Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Oligomerization of Substituted Phenyl Glycidyl Ethers with Tertiary Amine

Yoshio Tanaka[a]; Masao Tomio[ab]; Hiroshi Kakiuchi[a]
[a] DEPARTMENT OF APPLIED CHEMISTRY, FACULTY OF ENGINEERING, YOKOHAMA NATIONAL UNIVERSITY, YOKOHAMA, JAPAN [b] Showa Electro-Chemical Industry Co., Ltd., Kawasaki, Japan

To cite this Article Tanaka, Yoshio , Tomio, Masao and Kakiuchi, Hiroshi(1967) 'Oligomerization of Substituted Phenyl Glycidyl Ethers with Tertiary Amine', Journal of Macromolecular Science, Part A, 1: 3, 471 — 491

To link to this Article: DOI: 10.1080/10601326708053984

URL: http://dx.doi.org/10.1080/10601326708053984

J. MACROMOL. SCI. (CHEM.), A1(3), 471–491 (1967)

Oligomerization of Substituted Phenyl Glycidyl Ethers with Tertiary Amine*

YOSHIO TANAKA, MASAO TOMIO,†
and HIROSHI KAKIUCHI
DEPARTMENT OF APPLIED CHEMISTRY,
FACULTY OF ENGINEERING,
YOKOHAMA NATIONAL UNIVERSITY,
MINAMI-KU, YOKOHAMA, JAPAN

Summary

The oligomerization of substituted phenyl glycidyl ethers was studied kinetically in the presence of dimethylbenzylamine using toluene or dioxane as a solvent. The infrared spectra of the resultant oligomers suggest that the reaction products have the internal carbon-carbon double-bond unsaturation, which is confirmed by the catalytic hydrogenation. The molecular weights of the oligomers also suggest that γ-phenoxy allyl alcohol produced by the initial reaction step, in which the γ-proton of phenyl glycidyl ether is attracted by a base, amine, reacts with other phenyl glycidyl ether and thus proceeds further, yielding the oligomer. The value of the reaction constant ρ is obtained positive for this reaction, which indicates that electron-withdrawing substituents of phenyl gylcidyl ethers increase the rate of oligomerization. A kinetic analysis shows that the proposed reaction sequence accounts for all the characteristics of the polymerization including sigmoidal shapes of monomer consumption curves, reaction rates, and induction periods.

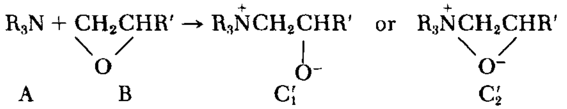
Several workers have studied the polymerization of phenyl glycidyl ether (PGE) by tertiary amines (*2–6*). The mechanism of polymerization, however, including roles of amine and proton-supplying substances such as water and alcohol, propagating species, and property of polymers, have been somewhat obscure.

---

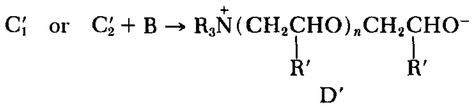
[*] Part X in a series on epoxy compounds (*1*).

[†] Present address: Showa Electro-Chemical Industry Co., Ltd., Chidorimachi 5, Kawasaki, Japan.

The first study of the polymerization mechanism was reported by Narracott. (2). He found that the polymer of PGE formed with various tertiary amines divided into two crystalline (molecular weights of 1200 and 950, respectively) and a viscous liquid (molecular weight of 800) fractions containing about one hydroxyl group per molecule together with 0.2 or 0.3 percentages of nitrogen, and that a small quantity of gas evolved was identified as ethylene, nitrogen, oxygen, and amine. He also stated that water and alcohol accelerated the polymerization and suggested the anionic mechanism for this polymerization as shown below.



(1)

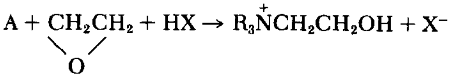


$$C_1' \text{ or } C_2' + B \rightarrow R_3\overset{+}{N}(CH_2\underset{R'}{CH}O)_nCH_2\underset{R'}{CH}O^- \qquad (2)$$

D'

where R are the alkyl groups such as ethyl, *n*-propyl, and *n*-butyl, R' is $C_6H_5OCH_2-$ and $n = 1, 2, \ldots$

Eastham and his co-workers (7,8) considered that the reaction of ethylene oxide with amines followed the same course (3), whether or not amine contained hydrogen attached to nitrogen:



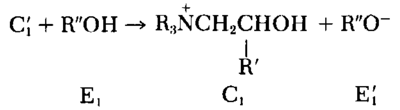
(3)

where HX is a proton-supplying substance. In aqueous solution the reactions were independent of the proton-supplying substance. When the reactions were conducted in pure amine solution they were sensitive to the proton source and the rate was proportional to the concentrations of ethylene oxide and the proton source.

Schechter and Wynstra (3) studied the reaction of PGE with isopropyl alcohol using benzyldimethylamine or dimethylaniline, and reported that after a nearly complete consumption of epoxide, about 80% of the charged alcohol was recovered unreacted, indicating that the reaction was largely a self-polymerization of epoxide. The reaction rate was sharply dependent on hydroxyl concentration; in the absence of alcohol this catalyst did not polymerize PGE.

Hence, he considered the following mechanism: A quaternary base C_1' is generated from the amine and the epoxide as shown by

Eq. (1). This base then reacts with alcohol to form a new alkoxide ion which can continue to add epoxide;


(4)

$$C_1' + \underset{E_1}{R''OH} \rightarrow \underset{C_1}{R_3\overset{+}{\underset{|\atop R'}{N}}CH_2CHOH} + \underset{E_1'}{R''O^-} \tag{4}$$

$$E_1' + B \rightarrow \underset{E_{2,n}'}{R''(OCH_2CHR')_nO^-} \tag{5}$$

The contact of $E_{2,n}'$ with another molecule of alcohol results in termination of this polymer chain and generation of a new alkoxide ion E_1' or $E_{2,m}'$ to start the polymerization process over again:

$$E_{2,n}' + E_1 \rightarrow \underset{E_{2,n}}{R''(OCH_2CHR')_nOH} + E_1' \tag{6}$$

$$E_{2,n}' + E_{2,m} \rightarrow E_{2,n} + E_{2,m}' \tag{7}$$

where R″ is the alkyl group, such as methyl and ethyl.

Narracott (2) suggested that polymerization might also be terminated by the elimination from the end product of tertiary amine, D, giving rise to a double bond or might be terminated by removal of an olefine, where D is $R_3N(CH_2CHR'O)_nCH_2CHR'OH$.

Lidarik and his co-workers (4,5) found that the polymerization rate of PGE with tributylamine at 20 to 80°C and molecular weight of polymer increased with the addition of water, and that this catalyst did not polymerize PGE without a cocatalyst.

In the previous paper (6), crystalline (47 to 50% crystallinity) and amorphous oligomers have been obtained from polymerization of PGE in the presence of various tertiary amines. We found (6) also that the polymerization seemed to increase but the molecular weight of oligomer decreased with water, and that the resulting oligomer had the internal carbon-carbon double-bond unsaturation.

This paper deals with the kinetic studies of substituted PGE using the dilatometric method in the presence of benzyldimethylamine with or without *n*-butanol as a cocatalyst, and with some properties of the resulting oligomer, and proposes a new mechanism for this oligomerization.

EXPERIMENTAL

Reagents

Reagent-grade PGE was dried over calcium hydride for several days and distilled at reduced pressure. The distillate at 103°C/6 mm Hg was used for polymerization. Substituted PGE were prepared from epichlorohydrin and corresponding substituted phenols with an aqueous solution of sodium hydroxide by the one-step method used previously by Kuwamura et al. (9). Substituted PGE were used for the polymerization after distillation at reduced pressure or recrystallization using the methanol-water system. The preparation and properties of the substituted PGE were reported adequately in the previous papers (*1b,10*).

Reagent-grade N,N-dimethylbenzylamine was used after distillation at reduced pressure. *n*-Butanol was reagent grade and dehydrated with calcium oxide and distilled at reduced pressure before use.

Solvents were purified as usual (*11*). Toluene and dioxane were dried over calcium chloride, refluxed over sodium for several hours, and fractionally distilled. Dimethyl formamide was dried over sodium sulfate and fractionally distilled at reduced pressure.

Polymerization Procedure

Catalyst solutions were prepared by dissolving N,N-dimethylbenzylamine and *n*-butanol into toluene or dioxane. The mixture of PGE and catalyst solutions was cooled using the dry ice–methanol system, and then introduced into a dilatometer after being degassed. The rate of polymerization was followed by measuring the decrease in the volume at various temperatures (70.0, 80.0, and 90°C). Attempts were made to hold the temperature of the reaction mixtures constant (±0.05°C).

The oligomerization of PGE was also studied in a sealed test tube at 90 to 95°C. A sample of PGE, together with the catalyst, was degassed in vacuo, sealed in a test tube after the test tube had been flushed with dry nitrogen, and placed in a constant-temperature bath. At the end of the reaction time the test tube was cooled and opened. The reaction mixture was dissolved into a small amount of benzene, poured into a methanol-HCl solution to remove the catalyst, and dried in vacuo.

Infrared Absorption Spectrum

The infrared absorption spectrum in the region 650 to 4000 cm^{-1} was measured for the resulting oligomer, a viscous transparent resin, by a Hitachi Model EPI-2 infrared spectrophotometer equipped with a NaCl prism.

Molecular Weight

The molecular weight of the oligomer was determined by a cryoscopic method with benzene or done with a Mechrolab vapor pressure Model 301-A osmometer.

Carbon-Carbon Double-Bond Unsaturation

The contents of carbon-carbon double-bond unsaturation were estimated by catalytic hydrogenation with palladium charcoal as a catalyst in the atmospheric pressure (*12*).

RESULTS

Infrared Absorption Spectrum Intensity of Epoxy Group and Volume Change in Reaction System

The intensity of infrared absorption spectrum of the epoxy group has been found to decrease in proportion to the decrease of epoxide in the reaction system (*13,14*). If the decrease of the intensity of 10.9 μ, which is a characteristic band of the epoxy group in PGE (*15*), is proportional to the decrease of the volume of the reaction

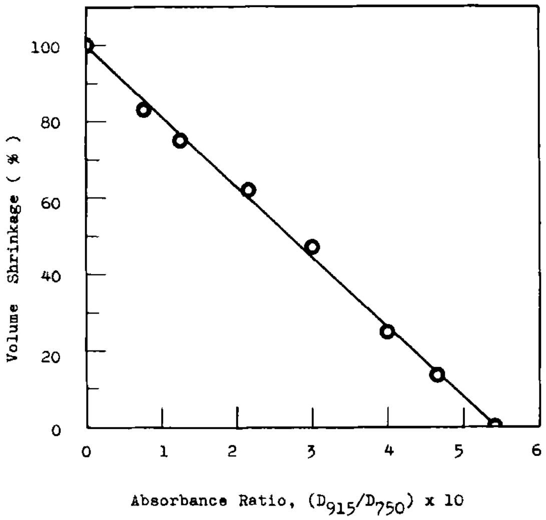


FIG. 1. Relationship between the volume shrinkage and the absorbance ratio, D_{915}/D_{750}, of the infrared spectrum of the reaction system.

system, the decrease of the volume is directly proportional to the decrease of epoxide (*16,17*). For this study, the aliquots of the reaction mixtures were taken out at convenient intervals and the intensity of the band at 10.9 μ was measured. The characteristic band of the phenyl group at 13.3 μ (*18*) was adopted for the standard because its intensity does not change during the reaction.

As shown in Fig. 1, a good linear relationship was found between the volume change and the relative intensity change of 10.9 to 13.3 μ. The volume change, therefore, is proportional to the change of the epoxide content. This result is in good agreement with those found in the polymerizations of ethylene oxide and propylene oxide catalyzed by sodium alkoxides (*17,19*).

Effect of PGE Concentration

The results of typical experiments are plotted in Fig. 2, in which the volume change of the reaction system is plotted against the

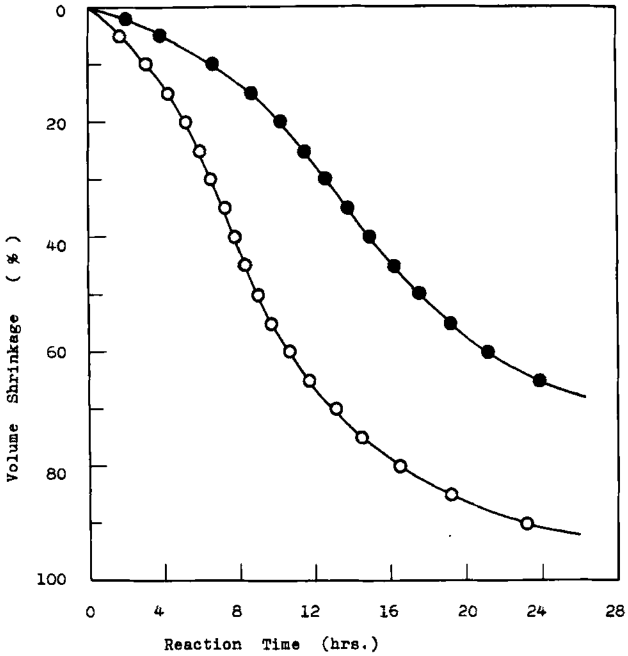


FIG. 2. Time-conversion curves for the polymerization of PGE (4.6 moles/liter) catalyzed by N,N-dimethylbenzylamine and *n*-butanol in dioxane at 70°C. [N,N-dimethylbenzylamine] = [*n*-butanol]. The catalyst concentration is 0.12 mole/liter for ● and 0.23 mole/liter for ○.

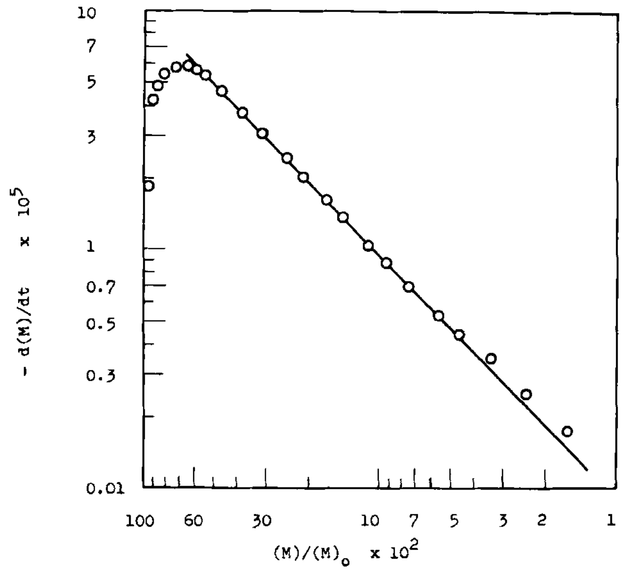


FIG. 3. Relationship between $-d[M]/dt$ and $[M]/[M]_0$ for the polymerization of PGE (4.6 moles/liter) catalyzed by N,N-dimethylbenzylamine (0.23 mole/liter) and *n*-butanol (0.23 mole/liter) in dioxane at 70°C.

reaction time and follows a sigmoidal curve showing an induction period. The induction period was found to be dependent on the concentration of catalyst. Since the volume change is found to be proportional to the change of epoxide content, $[M]$, as mentioned above, the relationship between ln $(-d[M]/dt)$ and ln $[M]$ can be obtained by differentiating the sigmoidal curve in Fig. 2. The result is shown in Fig. 3, in which the slope of the line was almost 1, except in the initial stage of the reaction. Then the rate of disappearance of epoxide is of first order with respect to epoxide except in the initial stage of the reaction. The rate equation is

$$-d[M]/dt = k[M] \tag{8}$$

where k is the observed first-order rate constant containing the catalyst concentration. The same rate equations were obtained for various PGE concentrations of 3 to 6 moles/liter in such solvents as toluene, dioxane, and dimethyl formamide at various temperatures.

Effect of Catalyst

The order of reaction with respect to the concentration of N,N-dimethylbenzylamine was determined through a series of experi-

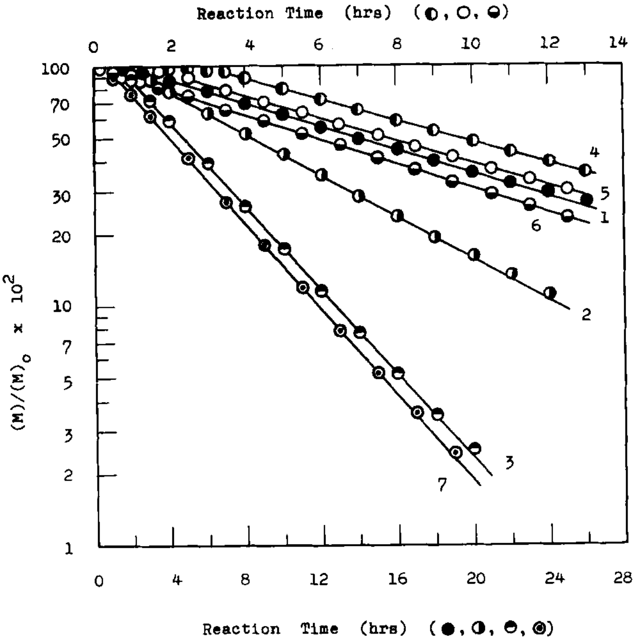


FIG. 4. Guggenheim plots for the polymerization of PGE (4.6 moles/liter) catalyzed by various concentrations of N,N-dimethylbenzylamine and *n*-butanol in dioxane at 70°C.

No.	Symbol	N,N-dimethylbenzylamine, mole/liter	*n*-butanol, mole/liter
1	●	0.12	0.23
2	◑	0.23	0.23
3	◓	0.46	0.23
4	◐	0.23	0.12
5	○	0.23	0.23
6	◒	0.23	0.46
7	⊙	0.46	0.46

ments carried out by keeping the initial concentration of PGE constant of 4.6 moles/liter and by varying the concentrations of a mixture solution of equimolar quantities of *n*-butanol and N,N-dimethylbenzylamine from 2 to 10 mole-% for PGE (0.23 to 0.46 mole/liter) at 70.0°C. The variations of the ratios, $[M]/[M]_0$, are shown in Fig. 4 (Nos. 2 and 7). The various values of the slope of the linear part of these curves were plotted against the initial con-

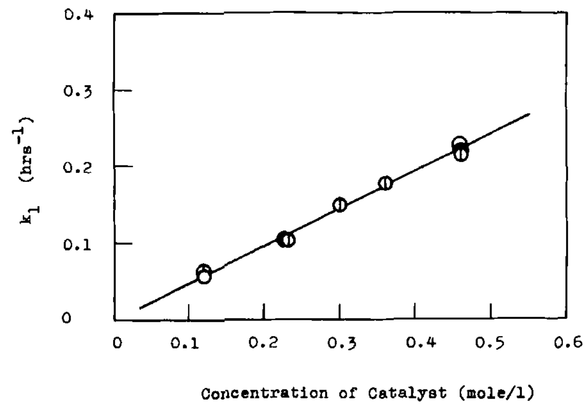


FIG. 5. Effect of N,N-dimethylbenzylamine on the polymerization of PGE (4.6 moles/liter) in dioxane at 70°C. ◐, [N,N-dimethylbenzylamine]/[*n*-butanol] = 1; ○, [N,N-dimethylbenzylamine]/[*n*-butanol] = 0.52; ●, [N,N-dimethylbenzylamine]/[*n*-butanol] = 2.

centrations of catalyst solutions and a straight line was obtained, as shown in Fig. 5. The reaction rate, therefore, is found to be of the first order with respect to the catalyst solution and can be expressed as

$$-d[M]/dt = k'[\text{catalyst}][M] \tag{9}$$

where k' is the second-order rate constant and [catalyst] the initial concentration of the catalyst.

The order of reaction with respect to the concentration of *n*-butanol was determined through a series of the experiments carried out by keeping the initial concentration of PGE and N,N-dimethylbenzylamine constant of 4.6 and 0.23 mole/liter and by varying the concentration of *n*-butanol from 0.12 to 0.46 mole/liter at 70.0°C. The variations of the ratios, $[M]/[M]_0$, are shown in Fig. 4 (Nos. 4, 5, and 6). The slope of the linear part of the curves was found to not change with regard to the concentration change of *n*-butanol, but the induction period decreases according to the increase of *n*-butanol content.

The variations of the conversion of PGE at various concentrations of N,N-dimethylbenzylamine from 0.12 to 0.46 mole/liter are shown in Fig. 4, in which the initial concentrations of PGE and *n*-butanol were kept constant at 4.6 and 0.23 mole/liter at 70.0°C. The reaction rate increases in proportion to the amine concentrations, and the induction period hardly changes. (Nos. 1, 2, and 3 in Fig. 4).

Effect of Substituents of PGE

The effect of substituents of PGE on this oligomerization in the presence of N,N-dimethylbenzylamine and *n*-butanol (4.6, 0.23, and 0.23 mole/liter, respectively) at 70.0°C and in various solvents is shown in Table 1, in which the σ_p values used in this calculation

TABLE 1

Observed Second-Order Rate Constants and Hammett's ρ Value for Oligomerization of Substituted PGE at 70.0°C[a]

R, in PGE[b]	$10^4 k_i'$,[c] liters/mole/sec	Solvent	k_i'/k_H'
p-CH_3O	1.20	Toluene	0.71
p-CH_3	1.35	Toluene	0.79
H	1.70	Toluene	1.0
H	1.37	Dioxane	1.0
H	1.92	Dimethyl formamide	1.0
p-Cl	2.21	Dioxane	1.6
p-NO_2	4.20	Dimethyl formamide	2.2
Hammett's ρ value	0.5		

---

[a] The initial concentrations of PGE, N,N-dimethylbenzylamine, and *n*-butanol are 4.6, 0.23, and 0.23 mole/liter, respectively.

[b] R is a substituent in

$R{-}C_6H_4OCH_2\underset{\diagdown O \diagup}{CHCH_2}$.

[c] Shown by Eq. (9).

have been taken trom Jaffe's review (*20*). Dioxane and N,N-dimethyl formamide were used as solvents in the case of *p*-chloro- and *p*-nitrophenoxy 1,2-epoxypropanes, respectively, because of their poor solubilities in toluene. Hammett's plots of the logarithms of the observed relative rate constants, k_i'/k_H' ($i = CH_3O^-$, CH_3^-, H^-, Cl^-, and NO_2^-, respectively) versus σ_p gave us a straight line for the oligomerization of substituted PGE and, from the slope, ρ value is found to be 0.5. Where k_i' ($i = CH_3O^-$, CH_3^-, H^-, Cl^-, and NO_2^-, respectively) are the observed second-order rate constants for the oligomerizations of substituted PGE, B, in which R′ are p-CH_3O^-, p-CH_3^-, H^-, p-Cl^-, and p-NO_2^- phenoxymethylene groups, respectively. The fact that ρ is positive indicates that the electron-withdrawing substituents increase the rate and that the oligomerization is that of S_N2 type.

Effect of Concentrations of Amine and Alcohol on Molecular Weight of Oligomer

Molecular weights of the resulting oligomers were about 400 to 450, which are equal to those of dimers and trimers of PGE, in the case of the concentrations of N,N-dimethylbenzylamine being changed from 10 to 50 mole-% and of *n*-butanol being kept constant at 5 mole-% for PGE. The result is shown in Table 2.

TABLE 2

Effect of Amine and Alcohol on Molecular Weight of Oligomer and Carbon-Carbon Double-Bond Unsaturation[a]

Concentration, mole-%[b]				
N,N-dimethylbenzylamine	*n*-butanol	Yield,[b] %	Molecular weight[c]	Carbon-carbon double-bond unsaturation, number/mole
10.0	0.0	95	650	0.93
10.0	5.0	95	440	0.57
10.0	10.0	90	450	0.46
10.0	20.0	93	460	0.38
10.0	50.0	90	400	0.18
10.0	100.0	95	280	0.00
20	5.0	90	435	0.58
50	5.0	90	405	0.60

[a] The initial concentration of PGE is 7.37×10^{-2} mole/liter in toluene. The reaction temperature and time are 90 to 95°C and 8 days, respectively.

[b] Ratio to PGE.

[c] By a cryoscopic method and on the Mechrolab Model 301-A vapor-pressure osmometer with benzene at 30°C.

The effect of alcohol on the molecular weight of the oligomer was determined through a series of the experiments carried out by keeping the initial concentrations of PGE and N,N-dimethylbenzylamine at constant of 7.37×10^{-2} mole/liter and 0.737×10^{-2} mole/

liter (10 mole-% for PGE), respectively, and by varying the concentration of tri-*n*-butylamine from 0 to 100 mole-% in toluene at 90 to 95°C for 8 days. Molecular weight of oligomer was 400 to 450 for 5 to 50 mole-% of *n*-butanol and 280 for 100 mole-% of *n*-butanol. The molecular weight of the oligomer without *n*-butanol was 650, as shown in Table 2. These oligomers were all viscous liquid, soluble in benzene and acetone, and insoluble in water and alcohol.

Infrared Spectra of Oligomers

The infrared spectra of the oligomers have been obtained in the region of 650 to 4000 cm^{-1} as shown in Fig. 6. Comparison of the spectrum of the oligomer with that of PGE shows that a characteristic band of the epoxy group, 10.9 μ, disappears and that new bands at 1650 to 1675 cm^{-1} appear. These new bands seem to belong to the bands arising from the vibrations of the carbon-carbon double-bond unsaturation in the oligomer chain, and disappeared after the hydrogenation of the oligomer as shown in Fig. 6.

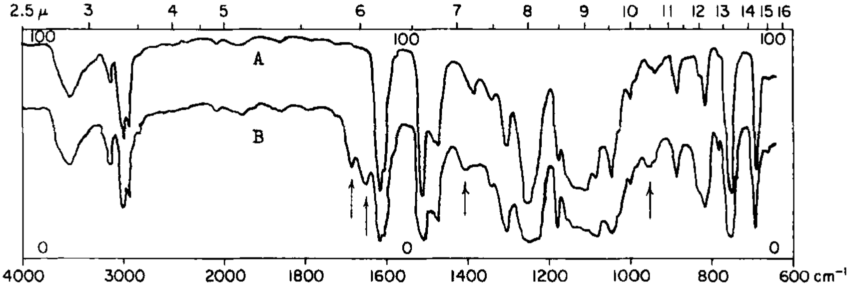


FIG. 6. IR spectra of the oligomers obtained with N,N-dimethylbenzylamine of 20.0 mole-% and *n*-butanol of 5 mole-% at 90 to 95°C for 8 days, before and after catalytic hydrogenation. Molecular weight of 435 and carbon-carbon double-bond unsaturation of 0.58/mole. A, after hydrogenation; B, before hydrogenation.

Carbon-Carbon Double-Bond Unsaturation

The contents of carbon-carbon double-bond unsaturation in oligomers were measured by the catalytic hydrogenation with palladium charcoal as a catalyst in atmospheric pressure (*12*). As shown in Table 2, the carbon-carbon double-bond unsaturation seems to be not affected by the concentration change of N,N-dimethylbenzylamine but affected by the concentration of *n*-butanol.

DISCUSSION

Data on the molecular weight, infrared spectra, and hydrogenation of the oligomer show that the oligomerization products should consist of the mixtures of the saturated and unsaturated compounds. The infrared spectra of the oligomers, the assignments of which were discussed in detail in the previous paper (*1b*), have the characteristic bands at 1675 cm^{-1} assigned (*21*) to the stretching modes of the carbon-carbon double bond of *trans*-alkene, and at 1650 cm^{-1} assigned to the stretching vibration of the carbon-carbon double bond of *cis*-alkene. The bands assigned (*21*) to the in-plane hydrogen deformation mode of *cis*-alkene and to the out-of-plane hydrogen deformation mode of *trans*-alkene are found at 1405 and 955 cm^{-1}, respectively, in the infrared spectra of the oligomers. These bands disappeared after hydrogenation. It can be estimated, therefore, that the unsaturation should be of the internal carbon-carbon double-bond structure. The molecular structure of PGE seems to suggest that $C_6H_5CH{=}CH_2O^-$ is only an available structure for such an internal unsaturation. In the infrared spectra of phenyl vinyl ether (22), the bands assigned to those arising from the carbon-carbon double-bond unsaturation and from the characteristic band of vinyl group have been found to be at 1644 and 806 cm^{-1}, respectively. The vibrational band near at 806 cm^{-1} of the oligomer of PGE did not change its intensity and sharpness even after the catalytic hydrogenation, and the band near at 890 cm^{-1}, which seems to correspond to the band assigned to the out-of-plane hydrogen deformation of a vinylidene type of structure (*21*) also did not change. These facts should suggest an internal olefinic structure for the oligomers of PGE, as mentioned above.

It seems to be difficult to consider a vinylidene type of structure for these oligomers, because the structure, $C_6H_5OCH_2C({=}CH_2)O^-$, may be obtained only from the quaternary bases of C_1' or C_2' and D′, which have been considered too unstable to exist (*23*). Table 3 shows the result of the oligomerization of γ-butoxy α,β-epoxypropane (butyl glycidyl ether, BGE), whose γ-hydrogen is considered to be less mobile than that of PGE. The experiment with the low concentrations of benzyl alcohol gave no oligomers but unreacted BGE. The products have no carbon-carbon double-bond unsaturation. Table 3 also shows that N,N-dimethylbenzylamine is more effective than tri-*n*-butylamine.

TABLE 3

Effect of Amine and Alcohol on Oligomerization of Butyl Glycidyl Ether[a]

Concentration, mole-%[b]			
tri-*n*-Butylamine	Benzyl alcohol	Yield,[b] %	Molecular weight[c]
5.0	5.0	[d]	—
5.0	10.0	[d]	—
5.0	20.0	Trace	—
5.0[e]	30.0	70	310
5.0	50.0	43	215
5.0	100.0	90	230

[a] The initial concentration of butyl glycidyl ether (BGE) is 7.37×10^{-2} mole/liter in toluene. The reaction temperature and time are 90 to 95°C and 14 days, respectively.

[b] Ratio to BGE.

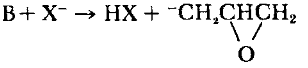
[c] By a cryoscopic method and on the Mechrolab Model 301-A vapor-pressure osmometer with benzene.

[d] Unreacted BGE was recovered.

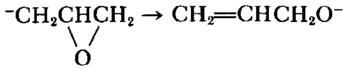
[e] N,N-dimethylbenzylamine was used.

The content of the carbon-carbon double bond was about 1 per mole for the oligomers without any alcohol, as shown in Table 2. This suggests that the oligomerization of PGE can be carried out by a tertiary amine alone. Lidarik and his co-workers (*4*) reported that the ionic polymerization of PGE with triethylamine did not proceed without a cocatalyst such as water at 20 to 80°C, and found that the concentration change of an amine did not alter the polymerization rate in the case of keeping water concentration constant. It is not clear why our result disagrees with Lidarik et al. (*4*). Overberger and Tobkes (*24*) studied the copolymerization of propylene oxide and aziridine and reported that the homopolymerization of propylene oxide took place by triethylamine alone.

It is well known (*25,26*) that the polymers of propylene oxide by potassium hydroxide have a considerable amount of the carbon-carbon double-bond unsaturation, and that an allylate anion produced with a base which should attract and eliminate a hydrogen from the methyl group of propylene oxide might initiate the polymerization. The mechanism is considered to be as follows (*26*):



$$B + X^- \rightarrow HX + {}^-CH_2\underset{\diagdown O \diagup}{CHCH_2} \quad (10)$$



$$^{-}\underset{\diagdown\,O\,\diagup}{CH_2CHCH_2} \rightarrow \underset{G'_1}{CH_2{=}CHCH_2O^{-}} \qquad (11)$$

$$G'_1 + B \rightarrow \underset{G'_2}{CH_2{=}CHCH_2OCH_2CH(CH_3)O^{-}} \qquad (12)$$

where R′ in B is CH_3, and X^- is a base whose counterion seems to be potassium cation. The ion-pair polymerization mechanism was also proposed for the polymerization of ethylene oxide and propylene oxide by sodium alkoxide (*17,19*).

Under our experimental condition, however, the propagation by a free ion or an ion pair as shown by Eqs. (10) to (12) is difficult to consider because of the solvents used being nonpolar and because of the counterion being considered to be a tertiary ammonium salt which can give a proton easily.

In order to explain the available data, the following reaction sequence, a modification of that initially suggested by St. Pierre and Price (*25*), and used recently by Steiner et al. (*26*) for the polymerization of propylene oxide by potassium hydroxide, is proposed:

$$A + B \xrightarrow{k_1} \underset{G_1}{C_6H_5OCH{=}CHCH_2OH} + A \qquad (13)$$

$$A + G_1 + B \xrightarrow{k_2} \underset{G_n}{C_6H_5OCH{=}CHCH_2OCH_2CH(CH_2OC_6H_5)OH} + A \qquad (14)$$

$$A + E_1 + B \xrightarrow{k_3} \underset{E_{2,n}}{C_6H_5OCH_2CH(OH)CH_2OR''} + A \qquad (15)$$

where R are methyl or methyl and benzyl groups of tertiary amines, R′ of B is $C_6H_5OCH_2^-$, R″ of the alcohol is *n*-butyl or benzyl group, n is 1, 2, . . . , and k_i ($i = 1$ to 3) are the rate constants of reactions (13) to (15).

Elimination and rearrangement of γ-hydrogen of PGE should lead to isomerization of PGE into γ-phenoxy allyl alcohol, as shown by Eq. (13). This alcohol reacts further with PGE to give the oligomer of PGE[Eq. (14)]. On the other hand, *n*-butanol added initially reacts with PGE to produce 1-phenoxy 3-butoxypropanol-2, which can react further with PGE to give oligomers.

Reaction (13) can explain that the polymerization products had the internal carbon-carbon double-bond unsaturation. The existence of saturated compounds can be explained easily by the reaction (15). It was found that there is an induction period during which the amounts of double bonds and hydroxy groups increase to a somewhat significant level by infrared spectrum analysis. The induction period in the reaction, therefore, is readily explained by the proposed reaction sequence. At the beginning of the polymerization there is a slow buildup of hydroxylic materials attributed to reaction (13). The proposed mechanism illustrated by equations [(14) and (15)], involving a termolecular reaction, would require a large negative entropy change. There is a slight probability for such a postulation as described above, but since no measurements were made, a more probable mechanism, which would allow the same kinetic order but which is indistinguishable from the above mechanism on a purely kinetic basis, is shown in Eqs. (16) and (17):

$$\mathrm{G_1} \quad \text{or} \quad \mathrm{E_1 + A} \underset{k_5}{\overset{k_4}{\rightleftharpoons}} \underset{\mathrm{J}}{[\mathrm{R'''OH} \cdots \mathrm{NR_3}]} \tag{16}$$

$$\mathrm{J + B} \xrightarrow{k_6} \mathrm{G}_n \quad \text{or} \quad \mathrm{E}_{2,n} + \mathrm{A} \tag{17}$$

where R''' is $C_6H_5OCH{=}CHCH_2^-$ or R'' (*n*-butyl in this case), *n* is 1, 2, . . . , and k_i ($i = 4$ to 6) are the rate constants of reactions of (16) and (17).

These hydroxylic materials, G_n ($n = 1, 2, \ldots$), might be converted to their associated complexes by the tertiary amine as shown by Eq. (16). As the complex J is formed, reaction (17) becomes [then reactions (14) and (15) become] significant and is autocatalytic in the presence of a tertiary amine. Hence, the over-all rate of formation of growing polymer chains is increasing and gives the typical induction period. If this situation is obtained, the addition of hydroxylic materials such as water and alcohol should eliminate the induction period and increase the over-all rate of polymerization. This is so, as is shown in Fig. 4 (Nos. 6 and 7).

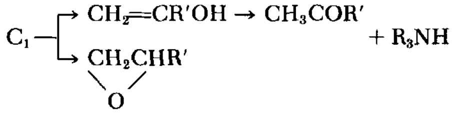
The hydroxylic compounds G_n and $E_{2,n}$ ($n = 1, 2, \ldots$) produced in reactions of (14) and (15) seem to be less reactive than E_1 and G_1, produced in reaction (13), because G_n and $E_{2,n}$ are secondary hydroxylic compounds and have the larger substituent, whereas the latter is primary.

If the reaction proceeds as shown by Eqs. (1) and (2), which were proposed by Narracott (2), the carbon-carbon double-bond unsaturation of a vinylidene type may be obtained as follows:

$$D' \rightarrow A + CH_2{=}CR'O(CH_2CHR'O)_nCH_2CHR'OH \qquad (18)$$

However, the amphi-ion D′, as shown by Eq. (2), seems to be too unstable to exist under this experimental condition.

If the reaction proceeds as shown by Eqs. (1), (4), and (5), which were proposed by Shechter and Wynstra (3), a ketone or an epoxide should be obtained as



$$C_1 - \left[\begin{array}{l} \rightarrow CH_2{=}CR'OH \rightarrow CH_3COR' \\ \rightarrow \underset{\diagdown O \diagup}{CH_2CHR'} \end{array}\right. + R_3NH \qquad (19)$$

The infrared spectra of oligomerization products, however, suggest that no carbonyl and epoxy compounds are produced under these experimental conditions; that is, these results seem to suggest that Narracott's (2) and Shechter and Wynstra's (3) mechanisms are unsuitable for the oligomerization of PGE.

The kinetic model is

$$dG_1/dt = k_1AB - k_4AG_1 + k_5J_{G_1} \qquad (20a)$$

$$dG_n/dt = -k_4AG_n + k_5J_{G_n} + k_6BJ_{G_{n-1}} \qquad (20b)$$

$$dE_{2,1}/dt = -k_4AE_{2,1} + k_5J_{E_{2,1}} + k_6BJ_{E_1} \qquad (20c)$$

$$dJ_{G_n}/dt = k_4AG_n - k_5J_{G_n} - k_6J_{G_n}B \qquad (20d)$$

$$dJ_{E_i}/dt = k_4AE_i - k_5J_{E_i} - k_6J_{E_i}B \qquad (20e)$$

where A and B are the concentrations of amine and epoxide, and E_i ($i = 1$ and $2,n$; $n = 1, 2, \ldots$), G_n ($n = 1, 2, \ldots$), J_{G_n} ($n = 1, 2, \ldots$), and J_{E_i} ($i = 1$ and $2,n$; $n = 1, 2, \ldots$) are the concentrations of alcohol added initially; hydroxylic compounds of $E_{2,n}$ ($n = 1, 2, \ldots$), G_n ($n = 1, 2, \ldots$) shown by Eqs. (13) to (15); the hydrogen-bonded complexes of A with G_n ($n = 1, 2, \ldots$); and E_i ($i = 1$, and $2,n$: $n = 1, 2, \ldots$) as shown by Eq. (16), respectively. Since the reactivity of G_n ($n \geqslant 3$) seems to be the same as that of $E_{2,n}$ ($n \geqslant 2$), both of them and their hydrogen-bonded complexes with A are symbolized as G_n and J_{G_n}, respectively. Material balance for this system gives us the following relation:

$$B_0 - B = E_{2,1} + J_{E_{2,1}} + \sum_{1}^{n} nG_n + \sum_{1}^{n} nJ_{G_n} \qquad (21)$$

where B_0 is the initial concentration of epoxide B. From Eqs. (20) and (21) we can obtain

$$-dB/dt = d\left(E_{2,1} + J_{E_{2,1}} + \sum_1^n nG_n + \sum_1^n nJ_{G_n}\right)$$
$$= B\left[k_1A + k_6\left(\sum_1^{n-1} J_{G_m} - nJ_{G_n} + J_{E_1} - J_{E_{2,1}}\right)\right] \tag{22}$$

If $J_{G_n}/(A\cdot G_n) = J_{E_i}/(A\cdot E_i) = K$, Eq. (22) takes the form

$$-dB/dt = AB\left[k_1 + k_2\left(\sum_1^{n-1} G_m - nG_n\right) + k_3(E_1 - E_{2,1})\right] \tag{23}$$

Equation (23) can be derived directly from Eqs. (13) to (15). Here $k_2 = k_6K$ and $k_3 = k_6K$, respectively.

In the case of $E_1 = 0$ or $k_3(E_1 - E_{2,1})$ being smaller than $k_1 - k_2(\Sigma_1^{n-1} G_m - nG_n)$, Eq. (23) takes the form

$$-dB/dt = (1 + KA)d\sum_1 nG_n/dt$$
$$= A\left(B_0 - (1 + KA)\sum nG_n\right)\left[k_1 + k_2\left(\sum_1^{n-1} G_m - nG_n\right)\right] \tag{24}$$

The explicit integration of Eq. (24) is impossible, but an approximate solution giving $(\Sigma_1^{n-1}G_m - nG_n)$ as a function of $\Sigma_1 nG_n$, $f\Sigma_1 nG_n$, can be obtained as

$$\frac{1}{k_1(1 + KA) + k_2fB_0}\log\frac{k_1 + k_2f\sum_1 nG_n}{B_0 - (1 - KA)\sum_1 nG_n} = \frac{A}{1 + KA}t \tag{25}$$

The monomer consumption curves shown by Eq. (25) should give the typical sigmoidal shapes shown in Fig. 2.

In the case of $k_3(E_1 - E_{2,1}) \gg k_1 + k_2(\Sigma_1^{n-1}G_m - nG_n)$, we can obtain

$$-dB/dt = k_3(E_1 - E_{2,1})AB \tag{26a}$$

and Eq. (26a) takes the form

$$-dB/dt = k_3ABE_1^{\circ} \tag{26b}$$

at the initial stage of the reaction, where E_1° is the initial concentration of n-butanol.

The amount of the resulting hydroxylic compounds, $\Sigma^n G_n$ ($n = 1, 2, \ldots$), is considered to be constant at the middle or last stages of the reaction, and we can obtain the following equation from Eq. (23):

$$-d\mathrm{B}/dt = K'\mathrm{AB} \tag{27}$$

where K' is constant and may be a function of k_2 and the concentration of the hydroxylic compound G_n. Equations (26) and (27) show that the rate of polymerization is of first order with respect to amine and epoxide, respectively. This can explain more reasonably the experimental results shown in Figs. 3 to 5.

Yamashita (27) has reported the ρ value of 1.0 for the anionic polymerization of styrene oxide by sodium phenoxide, from the data of log $1/r_1$ versus Hammett's σ constants. The smaller ρ value in the polymerization of PGE may be considered to be due to the greater distance of the substituents of PGE from the reaction site.

REFERENCES

1. *a.* Presented first at the 13th Annual Meeting of the High Polymer Society of Japan, Kyoto, Japan, June 1964; *b.* Part IX of this series, Y. Tanaka and H. Kakiuchi, *J. Macromol. Chem.*, **1**(2), 307 (1966).
2. E. S. Narrcott, *Brit. Plastics*, **26,** 120 (1953).
3. L. Schechter and J. Wynstra, *Ind. Eng. Chem.*, **48,** 86, 94 (1956).
4. M. Lidarik, S. Stary, and I. Mleziva, *Vysokomolekul. Soedin.*, **5,** 1748 (1963).
5. M. Lidarik, S. Stary, N. Soukalova, and S. Pokorny, *Kunststoff-Rundschau,* **10,** 498 (1963).
6. Y. Tanaka and H. Kakiuchi, *J. Polymer Sci.*, **A1,** 4, 109 (1966).
7. A. M. Eastham, B. de B. Darwent, and P. E. Beaubien, *Can. J. Chem.*, **29,** 575 (1951).
8. A. M. Eastham and B. de B. Darwent, *Can. J. Chem.*, **29,** 585 (1951).
9. T. Kuwamura, *Kogyo Kagaku Zasshi*, **63,** 595 (1960).
10. H. Kakiuchi and Y. Tanaka, *J. Org. Chem.*, **31,** 1559 (1966).
11. J. A. Riddick and E. E. Toops, Jr., *Organic Solvents,* 2nd ed., Wiley (Interscience), New York, 1955.
12. R. L. Burwell, *Chem. Rev.*, **57,** 895 (1957).
13. L. A. O'Neill and C. P. Cole, *J. Appl. Chem.*, **6,** 356 (1956).
14. Te-Ho Chang, *Sci. Sinica (Peking)*, **12**(9), 1398 (1963).
15. *a.* O. D. Shreve, M. R. Heether, H. B. Knight, and D. Swern, *Anal. Chem.*, **23,** 277 (1951); *b.* W. A. Patterson, ibid., **26,** 823 (1954); *c.* J. Bomstein, ibid., **30,** 544 (1958).
16. G. Gee, W. C. E. Higginson, P. Levesiey, and K. J. Taylor, *J. Chem. Soc.*, **1959,** 1338.
17. G. Gee, W. C. E. Higginson, and G. T. Merrall, *J. Chem. Soc.*, **1959,** 1345.

18. H. W. Mackinney and J. T. Spalik, *SPE Trans.*, **5**, 39 (1965).
19. G. Gee, W. C. E. Higginson, K. J. Taylor, and M. W. Trenholme, *J. Chem. Soc.*, **1961**, 4298.
20. H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).
21. *a.* L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, 1958; *b.* T. Shimanouchi, *Sekigaisen Kyushu Supekutoru Kaisekiho* (*Analysis of Infrared Spectra*), Nankodo, Tokyo, 1960; *c.* K. Nakanishi, *Sekigaisen Kyushu Supekutoru* (*Infrared Absorption Spectra*), Nankodo, Tokyo, 1962.
22. Y. Mikawa, *Bull. Chem. Soc. Japan*, **29**, 110 (1956).
23. I. T. Smith, *Polymer*, **2**, 95 (1961).
24. C. G. Overberger and M. Tobkes, *J. Polymer Sci.*, **A2**, 2481 (1964).
25. L. E. St. Pierre and C. C. Price, *J. Am. Chem. Soc.*, **78**, 2432 (1956).
26. E. C. Steiner, R. R. Pelletier, and R. O. Trucks, *J. Am. Chem. Soc.*, **86**, 4678 (1964).
27. Y. Yamashita, *Kagaku* (*Kyoto*), **20**, 185 (1965).

Zusammenfassung

Die Oligomerisation von substituierten Glycidäthern wurde kinetisch in Gegenwart von Dimethylbenzylamin in Toluol oder Dioxan als Lösungsmittel untersucht. Die Infrarotspektren der resultierenden Oligomeren weisen darauf hin, dass die Reaktionsprodukte ungesättigte Kohlenstoff-Kohlenstoff Doppelbindungen enthalten, was durch katalytische Hydrierung bestätigt wurde. Die Werte der Molekulargewichte der Oligomeren weisen ebenfalls darauf hin, dass der primär entstehende α-Phenoxyallylalkohol mit weiterem Phenylglycidäther reagiert und so weitere Oligomere produziert. Der Wert der Reaktionskonstanten, ρ, hatte für diese Reaktion positive Werte. Dies bedeutet, dass elektronenanziehende Substituenten des Phenylglycidäthers die Oligomerisationsgeschwindigkeit erhöhen. Eine kinetische Analyse zeigt, dass die vorgeschlagene Reaktionsfolge alle charakteristischen Merkmale der Polymerisation erklären kann, sowohl die sigmoiden Formen der Abbaukurven der Monomeren als auch die Reaktionsgeschwindigkeiten und Induktionszeiten.

Résumé

Les auteurs presentent une étude cinétique de l'oligomérisation des éthers phényl glycidiques substitués, en presence de la diméthylbenzylamine avec le toluène ou le dioxanne comme solvant. Les spectra infrarouges des oligomères obtenus suggèrent que les produits de la réaction possèssent l'insaturation interne d'une double liaison carbon-carbon, fait confirmé par l'hydrogénation catalytique. Les masses moléculaires de ces oligomères suggèrent egalement que l'alcool γ-phenoxyallylique, produit dans le premier stade de la réaction, quand le proton γ de l'ether phényl glycidique est attiré par la base, l'amine, réagit avec l'ether phényl glycidique présent et donne ainsi l'oligomère. La valeur de la constante de

réaction est positive pour cette réaction, indicant que les substituants, attracteurs d'éléctrons de l'ether phényl glycidique augmentent la vitesse d'oligomérisation. L'analyse cinétique montre que la sequence de réactions proposée rend compte de tous les traits caractéristiques de cette polymérisation, y compris l'allure sigmoidalle des courbes de la consommation du monomère, des vitesses de réaction et des periodes d'induction.

Received by editor July 22, 1966
Submitted for publication November 14, 1966