Macromolecules **1994**, *27*, 7589−7600 **7589**

Reaction Kinetics of Epoxy/Amine Model Systems. The Effect of Electrophilicity of Amine Molecule

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Received April 11, 1994; Revised Manuscript Received September 19, 1994[®]

ABSTRACT: An investigation was carried out on the effect of electrophilicity of amine molecule on the epoxy/amine reaction kinetics. Model systems, containing amines with different electron-donating and/or -withdrawing characteristics, were prepared, reacted, and investigated by high-performance liquid chromatography (HPLC). Reaction rate constants and activation energies were determined for all systems based upon a kinetic model of epoxy/amine reactions. It was established that an electron-donating group on the amine molecule enhanced the reaction rate and lowered the activation energy. It was also found that the reactivity ratio of primary amine/epoxy and secondary amine/epoxy reactions was dependent on the amine structure, but independent on temperature.

I. Introduction

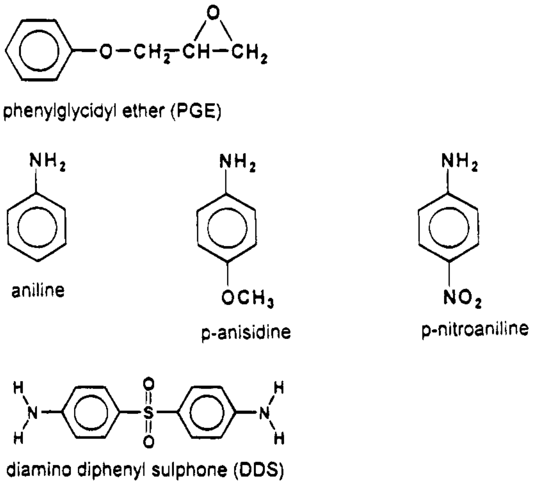
The subjects of mechanism and rates of epoxy/amine reactions have been studied by numerous investigators, and their findings were described in several books and key reviews.[1−6] But despite the wealth of available information, the fundamental and applied aspects of epoxy/amine reactions continue to attract considerable interest in the scientific community. There remain contradictory findings and unsolved questions regarding the substitution effect and the reactivity ratio (i.e., the effect of primary amine/epoxy reaction on the subsequent secondary amine/epoxy reaction), the nature of noncatalyzed and autocatalyzed reaction paths, the conditions under which etherification, homopolymerization, and intramolecular cyclization occur, and the effect of chemical structure and molecular archittecture of reactive components on the reaction kinetics.

A comprehensive research program aimed at answering those questions on the basis of a fundamental mechanistic approach has been underway at the Polytechnic University for several years. In an earlier paper from our group, we have proposed and verified a mechanistic kinetic model of epoxy/amine cure based upon the existence of different hydrogen-bonded transition complexes, whose formation and dissociation during the reaction control the kinetics.[7] The main objective of the work reported here, which was completed during the past 2 years, was to investigate epoxy/amine kinetics using a series of model systems containing amine molecules of different chemical composition. Specifically, we are interested in the effect of electrophilicity of amine molecules on the ensuing kinetics and the conditions under which the kinetic parameters of model systems are applicable to multifunctional epoxy formulations.

II. Experimental Section

A. Materials. All model systems contained stoichiometric amounts of the same epoxy and various amines (Aldrich). Model epoxy was 1,2-epoxy-3-phenoxypropane. This compound is also known as phenyl glycidyl ether, or PGE, and will be referred to by its acronym. Model amines included aniline, *p*-nitroaniline, *p*-anisidine (or *p*-methoxyaniline), and diaminodiphenyl sulfone (or DDS). The structures of all compounds are shown in Chart 1.

Chart 1. Chemical Formulas of Model Compounds



B. Sample Preparation. Amines (except aniline) were first dissolved in PGE at an elevated temperature which was then raised to the reaction temperature. Approximately 40 mL of the sample was placed in a 100 mL three-neck bottle which was immersed in an oil bath and purged with purified nitrogen. An Omega CN 2010 controller was used to control the temperature. Small aliquots were extracted at desired time intervals and quenched prior to the subsequent analysis.

C. Analytical Technique. High-performance liquid chromatography (HPLC) analysis was conducted on a Perkin-Elmer LCI laboratory computing integrator equipped with a pump, UV detector, and a reversed-phase C18 column. Gradient elution of methanol−water system (from 20% to pure methanol) was used at a constant flow rate of 1.75 mL/min. Twenty μL of sample in the form of ca. 0.5 wt % solution in methanol was injected in the column. The UV detector set at 254 nm was used to monitor eluted species. Concentrations of various species were calculated from the peak areas using the calibration curves of pure compounds. In PGE/aniline system, secondary amine product was prepared by reacting PGE with excess aniline (1:10 molar ratio) at 80 °C for 24 h, after which the excess aniline was distilled off. Tertiary amine product was obtained from the stoichiometric mixture reacted at 120 °C for 15 h. The intermediate (secondary amine) products in other model systems were obtained using a fractional collector connected to the HPLC unit. A series of typical chromatograms which trace the progress of reaction is displayed in Figure 1.

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[®] Abstract published in *Advance ACS Abstracts*, November 15, 1994.

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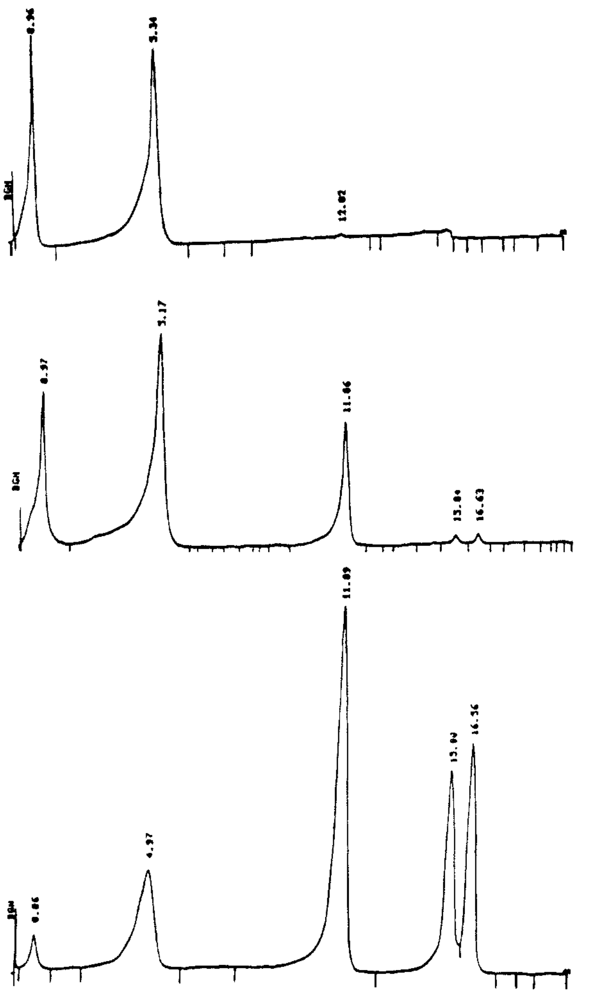

Figure 1. HPLC chromatograms for PGE/aniline reaction at 100 °C for (a) 2, (b) 30, and (c) 80 min.

III. Results and Discussion

Modeling Aspects. The following reactions are possible in an epoxy/amine mixture: primary amine (PA)–epoxy (E), secondary amine (SA)–epoxy, hydroxyl (OH)–epoxy, and epoxy–epoxy. It is further known that a hydroxyl group, or a proton donor(XH) in general, can act as a catalyst for epoxy–amine and epoxy–hydroxyl reactions. On that basis, a general equation for epoxy/amine kinetics in terms of the rate of disappearance of epoxy groups can be written as follows:

$$-\mathrm{d(E)}/\mathrm{d}t = k_1\mathrm{(E)(PA)} + k_1'\mathrm{(E)(PA)(XH)} + k_2\mathrm{(E)(SA)} + k_2'\mathrm{(E)(SA)(XH)} + k_3\mathrm{(E)(OH)} + k_3'\mathrm{(E)(OH)(XH)} + k_4\mathrm{(E)(E)} \quad (1)$$

By neglecting etherification, which is known to occur only at high temperature and advanced degrees of cure,[8-11] and homopolymerization, which is contingent upon the presence of Lewis acid and/or base catalysts,[6,12,13] eq 1 can be simplified as follows:

$$-\mathrm{d(E)}/\mathrm{d}t = k_1\mathrm{(E)(PA)} + k_1'\mathrm{(E)(PA)(XH)} + k_2\mathrm{(E)(SA)} + k_2'\mathrm{(E)(SA)(XH)} \quad (2)$$

The model systems selected herein are conducive to the application of simplifying assumptions reflected in eq 2 due to (1) the nonpolymer forming character of model systems which renders intramolecular cyclization inconsequential and (2) the fact that the temperature range used and the absence of Lewis base (or acid) type accelerators allow etherification and homopolymerization to be neglected. Both assumptions were corroborated by HPLC and FTIR measurements in the course of this investigation. Cyclization in diglycidyl epoxy/aromatic amine networks has been investigated by Johncock and co-workers.[14,15] One must keep in mind, however, that albeit model systems are of great help in elucidating the reaction mechanism, the kinetic parameters generated in a model study cannot be, as a rule, substituted for the corresponding kinetic parameters of multifunctional systems. The conditions under which this is possible is an issue of major interest and will be addressed later in the text.

In addition to monitoring the change in the concentration of epoxy groups, kinetics of epoxy/amine reactions could be also evaluated by measuring the rate of disappearance of primary amine (PA) and/or the rate of appearance of tertiary amine (TA). The appropriate rate expressions were those of our model, which was described in detail elsewhere[7,16] and hence only its salient features will be recapped here. The model is based upon the existence of three intermediate hydrogen-bonded transition complexes; (a) epoxy–amine, (b) epoxy–hydroxyl, and (c) amine–hydroxyl. These three transition complexes control the rate of epoxy–amine reactions according to the following general scheme:

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

We have previously identified three hydrogen-bond complexes that can form and participate in the reactions. Amino groups are consumed (and/or formed) via the three proposed routes (termed a, b, and c above), and one can write the following equations for the rate of disappearance of primary amine and the rate of formation of tertiary amine, respectively

$$-\mathrm{d(PA)}/\mathrm{d}t = -[\mathrm{d(PA)}_a/\mathrm{d}t + \mathrm{d(PA)}_b/\mathrm{d}t + \mathrm{d(PA)}_c/\mathrm{d}t] = W_1k_{a1}\mathrm{(PA)}^2\mathrm{(E)} + W_2\mathrm{(PA)(E)}[k_{b1} + k_{b1}'\mathrm{(OH)}] + W_3k_{c1}\mathrm{(PA)(E)(OH)} - [\mathrm{(PA)/(OH)}][\mathrm{d(OH)}/\mathrm{d}t] \quad (3)$$

and

$$\mathrm{d(TA)}/\mathrm{d}t = [\mathrm{d(TA)}_a/\mathrm{d}t + \mathrm{d(TA)}_b/\mathrm{d}t + \mathrm{d(TA)}_c/\mathrm{d}t] = W_1k_{a2}\mathrm{(SA)}^2\mathrm{(E)} + W_2\mathrm{(SA)(E)}[k_{b2} + k_{b2}'\mathrm{(OH)}] + W_3k_{c2}\mathrm{(SA)(E)(OH)} - [\mathrm{(SA)/(OH)}][\mathrm{d(OH)}/\mathrm{d}t] \quad (4)$$

where k's are reaction rate constants, subscripts a, b and c refer to the above-defined reaction paths that involve transition complexes, subscripts 1 and 2 define primary and secondary amine, respectively, and superscript ′, denotes catalyzed reaction. The weight factor W_i is zero when the consumption of epoxy groups by ith mechanism is negligible and 1 when it is not.

In the absence of initially present electrophilic groups (i.e., by neglecting route a) and before the critical concentration of hydroxyl groups is reached (i.e., prior to the engagement of route c), eqs 4 and 5 reduce to the following form:

$$-\mathrm{d(PA)}_b/\mathrm{d}t = W_2\mathrm{(PA)(E)}[k_{b1} + k_{b1}'\mathrm{(OH)}] \quad (5)$$

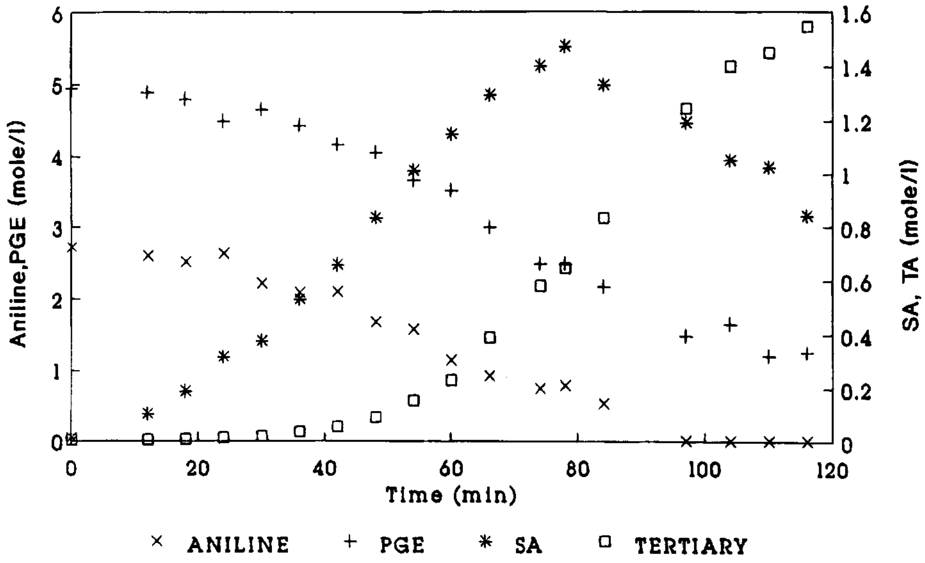

Figure 2. Concentration of components as a function of reaction time in a PGE/aniline system at 110 °C.

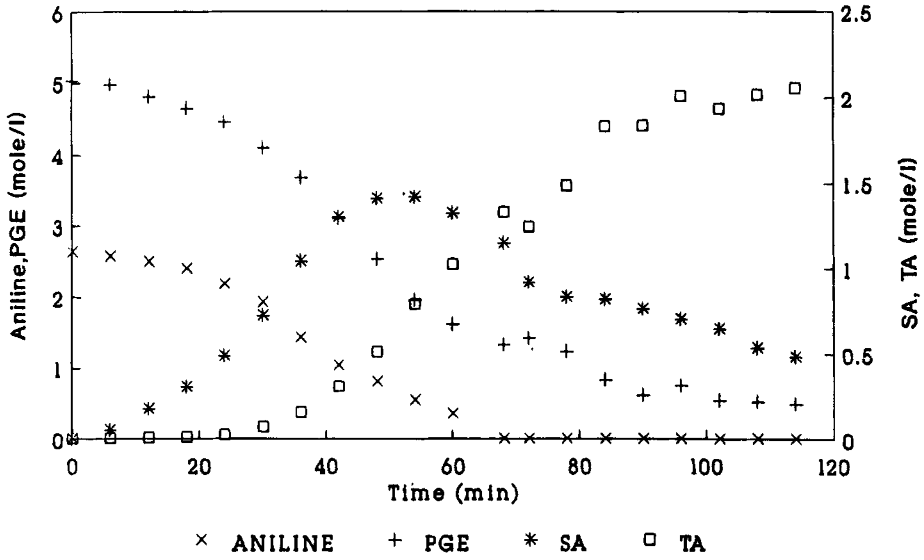

Figure 3. Concentration of components as a function of reaction time in a PGE/aniline system at 120 °C.

and

$$\mathrm{d(TA)_b/d}t = W_2\mathrm{(SA)(E)}[k_{b2} + k_{b2}'\mathrm{(OH)}] \qquad (6)$$

We note that eqs 5 and 6 are de facto analogous to the equations previously reported by Horie and co-workers.[17]

It is intuitively expected that the rates of primary amine–epoxy and secondary amine–epoxy reaction should be different. The ratio of the corresponding rate constants, i.e., k_2/k_1 or k_2'/k_1', is known as relative reactivity. The secondary amine formed during reaction is sterically hindered and has restricted mobility that is expected to reduce the reactivity of the remaining hydrogen. The value of the reactivity ratio is a measure of the "substitution effect", which is termed "negative" when secondary amine is less reactive than primary amine, and "positive" when the opposite is true. The value of k_2'/k_1' is an important factor in the formation of network morphology in multifunctional polymers. A large value of k_1' will favor the initial formation of a predominantly linear polymer, while commensurate values of k_1' and k_2' will result in a randomly crosslinked network. In this study we shall utilize exclusively the catalyzed reaction rate constants, and hence the reactivity ratio will be defined as k_2'/k_1'. We shall now describe our results for all systems investigated.

PGE/Aniline. Examples of experimental results for the PGE/aniline system obtained at 110 and 120 °C are shown in Figures 2 and 3, respectively. The mass balances were checked continuously during the course of reaction by comparing the amount of sample injected in the column with the calculated calibration values. The observed deviation never exceeded 5%, and the accuracy was also verified by titration.

We first tried to fit our kinetic data to eqs 7 and 8, shown below. That was accomplished by rewriting eqs 5 and 6 as follows

$$-\mathrm{d(PA)_b/d}t\mathrm{(PA)(E)} = k_{b1} + k_{b1}'\mathrm{(OH)} \qquad (7)$$

and

$$\mathrm{d(TA)_b/d}t\mathrm{(SA)(E)} = k_{b2} + k_{b2}'\mathrm{(OH)} \qquad (8)$$

and plotting reduced rate (left hand side of eqs 7 and 8) as a function of hydroxyl concentration. Absolute values for the rate constants were generated by first calculating the reduced rates from the slopes of the concentration profiles and the instantaneous concentrations of various

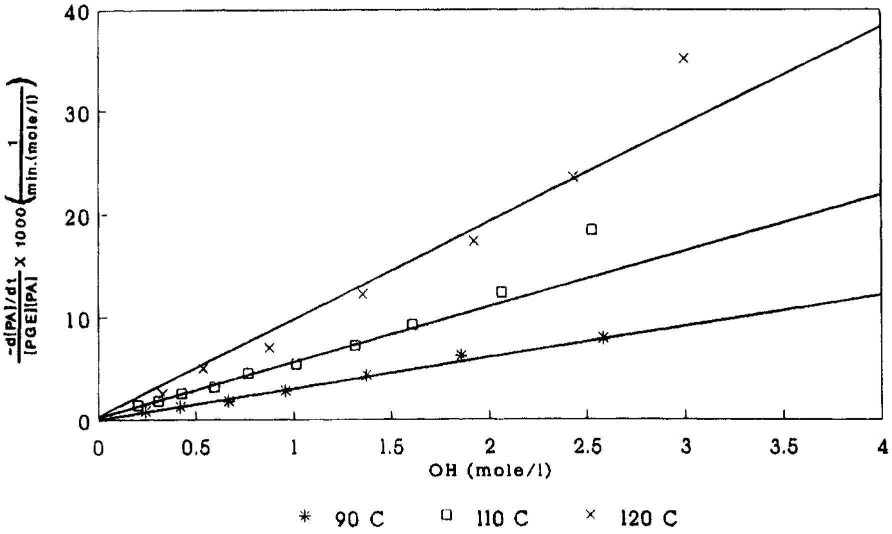

Figure 4. Primary amine/epoxy reduced rate as a function of hydroxyl concentration in PGE/aniline, with reaction temperature as a parameter.

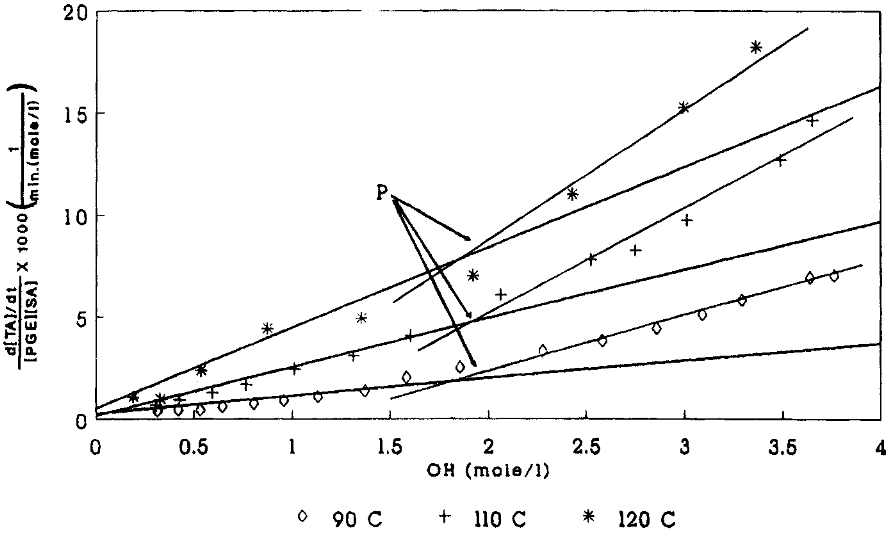

Figure 5. Secondary amine/epoxy reduced rate as a function of hydroxyl concentration in PGE/aniline, with reaction temperature as a parameter.

components in the reactive mixture. The reduced rates were then plotted as a function of hydroxyl concentration and the rate constants extracted from the corresponding values of slope and intercept. Let us first consider the primary amine–epoxy reaction, which dominates the early stages of reaction characterized by a high concentration of primary amine. Figure 4 was generated by plotting the reduced reaction rate of eq 7 as a function of hydroxyl concentration at several temperatures. A linear correlation was observed suggesting the validity of the kinetic model described by eq 7. Values of the kinetic rate constants for catalyzed and noncatalyzed reactions obtained from the slopes and intercepts of best-fit reduced rate plots are summarized in Table 1. The noncatalyzed rate constant, k_1, was very sensitive to the presence of traces of impurities and its value should be considered an estimate. The values of k_1', on the other hand, were very accurate and reproducible within 5%.

To analyze the rate of formation of tertiary amine, the reduced rate of eq 8 was plotted as a function of hydroxyl concentration, with temperature as a parameter, as shown in Figure 5. At hydroxyl group concentration below 2.0 mol/L, data points fell on straight lines at all temperatures, thus supporting the proposed mechanism. However, a decisive deviation from the straight line was observed at concentrations in excess of the critical value of 2.0 mol/L, clearly indicating that epoxy/amine reactions cannot be described exclusively by the underlying mechanism of eqs 7 and 8. The slope changes dramatically at point *P*, which corresponded to the "critical" hydroxyl concentration of approximately 2.0 mol/L and is independent of temperature. This further implies that the change in the mechanism, whose nature is discussed below, depends on the composition of the reaction mixture but is not thermally driven. The plot shown in Figure 5 and the corresponding plots for other systems investigated in this study were consistently well-represented by two straight lines intersecting at a critical point.

Table 1. Rate Constants for Epoxy/Amine Reactions in PGE/Aniline Model System

rate constant	90 °C	110 °C	120 °C
k_1 (L/mol)/t	0.05×10^{-3}	0.28×10^{-3}	0.35×10^{-3}
k_1' (L/mol)^2/t	3.00×10^{-3}	5.40×10^{-3}	9.50×10^{-3}
k_2 (L/mol)/t	0.10×10^{-3}	0.20×10^{-3}	0.58×10^{-3}
k_2' (L/mol)^2/t	0.97×10^{-3}	2.34×10^{-3}	4.04×10^{-3}
k_{2c}' (L/mol)^3/t	0.43×10^{-3}	0.86×10^{-3}	1.29×10^{-3}

The concentration of the primary amine groups is already very small at the critical hydroxyl concentration, where over 90% of the primary amine groups have been

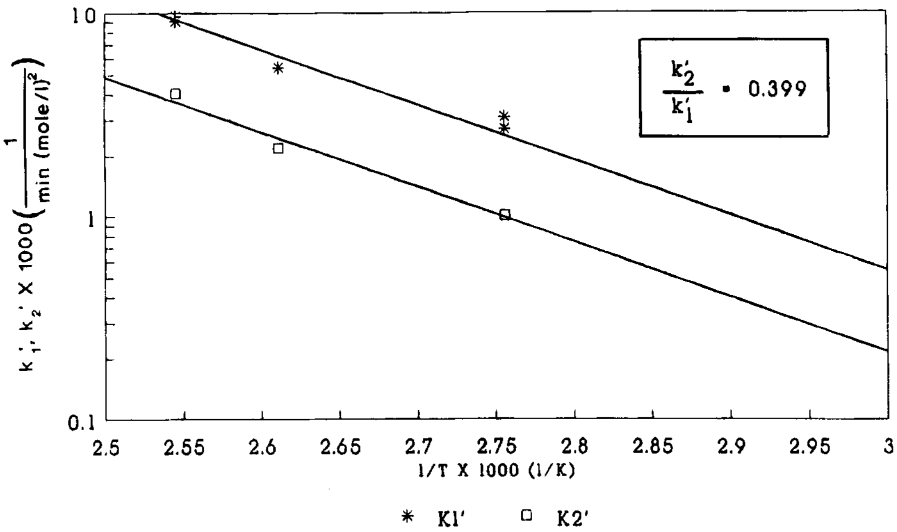

Figure 6. Reaction rate constants as a function of temperature for PGE/aniline.

converted to secondary amine. The principal reaction in the mixture beyond that point, as the concentration of primary amine decreases to zero, is the conversion of secondary to tertiary amine. This has important implications in the multifunctional epoxy–amine systems, in that the morphology of those networks depends on the relative reactivity of the amino groups (k'_2/k'_1) prior to point P, but not after.

The effect of temperature on the kinetic rate constants is seen in the Arrhenius plots of Figure 6. The same value of activation energy, ca. 12.5 kcal/mol, characterizes both rate constants. The relative reactivity ratio was found to be independent of temperature and equal to 0.4. This value agrees with the value reported by Enikolopyan.[18]

An explanation of the underlying mechanism responsible for the observed shift in kinetics at point P is offered in terms of the additional interactions between epoxy–hydroxyl and amine–hydroxyl complexes, brought about by a sufficiently high concentration of the hydroxyl groups. In the early stages of reaction, hydroxyl groups tend to form complexes with epoxy groups due to the high value of the equilibrium constant.[3] The concentration of hydroxyl groups increases during the reaction, while that of epoxy groups decreases, resulting in the changes of concentration ratios of various complexes. Beyond the critical value of hydroxyl concentration, the concentration of amine–hydroxyl complex assumes a significant role in the kinetic scheme despite its low equilibrium constant, and the route c in our mechanism, which involves the amine–hydrogen complex and has been first reported by our group, becomes activated. Kinetically, that route can be represented by the last term on the right hand side of eqs 3 and 4, as proposed earlier, or by the following equations which gave equally good results:[19]

$$-\mathrm{d(PA)}_c/\mathrm{d}t = k_{1c}'\mathrm{(PA)(E)(OH)}^2 \qquad (9)$$

and

$$\mathrm{d(TA)}_c/\mathrm{d}t = k_{2c}'\mathrm{(SA)(E)(OH)}^2 \qquad (10)$$

Equations 7 and 8 can now be combined with eqs 9 and 10, in order to describe the entire reaction path as follows:

$$\begin{aligned}-\mathrm{d(PA)}/\mathrm{d}t &= -[\mathrm{d(PA)}_b/\mathrm{d}t + \mathrm{d(PA)}_c/\mathrm{d}t] \\ &= k_{1b}\mathrm{(PA)(E)} + k_{1b}'\mathrm{(PA)(E)(OH)} + k_{1c}'\mathrm{(PA)(E)(OH)}^2 \\ &= k_{1b}\mathrm{(PA)(E)} + \mathrm{(PA)(E)(OH)}[k_{1b}' + k_{1c}'\mathrm{(OH)}] \qquad (11)\end{aligned}$$

and

$$\begin{aligned}\mathrm{d(TA)}/\mathrm{d}t &= [\mathrm{d(TA)}_b/\mathrm{d}t + \mathrm{d(TA)}_c/\mathrm{d}t] \\ &= k_{2b}\mathrm{(SA)(E)} + k_{2b}'\mathrm{(SA)(E)(OH)} + k_{2c}'\mathrm{(SA)(E)(OH)}^2 \\ &= k_{2b}\mathrm{(SA)(E)} + \mathrm{(SA)(E)(OH)}[k_{2b}' + k_{2c}'\mathrm{(OH)}] \qquad (12)\end{aligned}$$

The proposed model was checked by plotting the reduced rate of formation of tertiary amine as a function of $(\mathrm{OH})^2$, with temperature as a parameter. The data at higher concentration of hydroxyl groups fall on straight lines, as shown in Figure 7, and hence support the model. The values of k_{2c}' obtained from the slopes are also given in Table 1. The values of k_{2c}' are smaller than those of k_2', as a result of the lower reactivity of amino–hydrogen in the amine–hydroxyl complex. In the complex, the amino hydrogen is "tied" by the hydrogen bond which decreases its reactivity.

When we compared the findings of the PGE–aniline study with previously generated data on the kinetics of a diglycidyl ether of bisphenol A(DGEBA)–diamonidiphenyl sulfone (DDS), we found out that the latter system had to be heated to higher temperature in order to induce commensurate reaction rates. This led to an examination of the nature of required similarities between model systems and network-forming multifunctional systems that would have to exist if these two systems were to have the same kinetics. The size of reactive molecules was considered first. In multifunctional systems of the DGEBA–DDS type, molecular weight increases during reaction. The size of growing molecules, however, is not a factor here: it affects the reaction rate only when the latter is diffusion controlled, the condition not met prior to vitrification. The effect of steric hindrance is minor, since the functional groups of multifunctional molecules are separated by a sufficiently long distance. Thus, the major role in deter-

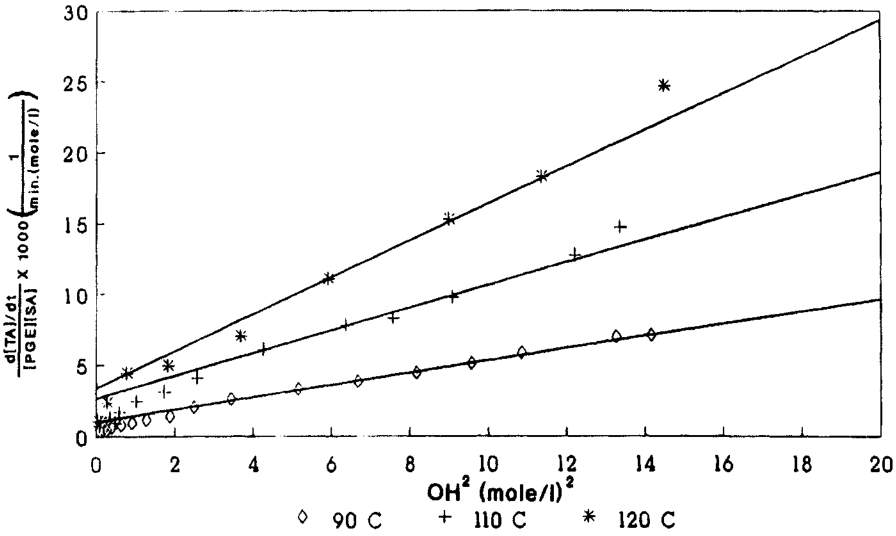

Figure 7. Secondary amine/epoxy reduced rate as a function of the square of hydroxyl concentration in PGE/aniline, with reaction temperature as a parameter.

mining the reaction rate is played by the electrophilicity of the substituent group on amine molecules, which can affect the electron density of the reactive group and hence alter the corresponding kinetics. The electrophilicity of the epoxy benzene ring substituent is of lesser importance. The epoxy group in either PGE or DGEBA is separated from the benzene ring by the $-OCH_2-$ segment, and due to small inductive effect, a substituent on the benzene ring should not affect the electron affinity of the epoxy group and thereby its reactivity. A well-known example of such a trend is the effect of phenyl group on the acidity of a series of phenylalkanoic acids; the acid strengthening effect of the phenyl group is attenuated rapidly down the alkyl chain. The amino group in aniline or DDS, on the other hand, is attached directly to the benzene ring. A substituent group on the benzene ring can therefore affect the electron density of the amino group through the resonance effect and cause different kinetics in PGE/aniline and DGEBA/DDS systems.

In the continuation of our investigation we looked into the effect of the type of amine substituent on the reaction kinetics. Since the secondary amine–epoxy reaction rate order changes at the critical concentration of hydroxyl groups, as shown above, it is important to select a proper rate constant for the evaluation of relative reactivity. In this discussion, k_2' is chosen over k_{2c}', since the former describes the region where both primary amine–epoxy and secondary amine–epoxy reactions occur and hence their relative rates can be compared.

PGE/*p*-Anisidine. We first investigated *p*-anisidine, an aniline with the methoxy group in the para position. Methoxy is a strong electron-donating group. Reactions between PGE and *p*-anisidine are described in Figure 8 (top), and an HPLC plot of concentration of components as a function of reaction time is given in Figure 8 (bottom). Reaction rate constants were evaluated at a series of temperatures using the procedure described for the PGE/aniline system. An example of reduced rate of tertiary amine as a function of hydroxyl concentration is shown in Figure 9. Similar trends were observed as in the case of the PGE–aniline system; the reduced rate for primary amine–epoxy reaction was linearly proportional to hydroxyl concentration, while the reduced rate for the secondary amine–epoxy reaction was characterized by the same change from first to second order at the critical hydroxyl concentration of ca. 2.0 mol/L. From the Arrhenius plot of Figure 10 the energy of activation of both reactions was calculated to be 8.9 kcal/mol, lower than the corresponding value for the PGE–aniline system. A slight positive substitution effect was determined ($k_2'/k_1' = 0.549$) but the reactivity ratio was independent of temperature. A comparison of Figures 6 and 10 shows that, for a given temperature, the reaction rate constants for PGE/*p*-anisidine are higher than those of PGE/aniline system. The enhancement of the reaction rate is caused by the electron-donating effect of the methoxy group which increases the basicity (electron density) of aniline.

PGE/*p*-Nitroaniline. We next investigated *p*-nitroaniline, an aniline with a nitro group in the para position. The nitro group is a strong electron-withdrawing group. Reactions between PGE and *p*-nitroaniline are described in Figure 11 (top), and an HPLC plot of concentration of components as a function of reaction time is given in Figure 11 (bottom). Reaction rate constants were evaluated at a series of temperatures using the procedure described for PGE/aniline system. An example of reduced rate of tertiary amine as a function of hydroxyl concentration is shown in Figure 12. Similar general trends were observed as in the case of PGE/aniline and PGE/*p*-anisidine systems; the reduced rate for primary amine–epoxy reaction was linearly proportional to hydroxyl concentration, while the reduced rate for secondary amine–epoxy reaction was characterized by the same change from first to second order at the critical hydroxyl concentration of ca. 2.0 mol/L. From the Arrhenius plot of Figure 13 the energy of activation of both reactions was calculated to be 14.9 kcal/mol, higher than the corresponding values for PGE–aniline and PGE–*p*-anisidine systems. A strong negative substitution effect was determined ($k_2'/k_1' = 0.089$) but the reactivity ratio was again independent of temperature. A comparison of Figure 13 with Figures 6 and 10 shows that, for a given temperature, the reaction rate constants for the PGE/*p*-nitroaniline system are lower than the corresponding values for PGE/aniline and PGE/*p*-anisidine systems. A nitro group in the para position significantly reduces the basicity of aniline as a result of direct conjugation with the amino group, which thus reduces the reactivity of the amine.

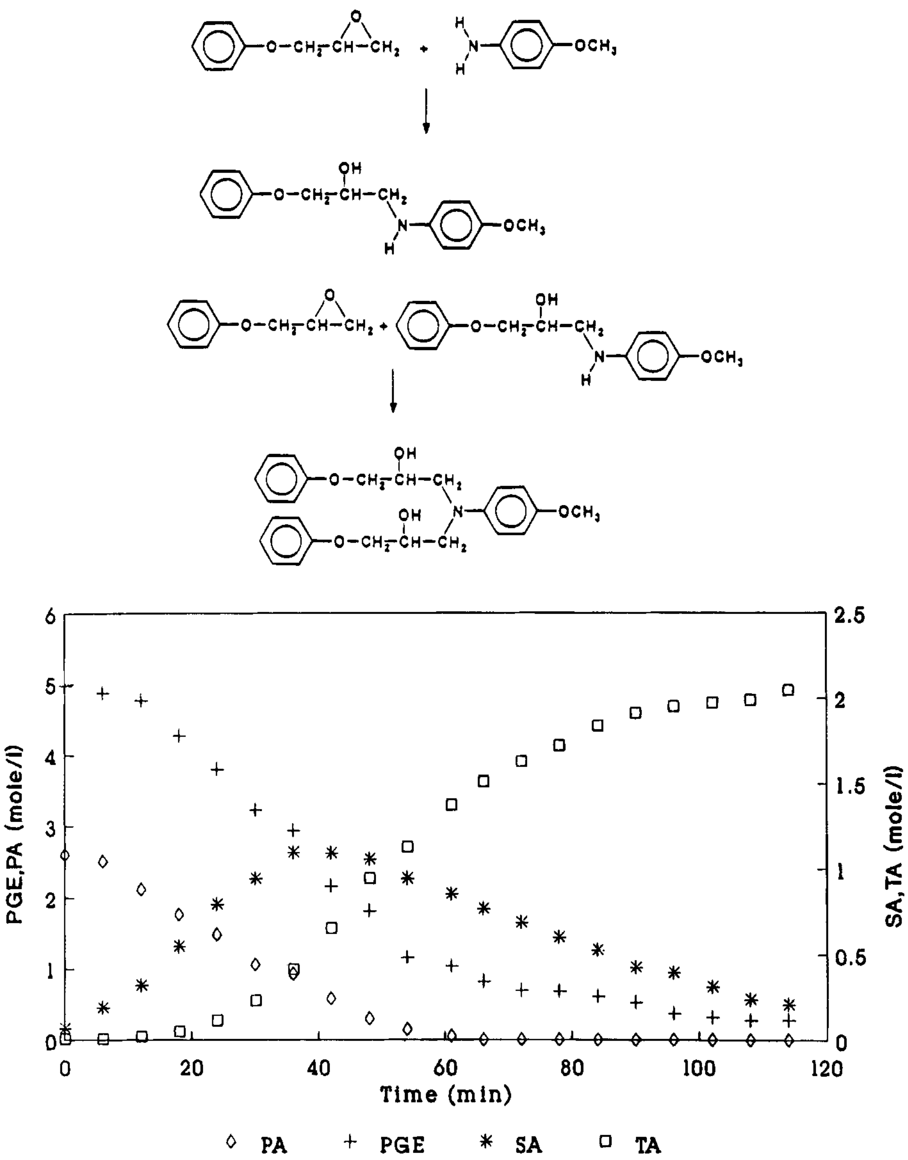

Figure 8. (Top) PGE/*p*-anisidine reaction scheme. (Bottom) concentration of components as a function of reaction time in PGE/*p*-anisidine system at 98 °C.

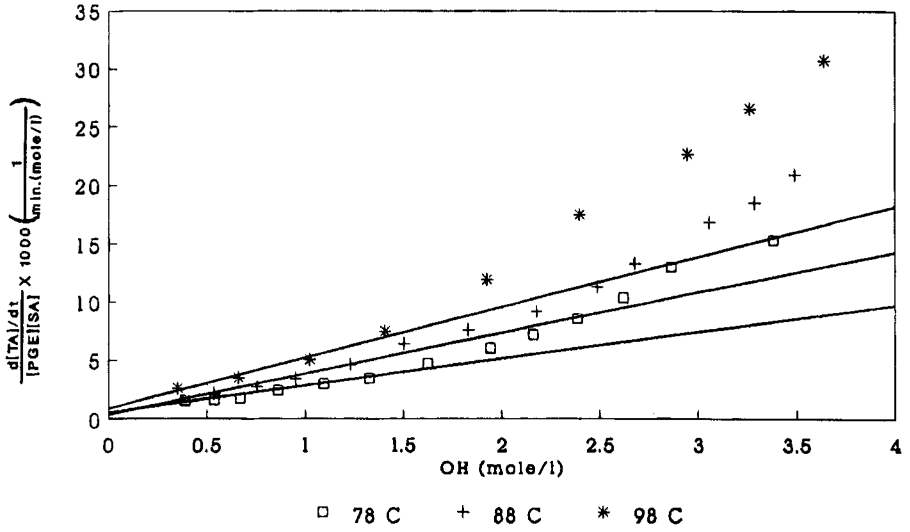

Figure 9. Secondary amine/epoxy reduced rate as a function of hydroxyl concentration in PGE/*p*-anisidine, with reaction temperature as a parameter.

PGE/DDS. Unlike the amines discussed thus far, DDS has two primary amine groups per molecule, resulting in a multitude of possible products and reaction paths. A more detailed description of the reaction mechanism in PGE/DDS system is given elsewhere,[20] and only the results of direct relevance to this work will be presented here. An HPLC plot of concentration of components in the reaction mixture as a function of time

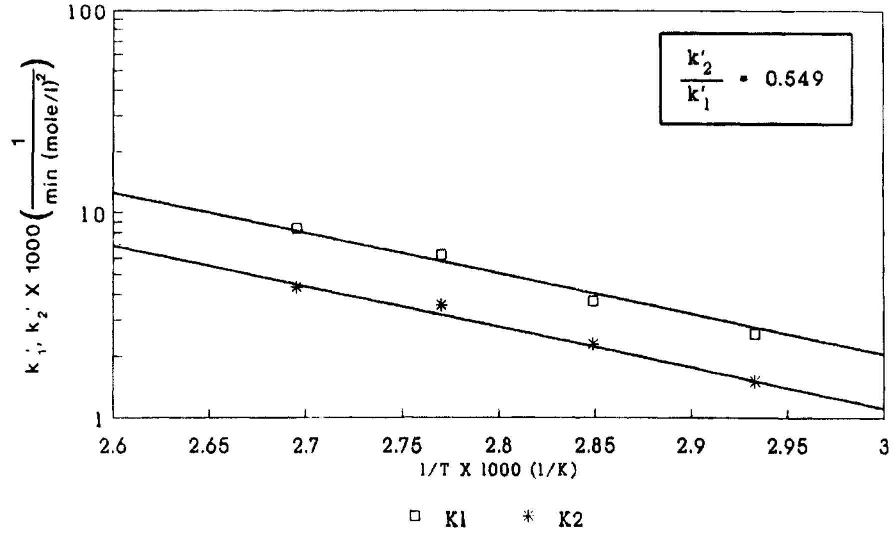

Figure 10. Reaction rate constants as a function of temperature for PGE/*p*-anisidine.

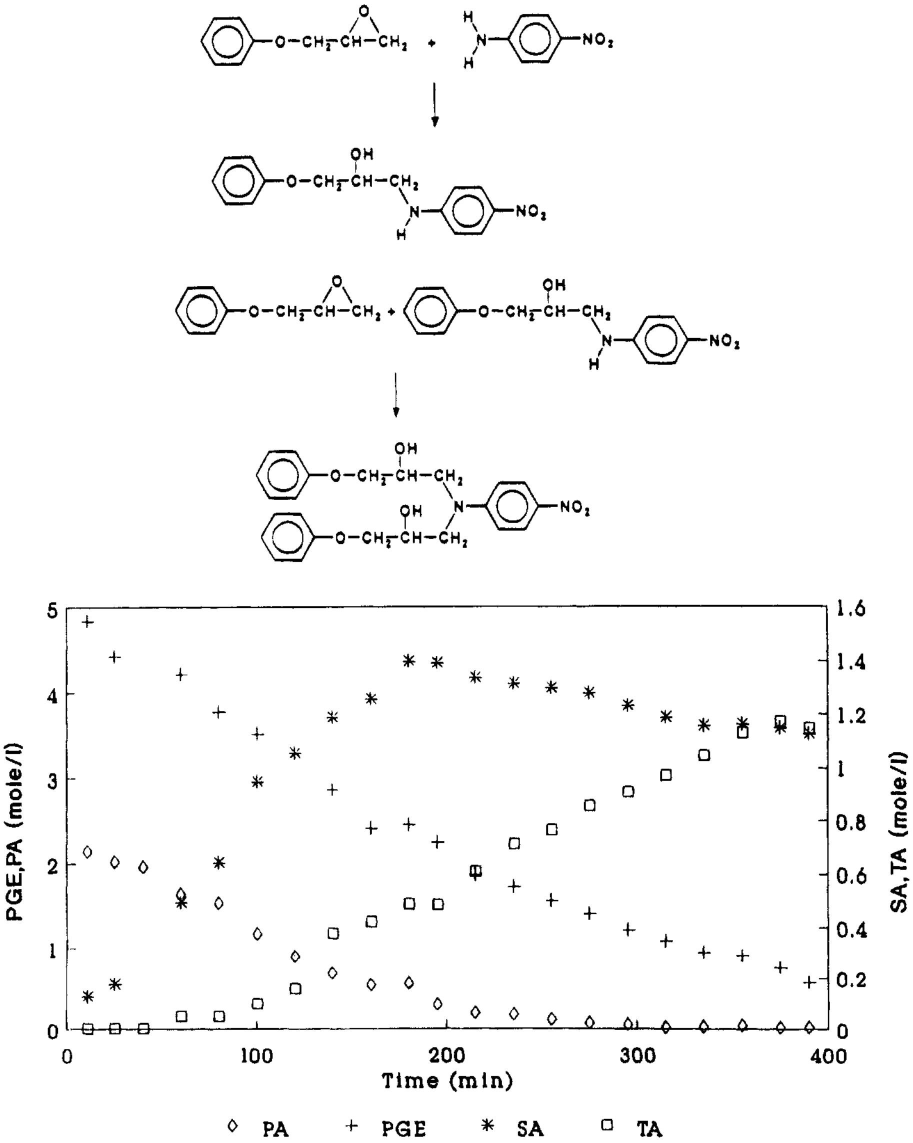

Figure 11. (Top) PGE/*p*-nitroaniline reaction scheme. (Bottom) concentration of components as a function of reaction time in PGE/*p*-nitroaniline system at 150 °C.

is shown in Figure 14. Analogous runs were made at a series of temperatures. The products labeled 1SUBST, 2SUBST, 3SUBST, and 4SUBST refer to the DDS molecules that have reacted with one, two, three, and four epoxy groups, respectively. It was found that the size of any of those components had no effect on the kinetics. Examples of the reduced reaction rate of formation of 1SUBST (by primary amine–epoxy reaction) and 4SUBST (by secondary amine–epoxy reaction) as a function of hydroxyl concentration are presented

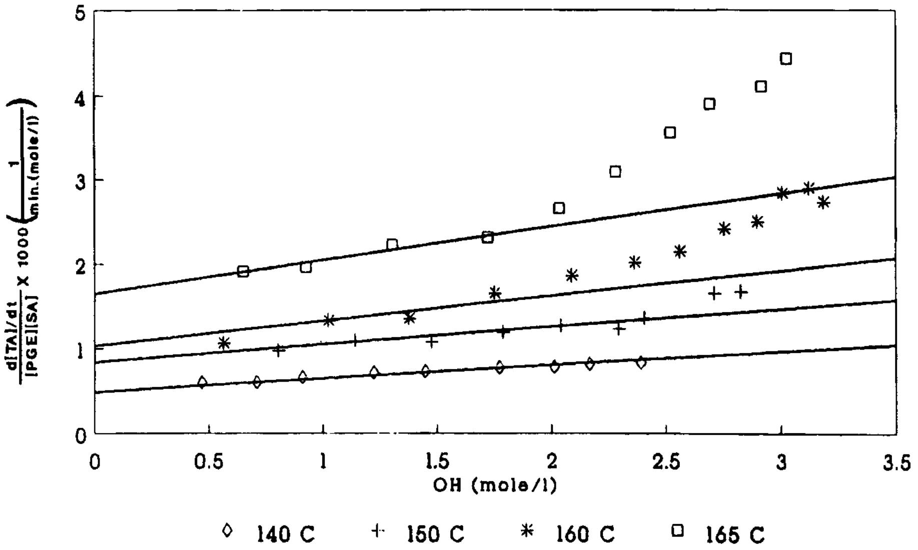

Figure 12. Secondary amine/epoxy reduced rate as a function of hydroxyl concentration in PGE/*p*-nitroaniline, with reaction temperature as a parameter.

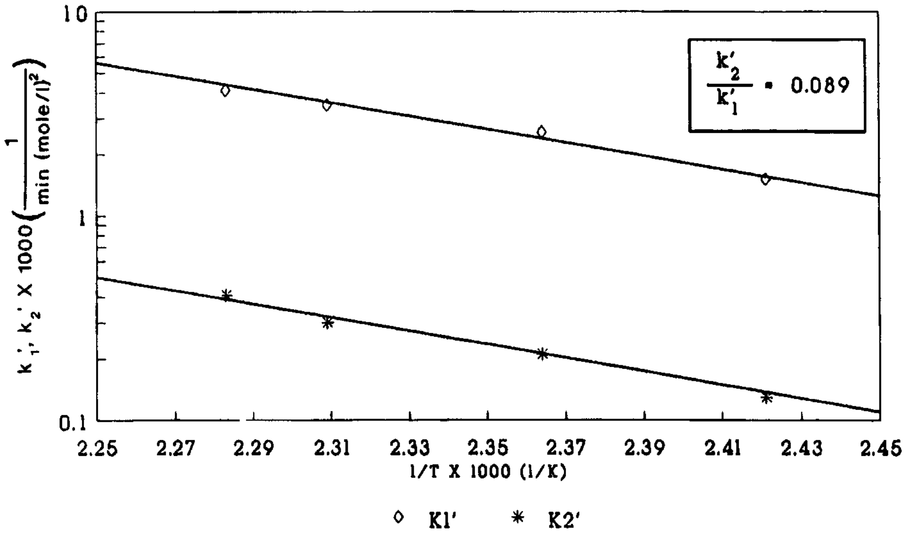

Figure 13. Reaction rate constants as a function of temperature for PGE/*p*-nitroaniline.

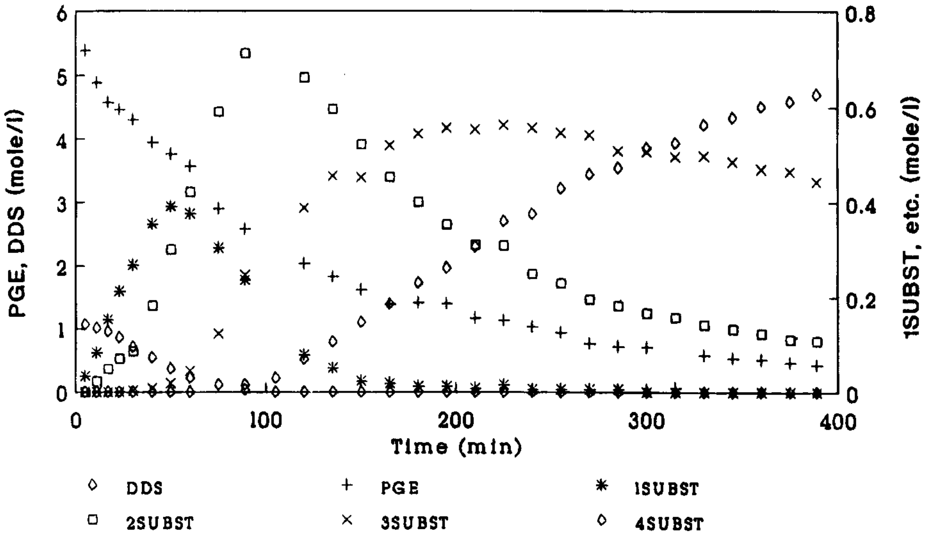

Figure 14. Concentration of components as a function of reaction time in PGE/DDS system at 143 °C.

in Figures 15 and 16, respectively. From the Arrhenius plot of Figure 17 the energy of activation of both reactions was calculated to be 13.9 kcal/mol, higher than the corresponding values for PGE/aniline and PGE/*p*-anisidine systems but slightly lower than that of the PGE/*p*-nitroaniline system. A strong negative substitution effect was determined ($k_2'/k_1' = 0.223$) but the reactivity ratio was again independent of temperature. Slower kinetics with respect to PGE/aniline were observed and, as in the case of PGE/*p*-nitroaniline, were

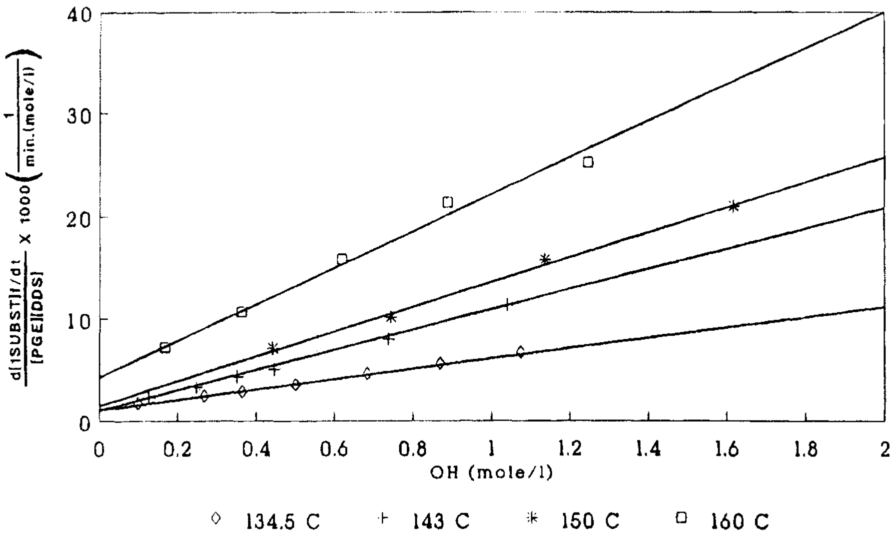

Figure 15. Primary amine/epoxy reduced rate as a function of hydroxyl concentration in PGE/DDS based on the formation of 1SUBST, with reaction temperature as a parameter.

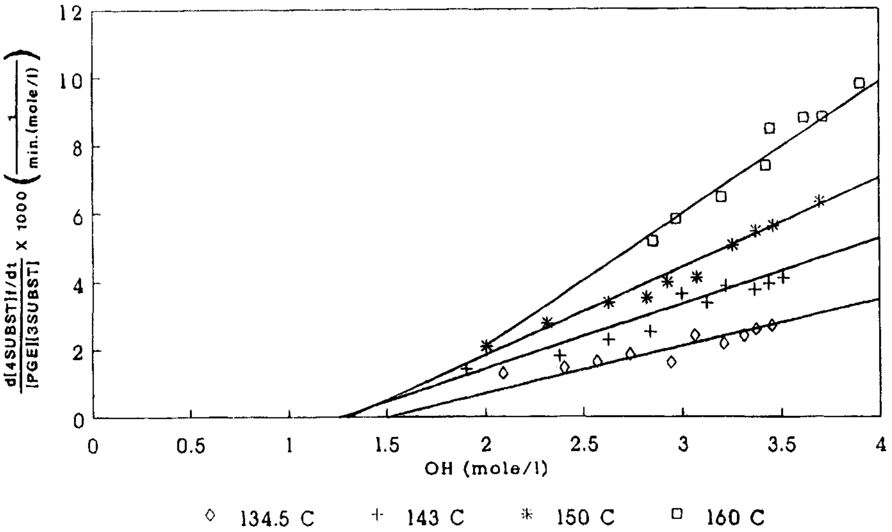

Figure 16. Secondary amine/epoxy reduced rate as a function of hydroxyl concentration in PGE/DDS based on the formation of 4SUBST, with reaction temperature as a parameter.

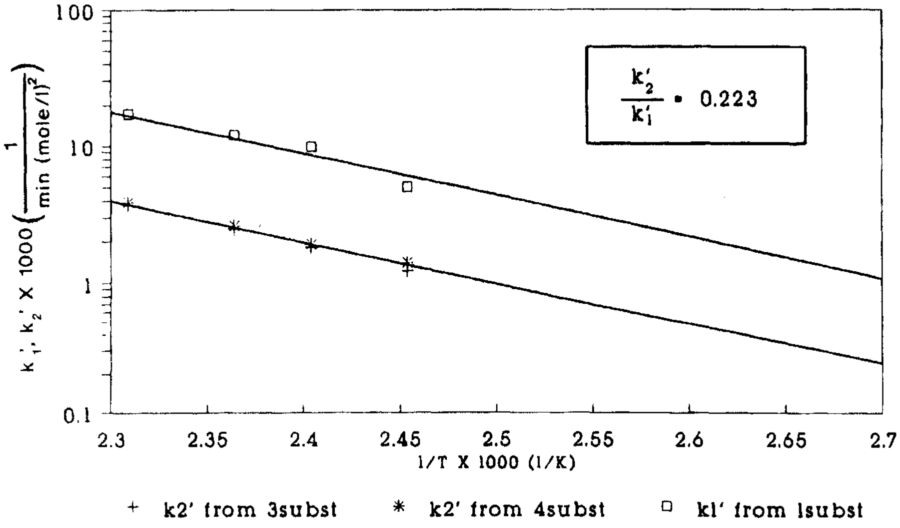

Figure 17. Reaction rate constants as a function of temperature of PGE/DDS.

ascribed to the reduction of amine basicity by the $-SO_2-$ group. A summary of the calculated activation energies for reactions between PGE and various aromatic amines is given in Table 2.

Effect of Electrophilicity. In the absence of etherification and/or homopolymerization, the morphology of multifunctional epoxy/amine networks is determined by their relative reactivity, i.e., the ratio k_2'/k_1'. The

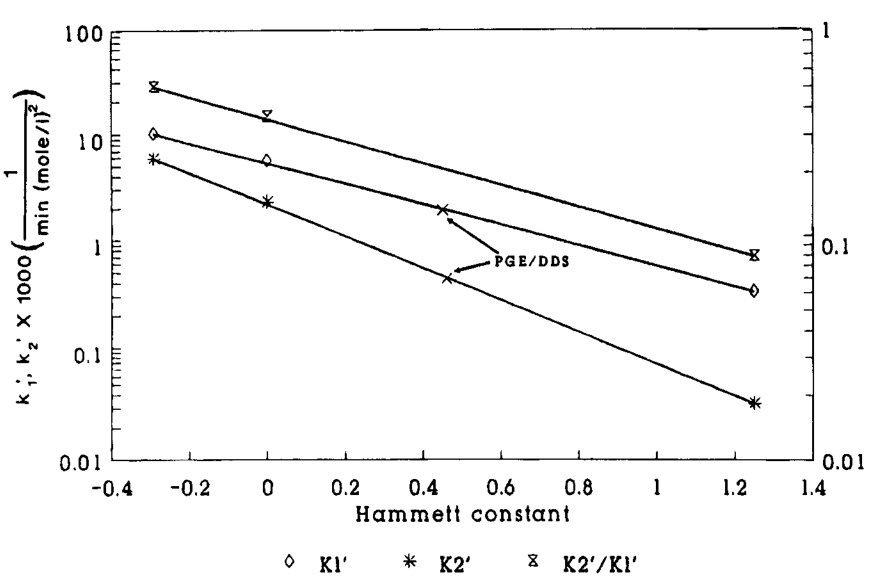

Figure 18. Reaction rate constants and reactivity ratios for various amines as a function of the Hammett constant, σ, at 110 °C.

Table 2. Activation Energies for Model Systems

system	type of substituent	activation energy (kcal/mol)
PGE/*p*-anisidine	electron donating	8.9
PGE/aniline	none	12.5
PGE/*p*-nitroaniline	electron withdrawing	14.9
PGE/DDS	electron withdrawing	13.9

Table 3. Relative Reactivity Ratio (k_2'/k_1') for Model Systems

system	k_2'/k_1'
PGE/aniline	0.399
PGE/*p*-anisidine	0.549
PGE/*p*-nitroaniline	0.089
PGE/DDS	0.223

negative substitution effect reported herein is in agreement with some[21-28] and disagreement with other[29,30] reports. Relative reactivity was independent of temperature in each of the four systems investigated here, suggesting that the morphology of an epoxy/amine network characterized by such kinetics is not a function of thermal history. Nonetheless, one cannot arbitrarily increase the curing temperature to reduce the curing time, since etherification reactions, as pointed out earlier, become pronounced at higher temperature. Our findings regarding the temperature dependence of the reactivity ratio are in agreement with most authors and disagreement with a few,[28] including an earlier report of ours[7] in which the values of k_2'/k_1' were calculated using "Simusolv" modeling and simulation software that adjusts parameters to get the best fitting for a given mathematical model.[16] The "Simusolv" method produced best fits over the entire range of hydroxyl concentration, but its outcome is judged less reliable since it lumps together data on both sides of the critical concentration of hydroxyl groups without distinguishing between two distinct mechanisms on either side of the critical point. Wang and Gillham,[28] who also reported the effect of temperature on relative reactivity, relied mainly on the data obtained at a high conversion of primary amine, between ca. 85 and 95%. At such high values of the degree of cure (α), the calculated value of their reduced variable $(1 - \alpha_{PA})^{(k2-k1)/k1}$ is very sensitive to the value of α_{PA} and will be dramatically affected by a small error in $(1 - \alpha_{PA})$.

The calculated values of relative reactivity for all four systems are listed in Table 3 in the order of increasing negative substitution effect. The most pronounced effect is observed in the presence of a nitro group, which has a strong electron-withdrawing character. The sulfone group ranks next; it is also an electron-withdrawing group which, in this case, is "shared"; it interacts simultaneously with the amine groups on both ends of DDS molecule. Aniline is considered as a reference, and the negative substitution effect here is taken to represent its intrinsic kinetic characteristic. The introduction of an electron-donating group in *p*-anisidine raises the value of relative reactivity slightly above 0.5.

The effects of structure on reactivity are generally classified as steric, inductive, and resonance. In this study, the substituent and the amine group are in the para position, sufficiently far apart to justify the assumption of negligible steric effects on reactivity. The variation in the reaction rate in our systems is caused by inductive and/or resonance effects, which are difficult to separate and are frequently lumped together as the electronic effect. Quantitative correlations between the electronic effect and reactivity can be obtained with the Hammett equation, which has been widely used by organic chemists to relate the effect of meta and para substituents in aromatic compounds on their equilibrium and rate constants.[31] The Hammett equation is based upon the concept that a given substituent will affect related reactions in more or less analogous way. For example, if the acidity of acetic acid is increased by replacing hydrogen with bromine, then one could expect that the introduction of bromine in the α-position on propionic acid would enhance its acidity too. The Hammett equation is expressed in the logarithmic form as

$$\log K_i/K_H = \varrho\sigma_i \tag{13}$$

where K_i is the equilibrium or rate constant of the compound with substituent i and K_H is the equilibrium or rate constant of the nonsubstituted compound (i.e., H is the substituent). The substituent constant, σ_i, is a number (positive or negative) that indicates the relative electronic effect of that substituent. Positive σ_i indicates an electron-withdrawing substituent and negative σ_i denotes an electron-donating substituent. The larger the magnitude of σ_i, the greater the effect of the substituent on the rate or equilibrium constant. The

Table 4. Hammett Substituent Constant for Model Systems

system	Hammett substituent constant, σ	k_2'/k_1'
PGE/aniline	0	0.399
PGE/*p*-anisidine	−0.293	0.549
PGE/*p*-nitroaniline	1.25	0.089
PGE/DDS	NA	0.223

constant ϱ is a number (again, positive or negative) which indicates the susceptibility of a given equilibrium or reaction rate to electronic effects. Positive ϱ signifies that the equilibrium, or reaction, is helped by an electron-withdrawing substituent. In order to assign numerical values to various ϱ's and σ_i's, an arbitrary convention must be adopted. For that purpose, ϱ_0 is taken as unity when K's in eq 13 are the ionization constants of substituted benzoic acids in water at 25 °C. Values of σ_i can then be calculated from the measurements of acid dissociation constants of substituted benzoic acids.

Calculated values of the Hammett substituent constant for our systems are summarized in Table 4. Since the relative reactivity of our systems was not a function of temperature, a correlation between relative reactivity and the Hammett constant could be sought at any temperature. We chose 110 °C. Plots of the rate constants k_1' and k_2' as a function of the Hammett constant at 110 °C are shown in Figure 18. Data were found to fit on two straight lines with different slopes. The higher slope is observed for k_2', suggesting that the secondary amine−epoxy reaction is more sensitive to the character of the substituent than the primary amine−epoxy reaction. We also found a specific relationship between relative reactivity and the Hammett substituent constant, seen in Figure 18. This is in contrast to the findings of Dobas et al.[30] who reported the same relative reactivity for various substituents. Their results were generated in dilute ethanol solutions, however, where the effect of the presence of large excess of hydroxyl groups on the reaction rate could be significant. To check our findings further, we calculated the reaction rate constants k_1' and k_2' for the PGE/DDS system at 110 °C, plotted them in Figure 18, and read off the value of the Hammett constant. As seen in Figure 18, the thus predicted values of the Hammett substituent constant are practically identical, which supports our tenet.

IV. Conclusions

We have completed an investigation of the effect of electrophilicity of the amine para-substituent on the kinetics of model epoxy/amine reactions. Four model amines, differing in their electron-withdrawing and/or -donating character, were investigated.

The kinetic analysis was performed using an earlier model of ours. It was found that the kinetics of secondary amine−epoxy reaction change from first to second order in hydroxyl group, upon depletion of the primary amine. A negative substitution effect (i.e., $k_2'/k_1' < 0.5$) was observed in the presence of an electron-withdrawing p-substituent. An electron donating p-substituent, on the other hand, contributes to the lowering of the activation energy and an increase in the reaction rate. The relative reactivity ratio (k_2'/k_1') of our model systems was found to vary in a systematic manner with the Hammett constant.

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