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Addition Copolymerization of Sulfur Dichloride and Sulfur Monochloride with 1,3-Butadiene

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Addition Copolymerization of Sulfur Dichloride and Sulfur Monochloride with 1,3-Butadiene

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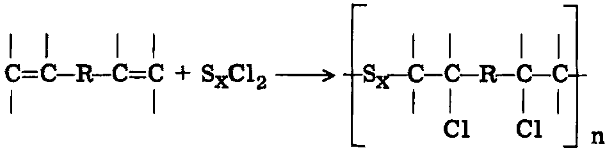
SUMMARY

Poly(dichlorobutane sulfide) I and poly(dichlorobutane disulfide) II have been prepared in 97% yield by addition copolymerization of butadiene with sulfur dichloride and sulfur monochloride, respectively. The polymers were characterized by elemental analysis, infrared spectrum, inherent viscosity, and thermogravimetric analysis. The reactions of several dienes with sulfur dichloride (but not with sulfur monochloride) have been reported in the literature. All were reported to give mainly the intramolecular addition products. However, it has very recently been found that diolefins with double bonds rigidly separated from each other, or with double bonds so situated that intramolecular reaction is thermodynamically unfavorable, preferentially undergo polymerization with sulfur monochloride or sulfur dichloride. In the case of butadiene, polymerization is thermodynamically more feasible than intramolecular addition due to the dipole repulsion and eclipsing chain which would be present in the intramolecular reaction products.

INTRODUCTION

Recent work in this laboratory has shown that sulfur dichloride and sulfur monochloride each undergo addition polymerization with selected diolefins to form the corresponding sulfide and disulfide addition polymers [1-3]. These reactions, which are the first reported addition polymerizations of sulfur dichloride or sulfur monochloride, proceed as follows:*



$$\mathrm{\overset{|}{\underset{|}{C}}{=}\overset{|}{C}{-}R{-}\overset{|}{C}{=}\overset{|}{\underset{|}{C}}} + S_xCl_2 \longrightarrow \left[-S_x-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{\underset{Cl}{|}}{C}}-R-\overset{|}{\underset{\underset{Cl}{|}}{C}}-\overset{|}{\underset{|}{C}}- \right]_n$$

The reactions of several dienes with sulfur dichloride (but not with sulfur monochloride) have been reported in the literature. 1, 5-Cyclooctadiene [4] bicycloheptadiene [5], 1, 5-hexadiene [6], 2, 3-dimethylbutadiene [7], etc., were reported to give mainly the intramolecular double addition products. In contrast, we have found that diolefins with double bonds rigidly separated from each other [1],

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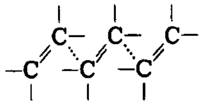
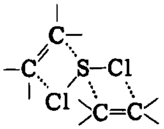
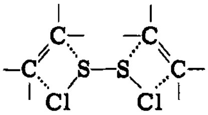
*It is significant to note that this new polymerization reaction, while it may be grossly termed addition polymerization, is actually an example of a new polymerization category. The formation of polymers via addition polymerization formally involves one atom of each monomer and thus may be termed a two-center reaction. Of course, in actuality, the π-electron cloud of the monomer which is to undergo addition overlaps the terminal atom of the growing polymer chain. By contrast, the addition of a sulfenyl chloride bond formally involves two atoms of each monomer and thus may be termed a four-center addition polymerization (even though the actual mechanism may involve stepwise addition of a chloride ion and a sulfonium ion).



Two-center



and Four-center



or with double bonds situated so that intramolecular reaction is thermodynamically unfavorable, preferentially undergo polymerization with sulfur dichloride or sulfur monochloride [2, 3]. Specifically, we have found that bis(1, 2, 3, 6-tetrahydrophthalimide), in which the double bonds are rigidly separated, and cyclopentadiene, a molecule whose intramolecular addition products would consist of highly strained bicyclic sulfides, undergo polymerization with either sulfur dichloride or sulfur monochloride.

The possibility of obtaining addition polymers from the copolymerization of 1, 3-butadiene with sulfur dichloride or sulfur monochloride is of particular interest because of the ready availability and low cost of the monomers. Further, it is readily apparent that the driving force for the intramolecular reaction of butadiene with sulfur dichloride would be reduced over that for the intramolecular reaction of other linear diolefins due to the eclipsing strain inherent in the five-membered ring vicinally substituted with chlorine atoms which would be the result of intramolecular addition. Similarly, it is apparent that the intramolecular addition product of sulfur monochloride with butadiene (a six-membered ring) would be thermodynamically less favored than the polymer due to chlorine atom dipole repulsion, which could be minimized in the antirotamer of the polymer but only partially minimized in the intramolecular product. Indeed 1, 3-butadiene gives a 97% yield of the corresponding addition polymer when reacted with sulfur dichloride and a 97% yield of the corresponding disulfide addition polymer when reacted with sulfur monochloride.

RESULTS

Copolymerization of 1, 3-Butadiene with Sulfur Dichloride

Sulfur dichloride (20.6 g, 0.2 mole) was added dropwise to 1, 3-butadiene (10.4 g, 0.2 mole) in methylene chloride (50 ml) at —20°C with stirring, over a period of 2 hours. After addition of sulfur dichloride, the reaction mixture was stored at —20°C for 3 days to give a transparent yellow solution with no precipitate. Methylene chloride was stripped under vacuum at room temperature, giving 29.3 g (97%) yield of a yellow, putty-like polymer from which long fibers could be pulled. This material had an inherent viscosity, 0.5% solids in toluene of 0.08; and the infrared spectrum (Fig. 1) had very weak olefinic bands at 1640, 3010, 3050, and 3090 cm^{-1}. Thermogravimetric analysis showed thermal instability at approximately 200°C in nitrogen.

Analysis calculated for $(C_4H_6SCl_2)_n$: C, 30.59; H, 3.85; S, 20.42; Cl, 45.15. Found: C, 32.14; H, 4.03; S, 19.46; Cl, 44.13.

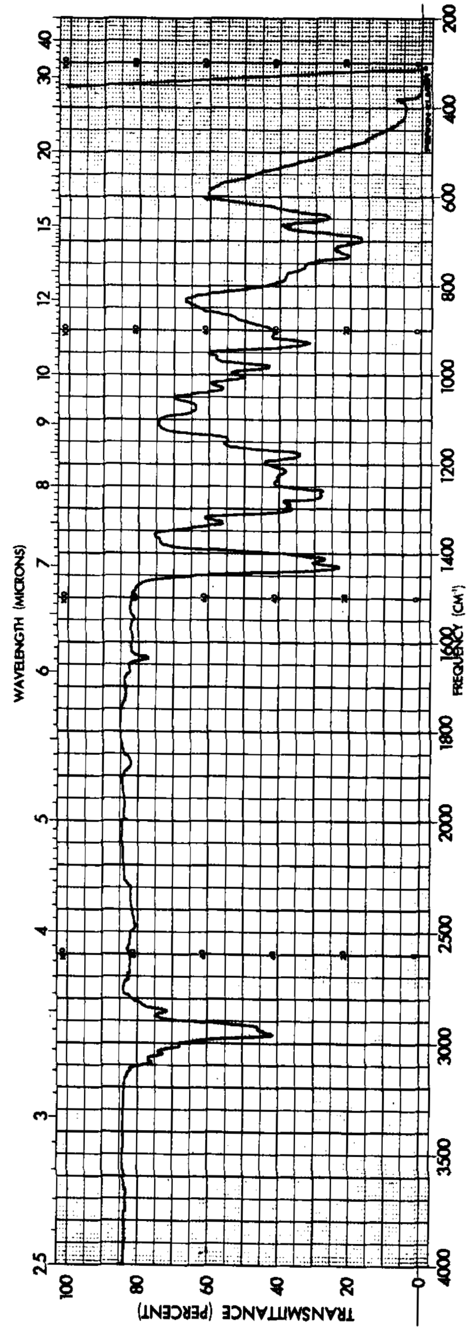


Fig. 1. Infrared spectrum of polymer I.

Copolymerization of 1, 3-Butadiene with Sulfur Monochloride

Sulfur monochloride (27.0 g, 0.2 mole) was added dropwise to 1, 3-butadiene (10.4 g, 0.2 mole) in methylene chloride as above to give 36.6 g (97% yield) of a brownish yellow, putty-like polymer which could be pulled into long strands. An inherent viscosity, 0.5% solids in toluene of 0.04 was obtained; and the infrared spectrum (Fig. 2) had very weak olefinic bands at 1630, 3010, 3050 and 3090 cm^{-1}. Thermogravimetric analysis showed thermal instability at approximately 200°C in nitrogen.

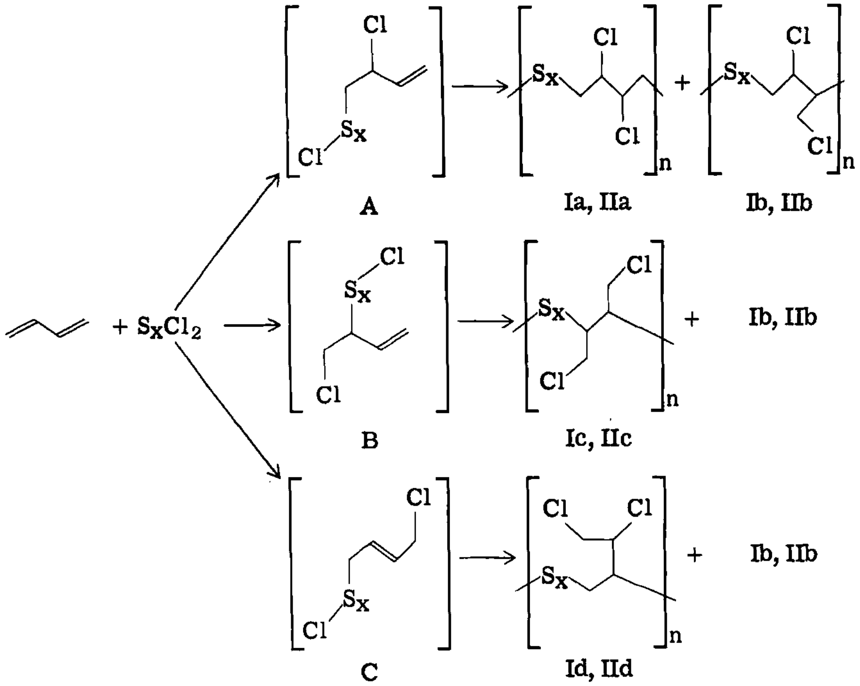
Analysis calculated for $(C_4H_6S_2Cl_2)_n$: C, 25.40; H, 3.20; S, 33.91; Cl, 36.49. Found: C, 26.39; H, 3.37; S, 33.77; Cl, 36.03.

DISCUSSION

Previous work in this area by Baker and Stratling reported that 2, 3-dimethyl-1, 3-butadiene, isoprene, and 1, 3-butadiene react with sulfur dichloride to give less than 1% yields of the intramolecular addition products for the former two derivatives, and tetrachlorobutane in the case of the reaction of 1, 3-butadiene with sulfur dichloride [7]. The major portion of the reaction products was not analyzed.

The present work, which is addressed to the major portion of the yield, shows that 1, 3-butadiene copolymerizes with either sulfur dichloride or sulfur monochloride to give the monosulfide (polymer I) and the disulfide (polymer II) addition copolymers in 97% yield. The minor yields of monomeric products reported by Baker and Stratling may indeed be present, but their presence or absence is of minor consequence. These results are in concert with those obtained for the polymerization of cyclopentadiene with sulfur dichloride and sulfur monochloride [2, 3]. The present polymers, like those from cyclopentadiene, may be a combination of mers consisting of positional isomers Ia, Ib, Ic, and Id and IIa, IIb, IIc, and IId, in which one isomer or the other might predominate.

It has been shown that the sulfenyl halide bond undergoes classical electrophilic addition to nonconjugated olefins [8] with the sulfur atom taking on a positive charge (sulfonium ion) and the chloride taking on a negative charge (chloride ion). Classical electrophilic addition to conjugated olefins, e.g., hydrogen chloride to 1, 3-butadiene, yields mainly 1, 2 addition (with the nucleophile attacking the allylic carbonium ion position) rather than 1, 4 addition. More specifically, the addition of hydrogen chloride to 1, 3-butadiene gives 1-hydro-2-chloride (75%), 1-hydro-4-chloride (25%), and no 2-hydro-1-chloride [9]. Thus, it is likely that polymers I and II are formed mainly through intermediate A and consist mainly of a mixture of isomers Ia, Ib, and IIa, and IIb.



SCl_2 where x = 1 obtain Ia, Ib, Ic, and Id
S_2Cl_2 where x = 2 obtain IIa, IIb, IIc, and IId

Interestingly, the thermogravimetric analyses of polymers I and II show major thermal decomposition at approximately 200°C, as do the corresponding polymers from cyclopentadiene [2, 3] and bis(1, 2, 3, 6-tetrahydrophthalimide) [10]. It appears that the mechanism of thermal degradation at this temperature range probably involves reversion to the two monomers, butadiene and sulfur dichloride, in one case and butadiene and sulfur monochloride in the other case.

EXPERIMENTAL

Infrared spectra were determined on a Perkin Elmer Model 521 grating spectrophotometer (film on NaCl plate). Thermogravimetric analyses were run on an American Instrument Co. apparatus at 9°/min under 30 cc/min nitrogen flow. Inherent viscosities were determined using a Cannon Fenske viscometer in a bath at 25°C. Elemental analyses were obtained from the Elek Microanalytical Laboratories.

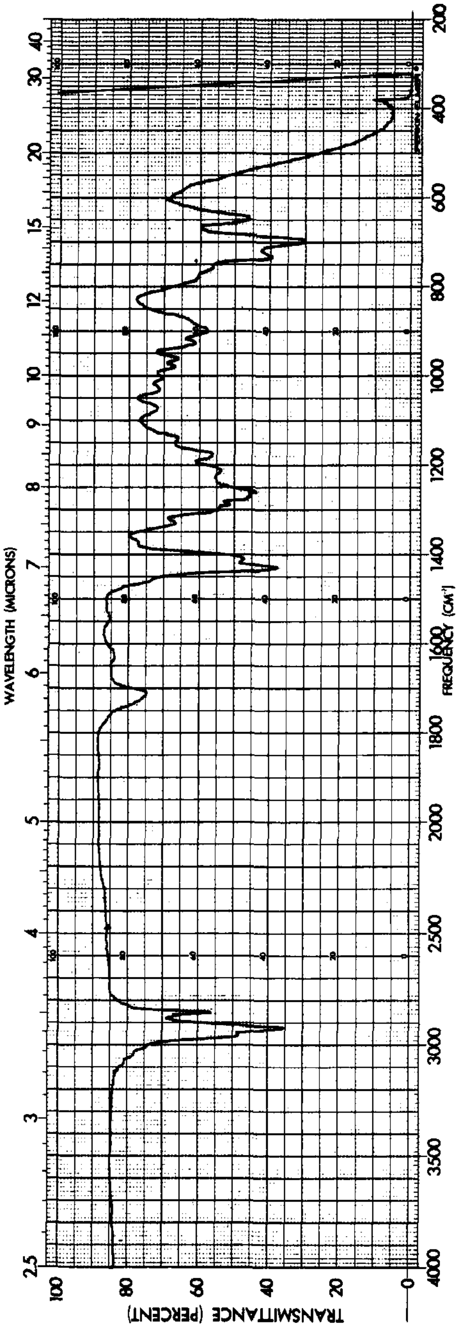


Fig. 2. Infrared spectrum of polymer II.

Sulfur dichloride and sulfur monochloride (Matheson, Coleman and Bell Tech. Grade) were distilled using a Vigruex column. (Defractions boiling at 58-59°C and 55°C/44 mm, respectively, were collected.) 1, 3-Butadiene (J.T. Baker C.P. grade, 99.0%) was used without further purification.

REFERENCES

[1] R.A.Meyers and E.R.Wilson, *Polymer Letters*, **6**, 531 (1968).
[2] R.A.Meyers and E.R.Wilson, *Polymer Letters*, **6**, 581 (1968).
[3] R.A.Meyers and E.R.Wilson, *Polymer Letters*, **6**, 587 (1968).
[4] E.D.Weil, K.J.Smith, and R.J.Gruber, *J. Org. Chem.*, **31**, 1669 (1966).
[5] E.J.Corey and E.Block, *J. Org. Chem.*, **31**, 1663 (1966).
[6] F.Lautenschlager, paper presented at the Conference on the Chemistry of Sulfenyl Compounds, Santa Monica, Calif., November 1967.
[7] J.Baker and J.Stratling, *Rec. Trav. Chem.*, **54**, 52 (1935).
[8] P.B.D.De La Mare and R.Bolton, *Electrophilic Additions to Unsaturated Systems*, Elsevier, New York, 1966, pp. 166-171.
[9] M.S.Kharasch, et al., *J. Org. Chem.*, **2**, 489 (1938).
[10] R.A.Meyers and E.R.Wilson, 156th National Meeting of the American Chemical Society, Atlantic City, N.J., *Polymer Preprints*, **9** (2), 1663 (1968).

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