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REACTIVE IONIC OLIGOMERS. I. PRECURSORS FOR WATER-SOLUBLE CATIONIC POLYMERS OBTAINED BY THE REACTION OF DIMETHYLAMINE WITH EPICHLOROHYDRIN

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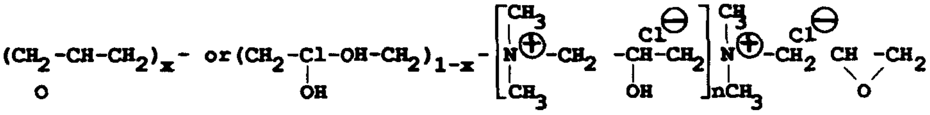
ABSTRACT

The reaction between dimethylamine and epichlorohydrin (in excess) was studied with the purpose of obtaining compounds with ammonium quaternary groups and reactive groups like 2,3-epoxypropyl and 2-hydroxy-3-chloropropyl. It was found that the ionic products of this reaction are mixtures of oligomers described by the following chemical formula:



$$(\underset{O}{CH_2-CH-CH_2})_x-\text{ or }(CH_2-\underset{OH}{Cl}-OH-CH_2)_{1-x}-\left[\overset{CH_3}{\underset{CH_3}{N^{\oplus}}}-CH_2\ -\overset{Cl^{\ominus}}{\underset{OH}{CH}}-CH_2\right]_n\overset{CH_3}{\underset{CH_3}{N^{\oplus}}}-CH_2\overset{Cl^{\ominus}}{}\ \underset{O}{CH\ -CH_2}$$

where, depending of the reaction conditions, the parameters *n* and *x* take values in the ranges 0–1.5 and 0–0.75, respectively. It is shown how these structure parameters are affected by the ratio of reactants, the solvent, the temperature, and the time of reaction.

INTRODUCTION

Functionalized oligomers offer an attractive way to induce new properties for common polymers. For example, it was reported recently that

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a network of epoxy resins can be modified by using oligomers with reactive groups [1].

There are few studies about the synthesis of ionic and reactive oligomers. Possible routes to these compounds are given by the reaction of epichlorohydrin (ECH) with amines. For example, the reaction with ammonia and primary amines leads, under certain conditions, to tertiary amines substituted with two or three 2,3-epoxypropyl groups [2–4]. Reaction with secondary amines generates *N,N*-dialkyl-2,3-epoxypropylamines [5, 6] or cationic polymers like poly[(*N,N*-dialkyl-2-hydroxypropylene ammonium)chloride] [7]. *N,N′*-Dimethyl-bis(2,3-epoxypropyl)polymethylenediamine, formed from the reaction of the corresponding secondary amines with ECH [8], was used to modify cellulose to generate anion-exchange resins [9]. Other compounds mentioned in the literature obtained by reacting ECH with tertiary amines are 2,3-epoxypropyl monosubstituted ammonium quaternary salts [10], ammonium diquaternary salts [11], and [(3-hydroxy-1-propenyl)trimethyl-ammonium]chloride [12].

There is little information regarding the use of the reaction between ECH and secondary amines to get low molecular compounds or oligomers containing ammonium quaternary salt groups and reactive groups on the same molecule.

The present paper shows some results of the reaction between ECH with dimethylamine (DMA) which was carried out at ECH/DMA molar ratios higher than 1.5:1. The purpose of this study was to find the reaction conditions of epoxide and ammonium quaternary salt groups which would lead to precursors of cationic polymers.

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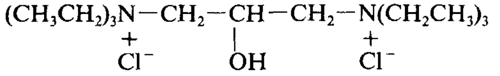
EXPERIMENTAL

Materials

DMA was used as solutions in water, anhydrous ethanol, and chloroform. *ECH was purified before being used by boiling on KOH for 8 h* followed by distillation at atmospheric pressure; only the 116–117°C fraction was retained. The following compounds were used as received: anhydrous ethanol (EtOH anh.), chloroform ($CHCl_3$), acetone, and anhydrous diethylether.

[2-Hydroxytrimethylene-1,3-bis(triethylammonium)] chloride (Bis Q) was synthesized in order to aid in the interpretation of ^{1}H-NMR spectra of the reaction products. Bis Q was obtained by reacting ECH and triethylamine hydrochloride (TEA.Ch) under the following conditions: ECH/TEA.Ch = 1:1, EtOH anh. as the reaction medium, 50°C, and a reaction time of 50 h. The final reaction mixture was treated with anhydrous diethylether. Bis Q was obtained as a crystalline product from the insoluble fraction after a washing with acetone. A final purification was carried out by recrystallization from dimethylformamide.

Elemental analysis for



$$\underset{\mathrm{Cl}^-}{\overset{+}{(\mathrm{CH_3CH_2})_3\mathrm{N}}}-\mathrm{CH_2}-\underset{\mathrm{OH}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\underset{\mathrm{Cl}^-}{\overset{+}{\mathrm{N}(\mathrm{CH_2CH_3})_3}}$$

(Bis Q)

Calculated: C, 54.38%; H, 10.87%; N, 8.46%; Cl_i, 21.45%. Found: C, 54.69%; H, 10.52%; N, 8.13%; Cl_i, 21.05%.

^{1}H-NMR spectrum in DMSO-d_6 at 100°C: 1.2 ppm, triplet arising from all methyl groups; 3.75 ppm, multiplet resulting from the overlap of signals from the two types of methylene groups; and 4.9 ppm, unresolved multiplet arising from methine protons.

Methods

All reactions of ECH with DMA were carried out in a 250-mL glass reactor provided with stirrer, thermometer, dropping funnel, and heating mantle. First, ECH was poured into the reactor, and the temperature was adjusted to 18°C. Then the solution of DMA was dropped to such a low flow rate that the temperature was maintained at 18–20°C. Reaction progress was monitored by analyzing samples extracted at various times. In order to separate the ionic products, these samples were treated with acetone (when the reaction was carried out in water) or anhydrous diethylether (when the reaction was carried out in EtCH anh. or $CHCl_3$). The products were dried under vacuum with P_2O_5. Secondary reaction products and the unreacted ECH were isolated by fractional distillation.

All reaction products were characterized by IR spectroscopy and elemental analysis. Additionally, the ionic products were characterized by ^{1}H-NMR spectroscopy from which the epoxide group content was determined. The identification of ^{1}H-NMR signals arising from OH and epoxide groups was realized by an *in-situ* acidification with CF_3COOH. The epoxide coefficient (EC), defined as the epoxide group equivalent per 100 g of sample, was determined by HBr addition in glacial acetic acid [13].

The IR spectra were recorded on a Perkin-Elmer Model 577 spectrom-

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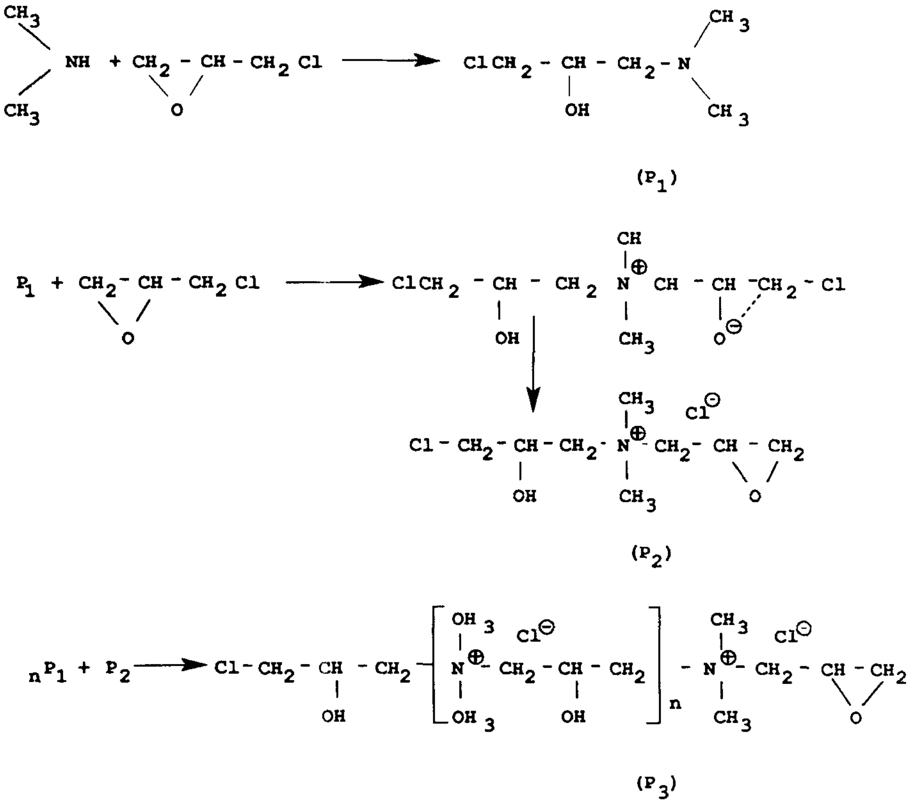

SCHEME 1.

eter. The ^{1}H-NMR spectra were obtained at 60 MHz on a JNM-C-60 HL spectrometer by using DSMO-d_6 as the solvent.

RESULTS AND DISCUSSION

It is known that the main reaction between ECH and dialkylamines is determined by the nucleophilic attack of the amine on the epoxide ring [2, 14], but other reactions are expected to occur when ECH is taken in excess. A possible mechanism of the reaction between ECH and DMA at a ECH/DMA molar ratio > 1 is presented in Scheme 1.

It is observed that the formation of the products P_2 and P_3 is supposed to take place by a nucleophilic attack of the tertiary amine P_1 on the epoxide groups of ECH and P_2 product, respectively.

The Average Chemical Structure of Ionic Reaction Products

The reaction conditions and the analytical characteristics of the ionic products obtained by reacting ECH and DMA are given in Table 1.

The ^{1}H-NMR spectrum of the product D_1, which is quite similar to the spectra of the other products in Table 1, is shown in Fig. 1.

By comparing this spectrum with the spectra of known compounds which contain glycidyl groups, it is concluded that the multiplet signal at 2.5–3.1 ppm arises from the CH_2 protons in an epoxide ring. Also, the presence of H_3C-N^+ groups is confirmed by the strong singlet signal at 3.3 ppm, and the absence of any signal at 2.0–2.5 ppm excludes the presence of H_3C-N groups. The assignment of the signal at 5.0 ppm is based on the spectrum of Bis Q compound (see the Experimental Section). It is concluded that the product D_1 has the chemical structure of compound P_3 in Scheme 1. It should be mentioned that the relative intensity of the signal at 5.0 ppm, which arises from the proton CH in $^+N-CH_2-CH(OH)-CH_2-N^+$ groups, is a measure of the degree of oligomerization.

The proposed structure of P_3 is not comprehensive enough to describe all the products in Table 1.

A decrease in the content of covalent chlorine (Cl_c) and a simultaneous increase of EC with reaction time have been observed, especially for ECH/DMA ratios $> 2/1$ (Fig. 2 and Samples F and G, Table 1).

In these cases the value of the (Cl_c/EC) ratio is lower than 35.5 – a value corresponding to the product P_3. This fact can be explained by assuming a partial transformation of chlorohydrin groups into epoxide groups if the mechanism in Scheme 2 is taken into account.

This transformation mechanism is based on the nucleophilic attack of Cl^- anion on the epoxide ring, which generates 1,3-dichloro-2-propanol. For example, in the case of the G_4 product the molar ratio between this compound and DMA was found to be about 1/2. The ^{1}H-NMR spectrum of the G_4 product also contains of signal at 2.6–3.1 ppm which corresponds to a structure similar to a diepoxide compound (Fig. 3).

Consequently, it is concluded that the ionic products in Table 1 are mixtures with the general formula P:

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TABLE 1. The Ionic Products Obtained by Reacting ECH and DMA: According to Formula P

	Reaction conditions					
Sample	ECH/DMA molar ratio	Solvent	Temperature, °C	Time, h	Cl_i, %	Cl_t, %
A_1	2/1	H_2O	30	0	18.00	26.00
A_2	2/1	H_2O	30	3	17.27	28.92
B_1	12/1	H_2O	50	3	16.91	22.68
B_2	2/1	H_2O	50	6	17.22	22.77
C_1	1.6/1	H_2O	30	0	18.13	26.37
C_2	1.6/1	H_2O	30	1	17.56	25.95
C_3	1.6/1	H_2O	30	2	17.49	26.36
C_4	1.6/1	H_2O	30	3	17.29	26.31
D_1	2/1	EtOH	30	0	17.34	27.45
D_2	2/1	EtOH	30	1	16.78	26.94
D_3	2/1	EtOH	30	2	15.87	27.95
D_4	2/1	EtOH	30	3	15.78	28.24
D_5	2/1	$CHCl_3$	30	3	16.64	25.75
F_1	6/1	EtCH	30	0	14.84	28.75
F_2	6/1	EtCH	30	1	14.91	27.04
F_3	6/1	EtOH	30	3	15.10	25.03
F_4	6/1	EtOH	30	5	15.83	23.96
F_5	6/1	EtOH	30	9	15.96	23.38
F_6	6/1	EtCH	30	20	16.25	21.93
G_1	10/1	EtCH	30	0	14.59	29.77
G_2	10/1	EtOH	30	3	15.57	23.22
G_3	10/1	EtOH	30	8	15.87	21.77
G_4	10/2	EtOH	30	20	16.95	20.75
$(P_2)^c$	—	—	—	—	15.43	30.86

[a] Cl_i = ionic chlorine; Cl_t = total chlorine; Cl_c = covalent chlorine = $Cl_t - Cl_i$; EC = epoxide coefficient.

[b] M = the molecular weight; n = the degree of oligomerization; x = the degree of transformation of chlorohydroxypropyl groups into epoxide groups.

[c] Calculated values for $C_8H_{17}NO_2Cl_2$.

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Reaction Conditions, Analytical Data, and Parameters of Structure

Analytical data[a]				Parameters of structure[b]		
Cl_c, %	EC, epoxy equiv/100 g	Cl_i/EC	Cl_c/EC	M	n	x
8.00	0.227	79.30	35.20	443.70	1.24	0.004
10.05	0.276	62.70	36.20	358.60	0.75	0.017
5.77	0.310	54.50	18.60	422.60	1.01	0.312
5.55	0.268	64.20	20.70	473.30	1.28	0.263
8.24	0.218	83.20	37.80	444.00	1.27	−0.030
8.39	–	–	–	–	–	–
8.87	–	–	–	–	–	–
9.02	0.240	72.00	37.60	406.00	0.97	−0.030
10.11	0.278	62.20	36.60	355.00	0.73	−0.011
10.16	0.281	60.00	36.40	353.00	0.67	−0.012
12.08	0.374	42.50	32.20	279.00	0.25	0.067
12.46	0.395	40.00	31.60	268.00	0.19	0.058
9.11	0.357	46.60	25.50	326.00	0.53	0.164
13.91	–	–	–	–	–	–
12.13	0.390	38.20	31.10	273.00	0.15	0.070
9.93	0.535	28.20	18.60	245.00	0.04	0.310
8.13	–	–	–	–	–	–
7.42	–	–	–	–	–	–
5.68	0.544	29.90	10.40	284.00	0.30	0.550
15.18	0.429	33.95	35.35	233.50	−0.05	0.002
7.65	0.585	26.66	13.08	256.00	0.10	0.440
5.90	0.643	24.70	9.17	247.30	0.10	0.590
3.80	0.742	22.80	5.12	236.70	0.12	0.750
15.43	0.435	–	–	230.00	0	0

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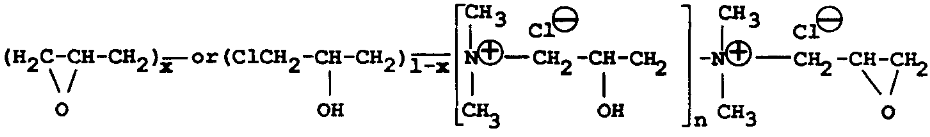

(P)

This general structure is also confirmed by the IR spectra (Fig. 4) where the following characteristic absorption bands are present: 860, 920, and 1260 cm^{-1} for epoxide rings; 690 cm^{-1} (weak) for C—Cl bonds; and 1050–1100 cm^{-1} for OH groups. It was observed that the characteristic epoxide ring bands are more intense if the products are obtained with a higher ECH/DMA molar ratio.

Dependence of Chemical Structure on the Reaction Conditions

According to the general chemical formula P, each product in Table 1 can be characterized by the parameters *n* (the degree of oligomeriza-

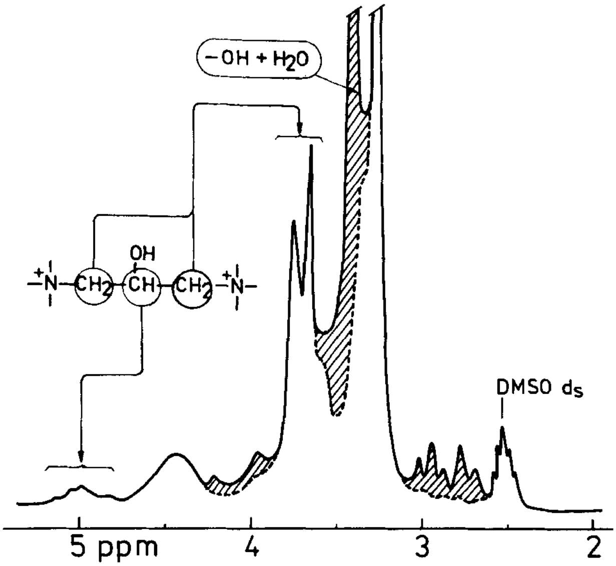

FIG. 1. ^1H-NMR spectrum of the product D_1 in DMSO-d_6 at 40°C. The cross-hatched signals disappear upon acidification with CF_3COOH.

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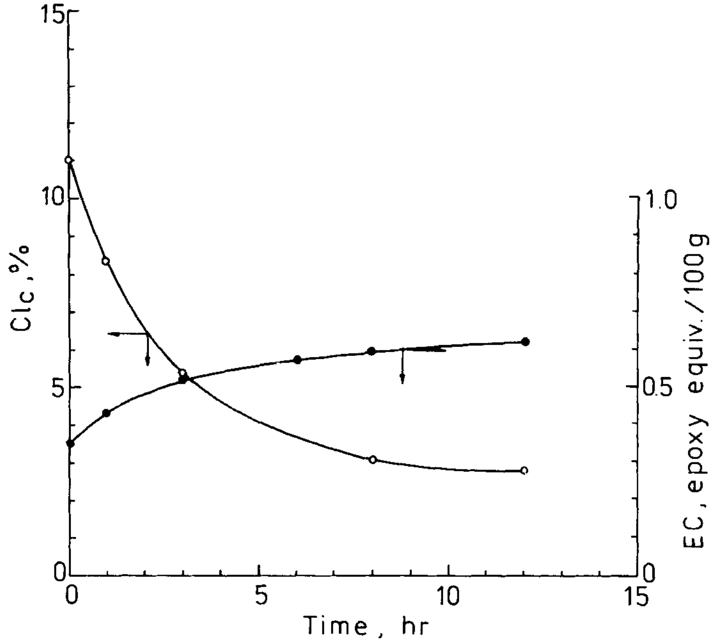

FIG. 2. Dependence of Cl_c (○) and EC (●) contents on reaction time. Reaction conditions: EtOH anh., 30°C, ECH/DMA = 3:1.

tion) and x (the degree of transformation of chlorohydroxy propyl groups into epoxide groups).

In order to determine these parameters, the following experimental data were used: the percent ionic chlorine (Cl_i), the percent total chlorine (Cl_t), the percent covalent chlorine (Cl_c) = $Cl_t - Cl_i$, and EC.

By considering the general formula P, the following equations can be formulated:

$$Cl_i = \frac{(n + 1) \times 35.5 \times 100}{M} \tag{1}$$

$$Cl_c = \frac{(1 - x) \times 35.5 \times 100}{M} \tag{2}$$

$$EC = \frac{(1 + x) \times 100}{M} \tag{3}$$

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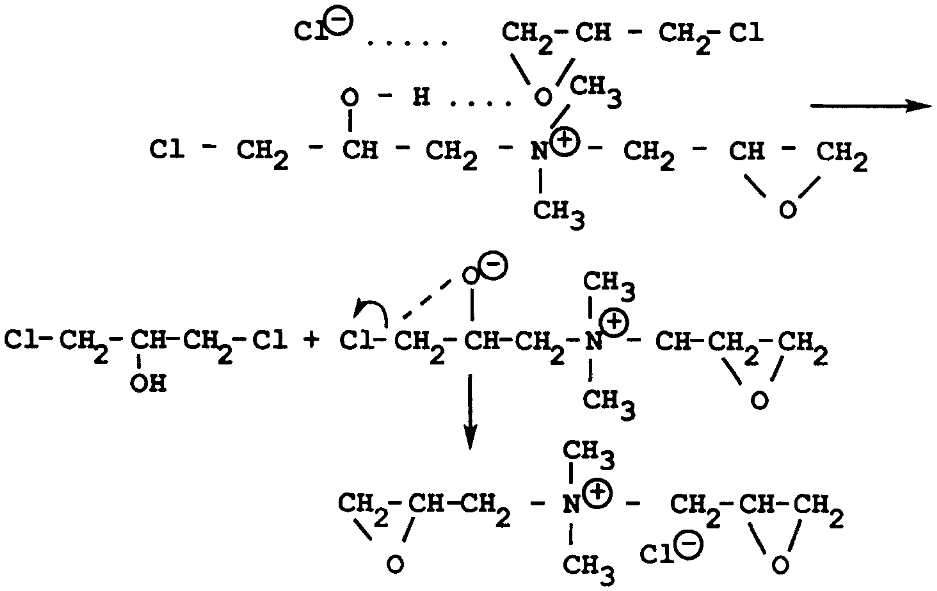

SCHEME 2.

where M is the molecular weight.

By using Eqs. (1), (2), and (3), the following relationships for structural parameters can be derived:

$$n = \frac{2(\mathrm{Cl_i/EC})}{35.5 + (\mathrm{Cl_i/EC})} - 1 \qquad (4)$$

$$x = \frac{35.5 - (\mathrm{Cl_c/EC})}{35.5 + (\mathrm{Cl_c/EC})} \qquad (5)$$

$$M = \frac{7100}{\mathrm{Cl_c} + 35.5 \times \mathrm{EC}} \qquad (6)$$

The number 35.5 in these equations is the value of the (Cl_c/EC) ratio for $n = 0$ and $x = 0$ for compound P_2 in Scheme 1. This compound is best described by the product G_1 in Table 1.

The values of n and x determined for each reaction product are also

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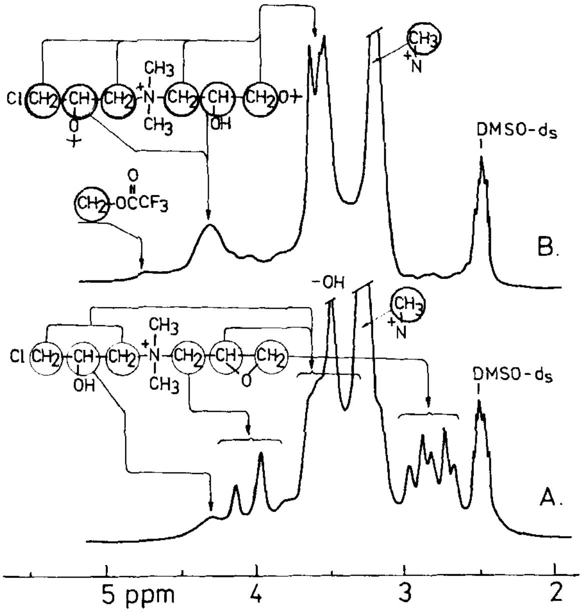

FIG. 3. ^{1}H-NMR spectra of the product G_4. (A) The spectrum of a solution in DMSO-d_6 at 40°C. (B) The spectrum of the same solution after acidification with CF_3COOH.

given in Table 1. Some effects of the reaction conditions on the chemical structure are described below.

Solvent Effects

By comparing the products A_2, D_4, and D_5, which are obtained at ECH/DMA = 2/1, 30°C, a reaction time of 3 h, and different solvents, it is observed that $n_{(H_2O)} > n_{(CHCl_3)} > n_{(EtOH)}$ and $x_{(CHCl_3)} > x_{(EtOH)} \simeq x_{(H_2O)}$. This indicates that water promotes oligomerization better than EtOH and $CHCl_3$.

Temperature Effects

By comparing the products A_2 and B_1, it is observed that the parameter x increases with temperature, at least for the following conditions:

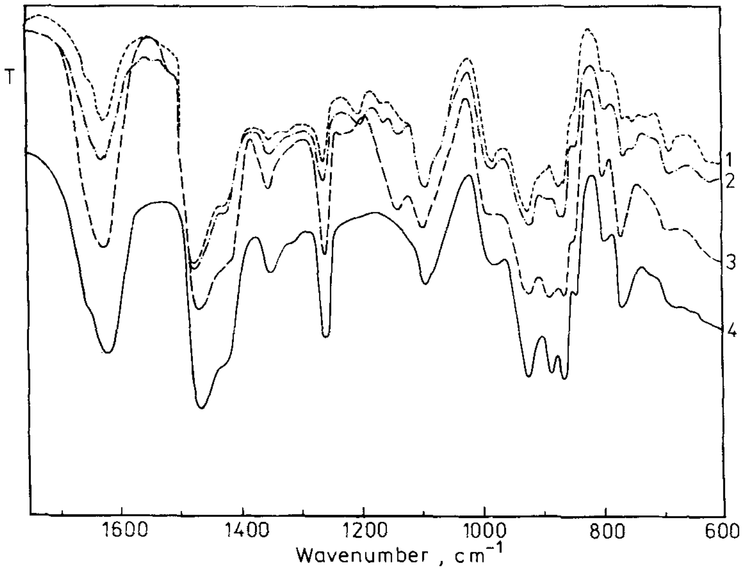

FIG. 4. IR spectra of some products obtained in EtOH at 30°C: (1) ECH/DMA = 2:1, collected at the beginning of reaction (D_t): (2) ECH/DMA = 2:1, after 3 h (D_4); (3) ECH/DMA = 3:1, after 8 h (Fig. 2); and (4) ECH/DMA = 6:1, after 20 h (F_6).

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ECH/DMA = 2/1, water as solvent, and a reaction time of 3 h. No clear effect is observed for *n*.

Effects of ECH/DMA Ratio

Parameter *x* increases with the ECH/DMA ratio, at least for the following conditions: EtOH as solvent, 30°C, and a reaction time of 3 h (the products D_4, F_3, and G_2). It seems that the parameter *n* decreases with the ECH/DMA ratio.

Effects of Reaction Time

These effects cannot be well separated from those of the ECH/DMA molar ratio and the solvent. However, the following observations are of interest: 1) *n* decreases with the reaction time if the ECH/DMA ratio

= 1.6–2 (see products C and D), but no effect is observed if the ECH/DMA ratio is higher (see product G); 2) x increases with the reaction time, especially for high ECH/DMA ratios (see products F and G).

The decrease of n with reaction time can be explained by supposing that the oligomers with $n > 1$ appear predominantly at the beginning of the reaction; fragmentation of molecules is less likely.

CONCLUSIONS

The ionic products obtained in the reaction of DMA and ECH (in excess) are generally mixtures with the chemical formula P.

Oligomerization is promoted by water as the solvent and an ECH/DMA molar ratio lower than 2/1. It is proposed that this process occurs predominantly at the beginning of the reaction. For the reaction conditions in the present study, the degree of oligomerization n does not exceed 1.5.

The transformation of chlorohydroxy propyl groups into epoxide groups is favored by high ECH/DMA ratios, long reaction times, and temperature.

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