Mechanistic Modeling of Epoxy–Amine Kinetics. 1. Model Compound Study

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ABSTRACT: An investigation was carried out of the mechanism and rate of epoxy–amine reactions using model compounds. High-performance liquid chromatography was used to generate experimental results. A mechanistic reaction model based on the existence of different transition complexes was proposed, and the corresponding kinetic parameters were evaluated. Excellent agreement was observed between model predictions and experimental data.

I. Introduction

Since Pierre Castan's seminal work, over half a century ago,[1] epoxy resins have graduated from a laboratory curiosity to a multitude of applications, becoming an integral part of the adhesives industry, printed board circuitry, and various aircraft and spacecraft designs. Depending on the intended use, one can nowadays choose between numerous epoxy formulations, differing in the composition and chemical structure of the ingredients. Formulations consisting of epoxy resins and aromatic amines are the most widely used thermoset polymer matrices in advanced composites, and that fact has provided the major impetus for this study.

Thermoset polymers are processed by cure, which entails conversion of liquid monomers, or prepolymers, into three-dimensional networks. The mechanism and kinetics (rate) of cure determine the network morphology, which, in turn, dictates the physical and mechanical properties of the cured product. For that reason, a fundamental understanding of cure is the first prerequisite for the studies of modeling and the optimization and design of processing of composites.

Many a researcher studied the mechanism and kinetics of epoxy–amine reactions, and several fine reviews of the subject have been published,[2-5] including a recent one with 630(!) references.[6] But despite the wealth of information in the literature, the subject of epoxy–amine systems has continued to attract considerable scientific efforts, primarily because of the contradictory findings and unresolved questions regarding some crucial aspects of the epoxy–amine reactions. The principle uncertainties arise from the conflicting results concerning the following questions: (1) Is the rate of secondary amine–epoxy reaction affected by the preceding reaction between primary amine and epoxy (i.e., is there a substitution effect)? (2) Is the reactivity ratio (ratio of secondary amine–epoxy to primary amine–epoxy reaction rate constants) a function of temperature and/or degree of cure? (3) What is the ratio of noncatalyzed and autocatalyzed rates (or rate constants) for various reaction paths in the overall mechanism of epoxy–amine cure? (4) What are the conditions under which etherification, homopolymerization, and intramolecular cyclization become important in epoxy–amine cure?

At Polytechnic, we have recently embarked upon a comprehensive research program aimed at answering these questions from fundamental mechanistic studies. The phenomenological approach to modeling epoxy–amine cure, which has been explored by many authors,[7-13] including our group,[14-17] is not considered in this study due to its batch specificity and thus limited applicability to modeling and optimization of processing from the first principles.

The main objectives of the work reported in this paper are (1) to conduct a fundamental investigation of epoxy–amine reactions using model compounds, (2) to elucidate the reaction mechanism, and (3) to develop the corresponding mechanistic kinetic model.

II. Experimental Section

A. Materials. The model compound formulation consisted of aniline (99.55%, Aldrich) and 1,2-epoxy-3-phenoxypropane (99%, Aldrich). The latter compound is also known as phenyl glycidyl ether, or PGE, and will be referred to in the text by its acronym.

B. Sample Preparation. Stoichiometric amounts of aniline and PGE were mixed at room temperature and stored in dry ice for a maximum of 72 h. The reaction kinetics were studied in the temperature range 90–120 °C. Forty milliliters of the sample was placed in a 100-mL three-neck bottle, which was immersed in an oil bath and purged with purified nitrogen. A reflux condenser was attached to prevent the evaporation of aniline. Temperature was controlled with an Omega CN2010 controller. At desired time intervals, small aliquots of the reaction mixture were removed and quenched, prior to the subsequent analysis.

C. Techniques. 1. High-Performance Liquid Chromatography (HPLC). High-performance liquid chromatography (HPLC) analysis was conducted with a Perkin-Elmer LCI-laboratory computing integrator equipped with a reverse-phase C18 column. Gradient elution of the methanol–water system was utilized at a constant flow rate of 1.75 mL/min for 20 min. The solvent had been purged with helium, and a Perkin-Elmer LC 235 ultraviolet detector set at 254 nm was used to monitor the concentration of the species.

Typically, 5–15 mg of a sample was combined with 10–15 mL of methanol. About 20 μL of the sample was injected. The concentrations of aniline, PGE, secondary amine (SA), and tertiary amine (TA) were calculated from peak areas using calibration constants established for the pure compounds. TA was prepared by reacting stoichiometric amounts of aniline and PGE for 15 h at 120 °C. SA was made by reacting an excess of aniline with PGE for 12 h at 80 °C, after which time excess aniline was distilled off. Progress of reaction was monitored from chromatograms taken at different times, as shown in Figure 1.

2. Titration. The argentimetric method was used to follow the concentration of epoxy groups. This method involves hydrochlorination reaction followed by a measurement of the consumption of chloride ions.

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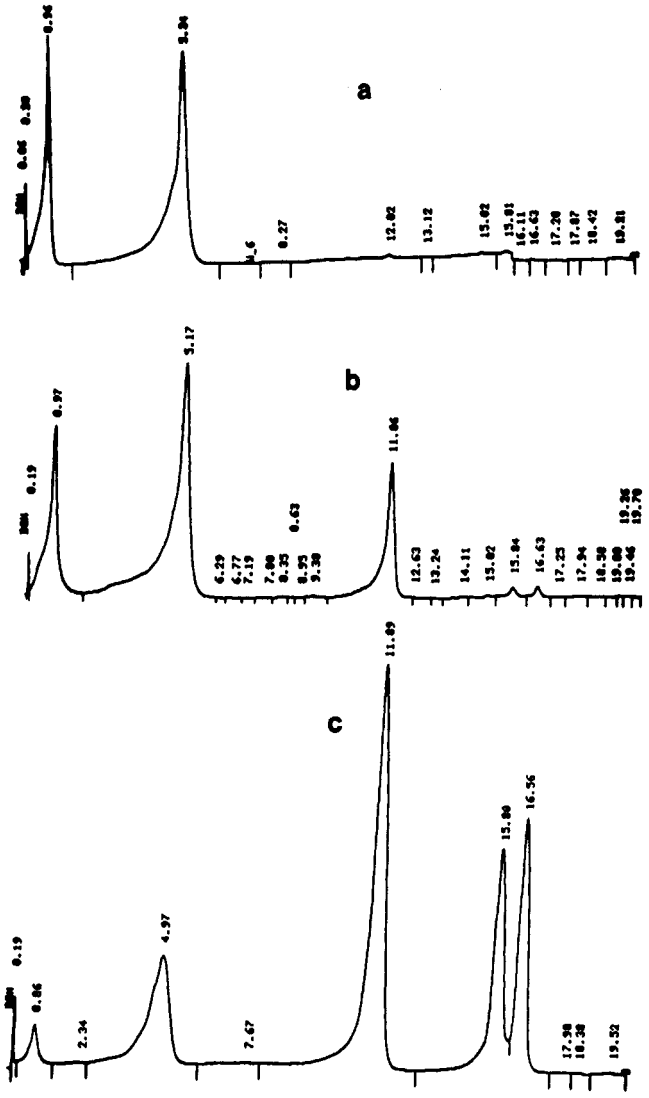

Figure 1. HPLC chromatograms for the PGE/aniline reaction at 100 °C for (a) 2, (b) 30, and (c) 80 min.

III. Results and Discussion

A. Model Development. Since the early work on the mechanism of epoxy–amine reactions by Shechter et al.,[18,19] Chapman et al.,[20] and Smith,[21] many a researcher has contributed to this field of study, and several excellent reviews, cited in the Introduction, have appeared in the literature. We shall make no attempt to write another review; instead, we shall briefly recap the current understanding of the mechanism of epoxy–amine reactions and then focus our attention to the modeling scheme put forward in this work. It is generally agreed that, under appropriate kinetic conditions, the following reactions are possible in an epoxy–amine mixture: primary amines (PA)–epoxy (E), secondary amine (SA)–epoxy, hydroxyl (OH)–epoxy, and epoxy–epoxy. Furthermore, it is also well-known that compounds containing oxygen–hydrogen or nitrogen–hydrogen bonds (abbreviated here as XH) can act as catalysts for epoxy–amine and epoxy–hydroxyl reactions. Since every one of those reactions yields a new hydroxyl group, the autocatalytic path in epoxy–amine mixtures must be taken into account. On the basis of the above mechanism one can proceed to write the following general equation for the rate of epoxy–amine reactions in terms of the rate of disappearance of epoxy groups:

$$-d(E)/dt = k_1(E)(PA) + k_1'(E)(PA)(XH) + k_2(E)(SA) + k_2'(E)(SA)(XH) + k_3(E)(OH) + k_3'(E)(OH)(XH) + k_4(E)(E) \quad (1)$$

The terms in parentheses in eq 1 are concentrations of different components, and k's are the reaction rate constants. Subscripts 1, 2, 3, and 4 refer to epoxy–primary amine, epoxy–secondary amine, epoxy–hydroxyl, and epoxy–epoxy reactions, respectively. The prime denotes catalyzed reactions. Since eq 1 is completely general, specific modifications must be made whenever the situation requires. For example, a more complicated scheme ensues when intramolecular cyclization becomes effective, which is important in tetrafunctional epoxy formulations of the type used in advanced composites. A fine treatment of this subject appears in a recent series of papers by two groups in Czechoslovakia[22,23] and by Pyun and Sung.[24] Fortunately, equation 1 can also be simplified by a judicious choice of components and reaction conditions. First, epoxy homopolymerization is reported to occur only in the presence of Lewis base (or acid) type catalysts[25,26] and can be neglected in their absence. Second, the importance of the etherification reaction between epoxy and hydroxyl groups has not been firmly established, and, more often than not, it is said to occur only at high temperatures and degrees of cure[27,28] or in the presence of a large excess of epoxy groups.[29,30] When those conditions prevail in epoxy–amine mixtures, the rate of disappearance of epoxy groups can be rewritten in the form analogoues to that proposed by Horie and co-workers:[31]

$$-d(E)/dt = k_1(E)(PA) + k_1'(E)(PA)(XH) + k_2(E)(SA) + k_2'(E)(SA)(XH) \quad (2)$$

Several authors[4,29,32,33] assumed that the epoxy–amine reactions could be described exclusively by the autocatalytic path, in which case the following equation is obtained:

$$-d(E)/dt = k_1'(E)(PA)(XH) + k_2'(E)(SA)(XH) \quad (3)$$

Dusek et al.[29] reported good agreement between experimental and theoretical results using the following rate expression:

$$-d(E)/dt = k_2(E)(SA)^2 + k_2'(E)(SA)(OH) \quad (4)$$

The second-order dependence of the epoxy consumption rate on the concentration of secondary amine suggests that in the absence of a proton donor the amine has a dual role as a participant in the formation of an intermediate complex with the epoxy and as a nucleophilic reagent which reacts with the epoxy–amine complex.

We begin our analysis by parlaying the above findings into the development of our model, as described below. The use of model compounds allowed us to simplify the analysis by introducing two important assumptions: (1) due to the chemical structures of the model compounds (i.e., monofunctionality), intramolecular cyclization is inconsequential, and (2) in the absence of Lewis base (or acid) type accelerators and in the temperature range employed in this study, etherification (epoxy–hydroxyl) and homopolymerization (epoxy–epoxy) reactions can be neglected. Both assumptions were borne out by the experimental evidence acquired from HPLC and FTIR studies.

Conceptually, our analysis is based upon the existence of a transition complex, whose formation is the rate-

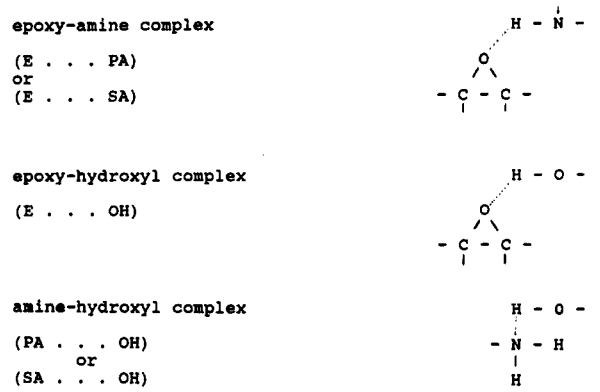

Figure 2. Three types of hydrogen bond complexes in epoxy–amine systems.

controlling step in the reaction between an epoxy and an amine. This mechanism requires an initial interaction between epoxy or amino groups with proton donor molecules, leading to the formation of a hydrogen bond complex. Proton donor molecules may be hydroxyl- or amine-containing moieties or impurities present in the reaction mixture. Upon a careful examination of epoxy–amine reaction mechanisms, we have identified the following three types of hydrogen bond complexes which can form and are likely to participate in the reactions: (1) epoxy–amine, (2) epoxy–hydroxyl, and (3) amine–hydroxyl. They are schematically presented in Figure 2. Other complexes, such as epoxy–epoxy and amine–amine may form but can be neglected in the kinetic analysis, as successfully argued by several researchers.[3,33] Once formed, a hydrogen bond complex will next react with an amine, the latter being available either as a separate amine molecule or as an amine–hydroxyl complex. Reaction between a hydrogen bond complex and PA or SA will lead to SA or TA, respectively, in both cases via an intermediary transition complex, as indicated by eq 5:

$$\text{(hydrogen bond complex)} + \text{(amine)} \rightarrow \text{(transition complex)} \rightarrow \text{SA or TA} \quad (5)$$

Within the general path described by eq 5 we have identified three specific routes leading to the formation of secondary or tertiary amines. These include route a, the reaction between an epoxy–amine complex and an amino group, route b, the reaction between an epoxy–hydroxyl complex and an amino group, and route c, the reaction between an epoxy–hydroxyl complex and an amine–hydroxyl complex. A schematic presentation of these three routes is shown in Figure 3, and a brief discussion of their salient features follows.

The first route (route a, Figure 3a), between an epoxy–amine complex and an amino group, was investigated by Arutyunyan et al.,[34] who suggested that amino groups may act both as electrophilic groups in forming epoxy–amine complex and as nucleophilic groups that react with the complex to yield secondary or tertiary amines. Arutyunyan et al. worked with highly purified systems, and their mechanism is important as it accounts for epoxy–amine reactions in the absence of hydroxyl groups. Nonetheless, this mechanism is significantly only in the earliest stages of reaction, where the initial concentration of hydroxyl groups remains low. Equations 6 and 7 describe this mechanism in terms of the rate of consumption of primary amine and the rate of production of tertiary amine, respectively:

$$-\mathrm{d(PA)_a}/dt = W_1 k_{1a}(\mathrm{PA})(\mathrm{E\cdots PA}) = W_1 k_{1a} K_{\mathrm{e\cdots PA}}(\mathrm{PA})^2(\mathrm{E}) \quad (6)$$

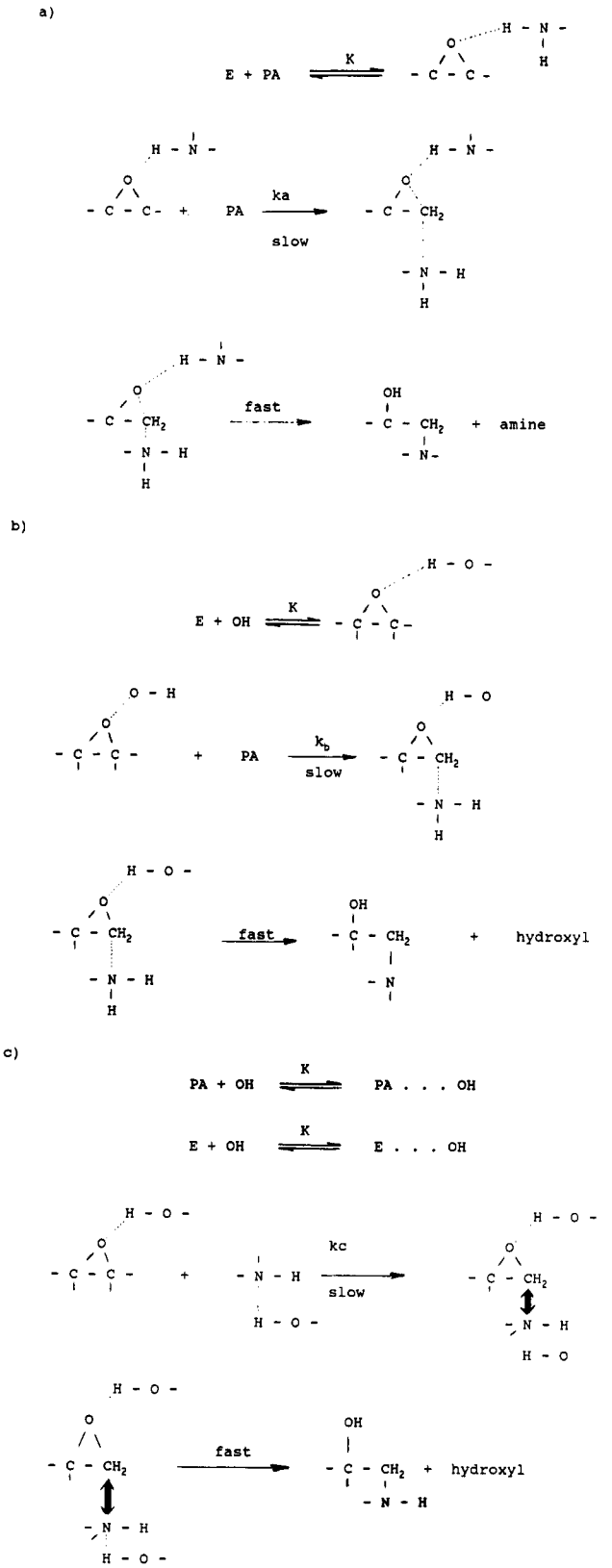

Figure 3. Three types of intermediary transition complexes in epoxy–amine systems.

$$\mathrm{d(TA)_a}/dt = W_1 k_{2a}(\mathrm{SA})(\mathrm{E\cdots SA}) = W_1 k_{2a} K_{\mathrm{E\cdots SA}}(\mathrm{SA})^2(\mathrm{E}) \quad (7)$$

where k_a is the kinetic rate constant for route a, K is the equilibrium constant, and E···PA and E···SA are epoxy–primary amine and epoxy–secondary amine hydrogen bond complexes, respectively. Subscripts 1 and 2 refer to the primary amine reactions (eq 6) and tertiary amine reactions

(eq 7), respectively. The weight factor W_1 is 0 when the consumption of epoxy groups by this mechanism is negligible and 1 when it is not.

The second reaction route (route b, Figure 3b) involves interactions between an epoxy–hydroxyl complex and an amino group and is described by the following general equations:

$$-d(PA)_b/dt = W_2\sum k_{b1i}(PA)(E\cdots XH) = W_2\sum k_{b1i}K_{b1iE\cdots XH}(PA)(XH)(E) \quad (8)$$

$$d(TA)_b/dt = W_2\sum k_{b2i}(SA)(E\cdots XH) = W_2\sum k_{b2i}K_{b2iE\cdots XH}(SA)(XH)(E) \quad (9)$$

where summation is made over i electrophilic groups and other symbols are as defined earlier. The weight factor W_2 is equal to 1 when this route is engaged and 0 when it is not. For controlled systems, such as ours, where the only electrophilic groups are the traces of initially present hydroxyl groups and the hydroxyl groups formed in the course of the reaction, eqs 8 and 9 reduce to a more convenient form:

$$-d(PA)_b/dt = W_2(PA)(E)(k_{b1} + k_{b1}'(OH)) \quad (10)$$

$$d(TA)_b/dt = W_2(SA)(E)(k_{b2} + k_{b2}'(OH)) \quad (11)$$

Rate constants with primes describe reactions involving hydroxyl groups produced during reaction, while rate constants without primes describe reactions involving the initially present hydroxyls. The concentration of the initially present hydroxyl groups is comprised in the value of the reaction rate constant. We note that eqs 10 and 11 are de facto analogous to eq 2 derived by Horie and coworkers.

The third reaction route (route c, Figure 3c) is based on the interaction between epoxy–hydroxyl and amine–hydroxyl complexes. The following equations describe the reaction sequence:

$$(PA) + (OH) \overset{K_{eq1}}{\leftrightarrow} (PA\cdots OH); \quad (PA\cdots OH) = K_{eq1}(PA)(OH) \quad (12)$$

$$(E) + (OH) \overset{K_{eq2}}{\leftrightarrow} (E\cdots OH); \quad (E\cdots OH) = K_{eq2}(E)(OH) \quad (13)$$

$$(PA\cdots OH) + (E\cdots OH) \overset{k_1}{\rightarrow} (SA) + \text{hydroxyl} \quad (14)$$

From eqs 12–14 one can proceed to write an expression for the rate of disappearance of amine–hydroxyl complex as follows:

$$d(PA\cdots OH)/dt = K_{eq1}(OH)\, d(PA)/dt + K_{eq1}(PA)\, d(OH)/dt = k_1(PA\cdots OH)(E\cdots OH) \quad (15)$$

Equations 12–15 can now be combined to obtain the following expression for the rate of disappearance of primary amine by route c:

$$d(PA)/dt = k_1K_{eq2}(PA)(E)(OH) - [(PA)/(OH)]\, d(OH)/dt = k_{c1}(PA)(E)(OH) - [(PA)/(OH)]\, d(OH)/dt \quad (16)$$

The rate of production of tertiary amine by route c can be derived by the analogous approach. The main feature of this route is that it goes into effect only after the hydroxyl concentration, which increases during reaction, has exceeded a certain critical value. Beyond that point, amine and hydroxyl groups interact to form a complex, which then reacts with epoxy–hydroxyl complex to produce secondary or tertiary amines. It is important to emphasize here that this reaction path has not been hitherto reported in the studies of epoxy–amine kinetics. Upon inclusion of route c in the model we were able to arrive at the excellent agreement between predicted and experimental results observed in this study.

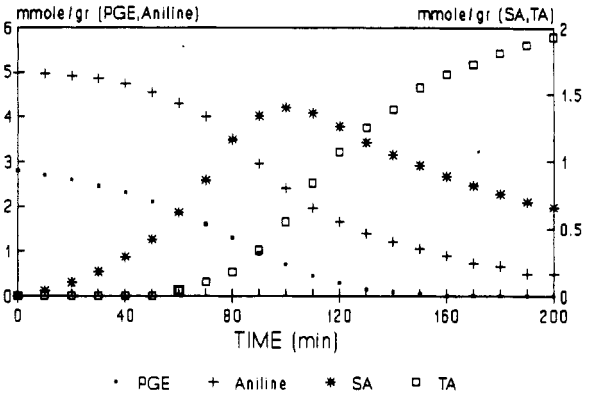

Figure 4. Concentration of components as a function of reaction time in the PGE/aniline system at 100 °C.

Assuming that the amino groups are depleted (and/or formed) via all three routes (a, b, and c), one can write the following equations for the rate of disappearance of primary amine or the rate of production of tertiary amine:

$$-d(PA)/dt = -[d(PA)_a/dt + d(PA)_b/dt + d(PA)_c/dt] \quad (17)$$

$$d(TA)/dt = d(TA)_a/dt + d(TA)_b/dt + d(TA)_c/dt \quad (18)$$

Using eqs 6–16 and substituting for each corresponding term in eqs 17 and 18, one obtains

$$-d(PA)/dt = W_1k_{a1}(PA)^2(E) + W_2(PA)(E)[k_{b1} + k_{b1}'(OH)] + W_3k_{c1}(PA)(E)(OH) - [(PA)/(OH)]/(d(OH)/dt) \quad (19)$$

$$d(TA)/dt = W_1k_{a2}(SA)^2(E) + W_2(SA)(E)[k_{b2} + k_{b2}'(OH)] + W_3k_{c2}(SA)(E)(OH) - [(SA)/(OH)]/(d(OH)/dt) \quad (20)$$

where k_{a1} and k_{a2} are equal to $k_{1a}K_{E\cdots PA}$ and $k_{2a}K_{E\cdots SA}$ in eqs 6 and 7, respectively. Equations 19 and 20 represent the mechanistic model for epoxy–amine cure kinetics used in this study.

B. Analysis of Results. 1. Reaction Rates. A typical result of an HPLC experiment is shown in Figure 4, where concentrations of aniline, PGE, secondary amine (SA), and tertiary amine (TA) are plotted as a function of reaction time at 100 °C. Analogous results were generated at other temperatures, and repeated runs were conducted to establish a high degree of reliability and reproducibility of data. Mass balances were calculated continually throughout the reaction course, and the observed deviation never exceeded 5%. The accuracy of the results was also verified by comparing HPLC and titration data, as shown in Figure 5. The computational analysis of data was conducted with the SIMUSOLV modeling and simulation software (available from Dow Chemical Co. and MGA Inc., Concord, MA), which is designed for development of mathematical models of dynamic systems. To discriminate between possible models, the program uses the maximum likelihood function; the larger it is, the better the fit. The mathematical model used in this work was written in Advanced Continuous Simulation Language (ACSL) and is described in detail elsewhere.[33]

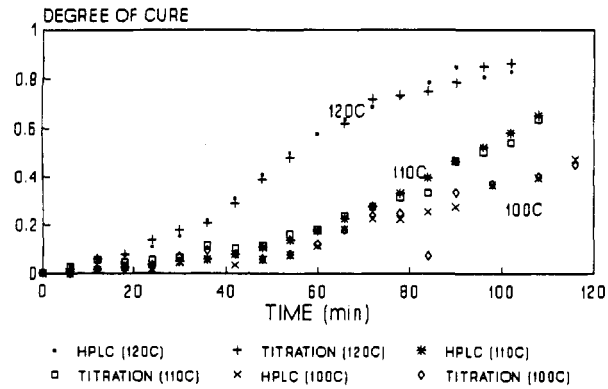

Figure 5. Comparison of HPLC and titration results for the PGE/aniline system at various temperatures.

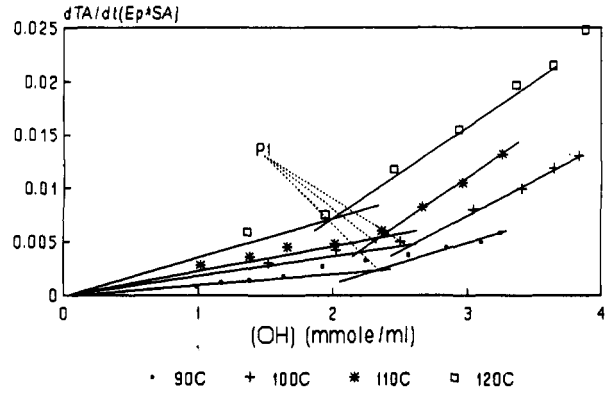

Figure 6. Reduced rate of production of tertiary amine as a function of hydroxyl concentration.

As stated earlier, our results have clearly shown that the reaction path termed route c must be incorporated in the model, although several previous investigators have suggested that the epoxy–amine reaction mechanism could be adequately described solely by route b, i.e., the reaction between an epoxy–hydroxyl complex and an amino group, represented by eqs 10 and 11. The validity of that assumption can be checked by rewriting eq 11 as

$$d(TA)_b/dt(SA)(E) = k_{b2} + k_{b2}'(OH) \qquad (21)$$

and plotting the reduced rate of production of tertiary amine (left-hand side of eq 21) as a function of hydroxyl concentration, as shown in Figure 6. It is clear from this figure that the assumption is correct only below the critical value of hydroxyl concentration, which, at the conditions of this study, is about 2 mmol/mL. Above that value, the rising importance of amine–hydroxyl complexes necessitates that route c be included in the model. At the conditions of this study, the critical value of hydroxyl concentration was found to be independent of temperature. A comparison between model predictions and experimental results is given in Figures 7 and 8. An excellent agreement is apparent.

2. Reaction Rate Constants. The following approach was applied in the calculation of the kinetic rate constants associated with various reaction routes in the overall kinetic scheme. Route a was assumed negligible and the corresponding rate constants were omitted from the analysis. The statistical error in calculating the rate constants for route b reactions involving the hydroxyl groups initially present in traces of impurities (i.e., k_{1b} and k_{2b}) was deemed too high, and hence their values were considered unreliable. The reproducibility and accuracy of the remaining constants shown in Table I, which include k_{1b}', k_{2b}', k_{1c}' and k_{2c}', were remarkable. The corresponding values of

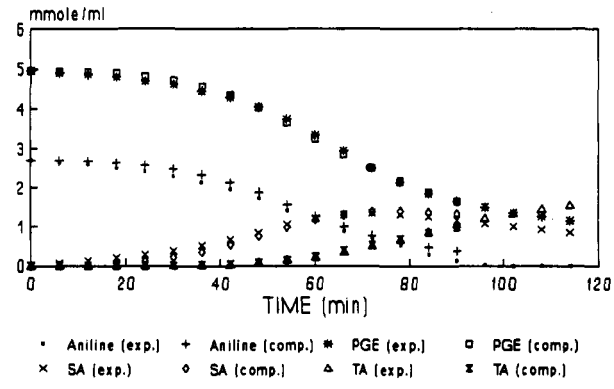

Figure 7. Comparison between model prediction and experimental results for PGE/aniline reactions at 110 °C.

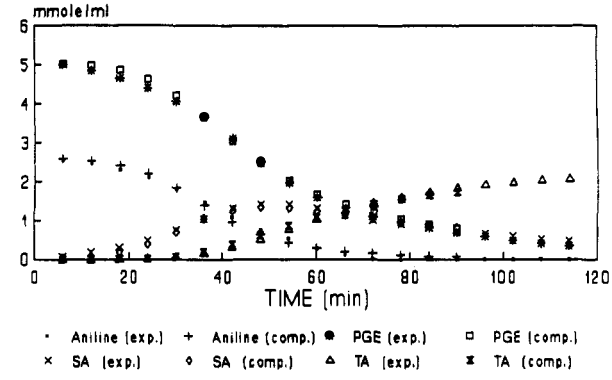

Figure 8. Comparison between model prediction and experimental results for PGE/aniline reactions at 120 °C.

Table I
Kinetic Parameters of the Model

	T, °C				
k, L²/(mol² min)	90	100	110	120	E_a, cal/mol
k_{1b}'	0.00304	0.0055	0.0073	0.0085	9.5
k_{2b}'	0.0019	0.0023	0.0026	0.0027	2.8
k_{2b}'/k_{1b}'	0.31	0.22	0.21	0.16	
k_{1c}'		0.0065	0.0087	0.0123	8.8
k_{2c}'	0.0002	0.0050	0.0074	0.0110	12.7
k_{2c}'/k_{1c}'		0.38	0.42	0.45	

activation energies, obtained from Arrhenius-type plots, are also listed. Another entry in this table is the reactivity ratio, defined as k_{2i}'/k_{1i}', an important kinetic parameter which influences the morphology and properties of networks. The subscript i implies that the reaction can proceed by either route b or route c, each of which is characterized by its own reactivity ratio. In essence, the reactivity ratio is a measure of the effect of consumption of primary amine hydrogen atom on the reactivity of secondary amine hydrogen atom on the same amino group. This effect is also known as the substitution effect. A negative substitution effect signifies a decrease in the reactivity of the secondary amine hydrogen atom, while its absence (i.e., no substitution effect) implies an equal reactivity of primary and secondary amine hydrogens. The importance of the substitution effect is perhaps best conveyed by considering its implications regarding the network morphology. In the absence of substitution effect, the equal reactivity of all amine hydrogens would favor the formation of a randomly cross-linked network. However, when primary amine hydrogens are much more reactive than their secondary amine counterparts, one would intuitively expect an initial predominance of linear chains followed by subsequent cross-linking, resulting in a different network morphology and hence properties. The

Table II
Reported Studies of the Relative Reactivity Ratio

system	reacn medium/temp (K)	k_2/k_1	method of anal.	ref
TGEB/DDS	bulk/413–453	0.5	UV–vis	46
DGEBA/DDS	bulk/413–453	0.5	UV–vis	34, 46
DGEBA/*N*-methylaniline	bulk/373, 425	0.5	GPC	41
BADGE/DDS	bulk/383–473	0.4	DSC	28
TGMEDA/DGA 4,4′-DDS, 3,3′-DDS	bulk/413, 433	0.5	DSC	42
TGE/*p*-methoxyaniline	ethanol/333	0.4 or 0.29	titration	37
TGE/*p*-nitroaniline	ethanol/333	0.62 or 0.26	titration	37
TGE/*p*-toluidine	ethanol/333	0.24	titration	37
TGE/aniline	ethanol/333	0.25	titration	37
TGE/*p*-cyanoaniline	ethanol/333	0.24	titration	37
TGE/*p*-chloroaniline	ethanol/333	0.24	titration	37
TGE/*p*-bromoaniline	ethanol/333	0.25	titration	37
TGE/*p*-iodoaniline	ethanol/333 (0.1–0.4 mol/L)	0.30	titration	37
TGE/benzidine	ethanol/333 (0.1–0.4 mol/L)	0.31	titration	38
TGE/phenylenediamine	ethanol/333 (0.1–0.4 mol/L)	0.35	titration	38
TGE/4,4′-diaminodiphenylmethane	ethanol/333 (0.1–0.4 mol/L)	0.33	titraton	38
TGE/4,4′-diaminodiphenyl sulfone	ethanol/333 (0.1–0.4 mol/L)	0.52	titration	38
DGEBA/TMAB	bulk/373–433	0.16–0.33	FTIR	49
PGE/MPDA	THF/343	1 ± 0.5	GPC	32
RDGE/aniline	THF/343	1 ± 0.5	GPC	32
DGEBA/Tonox	bulk/297–338	0.1–0.2	FTIR	45
DGEBA/DDS	bulk/450	0.1	FTIR	44
4-methylphenylglycidyl ether/benzylamine	bulk/373	0.42	NMR	47
PGE/aniline	*o*-dichlorobenzene/363–403	0.25	titration	34
BADGE/DDM	bulk/353	0.2	titration FTIR	39
TGDDM/DDS	bulk/423–450	0.05–0.06	DSC, FTIR	48
DGER/2,6-diaminopyridine	bulk/360	1.12		43
DGEBA/MDA	excess amine, bulk/333–423	0.08–0.14	titration	36

value of the reactivity ratio, and hence the presence or absence of the substitution effect, constitutes a major unresolved issue in studies of epoxy–amine kinetics. At this point, it is instructive to peruse Table II, where the reported values of reactivity ratios for various epoxy–aromatic amine systems are summarized and seen to vacillate by more than an order of magnitude. We note the absence of subscript i on the rate constants in Table II, because the hitherto reported studies of epoxy–amine reaction mechanisms have not accounted for reaction routes other than the one corresponding to route b in this study. At this point, it is instructive to stress that the value of the reactivity ratio can be expressed in terms of the reactivity of either amino groups or hydrogen atoms on the amino group. In this study, a value of $k_{2i}'/k_{1i}' = 0.5$ signifies the absence of substitution effect. The relative reactivity values in Table II were normalized accordingly. Our results of the reactivity ratio for route b (i.e., k_{2b}'/k_{1b}') clearly reveal a negative substitution effect, which is in agreement with some authors (e.g., refs 34, 36–39, 43, 44, and 47–49) and disagreement with others (e.g., refs 24, 28, 41, 42, and 46). In addition, there is an obvious temperature effect on the reactivity ratio, a fact that must be considered in modeling studies but, unfortunately, has been neglected until recently.[46] In the later stages of reaction, when route c comes into play, a weak negative substitution effect is observed, as the k_{2c}'/k_{1c}' ratio decreases with decreasing temperature.

IV. Conclusions

We have successfully completed a fundamental investigation of epoxy–amine reactions using model compounds. A stoichiometric mixture of aniline and 1,2-epoxy-3-phenoxypropane was prepared and studied in the temperature range 90–120 °C. Experimental results were obtained from high-performance liquid chromatography. A mechanistic reaction scheme was put forward, involving the initial formation of hydrogen bond complexes which, via the intermediary transition complexes, lead to the reaction products by three major routes. From the proposed set of equations we were able to derive all significant kinetic parameters. The observed agreement between the model predictions and the experimental results was superb. It was unambiguously shown that the kinetic mechanism is characterized by a temperature-dependent negative substitution effect.

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