamide. The polymers obtained in good yields had inherent viscosities up to 0.66. The polymers derived from 1,3-di-4-piperidylpropane were soluble in organic solvents, such as dichloromethane and chloroform, and gave transparent, tough films from the solution. These polymers decomposed upon UV irradiation, with the liberation of carbon disulfide. The photopolymerization of methyl methacrylate in the presence of the polymer has also been studied.

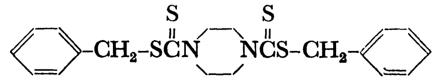
The facile condensation of Na or K dithiocarbamates with alkyl halides is well known and has been extensively studied.[2] This reaction has been employed to introduce a dithiocarbamate side chain into polymers. Some of these polymers can serve as the backbone for photografting and as photosensitive resin.[3,4] However, the condensation reaction has not been extended to the preparation of high molecular-weight linear polymers. Although Zochniak has prepared polydithiocarbamates by the polycondensation of di-Na alkylene bisdithiocarbamates with bischloromethylated diphenyl ether, the polymers are insoluble in organic solvents.[5] This presents a major obstacle to the solution characterization of the products.

We have been interested in the polymers containing photosensitive groups in the main chain.[6-8] In the course of our studies, it was found that fairly high molecular-weight polydithiocarbamates (**3**) with good solubility characteristics can be prepared from di-K or di-Na bisdithiocarbamates based on secondary diamines (**1**) and bischloromethylated aromatics (**2**).[9] This paper will describe the synthesis and properties of the polydithiocarbamates. Their photochemical behavior will also be discussed in some detail.

Results and Discussion

Synthesis. The bisdithiocarbamate salts, **1**, were prepared from secondary diamines, carbon disulfide, and alkali metal hydroxides [Eq. (1)]. Their structures were confirmed as dibenzyl derivatives, (**4**) and (**5**). The polycondensation of **1** with **2** proceeds according to Eq. (2). The polymer formation was carried out by stirring an equimolar mixture of **1** and **2** in *N,N*-dimethylformamide (DMF) for 1 hr at room temperature followed by heating the mixture up to 110 °C over a 30 min period. The polymer which was precipitated





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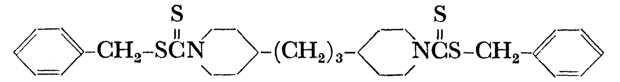

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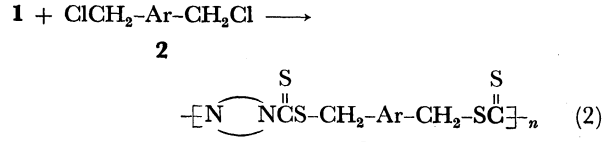

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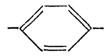
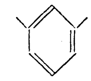
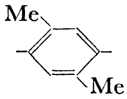
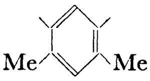
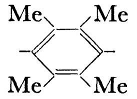
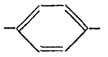
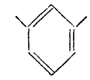
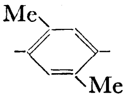
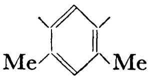
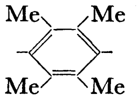
Table 1. Preparation of polydithiocarbamates (**3**)

Polymer No.	1	2 -Ar-	Yield (%)	Softening point (°C[a])	Dec. point (°C[b])	η_{inh}
3a	a		83	251—254 (dec.)	271	0.43[c]
3b	a		83	202—208	278	0.54[c]
3c	a		90	285—293 (dec.)	274	0.41[c]
3d	a		91	242—248 (dec.)	282	0.54[c]
3e	a		91	>300	295	0.38[c]
3f	b		95	167—178	277	0.63[d]
3g	b		98	141—150	286	0.53[d]
3h	b		94	173—185	276	0.66[d]
3i	b		95	162—178	273	0.47[d]
3j	b		90	258—266	273	0.60[d]

a) Determined by a hot-stage microscope. b) Determined by DTA (heating rate 10 °C/min). c) Measured in methanesulfonic acid (0.5 g/100 ml, 30 °C). d) Measured in TCE (0.5 g/100 ml, 30 °C).

during the reaction was washed with water and methanol and dried at 50 °C under a vacuum. Using different combinations of **1** and **2**, a variety of different polymers with novel backbone structures were prepared. Table 1 contains a listing of these polymers, together with a partial compilation of their properties. Polymers were obtained in good yields regardless of the combinations of **1** and **2**. The inherent viscosities of the polymers ranged from 0.38 to 0.66, indicating that these polymers were of a fairly high molecular weight.

Other solvents, such as benzene–water, chloroform–water, and *sym*-tetrachloroethane (TCE), can also be used in the polycondensation; however, they usually give polymers with low inherent viscosities. The prominent feature of DMF may be attributed to its ability to increase the nucleophilicity of anions and to activate halogenated compounds by forming ionic complexes.[10)]

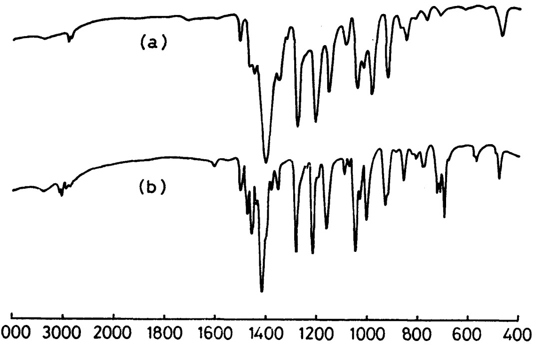


Fig. 1. The IR spectra of (a) polymer **3a** and (b) model compound **4** (KBr disks).

The polymers showed essentially the same results of elemental analyses as polydithiocarbamates. The IR spectra of the **3a**—**3e** polymers (piperazine polymers) were virtually identical and compared favorably with that of the corresponding model compound, **4** (Fig. 1). The bands at 1280, 990, and 930 cm^{-1} are characteristic of the dithiocarbamate group and are assigned to $\nu_{\text{C-N}}$, $\nu_{\text{C=S}}$, and $\nu_{\underset{\|}{\text{C}}\text{-S}}$, respectively. It is interesting to note that the band at 1470 cm^{-1} due to the polar C–N partial double bond[11)] is not so intense. On the other hand, the IR spectra of the **3f**—**3j** polymers (dipiperidylpropane polymers) and the model compound **5** displayed an intense absorption of $\nu_{\text{C=N}}$ at 1480 cm^{-1}. The NMR spectra provided further support for the assigned polymer structures; these polymers showed a triplet, centered at $\delta\sim3.1$ ($J=12$ Hz), for the four axial *N*-methylene protons, a broad signal centered at δ 5.1—5.2 for the four equatorial *N*-methylene protons, and a singlet at δ 4.5—4.6 for the four benzylic protons. As is shown in Fig. 2, the NMR spectrum of the **3f** polymer is quite similar to that of **5**.

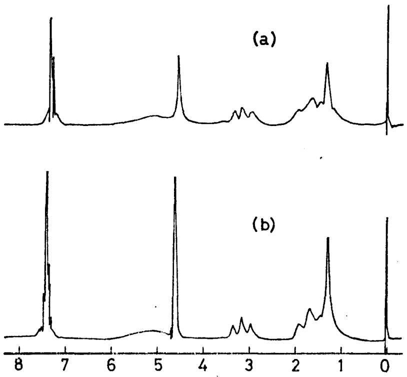


Fig. 2. The NMR spectra of (a) polymer **3f** and (b) model compound **5** (CDCl$_3$–TMS).

General Properties. The softening points of the piperidylpropane polymers lie below those of the corresponding piperazine polymers and tend to increase with an increase in the number of methyl substituents per unit. The introduction of symmetrical 1,4-phenylene ring structures into the polymer chain also increases the softening point. All the polymers decomposed on heating above 270 °C. The decomposition was exothermic, according to DTA.

The piperazine polymers were soluble in methanesulfonic acid and insoluble in organic solvents, whereas the dipiperidylpropane polymers were soluble in dichloromethane, chloroform, TCE, and *m*-cresol in addition to methanesulfonic acid, and the resulting polymer solutions gave transparent, tough films when cast upon a glass plate. This made possible an investigation of the photochemical properties of the polymers.

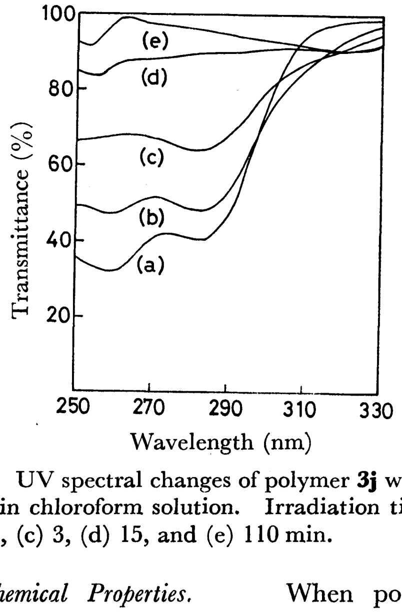


Fig. 3. UV spectral changes of polymer **3j** with irradiation in chloroform solution. Irradiation time; (a) 0, (b) 1, (c) 3, (d) 15, and (e) 110 min.

Photochemical Properties. When polymer films were exposed to the UV light from a 450 W high-pressure mercury lamp, they decomposed with a noticeable color change. The photolysis of the **3j** polymer was followed by means of the UV and IR spectra in an appropriate solvent. Figure 3 depicts the changes in the UV spectra on irradiation. The unirradiated sample showed two bands at 260 and 283 nm assignable to the S–C=S conjugation and the N–C=S conjugation, respectively.[12)] These bands decreased in intensity with time and finally disappeared, while two new bands appeared. The band in the 252—255 nm range showed a shift to a shorter wavelength with continued exposure; it was unaccounted for. The band at approximately 320 nm coincided in position with that of carbon disulfide. The formation of carbon disulfide

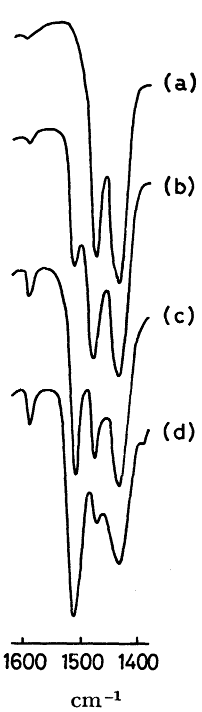
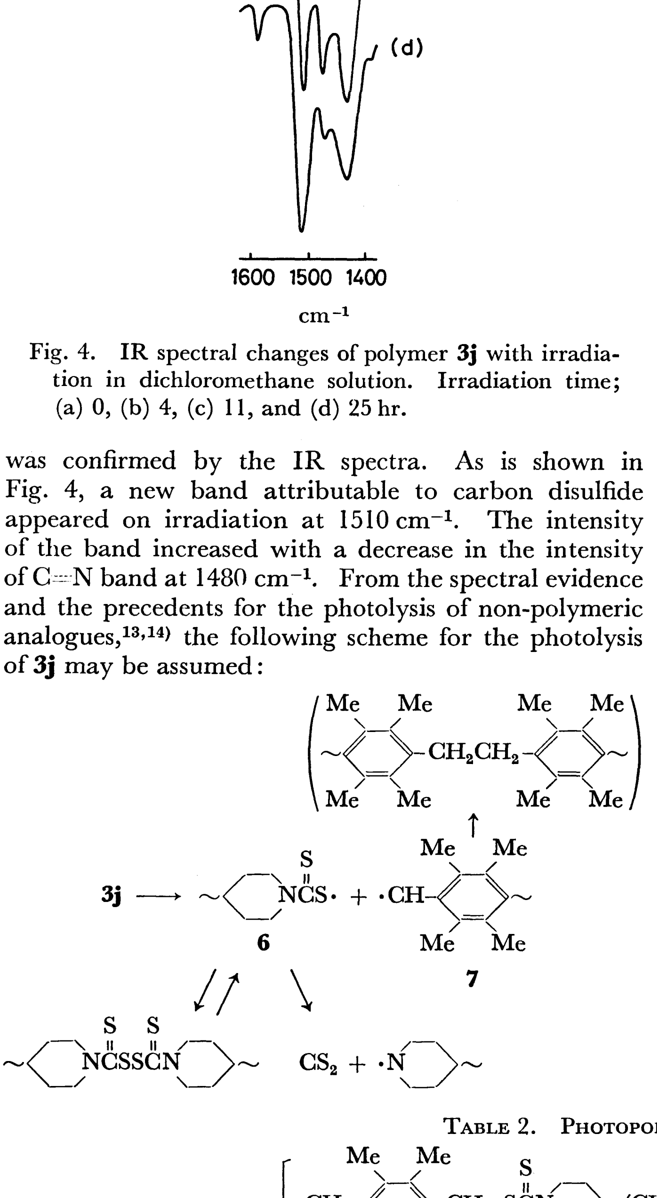


Fig. 4. IR spectral changes of polymer **3j** with irradiation in dichloromethane solution. Irradiation time; (a) 0, (b) 4, (c) 11, and (d) 25 hr.

was confirmed by the IR spectra. As is shown in Fig. 4, a new band attributable to carbon disulfide appeared on irradiation at 1510 cm^{-1}. The intensity of the band increased with a decrease in the intensity of C=N band at 1480 cm^{-1}. From the spectral evidence and the precedents for the photolysis of non-polymeric analogues,[13,14] the following scheme for the photolysis of **3j** may be assumed:



The initial photochemical step involves the formation of a dithiocarbamoyl radical (**6**) and a benzyl radical (**7**). The former either dimerizes to a thiuram disulfide or dissociates to carbon disulfide and an amino radical.[15] The **7** radical may dimerize to give a bibenzyl derivative, but this point is not clear.

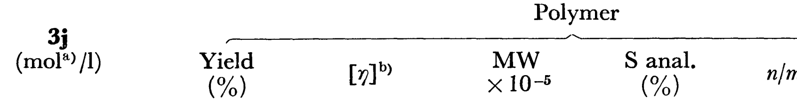
Photopolymerization of Methyl Methacrylate (MMA). In view of the above results and the known tendency of dithiocarbamate to initiate the photopolymerization of vinyl monomers,[3,13,16] we expected that a new type of block copolymers could be obtained by using the **3** polymer as the initiator of the vinyl polymerization. Chloroform solutions containing MMA and **3j** were irradiated in a Pyrex tube (frozen and vacuum sealed) at room temperature. A linear relationship was noticed between the polymer yield and the reaction time. The IR spectra of the polymers obtained were identical with that of poly MMA, but the UV spectra exhibited characteristic absorption of **3j** at 259 and 283 nm, showing that some units of **3j** were incorporated in the polymer. Table 2 shows the effect of **3j** on the polymerization of MMA, the polymerization time being 2 hr. The molecular weights of the polymers were determined viscometrically in toluene at 30 °C with the aid of the relation, $[\eta]=7.0\times10^{-5}\,M^{0.71}$, given by Stanley.[17] Compared to the polymerization without additives, the polymerization in the presence of **3j** gave a polymer with a lower molecular weight in higher yield. Thus, it may be concluded that **3j** functions not only as an initiator but also as a chain-transfer agent. A similar observation has been reported for benzyl diethyldithiocarbamate.[3] The ratio of the **3j** unit and the MMA unit in the polymer (m: n), as estimated on the basis of sulfur analysis, was 1: 64.[18] This means that each polymer molecule contains about 11 units of **3j**. Furthermore, the ratio of the durene unit and the MMA unit obtained from the NMR spectrum[19] was 1: 72. These values are indicative of the block character of the copolymer.

Experimental

Instrumentation. The following instruments were used in this study: a Hitachi EPI-G3 grating infrared spectrophotometer, a Varian T-60 NMR spectrometer, a Hitachi EPS-3 recording spectrophotometer, and an AGNE TGD-1500 thermal balance.

Materials. 2,5-Bis(chloromethyl)-*p*-xylene and 4,6-bis(chloromethyl)-*m*-xylene were prepared by the reaction of the corresponding xylene with formaline and hydrochloric acid.

TABLE 2. PHOTOPOLYMERIZATION OF MMA



MMA (mol/l)	3j (mol[a]/l)	Polymer					
		Yield (%)	$[\eta]$[b]	MW $\times 10^{-5}$	S anal. (%)	n/m[c]	m per molecule
2.83	0	1.0	0.60	3.47	—	—	—
2.83	9.6×10^{-3}	14.5	0.21	0.79	1.85	64	11.4

a) Based on recurring unit. b) Measured in toluene at 30 °C. c) Estimated from sulfur analysis.

2,5-Bis(chloromethyl)-*p*-xylene; mp 134 °C (lit,[20]) mp 132—134 °C). 4,6-Bis(chloromethyl)-*m*-xylene; mp 98—99 °C (lit,[21]) mp 99 °C). Piperazine, 1,3-(di-4-piperidyl)propane, *α,α'*-dichloro-*p*-xylene, -*m*-xylene, and 3,6-bis(chloromethyl)-durene were used as received. MMA was purified by distillation in the usual manner.[22])

*Di-K Piperazine-*N,N'*-biscarbodithioate (1a).* To a solution of 8.6 g of piperazine and 13.1 g of potassium hydroxide in 200 ml of ethanol was added dropwise a solution of 15.2 g of carbon disulfide in 40 ml of ether below 10 °C; the mixture was then stirred for 1 hr. The solid product was used for a subsequent reaction after one reprecipitation from water into acetone, followed by drying at 80 °C under a vacuum. The yield was 23.2 g.

*Di-Na 1,3-Di-4-piperidylpropane-*N,N'*-biscarbodithioate (1b).* To a stirred solution of 21.0 g of 1,3-(di-4-piperidyl)propane and 9.0 g of sodium hydroxide in 200 ml of ethanol was added dropwise a solution of 15.2 g of carbon disulfide in 40 ml of ether below 10 °C after which the mixture was stirred for 1 hr. The mixture was then filtered into a large volume of ether. The white precipitate was used for a subsequent reaction after one reprecipitation from ethanol into ether, followed by drying at 80 °C under a vacuum. The yield was 36.0 g.

*Dibenzyl Piperazine-*N,N'*-biscarbodithioate (4).* A solution of 6.28 g of **1a** in 150 ml of water was mixed with a solution of 5.07 g of benzyl chloride in 50 ml of chloroform. The mixture was stirred vigorously for 3 hr under reflux. The chloroform layer was then separated, washed with water, dried over anhydrous magnesium sulfate, and concentrated to give 7.85 g (94%) of **4**; mp 122—123 °C (from benzene-*n*-hexane). The IR spectrum is shown in Fig. 1.

NMR ($CDCl_3$); δ 4.33 (s, 8H), 4.70 (s, 4H), 7.48 (m, 10H).

Found: C, 57.42; H, 5.13; N, 6.59; S, 30.66%. Calcd for $C_{20}H_{22}N_2S_4$: C, 57.38; H, 5.30; N, 6.69; S, 30.63%.

*Dibenzyl 1,3-(Di-4-piperidyl)propane-*N,N'*-biscarbodithioate (5).* A mixture of 8.13 g of **1b**, 5.07 g of benzyl chloride, 150 ml of water, and 50 ml of chloroform was refluxed for 3 hr with vigorous stirring. From the reaction mixture, 10.4 g of an oily product was obtained after the same work-up as above. The product was treated with 100 ml of ether to give 8.90 g (82%) of **5**; mp 122—124 °C (from ethanol). The NMR spectrum is shown in Fig. 2.

Found: C, 64.40; H, 6.89; N, 5.17; S, 23.84%. Calcd for $C_{29}H_{38}N_2S_4$: C, 64.16; H, 7.06; N, 5.16; S, 23.62%.

Polycondensation. The polycondensation of **1** with **2** was carried out in DMF. The results are summarized in Table 1. The following is a typical example. A mixture of 2.03 g of **1b**, 1.16 g of 3,6-bis(chloromethyl)durene, and 30 ml of DMF was stirred for 1 hr at room temperature and then heated up to 110 °C over a 30 min period. The mixture was cooled and kneaded with 50 ml of methanol. The solvents were decanted. This treatment was repeated until the polymer solidified completely. The polymer was filtered with suction, washed with water and methanol, and dried at 50 °C under a vacuum. The yield of the **3j** polymer was 2.33 g (90%).

NMR ($CDCl_3$); δ 0.8—2.0 (m, 16H), 2.33 (s, 12H), 3.12 (t, J=12 Hz, 4H), 4.50 (s, 4H), ~5.1 (broad signal, 4H).

The polymer was purified by two reprecipitations from chloroform into methanol and was then used for analysis and photolysis.

Found: C, 62.35; H, 7.61; N, 5.25; S, 24.57%. Calcd for $(C_{27}H_{40}N_2S_4)_n$: C, 62.26; H, 7.74; N, 5.38; S, 24.62%.

Photolysis of 3j. Irradiations were carried out with a 450 W high-pressure mercury lamp (Ushio UM-452) centrally situated in a water-cooled Pyrex cold-finger. A chloroform solution of **3j** (1.1×10^{-5} mole-based on the repeating unit/l) was irradiated in a 1 cm quartz cell at a distance of 60 cm from the lamp. The UV spectral measurements were made immediately after the removal of the sample from the exposure unit. The results are shown in Fig. 3.

A dichloromethane solution of **3j** (*ca.* 6×10^{-2} mol-based on the repeating unit/l) was irradiated in a 0.1 mm NaCl closed cell at a distance of 20 cm from the UV lamp. The IR spectral changes around 1500 cm^{-1} are shown in Fig. 4.

Photopolymerization of MMA. A solution of 0.05 g of **3j** and 3 ml of MMA in 10 ml of chloroform was placed in a Pyrex tube, 2 cm in diameter. The tube was degassed under a vacuum by the usual freezing and thawing technique and then sealed. The tube was irradiated at a distance of 40 cm from the UV lamp. After a given interval the mixture was concentrated under reduced pressure, dissolved in acetone, and filtered into a large volume of methanol. The yield was calculated from the weight of the polymer obtained in the dry state. Viscosity measurements were made in toluene with a Ubbelohde viscometer at 30 °C. The IR spectra of the polymers were identical with that of poly MMA. The UV spectra exhibited the weak absorptions at 259 and 283 nm characteristic of **3j**.

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