Kinetics of Epoxy Resins Formation from Bisphenol-A, Tetrabromobisphenol-A, and Epichlorohydrin

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SYNOPSIS

The kinetics of formation of epoxy resins derived from bisphenol-A, tetrabromobisphenol-A, and epichlorohydrin under stoichiometric conditions was considered. The kinetics of reaction was studied by taking into account the consumption of the added alkali and epoxide group of epoxide oligomers. The obtained results satisfactorily explained that the reactivity of bisphenol-A with epichlorohydrin is higher than that of tetrabromobisphenol-A. The rate of dehydrochlorination of chlorohydrin ether in the presence of alkali and water is much higher than that of the rate of condensation of phenolic hydroxyl group with epichlorohydrin. The apparent reaction order of phenolic groups with epichlorohydrin and terminal epoxide groups in the oligomer are second order. The rate constants and reaction activation energy were determined. The results are discussed. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Bromo-epoxy resins based on epichlorohydrin (ECH), bisphenol-A (BPA) and tetrabromobisphenol-A (TBBPA) had been synthesized.[1-3] These resins are a relatively fire-resistant compound when the content of bromine is over 10%. They are usually used for a fire-resistant material. The kinetics of formation of epoxy resins based on ECH and BPA had been considered. Attempts to develop a mathematical model of the synthesis of epoxy resins had also been made.[4,5] In some case, a qualitative coincidence of theoretical and experimental data were obtained. However, the process of this reaction is rather complicated, and, in spite of having made some progress, more complete kinetic data and description of the synthesis have been lacking until now. The reaction order is not given in Experimental.

The kinetics analysis of synthesis of bromo-epoxy resins is the purpose of the present investigation. The kinetics of formation of these epoxy resins under stoichiometric conditions is considered. The reactivity of bisphenol-A and tetrabromobisphenol-A with ECH and the terminal epoxide group (EG) in oligomer were investigated by taking into account the consumption of the added alkali and epoxide group.

EXPERIMENTAL

Materials

Bisphenol-A and tetrabromobisphenol-A
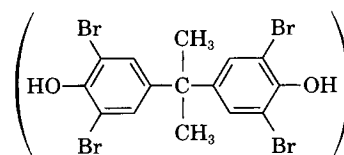
were purified by recrystallized in toluene, mp are 160 and 180°C, respectively; epichlorohydrin, dioxane, acetone, ethyl alcohol, hydrochloric acid, NaOH, and KOH were all analytically pure grade.

Synthesis of Diglycidyl Ethers of BPA and TBBPA

Diglycidyl ethers of BPA and TBBPA were synthesized respectively according to the Ref. 6. The epoxide values were determined in accordance with the method of Ref. 7. The epoxide values of diglycidyl ethers of BPA and TBBPA are 0.53 mol/100 g and 0.28 mol/100 g, respectively.

Determination of Conversion Rate of Reactants

The kinetics of reaction of BPA and TBBPA with ECH was investigated by taking into account the consumption of added alkali. The initial mole ratio of BPA and/or TBBPA, ECH, and NaOH is 1. To a four-necked flask equipped with a stirrer, a thermometer, and a condenser was added 0.025 mol TBBPA and 0.025 mol NaOH, 30 mL dioxane and 15 mL distilled deionized water (DDi water). The mixture was rapidly stirred and heated to a reaction temperature ($\pm 0.2°C$). Then 0.025 mol ECH was added and stirred rapidly. A sample of mixture was removed at regular time intervals for analysis. The conversion of reactants was determined potentiometrically with 0.1 mol HCl solution. The data were treated by a computer.

Under the same concentration and initial mole ratio of $[EG]:[-phOH]:[NaOH] = 1:1:1$, the reaction rate of the terminal epoxide group in oligo-

mer with phenolic group was determined by taking into account the consumption of the epoxide group.

Determination of NMR Spectrum

The product at different reaction times was purified by passing it through benzene and washing with dilute alkali solution and distilled deionized water. Then the water and solvent were distilled under vacuum. The epoxy resin was dissolved in D-acetone. The resultant product was scanned with an NMR spectrometer. The absorption peak of proton of benzene ring in BPA is 6.85–7.35 ppm and in TBBPA 7.6 ppm.
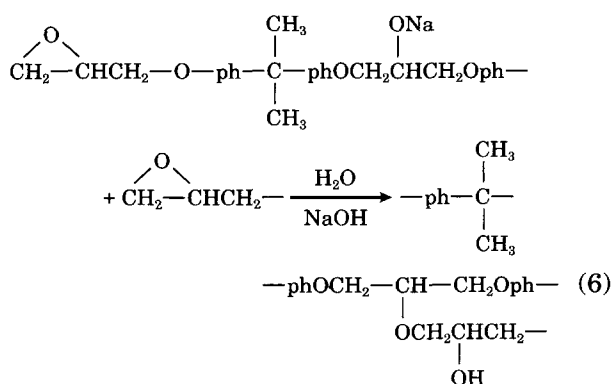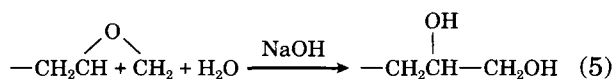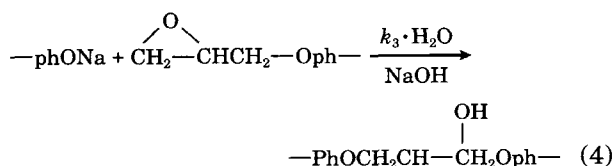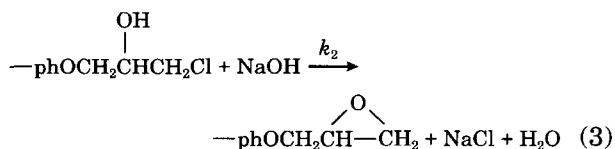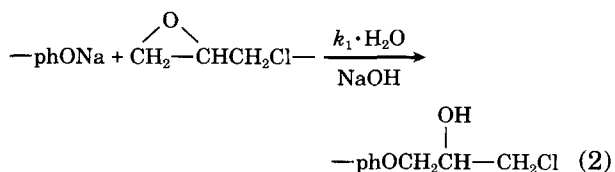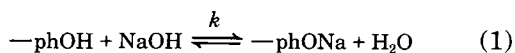
RESULTS AND DISCUSSION

The epoxy resins derived from BPA, TBBPA, and ECH are more complicated; one of them has the following approximate form:
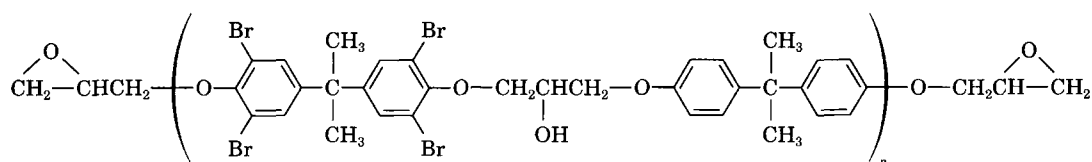
where $n = 1-2$. It is possible that the bisphenol in the one molecular chain are all BPA or are all TBBPA. It is also possible to have diglycidyl ether of BPA or TBBPA.

The reaction during the interaction of bisphenol with ECH in the presence of alkali in water-organic media have the following main process:

$$-phOH + NaOH \overset{k}{\rightleftharpoons} -phONa + H_2O \qquad (1)$$

$$-phOCH_2\overset{OH}{\underset{|}{CH}}-CH_2Cl \qquad (2)$$

$$-phOCH_2\overset{O}{\overset{/\backslash}{CH-CH_2}} + NaCl + H_2O \qquad (3)$$

$$-PhOCH_2\overset{OH}{\underset{|}{CH}}-CH_2Oph- \qquad (4)$$

Because the concentration of phenolic group in the first stage of the synthesis is higher than that of alkali, all alkali is bound as phenolate ions owing to the high acidity of phenolic hydroxyl groups. The side reaction of hydrolysis and alcoholysis of ECH and the epoxide group are practically absent; the chain branching reactions are also not considered. Only the main reactions (1)–(4) occur in this system.

We postulate the following:

1. All phenolic groups in monomer and chain end have the same reactivity about the same phenol hydroxyl groups.
2. The reaction (1) is faster than that of (2) and (4), so that $[-\text{phONa}] = [\text{NaOH}]$.
3. The rate of dehydrochlorination of chlorohydrin ether (CHE) in the presence of alkali in the amount required for complete dehydrochlorination is much higher than the rate of condensation of phenolic hydroxyl groups with ECH and the reaction rate of phenolic hydroxyl groups with terminal epoxide groups. That is, $k_2 \gg k_1, k_3$.

The kinetic equation has the following main form:

$$-\frac{d[\text{ECH}]}{dt} = k_1[-\text{phOH}][\text{ECH}]$$

$$= k_1[\text{NaOH}][\text{ECH}] \qquad (7)$$

$$-\frac{d[\text{NaOH}]}{dt} = k_2[\text{NaOH}][\text{CHE}]$$

$$= k_1^{\text{r}}[\text{NaOH}][\text{ECH}] \qquad (8)$$

$$-\frac{d[\text{EG}]}{dt} = k_3[\text{NaOH}][\text{EG}]$$

$$= k_1[\text{NaOH}][\text{ECH}] \qquad (9)$$

where [NaOH], [ECH], [CHE], and [EG] are the current concentration of NaOH, ECH, CHE, and the terminal epoxide group in oligomer.

Kinetics of Reaction of ECH with TBBPA and BPA

If we consider the reaction order of reactants, the reaction rate equation of ECH with $-\text{phONa}$ is

$$-\frac{d[\text{NaOH}]}{dt} = km[\text{phONa}]^a[\text{ECH}]^e \qquad (10)$$

where a and e are the order of phOH and ECH, respectively, and m is the overall order of this reaction, $m = a + e$. Let

$$R = [\text{phOH}]_0/[\text{ECH}]_0 = [\text{NaOH}]_0/[\text{ECH}]_0$$

$$\alpha = [\text{NaOH}]/[\text{NaOH}]_0$$

and the reaction be performed stoichiometrically ($R = 1$). Equation (1) becomes

$$-\frac{d[\text{NaOH}]}{dt} = km[\text{NaOH}]_0^m\alpha^m = k_m'\alpha^m \qquad (11)$$

According to experimental determination of reaction conversion, the reaction of ECH with TBBPA was carried out as 70, 80, and 90°C, respectively. The relationship between $1/\alpha$ and reaction time t is obtained in Figure 1. As seen from the data in Figure 1, the reaction is apparently second order. To determine the order of reactants, we used the method of changing the molar concentration of reactants to perform the experiment,[8,9] it had been apparently shown that the reaction of ECH with phenol is first order with respect to phenol and first order in ECH. The results show that the postulate (3) is right, that is, reactions (2) and (3) may be considered to proceed in one state under these conditions. The kinetic equation in the first stage of this reaction is

$$\frac{-d[\text{ECH}]}{dt} = k_1[\text{NaOH}][\text{ECH}] \qquad (12)$$

The rate constants $k_{1\text{BA}}$ of reaction of TBBPA with ECH were listed in Table I. Under the same condition, the reaction of ECH with BPA was carried out at 60, 70, and 80°C, respectively. The plot of $1/\alpha$ against t is given in Figure 2. The rate constants $k_{1\text{A}}$ are listed in Table I. According to the Arrhenius equation $k = Ae^{-E/RT}$, a plot of $\ln k_1$ against $1/T$ are obtained in Figure 3. The reaction activation energy E_{BA} and E_A are 64.04 kJ/mol and 76.56 kJ/mol, respectively. The ΔS_{BA} and ΔS_A are -144.91 J/K° mol and -69.47 kJ/K° mol, respectively.
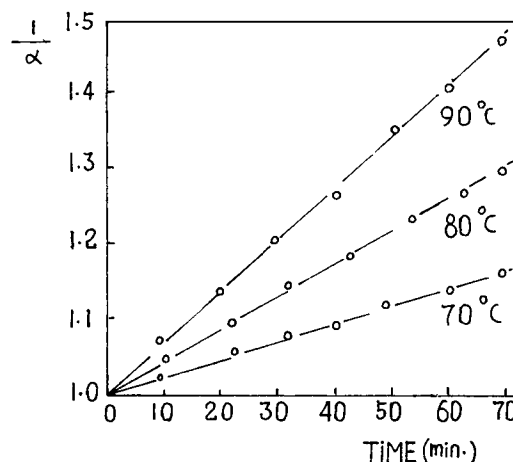

Figure 1 Plot of $1/\alpha$ vs. reaction time t in the reaction of ECH with TBBPA.

Table I Rate Constant k_1, k_3, and r at Various Temperatures[a]

	k	60°C	70°C	80°C	90°C
a	$10^4 \times k_{1BA}$ (mol L)$^{-1}$ S^{-1}		0.3821	0.6844	1.3216
b	$10^4 \times k_{3BA}$ (mol L)$^{-1}$ S^{-1}		0.2885	0.5042	0.9504
c	r_{BA} (k_{1BA}/k_{3BA})		1.3243	1.3575	1.3972
d	$10^4 \times k_{1A}$ (mol L)$^{-1}$ S^{-1}	12.531	30.493	68.202	
e	$10^4 \times k_{3A}$ (mol L)$^{-1}$ S^{-1}	1.1860	2.3793	4.8249	
f	r_A (k_{1A}/k_{3A})	10.55	12.82	14.14	

[a] Note: 1. The linear correlation coefficients of k are usually between 0.9925 and 0.9992. 2. The concentration of reactants are all 0.37 mol/L.

Kinetics of Reaction of Phenol with EG in Oligomer

The reaction of TBBPA diglycidyl either with TBBA was carried out in solvents (dioxane–water) and alkali with initial mole ratio of EG : TBBPA : NaOH = 1 : 1 : 1. The kinetic equation of consumption of epoxide group had the following form:

$$-\frac{d[EG]}{dt} = k_{3BA}[EG][-phoNa] \quad (13)$$

When the concentrations of reactants are as large as the reaction of ECH with TBBPA, the relationship of $1/\alpha$ with time t is given in Figure 4. As is seen from the data in Figure 4, this reaction is also second order. The rate constants k_{3BA} and r_{BA} (r_{BA} = k_{1BA}/k_{3BA}) are listed in Table I— b, and c, respectively. Under the same conditions, k_{3A} and r_A are obtained (Table I—e, f).

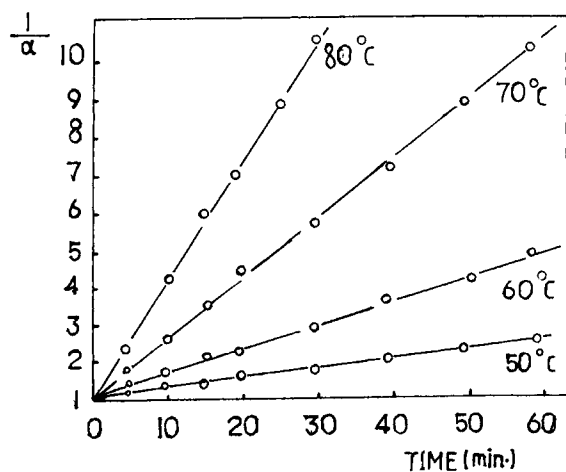From Table I, we have at 80°C k_{1BA} = 1.3575k_{3BA}, k_{1A} = 14.14k_{3A}, respectively. Inserting k_{1BA} =

1.3575k_{3BA} and k_{1A} = 14.14k_{3A} into eq. (9), respectively, we obtain

$$-\frac{d[EG]}{dt} = k_{3BA}[NaOH][EG-1.3575ECH] \quad (14)$$

$$-\frac{d[EG]}{dt} = k_{3A}[NaOH][EG-14.14ECH] \quad (15)$$

It is shown this reaction was proceed in two stages. In the first stage, the reactions (2) and (3) dominate. Theoretically, in the reaction of TBBPA with ECH, when the current concentration of the end epoxide group in oligomer is higher than 1.357 [ECH], the reaction (4) was run. At this time the conversion of ECH is over 58%, but in the reaction of BPA with ECH it is over 93%.

This result is well illustrated for industrial production. In the synthesis of BPA epoxy resin, the resin which has a higher epoxide value can be obtained easily with a general method, but it is difficult
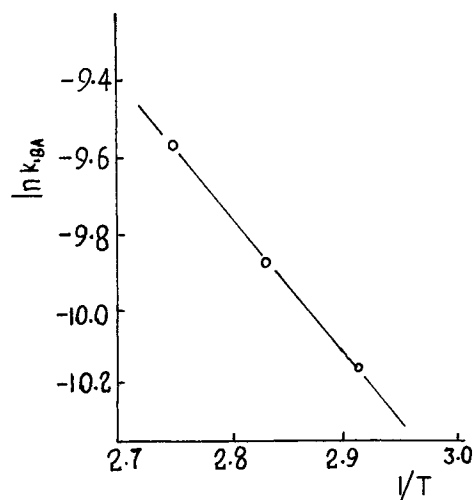

Figure 2 Relationship between $1/\alpha$ and time t in the reaction of ECH with BPA.

Figure 3 Plot of ln k_{1BA} against $1/T$ in the reaction of ECH with TBBPA.
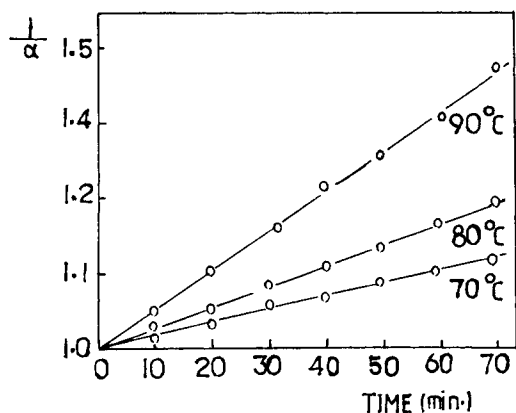
Figure 4   Relationship between $1/\alpha$ and reaction time t in the reaction of TBBPA epoxy resin with TBBPA.

Figure 5   NMR spectra of bromo-epoxy resins based on ECH, BPA, and TBBPA, D-acetone as solvent.

for the TBBPA epoxy resin. The TBBPA epoxy resin of higher epoxide value must be synthesized by the method of dichlorohydrin ether or used a large ratio of ECH to TBBPA.

Comparison of Reactivity of TBBPA and BPA

As seen from Table I, k_{1A} is nearly 100 times more than k_{1BA} and k_{3A} is nearly 10 times greater than k_{3BA}. It is show that the reactivities of BPA and BPA epoxy resin are much higher than those of TBBPA and the TBBA epoxy resin. This result can be proved from analysis of reaction product at different times.

Table II illustrates the NMR analysis for the reaction product of TBBPA and BPA with ECH under stoichiometric condition. As seen from Table II, it is right about the theory of reactivity of BPA and TBBPA. The BPA was consumed more rapidly than that of TBBPA in the early stage of synthesis. Figure 5 is the NMR spectrum of a bromo-epoxy resin.

CONCLUSIONS

1. The reaction of BPA and TBBPA with ECH in the presence of alkali in water-organic medium are apparently second order. The re-

Table II   The Content (%) of TBBPA in the Product at Different Reaction Times[a]

t (min)	20	35	50	65	80
TBBPA (%)	4	8.5	18.6	25.1	40.7

[a] Note: reaction temperature is 60°C.

action of epoxide group in molecular chain end with phenol in alkali medium is also second order.

2. Because the ratio of k_{1BA} to k_{3BA} is smaller, TBBPA epoxy resin which has a higher epoxide value must be synthesized by the method of TBBPA dichlorohydrin ether.[7] This diglycidyl ether is prepared from ECH and TBBPA in an anhydrous, aprotic medium in the presence of catalyst.

3. The reactivity of BPA is higher than that of TBBPA. Hence, the content of BPA in the product at early stage of the reaction is higher than that of TBBPA. If high molecular bromo-epoxy resin based on TBBPA, BPA, and ECH was prepared, the two-step method which used TBBPA diglycidyl ether to reaction with BPA worked well.[10]

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