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Kinetic Analysis of Competing Intramolecular and Intermolecular Polymerization Reactions

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H. Noureddini and **D. C. Timm,** *Kinetic Analysis of Competing Intramolecular and Intermolecular Polymerization Reactions,* Macromolecules; 1992; 25(6); 1725-1730.

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ABSTRACT: Kinetic reaction theory was used to model a step-growth, thermoset polymerization of a monomer of even functionality f. Intermolecular additions were represented by second-order and intramolecular reactions were expressed by first-order rate expressions. All functional groups were assumed to react with equal reactivity. Independent variables are degree of polymerization i, extent of cross-linking j, and conversion ρ. The normalized rate constant for intramolecular reactions is ϵ. The solution for the normalized population density distribution is

$$P_{i,j} = \frac{f(i-1-j)![(f-2)i/2]!}{2![(f-2)i-j+1]!\,j!\,[(f-2)i/2-j-1]!} \frac{\epsilon^j \rho^{i+j-1}[(1-\rho+\epsilon)(1-\rho)]^{(f-2)i/2-2j}}{(1+\epsilon)^{(f-2)i/2}}$$

subject to $0 \le j \le (f-2)i/2 - 1$ and $\epsilon \ge 0$. Formulas for the number-, mass-, and cross-link-average molecular weights were derived.

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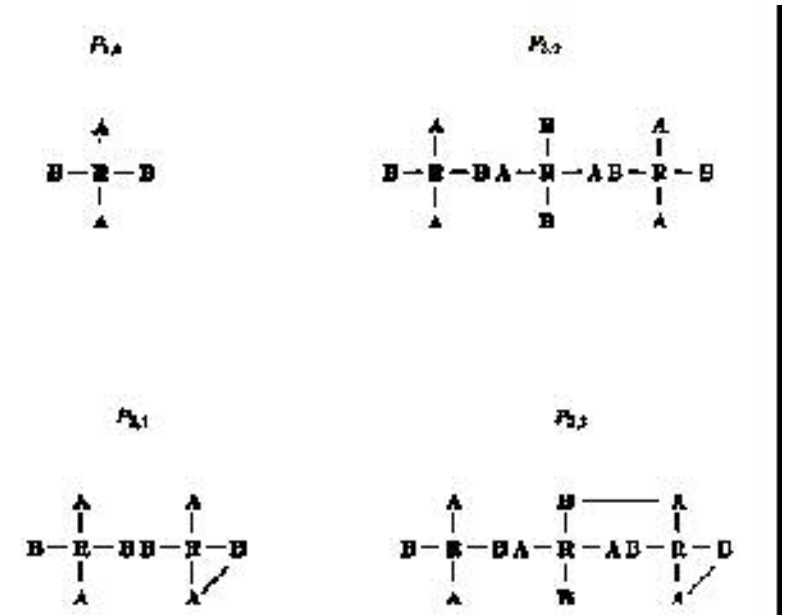

Figure 1. Examples of monomeric and oligomeric molecules, $f = 4$.

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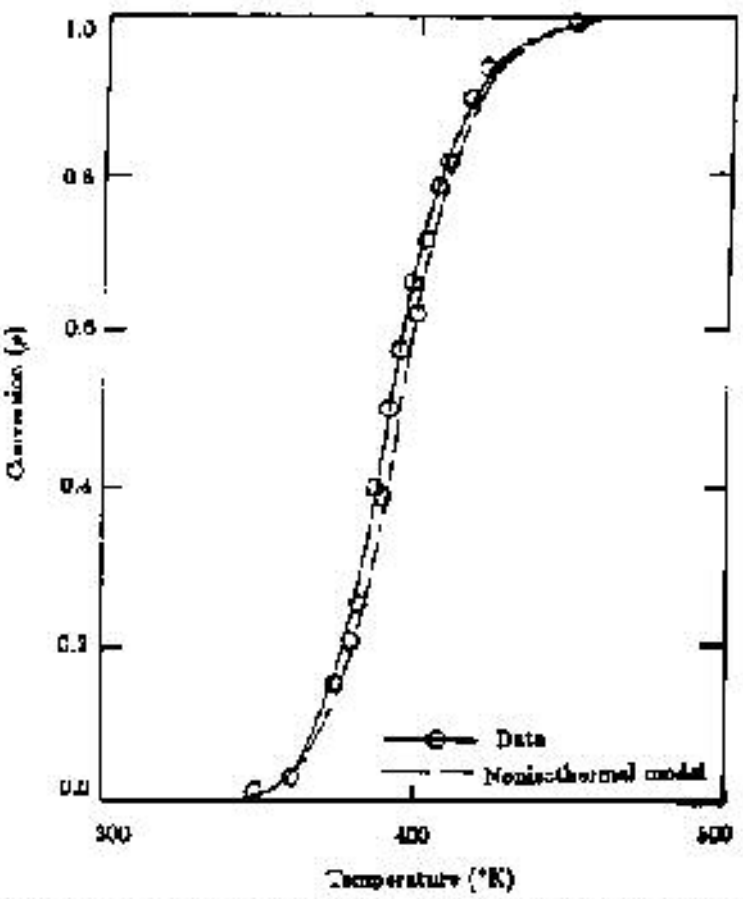

Figure 2. Calculated vs actual degree of cure for a 2 K/min scan by DSC analysis.