

Composition of condensation products of bisphenol-A and epichlorohydrin

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Received: 6 December 1995/Revised version: 3 March 1998/Accepted: 5 March 1998

Summary

Theoretical equations based on kinetic scheme were developed to predict the average oligomerization number of products of Bisphenol-A and epichlorohydrin condensation catalysed by a quaternary ammonium salt. Ratio of rate constants of the terminal groups formation and chain extension reaction was found. The reactivity ratio varies from 0.05 at 25° to 0.50 at 120°.

Introduction

Condensation of epichlorohydrin (ECH) with polyfunctional hydroxyl compounds leads to the formation of a number of valuable polymers (1); e.g. epoxy resin based on Bisphenol-A (BPA).

The kinetics of the reaction of BPA with epichlorohydrin catalysed by sodium alkali and the composition of reaction products has been studied in detail (2). Mathematic models for the calculation of average molecular weight (M_n), weight per epoxy equivalent and average oligomerization number (\bar{n}) were developed (3,4).

It was assumed (2-4) that the reactivity of the epoxy ring of epichlorohydrin is higher than the reactivity of rings of the BPA glycidyl ethers. The ratio of the ring opening rate constants of ECH and glycidyl ethers ($\epsilon=0.6$) was determined by Fish (5) and it was used for calculating the epoxy resin molecular weight distribution. In more recent papers either the value of the reactivity ratio determined by Fish (4,6) or a close value (3) was used. Dependence of the reactivity ratio on temperature and other reaction conditions has not been discussed. There are no determined values of reactivity ratio for the reaction catalysed by other catalyst than sodium hydroxide.

Sodium hydroxide is used both as a catalyst of the condensation reaction and as a dehydrochlorination agent for intermediate Bisphenol-A chlorohydrin ethers. When condensation reaction is catalysed by non basic catalyst, e.g. quaternary ammonium halides, dehydrochlorination of chlorohydrin ethers occurs by reversible reaction with epichlorohydrin (trans-epoxidation reaction) (7,8). Although, trans-epoxidation reaction is used for preparation of epoxy resins (9), it has not been studied in detail.

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Quaternary ammonium salts (QAS) and salts of phosphonium are used as a catalyst of the condensation reaction of epichlorohydrin with Bisphenol-A (10), novolac resins (11), fluorinated phenols (12), and fluorinated alcohols (13).

We have studied the condensation reaction of BPA with epichlorohydrin catalysed by QAS. Our aim was to develop a simple kinetic scheme to describe the composition of products of bisphenol-A and epichlorohydrin condensation catalysed by QAS.

Experimental

Starting materials.

Epichlorohydrin was purified by distillation; the fraction boiled at 116-117° was collected and dried under molecular sieves 4Å for 24 hours. Tetramethylammonium chloride was dried under vacuum for 24 hours at 80°; Bisphenol-A, chloroform and hexane were used without additional purification.

Preparation of oligomers.

The reaction was carried out in a thermostat reactor supplied with magnetic stirrer. Initial proportion of epichlorohydrin to Bisphenol-A ranged from 3 to 20 mole/mole. Catalyst concentration (Me_4NCl) was 0.01 mole per kg of the mixture.

Technique of analysis.

The analysis was carried out on "Waters" chromatograph with the column "Nova-Pack Silica" (14).

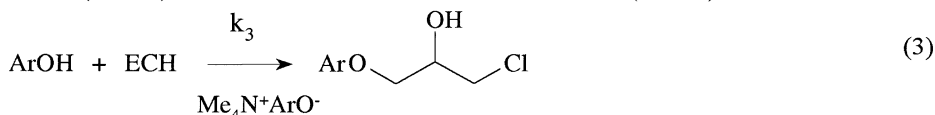
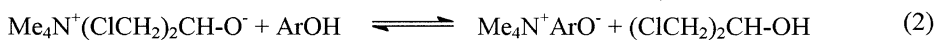
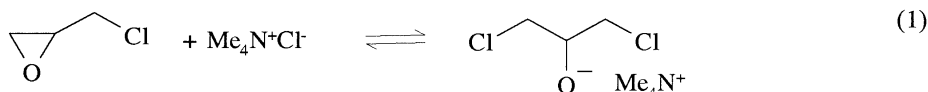
Results and discussion.

The epoxidation of phenolic hydroxyl groups catalysed by quaternary ammonium salts takes place through by reactions showed in scheme 1. There are two groups of reactions. The first one is the transformation reactions of the catalyst. Those reactions have been proved to take place through the formation of the intermediate alcoholate ion (8) followed by the formation of phenoxide of quaternary ammonium ($\text{Me}_4\text{N}^+ \text{ArO}^-$) as a result of the exchanged reaction with BPA (reaction 1, 2).

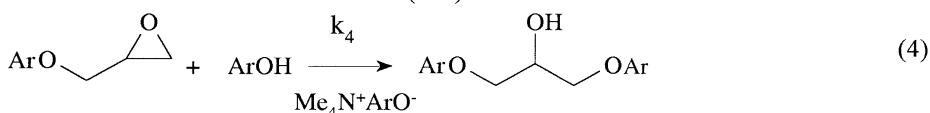
The second group of reactions is the condensation reactions catalysed by a base, i.e. the phenoxide ion. The phenoxide ion formed reacts with epichlorohydrin in the presence of BPA (reaction 3) to give BPA chlorohydrin ethers (**CH**) and with BPA glycidyl ethers (reaction 4) to give glycerol chain groups ($\text{ArOCH}_2\text{-CH(OH)-CH}_2\text{-OAr}$, **E**). Phenoxide ion is the catalyst of reaction 3 and 4 and it is not consumed.

The glycidyl ethers of BPA (**GL**) are formed by reaction of the phenoxide ion with the chlorohydrin ethers of BPA (reaction 5). Consumed phenoxide ion is regenerated by reactions 1 and 2.

Scheme 1.

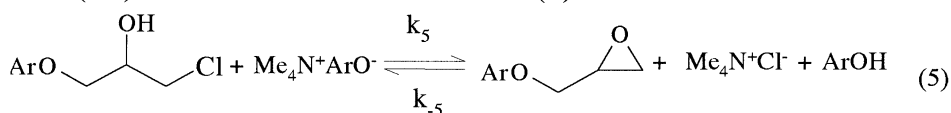


(CH)

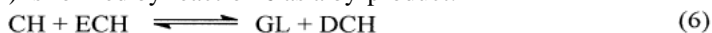


(GL)

(E)



Together reaction 5 and reactions 1 and 2 give the reaction between the chlorohydrin ether of BPA and epichlorohydrin (trans-epoxidation reaction 6). Glycerol dichlorohydrin (**DCH**) is formed by reaction 6 as a by-product.



The average oligomerization number of epoxy resin may be calculated by dividing the total number of the glycerol chain to the total number of moles of resin. By calling $[\text{ArOH}]$ - current and $[\text{ArOH}]_0$ - initial concentrations of phenolic hydroxyls we get:

$$\bar{n} = [\text{E}] / (0.5 \cdot [\text{ArOH}]_0 - [\text{E}]) \quad (7)$$

Equation 7 assumes that every time the chain extension step occurs, the total number of moles is decreased by one unit, i.e. no intermolecular rings are formed. The above equation may be rewritten in terms of the selectivity of glycerol chain formation $\Phi_{\text{ArOH}}^{\text{E}} = 2 \cdot [\text{E}] / ([\text{ArOH}]_0 - [\text{ArOH}])$. When conversion degree of phenolic hydroxyls $x_{\text{ArOH}} = ([\text{ArOH}]_0 - [\text{ArOH}]) / [\text{ArOH}]_0$ is high and $[\text{ArOH}] \cong 0$ we get:

$$\bar{n} = \Phi_{\text{ArOH}}^{\text{E}} / (1 - \Phi_{\text{ArOH}}^{\text{E}}) \quad (8)$$

According to equations 3 and 4, the rates of formation of terminal glycidyl and chlorohydrin groups (**GL** and **CH**) and glycerol fragments (**E**) can be described by the following kinetic equations:

$$\frac{d([\text{GL}] + [\text{CH}])}{dt} = k_3 \cdot [\text{ECH}] \cdot [\text{ArOH}] \cdot [\text{Me}_4\text{N}^+\text{ArO}^-] - k_4 \cdot [\text{GL}] \cdot [\text{ArOH}] \cdot [\text{Me}_4\text{N}^+\text{ArO}^-] = r_3 - r_4 \quad (9)$$

$$r_3 = k_3 \cdot [ECH] \cdot [ArOH] \cdot [Me_4N^+ArO^-]. \quad (10)$$

$$r_4 = d([E]) / dt = k_4 \cdot [GL] \cdot [ArOH] \cdot [Me_4N^+ArO^-]. \quad (11)$$

By calling $R=[GL]/[ECH]$ and $\varepsilon=k_4/k_3$ we get the following equation for the differential selectivity of the formation of glycerol group:

$$\phi_{ArOH}^E = \frac{-2d[E]}{d[ArOH]} = \frac{2d[E]}{dx_{ArOH}} = \frac{2r_4}{r_3 + r_4} = \frac{2\varepsilon \cdot R}{1 + \varepsilon \cdot R} \quad (12)$$

By integrating equation 12 we get:

$$\Phi_{ArOH}^E = \frac{1}{x_{ArOH}} \int_0^{x_{ArOH}} \phi_{ArOH}^E \quad (13)$$

Equation 13 allow us calculate concentrations of glycerol groups and terminal (glycidyl and chlorohydrin) groups.

$$[E] = x_{ArOH} \cdot \Phi_{ArOH}^E \quad (14)$$

$$[TG] = [GL]+[CH] = x_{ArOH} \cdot (1 - \Phi_{ArOH}^E) \quad (15)$$

According to equations 12 and 13, the selectivity of the glycerol group formation depends on the ratio of ring opening rate constant of glycidyl ethers and ECH (ε) and the ratio of the concentrations glycidyl group and epichlorohydrin (R).

Current concentration of epichlorohydrin can be calculated by the following equation:

$$[ECH] = [ECH]_{,0} - 2 \cdot [GL] - [CH] - 2 \cdot [E] = [ECH]_{,0} - [GL] - [TG] - 2 \cdot [E] \quad (16)$$

Equation 16 assumes, that formation of a glycidyl group requires two moles of epichlorohydrin: one mole for chlorohydrin group formations (reaction 3) and another mole for dehydrochlorination reaction 6. Consequently, a glycerol group is formed from two moles of epichlorohydrin and two equivalents of phenol.

The small amount of epichlorohydrin is used for generation of phenoxide ion. The concentration of the phenoxide ion, in accordance with equation 1, can not be higher than initial concentration of $Me_4N^+Cl^-$. Because initial concentration of $Me_4N^+Cl^-$ is less than 0.3% from initial concentration of epichlorohydrin and conversion degree of $Me_4N^+Cl^-$ to $Me_4N^+ArO^-$ varies from 1 to 75% (15), it is possible to ignore the contribution of reactions 1 and 2 deriving equation 13.

For calculating the concentration of glycidyl group we can find the concentration of terminal (chlorohydrin and glycidyl) groups and find the amount of chlorohydrin converted into glycidyl groups. It was assumed that there are no chlorohydrin groups present in the reaction mixture for the reaction condensation of BPA and ECH catalysed by sodium hydroxide (7-10). On the other hand, for condensation reaction catalysed by a non alkaline catalysts, as a quaternary ammonium salt, only a part of chlorohydrin groups is converted into glycidyl ones by reversible reaction 6.

Table 1 shows conversion degree of chlorohydrin groups at different initial ratio of epichlorohydrin and BPA.

Equilibrium constant of the trans-epoxidation reaction (reaction 6)

$$K = ([GL] \cdot [DCH]) / ([ECH] \cdot [CH]) \quad (17)$$

was found to be equal to $K=0.46 \pm 0.05$. Glycerol dichlorohydrin is formed by

$$\text{reaction 6 and its concentration is } [DCH] = [E] + [GL]. \quad (18)$$

Table 1

Initial ratio of epichlorohydrin to BPA (β), mole/mole	3	5	7	10	15	20
Conversion degree chlorohydrin groups to glycidyl ones, %	29.8	53.4	67.8	72.4	79.2	82.8

The small amount of glycerol dichlorohydrin also generated in accordance with equations 1 and 2, but it is possible to ignore the contribution of reactions 1 and 2 deriving equation 15 because phenoxide ion concentration is many times less than the concentration of other products of reaction.

By using equations 15, 17 and 18 we get:

$$K = \frac{[GL] \cdot ([E] + [GL])}{([ECH] \cdot ([TG] - [GL]))} \quad (19)$$

By solve equation 19 we get:

$$[GL] = \frac{-[E] - K \cdot [ECH] + \sqrt{([E] + K \cdot [ECH])^2 + 4 \cdot K [TG] \cdot [ECH]}}{2} \quad (20)$$

The system of equations 13-16 and 19 allows us to calculate the selectivity of glycerol group formation, the concentrations of terminal groups and, using equation 8, the average oligomerization number of Bisphenol-A based epoxy resin.

Fig. 1 shows values of \bar{n} , calculated at a different reactivity ratio e , as a function of the initial ratio of ECH to BPA (solid lines). Points represent experimental data.

Good correlation is observed between experimental and calculated values of \bar{n} .

Fig. 2 shows average oligomerization numbers of epoxy resins prepared at a different temperature. Significant dependence of average oligomerization number on temperature is observed. The reactivity ratio e is the ratio of rate constants of reaction 4 and reaction 3, consequently. The e dependence on temperature is described by the equation:

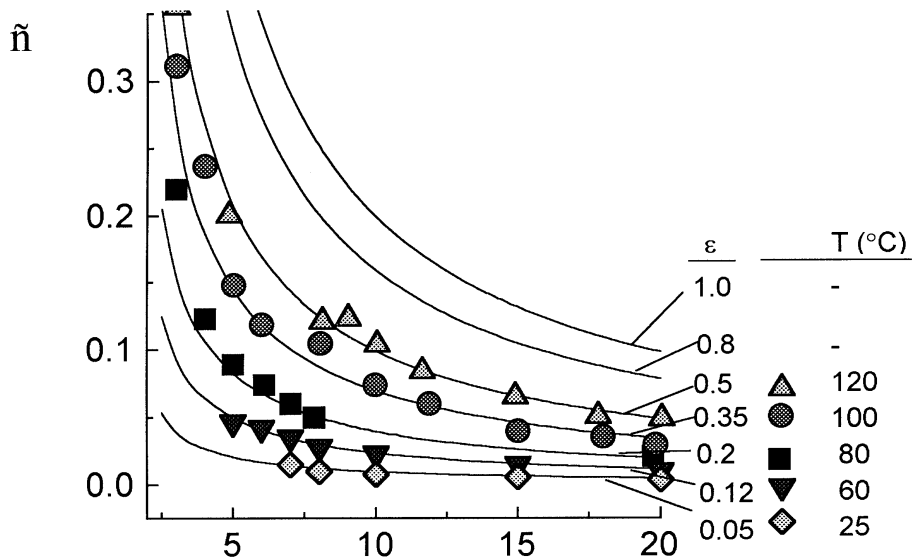
$$e = \frac{k_4}{k_3} = \frac{A_4}{A_3} \exp\left(-\frac{E_4 - E_3}{RT}\right) \quad (21)$$

The difference in activation energies for reactions 4 and 3 $\Delta E = (E_4 - E_3)$ is 24 KJ/mol.

A close value of $\Delta E = 25.6$ KJ/mol was found for the reaction of phenol with epichlorohydrin (16).

The difference in activation energies of the reactions 4 and 3 is suggested to be so large due to the marked bulk hindering in transition complex of the reaction of BPA glycidyl ethers with BPA.

The opening of the epoxy ring by the action of the phenoxide ion proved to be the rate limiting step of the addition reaction of BPA to epichlorohydrin (reaction 3) and BPA glycidyl ethers (reaction 4).

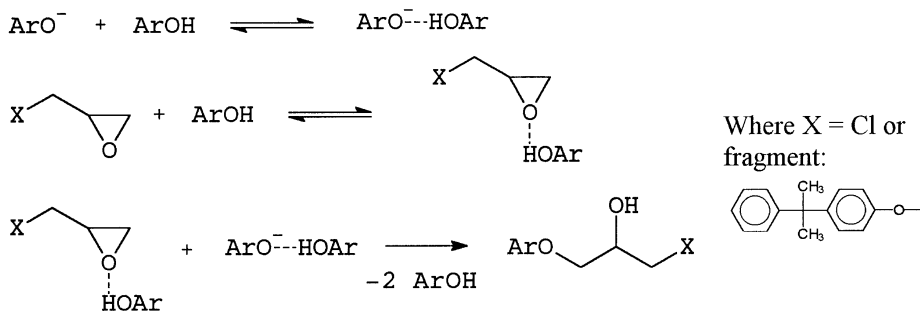


Initial ratio of epichlorohydrin to Bisphenol-A, mole/mole.

Fig. 1. Average oligomerization numbers as a function of ratio of initial concentrations of epichlorohydrin to Bisphenol-A. Solid lines represent values of \bar{n} calculated at different reactivity ratio ϵ ; points represent experimental data obtained at different temperatures.

Phenols give a complex both with epoxide (17) and phenoxide ions (18). Thus the following scheme of the process can be proposed.

Scheme 2.



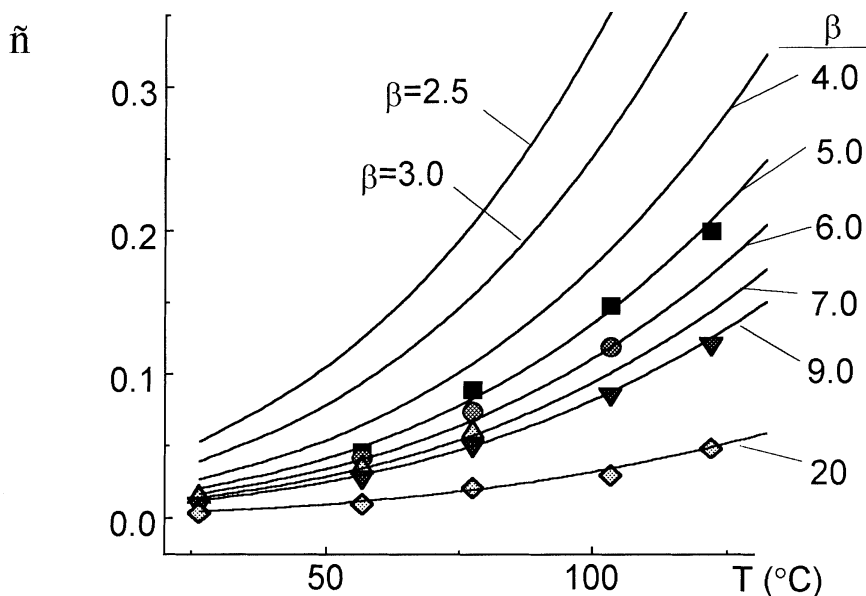
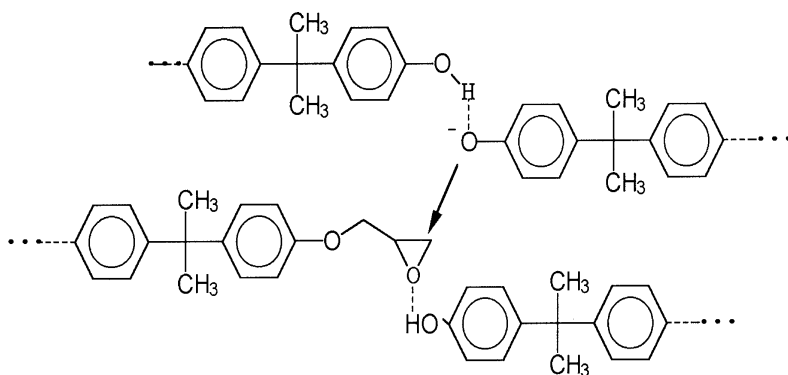


Fig. 2. Average oligomerization numbers as a function of temperature of synthesis. Solid lines represent values of \bar{n} calculated at different ratio of initial concentrations of epichlorohydrin and Bisphenol-A (β); points represent experimental data.

There are many bulk groups in the transition complex of the chain propagation reaction (reaction 4), i.e. the reaction of BPA glycidyl ethers with BPA.



During the reaction with epichlorohydrin the decrease in bulk hindering of the transition complex is due to a smaller atom of chlorine.

Conclusion.

The model proposed makes it possible to determine the composition and average oligomerization number of the condensation products of epichlorohydrin with Bisphenol-A catalysed by quaternary ammonium salts.

The relationship between reactivities of Bisphenol-A glycidyl ethers and epichlorohydrin (ϵ) and its temperature dependence has been found.

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