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

JUNGANG GAO, MIN ZHAO, LITING YANG

Department of Chemistry, Hebei University, Hebei Province, Baoding, People's Republic of China

ABSTRACT: The kinetics of formation of epoxy resins derived from bisphenol-S, 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 the epoxide group of the epoxide oligomers. The obtained results satisfactorily explained that the reactivity of bisphenol-S with epichlorohydrin is higher than that of tetrabromobisphenol-A. The rate of dehydrochlorination of chlorohydrin ether in the presence of alkali and water was much higher than that of the rate of condensation of the phenolic hydroxyl group with epichlorohydrin. The apparent reaction order of the phenolic groups with epichlorohydrin and the terminal epoxide groups in the oligomer were second order. The rate constants and reaction activation energy were determined and results discussed. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 1137–1142, 1997

INTRODUCTION

Bromoepoxy resins, based on epichlorohydrin (ECH), bisphenol-A (BPA), and tetrabromobisphenol-A (TBBPA), were synthesized.[1,2] These resins are relatively fire resistant when the content of bromine is over 10%. They are usually used as fire-resistant materials. Epoxy resins based on ECH and BPS were synthesized.[3,4] These polymers have better heat resistance, gel time, and mechanical properties than those of epoxy resins prepared from ECH and BPA. The kinetics of formation of epoxy resins based on ECH and BPA have been considered and attempts to develop a mathematical model for the synthesis of epoxy resins have also been made.[5,6] In some cases, a qualitative coincidence of theoretical and experimental data were obtained. However, the process of this reaction is rather complicated, despite some progress made. The complete kinetic data and the description of the synthesis have been lacking until now. The reaction order was not discussed.

The kinetics analysis of synthesis of bromoepoxy resins from TBBPA, BPS, and ECH was the purpose of the present investigation. The kinetics of formation of these epoxy resins under stoichiometric conditions was considered. The reactivity of BPS and TBBPA with ECH and the terminal epoxide group (EG) in the oligomer were investigated by taking into account the consumption of the added alkali and the epoxide group.

EXPERIMENTAL

Materials

BPS and TBBPA have the following structures:
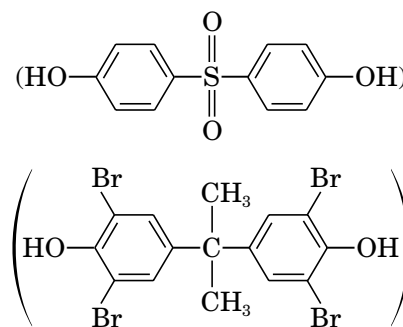
They were purified by recrystallization in toluene (mp 240 and 180°C, respectively). ECH, dioxane, acetone, ethyl alcohol, hydrochloric acid, NaOH, and KOH were all of analytically pure grade.

Synthesis of Diglycidyl Ethers of BPS and TBBPA

Diglycidyl ethers of BPS and TBBPA were synthesized according to Rainer et al.[7]: 0.1 mol BPS or TBBPA, 0.4 mol ECH, and 0.001 mol $Et_4N^+Br^-$ were stirred at 353 K for 5 h. After adding xylene and cooling to 308 K, 0.2 mol 20% NaOH was added; heating at 348 K for 30 min removed the H_2O, NaCl, ECH, and xylene, which yielded a resin. The epoxide values were determined in accordance with the method of Jay.[8] The epoxide values of diglycidyl ethers of BPS and TBBPA are 0.34 and 0.25 mol/100 g, respectively.

Determination of Conversion Rate of Reactants

The kinetics of the reaction of BPS and TBBPA with ECH was investigated by taking into account the consumption of added alkali. The initial mole ratio of BPS and/or TBBPA, ECH, and NaOH was 1. To a four-necked flask, equipped with a stirrer, a thermometer, and a condenser, were added 0.025 mol TBBPA, 0.025 mol NaOH, 25 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. Samples of the mixture were removed at regular time intervals for analysis. The conversion of reactants was determined potentiometrically with 0.1 mol HCl-acetone solution. The data were processed using 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 the oligomer with the phenolic group was determined by taking into account the consumption of the epoxide group, in accordance with a method found in the literature.[9]

Infrared Analysis

The content of the sulfone group in the epoxy resin formed from BPS, TBBPA, and ECH was analyzed by the method of Patts.[10] The characteristic absorption peak of the sulfone group $O=S=O$ in BPS is 1110 cm^{-1}, the absorption peak of isopropene (CH_3-C-CH_3) in TBBPA is 1180 cm^{-1}.
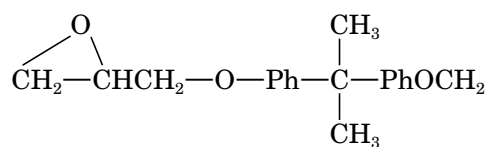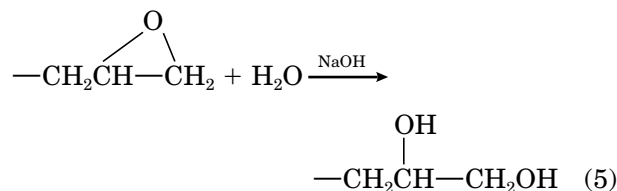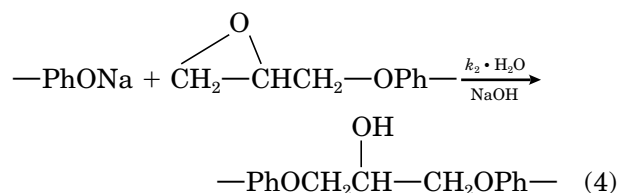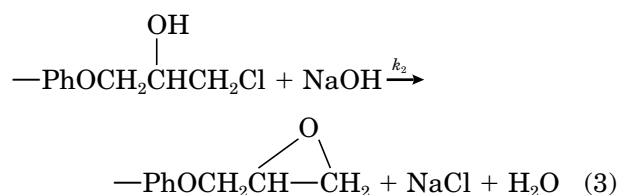
RESULTS AND DISCUSSION

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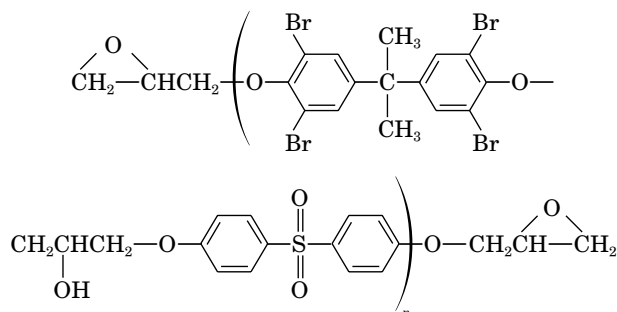
where $n = 1-2$. It is possible that the bisphenols in the one molecular chain are all BPS or are all TBBPA. It is also possible to have diglycidyl ether of BPS or TBBPA.

The reaction between bisphenol and ECH in the presence of alkali in water–organic media have the following main steps:

$$-PhOH + NaOH \underset{}{\overset{k}{\rightleftharpoons}} -PhONa + H_2O \qquad (1)$$

$$-\underset{\overset{|}{\text{CHCH}_2\text{OPh}}}{\overset{\overset{\text{ONa}}{|}}{}} + \underset{\text{CH}_2}{\overset{\overset{\text{O}}{\diagup\diagdown}}{}}-\text{CHCH}_2- \xrightarrow[\text{NaOH}]{\text{H}_2\text{O}}$$

$$-\text{Ph}-\underset{\overset{|}{\text{CH}_3}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}}-\text{PhOCH}_2-\underset{}{\text{CH}}-\underset{\overset{|}{\text{OCH}_2\text{CHCH}_2-}}{\text{CH}_2\text{OPh}}- \quad (6)$$

$$\underset{\overset{|}{\text{OH}}}{}$$
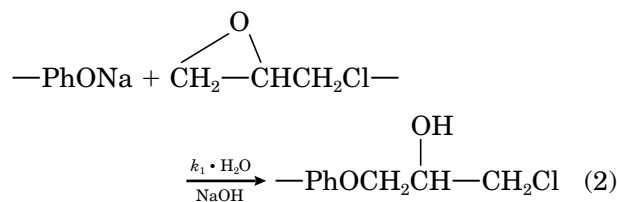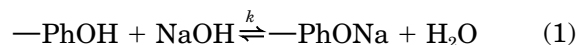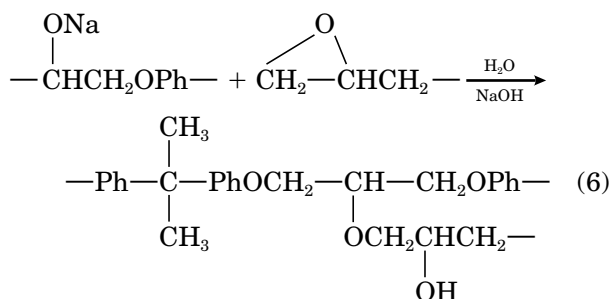
Because the concentration of the phenolic group in the first stage of the synthesis was higher than that of the alkali (phenolic-OH : NaOH = 1 : 0.50), all the alkali was bound as phenolate ions owing to the high acidity of the phenolic hydroxyl groups. The side reaction of hydrolysis and alcoholysis of ECH and the epoxide group were practically absent; the chain branching reactions were also not considered. Only the main reactions (1)–(4) occurred in this system. We postulate the following:

1. All phenolic groups in the monomer and chain end have the same reactivity about the same phenol hydroxyl groups.
2. Reaction (1) is faster than reactions (2) and (4), so that [−phONa] = [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:

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

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

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

$$= k_1[\text{NaOH}][\text{ECH}] \quad (8)$$

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

$$= k_3[\text{NaOH}][\text{EG}] - k_1[\text{NaOH}][\text{ECH}], \quad (9)$$

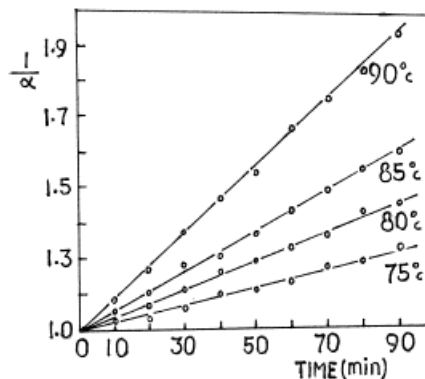where [NaOH], [ECH], [CHE], and [EG] are the

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

current concentration of NaOH, ECH, CHE, and the terminal epoxide group in the oligomer, respectively.

Kinetics of Reaction of ECH with TBBPA and BPS

If we consider the reaction order of reactants, the reaction rate equation of ECH with −phONa is

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

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

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

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

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

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

According to the experimental determination of reaction conversion, the reaction of ECH with TBBPA was carried out at 75, 80, 85, 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.[11] 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 postulate (3) is right; that is, reac-
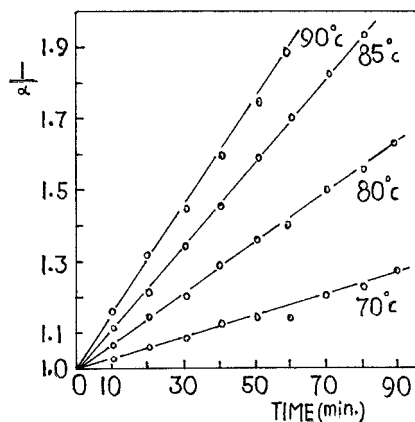
Figure 2 Plot of $1/\alpha$ vs. reaction time t in the reaction of ECH with BPS.

tions (2) and (3) may be considered to proceed in one stage 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 the reaction of TBBPA with ECH are listed in Table I. Under the same condition, the reaction of ECH with BPS was carried out at 70, 80, 85, and 90°C, respectively. The plot of $1/\alpha$ against t is given in Figure 2. The rate constants $k_{1\text{S}}$ are listed in Table I. According to the Arrhenius equation $k = Ae^{-E/RT}$. Plotting $\ln k - [1\text{BA}]$ and $\ln k_{1\text{S}}$ against $1/T$ gave the activation energies E_{BA} and E_{S}, obtained from linear regression analysis as 94.77 and 96.72 kJ/mol, respectively.

Kinetics of Reaction of Phenol with EG in Oligomer

The reaction of BPS diglycidyl either with BPS was carried out in solvents (dioxane–water) and
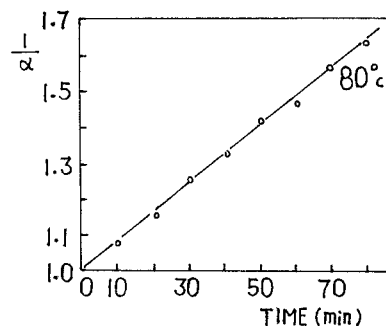

Figure 3 Relationship between $1/\alpha$ and reaction time t in the reaction of BPS epoxy resin with BPS.

alkali with an initial mole ratio of EG : BPS : NaOH = 1 : 1 : 1. The kinetic equation of consumption of epoxide group had the following form:

$$-\frac{d[\text{EG}]}{dt} = k_{3\text{S}}[\text{EG}][-\text{phoNa}] \qquad (13)$$

When the concentrations of the reactants were as large as the reaction of ECH with BPS, the relationship of $1/\alpha$ with time t is as given in Figure 3. As seen from the data in Figure 3, this reaction is also of second order. The rate constants $k_{3\text{S}}$ and r_{S} ($r_{\text{S}} = k_{1\text{S}}/k_{3\text{S}}$) are listed in Table I. Under the same conditions, $k_{3\text{BA}}$, r_{BA}, $k_{3\text{BA-S}}$, and $k_{3\text{S-BA}}$ are obtained (Table I).

From Table I we have at 80°C $k_{1\text{BA}} = 1.35 k_{3\text{BA}}$, $k_{1\text{S}} = 1.65 k_{3\text{S}}$, respectively. Inserting $k_{1\text{BA}} = 1.35 k_{3\text{BA}}$ and $k_{1\text{S}} = 1.65 k_{3\text{S}}$ into eq. (9) we obtain

$$-\frac{d[\text{EG}]}{dt} = k_{3\text{BA}}[\text{NaOH}][\text{EG} - 1.35\text{ECH}] \qquad (14)$$

$$-\frac{d[\text{EG}]}{dt} = k_{3\text{S}}[\text{NaOH}][\text{EG} - 1.65\text{ECH}] \qquad (15)$$

This reaction proceeded in two stages. In the

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

k	70°C	75°C	80°C	85°C	90°C
$10^4 \times k_{1\text{BA}}$ (mol L)$^{-1}$ S^{-1}		0.369	0.591	0.893	1.435
$10^4 \times k_{3\text{BA}}$ (mol L)$^{-1}$ S^{-1}			0.438		
r_{BA} ($k_{1\text{BA}}/k_{3\text{BA}}$)			1.35		
$10^4 \times k_{1\text{S}}$ (mol L)$^{-1}$ S^{-1}	0.772		2.197	3.863	4.535
$10^4 \times k_{3\text{S}}$ (mol L)$^{-1}$ S^{-1}			1.332		
r_{S} ($k_{1\text{S}}/k_{3\text{S}}$)			1.65		
$10^4 \times k_{3\text{BA-S}}$ (mol L)$^{-1}$ S^{-1}			0.459		
$10^4 \times k_{3\text{S-BA}}$ (mol L)$^{-1}$ S^{-1}			1.065		

The linear correlation coefficients of k are usually between 0.9907 and 0.9995. The concentration of reactants are all 0.37 mol/L.

first stage, reactions (2) and (3) dominated. Theoretically, in the reaction of TBBPA with ECH, when the current concentration of the end epoxide group in oligomer was higher than 1.35[ECH], the reaction (4) was run. At this time the conversion of ECH was over 58%, but in the reaction of BPS with ECH it was over 62%.

Under the same condition, from the synthesis of BPA epoxy resin based on BPA and ECH, we had obtained $k_{1A} = 14.14k_{3A}$. According to this theory, when the current concentration of the end epoxide group in oligomer is higher than 14.14[ECH], the reaction (4) was run. At this time the conversion of ECH is over 93%.

This result is well illustrated in 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 for the TBBPA and PBS epoxy resins. The TBBPA and PBS epoxy resins of higher epoxide value must be synthesized by the method of dichlorohydrin ether or using a large ratio of ECH to phenol.

Comparison of Reactivity of TBBPA and BPS

As seen from Table I, k_{1S} is 3.7 times more than k_{1BA} and k_{3S} is 2.3 times greater than k_{3BA}. The reactivities of BPS and BPS epoxy resin were higher than those of TBBPA and TBBPA epoxy resin. Because k_{1S} and k_{3S} were not much higher than k_{1BA} and k_{3BA}, the consumption of PBS was more rapid than that of TBBPA in the early stages of synthesis, causing the consumption to become near equality. If the TBBPA and BPS had the same reactivity, the mole content (%) in the product at different reaction times would be near equality. IR analysis of epoxy resin formation from PBS, TBBPA, and ECH under stoichiometric conditions at different reaction times are shown in Table II. These experiments and theory are correct as seen from Table II. Figure 4 shows the IR spectrum of this epoxy resin.
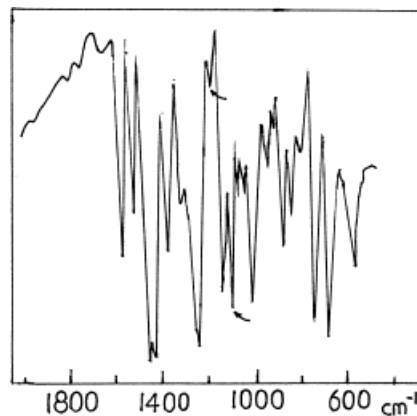

Figure 4 Infrared spectrum of epoxy resin formed from TBBPA, BPS, and ECH.

CONCLUSIONS

1. The reaction of BPS and TBBPA with ECH in the presence of alkali in water−organic medium were apparently second order. The reaction of the epoxide group in the molecular chain end with phenol in the alkali medium were also second order.
2. Because the ratio of k_{1BA} to k_{3BA} and k_{1S} to k_{3S} was smaller, epoxy resins that had a higher epoxide value must be synthesized by the method of dichlorohydrin ether.[7] These diglycidyl ethers were prepared from ECH, PBS, and TBBPA in an anhydrous, aprotic medium in the presence of a catalyst.
3. The reactivity of BPS was higher than that of TBBPA. Hence, the content of BPS in the product at early stages of the reaction was higher than that of TBBPA. If high molecular bromoepoxy resin based on TBBPA, BPS, and ECH was prepared, the two-step method, which used TBBPA diglycidyl ether to react with BPS, worked well.[7]

Table II Mole Content (%) in Product at Different Reaction Times

t (min)	20	30	40	50	60
TBBPA (%)	30.5	45.2	48.7	49.2	49.5

Reaction temperature is 55°C.

REFERENCES

1. Asahi Chemical Industry Co. Ltd., Jpn. Pat. 82,109,882 (1982).
2. D. W. Fox, Ger. Pat. 2,757,557 (1978).
3. V. Sykora and V. Spacek, *J. Appl. Polym. Sci.,* **54,** 1463 (1994).
4. J. G. Gao, Y. H. Liu, F. L. Wang, and L. Q. Shi, *Technol. Adhesion Sealing,* **7,** 5 (1986).

5. N. S. Engkolopyan, N. A. Markevitch, L. S. Sakhoneko, S. Z. Rogovina, and V. G. Oshmyan, *J. Polym. Sci. Chem.,* **20,** 1231 (1982).

6. H. Batzer and S. A. Zahir, *J. Appl. Polym. Sci.,* **21,** 1843 (1977).

7. E. Rainer, G. Udo, H. W. Heinrich, and B. Eruin, Ger. Pat. 228,279 (1985).

8. R. R. Jay, *Anal. Chem.,* **36,** 665 (1964).

9. The Group of Polymers, Fudan Univ., *Experimental Technology in Polymer Science,* Fudan Univ. Publishing Company, Shanghai, 1983, p. 275.

10. W. J. Patts, Jr., *Chemical Infrared Spectroscopy,* Vol. 1, Wiley, New York, 1963, p. 191.

11. S. H. Maroh and J. B. Lando, *Fundamentals of Physical Chemistry,* Macmillan, New York, 1974, p. 681.