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Reaction Kinetics Analyses of Amine-Cured Epoxies: First Shell Substitution Effects

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ABSTRACT:

Kinetic reaction theory was used to model first shell substitution effects for several amine-cured epoxy resins, subject to the constraint of intermolecular reactions. Moment analysis will allow numerical simulations to be extended beyond the gel point. Functionalities for several chemical moieties were correlated as a function of conversion. Simulations also incorporated population density distribution dynamics. Analyses of several oligomers clearly demonstrated the dependency of oligomeric weight fractions on first shell substitution effects and conversion. The ratio of rate constants for reactions of secondary amino hydrogens relative to reactions of primary amino hydrogens ranged from 0.5 to 1.2 for the resins analyzed.

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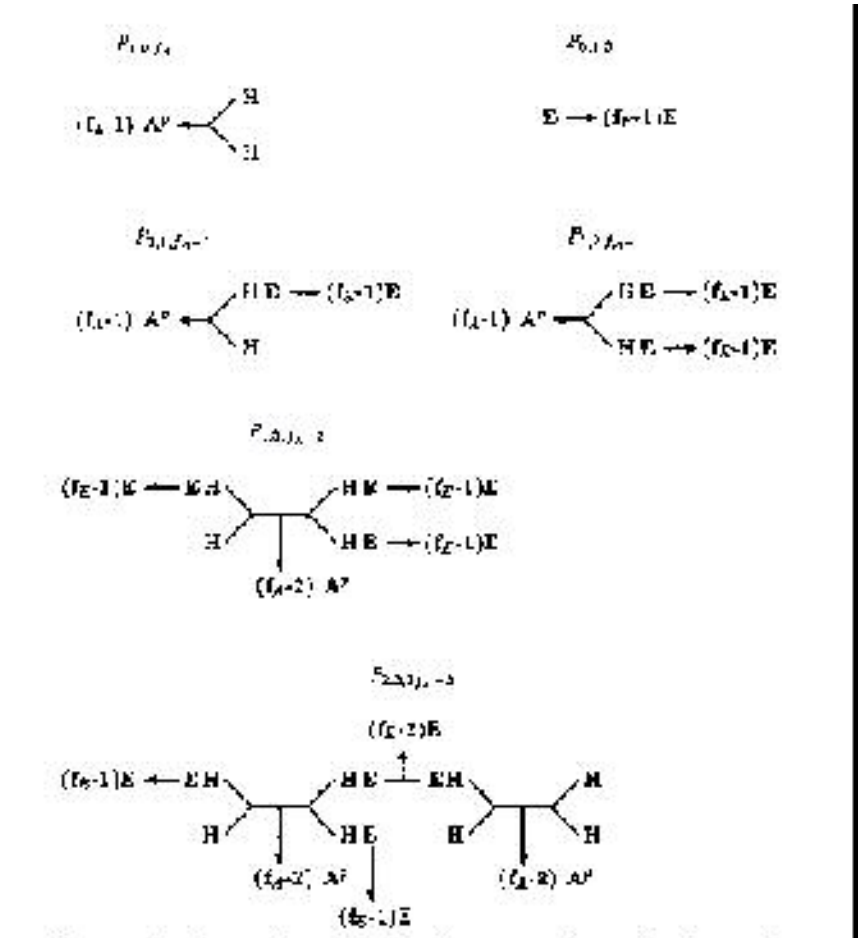

Figure 1. Examples of typical monomeric and oligomeric molecules resulting from the reaction of polyepoxides with polyamines.

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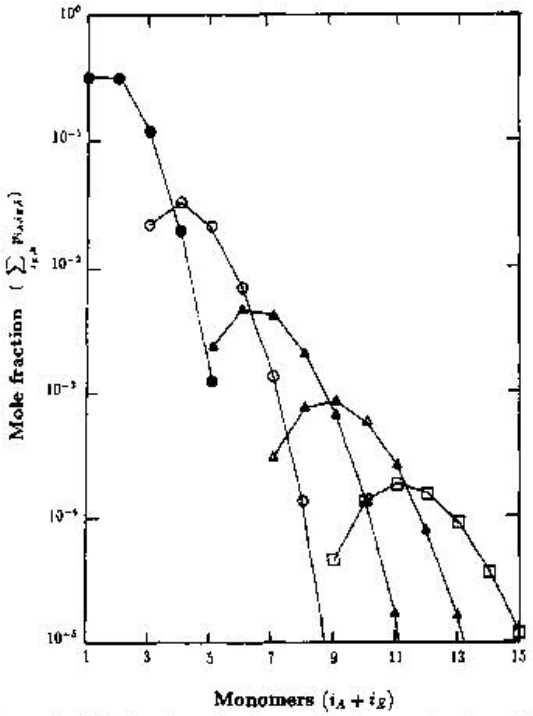

Figure 2. Mole fraction of various molecules as a function of the total number of epoxy and amine monomers at conversion equal to 0.250, subject to $c_1 = 1.0$, $\zeta = 2.0$, $f_A = f_E = 2$ and second-order kinetics. (●) $\sum_{i_E,k} p_{1,i_E,k}$; (○) $\sum_{i_E,k} p_{2,i_E,k}$; (▲) $\sum_{i_E,k} p_{3,i_E,k}$; (△) $\sum_{i_E,k} p_{4,i_E,k}$; (□) $\sum_{i_E,k} p_{5,i_E,k}$.

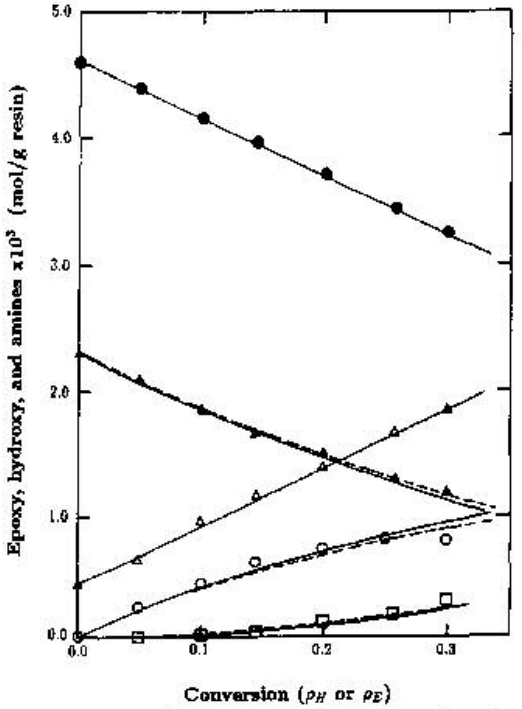

Figure 3. Numerical simulations and experimental results of functional groups as a function of conversion in the system DGEBA/DAB subjec to $\zeta = 2.0$ and third-order kinetics. (●) Epoxy groups; (▲) primary amines; (△) hydroxyl groups; (○) secondary amines; (□) tertiary amines; (—) $c_1 = 1.00$; (- - -) $c_t = 1.20$.

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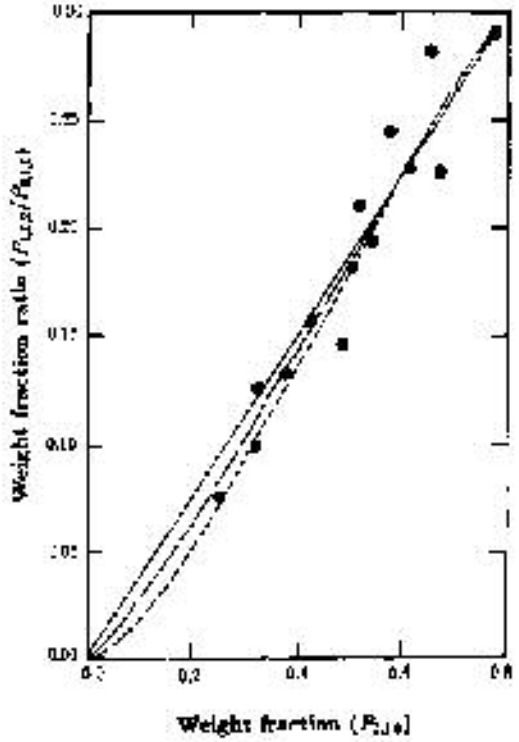

Figure 4. Theoretical and experimental relative moles of $P_{1,2}$ and $P_{0,1}$ compared to $P_{0,1}$ in the system DGEBA/DDM subject to $\zeta = 2.0$ and second-order kinetics. (●) Experimental data; (—) $c_1 = 1.00$; (- - -) $c_1 = 0.80$; (- · -) $c_1 = 0.60$.

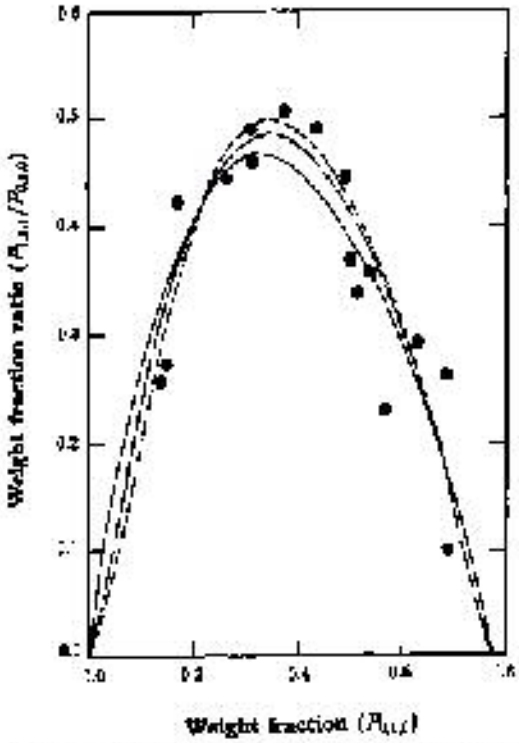

Figure 5. Theoretical and experimental relative moles of $P_{1,1}$ and $P_{1,0}$ compared to $P_{0,1}$ in the system DGEBA/DDM subject to $\zeta = 2.0$ and second-order kinetics. (●) Experimental data; (—) $c_1 = 1.00$; (- - -) $c_1 = 0.80$; (- · -) $c_1 = 0.60$.

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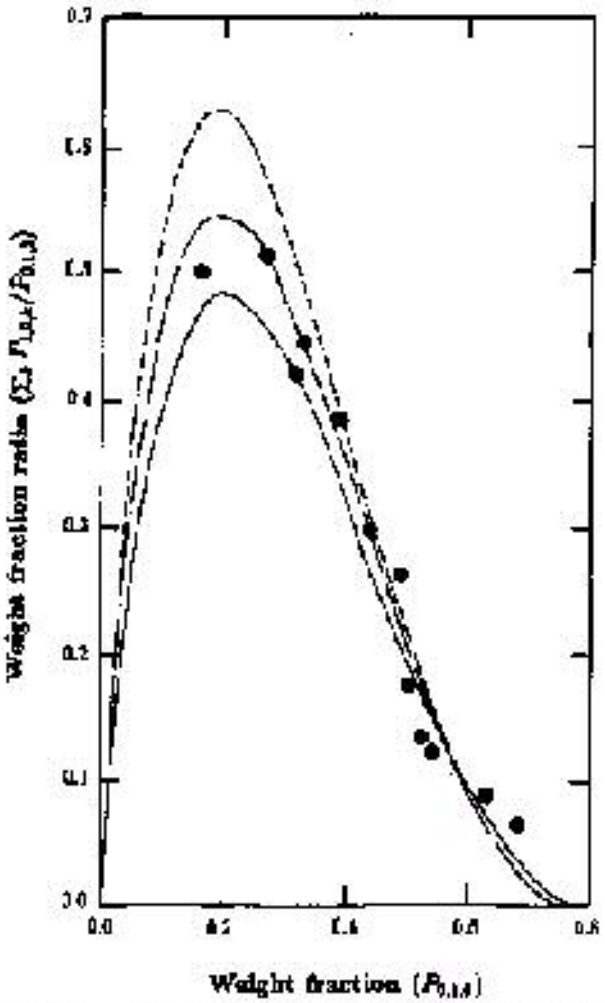

Figure 6. Theoretical and experimental relative moles of $\Sigma_A P_{1,A,t}$ and $P_{0,1,t}$ compared to $P_{0,1,0}$ in the system DGEBA/DDM subject to $f = 2.0$ and second-order kinetics (●) Experimental data; (—) $c_1 = 1.00$; (- -) $c_1 = 0.80$; (- - -) $c_1 = 0.60$.

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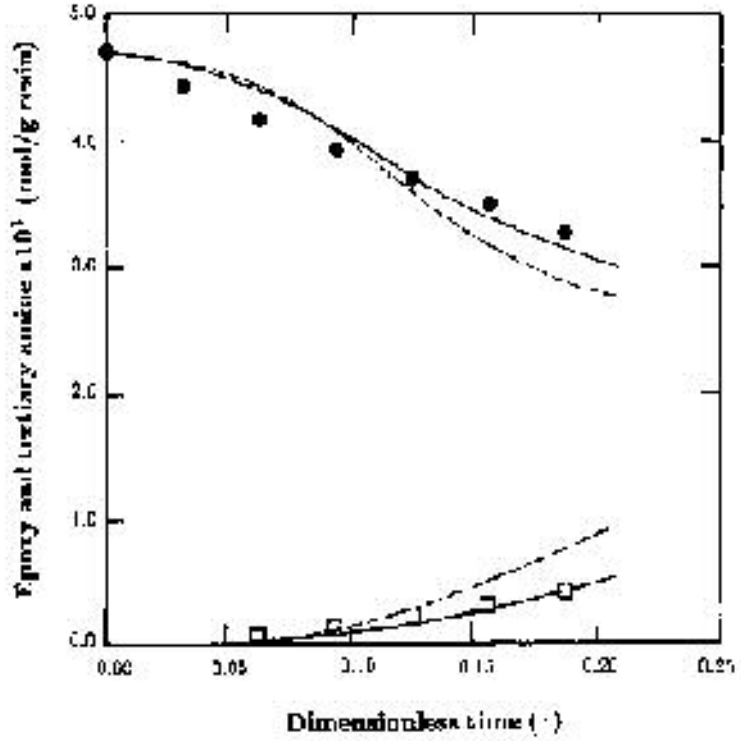

Figure 7. Numerical simulations and experimental results for epoxy groups and tertiary amines as a function of time in the system DGEBA/DDE subject to f = 4.0 and third-order kinetics. (●) Epoxy groups; (□) tertiary amines; (— —) α_1 = 0.50; (- - -) α_1 = 1.00.