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SULFUR-CONTAINING POLYMERS. XIV.

POLY(BISCARBAMOYL DISULFIDES). A NEW TYPE OF PHOTOSENSITIVE POLYMERS[1]

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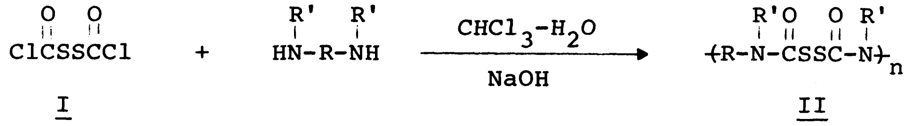
Poly(biscarbamoyl disulfides) have been synthesized by the interfacial polycondensation of dithiobis(carbonyl chloride) with secondary diamines. The polymers obtained in good yields were of sufficiently high molecular weight to form films. The polymer films decomposed by UV irradiation with liberation of carbonyl sulfide.

A variety of structural features have been incorporated into macromolecules in order to obtain uique or modified properties. The introduction of -XC(=O)SY- (X, Y = N, O, or S) linkages in the polymer backbone is of interest because of the effect the linkages can have on the photochemical properties of the polymers. Recent studies in this laboratory have shown that polymers having $>$NC(=O)SN$<$,[2,3] -OC(=O)SN$<$,[4] $>$NC(=O)SS-,[5] or -OC(=O)SS-[6] linkages in the main chain decompose with liberation of carbonyl sulfide on being subjected to UV irradiation. The finding of this phenomenon led us to prepare new photosensitive polymers. We now wish to report the synthesis of novel polymers containing $>$NC(=O)SSC(=O)N$<$ linkages whose potential for incorporation in polymers has not yet been evaluated. The polymers were conveniently prepared by the polycondensation of dithiobis(carbonyl chloride)[7] (I) with secondary diamines.

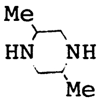
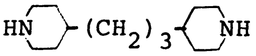
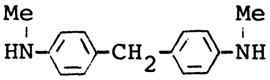
I was prepared by the partial hydrolysis of bis(trichloromethyl) disulfide in concentrated sulfuric acid as described previously[7] and was freshly distilled before the polymerization reaction. Polycondensation of I with diamines proceeds according to eq. (1). Formation of polymer was carried out by interfacial polymerization in chloroform-water, sodium hydroxide being used as an acid acceptor. An aqueous solution containing a diamine[8] and sodium hydroxide (2 mole equivalents) was cooled



$$\underset{\underline{I}}{\mathrm{ClCSSCCl}} \text{ (C=O, C=O)} + \mathrm{HN(R')\text{-}R\text{-}NH(R')} \xrightarrow[\mathrm{NaOH}]{\mathrm{CHCl_3\text{-}H_2O}} \underset{\underline{II}}{\left(\mathrm{R\text{-}N(R')\text{-}C(=O)SSC(=O)\text{-}N(R')}\right)_n} \qquad (1)$$

in an ice bath. To this solution was quickly added a solution of I (1 mole equivalent) in chloroform with vigorous stirring and the resultant mixture was stirred for 10 min. The behavior of the polymers in the polymerization system varied with the nature of diamine used. With trans-2,5-dimethylpiperazine, 1,3-di-4-piperidylpropane, and N,N'-dimethyl-4,4'-diaminodiphenylmethane, the polymers remained in solution until after completion of the polymerization. With piperazine, however, the polymer precipitated from the reaction system. In all cases the reaction mixture was treated with a large volume of methanol. The resulting nonswollen precipitates were filtered, washed with methanol, and dried under vacuum. The results are summarized in Table 1. The poly(biscarbamoyl disulfides) (II) thus obtained in good yields had inherent viscosities up to 1.08, indicating that they were of high molecular weight.9)

Table 1. Poly(biscarbamoyl disulfides)

No.	Diamine	Yield (%)	Softening point (°C a))	Dec. point (°C b))	η_{inh}
IIa		88	230-236 (dec)	238	0.57 c)
IIb	 (trans)	91	252-254 (dec)	264	1.08 d)
IIc		91	218-220 (dec)	225	0.81 d)
IId		98	224-230	283	0.30 d)

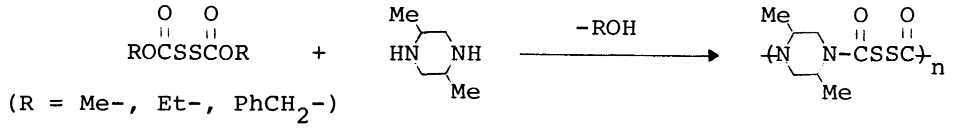
a) Determined by a hot-stage microscope.

b) Determined by differential thermal analyses.

c) Measured at 0.5 g/100 ml of m-cresol at 30°C.

d) Measured at 0.5 g/100 ml of chloroform at 30°C.

As an alternate route to poly(biscarbamoyl disulfides), the reaction of bis(alkoxycarbonyl) disulfide10) with diamine was studied. When an equimolar mixture of bis(methoxycarbonyl) disulfide and trans-2,5-dimethylpiperazine was stirred in dichloromethane at room temperature, polymer with inherent viscosity 0.33 was obtained in 41% yield. The IR and NMR spectra of this polymer agreed with those of polymer IIb.



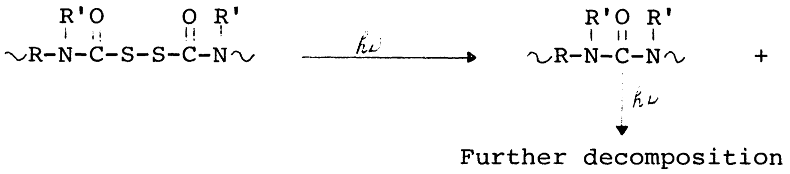
(2)

Bis(ethoxycarbonyl) disulfide and bis(benzyloxycarbonyl) disulfide can also be used in this reaction, but the inherent viscosity of the polymer formed was usually low (0.20-0.26). The main disadvantage of this method is the lack of generality; no polymer was obtained from N,N'-dimethyl-4,4'-diaminodiphenylmethane and piperazine.

The IR spectra of the polymers were characterized by a prominent band for the carbonyl group at 1675-1680 cm^{-1}, and compared favorably with those of the nonpolymeric analogues.[7)] Furthermore, elemental analyses and the NMR spectra were consistent with the proposed polymer structures.

The polymers resemble poly(carbamoyl disulfides)[5)] very closely in solubility characteristics. Polymer IIa derived from piperazine was soluble in m-cresol, methanesulfonic acid, and concentrated sulfuric acid and insoluble in halogenated hydrocarbons. On the other hand, polymers IIb-IId were readily soluble in chloroform and sym-tetrachloroethane. These polymers gave transparent tough films when chloroform solutions were cast upon a glass plate.

The polymers prepared here were, as expected from analogy with the polymers having -XC(=O)SY- linkages, found to be sensitive to light. The films of aliphatic polymers IIb and IIc colored brown and became brittle during storage for 3 weeks under diffused light, while in the dark these films can be stored indefinitely without change. The photochemical decomposition of polymer films was monitored by IR spectra. The film of polymer IIc was exposed to UV light from 450-W high-pressure mercury lamp. The IR spectrum of the film after irradiation for 10 min showed a new band at 2025 cm^{-1} due to carbonyl sulfide occluded in the film. The carbonyl band at 1675 cm^{-1} gradually decreased in intensity, while a new band appeared at 1640 cm^{-1} characteristic of substituted urea; after 2.5 hr the band at 1675 cm^{-1} had been almost completely replaced by the band at 1640 cm^{-1}. The film was torn with a noticeable color change by prolonged irradiation. These IR spectral changes are quite similar to those observed previously for poly(carbamoyl disulfides).[5)] It can therefore be presumed that the photochemical decomposition of II proceeds as outlined in eq. (3).



$$\sim R-\overset{R'}{N}-\overset{O}{\overset{\|}{C}}-S-S-\overset{O}{\overset{\|}{C}}-\overset{R'}{N}\sim \xrightarrow{h\nu} \sim R-\overset{R'}{N}-\overset{O}{\overset{\|}{C}}-\overset{R'}{N}\sim + COS + S \qquad (3)$$

$$\downarrow h\nu$$

Further decomposition

REFERENCES

1) Part XIII, N. Kobayashi, A. Osawa, and T. Fujisawa, Bull. Chem. Soc. Japan, 47, 2287 (1974).

2) N. Kobayashi and T. Fujisawa, Macromolecules, 5, 106 (1972).

3) N. Kobayashi and T. Fujisawa, J. Polym. Sci., A-1, 10, 1233 (1972).

4) N. Kobayashi and T. Fujisawa, J. Polym. Sci., A-1, 10, 3165 (1972).

5) N. Kobayashi, A. Osawa, and T. Fujisawa, J. Polym. Sci., Polym. Chem. Ed., 11, 553 (1973).

6) N. Kobayashi, A. Osawa, and T. Fujisawa, J. Polym. Sci., Polym. Chem. Ed., 11, 2099 (1973).

7) N. Kobayashi, A. Osawa, and T. Fujisawa, Chem. Lett., 1973, 1315.

8) 1,3-Di-4-piperidylpropane and N,N'-dimethyl-4,4'-diaminodiphenylmethane were dissolved in a small amount of chloroform.

9) The molecular weight of polymer IIb was 22,900 as determined by a vapor pressure depression method.

10) N. Kobayashi, A. Osawa, and T. Fujisawa, J. Polym. Sci., Polym. Lett. Ed., 11, 225 (1973).

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