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Selectivity and Kinetics of Epoxy Resin-Bisphenol A Reaction Catalyzed by Certain Guanidine Derivatives

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Synopsis

The reaction of bisphenol A with a diglycidyl ether of bisphenol A may lead to linear polymers if a selective catalyst is used. Selective catalysts promote linear polymer formation while nonselective catalysts increase the rate of crosslinking. Selectivity in epoxy resin-bisphenol A reactions depends upon the nature of the catalyst used. In order to understand these catalyst-structure relationships better, we measured the effects of catalysts on the rate of polymerization (k_1) and the rate of crosslinking (k_2) during epoxy resin cures. The knowledge of the ratio k_1/k_2 aids in the selection of catalysts specific for the linear polymerization of epoxy resins. We related this specificity to catalyst basicity. We found that less basic catalysts tend to give large k_1/k_2 values, indicating that little crosslinking occurs with these highly selective catalysts. We demonstrated that the linear polymer obtained from epoxy resin polymerized by triethanolamine, a very selective catalyst, and the linear polymer prepared using 3-*p*-chlorophenyl-1,1-dimethylurea,[1] a catalyst with low selectivity, are essentially the same. Finally, we caution that quantitative comparisons of selectivity should be restricted to those reactions whose kinetic reaction orders are the same.

INTRODUCTION

Many workers have studied the reaction of phenols with epoxides.[2,3] Recently, Alvey published a paper describing a convenient method for determining the selectivity of amine catalysts in an epoxide–phenol reaction.[4] We demonstrated that this method is valid. However, we found that quantitative comparisons of selectivity are meaningful only when the reactions have reaction orders that are zero order with respect to the epoxide concentration.

Briefly, Alvey's method is based on the bulk polymerization of bisphenol A diglycidyl ether (DGE) and bisphenol A (BPA) (in a 2:1 mole ratio) in the presence of a catalyst. He follows the reaction by titrating the unreacted epoxide. A plot of per cent epoxide reacted versus reaction time gives two straight lines with an inflection point around 50% epoxide reaction (see Fig. 1). The slopes of these lines correspond to the rate constant for a linear polymerization (k_1) and the rate constant for crosslinking (k_2). A selective catalyst, therefore, shows a high k_1/k_2 value and a sharp inflection point.

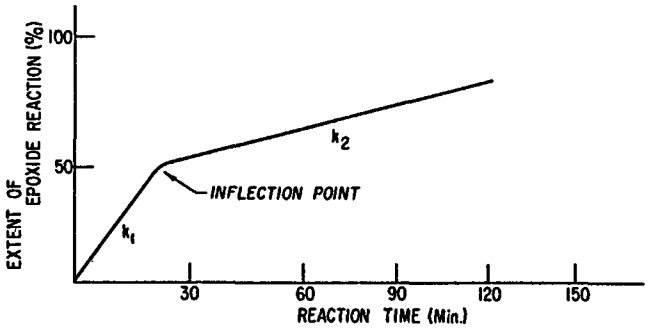


Fig. 1. A typical zero-order plot of DGE-BPA reaction in the presence of a catalyst.

RESULTS AND DISCUSSION

Catalysts

The catalysts we used in this work are derivatives of 1,1,3,3-tetramethylguanidine (TMG). They are new compounds. However, during the preparation of this report two papers were published on the syntheses of 2-acetyl and 2-benzoyl TMG derivatives.[5,6] Their syntheses differ from ours. We compared these TMG derivatives with commercially available catalysts such as triethanolamine, 2-dimethylaminoethanol, TMG, and 3-(*p*-chlorophenyl)-1,1-dimethylurea.

The TMG derivatives are readily prepared by the reaction of acyl chlorides or alkanesulfonyl chlorides with TMG in the presence of triethylamine (Scheme 1).

$$RCCl + HN=C(NMe_2)_2 \xrightarrow{Et_3N} RCN=C(NMe_2)_2$$

1

1a R = CH_3

1b R = ϕ

1c R = Cl-C$_6$H$_4$-

1d R = O_2N-C$_6$H$_4$-

$$RSO_2Cl + HN=C(NMe_2)_2 \xrightarrow{Et_3N} RSO_2N=C(NMe_2)_2$$

2

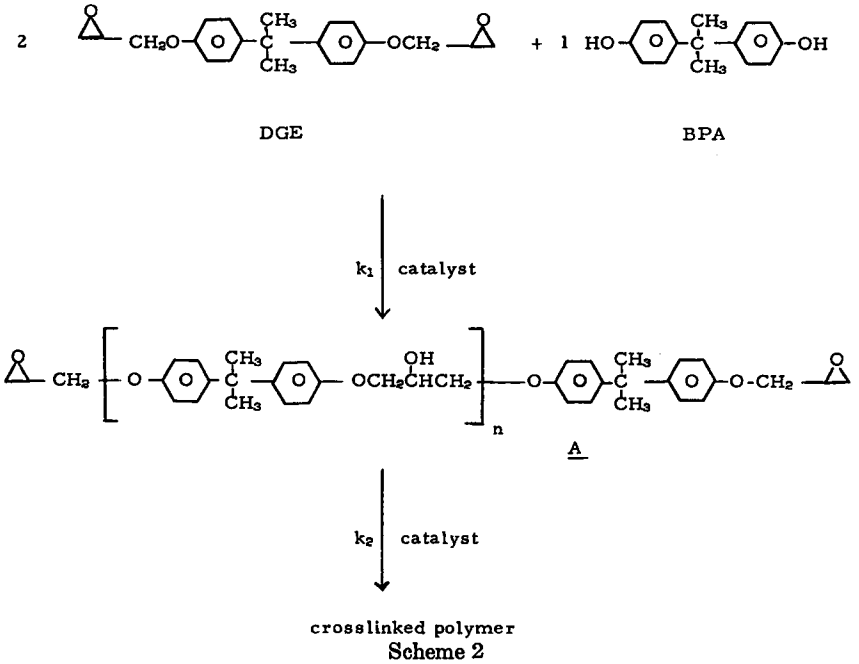
2a R = CH_3

2b R = $CH_2\phi$

Scheme 1

A brief examination of Table I reveals that triethanolamine stands out as the most selective catalyst of those we evaluated. Its k_1/k_2 value is 340.00. The sharp inflection point near 50% epoxide reaction and a long gel time (over 116.5 hr) further indicate its selectivity. On the other hand, the selectivity of the reaction catalyzed by 3-(*p*-chlorophenyl)-1,1-dimethylurea is only 15.57, and gel forms within 3 hr.

However, it is surprising that in both reactions the same type of high molecular weight linear polymers are formed just prior to crosslinking. We did not detect the 2:1 adduct (structure A with $n = 2$ in Scheme 2) as postulated by Alvey.[4]



Scheme 2

Gel permeation chromatography (GPC) analyses of samples withdrawn before and after the inflection point are shown in Fig. 2 through 4. In all three cases we noticed the presence of unreacted DGE, which we identified by comparison with the GPC peak of DGE alone. As far as chain lengths of the two separated peaks are concerned, Figures 3 and 4 are superimposible. We confirmed that these peaks are due to linear polymers and not due to crosslinked polymers, by following the disappearance of BPA in the 3-(*p*-chlorophenyl)-1,1-dimethylurea catalyzed reaction. Within experimental error the rate of disappearance of BPA is twice (k_1 = 7.14%/min) that of DGE (k_1 = 3.58%/min); that is,

$$\frac{-d[\text{BPA}]}{dt} = 2\frac{-d[\text{DGE}]}{dt}.$$

TABLE I
Reaction Selectivity of Bisphenol A Diglycidyl Ether (1.000) and Bisphenol A (0.500) Reaction at 120°C

	Reaction rate, %/min		Selectivity	Gel time,[a]
	k_1	k_2	k_1/k_2	hr
3-(*p*-Chlorophenyl)-1,1-dimethylurea	3.58 7.14[b]	0.23	15.57	1.8–2.0
2-Dimethylaminoethanol	4.76	0.14	34.00	2.3–2.8
Triethanolamine	2.04	0.006	340.00	>116.5
1,1,3,3-Tetramethylguanidine	14.29	0.78	18.32	1.3–1.5
1,1,3,3-Tetramethyl-2-acetylguanidine	6.96	0.47	14.81	1.6–1.8
1,1,3,3-Tetramethyl-2-benzoylguanidine	2.93	0.21	13.95	3.3–4.3
1,1,3,3-Tetramethyl-2-*p*-chlorobenzoyl-guanidine	2.38	0.14	17.00	5.0–6.0
1,1,3,3-Tetramethyl-2-*p*-nitrobenzoyl guanidine	1.20	0.008	150.00	7.5–22.9
1,1,3,3-Tetramethyl-2-methanesulfonyl-guanidine	0.50	0.014	35.71	45.9–51.4

[a] The time when the sample failed to dissolve in MEK–HCl solution.

[b] Rate of bisphenol A disappearance in 3-(*p*-chlorophenyl)-1,1-dimethylurea-catalyzed reaction.

This means that in the absence of the formation of cyclic polymers, which is very unlikely, the first reaction involves only linear polymerization. In addition, the presence of unreacted DGE and the absence of the 2:1 adduct near the inflection point suggest that 2 moles of the 2:1 adduct can react with 1 mole of BPA to form a 4:3 adduct (structure *A* with $n = 6$ in Scheme 2). Similarly, 2 moles of 4:3 adduct can react further with 1 mole of

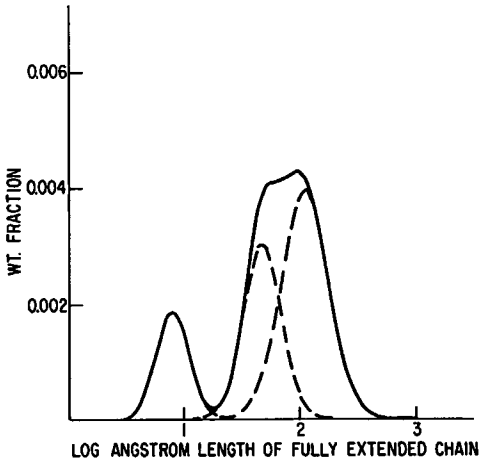


Fig. 2. GPC analysis: the superposition of experimental (solid line) and best-fit curve separation by computer (dotted line) for triethanolamine-catalyzed DGE–BPA reaction. The sample was withdrawn about 10 min before the inflection point which was shown in Fig. 6.

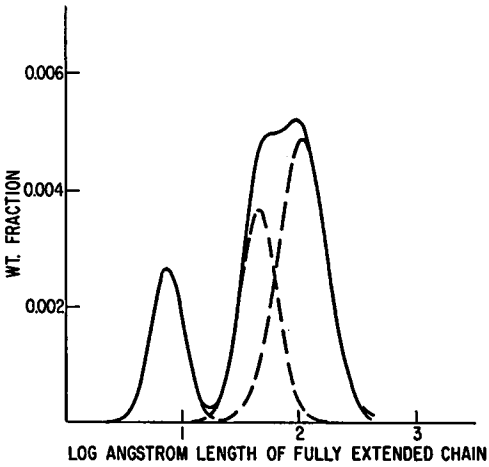


Fig. 3. GPC analysis: the superposition of experimental (solid line) and best-fit curve separation by computer (dotted line) for triethanolamine-catalyzed DGE–BPA reaction. The samples was withdrawn about 40 min after the inflection point which was shown in Fig. 6.

BPA to form a 8:7 adduct (structure A with $n = 14$ in Scheme 2), and so on. We measured the chain lengths of these adducts using Fisher-Hirchfelder-Taylor models. We also determined the relative lengths of fully extended chains of the two separated peaks with respect to DGE from Figure 4 (or computer print-out data). These measurements indicate that these peaks correspond to 4:3 and 8:7 adducts. The latter polymer has a molecular weight of 4316. Figure 2 is similar to Figures 3 and 4 except it has less high molecular weight polymer.

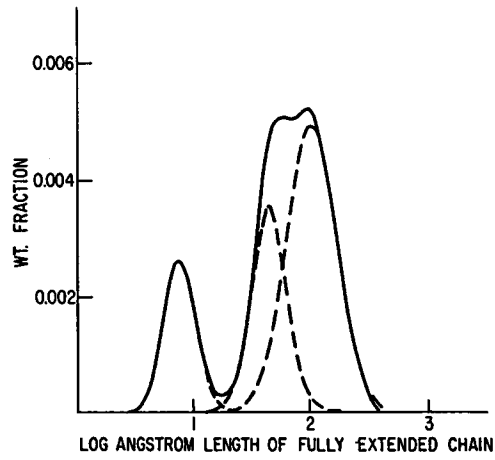


Fig. 4. GPC analysis: the superposition of experimental (solid line) and best-fit curve separation by computer (dotted line) and 3-(*p*-chlorophenyl)-1,1-dimethylurea-catalyzed DGE–BPA reaction. The sample was withdrawn 2 min before the inflection point which was shown in Fig. 6.

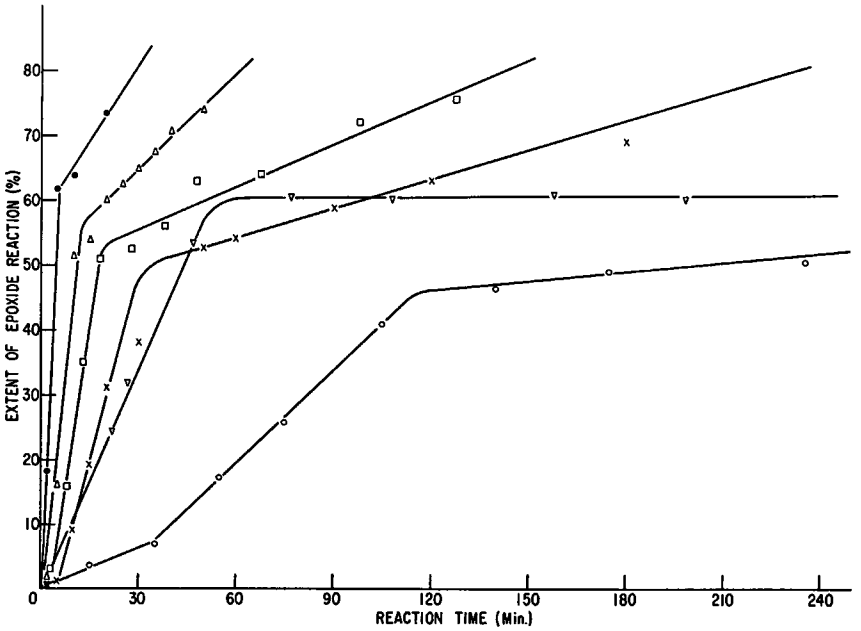


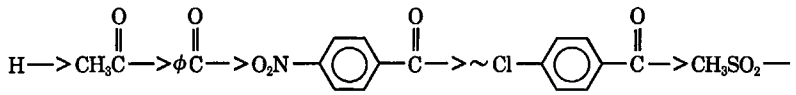
Fig. 5. Extent of epoxide reaction (%) vs. time for the reaction of bisphenol A diglycidyl ether (1.000) with bisphenol A (0.500) at 120°C with various catalysts (0.020): (●) 1,1,3,3-tetramethylguanidine; (△) 1,1,3,3-methyl-2-acetylguanidine; (□) 1,1,3,3-tetramethyl-2-benzoylguanidine; (×) 1,1,3,3-tetramethyl-2-*p*-chlorobenzoylguanidine; (▽) 1,1,3,3-tetramethyl-2-*p*-nitrobenzoylguanidine; (○) 1,1,3,3-tetramethyl-2-methanesulfonyl guanidine.

One explanation for the high selectivity of triethanolamine or other β-hydroxyethyl catalysts is that the β-hydroxyl group can form an intramolecular hydrogen bond with the nitrogen atom.[4] This reduces the ability of the catalyst to activate the secondary hydroxyl groups of the polymer. This activated complex of polymer and catalyst is required for the cross-linking reaction.[7]

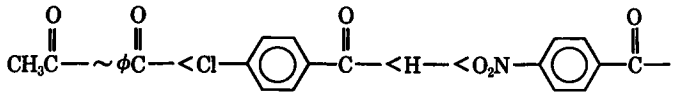
However, we observed that 2-dimethylaminoethanol was not a selective catalyst (k_1/k_2 = 33.3). Thus, in addition to hydrogen bonding between the β-hydroxyl group and the nitrogen atom, the basicity of the catalyst also plays an important role in determining the selectivity of catalyst in DGE and BPA reaction. This explanation is further amplified in the following discussion.

The data from the DGE–BPA reaction in the presence of TMG or its derivatives are plotted and summarized in Figure 5 and Table I.

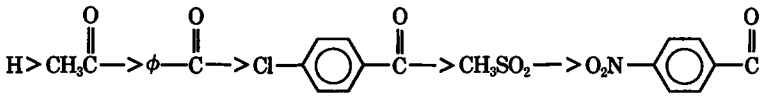
In an attempt to correlate selectivity with catalyst basicity, the basicities of TMG and 2-substituted TMG derivatives were determined (see experimental section). Their basicities decrease in the following order (only R groups of $(Me_2N)_2C{=}N{-}R$ are indicated):



On the other hand, the selectivity increases as follows:



Thus, there is no simple correlation between basicity and selectivity. However, except for TMG, more basic catalysts are not as selective as the less basic ones. A better correlation can be found between basicity of catalysts and k_2 values which decrease in the following order:



Moreover, α-hydrogen containing 2-substituted TMG derivatives such as 1,1,3,3-tetramethyl-2-acetylguanidine and 1,1,3,3-tetramethyl-2-methanesulfonylguanidine may be capable of releasing ketene and sulfene, respectively, along with free TMG in situ. This may explain why 1,1,3,3-tetramethyl-2-methanesulfonylguanidine is more reactive than *p*-nitrobenzoyl TMG derivatives.

Reaction Order

The reaction selectivity we referred to in the preceding discussion is based on k_1 and k_2 values obtained from zero-order plots (Figs. 4 and 6). In general, these plots give straight lines. But there are exceptions. For ex-

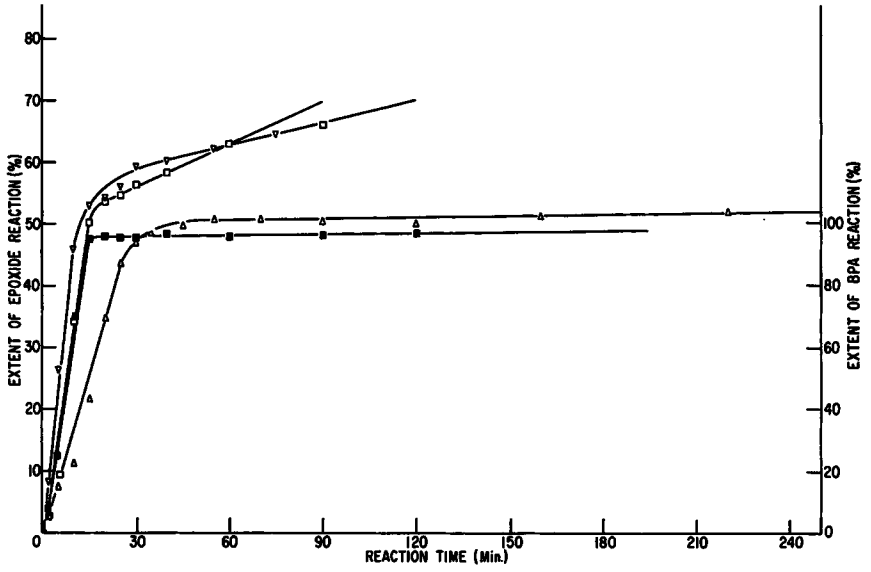


Fig. 6. Extent of epoxide reaction (%) vs. time for the reaction of bisphenol A diglycidyl ether (1.000) and bisphenol A (0.500) at 120°C with various catalysts (0.020): (▽) 2-dimethylaminoethanol; (□) 3-(*p*-chlorophenyl)-1,1-dimethylurea; (■) extent of BPA reaction (%) which is catalyzed by 3-(*p*-chlorophenyl)-1,1-dimethylurea; (△) triethanolamine.

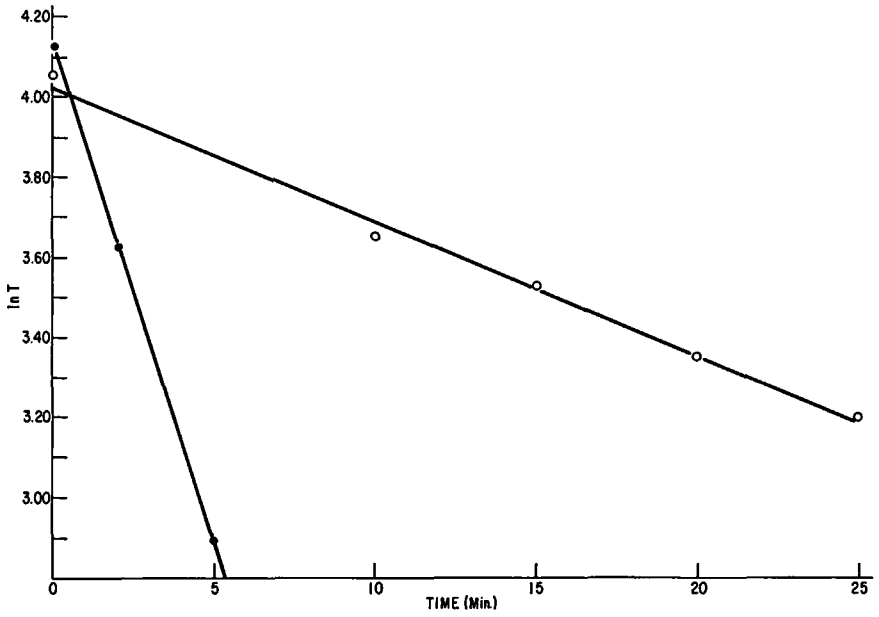
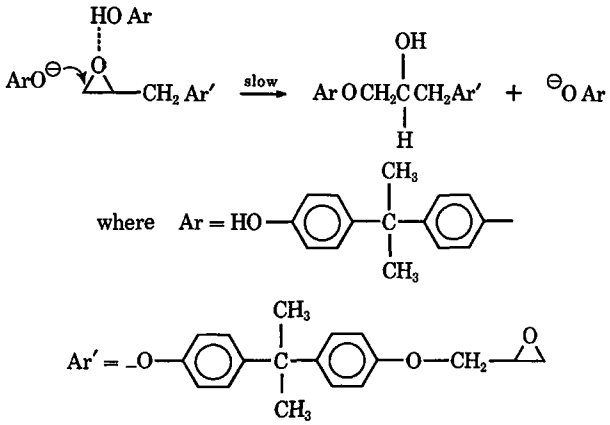


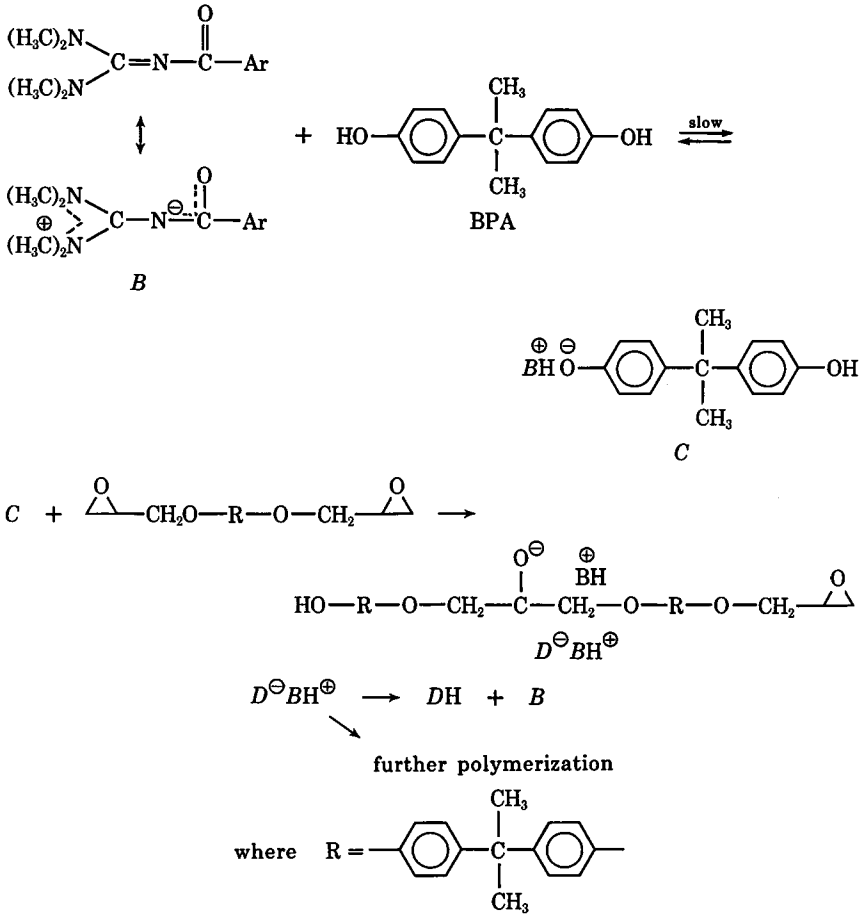
Fig. 7. First-order plots of bisphenol A diglycidyl ether (1.000) and bisphenol A (0.500) reaction at 120°C with a catalyst (0.020): (●) 1,1,3,3-tetramethylguanidine ($k = 4.15 \times 10^{-3}$ sec^{-1}); (O) triethanolamine ($k = 5.47 \times 10^{-4}$ sec^{-1}). (T = titre (ml)/weight of sample (g)).

ample, the triethanolamine or TMG-catalyzed DGE–BPA reaction is first order with respect to epoxide concentration (see Fig. 7). A possible mechanism for these reactions involves the following rate-determining step:



The nucleophilic attack by the anion of BPA on the epoxide carbon atom is facilitated by hydrogen bonding[8] between BPA hydroxy group and the epoxide. Thus, the reaction rate would depend not only on the concentration of BPA but also on the concentrations of catalyst and DGE. We plan to do further work in this area.

On the other hand, the kinetic data for 2-substituted TMG-catalyzed reactions, fit best for pseudo zero-order reactions with respect to epoxide concentration. Probably, the slow step involves the activation of the catalyst. As we mentioned earlier, α-hydrogen containing catalysts such as 1,1,3,3-tetramethyl-2-acetylguanidine and 1,1,3,3-tetramethyl-2-methanesulfonylguanidine could release TMG in the rate determining step. However, those TMG derivatives which have no α-hydrogen atoms may involve activation by BPA, forming an ion pair *C*.



The activated catalyst *C* can then attack the epoxide group of DGE to form a new ion pair $D^{\ominus}BH^{\oplus}$. The latter can either attack DGE again or terminate the reaction temporarily by picking up a proton to form *D*H. Similar phenomena were observed in the polymerization of epoxide resin in the presence of acid anhydride and tertiary amine. In this study, Feltzin et al.[9] found that the rate of the polymerization was first order with respect to catalyst, but appeared to be zero order in epoxy and anhydride. Fur-

thermore, they also found that the rate-controlling step was activation of the catalyst by water.

In summary, comparison of selectivity values (k_1/k_2) is more meaningful if one confines the comparison to those reactions which follow the same kinetics.

EXPERIMENTAL

Preparation of 1,1,3,3-Tetramethylguanidine (TMG) Derivatives

1,1,3,3-Tetramethyl-2-benzoylguanidine (1b). The experimental procedures for preparing TMG derivatives are essentially the same. Therefore, a detailed description of experimental conditions is given only for the synthesis of 1,1,3,3-tetramethyl-2-benzoylguanidine (1b).

In a flame-dried 2-liter flask were placed 57.6 g (0.5 mole) TMG and 50.6 (0.5 mole) triethylamine in 400 ml THF. The solution was cooled to 9°C by an ice water bath. To this stirred solution was added dropwise 70.3 g (0.5 mole) benzoyl chloride in 200 ml THF. A white precipitate formed immediately. During the addition, about 1 hr, the reaction temperature was maintained at 9–18°C. After the benzoyl chloride solution had been added the ice water bath was removed. The resulting white slurry was allowed to stir 2 additional hours, filtered, and the precipitate washed with THF. The combined washings and the filtrate were concentrated on a rotary evaporator to yield 110 g (86% of theory) of yellow syrup. It failed to distill at 140°C/0.6 mm. However, Kessler and Leibfritz[6] reported a boiling point of 138–140°C/0.25 mm for this residue. Without purification, the yellow syrup gave the correct elemental analysis, and its structure was further confirmed by NMR, IR, and mass spectroscopy.

NMR ($CDCl_3$): δ 2.87 (singlet), δ 7.36 (multiplet), δ 8.12 (multiplet) in ratio of 12:3:2.

ANAL. Calcd for $C_{12}H_{17}N_3O$: C, 65.72; H, 7.82; N, 19.17. Found: C, 65.36; H, 7.77; N, 19.49.

1,1,3,3-Tetramethyl-2-acetylguanidine (1a). This was prepared similarly from acetyl chloride and TMG on a 1-mole scale. Instead of THF, anhydrous ether was used as the solvent. After stirring overnight, the resulting yellow slurry was filtered. The mother liquor was concentrated to leave 122 g of a dark-brown liquid, which was fractionated to give 92.3 g of crude product (58.9% of theory), bp 82–86°C/0.4–0.2 mm, (reported 78–81°C/0.1 mm[5]; 142–143°C/0.26 mm[6]). A pure sample was isolated by preparative gas chromatography and subsequently recrystallized from hexane. Tne resulting hygroscopic white needles melt at 56.0–56.5°C. Spectroscopic data and elemental analysis support the structure.

ANAL. Calcd for $C_7H_{15}N_3O$: N, 26.73. Found: N, 26.06.

1,1,3,3-Tetramethyl-2-(*p*-nitrobenzoyl)guanidine (1d). This was prepared similarly on a 0.5-mole scale. THF was used as the solvent. After

work-up, the crude product was isolated as a yellow solid (129.5 g), mp 89–94°C. Recrystallization from water gave a white solid, mp 100–101°C. Spectroscopic data and elemental analysis support the structure.

ANAL. Calcd for $C_{12}H_{16}N_4O_3$: N, 21.20. Found: N, 21.59.

1,1,3,3-Tetramethyl-2-(*p*-chlorobenzoyl)guanidine (1c). It was prepared similarly in THF. After usual work-up, a yellow-brown liquid was obtained. It failed to distill at 150°C/0.5 mm. The NMR ($CDCl_3$) spectroscopy of the product was consistent with the structure δ2.94 (singlet), δ7.72 (the center of a quartet) in a 3:1 ratio.

1,1,3,3-Tetramethyl-2-methanesulfonylguanidine (2a). It was prepared similarly from methanesulfonyl chloride and TMG in the presence of triethylamine. A 0.5-mole-sclae reaction was run using anhydrous ether as the solvent. After usual work-up, a mixture of a solid and an oil was obtained. The solid was isolated by washing with methanol. The crude product weighed 31.0 g (33.1% yield), mp 107–109°C. An analytical sample was obtained by sublimation. The resulting white crystals melt at 108.5–110°C. NMR ($CDCl_3$) showed a single peak at δ2.97. The mass spectrum and IR spectrum agree with the proposed structure.

ANAL. Calcd for $C_6H_{15}N_3O_2S$: C, 37.29; H, 7.82; N, 21.74; S, 16.59. Found: C, 37.45; H, 7.77; N, 22.86; S, 16.26.

1,1,3,3-Tetramethyl-2-phenylmethanesulfonylguanidine (2b). It was prepared by the same procedure used to prepare 2a. A 0.12-mole-scale reaction was run in dry benzene. After the usual work-up, an orange solid was obtained. Recrystallization from hexane–benzene (5:1 ratio) gave 15.4 g (47.7% yield) of crude product, mp 105–110°C. An analytical pure sample was obtained by further recrystallization from ethyl acetate. This water white solid has a mp 111–112°C. No cycloadduct was found. The structure was confirmed by NMR, IR, and mass spectra.

ANAL. Calcd for $C_{12}H_{19}N_3O_2S$: C, 53.51; H, 7.11; N, 15.60; S, 11.90. Found: C, 53.60; H, 7.35; N, 15.68; S, 11.51.

Reaction Procedure

All the polymerization reactions were carried out in a 500-ml three-necked flask equipped with stirrer, condenser, and thermometer. The bath temperature was maintained at 120°C (± 1°C). A mixture of DGE and BPA (2:1 mole ratio) was heated to 120°C and then the catalyst (0.02 mole of DGE) was added. This was taken as zero time. Usually an exothermic reaction followed the addition of a catalyst. As the reaction proceeded, the viscosity of the reaction mixture increased. Samples were withdrawn at desired intervals and analyzed as described in the following section. When stirring became difficult, the reactants were transferred quickly into aluminum dishes and allowed to react further in an oven maintained at 120°C (± 1°C).

Analysis

Disappearance of the epoxide was followed by titrating samples according to the Jung and Kleeberg method.[10] Disappearance of BPA was followed by potentiometric titration, using tetrabutylammonium hydroxide as titrant in pyridine.[11,12,13]

The relative basicity of TMG derivatives was determined by potentiometric titration with 0.1*N* $HClO_4$ in glacial acetic acid. Methyl cellosolve was used as the solvent.

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