Selectivity of the Epoxide Phenol Reaction

FRANCIS B. ALVEY, PH.D., *Celanese Coatings Company,*
Louisville, Kentucky*

Synopsis

A method for determining the relative amount of alcohol side reaction which occurs in reactions of epoxy compounds with active hydrogen compounds has been investigated. It involves determining the ratio of rates of the successive reactions, epoxide-active hydrogen compound and epoxide-generated secondary alcohol, in the reaction of epoxide and active hydrogen compound at respectively a 2:1 mole ratio. Rate ratios are reported for the bulk reaction of bisphenol-A and the diglycidyl ether of bisphenol-A under different reaction conditions. The data correlated with the properties of high molecular weight polymers. Amines with β-hydroxyl groups were very selective catalysts.

INTRODUCTION

The reaction of epoxy compounds with active hydrogen compounds yields hydroxylalkyl products. Thus, carboxylic acids, phenols and alcohols yield respectively hydroxylalkyl-esters, -aromatic ethers, and -aliphatic ethers. The direction of ring opening of the epoxide compound has been extensively studied, it depends on electronic and steric factors and the reaction environment. In terminal epoxides, the ring opening occurs generally to yield the secondary alcohol group.[1-3] An important facet of such epoxide-active hydrogen compound reactions is the degree of reaction of the unreacted epoxide compound with the generated secondary alcohol group of the hydroxylalkyl products.

We refer to epoxy-active hydrogen reactions which proceed without reaction of the secondary hydroxyl group as selective reactions. The degree of selectivity of reaction will depend on the active hydrogen compound employed, catalysts, temperature and other reaction variables. Selectivity considerations are important in epoxy reactions which yield thermoset and thermoplastic polymers. Thermoset epoxy plastics, in order to have optimum physical and chemical properties, should generally be formulated to have stoichiometric quantities of reactants. Nonselective reaction of the generated secondary hydroxyl group can upset stoichiometry in these reactions and thus reduce properties. Reaction of diepoxide monomers with difunctional active hydrogen compounds to produce high molecular

* The author is currently a Research Associate in the Pharmacology Department of the University of Louisville School of Medicine.

weight polyhydroxyl polymers can lead to gelation in the final stages of polymerization if a selective reaction does not prevail.

We have been concerned with reaction selectivity in the bulk polymerization of bisphenol-A (BPA) and bisphenol-A-digylcidyl ether (DGE) in essentially equivalent quantities to yield high molecular weight polyhydroxylether polymers (PHE). Some information has been given in the literature relating to the amount of epoxy-secondary alcohol reaction that might be expected to occur in the polymerization of diepoxides and diphenols. Shechter and Wynstra have studied reactions of phenylglycidyl ether with acids, phenols and alcohols.[4] They reported that under mineral base catalysis, in the reaction of phenylglycidyl ether and phenol, nearly all epoxide reaction was with phenol. They also showed that dipropyleneglycol reacted with phenylglycidyl ether under conditions similar to those used in the phenol reaction, at a rate faster than phenol. These same workers reported that amine epoxide reactions occur with no alcohol reaction, within experimental error.[5] This work was based on primary and secondary amine reactions with phenylglycidyl ether. Tanaka and Takiuchi studied gel times in the thermosetting reaction of DGE and hexahydrophthalic anhydride with amine and alcohol catalysts[6] and concluded that epoxide-alcohol reaction did not take place. In a study of the product distribution from the reaction of phenol and epichlorohydrin under base catalysis in ethanol solvent, about 2% of the product mix related to reaction of phenylglycidyl ether with ethanol.[7] However, primary alcohol is more reactive than secondary and tertiary alcohol with epoxide.[4] Belanger and Denham studied the dilute solution kinetics of the reaction of phenylglycidyl ether with active hydrogen compounds in pyridine solvent. They reported that at 90°C the rate of reaction of phenylglycidyl ether with phenol is 5 to 8 times as fast as that with primary, secondary, and tertiary alcohols.[8] Several of these workers indicated experimental difficulties in determining the alcohol reaction.[5-8] Generally, we concluded that only a small amount of nonselective reaction would occur in the DGE, BPA polymerization. However, just a small degree of this reaction can cause gelation in the final stages of polymerizations designed to yield high molecular weight linear polymers. It was apparent from the literature that analysis for any small percentage of epoxide-secondary alcohol reaction would be difficult.

We developed an empirical technique to characterize the DGE-BPA reaction with respect to the relative degree of reaction selectivity that might occur under one set of reaction conditions compared to another in bulk polymerizations. Our method involves measuring the rate of epoxide disappearance in the bulk reaction of DGE and BPA in a 2:1 mole ratio as shown in Figure 1. In this idealized representation of the bulk reaction, DGE reacts chiefly with BPA in fast Reaction 1 to yield a higher molecular weight dihydroxydiepoxide (DHDE). If no further reaction occurs, the process is completely selective and the overall degree of reaction of epoxide is 50%. However, Reaction 2 can occur. This is a much slower reaction

REACTION 1: EPOXIDE-PHENOL

REACTION 2: EPOXIDE-SECONDARY ALCOHOL
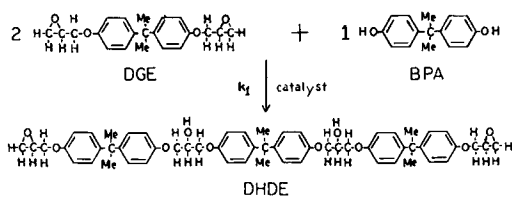
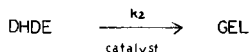$$\text{DHDE} \xrightarrow[\text{catalyst}]{k_2} \text{GEL}$$

Fig. 1. Reaction of bisphenol-A (1.0) and the diglycidyl ether of bisphenol-A (2.0).

than is Reaction 1 and produces a gelled three dimensional polymer structure.

Plots of percent conversion versus time for the 2:1 mole ratio bulk polymerization show a major rate break in the region of 50% which relates to the end of the epoxide phenol reaction. It is apparent that as the reaction process becomes more selective, that is, as the rate of Reaction 2 approaches zero, the ratio of the observed rates of the first and second reactions approaches infinity. Our empirical method for evaluating selectivity of reaction for the bulk, equimolar polymerization of DGE and BPA under various reaction conditions simply entails determining this rate ratio for the 2:1 mole ratio reaction under those conditions. The rate ratio serves as a relative selectivity index for any series of polymerizations. Most of the polymerizations we studied gave linear rate curves for the initial and final reactions. In cases where linearity was not observed, the rate ratios were based on the slope of the rate plot at selected degrees of conversion. The linearity of the rate curves suggests that the reactions were independent of the concentration of DGE and BPA. This type of behavior has been observed before for the reaction of phenylglycidyl ether and phenol[7] and for epoxy anhydride reactions.[9]

In addition to the rate ratios, the shape of the percent reaction versus time curves in the region of 50% reaction, the gel time, and the percent conversion in the gel also serve to indicate reaction selectivity. Thus, the more selective reactions should have high rate ratio values, sharp inflection points in the rate curves near 50% conversion, long gel times, and higher degrees of conversion in the gel structure. In addition to the DGE, BPA polymerization, this method can be applied to the reaction of other active hydrogen compounds with epoxides. In all cases, the effect of catalyst type, catalyst concentration, reaction temperature and other reaction variables can be determined.

Experimental

Materials. The DGE used in these experiments was a resinous grade commercially available from Celanese Resins, Epi-Rez 509. All resins em-

ployed had less than 0.1% hydrolyzable chlorine. The BPA was obtained from Union Carbide (high purity), freezing point 156°C or from Monsanto, freezing point 153°C. The Union Carbide BPA was employed in the 2:1 reactions; the Monsanto BPA in the polymerizations of Table III. Generally, in all comparison series, the same quantity of DGE and BPA was employed. Other reactants were obtained as follows: p-toluenesulfonamide, Monsanto; adipic acid, DuPont; azelaic acid, Emery. Catalysts were obtained as follows: tri-n-butylamine and 1,1,3,3-tetramethylguanidine, Eastman Grade, Eastman; lithium hydroxide, Merck; n-butylamine, di-n-butylamine, triethanolamine, triisopropanolamine, technical grade, Union Carbide. The catalysts were employed as received. The di-(3-phenoxy-2-hydroxylpropyl), n-butylamine was prepared from n-butylamine and phenylglycidyl by stirring 2 hr at 60°C, followed by 2 hr at 95°C. Volatiles were vacuum distilled (to 125°C; 4 mm). The product was a yellow viscous liquid having no epoxide content by infrared; yield 99.5%.

Reaction Procedure. Bulk reactions of DGE and BPA at all mole ratios were carried out in open metal reaction vessels with stirring. The reactants were heated to reaction temperature and the catalyst was added. The time of catalyst addition was taken as zero time. The reactions were stirred during the exothermic initial stages, generally for 1 to 7 hr in the 2:1 mole ratio reactions and for 1 hr in the polymerizations listed in Table III. The reaction mixtures were then placed in an oven equilibrated at the reaction temperature. Temperatures were held at ±1°C during the stirring phase and at ±0.5°C during the unagitated oven aging. Aliquots were removed for analysis. Reactions with dicarboxylic acids were run in three neck flasks equipped with reflex condensers. Molecular weights used for all reactants were based on epoxide and acid titrations.

Analyses. Epoxide equivalents were determined by the methylethyl ketone hydrochloric acid technique with cresol red indicator.[10] The gels were analyzed by the same method on samples swelled and pulverized in methylene ketone. The epoxide analyses of DGE-dicarboxylic acid reactions were corrected for acid content.

Results and Discussion

Low Molecular Weight Polymers; Reaction Selectivity

We have applied this technique of rate ratios to ten different catalysts, three active hydrogen compounds, at several temperatures, and at several catalyst concentrations.

In applying this technique, we are assuming that Reaction 1 of Figure 1 below 50% conversion is essentially all epoxide-phenol and Reaction 2, above 50%, all epoxide-alcohol. The reactions of Figure 1 can be represented by the following expressions:

Reaction 1: Epoxide-Phenol

$$\text{Rate}_1 = k_1(\text{Epoxide})^a(\text{Phenol})^b \qquad (1)$$

TABLE I
Reaction of Bisphenol-A Diglycidyl Ether (1.000) with Bisphenol-A (0.5000)

Catalyst	Catalyst moles	Reaction temperature °C	Reaction rate[a] %/min		Rate ratio	Gel[b] time hr	Percent[b] conversion in gel
			Reaction 1	Reaction 2			
lithium hydroxide[c]	0.0200	125	1.3	0.078	17.0	3.0-4.0	60-65
tri-n-butylamine	0.0200	125	8.4	0.080	100	1.5-2.0	71-74
di-n-butylamine	0.0200	125	3.3	0.018	190	23-28	70-72
n-butylamine	0.0200	125	1.3	0.0041	320	>165	—
N,N-dimethylacetamide	0.0200	125	0.66	0.013	51	16-21	70-73
tetramethylurea	0.0200	125	0.58	0.016	36	9-17	65-72
1,1,3,3-tetramethylguanidine	0.0200	125	12.0	0.76	16	0.2-0.5	72-78
triisopropanolamine	0.0200	125	0.68	0.0050	140	>128	—
triethanolamine	0.0200	125	1.7	0.0040	430	>108	—
di-(3-phenoxy-2-hydroxyl),n-butylamine	0.0200	125	1.3	0.0063	210	>300	—
N,N-dimethylacetamide	0.0200	90	0.040	0.0013	31	127-145	65-66
N,N-dimethylacetamide	0.0200	125	0.50	0.012	43	51-56	72-74
N,N-dimethylacetamide	0.0200	150	2.30	0.0046	500	167-215	74-76
tri-n-butylamine	0.0100	125	2.30	0.0040	590	22-29	70-72
tri-n-butylamine	0.00100	125	0.27	0.00025	1100	>150	—

[a] See Figure 1 for Reactions 1 and 2.

[b] Values shown are for last sample before gel and first gelled sample.

[c] Catalyst not completely soluble in reaction medium.

Reaction 2: Epoxide-Secondary Alcohol

$$Rate_2 = k_2(Epoxide)^c(Alcohol)^d \qquad (2)$$

The ratio is simply:

$$\frac{Rate_1}{Rate_2} = \frac{k_1(Epoxide)^a(Phenol)^b}{k_2(Epoxide)^c(Alcohol)^d} \qquad (3)$$

As reaction selectivity increases, the ratio expressed by eq. (3) increases in numerical value and approaches theoretical values. The method is most accurate when reaction selectivity is indicated. Furthermore, the method was found useful because: (1) it avoids the need for accurate determination of actual secondary alcohol reaction, (2) it gives a selectivity rating, the rate ratio, which is based on the actual reactants to be employed in the high molecular polymerization reaction, (3) it minimizes error relating to reactant purity and experimental technique.

Table I gives rate data for Reactions 1 and 2 and the ratio of these rates for a series of reactions wherein we have varied catalysts, temperatures, catalysts concentrations. Table II gives similar data for other active hydrogen compounds. For the DGE-BPA reactions at 125°C with 0.02 moles of catalyst per mole of DGE, initial reaction rates varied from 0.50% to 12% per min. The second reaction rate varied from 0.016% to 0.76% per min. Rate ratios observed were from about 16 to greater than 1000. A high reaction rate in Reaction 1 did not correlate with high reaction selectivity. Thus, 1,1,3,3-tetramethylguanidine gave the greatest initial rate and final rate values and the lowest reaction selectivity or rate ratio. The low selectivity of 1,1,3,3-tetramethylguanidine agrees with the work of Sherr and Krupnik who have shown that this catalyst is very effective
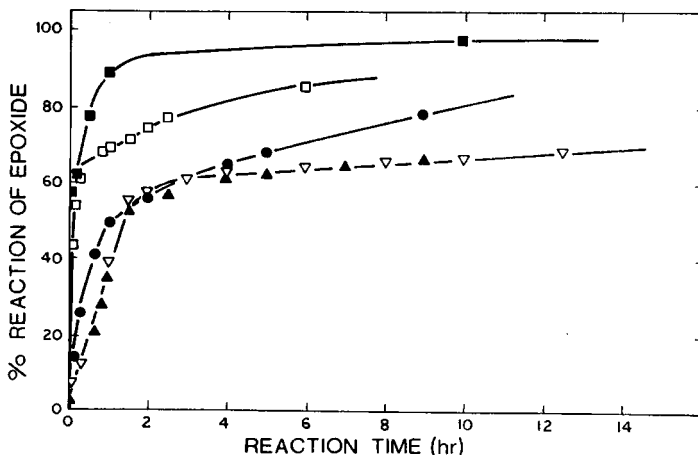

Fig. 2. % Reaction versus time for the reaction of bisphenol-A diglycidyl ether (1.000) and bisphenol-A (0.5000) at 125°C with several catalysts (0.0020): ■, 1,1,3,3-tetramethylguanidine; □, tri-n-butylamine; ●, lithium hydroxide; ▽, N,N-dimethyl-acetamide; ▲, tetramethylurea.

TABLE II
Reaction of Bisphenol-A Diglycidyl Ether (1.000) with Active Hydrogen Compounds (0.500)

Active hydrogen compound	Catalyst[a]	Reaction temperature °C	Reaction rates[b] %/min		Rate ratio	Gel[c] time hr	Percent[c] conversion in gel
			Reaction 1	Reaction 2			
bisphenol-A	N,N-dimethylacetamide	125	0.52	0.023	22	14–20	71–74
p-toluenesulfonamide	N,N-dimethylacetamide	125	0.40	0.050	8.1	4–6	61–67
adipic acid	tri-n-butylamine	125	2.6	1.0	2.6	0.5	68
azelaic acid	tri-n-butylamine	125	4.0	0.75	5.3	0.5	71

a 0.02 mole per mole of DGE.
b See Figure 1 for Reactions 1 and 2.
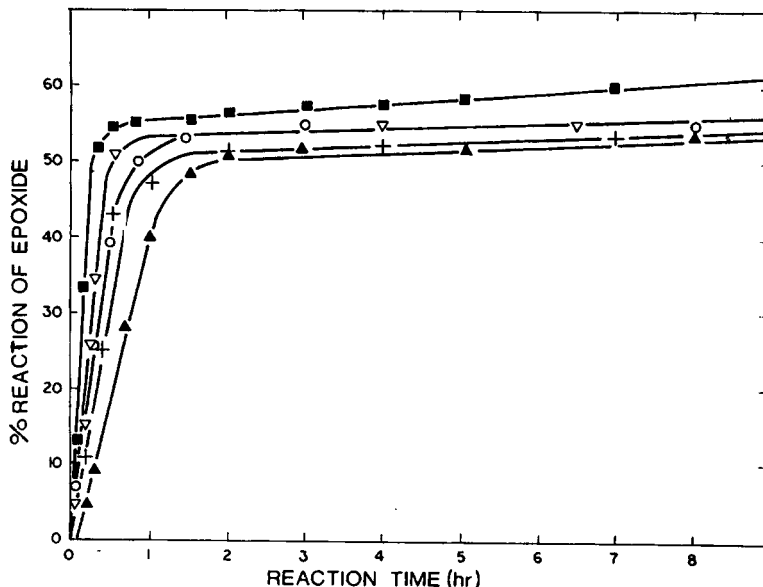c Values are for gel sample or for last sample before gel and first gelled sample.

Fig. 3. % Reaction versus time for the reaction of bisphenol-A diglycidyl ether (1.000) and bisphenol-A (0.5000) at 125°C with several catalysts (0.0200): ■, di-*n*-butylamine; O, *n*-butylamine; ▲, triisopropanolamine; ∇, triethanolamine; +, di-(3-phenoxy-2-hydroxylpropyl), *n*-butylamine.

for curing DGE by polyetherification mechanism.[11] Gel times given in Table I, for comparable reaction types, correlate with the reaction rate ratios, high ratios giving long gel times. Percent conversion in the gels appears to be about 70% to 75%.
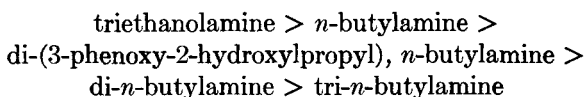
Lithium hydroxide, which was partially insoluble under the conditions of the experiment, seemed to be different in nature from the other catalysts. Its rate curve was not linear and it produced gelation at a lower degree of conversion. To estimate the rate ratio for lithium hydroxide, we measured the rate for the initial reaction at 25% and for the final rate the slope obtained from the data of the 50% and 70% conversion points. For the other curves, we employed the most linear part of the initial rate curve and the most linear part of the final curve below 70% to 80% where we assumed that the rate would be reduced by increasing immobility of the reaction system.

Figures 2 and 3 give plots for DGE, BPA reactions at 125°C with 0.02 moles of the various catalysts per mole of DGE. Generally, the curves for the systems with the greatest selectivity based on the rate ratios have the sharpest rate curve transitions from the fast to the slow rate. Further, the transition occurs closer to the theoretical value of 50% for the more selective catalysts. These curve characteristics would be those expected under selective conditions. The least selective catalyst, 1,1,3,3-tetramethyl-guanidine shows a very minor rate transition at about 60% reaction of

epoxide. The rate decrease beginning at 80% to 90% conversion, after initial gelation at about 75%, is probably the result of both the increasing immobility of the reaction medium and reduction in concentration of reactant species. It is interesting that rate reduction in the second reaction stage occurs beyond gelation in all cases. It seems that in these unagitated reactions, initial gelation does not reduce reaction rate. The curves for the tri-n-butylamine and lithium hydroxide show this same effect.

The curves for N,N-dimethylacetamide and tetramethylurea in Figure 2 show rate reductions in the initial stages of the second reaction between 50% and 60%. We have no explanation for this and have based our rate ratios on the second linear portion of the reduced rate curve. We included these two catalysts in this study to be representative of alkyl acid amide catalysts which we have reported to be effective catalysts for the epoxide-phenol reaction.[12]

Figure 3 shows rate curves for the more selective catalysts, when employed at the 0.02 mole concentration. These catalysts, in the order of their selectivity, based on rate ratios are:

<div align="center">

triethanolamine > n-butylamine >

di-(3-phenoxy-2-hydroxylpropyl), n-butylamine >

di-n-butylamine > tri-n-butylamine

</div>

The rate transition of the curves occurs near 50% conversion and is quite sharp. These catalysts all have hydroxyl groups β to the tertiary amine nitrogen. In the case of di- and n-butylamine, the β-hydroxyl group would form by an initial reaction with epoxide in the first reaction stage probably prior to reaction of BPA.[5] We propose that the β-hydroxyl groups do not interfere with catalysis of the epoxide-phenol reaction because of the greater acidity of phenol in comparison to the β-hydroxyl group. However, they might reduce reaction of the secondary hydroxyl group of the DHDE structure of Figure 1 if the reaction mechanism involves a complex intermediate of catalyst and secondary hydroxyl.[13] The β-hydroxylalkyl amines should be non-complexing with secondary hydroxyl of the DHDE because of preferential intramolecular hydrogen bonding to form stable five membered ring structures as follows:

<div align="center">

—CH$_2$—CH—CH$_2$—N—
      |
     O—H

</div>
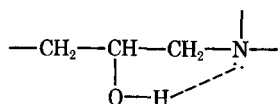
Shechter, Wynstra, and Kurkjy have reported that the reaction of excess epoxide with aliphatic amines gives essentially no epoxide-secondary alcohol reaction after consumption of amine.[5] They explained their observations on the basis of steric considerations. We feel that intramolecular hydrogen bonding can also explain this effect. We observe a greater reduction in epoxide-alcohol reaction when two β-hydroxyl groups are present. The epoxide-alcohol reaction with di-n-butylamine catalyst proceeds at a rate of

0.018% per min. The other β-hydroxyl catalysts with 2 and 3 hydroxyl groups give a rate of from 0.004% to 0.006% per min. At the 0.02 mole concentration at 125°C, the most selective catalyst on the basis of rate ratios was triethanolamine.

This method or rate ratios can be employed to determine relative reaction selectivity as a function of temperature. Figure 4 shows reaction rate curves for N,N-dimethylacetamide catalyst at 90°C, 125°C, and 150°C. The epoxide-phenol reaction rates are in the order predicted based on the temperature increase. The rate approximately doubles for each 10° rise in temperature. However, the epoxide-secondary alcohol reaction does not so increase with temperature. In fact, the rate is greatest at 125°C. The most selective reaction temperature, on the basis of rate ratio, is 150°C at
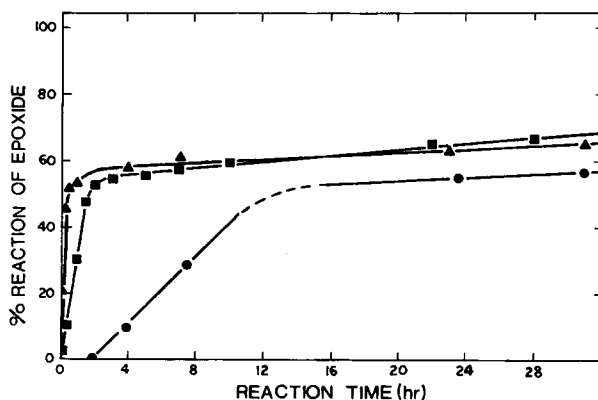

Fig. 4. % Reaction versus time for the reaction of bisphenol-A diglycidyl ether (1.000) with bisphenol-A (0.5000) with N,N-dimethylacetamide catalyst (0.0200) at 90°C (●); 125°C (■); 150°C (▲).

which temperature the epoxide-phenol reaction is 500 times faster than the epoxide-secondary alcohol reaction. Takahashi and Li, by proton magnetic resonance studies, have shown that the equilibrium constant for complex formation between N,N-dimethylacetamide and 2-propanol decreases as temperature rises.[14] At elevated temperatures, in the DGE, BPA reaction, it is possible that a hydrogen bonded complex catalytic species may be so reduced in concentration that the overall reaction rate becomes depressed.

The effect of catalyst concentration was determined with tri-n-butyl-amine as shown in Figure 5. It was found that the reaction selectivity increases as the catalyst concentration decreases. The reaction with 0.001 mole of tri-n-butylamine was the most selective reaction of the series. The epoxide-phenol reaction was about 1100 times as fast as the epoxide-secondary alcohol reaction. At the 0.01 mole concentration, a high degree of selectivity was also observed. The general characteristics of the curves and the observed gel times support the rate ratio selectivity data. The
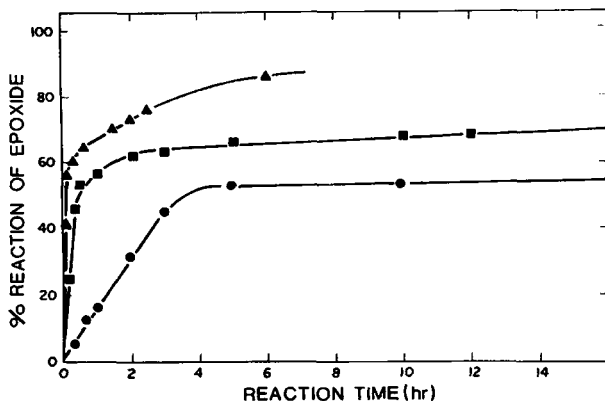
Fig. 5. % Reaction versus time for the reaction of bisphenol-A diglycidyl ether (1.000) and bisphenol-A (0.5000) at 125°C with tri-n-butylamine catalyst at several concentrations: ▲, (0.0200); ■, (0.0100); ●, (0.001).

rate transition in the $\%$ reaction versus time plots occurs at higher $\%$ conversions and are less sharp as the selectivity decreases.

The very high rate ratio for the 0.001 mole catalyst reaction could be the result of catalyst deactivation by reaction with the hydrolyzable chlorine of the DGE. Resinous grade DGE contains small amount of hydrolyzable chlorine resulting from incomplete dehydrohalogenation of the intermediate chlorohydrin ether in resin manufacture. The resin employed for this series of reactions had 0.03% hydrolyzable chlorine. This is equal to 0.003 moles of hydrolyzable chlorine in the reaction or a threefold excess over that equivalent to the catalyst. This explanation for the very high selectivity at the 0.001 mole catalyst concentration is supported by the work of Shechter and Wynstra who showed that while tertiary amine catalysis of the phenol-epoxide reaction is unaffected by hydrolyzable chlorine, catalysis of the alcohol-epoxide reaction is reduced.[4] This suggests that the effective sequence of reactions observed is: epoxide-phenol, tertiary amine-hydrolyzable chlorine, epoxide-alcohol. As the concentration of hydrolyzable chlorine exceeds that of the tertiary amine catalyst, the alcohol reaction decreases. It would seem that hydrolyzable chlorine might have some effect on the other catalysts employed. However, in the other cases, the concentration of catalyst was in large excess over that of the hydrolyzable chlorine. We have employed the same quantity of resin in all comparison series to minimize errors from this source.

Figure 6 shows curves for reactions of several active hydrogen compounds. It can be seen that at 125°C, the reaction of p-toluenesulfonamide with DGE under catalysis by N,N-dimethylacetamide is less selective than the comparable BPA reaction. This suggests that the β-hydroxyl group of N-alkyl sulfonamide is more reactive to epoxide than the β-hydroxyl group of alkyl aromatic ether. The curves for adipic and azelaic acid are only approximate. Early gelation in these systems at the temperature studied

impeded our work.   We did not determine the amount of acid-alcohol re-
action that occurred.   However, this reaction would contribute to gelation
and therefore gel time but not to epoxide reaction.   These results suggest
that reaction selectivity is less with carboxylic acids than with phenols.
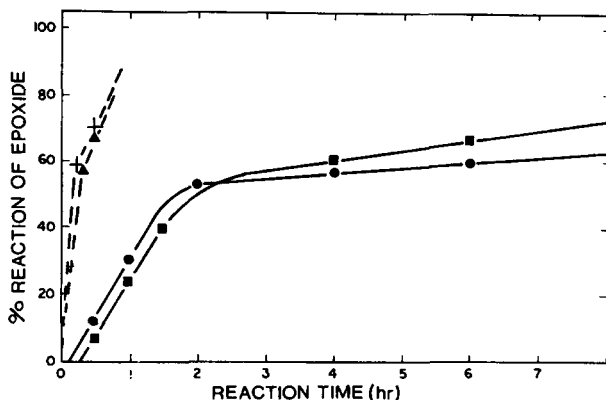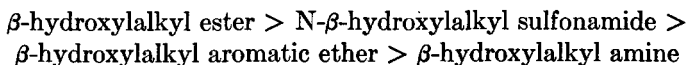Further study of this reaction is warranted.

Fig. 6. % Reaction versus time for the reaction of bipshenol-A diglycidyl ether (1.000)
with several active hydrogen compounds (0.5000) at 125°C; + and ▲ respectively
azelaic and adipic acid with tri-n-butylamine catalyst (0.0200); ● and ■ respectively
bisphenol-A and p-toluenesulfonamide with N,N-dimethylacetamide (0.0200).

For the series of active hydrogen compounds we have studied and the
literature,[5] the indicated order of reactivity of the generated secondary
hydroxyl with epoxide is as follows:

β-hydroxylalkyl ester > N-β-hydroxylalkyl sulfonamide >
β-hydroxylalkyl aromatic ether > β-hydroxylalkyl amine

This series is approximately one of increasing electron density on the hy-
droxyl oxygen resulting from inductive effects of the β-functional group.

High Molecular Weight Polymers

Table III lists a series of bulk polymerization reactions based on mole
ratios which will yield high molecular weight polymers.   The relative
properties of these polymers are in agreement with those that would be
predicted on the basis of the mole ratios of reactants and selectivity ratings
of the catalysts employed.   Concentrated solution viscosity measurements,
which were made by the Gardner Holdt method,[15] show the effect of branch-
ing in the primary polymer molecular structure.   At three different mole
ratios of DGE to BPA (1:1, 1:0.99, 1:0.98), a more selective catalyst was
compared to N,N-dimethylacetamide.   All polymerizations were conducted
under equivalent reaction conditions.

In each case, the rate of Reaction 1 for the more selective catalyst was
greater than that of N,N-dimethylacetamide as seen in Table I.   It was

found that, however, N,N-dimethylacetamide produced polymers with higher viscosities and higher melting properties than the more selective catalysts. This suggests that the higher viscosity and melting properties of the N,N-dimethylacetamide catalyzed polymerizations are the result of greater branching through the epoxide-secondary alcohol reaction.

TABLE III

Bulk Polymerizations of Bisphenol-A, Diglycidyl Ether, and Bisphenol-A[a]

Catalyst[b]	Moles DGE	BPA	Viscosity[c] (stokes)	Melting[d] range °C
N,N-dimethylacetamide	1.000	1.000	6.27	205–215
di-(3-phenoxy-2-hydroxylpropyl), n-butylamine	1.000	1.000	2.00	170–180
N,N-dimethylacetamide	1.000	0.9900	6.27–8.84	255–265
triisopropanolamine	1.000	0.9900	1.00–1.25	150–160
N,N-dimethylacetamide	1.000	0.9800	12.9	240–260
di-n-butylamine	1.000	0.9800	5.5	185–195

[a] Reaction conditions. One hour stirring at 125°C; 22 hr unagitated oven aging at 140°C.

[b] 0.02 moles per mole of DGE.

[c] Gardner Holdt. Values are Gardner limits or match. Ran at 25°C on 20% solutions in butyl carbitol.

[d] Determined on Fischer Hot Stage apparatus.

The viscosity and melting range properties for the PHE polymers from the DGE-BPA polymerizations catalyzed with N,N-dimethylacetamide increase as the mole ratio (DGE/BPA) increases or as the amount of excess epoxide increases. This further shows the effect of the branching reactions which occurs with this catalyst. If the reactions were completely selective, polymer termination with excess epoxide end group would have caused lower solution viscosities and melting characteristics with excess DGE.

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