A General Kinetic Model for Epoxy Polymerization

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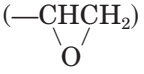
ABSTRACT: A general *kinetic* framework to study epoxy polymerization is developed. Best-fit values of five rate constants are obtained using some experimental chromatographic data available in the open literature on a system involving a single liquid phase. Detailed sensitivity studies are then carried out to identify the most important rate constants. Average molecular weights and the polydispersity index are predicted using these parameters. The present model is more general than earlier kinetic models, and does not have the drawbacks of probabilistic models. The present model is used to predict the effect of intermediate addition of NaOH, to illustrate how general it really is. The model can easily be extended to apply to industrial reactors, which have additional physico-chemical phenomena associated with them, as for example, non-isothermal polymerization, presence of two liquid phases, etc. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1859–1876, 1998

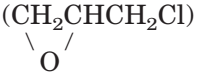
Keywords: kinetic model; epoxy polymerization

INTRODUCTION

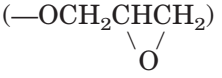
Epoxy polymers are formed by the reaction of an epoxy group



with a hydroxyl group. These resins are manufactured using two common processes: the taffy process, and the advancement process, but adaptations of these are not uncommon. In the taffy process, a diol, such as bisphenol A [HO—R—OH, where R is $C_6H_5(C—CH_3)_2—C_6H_5$] is reacted with a controlled excess of epichlorohydrin



to give a mixture of low molecular weight oligomers having glycidyl ether groups



at both ends. The lowest molecular weight oligomeric product is referred to as the diglycidyl ether of bisphenol A (DGEBPA). This process is carried out under the catalytic influence of an alkali such as sodium hydroxide. Water is present in the heterogeneous reaction mass, and it is claimed[1] that the reaction takes place at the water/organic medium interface. In the advancement process, bisphenol A is reacted with equimolar amounts of commercially available DGEBPA. This is a typical AA + BB step-growth polymerization,[2,3] in which complications are introduced by the presence of (over 10% of) impurities, for example, higher molecular weight diepoxides, monofunctional epoxides, etc.[4,5] Yet another process[5] involves the addition of bisphenol A to a solution of epichlorohydrin in a solvent (e.g., methyl cellosolve). Pulverized sodium hydroxide is added to

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this reaction mass in a controlled manner over a period of time. A specified temperature history is effected and intermediate washing with water and distillation under reduced pressure are used to give the final resin.

It is clear that a variety of physico-chemical phenomena are associated with the polymerization of epoxy resins in an industrial reactor. These are quite complex, and there is a definite need to study several of the interesting aspects of these polymerizations. Indeed, very few experimental or theoretical studies are available in the open literature on the modeling of *industrial* epoxy reactors.[5–7] This work intends to fill this gap to a small extent and attempts to provide a general mathematical framework for the study of the kinetics of the reactions. Limitations posed by heat and mass transfer effects can be incorporated subsequently, in order to develop a comprehensive reactor model.

The first systematic study of the kinetics of epoxy polymerization was done by Batzer and Zahir.[1,8–10] These workers have reported both experimental and theoretical work on the molecular weight distribution of epoxy resins. Their work was based on Flory's statistical method,[2,3] which in turn, assumes equal reactivity of the functional groups. Deviations of experimental results from theory have been explained due to[8,9] the presence of monofunctional epoxides in the resin and the possibility of branching reactions. These workers conclude that the reactivity of epichlorohydrin with the phenolic hydroxyl group is higher than with the aryl glycidyl ether group.

Ravindranath and Gandhi[4] improved the theoretical model developed by Batzer and Zahir and considered the unequal reactivity of epoxide groups. They used the probabilistic technique developed by Case[11] and observed improved agreement between model predictions and some of the experimental results of Batzer and Zahir. However, their model had two major drawbacks. It is well known that the alkali has a very important role to play in determining the molecular weight distribution (MWD) of the product. Because alkali leads to the production of phenoxide ions,[1] it is possible to have some degree of control over the concentration of the phenoxide anion by controlling the rate of intermediate addition of the alkali. This enables one to alter the MWD of the resin. Unfortunately, the effect of alkali addition on the MWD is not considered by Ravindranath and Gandhi. In addition, in their model, one of the intermediate reactions (dehydrochlorination) has been considered to be extremely fast and, hence, the concentration of the chlorohydrin species is zero. This is contrary to the experimental observations of Batzer and Zahir,[8] who do observe this species in their GPC studies. Moreover, the use of the probabilistic approach by Ravindranath and Gandhi[4] prevents its use in modeling industrial epoxy reactors, which are often operated in the semibatch mode (with intermediate addition of sodium hydroxide and vaporization of the volatiles). This study attempts to overcome these drawbacks, and presents a general *kinetic* framework, which can easily be adapted in the future to incorporate several important physico-chemical phenomena that are often present in industrial reactors.

Formulation

Any attempt to develop a mathematical model to describe the performance of an industrial semibatch epoxy reactor should first focus attention on the kinetics of the reaction, unencumbered by other influences. The detailed kinetic scheme[1,5] for epoxy polymerization incorporating most of the important reactions is shown in Table I. The different end groups, —A, —B, —E, and —F, are defined in this table. This scheme is more detailed than that used by Ravindranath and Gandhi[4] and takes care of the major weaknesses of their model. A study of the several reviews[5–7] in the open literature suggests that the scheme in Table I is fairly general, and so should be a good starting point for the study of epoxy reactors.

The various molecular species including the monomers present in the reaction mass at any time, are shown in Table II. AA_0 represents one of the monomers, bisphenol A, while EP represents the other monomer, epichlorohydrin. This description corresponds to the kinetic scheme of Table I. Table II also gives the molecular masses of all these species (for use in the computation of average molecular weights).

The kth moments ($k = 0, 1, 2, \ldots$) of the molecular species are defined in Table III. It is necessary to use $(n + 1)^k$ as the factor with the concentration, $[i_n]$, of any species of "length" n to avoid giving zero weightage to the smallest species. The number- and weight-average molecular weights, M_n and M_w , for this system have been obtained starting from the fundamental equations[2,3]

Table I Reaction Scheme for Epoxy Polymerization

1. $$\text{—OH} + \text{NaOH} \xrightarrow{k_1} \text{—ONa} + \text{H}_2\text{O}$$

$$\text{—A} + \text{NaOH} \xrightarrow{k_1} \text{—B} + \text{H}_2\text{O}$$

2. $$\text{—ONa} + \underset{\backslash\,/}{\text{CH}_2\text{CHCH}_2\text{Cl}}\text{O} \xrightarrow{k_2/\text{H}_2\text{O}} \text{—OCH}_2\underset{|}{\text{CH}}\text{CH}_2\text{ClH} + \text{NaOH}\quad (\text{OH})$$

$$\text{—B+EP} \xrightarrow{k_2/\text{H}_2\text{O}} \text{—F} + \text{NaOH}$$

3. $$\text{—OCH}_2\underset{|}{\text{CH}}\text{CH}_2\text{Cl} + \text{NaOH} \xrightarrow{k_3} \text{—OCH}_2\underset{\backslash\,/}{\text{CH}}\text{CH}_2 + \text{NaCl} + \text{H}_2\text{O}\quad (\text{OH},\ \text{O})$$

$$\text{—F} + \text{NaOH} \xrightarrow{k_3} \text{—E} + \text{NaCl} + \text{H}_2\text{O}$$

4. $$\text{—ONa} + \underset{\backslash\,/}{\text{CH}_2\text{CHCH}_2\text{O—}}\text{O} \xrightarrow{k_4/\text{H}_2\text{O}} \text{—OCH}_2\underset{|}{\text{CH}}\text{CH}_2\text{O—} + \text{NaOH}\quad (\text{OH})$$

$$\text{—B} + \text{E—} \xrightarrow{k_4/\text{H}_2\text{O}} \text{—(BE)—} + \text{NaOH}$$

5. $$\text{—ONa} + \text{ClCH}_2\underset{|}{\text{CH}}\text{CH}_2\text{O—}\ (\text{OH}) \xrightarrow{k_5} \text{—OCH}_2\underset{|}{\text{CH}}\text{CH}_2\text{O—} + \text{NaCl}\quad (\text{OH})$$

$$\text{—B} + \text{F—} \xrightarrow{k_5} \text{—(BF)—} + \text{NaCl}$$

End Groups Present in the Reaction Mass

—A	—OH
—B	—ONa
—E	$\text{—OCH}_2\underset{\backslash\,/}{\text{CH}}\text{CH}_2$ (O)
—F	$\text{—OCH}_2\text{CHOHCH}_2\text{Cl}$

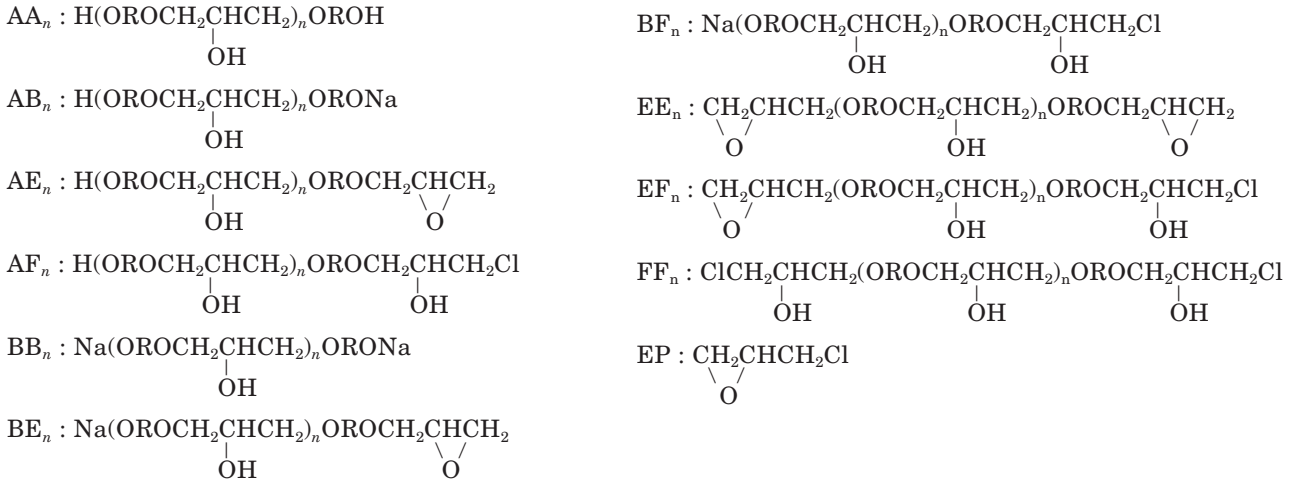
$$M_n = \sum_{\text{all species}} (\text{number fraction of } i\text{th species}) \times (\text{molecular weight of } i\text{th species}) \quad (1)$$

$$M_w = \sum_{\text{all species}} (\text{mass fraction of } i\text{th species}) \times (\text{molecular weight of } i\text{th species}) \quad (2)$$

The final expressions for M_n and M_w are also given in Table III. Two sets of average molecular weights have been described. In one, the contribution of the epichlorohydrin is incorporated, while in the other, this species is excluded from the computation. The latter is more appropriate and useful because experimental measurement of average molecular weights is usually performed after distilling out most of the epichlorohydrin from the reaction mass (there is negligible bisphenol A after some reaction has occurred).

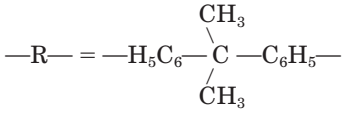
The mol balance equations for a well-mixed batch reactor for the various species shown in Table II can easily be written, and are given in Table IV. In these equations, extreme caution has been taken to account for all the possible formation and consumption terms of the individual molecular species. The detailed reactions between the several molecular species required to develop the equations in Table IV are given in the Appendix (Table A1). The mass balance equations in Table IV can be summed up analytically (using

Table II Different Molecular (Polymeric/Monomeric) Species Present in the Reaction Mass and Their Molecular Weights



$n = 0, 1, 2 \ldots$ for all cases

where,



Molecular Weights of Different Species

$$M_{AAn} = (n + 1)(M_{AA0} + M_{EP} - M_{HCl}) - M_{EP} + M_{HCl}$$
$$M_{ABn} = n(M_{AA0} + M_{EP} - M_{HCl}) + M_{AB0}$$
$$M_{AEn} = (n + 1)(M_{AA0} + M_{EP} - M_{HCl})$$
$$M_{AFn} = (n + 1)(M_{AA0} + M_{EP} - M_{HCl}) + M_{HCl}$$
$$M_{BBn} = n(M_{AA0} + M_{EP} - M_{HCl}) + M_{BB0}$$
$$M_{BEn} = (n + 1)(M_{AA0} + M_{EP} - M_{HCl}) + M_{AB0} - M_{AA0}$$
$$M_{BFn} = n(M_{AA0} + M_{EP} - M_{HCl}) + M_{AB0} + M_{EP}$$
$$M_{EEn} = (n + 1)(M_{AA0} + M_{EP} - M_{HCl}) + M_{EP} - M_{HCl}$$
$$M_{EFn} = (n + 1)(M_{AA0} + M_{EP} - M_{HCl}) + M_{EP}$$
$$M_{FFn} = (n + 1)(M_{AA0} + M_{EP} - M_{HCl}) + M_{EP} - M_{HCl}$$

$n = 0, 1, 2, \ldots$ for all cases

where,

M_{AA0} = molecular weight of bisphenol A; M_{EP} = molecular weight of epichlorohydrin; M_{HCl} = molecular weight of hydrochloric acid.

the definitions in Table III) to give the ordinary differential equations (ODEs) for the several moments (k = 0, 1, and 2). These are given in Table V. The concentrations of the four end groups can be written in terms of the concentrations of the individual molecular species. These are given in Table VI. Mole balance equations for the various end groups and for some of the lower molecular weight oligomers (for which experimental data[1] are available) can be written using the simplified kinetic scheme (in terms of end groups) of Table I. These are given in Table VII. The following checks were made to confirm the correctness of the balance equations: (a) it was found that the equations obtained by appropriately summing up the equations in Table IV (using Table VI), were identical to the balance equations for the end groups (given in Table VII and derived independently using the simplified kinetic scheme of Table I). The same check was made using the equa-

Table III *k*th Moments of Various Molecular Species

$$\lambda_{AA}^k = \sum_{n=0}^{\infty} (n+1)^k [AA_n] \qquad \lambda_{BE}^k = \sum_{n=0}^{\infty} (n+1)^k [BE_n]$$

$$\lambda_{AB}^k = \sum_{n=0}^{\infty} (n+1)^k [AB_n] \qquad \lambda_{BF}^k = \sum_{n=0}^{\infty} (n+1)^k [BF_n]$$

$$\lambda_{AE}^k = \sum_{n=0}^{\infty} (n+1)^k [AE_n] \qquad \lambda_{EE}^k = \sum_{n=0}^{\infty} (n+1)^k [EE_n]$$

$$\lambda_{AF}^k = \sum_{n=0}^{\infty} (n+1)^k [AF_n] \qquad \lambda_{EF}^k = \sum_{n=0}^{\infty} (n+1)^k [EF_n]$$

$$\lambda_{BB}^k = \sum_{n=0}^{\infty} (n+1)^k [BB_n] \qquad \lambda_{FF}^k = \sum_{n=0}^{\infty} (n+1)^k [FF_n]$$

where,

$$k = 0,\ 1,\ 2,\ \ldots$$

Average Molecular Weights

$$M_n = \frac{\begin{aligned}&[\{M_{AA0} + M_{EP} - M_{HCl}\}\{\lambda_{AA}^1 + \lambda_{AB}^1 + \lambda_{AE}^1 + \lambda_{AF}^1 + \lambda_{BB}^1 + \lambda_{BE}^1 + \lambda_{BF}^1 + \lambda_{EE}^1 + \lambda_{EF}^1 \\ &\quad + \lambda_{FF}^1 - \lambda_{AB}^0 - \lambda_{BB}^0 - \lambda_{BF}^0\} + M_{EP}\{\lambda_{EE}^0 + \lambda_{FF}^0 + \lambda_{EF}^0 + \lambda_{BF}^0 - \lambda_{AA}^0 + [EP]\delta_{m0}\} \\ &\quad + M_{HCl}\{\lambda_{FF}^0 + \lambda_{AA}^0 + \lambda_{AF}^0 - \lambda_{EE}^0\} + M_{AB0}\{\lambda_{AB}^0 + \lambda_{BE}^0 + \lambda_{BF}^0\} - M_{AA0}\lambda_{BE}^0 + M_{BB0}\lambda_{BB}^0]\end{aligned}}{\{\lambda_{AA}^0 + \lambda_{AB}^0 + \lambda_{AE}^0 + \lambda_{AF}^0 + \lambda_{BB}^0 + \lambda_{BE}^0 + \lambda_{BF}^0 + \lambda_{EE}^0 + \lambda_{EF}^0 + \lambda_{FF}^0 + [EP]\delta_{m0}}$$

$$M_w = \frac{\begin{aligned}&[\{M_{AA0} + M_{EP} - M_{HCl}\}^2\{\lambda_{AA}^2 + \lambda_{AB}^2 + \lambda_{AE}^2 + \lambda_{AF}^2 + \lambda_{BB}^2 + \lambda_{BE}^2 + \lambda_{BF}^2 + \lambda_{EE}^2 + \lambda_{EF}^2 + \lambda_{FF}^2\} \\ &\quad + 2\{M_{AA0} + M_{EP} - M_{HCl}\}\{(M_{HCl} - M_{EP})\lambda_{AA}^1 + (M_{AB0} + M_{HCl} - M_{AA0} - M_{EP})\lambda_{AB}^1 \\ &\quad + M_{HCl}\lambda_{AF}^1 + (M_{BB0} + M_{HCl} - M_{AA0} - M_{EP})\lambda_{BB}^1 + (M_{AB0} - M_{AA0})\lambda_{BE}^1 \\ &\quad + (M_{EP} + M_{HCl} + M_{AB0} - M_{AA0} - M_{EP})\lambda_{BF}^1 + (M_{EP} - M_{HCl})\lambda_{EE}^1 + M_{EP}\lambda_{EF}^1 \\ &\quad + (M_{EP} + M_{HCl})\lambda_{FF}^1\} + (M_{EP} - M_{HCl})^2(\lambda_{AA}^0 + \lambda_{EE}^0) \\ &\quad + (M_{AB0} + M_{HCl} - M_{AA0} - M_{EP})^2\lambda_{AB}^0 + M_{HCl}^2\lambda_{AF}^0 \\ &\quad + (M_{BB0} + M_{HCl} - M_{AA0} - M_{EP})^2\lambda_{BB}^0 + (M_{AB0} - M_{AA0})^2 \\ &\quad \times \lambda_{BE}^0 + (M_{EP} + M_{HCl} + M_{AB0} - M_{AA0} - M_{EP})\lambda_{BF}^0 \\ &\quad + M_{EP}^2\lambda_{EF}^0 + (M_{EP} + M_{HCl})^2\lambda_{FF}^0 + [EP]M_{EP}^2\delta_{m0}\end{aligned}}{\begin{aligned}&[\{M_{AA0} + M_{EP} - M_{HCl}\}\{\lambda_{AA}^1 + \lambda_{AB}^1 + \lambda_{AE}^1 + \lambda_{AF}^1 + \lambda_{BB}^1 + \lambda_{BE}^1 + \lambda_{BF}^1 + \lambda_{EE}^1 \\ &\quad + \lambda_{EF}^1 + \lambda_{FF}^1 - \lambda_{AB}^0 - \lambda_{BB}^0 - \lambda_{BF}^0\} + M_{EP}\{\lambda_{EE}^0 + \lambda_{FF}^0 + \lambda_{EF}^0 + \lambda_{BF}^0 - \lambda_{AA}^0 \\ &\quad + [EP]\delta_{m0} + M_{HCl}\{\lambda_{FF}^0 + \lambda_{AA}^0 + \lambda_{AF}^0 - \lambda_{EE}^0\} + M_{AB0}\{\lambda_{AB}^0 + \lambda_{BE}^0\lambda_{BF}^0\} \\ &\quad - M_{AA0}\lambda_{BE}^0 + M_{BB0}\lambda_{BB}^0]\end{aligned}}$$

$$PDI = \frac{M_w}{M_n}$$

where, $\delta_{m0} = 0$ for molecular weight determination without epichlorohydrin;
$\delta_{m0} = 1$ for molecular weight determination with epichlorohydrin

tions for the zeroth moments (Table V) and the equations matched with those in Table VII. This confirmed the correctness of the equations for the zeroth moment, as well as partially confirmed the correctness of the mol balance equations in Table IV. (b) In a batch reactor, the total mol of the aryl unit, R, is conserved, i.e., the mol of R at any time (distributed over the several molecular species given in Table II) must be equal to the mol of R initially (in bisphenol A). This has been checked out, and confirms that the equations are correct. (c) In a batch reactor, the sum of mol of the groups,

Table IV Mass Balance Equations for the Molecular Species

$$\frac{d[\mathrm{AA}_m]}{dt} = -2k_1[\mathrm{AA}_m][\mathrm{NaOH}] + k_4\{\sum_{i=0}^{m-1}[\mathrm{AB}_i][\mathrm{AE}_{m-1-i}]\}\delta_{m0} + k_5\{\sum_{i=0}^{m-1}[\mathrm{AB}_i][\mathrm{AF}_{m-1-i}]\}\delta_{m0}$$

$$\frac{d[\mathrm{AB}_m]}{dt} = k_1[\mathrm{NaOH}]\{2[\mathrm{AA}_m] - [\mathrm{AB}_m] - k_2[\mathrm{AB}_m][\mathrm{EP}] - k_4[\mathrm{AB}_m]\{\sum_{n=0}^{\infty}\{[\mathrm{AE}_n] + [\mathrm{BE}_n] + 2[\mathrm{EE}_n] + [\mathrm{EF}_n]\}$$
$$- k_5[\mathrm{AB}_m]\{\sum_{n=0}^{\infty}\{[\mathrm{AF}_n] + [\mathrm{BF}_n] + [\mathrm{EF}_n] + 2[\mathrm{FF}_n]\} + \{2k_4\sum_{i=0}^{m-1}[\mathrm{BB}_i][\mathrm{AE}_{m-i-1}]$$
$$+ k_4\sum_{i=0}^{m-1}[\mathrm{AB}_i][\mathrm{BE}_{m-i-1}] + 2k_5\sum_{i=0}^{m-1}[\mathrm{AB}_i][\mathrm{BF}_{m-i-1}] + 2k_5\sum_{i=0}^{m-1}[\mathrm{BB}_i][\mathrm{AF}_{m-i-1}]\delta_{m0}$$

$$\frac{d[\mathrm{AE}_m]}{dt} = -k_1[\mathrm{AE}_m][\mathrm{NaOH}] + k_3[\mathrm{AF}_m][\mathrm{NaOH}] - k_4[\mathrm{AE}_m]\{\sum_{n=0}^{\infty}\{[\mathrm{AB}_n] + [\mathrm{BE}_n] + 2[\mathrm{BB}_n] + [\mathrm{BF}_n]\}$$
$$+ \{k_4\sum_{i=0}^{m-1}[\mathrm{BE}_i][\mathrm{AE}_{m-i-1}] + 2k_4\sum_{i=0}^{m-1}[\mathrm{AB}_i][\mathrm{EE}_{m-i-1}]$$
$$+ k_5\sum_{i=0}^{m-1}[\mathrm{BE}_i][\mathrm{AF}_{m-i-1}] + k_5\sum_{i=0}^{m-1}[\mathrm{AB}_i][\mathrm{EF}_{m-i-1}]\delta_{m0}$$

$$\frac{d[\mathrm{AF}_m]}{dt} = -k_1[\mathrm{AF}_m][\mathrm{NaOH}] + k_2[\mathrm{AB}_m][\mathrm{EP}] + k_3[\mathrm{AF}_m][\mathrm{NaOH}] - k_5[\mathrm{AF}_m]\{\sum_{n=0}^{\infty}\{[\mathrm{AB}_n] + [\mathrm{BE}_n] + 2[\mathrm{BB}_n] + [\mathrm{BF}_n]\}$$
$$+ \{k_4\sum_{i=0}^{m-1}[\mathrm{BF}_i][\mathrm{AE}_{m-i-1}] + k_4\sum_{i=0}^{m-1}[\mathrm{AB}_i][\mathrm{EE}_{m-i-1}] + k_5\sum_{i=0}^{m-1}[\mathrm{BF}_i][\mathrm{AF}_{m-i-1}] + 2k_5\sum_{i=0}^{m-1}[\mathrm{AB_i}][\mathrm{FF}_{m-i-1}]\}\delta_{m0}$$

$$\frac{d[\mathrm{BB}_m]}{dt} = k_1[\mathrm{AB}_m][\mathrm{NaOH}] - 2k_2[\mathrm{BB}_m][\mathrm{EP}] - 2k_4[\mathrm{BB}_m]\{\sum_{n=0}^{\infty}\{[\mathrm{AE}_n] + [\mathrm{BE}_n] + 2[\mathrm{EE}_n] + [\mathrm{EF}_n]\}$$
$$- 2k_5[\mathrm{BB}_m]\{\sum_{n=0}^{\infty}\{[\mathrm{AF}_n] + [\mathrm{BF}_n] + 2[\mathrm{FF}_n] + [\mathrm{EF}_n]\} + \{2k_4\sum_{i=0}^{m-1}[\mathrm{BB}_i][\mathrm{BE}_{m-i-1}] + 2k_5\sum_{i=0}^{m-1}[\mathrm{BB}_i][\mathrm{BE}_{m-i-1}]\}\delta_{m0}$$

$$\frac{d[\mathrm{BE}_m]}{dt} = k_1[\mathrm{AE}_m][\mathrm{NaOH}] - k_2[\mathrm{BE}_m][\mathrm{EP}] + k_3[\mathrm{BF}_m][\mathrm{NaOH}]$$
$$- k_4[\mathrm{BE}_m]\{\sum_{n=0}^{\infty}\{[\mathrm{AE}_n] + [\mathrm{AB}_n] + 2[\mathrm{BB}_n] + 2[\mathrm{BE}_n] + [\mathrm{BF_n}] + 2[\mathrm{EE}_n] + [\mathrm{EF}_n]\}$$
$$- k_5[\mathrm{BE}_m]\{\sum_{n=0}^{\infty}\{[\mathrm{AF}_n] + [\mathrm{BF}_n] + [\mathrm{EF}_n] + 2[\mathrm{FF}_n]\} + \{k_4\sum_{i=0}^{m-1}[\mathrm{BE}_i][\mathrm{BE}_{m-i-1}]$$
$$+ 4k_4\sum_{i=0}^{m-1}[\mathrm{BB}_i][\mathrm{EE}_{m-i-1}] + k_5\sum_{i=0}^{m-1}[\mathrm{BE}_i][\mathrm{BF}_{m-i-1}] + 2k_5\sum_{i=0}^{m-1}[\mathrm{BB}_i][\mathrm{EF}_{m-i-1}]\delta_{m0}$$

Table IV *Continued*

$$\frac{d[\mathrm{BF}_m]}{dt} = k_1[\mathrm{AF}_m][\mathrm{NaOH}] + 22k_2[\mathrm{BB}_m][\mathrm{EP}] - k_2[\mathrm{BF}_m][\mathrm{EP}] - k_3[\mathrm{BF}_m][\mathrm{NaOH}]$$

$$- k_4[\mathrm{BF}_m]\{\sum_{n=0}^{\infty}[\mathrm{AE}_n] + [\mathrm{BE}_n] + 2[\mathrm{EE}_n] + [\mathrm{EF}_n]\}$$

$$- k_5[\mathrm{BF}_m]\{\sum_{n=0}^{\infty}\{[\mathrm{AF}_n] + [\mathrm{AB}_n] + [\mathrm{BE}_n] + 2[\mathrm{BB}_n] + 2[\mathrm{BF}_n] + [\mathrm{EF}_n] + 2[\mathrm{FF}_n]\}$$

$$+ \{k_4\sum_{i=0}^{m-1}[\mathrm{BF}_i][\mathrm{BE}_{m-i-1}] + 2k_4\sum_{i=0}^{m-1}[\mathrm{BB}_i][\mathrm{EF}_{m-i-1}]$$

$$+ k_5\sum_{i=0}^{m-1}[\mathrm{BF}_i][\mathrm{BF}_{m-i-1}] + 4\mathrm{k}_5\sum_{i=0}^{m-1}[\mathrm{BB}_i][\mathrm{FF}_{m-i-1}]\delta_{m0}$$

$$\frac{d[\mathrm{EE}_m]}{dt} = k_3[\mathrm{EF}_m][\mathrm{NaOH}] - 2k_4[\mathrm{EE}_m]\{\sum_{n=0}^{\infty}\{[\mathrm{AB}_n] + [\mathrm{BE}_n] + 2[\mathrm{BB}_n] + [\mathrm{BF}_n]\}$$

$$+ \{2k_4\sum_{i=0}^{m-1}[\mathrm{BE}_i][\mathrm{EE}_{m-i-1}] + k_5\sum_{i=0}^{m-1}[\mathrm{BE}_i][\mathrm{EF}_{m-i-1}]\}_{m0}$$

$$\frac{d[\mathrm{EF}_m]}{dt} = -k_3[\mathrm{EF}_m][\mathrm{NaOH}] + k_2[\mathrm{BE}_m][\mathrm{EP}] + 2k_3[\mathrm{FF}_m][\mathrm{NaOH}] - k_4[\mathrm{EF}_m]\{\sum_{n=0}^{\infty}\{[\mathrm{AB}_n] + 2[\mathrm{BB}_n] + [\mathrm{BE}_n] + [\mathrm{BF}_n]\}$$

$$- k_5[\mathrm{EF}_m]\{\sum_{n=0}^{\infty}\{[\mathrm{AB}_n] + 2[\mathrm{BB}_n] + [\mathrm{BE}_n] + [\mathrm{BF}_n]\} + \{2k_4\sum_{i=0}^{m-1}[\mathrm{BF}_i][\mathrm{EE}_{m-i-1}] + k_4\sum_{i=0}^{m-1}[\mathrm{BE}_i][\mathrm{EF}_{m-i-1}]$$

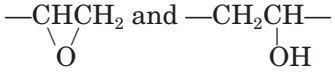
$$+ k_5\sum_{i=0}^{m-1}[\mathrm{BF}_i][\mathrm{EF}_{m-i-1}] + 2k_5\sum_{i=0}^{m-1}[\mathrm{BE}_i][\mathrm{FF}_{m-i-1}]\delta_{m0}$$

$$\frac{d[\mathrm{FF}_m]}{dt} = -2k_3[\mathrm{FF}_m][\mathrm{NaOH}] + k_2[\mathrm{EP}][\mathrm{BF}_m] - 2k_5[\mathrm{FF}_m]\{\sum_{n=0}^{\infty}\{[\mathrm{AB}_n] + 2[\mathrm{BB}_n] + 2[\mathrm{BE}_n] + [\mathrm{BF}_n]\}$$

$$+ \{k_4\sum_{i=0}^{m-1}[\mathrm{BF}_i][\mathrm{EF}_{m-i-1}] + 2k_5\sum_{i=0}^{m-1}[\mathrm{BF}_i][\mathrm{FF}_{m-i-1}]\}\delta_{m0}$$

$$\delta_{m0} = 0, \quad \text{for} \quad m = 0$$

$$\delta_{m0} = 1, \quad \text{for} \quad m > 0$$



should be constant with time and should be equal to the initial mol of epichlorohydrin present. An equation for the total number of the above repeat units (distributed over the several molecular species in Table II) was written (in terms of the moments). It was found that this check was also satisfied.

The above three checks were sufficient to confirm the correctness of the mol and moment balance equations in Tables IV and V.

The equations in Table V (along with those for [NaOH] and [EP] from Table VII) form a complete set of ODEs (initial value problem—IVP), which

Table V Moment Equations in a Batch Reactor

$$\frac{d\lambda^0_{AA}}{dt} = -2k_1[\text{NaOH}]\lambda^0_{AA} + k_4\lambda^0_{AB}\lambda^0_{AE} + k_5\lambda^0_{AB}\lambda^0_{AF}$$

$$\frac{d\lambda^0_{AB}}{dt} = -k_1[\text{NaOH}]\lambda^0_{AB} + 2k_1\lambda^0_{AA}[\text{NaOH}] - k_2\lambda^0_{AB}[\text{EP}] - k_4\lambda^0_{AB}\{\lambda^0_{AE} + 2\lambda^0_{EE} + \lambda^0_{EF}\}$$
$$- k_5\lambda^0_{AB}\{\lambda^0_{AF} + \lambda^0_{EF} + 2\lambda^0_{FF}\} + 2k_4\lambda^0_{BB}\lambda^0_{AE} + 2k_5\lambda^0_{BB}\lambda^0_{AF}$$

$$\frac{d\lambda^0_{AE}}{dt} = -k_1[\text{NaOH}]\lambda 0^0_{AE} + k_3\lambda^0_{AF}[\text{NaOH}] - k_4\lambda^0_{AE}\{\lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BF}\} + 2k_4\lambda^0_{AB}\lambda^0_{EE} + k_5\lambda^0_{BE}\lambda^0_{AF} + k_5\lambda^0_{AB}\lambda^0_{EF}$$

$$\frac{d\lambda^0_{AF}}{dt} = -k_1[\text{NaOH}]\lambda^0_{AF} + k_2\lambda^0_{AB}[\text{EP}] - k_3\lambda^0_{AF}[\text{NaOH}] - k_5\lambda^0_{AF}\{\lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BE}\} + k_4\lambda^0_{BF}\lambda^0_{AE} + k_4\lambda^0_{AB}\lambda^0_{EF} + 2k_5\lambda^0_{AB}\lambda^0_{FF}$$

$$\frac{d\lambda^0_{BB}}{dt} = k_1[\text{NaOH}]\lambda^0_{AB} - 2k_2\lambda^0_{BB}[\text{EP}] - 2k_4\lambda^0_{BB}\{\lambda^0_{AE} + 2\lambda^0_{EE} + \lambda^0_{EF}\} - 2k_5\lambda^0_{BB}\{\lambda^0_{AF} + \lambda^0_{EF} + 2\lambda^0_{FF}\}$$

$$\frac{d\lambda^0_{BE}}{dt} = k_1[\text{NaOH}][\lambda^0_{AE} - k_2\lambda^0_{BE}[\text{EP}] + k_3\lambda^0_{BF}[\text{NaOH}] - \text{k}_4\lambda^0_{BE}\{\lambda^0_{AE} + 2\lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BE} + \lambda\ ^0_{BF} + 2\lambda^0_{EE} + \lambda^0_{EF}\}$$
$$- k_5\lambda^0_{BE}\{\lambda^0_{AF} + \lambda^0_{EF} + 2\lambda^0_{FF}\} + 4k_4\lambda^0_{BB}\lambda^0_{EE} + 2k_5\lambda^0_{BB}\lambda^0_{EF}$$

$$\frac{d\lambda^0_{BF}}{dt} = k_1[\text{NaOH}]\lambda^0_{AF} + 2k_2\lambda^0_{BB}[\text{EP}] - k_2\lambda^0_{BF}[\text{EP}] - k_3\lambda^0_{BF}[\text{NaOH}] - k_4\lambda^0_{BF}\{\lambda^0_{AE} + 2\lambda^0_{EE} + \lambda^0_{EF}\}$$
$$- k_5\lambda^0_{BF}\{\lambda^0_{AF} + \lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BE} + \lambda^0_{BF} + \lambda^0_{EF} + 2\lambda^0_{FF}\} + 2k_4\lambda^0_{BB}\lambda^0_{EF} + 4k_5\lambda^0_{BB}\lambda^0_{FF}$$

$$\frac{d\lambda^0_{EE}}{dt} = k_3[\text{NaOH}]\lambda^0_{EF} - 2k_4\lambda^0_{EE}\{\lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BF}\} + k_5\lambda^0_{BE}\lambda^0_{EF}$$

$$\frac{d\lambda^0_{EF}}{dt} = k_2[\text{EP}]\lambda^0_{BE} - k_3\lambda^0_{EF}[\text{NaOH}] + 2k_3\lambda^0_{FF}[\text{NaOH}]$$
$$- k_4\lambda_{sx}\text{EF0}\{\lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BF}\} - k_5\lambda_{EF}{}^0\{\lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BE}\} + 2k_4\lambda^0_{BF}\lambda^0_{EE} + 2k_5\lambda^0_{BE}\lambda^0_{FF}$$

$$\frac{d\lambda^0_{FF}}{dt} = k_2[\text{EP}]\lambda^0_{BF} - 2k_3\lambda^0_{FF}[\text{NaOH}] - 2k_5\lambda^0_{FF}\{\lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BE}\} + k_4\lambda^0_{BF}\lambda^0_{EF}$$

$$\frac{d\lambda^1_{AA}}{dt} = -2k_1[\text{NaOH}][\lambda^1_{AA} + k_4\{\lambda^1_{AB}{}^0_{AE} + \lambda^0_{AB}\lambda^1_{AE}\} + k_5\{\lambda^1_{AB}\lambda^0_{AF} + \lambda^0_{AB}\lambda^1_{AF}\}$$

$$\frac{d\lambda^1_{AB}}{dt} = -k_1[\text{NaOH}]\lambda^1_{AB} + 2k_1\lambda^1_{AA}[\text{NaOH}] - k_2\lambda^1_{AB}[\text{EP}] - k_4\lambda^1_{AB}\{\lambda^0_{AE} + 2\lambda^0_{EE} + \lambda^0_{EF}\}$$
$$- k_5\lambda^1_{AB}\{\lambda^0_{AF} + \lambda^0_{EF} + 2\lambda^0_{FF}\} + 2k_4\{\lambda^1_{BB}\lambda^0_{AE} + \lambda^0_{BB}\lambda^1_{AE}\} + 2k_5\{\lambda^1_{BB}\lambda^0_{AF} + \lambda^0_{BB}\lambda^1_{AF}\} + k_4\lambda^0_{AB}\lambda^1_{BE} + k_5\lambda^0_{AB}\lambda^1_{BF}$$

$$\frac{d\lambda^1_{AE}}{dt} = -k_1[\text{NaOH}]\lambda^1_{AE} + k_3\lambda^1_{AF}[\text{NaOH}] - k_4\lambda^1_{AE}\{\lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BF}\}$$
$$+ k_4\lambda^1_{BE}\lambda^0_{AE} + 2k_4\{\lambda^1_{AB}\lambda^0_{EE} + \lambda^0_{AB}\lambda^1_{EE}\} + k_5\{\lambda^1_{BE}\lambda^0_{AF} + \lambda^0_{BE}\lambda^1_{AF}\} + k_5\{\lambda^1_{AB}\lambda^0_{EF} + \lambda^0_{AB}\lambda^1_{EF}\}$$

Table V *Continued*

$$\frac{d\lambda^1_{AF}}{dt} = -k_1[\mathrm{NaOH}][\lambda^1_{AF} + k_2\lambda^1_{AB}[\mathrm{EP}] - k_3\lambda^1_{AF}[\mathrm{NaOH}] - k_5\lambda^1_{AF}\{\lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BE}\}$$
$$+ k_4\{\lambda^1_{BF}\lambda^0_{AE} + \lambda^0_{BF}\lambda^1_{AE}\} + k_4\{\lambda^1_{AB}\lambda^0_{EF} + \lambda^0_{AB}\lambda^1_{EF}\} + k_5\lambda^1_{BF}\lambda^0_{AF} + 2k_5\{\lambda^1_{AB}\lambda^0_{FF} + \lambda^0_{AB}\lambda^1_{FF}\}$$

$$\frac{d\lambda^1_{BB}}{dt} = k_1[\mathrm{NaOH}]\lambda^1_{AB} - 2k_2\lambda^1_{BB}[\mathrm{EP}] - 2k_4\lambda^1_{BB}\{\lambda^0_{AE} + 2\lambda^0_{EE} + \lambda^0_{EF}\} - 2k_5\lambda^1_{BB}\{\lambda^0_{AF} + \lambda^0_{EF} + 2\lambda^0_{FF}\} + 2k_4\lambda^0_{BB}\lambda^1_{BE} + 2k_5\lambda^0_{BB}\lambda^1_{BF}$$

$$\frac{d\lambda^1_{BE}}{dt} = k_1[\mathrm{NaOH}]\lambda^1_{AE} - k_2\lambda^1_{BE}[\mathrm{EP}] + k_3\lambda^1_{BF}[\mathrm{NaOH}] - k_4\lambda^1_{BE}\{\lambda^0_{AE} + \lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BE} + \lambda^0_{BF} + 2\lambda^0_{EE} + \lambda^0_{EF}\}$$
$$- k_5\lambda^1_{BE}\{\lambda^0_{AF} + \lambda^0_{EF} + 2\lambda^0_{FF}\} + k_4\lambda^0_{BE}\lambda^1_{BE} + 4k_4\{\lambda^1_{BB}\lambda^0_{EE} + \lambda^0_{BB}\lambda^1_{EE}\} + k_5\lambda^0_{BE}\lambda^1_{BF} + 2k_5\{\lambda^1_{BB}\lambda^0_{EF} + \lambda^0_{BB}\lambda^1_{EF}\}$$

$$\frac{d\lambda^1_{BF}}{dt} = k_1[\mathrm{NaOH}]\lambda^1_{AF} + 2k_2\lambda^1_{BB}[\mathrm{EP}] - k_2\lambda^1_{BF}[\mathrm{EP}] - k_3\lambda^1_{BF}[\mathrm{NaOH}]$$
$$- k_4\lambda^1_{BF}\{\lambda^0_{AE} + 2\lambda^0_{EE} + \lambda^0_{EF}\} - k_5\lambda^1_{BF}\{\lambda^0_{AF} + \lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BE} + \lambda^0_{BF} + \lambda^0_{EF} + 2\lambda^0_{FF}\} + k_4\lambda^0_{BF}\lambda^1_{BE}$$
$$+ 2k_4\{\lambda^1_{BB}\lambda^0_{EF} + \lambda^0_{BB}\lambda^1_{EF}\} + k_5\lambda^0_{BF}\lambda^1_{BF} + 4k_5\{\lambda^1_{BB}\lambda^0_{FF} + \lambda^0_{BB}\lambda^1_{FF}\}$$

$$\frac{d\lambda^1_{EE}}{dt} = k_3[\mathrm{NaOH}]\lambda^1_{EF} - 2k_4\lambda^1_{EE}\{\lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BF}\} + 2k_4\lambda^1_{BE}\lambda^0_{EE} + k_5\{\lambda^1_{BE}\lambda^0_{EF} + \lambda^0_{BE}\lambda^1_{EF}\}$$

$$\frac{d\lambda^1_{EF}}{dt} = k_2[\mathrm{EP}]\lambda^1_{BE} - k_3\lambda^1_{EF}[\mathrm{NaOH}] + 2k_3\lambda^1_{FF}[\mathrm{NaOH}] - k_4\lambda^1_{EF}\{\lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BF}\}$$
$$- k_5\lambda^1_{EF}\{\lambda^0_{AB} + 2\lambda^0_{BB} + 2\lambda^0_{BE}\}\ *22)\ 2k_4\{\lambda^1_{BF}\lambda^0_{EE} + \lambda^0_{BF}\lambda^1_{EE}\} + k_4\lambda^1_{BE}\lambda^0_{EF} + k_5\lambda^1_{BF}\lambda^0_{EF} + 2k_5\{\lambda^1_{BE}\lambda^0_{FF} + \lambda^0_{BE}\lambda^1_{FF}\}$$

$$\frac{d\lambda^1_{FF}}{dt} = k_2[\mathrm{EP}]\lambda^1_{BF} - 2k_3\lambda^1_{FF}[\mathrm{NaOH}] - 2k_5\lambda^1_{FF}\{\lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BE}\} + k_4\{\lambda^1_{BF}\lambda^0_{EF} + \lambda^0_{BF}\lambda^1_{EF}\} + 2k_5\lambda^1_{BF}\lambda^0_{FF}$$

$$\frac{d\lambda^2_{AA}}{dt} = -2k_1[\mathrm{NaOH}]\lambda^2_{AA} + k_4\{\lambda^2_{AB}\lambda^0_{AE} + \lambda^0_{AB}\lambda^2_{AE} + 2\lambda^1_{AB}\lambda^1_{AE}\} + k_5\{\lambda^2_{AB}\lambda^0_{AF} + \lambda^0_{AB}\lambda^2_{AF} + 2\lambda^1_{AB}\lambda^1_{AF}\}$$

$$\frac{d\lambda^2_{AB}}{dt} = -k_1[\mathrm{NaOH}]\lambda^2_{AB} + 2k_1\lambda^1_{AA}[\mathrm{NaOH}] - k_2\lambda^2_{AB}[\mathrm{EP}] - k_4\lambda^2_{AB}\{\lambda^0_{AE} + 2\lambda^0_{EE} + \lambda^0_{EF}\} - k_5\lambda^2_{AB}\{\lambda^0_{AF} + \lambda^0_{EF} + 2\lambda^0_{FF}\}$$
$$+ 2k_4\{\lambda^2_{BB}\lambda^0_{AE} + \lambda^0_{BB}\lambda^2_{AE} + 2\lambda^1_{BB}\lambda^1_{AE}\} + 2k_5\{\lambda^2_{BB}\lambda^0_{AF} + \lambda^0_{BB}\lambda^2_{AF} + 2\lambda^1_{BB}\lambda^1_{AF}\}$$
$$+ k_4\{\lambda^0_{AB}\lambda^2_{BE} + 2\lambda^1_{AB}\lambda^1_{BE}\} + k_5\{\lambda^0_{AB}\lambda^2_{BF} + 2\lambda^1_{AB}\lambda^1_{BF}\}$$

$$\frac{d\lambda^2_{AE}}{dt} = -k_1\lambda^2_{AE}[\mathrm{NaOH}] + k_3\lambda^2_{AF}[\mathrm{NaOH}] - k_4\lambda^2_{AE}\{\lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BF}\} + k_4\{\lambda^2_{BE}\lambda^0_{AE} + 2\lambda^1_{BE}\lambda^1_{AE}\}$$
$$+ 2k_4\{\lambda^2_{AB}\lambda^0_{EE} + \lambda^0_{AB}\lambda^2_{EE} + 2\lambda^1_{AB}\lambda^1_{EE}\} + k_5\{\lambda^2_{BE}\lambda^0_{AF} + \lambda^0_{BE}\lambda^2_{AF} + 2\lambda^1_{BE}\lambda^1_{AF}\} + k_5\{\lambda^2_{AB}\lambda^0_{EF} + \lambda^0_{AB}\lambda^2_{EF} + 2\lambda^1_{AB}\lambda^1_{EF}\}$$

$$\frac{d\lambda^2_{AF}}{dt} = -k_1[\mathrm{NaOH}]\lambda^2_{AF} + k_2\lambda^2_{AB}[\mathrm{EP}] - k_3\lambda^2_{AF}[\mathrm{NaOH}] - k_5\lambda^2_{AF}\{\lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BE}\} + k_4\{\lambda^2_{BF}\lambda^0_{AE} + \lambda^0_{BF}\lambda^2_{AE} + 2\lambda^1_{BF}\lambda^1_{AE}\}$$
$$+ k_4\{\lambda^2_{AB}\lambda^0_{EF} + \lambda^0_{AB}\lambda^2_{EF} + 2\lambda^1_{AB}\lambda^1_{EF}\} + k_5\{\lambda^2_{BF}\lambda^0_{AF} + 2\lambda^1_{BF}\lambda^1_{AF}\} + 2k_5\{\lambda^2_{AB}\lambda^0_{FF} + \lambda^0_{AB}\lambda^2_{FF} + 2\lambda^1_{AB}\lambda^1_{FF}\}$$

$$\frac{d\lambda^2_{BB}}{dt} = k_1[\mathrm{NaOH}]\lambda^2_{AB} - 2k_2\lambda^2_{BB}[\mathrm{EP}] - 2k_4\lambda^2_{BB}\{\lambda^0_{AE} + 2\lambda^0_{EE} + \lambda^0_{EF}\}$$
$$-2k_5\lambda^2_{BB}\{\lambda^0_{AF} + \lambda^0_{EF} + 2\lambda^0_{FF}\} + 2k_4\{\lambda^0_{BB}\lambda^2_{BE} + 2\lambda^1_{BB}\lambda^1_{BE}\} + 2k_5\{\lambda^0_{BB}\lambda^2_{BF} + 2\lambda^1_{BB}\lambda^1_{BF}\}$$

Table V *Continued*

$$\frac{d\lambda^2_{BE}}{dt} = k_1[\text{NaOH}]\lambda^2_{AE} - k_2\lambda^2_{BE}[\text{EP}] + k_3\lambda^2_{BF}[\text{NaOH}] - k_4\lambda^2_{BE}\{\lambda^0_{AE} + \lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BE} + 2\lambda^0_{EE} + \lambda^0_{EF}\}$$
$$- k_5\lambda^2_{BE}\{\lambda^0_{AF} + \lambda^0_{EF} + 2\lambda^0_{FF}\} + k_4\{\lambda^0_{BE}\lambda^2_{BE} + 2\lambda^1_{BE}\lambda^1_{BE}\} + 4k_4\{\lambda^2_{BB}\lambda^0_{EE} + \lambda^0_{BB}\lambda^2_{EE} + 2\lambda^1_{BB}\lambda^1_{EE}\}$$
$$+ k_5\{\lambda^0_{BE}\lambda^2_{BF} + 2\lambda^1_{BE}\lambda^1_{BF}\} + 2k_5\{\lambda^2_{BB}\lambda^0_{EF} + \lambda^0_{BB}\lambda^2_{EF} + 2\lambda^1_{BB}\lambda^1_{EF}\}$$

$$\frac{d\lambda^2_{BF}}{dt} = k_1[\text{NaOH}]\lambda^2_{AF} + 2k_2\lambda^2_{BB}[\text{EP}] - k_2\lambda^2_{BF}[\text{EP}] - k_3\lambda^2_{BF}[\text{NaOH}] - k_4\lambda^2_{BF}\{\lambda^0_{AE} + 2\lambda^0_{EE} + \lambda^0_{EF}\}$$
$$- k_5\lambda^2_{BF}\{\lambda^0_{AF} + \lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BE} + \lambda^0_{BF} + \lambda^0_{EF} + 2\lambda^0_{FF}\} + k_4\{\lambda^0_{BF}\lambda^2_{BE} + 2\lambda^1_{BF}\lambda^1_{BE}\}$$
$$+ 2k_4\{\lambda^2_{BB}\lambda^0_{EF} + \lambda^0_{BB}\lambda^2_{EF} + 2\lambda^1_{BB}\lambda^1_{EF}\} + k_5\{\lambda^0_{BF}\lambda^2_{BF} + 2\lambda^1_{BF}\lambda^1_{BF}\} + 4k_5\{\lambda^2_{BB}\lambda^0_{FF} + \lambda^0_{BB}\lambda^2_{FF} + 2\lambda^1_{BB}\lambda^1_{FF}\}$$

$$\frac{d\lambda^2_{EE}}{dt} = k_3[\text{NaOH}]\lambda^2_{EF} - 2k_4\lambda^2_{EE}\{\lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BF}\} + 2k_4\{\lambda^2_{BE}\lambda^0_{EE} + 2\lambda^1_{BE}\lambda^1_{EE}\} + k_5\{\lambda^2_{BE}\lambda^0_{EF} + \lambda^1_{BE}\lambda^1_{EF}\}$$

$$\frac{d\lambda^2_{EF}}{dt} = k_2[\text{EP}]\lambda^2_{BE} - k_3\lambda^2_{EF}[\text{NaOH}] + 2k_3\lambda^2_{FF}[\text{NaOH}] - k_4\lambda^2_{EF}\{\lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BF}\}$$
$$- k_5\lambda^2_{EF}\{\lambda^0_{AB} + 2\lambda^0_{BB} + 2\lambda^0_{BE}\} + 2k_4\{\lambda^2_{BF}\lambda^0_{EE} + \lambda^0_{BF}\lambda^2_{EE} + 2\lambda^1_{BF}\lambda^1_{EE}\} + k_4\{\lambda^2_{BE}\lambda^0_{EF} + 2\lambda^1_{BE}\lambda^1_{EF}\}$$
$$+ k_5\{\lambda^2_{BF}\lambda^0_{EF} + 2\lambda^1_{BF}\lambda^1_{EF}\} + 2k_5\{\lambda^0_{BE}\lambda^0_{FF} + \lambda^0_{BE}\lambda^2_{FF} + 2\lambda^1_{BE}\lambda^1_{FF}\}$$

$$\frac{d\lambda^2_{FF}}{dt} = k_2[\text{EP}]\lambda^2_{BF} - 2k_3\lambda^2_{FF}[\text{NaOH}] - 2k_5\lambda^2_{FF}\{\lambda^0_{AB} + 2\lambda^0_{BB} + \lambda^0_{BE}\}$$
$$+ k_4\{\lambda^2_{BF}\lambda^0_{EF} + \lambda^0_{BF}\lambda^2_{EF} + 2\lambda^1_{BF}\lambda^1_{EF}\} + 2k_5\{\lambda^2_{BF}\lambda^0_{FF} + 2\lambda^1_{BF}\lambda^1_{FF}\}$$

can be integrated for any given set of initial conditions for a specified temperature history and specified rate constants (k_1–k_5). Similarly, the equations in Table VII form another complete set of ODE–IVPs and can be integrated separately. The numerical technique used to integrate these equations is Gear's algorithm.[12] The NAG library routine, D02EBF, which has a built-in step size control algorithm and is particularly useful for stiff systems, is used (with a tolerance, TOL, of 10^{-}) for this purpose. Changing the value of the parameter, TOL, led to almost identical results. The three checks described above were also made with the computer code to ensure the correctness of the simulation program.

Table VI Concentration of Various End Groups

$$[\text{A}] = \sum_{n=0}^{\infty} (2[\text{AA}_n] + [\text{AB}_n] + [\text{AE}_n] + [\text{AF}_n])$$

$$[\text{B}] = \sum_{n=0}^{\infty} (2[\text{BB}_n] + [\text{AB}_n] + [\text{BE}_n] + [\text{BF}_n])$$

$$[\text{E}] = \sum_{n=0}^{\infty} (2[\text{EE}_n] + [\text{AE}_n] + [\text{BE}_n] + [\text{BF}_n])$$

$$[\text{F}] = \sum_{n=0}^{\infty} (2[\text{FF}_n] + [\text{AF}_n] + [\text{BF}_n] + [\text{EF}_n])$$

With the mathematical model and computer code now developed, we can start obtaining some useful results. Some experimental data on isothermal (25°C) polymerization of bisphenol A with epichlorohydrin with NaOH catalyst (in methanol solvent) has been provided by Batzer and Zahir.[1] The reaction mass is a single phase, well-mixed mixture at constant temperature, and so is described well by the model presented here. These experimental data could be used to obtain curve-fit values for the five rate constants at 25°C. Similarly, curve fitting can be attempted at other temperatures when additional experimental data becomes available to give Arrhenius expressions for the rate constants (unfortunately, experimen-

Table VII Mol Balance Equations for the End Groups and Some Lower Oligomers in a Batch Reactor

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{NaOH}][\mathrm{A}]$$

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{NaOH}][\mathrm{A}] - k_2[\mathrm{EP}][\mathrm{B}] - k_4[\mathrm{E}][\mathrm{B}] - k_5[\mathrm{F}][\mathrm{B}]$$

$$\frac{d[\mathrm{E}]}{dt} = k_3[\mathrm{NaOH}][\mathrm{F}] - k_4[\mathrm{B}][\mathrm{E}]$$

$$\frac{d[\mathrm{F}]}{dt} = k_2[\mathrm{EP}][\mathrm{B}] - k_3[\mathrm{NaOH}][\mathrm{F}] - k_5[\mathrm{B}][\mathrm{F}]$$

$$\frac{d[\mathrm{EP}]}{dt} = -k_2[\mathrm{EP}][\mathrm{B}]$$

$$\frac{d[\mathrm{NaOH}]}{dt} = -k_1[\mathrm{NaOH}][\mathrm{A}] + k_2[\mathrm{EP}][\mathrm{B}] - k_3[\mathrm{NaOH}][\mathrm{F}] + k_4[\mathrm{B}][\mathrm{E}] = -\frac{d[\mathrm{H_2O}]}{dt}$$

$$\frac{d[\mathrm{NaCl}]}{dt} = k_3[\mathrm{NaOH}][\mathrm{F}] + k_5[\mathrm{B}][\mathrm{F}]$$

$$\frac{d[\mathrm{AA_0}]}{dt} = -2k_1[\mathrm{NaOH}][\mathrm{AA_0}]$$

$$\frac{d[\mathrm{AE_0}]}{dt} = -k_1[\mathrm{NaOH}][\mathrm{AE_0}] + k_3[\mathrm{AF_0}][\mathrm{NaOH}] - k_4[\mathrm{AE_0}][\mathrm{B}]$$

$$\frac{d[\mathrm{AF_0}]}{dt} = -k_1[\mathrm{NaOH}][\mathrm{AF_0}] + k_2[\mathrm{AB_0}][\mathrm{EP}] - k_3[\mathrm{AF_0}][\mathrm{NaOH}] - k_5[\mathrm{AF_0}][\mathrm{B}]$$

$$\frac{d[\mathrm{FF_0}]}{dt} = k_2[\mathrm{EP}][\mathrm{BF_0}] - 2k_3[\mathrm{FF_0}][\mathrm{NaOH}] - 2k_5[\mathrm{FF_0}][\mathrm{B}]$$

$$\frac{d[\mathrm{EE_0}]}{dt} = k_3[\mathrm{NaOH}][\mathrm{EF_0}] - 2k_4[\mathrm{EE_0}][\mathrm{B}]$$

$$\frac{d[\mathrm{AB_0}]}{dt} = -k_1[\mathrm{NaOH}]\{[\mathrm{AB_0}] - 2[\mathrm{AA_0}]\} - k_2[\mathrm{AB_0}][\mathrm{EP}] - k_4[\mathrm{AB_0}][\mathrm{E}] - k_5[\mathrm{AB_0}][\mathrm{F}]$$

$$\frac{d[\mathrm{BE_0}]}{dt} = k_1[\mathrm{NaOH}][\mathrm{AE_0}] - k_2[\mathrm{BE_0}][\mathrm{EP}] + k_3[\mathrm{BF_0}][\mathrm{NaOH}] - k_4[\mathrm{BE_0}]\{[\mathrm{B}] + [\mathrm{E}]\} - k_5[\mathrm{BE_0}][\mathrm{F}]$$

$$\frac{d[\mathrm{BB_0}]}{dt} = k_1[\mathrm{NaOH}][\mathrm{AB_0}] - 2k_2[\mathrm{BB_0}][\mathrm{EP}] - 2k_4[\mathrm{BB_0}][\mathrm{E}] - 2k_5[\mathrm{BB_0}][\mathrm{F}]$$

$$\frac{d[\mathrm{BF_0}]}{dt} = k_1[\mathrm{NaOH}][\mathrm{AF_0}] + 2k_2[\mathrm{BB_0}][\mathrm{EP}] - k_2[\mathrm{BF_0}][\mathrm{EP}] - k_3[\mathrm{BF_0}][\mathrm{NaOH}] - k_4[\mathrm{BF_0}]\{[\mathrm{B}] + [\mathrm{E}]\} - k_5[\mathrm{BF_0}][\mathrm{F}]$$

$$\frac{d[\mathrm{EF_0}]}{dt} = k_2[\mathrm{EP}][\mathrm{BE_0}] - k_3[EF_0][NaOH] + 2k_3[\mathrm{FF_0}][\mathrm{NaOH}] - k_4[\mathrm{EF_0}][\mathrm{B}] - k_5[\mathrm{EF_0}][\mathrm{B}]$$

tal work along the lines required are not available in the open literature). The Box complex procedure[13,14] is used to carry out the curve-fitting exercise for the data presented by Batzer and Zahir.[1] This technique minimizes an objective function, E, using a pattern-search technique. The objective function is chosen as a weighted sum of absolute errors between the values predicted by the model and experimental data. It is given by

$$E(k_1, k_2, k_3, k_4, k_5) = \sum_j w_j \frac{1}{N_{j,\text{exp}}} \sum_j \left| \frac{[j]_{i,\text{theor}} - [j]_{i,\text{exp}}}{[j]_{i,\text{exp}}} \right| \quad (3)$$

In the above equation, $[j]$ is the concentration of the jth molecular species for which experimental data is available,[1] W_j is the weightage factor assigned to the experimental data set for the jth oligomer (or summation of oligomers), and subscript i indicates the ith data point in a set for the jth species. Subscripts, exp and theor, represent experimental and the corresponding theoretical values for any concentration. N_j,exp indicates the number of experimental data points available for the ith species. Minimization of E while searching for values of k_1–k_5 leads to a best-fit set of values for these rate constants. The CPU time taken on a mainframe HP9000/850 S supermini computer for the parameter estimation (220 iterations) is 28.64 s.

RESULTS AND DISCUSSION

The Box complex algorithm is used with the experimental data of Batzer and Zahir[1] to obtain the best-fit values of the five parameters, k_1, k_2, k_3, k_4, and k_5, at 25°C. The initial conditions used are: $[AA_0]_0$ = 200 mol/m^3, $[EP]_0$ = 1280 mol/m^3, $[NaOH]_0$ = 400 mol/m^3. The parameters used in this program are given in Table VIII. The experimental data[1] used for curve fitting are the concentrations, $[AA_0]$ (bisphenol A), $[EE_0]$, $[EF_0]$, $[FF_0]$, and $([AE_0]+[AF_0])$, at different times. The actual data of Batzer and Zahir (representing uncorrected peak heights of chromatographic curves) were nondimensionalised using the corresponding maximum values, while the chromatographic peak data on $[AA_0]$ was transformed into concentrations using the given initial concentration, $[AA_0]_0$. The optimal values of the rate constants obtained finally are given in Table VIII.

Table VIII Data Used and Results Obtained in Optimal Parameter Estimation

Weightage Factors Used in Eq. 3

Data used	W_j
$[AA_0]$	1.0
$[EE_0]/[EE_0]_{max}$	1.0
$[EF_0]/[EF_0]_{max}$	1.0
$[FF_0]/[FF_0]_{max}$	5.0
$([AE_0] + [AF_0])/([AE_0] + [AF_0])_{max}$	1.0

Values of the Parameters Used in Box Complex Optimization

N = 7
α = 1.3
$\beta = 10^{-6}$
γ = 3
δ = 0.01 ($h_j - l_j$) where, h_j and l_j are the upper and lower bounds on the jth parameter

Initial Value of the Parameters

$[k_1, k_2, k_3, k_4, k_5] = [1.2 \times 10^{-3}, 3.1 \times 10^{-5}, 2.0 \times 10^{-4}, 6.4 \times 10^{-6}, 2.7 \times 10^{1}]$

Bounds on the Parameters

$$5.0 \times 10^{-4} \le k_1 \le 1.5 \times 10^{-3}$$
$$1.0 \times 10^{-5} \le k_2 \le 9.0 \times 10^{-5}$$
$$1.0 \times 10^{-4} \le k_3 \le 9.0 \times 10^{-4}$$
$$1.0 \times 10^{-6} \le k_4 \le 9.0 \times 10^{-6}$$
$$1.0 \times 10^{1} \le k_5 \le 9.0 \times 10^{1}$$

Optimized Values of the Parameters

$$\begin{bmatrix} k_1 \\ k_2 \\ k_3 \\ k_4 \\ k_5 \end{bmatrix} = \begin{bmatrix} 1.011378 \times 10^{-3} \\ 6.316743 \times 10^{-5} \\ 3.949022 \times 10^{-4} \\ 2.2321728 \times 10^{-6} \\ 3.3111607 \times 10^{1} \end{bmatrix}$$

Figure 1 shows how E varies with iteration number. It is observed that E slowly reaches its lowest value. Figures 2, 3, and 1 show how significant changes occur in the values of k_1–k_5 before they also settle down to their best-fit values.

The best-fit values of the rate constants (Table VIII) are used to generate the concentration histories of several lower oligomers. Figures 4–6 show experimental data as well as model predic-

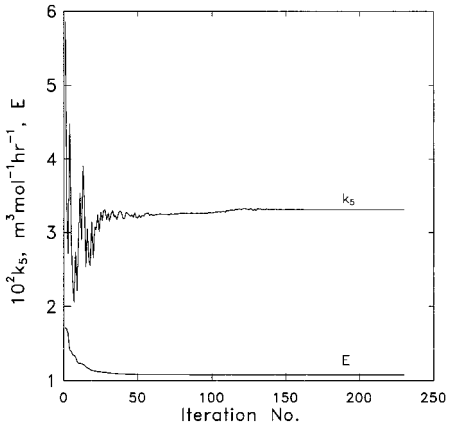


Figure 1 Variation of error and k_5 with iteration number.

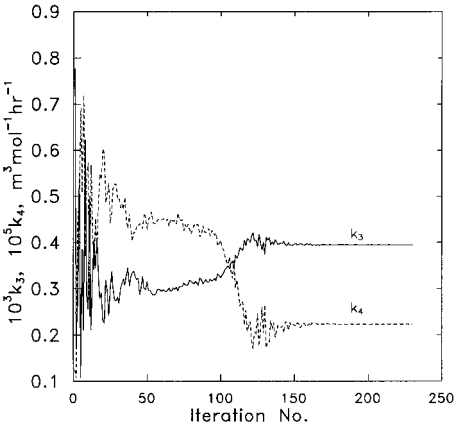


Figure 3 Variation of k_3 and k_4 with iteration number.

tions, and show that the quality of the curve fit of the experimental data is quite good. The theoretically predicted values of $[EE_o]/[EE_o]_{max}$ are found to be lower than the experimental values. The agreement could be improved, but only slightly, by increasing k_1 or k_2, but this worsens the other curve fits (particularly, of $[Ae_o]+[AF_o]$, and $[AA_o]$), and so this was not attempted. The lack of agreement for $[EE_o]/[EE_o]_{max}$ suggests that the kinetic scheme of Table I needs to be modified slightly (it is assumed that the experimental values of $[EE_o]/[EE_o]_{max}$ in the single comprehensive study of Batzer and Zahir[1] available in the open literature, are above suspicion). Figures 7 and 8 show the variations of [EP], [NaOH], [NaCl], and $[H_2O]$ with time (for which experimental data are not available), computed using the best-fit values of the rate constants. It is observed that reasonable amounts of NaOH are consumed leading to the production of water. The epichlorohydrin concentration does not change much with time because it is taken in excess. Small amounts of NaCl are produced during the polymerization. It is assumed that the H_2O and NaCl produced and the NaOH are all soluble in the reaction mass of Batzer and Zahir,[1] and that the latter remains as a single phase throughout the polymerization.

The optimized model parameters are used in the moment equations of Table V with $[AA_0]_0 = 200$ mol/m^3, $[EP]_0 = 1280$ mol/m^3, and $[NaOH]_0 = 400$ mol/m^3, to generate the number- and weight-average molecular weights, as well as the polydispersity index (with the help of Table III). Figure 9 shows the variation with time of the

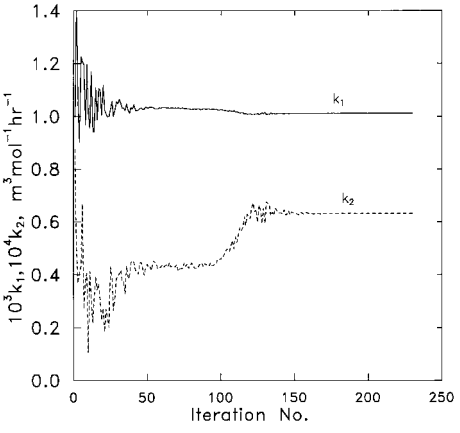


Figure 2 Variation of k_1 and k_2 with iteration number.

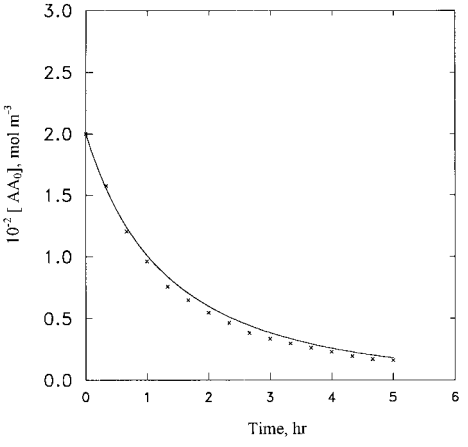


Figure 4 Variation of the concentration of bisphenol A with time. Experimental data of Batzer and Zahir[1] also shown. Curve indicates model predictions using the optimal parameters.

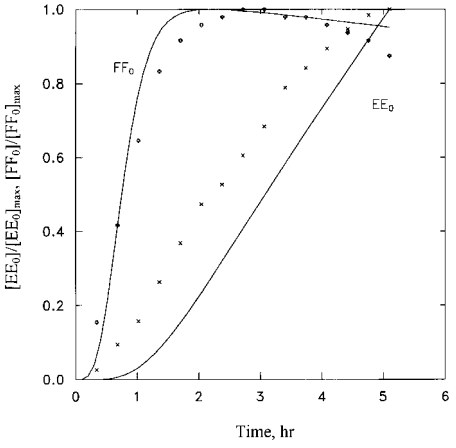


Figure 5 Variation of the dimensionless concentrations of EE_0 and FF_0 with time. Solid lines represent model predictions using optimal parameters. Symbols represent experimental data points of Batzer and Zahir.[1]

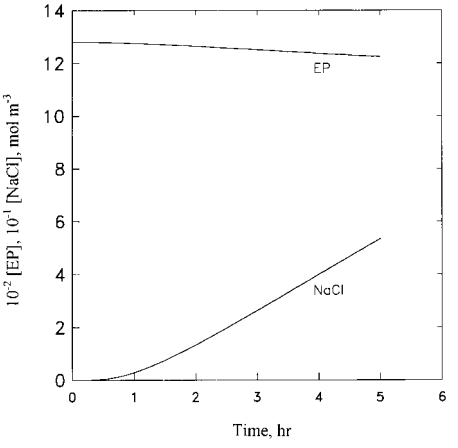


Figure 7 Variation of [EP] and [NaCl] with time. Optimal values of the rate constants used.

average molecular weights with and without the concentration of epichlorohydrin used in the computations. The value of M_n (without EP) is slightly over 342, the molecular weight of DGEBPA, near the end, and indicates that the end-capping of bisphenol A by excess epichlorohydrin is essentially complete. The PDI without EP rises from 1.0 to about 1.4 during this period. The PDI of about 1.4 at the end suggests that significant amounts of higher oligomers are also formed in this process.

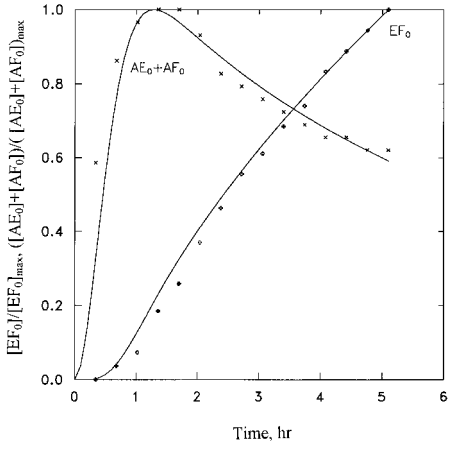


Figure 6 Variation of the dimensionless concentrations of AE_0+AF_0 and EF_0 with time. Solid lines represent model predictions using optimal parameters. Symbols represent the experimental data points of Batzer and Zahir.[1]

Detailed sensitivity tests are now performed to identify the most important parameters, so that greater care can be taken in estimating their values. Figure 10 shows that the bisphenol A concentration is somewhat sensitive to changes in the value of k_1. The other rate constants do not influence the concentration history of $[AA]_0$ as much. Similar sensitivities are observed for the concentration of NaOH. The concentration of NaCl, in contrast, is sensitive to variations in both k_1 and k_2, but not as sensitive to other rate constants. The epichlorohydrin concentration is not influenced much by any of the rate constants, because it is in excess. The value of M_n (without EP) is most sensitive to variations in k_1 and k_2. Figure 11 shows how higher values of M_n are attained when k_1 or k_2 is increased by about 20%

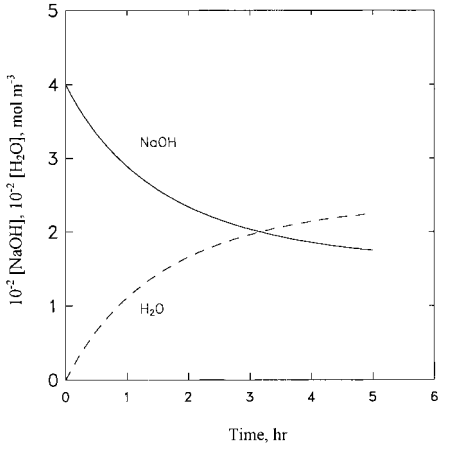


Figure 8 Variation of [NaOH] and $[H_2O]$ with time. Optimal values of the rate constants used.

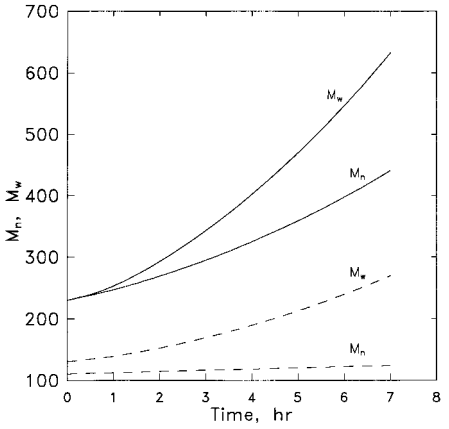


Figure 9 Variation of M_n and M_w with time. Dotted lines indicate average molecular weights incorporating epichlorohydrin. Solid lines indicate the variations excluding epichlorohydrin in the computation.

(over the optimal or reference values). The sensitivity of M_n to the remaining three rate constants is much less. Similar conclusions are obtained for the sensitivities of M_w and PDI to variations in the rate constants (detailed plots can be provided on request). A word of caution may be mentioned at this stage. The kinetic scheme of Table I indicates that the main chain-lengthening steps are reactions 4 and 5. The relative insensitivity of M_n and M_w to variations in k_4 and k_5 could possibly be because the rate constants have been obtained by curve-fitting experimental data on only the low molecular weight molecular species, rather than data on M_n or M_w, which is not available, and could thus be slightly biased.

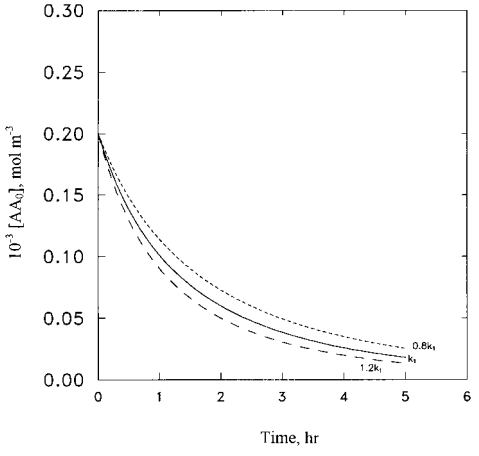


Figure 10 Sensitivity of the bisphenol A concentration to k_1. Sensitivity of M_n to k_1 and k_2. Epichlorohydrin excluded from computation of M_n.

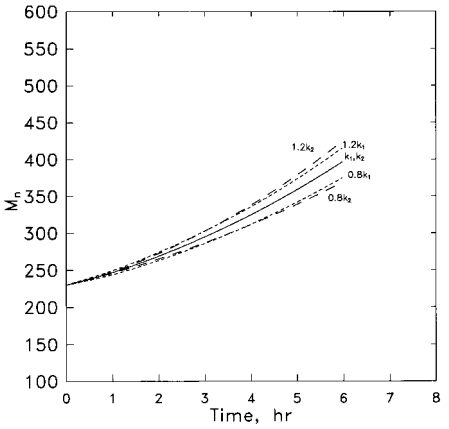


Figure 11 Sensitivity of M_n to k_1 and k_2. Epichlorohydrin excluded from computation of M_n.

We also studied the sensitivity of $[EE_o]$ to variations in k_1 and k_2, the two rate constants that would be expected to affect its value most. An increase in k_1 by 20% increased the value of $[EE_o]/[EE_o]_{max}$ very slightly, but led to a significant lowering of $[AA_o]$, and of the values of $([AE_o]+[AF_o])/([AE_o]+[AF_o])_{max}$ beyond the maximum (see Fig. 6). Thus, we inferred that it is futile to attempt to improve the agreement between the theoretical and experimental values of $[EE_o]/[EE_o]_{max}$ by changing the rate constants. This is not too important at this stage because in any case, one will have to "retune" the values of the rate constants when attempting to simulate industrial reactors.

An interesting simulation study is now made. Several industrial operations involve intermediate addition of NaOH. We run our simulation code to see the effect of sudden changes in NaOH concentration. The results so generated would give us some idea about the effects of NaOH addition in industrial epoxy reactors (which often involve two liquid phases, in contrast to the present study limited to single-phase polymerization). Figure 12 shows that slightly higher M_n and M_w are obtained with intermediate addition of NaOH. A similar effect would be expected if we distill off water/epichlorohydrin in between (the concentration of NaOH would increase). It may be added that the earlier probabilistic models cannot be used to provide such results, and demonstrates that our kinetic model is quite general.

CONCLUSIONS

A detailed kinetic model has been developed for epoxy polymerization. The rate constants have

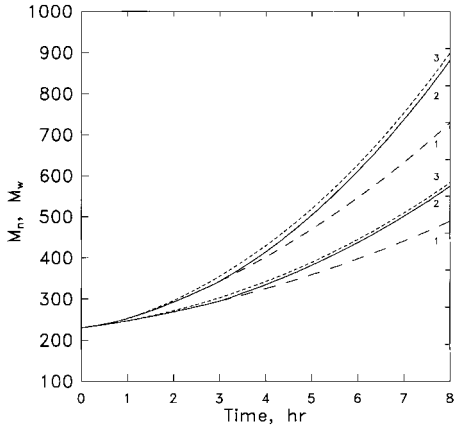


Figure 12 Effect of intermediate addition of NaOH. Curve 1: no intermediate addition of NaOH. Curve 2: [NaOH] increased by 400 mol/m^3 at 3 h (one step). Curve 3: [NaOH] increased by 80 mol/m^3 at t = 1, 2, 3, 4, and 5 h. Lower three curves indicate M_n, while the upper three represent M_w.

been curve fitted using one set of experimental data available in the open literature in which single-phase polymerization is carried out. The model incorporates the probabilistic model of Ravindranath and Gandhi[4] as a subset, but is far more powerful and general. The mathematical framework presented here can easily be extended to apply to industrial reactors that usually involve additional phenomena, as for example, nonisothermal operation, intermediate addition of NaOH or distillation of water/EP, presence of two liquid phases, etc. Industrial reactor data will be required to "tune" the parameters in these, more general, reactor models. Work along these lines is in progress.

NOMENCLATURE

A	hydroxyl end group
AA_n, AB_n, $\cdots$, FF_n,	molecular species defined in Table II
AA_0	bisphenol A (monomer)
B	sodium phenoxide end group
DGEBPA	diglycidyl ether of bisphenol A
E	glycidyl ether group; objective function
EP	epichlorohydrin
F	chlorohydrin end group
k_i	rate constant for the ith reaction (m^3 mol^{-1} h^{-1})
M_j	molecular mass of jth species
M_n	number-average molecular weight
M_w	weight-average molecular weight
$N_{j,\,\mathrm{exp}}$	number of experimental data points available for the jth species
PDI	polydispersity index
t	tme (h)
W_j	weightage factor assigned to the experimental data set for the jth oligomer, or summation of oligomers

Greek Letters

λ_j^k	kth moment of the jth species as given in Table III, k = 0, 1, 2

Subscripts/Superscripts

exp	experimental value
0	initial value
theor	theoretical value

Symbol

[ ]	concentration (mol/m^3)

REFERENCES

1. H. Batzer and S. A. Zahir, S. A., *J. Appl. Polym. Sci*., **21,** 1843 (1977).
2. W. H. Ray , *J. Macromol. Sci*., *Rev. Macromol. Chem*., **C8,** 1 (1972).
3. A. Kumar and S. K. Gupta, *Reaction Engineering of Step Growth Polymerization*, Plenum, New York, 1987.
4. K. Ravindranath and K. S. Gandhi, *J. Appl. Polym. Sci.,* **24,** 1115 (1979).
5. L. V. McAdams and J. A. Gannon, in *Encyclopedia of Polymer Science and Engineering,* vol. 6, 2nd ed., H. F. Mark, N. M. Bikales, C. G. Overberger, and G. Menges, Eds., Wiley, New York, 1986, p. 322.
6. K. Hodd, in *Comprehensive Polymer Science*, vol. 5, 1st ed., G. C. Eastmond, A. Ledwith, S. Russo, and P. Sigwalt, Eds., Pergamon Press, Oxford, 1989, p. 667.

7. S. Paul, in *Comprehensive Polymer Science*, vol. 6, 1st ed., G. C.Eastmond, A. Ledwith, S. Russo, and P. Sigwalt, Eds., Pergamon Press, Oxford, 1989, p.149.
8. H. Batzer and S. A. Zahir, *J. Appl. Polym. Sci.*, **19**, 585 (1975).
9. H. Batzer and S. A. Zahir, *J. Appl. Polym. Sci.*, **19**, 601 (1975).
10. H. Batzer and S. A. Zahir, *J. Appl. Polym. Sci.*, **19**, 609 (1975).
11. L. C. Case, *J. Polym. Sci.*, **29**, 455 (1958).
12. S. K. Gupta, *Numerical Methods for Engineers*, New Age International Publishers, New Delhi, India, 1995.
13. M. Box, *Comput. J.*, **8**, 42 (1965).
14. J. L. Kuester and J. H. Mize, *Optimization Techniques with Fortran,* McGraw-Hill, New York, 1973.

APPENDIX

Table A1 Different Reactions Taking Place

$$AA_n + NaOH \xrightarrow{2k_1} AB_n + H_2O$$
$$AB_n + NaOH \xrightarrow{k_1} BB_n + H_2O$$
$$AE_n + NaOH \xrightarrow{k_1} BE_n + H_2O$$
$$AF_n + NaOH \xrightarrow{k_1} BF_n + H_2O$$

$$AB_n + EP \xrightarrow{k_2/H_2O} AF_n + NaOH$$
$$BB_n + EP \xrightarrow{2k_2/H_2O} BF_n + NaOH$$
$$BE_n + EP \xrightarrow{k_2/H_2O} EF_n + NaOH$$
$$BF_n + EP \xrightarrow{k_2/H_2O} FF_n + NaOH$$

$$AF_n + NaOH \xrightarrow{k_3} AE_n + NaCl + H_2O$$
$$BF_n + NaOH \xrightarrow{k_3} BE_n + NaCl + H_2O$$
$$EF_n + NaOH \xrightarrow{k_3} EE_n + NaCl + H_2O$$
$$FF_n + NaOH \xrightarrow{2k_3} EF_n + NaCl + H_2O$$

$$AB_n + AE_m \xrightarrow{k_4/H_2O} AA_{n+m+1} + NaOH$$
$$BB_n + AE_m \xrightarrow{2k_4/H_2O} AB_{n+m+1} + NaOH$$
$$BE_n + AE_m \xrightarrow{k_4/H_2O} AE_{n+m+1} + NaOH$$
$$BF_n + AE_m \xrightarrow{k_4/H_2O} AF_{n+m+1} + NaOH$$

$$AB_n + BE_m \xrightarrow{k_4/H_2O} AB_{n+m+1} + NaOH$$
$$BB_n + BE_m \xrightarrow{2k_4/H_2O} BB_{n+m+1} + NaOH$$
$$BE_n + BE_m \xrightarrow{2k_4/H_2O} BE_{n+m+1} + NaOH$$
$$BF_n + BE_m \xrightarrow{k_4/H_2O} BF_{n+m+1} + NaOH$$

$$AB_n + EF_m \xrightarrow{k_4/H_2O} AF_{n+m+1}NaOH$$
$$BB_n + EF_m \xrightarrow{2k_4/H_2O} BF_{n+m+1}+NaOH$$
$$BE_n + EF_m \xrightarrow{k_4/H_2O} EF_{n+m+1} + NaOH$$
$$BF_n + EF_m \xrightarrow{k_4/H_2O} FF_{n+m+1} + NaOH$$

$$AB_n + AF_m \xrightarrow{k_5} AA_{n+m+1} + NaCl$$
$$BB_n + AF_m \xrightarrow{2k_5} AB_{n+m+1} + NaCl$$
$$BE_n + AF_m \xrightarrow{k_5} AE_{n+m+1} + NaCl$$
$$BF_n + AF_m \xrightarrow{k_5} AF_{n+m+1} + NaCl$$

$$AB_n + BF_m \xrightarrow{k_5} AB_{n+m+1} + NaCl$$
$$BB_n + BF_m \xrightarrow{2k_5} BB_{n+m+1} + NaCl$$
$$BE_n + BF_m \xrightarrow{k_5} BE_{n+m+1} + NaCl$$
$$BF_n + BF_m \xrightarrow{k_5} BF_{m+m+1} + NaCl$$

$$AB_n + EF_m \xrightarrow{k_5} AE_{n+m+1} + NaCl$$
$$BB_n + EF_m \xrightarrow{2k_5} BE_{n+m+1} + NaCl$$
$$BE_n + EF_m \xrightarrow{k_5} EE_{n+m+1} + NaCl$$
$$BF_n + EF_m \xrightarrow{k_5} EF_{n+m+1} + NaCl$$

$$AB_n + FF_m \xrightarrow{2k_5} AF_{n+m+1} + NaCl$$
$$BB_n + FF_m \xrightarrow{4k_5} BF_{n+m+1} + NaCl$$
$$BE_n + FF_m \xrightarrow{2k_5} EF_{n+m+1} + NaCl$$
$$BF_n + FF_m \xrightarrow{2k_5} FF_{n+m+1} + NaCl$$

$$AB_n + EE_m \xrightarrow{2k_4/H_2O} AE_{n+m+1} + NaOH$$

$$BB_n + EE_m \xrightarrow{4k_4/H_2O} BE_{n+m+1} + NaOH$$

$$BE_n + EE_m \xrightarrow{2k_4/H_2O} EE_{n+m+1} + NaOH$$

$$BF_n + EE_m \xrightarrow{2k_4/H_2O} EF_{n+m+1} + NaOH$$

where $m, n = 0, 1, 2, \cdots$