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Synthesis and Reactions of Functional Polymers. XXXIV. Low Polymerization of Ethylene Oxide with Sodium *N*, *N*-Dimethyldithiocarbamate in Dipolar Aprotic Solvents*[1]

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The low polymerization of ethylene oxide with sodium dimethyldithiocarbamate in a homogeneous system was studied. This reaction was verified as proceeding through a step-by-step addition mechanism, due to the enhanced nucleophilicity of the dithiocarbamate anion in dipolar aprotic solvents. The solvent effects and the catalyses of various dithiocarbamate salts were also examined. Epichlorohydrin was reacted with this salt in dimethylformamide to afford a polymer with a dithiocarbamate moiety through both ring-opening and substitution processes.

In previous papers[1] we have reported that polymers containing a dithiocarbamate moiety are effective as photosensitive resins. We prepared these polymers exclusively by polymer reactions since no monomer with a moiety has been readily available and since the radical polymerization of the monomers did not produce polymers of a high molecular weight. For example, *S*-vinyl-*N*, *N*-dialkyldithiocarbamates (I) were found to be polymerized with a radical initiator to give polymers of a low molecular weight, a low weight arising from the radical-stabilizing effect of the sulfur atom attached to the vinyl group (the *Q*-value for *N*, *N*-diethyl derivative is 0.45[2]). Thus, attempts have been made to prepare 1-*N*, *N*-dialkylthiocarbamylthio-2, 3-epoxy propane (II) by the reaction of epichlorohydrin (EPCl) with sodium dithiocarbamate and to produce a polymer by the ionic polymerization of the epoxide. As yet, however, we have not succeeded in the preparation of II.

During the course of our work on the reaction of EPCl with sodium dithiocarbamate in various solvents, it was found that epoxides were readily polymerized with sodium dithiocarbamate in dimethylformamide (DMF) at room temperature. This led us to our present study of the catalysis and of the solvent effect on the polymerization of ethylene oxide. It may be noted that this is in direct contrast to the observation that the transient dithiocarbamate anion (III) from triethylamine and carbon disulfide reacts with epoxides at 150°C under pressure, resulting in the formation of the corresponding ethylene trithiocarbonates *via* the episulfides, as is shown below,[3] just as in the well-known reactions of the alkylxanthate anion (⊖SCSOR) with epoxides at room temperature.[4]

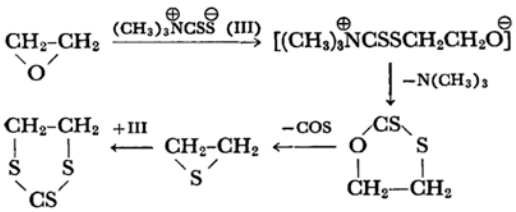
*[1] Presented at the 15th Annual Meeting of the Society of Polymer Science of Japan, Nagoya, May, 1966. Part XXIII: T. Nakagawa and M. Okawara, *J. Polymer Sci.*, in press.

1) a) M. Okawara, H. Yamashina, K. Ishiyama and E. Imoto, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **66**, 1383 (1963); b) M. Okawara, K. Morishita and E. Imoto, *ibid.*, **69**, 761 (1966); c) M. Okawara, M. Ori, T. Nakai and E. Imoto, *ibid.*, **69**, 766 (1966); d) M. Okawara and T. Nakai, *Bull. Tokyo Inst. Technol.*, **78**, 1 (1967). For photochemical behaviors of various dithiocarbamates, also see a) M. Okawara, T. Nakai, K. Morishita and E. Imoto, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **67**, 2108 (1964); b) M. Okawara, T. Nakai and E. Imoto, *ibid.*, **69**, 973 (1966); c) E. H. Hoffmeister and D. S. Tarbell, *Tetrahedron*, **21**, 35, 2857 (1966).

2) T. Nakai, K. Shioya and M. Okawara, *Makromol. Chem.*, **108**, 95 (1967).

3) J. A. Durden, Jr., H. A. Stranburg, Jr., and W. H. Catlette, *J. Am. Chem. Soc.*, **82**, 3082 (1960).

4) a) C. C. J. Culvenor, W. Davies and K. H. Pausacker, *J. Chem. Soc.*, **1946**, 1050; b) L. Owen *et al.*, *ibid.*, **1960**, 1024, 1030; c) C. G. Overberger and A. Drucker, *J. Org. Chem.*, **29**, 360 (1964).



On the other hand, although many earlier studies[5] of base catalyzed polymerization of epoxides have been carried out in heterogeneous systems, little information is available on the polymerization in a homogeneous system. Recently, however, Price and his co-workers[6] have reported the polymerization of epoxides with potassium *t*-buthoxide in dimethyl sulfoxide (DMSO).

This paper will describe how ethylene oxide can be polymerized with sodium dimethyldithiocarbamate in DMF at room temperature by means of a step-by-step addition mechanism.

Results and Discussion

Preliminary Experiments. Initially we attempted to react 2 mol of dithocarbamate salt with 1 mol of various epoxides in DMF, since we expected that the dithiocarbamate anion would react with epoxides in the same manner as the xanthate does.[4] Contrary to our expectations, however, many viscous materials were obtained, accompanied by a violent generation of heat, while the expected ethylene trithiocarbonates were not obtained at all. The presence of a non-volatile residue, after a portion of the liquid phase had been heated on a steam bath, was taken to be a positive criterion of polymerization. Thus, ethylene oxide (EO) and propylene oxide (PO) were reacted with about 5 mol% of sodium dimethyldithiocarbamate hydrate (MDTC) in DMF or in bulk at room temperature, resulting in the formation of viscous polymers of a low molecular weight, as is shown in Table 1. This led us to a detailed study of the polymerization of EO with MDTC.

Effect of MDTC Concentration on the Rate of Polymerization and on the Molecular Weight of the Resulting Polymer. In order to examine the mechanism for the initiation process of this polymerization, EO was polymerized in DMF at 30°C in the presence of various amounts of MDTC. As Fig. 1 shows the time-conversion curves were straight up to 80% of conversion.

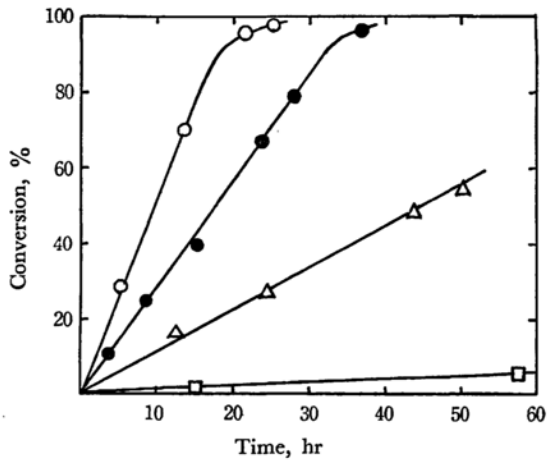


Fig. 1. Time-conversion curves.
EO 10.0 g; DMF 8.0 g; Temp. 30°C
MDTC=1.5 g (○), 0.8 g (●). 0.4 g (△) and 0.8 g (DMF none) (□)

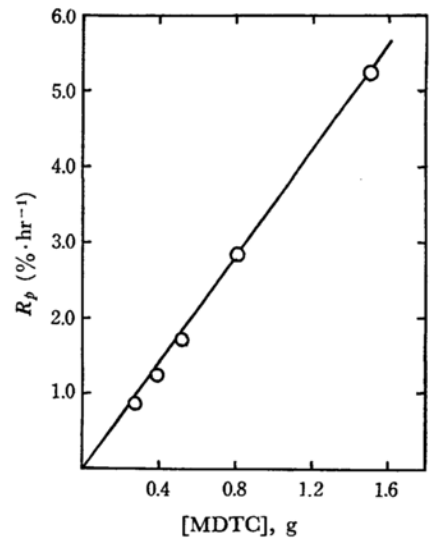


Fig. 2. Relationship between concentrations of MDTC and rates of polymerization.

The dependence of the rate of polymerization (R_p) on the concentration of MDTC is shown in Fig. 2. The relationship between the molecular weight of the resulting polymer and conversion is given in Fig. 3. These experimental results indicate the following facts; (i) the rate of polymerization is proportional to the concentration of MDTC; (ii) the molecular weight of the polymer increases gradually with conversion and (iii) the molecular weight of the polymer at the definite conversion increases with a decrease in the initial concentration of MDTC. These facts lead to the reasonable conclusion that this ring-opening polymerization proceeds through the anionic multistage polymerization mechanism, which is generally

5) For example, see a) L. E. St. Pierre and C. C. Price, *J. Am. Chem. Soc.*, **78**, 3432 (1956); b) G. Gee, W. C. E. Higgins and G. T. Merrall, *J. Chem. Soc.*, **1959**, 1345; c) E. C. Steiner, R. R. Pelletier and R. O. Trucks, *J. Am. Chem. Soc.*, **86**, 4678 (1964).

6) C. C. Price, C. D. Carmelite, R. Yamamoto and Y. Atarashi, International Symposium on Macromolecular Chem., Tokyo-Kyoto, Preprints I, p. 208 (1966).

TABLE 1. POLYMERIZATION OF EPOXIDES WITH MDTC*1

Epoxide, g		MDTC mol%	DMF ml	Product		
				Yield,*2 g	η_{rel} *3	Mol wt*4
EO	15.0	4.9	10	13.5	1.15	456
EO	14.3	3.2	0	4.3	1.11	374
PO	11.0	6.0	7	6.8	6.8	
PO	13.3	5.1	0	2.5		

*1 Temp.: room temperature Reaction time: 55 hr

*2 The product was isolated by the following procedure: the reaction mixture was poured into a large amount of ethyl acetate to form the precipitate, unreacted MDTC, which was then filtered off. The filtrate was distilled up to 80°C under 2 mmHg, giving a viscous residue in the flask, which was weighed.

*3 4% dioxane solution

*4 $[\eta]$ $(ml \cdot g^{-1}) = 0.083\, M^{0.59}$ (Ref. 5b; also see Experimental Section).

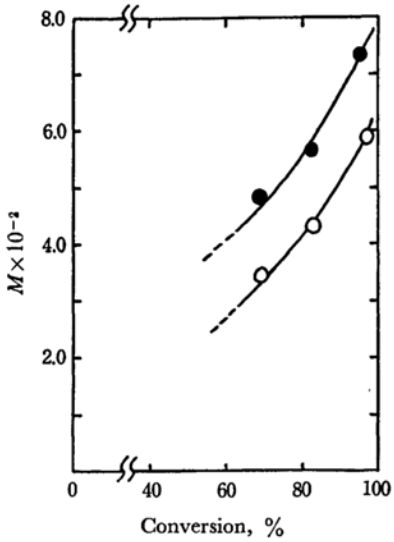


Fig. 3. Relationship between mol. wt. of polymers and conversions.
MDTC=0.8 g (●) and 1.5 g (○)

accepted for the ring-opening polymerization of epoxides with various anionic catalysts.[7] Consequently, the initiation and propagation reactions would be as follows:

$$Me_2NCSS^{\ominus}(Na^{\oplus}) + C_2H_4O \rightarrow$$

$$Me_2NCSSCH_2CH_2O^{\ominus}(Na^{\oplus})$$

$$Me_2NCSS(CH_2CH_2O)_{n-1}CH_2CH_2O^{\ominus}(Na^{\oplus}) \xrightarrow{C_2H_4O}$$

$$Me_2NCSS(CH_2CH_2O)_nCH_2CH_2O^{\ominus}(Na^{\oplus})$$

The IR spectrum (Fig. 4) of the resulting polymer shows absorptions of a double bond and of carbonyl groups, the formation of which might arise from the chain transfer or side reactions. The decolorization of bromine in carbon tetrachloride with the polymer also indicates the presence of the double bond. The treatment of the polymer with 2, 4-dinitrophenylhydrazine did not give the hydrazone, indicating that the polymer does not contain any ketone or aldehyde group. No further attempts were made to examine the chain-transfer reaction or to analyze the end groups.

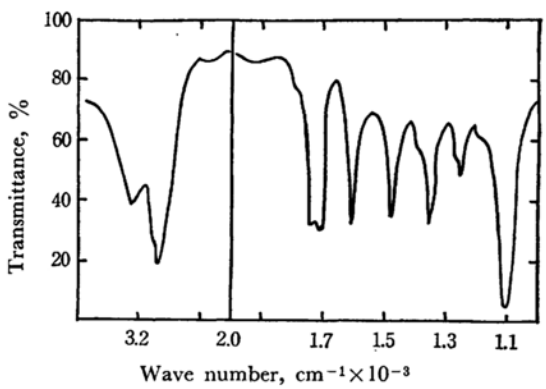


Fig. 4. IR spectrum of poly(EO) (liquid film).

According to Kagiya's equation[8] for successive high polymerizations, we tentatively calculated the catalytic activity coefficient (α), which denotes the number of active sites of MDTC:

$$\alpha = \frac{m \cdot M_p}{M \cdot C}$$

where m and M are molecular weights of the monomer and of the resulting polymer respectively, where M_p is the polymerized monomer (mol), and where C is the amount of MDTC (mol).

Table 2 indicates the α-values of MDTC thus obtained. It is surprising that the values ranged

7) For example, see a) S. Perry and H. Hibbert, *Can. J. Research*, **8**, 102 (1933); *J. Am. Chem. Soc.*, **62**, 2599 (1940); b) S. D. Holland, Brit. Pat., 821203 (1959).

8) a) T. Kagiya, M. Hatta and K. Fukui, *Kobunshi Kagaku (Chem. High Polymer)*, **20**, 737 (1963); b) T. Kagiya, T. Sano and K. Fukui, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **67**, 951 (1964); **68**, 1141 (1965).

TABLE 2. THE CATALYTIC ACTIVITY COEFFICIENT OF MDTC

C mol×10³	Time hr	M_p mol×10³	M	α
4.5	24	154	559	2.7
	28	179	568	3.0
	42	222	738	2.9
8.3	13	154	351	2.3
	17	181	450	2.2
	22	225	555	2.1

from 2 to 3; this variation cannot be reasonably explained at present. Alternatively, the application of the equation to low polymerizations remains in some doubt, since this equation has been originally devised for high-polymerization reactions.

Solvent Effect. It may be reasonably expected that the rate of polymerization is dependent on the nucleophilicity of the catalyst, varying with the nature of the solvent used. Thus, polymerizations were carried out in various aprotic solvents; the results are shown in Table 3.

TABLE 3. POLYMERIZATION IN VARIOUS SOLVENTS

Solvent	Dielectric constant	Polymerized monomer, g	Solubility of MDTC
DMF	37.6	8.4	soluble
DMSO	45.0	5.1	
CH_3CN	39.5	3.8	partially sol.
Acetone	21.2	0.5	insoluble
Dioxane	2.2	0.9	

EO 10.0 g; MDTC 0.5 g; Temp. 30°C; Time 65 hr; Solvent g

As expected, polymerization was accelerated in dipolar aprotic solvents in the following order: DMF > DMSO > CH_3CN, while the reaction was not accelerated in dioxane and acetone, in which MDTC is insoluble. This observation leads to the important conclusion that the major factor influencing the polymerization under homogeneous conditions is the enhanced nucleophilicity of the dithiocarbamate anion[9] in dipolar aprotic solvents; this is in agreement with many other observations[10] of nucleophilic substitutions and base-catalyzed reactions in these media. In the present case the catalysis of MDTC can be solely explained by the enhanced nucleophilicities of the thio anion in the initiation process and of the oxy anion in the propagation.

Catalysis of Various Dithiocarbamate Salts. Furthermore, we investigated the catalysis of various dithiocarbamate salts; the results are given in Table 4. It is not surprising that dithiocarbamate salts of bivalent metals, which are soluble in ordinary organic solvents, exhibit a small accelerating effect, or none at all, on this polymerization, since the metal-sulfur bonds in these dithiocarbamates are well-known to be chelate, not ionic bonds, and so the degree of the following dissociation is very small in solution.

$$M(SCSNR_2)_2 \rightleftarrows M^{2+} + 2R_2NCSS^-$$

It was also found that the ammonium salt of dithiocarbamate did not exhibit the catalysis on this polymerization; this implies a serious effect of the counter cation on the propagation process.

TABLE 4. CATALYSIS OF VARIOUS DITHIOCARBAMATE SALTS

Catalyst	polymerized monomer, g
$NaSCSNMe_2 \cdot 2H_2O$(MDTC)	6.6
$NaSCSNEt_2 \cdot 2H_2O$	7.7
$Nn(SCSNMe_2)_2$	2.7
$Zn(SCSNBu_2^n)_2$	0
$Ni(SCSNBu_2^n)_2$	2.0
$Et_2NHHSCSNEt_2$	0

EO 10.0 g; Catalyst 0.88 mol%; Temp. 30°C; Time 66 hr; DMF 8.0 g

Reaction of Epichlorohydrin with MDTC. Next, we attempted the reaction of epichlorohydrin (EPCl) with a small excess of MDTC in DMF. A DMF solution of MDTC was stirred into a DMF solution of EPCl to generate heat and to produce a precipitate (NaCl). After 20 hr, the mixture was poured into a large amount of water to give a white precipitate. The polymer obtained was soluble in DMF, DMSO, and acetonitrile, and was purified by reprecipitation (DMF-H_2O) to afford a white powder, which exhibited a negative Beilstein test. The reaction in DMSO gave a similar polymer. The experimental results are shown in Table 5.

Figure 5 indicates that the polymer exhibits characteristic bands of *S*-alkyl dithiocarbamate in the range from 1490 to 1375 cm^{-1} (–S–CS–N<), and ether linkage at 1140 cm^{-1} (>C–O–C<). The IR spectrum of this polymer was essentially identical with that of the polymer obtained by the reaction of epichlorohydrin rubber (V) (prepared by the Nihon Zeon Co.) with MDTC in a mixture of DMF and toluene, except in the range from 1700 to 1650 cm^{-1}. These observations indicate that the reaction of EPCl with MDTC involves the following two processes in affording the polyether

9) Dithiocarbamate anions are ranked with the strongest nucleophiles in aqueous solutions: R. E. Davis, "Survey of Progress in Chemistry," Vol. 2, ed. by A. Scott, Academic Press Inc., New York, N. Y. (1964), p. 189; R. E. Davis, H. Nakshbendi and A. Ohno, *J. Org. Chem.*, **31**, 2702 (1966).

10) For example, see a) D. J. Cram, C. A. Kingsbury and B. Rickborn, *J. Am. Chem. Soc.*, **83**, 3688 (1961); b) C. C. Price and W. H. Synder, *ibid.*, **83**, 1773 (1961); c) W. M. Weaver and J. D. Huchinson, *ibid.*, **86**, 261 (1964).

TABLE 5. REACTIONS OF EPCl WITH MDTC AT ROOM TEMPERATURE

EPCl g (mol)	MDTC mol	Solvent ml	Time hr	Product: Yield, g	Product: Elemental[a] analysis (%)	Product: $[\eta]^{30°C}_{DMF}$
9.3 (0.1)	1.8 DMF	50	20	19.0	C, 38.01; N, 7.55 H, 5.91; S, 37.74	—
4.7 (0.05)	0.08 DMF	50	19	8.3[b]	C, 37.01; N, 7.71 H, 6.00; S, 40.01	0.040
4.7 (0.05)	0.08 DMSO	50	21	12.2[c]	——	0.035

a) Calcd for $(C_6H_{11}NOS_2)_n$; C, 40.68; H, 6.21; N, 7.91; S, 36.13%.
b) Softing point 75—80°C c) Softing point 68—75°C

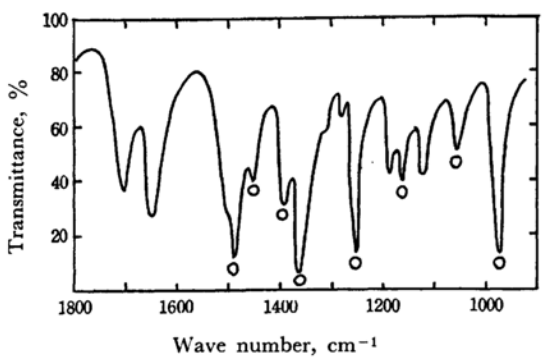


Fig. 5. IR spectrum of product from EPCl and MDTC (KBr disk). The sign ○ denotes the adsorption band observed CH_3-$SCSN(CH_3)_2$.

IV containing the dithiocarbamate moiety: the nucleophilic substitution (S_N) reaction on the chloromethyl carbon atom, and the ring-opening polymerization of the epoxy group. As is shown below, Chart, there are two possible mechanisms for the formation of the polymer IV. The first mechanism involves the initial polymerization of the EPCl catalyzed by MDTC, as has been verified above, followed by the S_N reaction (pathway a). The other consists of pathway b, which involves the initial formation of II, followed by the polymerization of II with MDTC. It seems reasonable to assume that pathway a is operative, since heat was usually evolved in the initial stage of the reaction and since EPCl reacted with less than 100 mol% of MDTC to give a viscous polymer, which exhibited a positive Beilstein test.

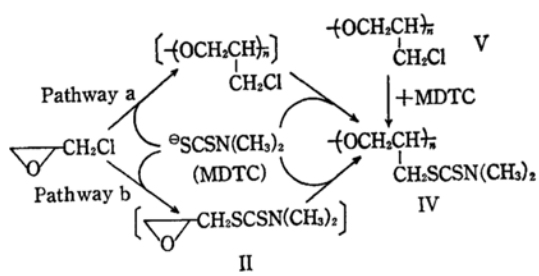
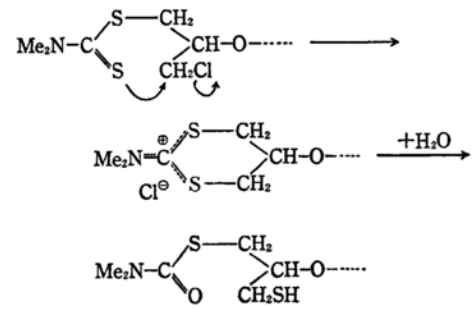


Figure 5 also indicates that the polymer IV exhibits two carbonyl bands, at 1700 and 1650 cm^{-1}. The former cannot be assigned, but the band was also observed for the polymer obtained by the polymerization of EO with MDTC (see Fig. 4). The latter band is assigned to the thiolcarbamate structure (–S–CO–N<) (1650 cm^{-1} for various *S*-alkyl *N, N*-dimethylthiolcarbamates); its formation can reasonably be explained by the following reaction sequence, involving the 1, 3-dithianylium ion (VI), through anchimerism by the dithiocarbamate function:[11]



The formation of the thiolcarbamate structure also provides another evidence for the initial polymerization of EPCl with MDTC (pathway a). Further, the equimolar reaction of EPCl with sodium *N, N*-diethyldithiocarbamate in dioxane or benzene did not give any polymeric materials, but a distillable liquid, bp 118—120°C/0.15 mmHg; n_D^{30} 1.5420. (Found: S, 31.09%. Calcd for $C_8H_{15}NOS_2$: S, 31.22%). This unidentified compound also exhibits a same strong carbonyl band at 1650 cm^{-1}. This observation gives another support to anchimerism by the dithiocarbamate function.

Experimental

Materials. *Sodium N, N-Dimethyldithiocarbamate Hydrate (MDTC).* Commercial MDTC was washed several times with chloroform and then dried *in vacuo.*

11) T. Nakai, Y. Ueno and M. Okawara, *Tetrahedron Letters,* No. 39, 3831 (1967).

According to the reported method,[12] it was determined that this salt contained two molecules of coordinated water. The other dithiocarbamate salts used were available commercially and were employed without further purification.

Epoxides and Solvents. EO and PO were purified by distillation over solid potassium hydroxide. EPCl was purified by distillation. The solvents employed were purified by the usual methods.

Polymerization Procedure. A purified, anhydrous monomer and the solvent were added to a given amount of MDTC in a hard-glass tube at −78°C. The tube was then sealed and immersed in the stirring-thermostat adjusted at 30°C. After a given interval, the tube was removed from the thermostat and opened at −78°C. The unreacted monomer was readily removed on the steam-bath. From the decrease in the weight observed, the weight of the polymerized monomer was calculated.

Procedure of Isolating the Polymer. Anhydrous benzene (*ca* 80 m*l*) was added to the reaction mixture, and the precipitate formed was removed off using the centrifuge. The benzene and the solvent were removed by heating the clear solution to 80°C under reduced pressure (1 mmHg), thus producing a viscous residue. Viscosity measurements were made in dioxane solutions with an Ostwald viscometer at 30°C. The molecular weight of the polymer was calculated using Gee's equation,[5b] $[\eta]$ $(ml \cdot g^{-1}) = 0.083\, M^{0.59}$. It has been verified that molecular weights ranging from 300 to 5100 can be determined by this equation, although no high precision is claimed.

Reaction of EPCl with MDTC. To a solution of 4.7 g (0.05 mol) of EPCl in 15 m*l* of DMF, 15 g (0.08 mol) of MDTC in 35 m*l* of DMF were added, little by little, at room temperature; the mixture was then stirred for 19 hr at room temperature. The white precipitate formed (NaCl) weighed 2.8 g (0.05 mol). The mixture was stirred into a large amount of water to give a white precipitate, which was collected by filtering and then dried *in vacuo* (yield 8.3 g). The product was purified by reprecipitation (DMF-H_2O). The reaction conditions and the results of individual experiments are shown in Table 5.

IR Spectra. The IR spectra were measured using a Hitachi Model EPI-2 Infrared Spectrometer.

12) D. G. Clarke *et al.*, *Anal. Chem.*, **23**, 1842 (1957).