Polymer Bulletin 1, 73-77 (1978)

Polymer Bulletin

Cationic Oligomerization of Isobutylene Oxide

Yuya Yamashita, Katsumi Iwao and Koichi Ito

Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464, Japan

Dioxolane type dimer and trioxane type trimer were the principal product in the cationic polymerization of isobutylene oxide at room temperature. At low temperature polymer formation accompanied by dioxane type dimer through back-biting reaction was predominant. At room temperature, hydride transfer occurs easily to form isomerized oligomers. The effect of solvents and initiators was discussed in correlation with the mechanism.

Introduction

In recent years it has become evident that cationic polymerization of cyclic monomers may lead to polymers containing considerable amounts of cyclic oligomers as reviewed by GOETHALS (1977). Since the discovery of crown ethers, oligomerization of epoxides has been interested as a new synthetic method of macrocyclic compounds. However, the mechanism of the oligomerization is still obscure except for the case of ethylene oxide by DALE (1977), and it seems necessary to clarify the effect of substituents and reaction variables on the selectivity of oligomer formation. In the case of isobutylene oxide, KAMBARA et al (1963) and VANDENBERG (1972) reported on the formation of oligomeric products in cationic polymerization, but the detailed nature of the reaction has not been clarified. In the present communication, the structure and distribution of cyclic oligomers in cationic polymerization of isobutylene oxide is discussed in correlation with mechanism.

Experimental

Monomer and solvents were dried and distilled by the usual procedure. Polymerization was carried out

0170-0839/78/0001/0073/$01.00

by adding isobutylene oxide dropwise during fifteen minutes to the initiator solution kept at fixed temperature and stirred for two hours. The reaction was terminated with triethylamine and the product distribution was determined by gas chromatography by using n-decane as an internal standard. Each product was identified by NMR, IR and MS.

Results and Discussion

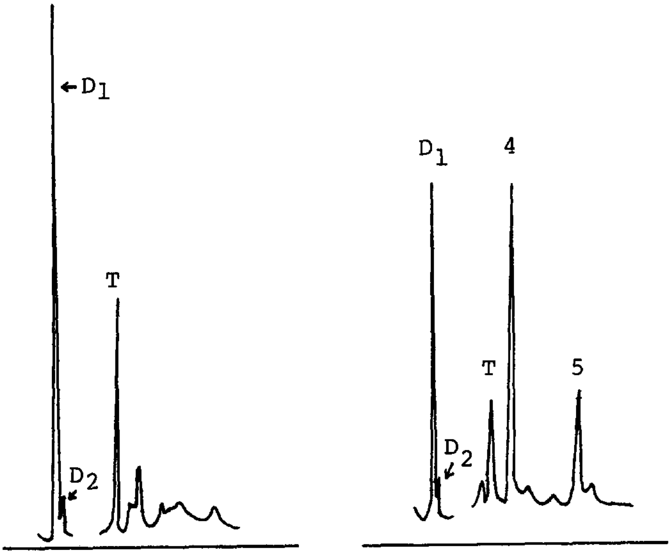
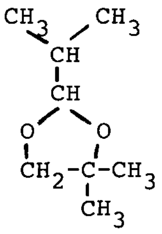
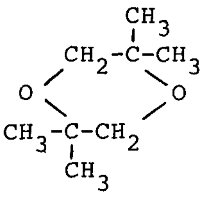


Fig. 1 Gaschromatogram of isobutylene oxide oligomers formed in dimethoxyethane at 20°C.
a) $BF_3\ Et_2O$ b) CF_3SO_3H

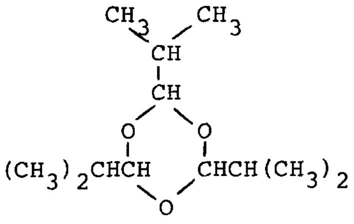
Typical chromatogram is shown in Figure 1. Two types of dimers and a trimer were isolated and confirmed to consist of the following structure.



D1



D2



T

D_1 : bp 135°C, NMR($CDCl_3$) δ 0.95 (6H, d, CH_3), 1.45 (6H, s, CH_3), 1.5~2.0 (1H, m, CH), 3.65 (2H, s, CH_2), 4.9 (1H, d, CH)
D_2 : bp 140°C, NMR($CDCl_3$) δ 1.12 (12H, s, CH_3), 3.34 (4H, s, CH_2)
T : mp 64°C, NMR($CDCl_3$) δ 0.95 (18H, d, CH_3), 1.5~2.2 (3H, m, CH), 4.55 (3H, d, CH)

TABLE 1.

Product distribution in oligomerization of isobutylene oxide[a)]

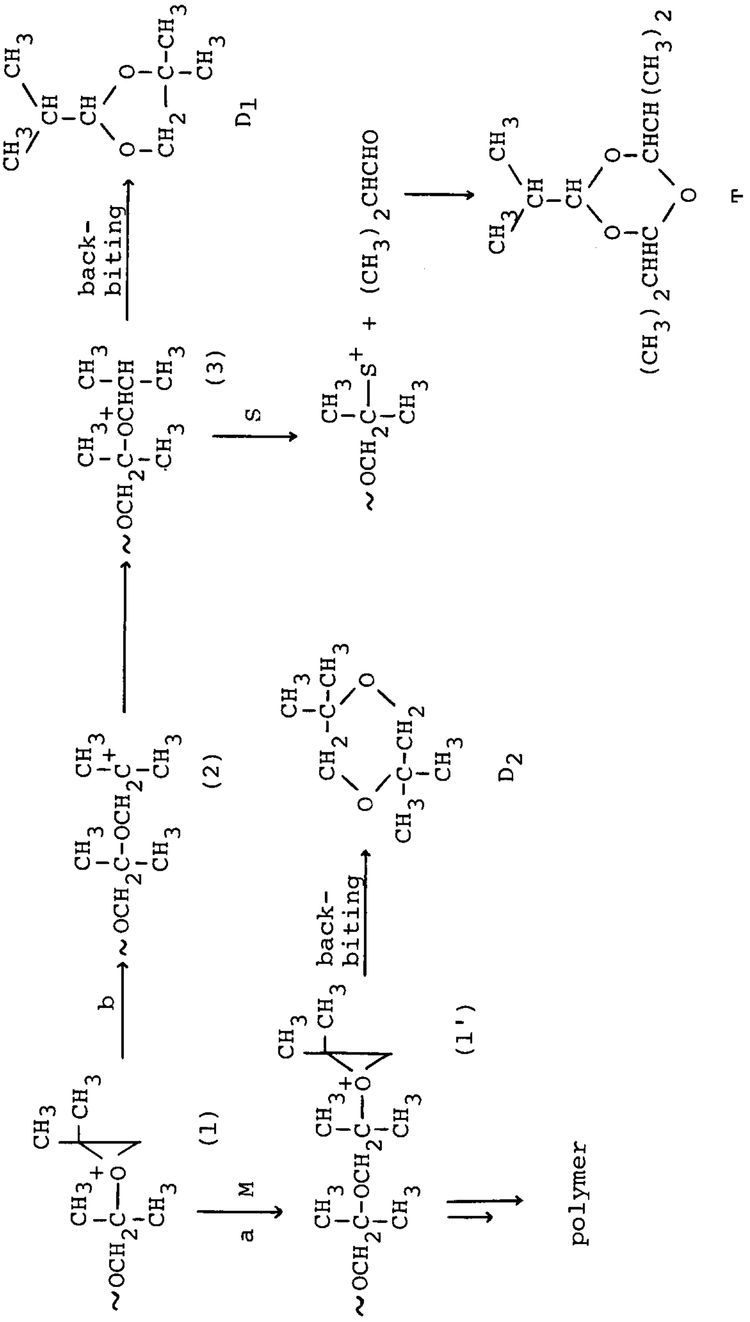
		Conversion	Yield%(based on IBO)		
Solvent	°C	%	D_1	D_2	T
dimethoxyethane	20	37.0	16.2	1.4	10.4
dimethoxyethane	-40	83.9	7.4	3.4	0.0
dioxane	20	36.4	13.7	1.8	13.4
nitromethane	20	73.7	47.4	3.6	0.0
dichloromethane	20	86.6	12.9	2.4	0.0
toluene	20	77.7	54.3	3.3	2.2
toluene	-40	87.6	35.8	5.4	0.0
toluene	-78	68.3	17.2	4.6	0.0
dimethoxyethane[b)]	20	78.7	20.3	0.8	0.8
toluene[b)]	20	91.5	22.3	0.8	0.3

a) $[M]_{overall}$=1.0 M, $[I]_{overall}$=0.1 M, $BF_3 \cdot Et_2O$, 2 hr.
b) CF_3SO_3H instead of $BF_3 \cdot Et_2O$

Table 1 shows the effect of the solvent and the initiator on the product distribution. The product consisted of oligomer and polymer. In case of Lewis acid such as boron fluoride etherate or stannic chloride as catalyst, dioxolane type dimer (D_1) was predominant accompanied with trimer (T) and small amount of dioxane type dimer (D_2). The structure of the polymer was found to consist of the normal head to tail structure and acetal proton formed by isomerization was not found in the NMR spectrum of the polymer. At lower temperature, the formation of D_1 and T was suppressed and the polymer becomes the main product of the reaction. The effect of solvent is noticeable, and the formation of T increased in dioxane and in dimethoxyethane although the reaction was considerably slow, but D_1 formed rapidly as the principal component in toluene and nitromethane.

Higher oligomers above trimer were formed in considerable amounts in the case of trifluoromethane sulfonic acid catalyst. Isolated oligomers by vacuum distillation correspond to tetramer and pentamer con-

SCHEME



taining principally isomerized structure by NMR. Addition of sodium and potassium tetrafluoroborate to the polymerization mixture did not change the product distribution, showing little tendency of the chelate formation as observed by DALE and DAASVATN (1976).

These results may be explained by the following scheme. At low temperature, polymerization proceeds through path a, but at room temperature S_N1 opening of the cyclic oxonium ion (1) proceeds through path b. The tertiary carbenium ion (2) easily isomerizes to oxycarbenium ion (3) by hydride transfer. Dioxolane type dimer (D_1) is formed by back-biting reaction of this oxycarbenium ion. In toluene and nitromethane, this becomes the main reaction path. In dioxane and dimethoxyethane, the oxycarbenium ion (3) is susceptible to nucleophilic attack by the ether oxygen atom and isobutyraldehyde is formed, which trimerizes to cyclic trimer (T). At low temperature, the cyclic oxonium ion (1) is relatively stable and polymer formation accompanied by dioxane type dimer (D_2) formed by back-biting reaction seems to be the predominant path.

DALE, J., and K. Daasvatn: J. Chem. Soc., Chem. Comm., 295 (1976)
DALE, J. et al: Makromol. Chem., 178, 873 (1977)
GOETHALS, E. J. : Adv. Polym. Sci., 23, 103 (1977)
KAMBARA, S. et al: Kobunshi Kagaku, 20, 497 (1963)
VANDENBERG, E. J. : J. Polym. Sci., A1, 10, 329 (1972)

Received June 5, 1978.