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Kinetic Analysis of Competing Intramolecular and Intermolecular Polymerization Reactions

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Kinetic Analysis of Competing Intramolecular and Intermolecular Polymerization Reactions

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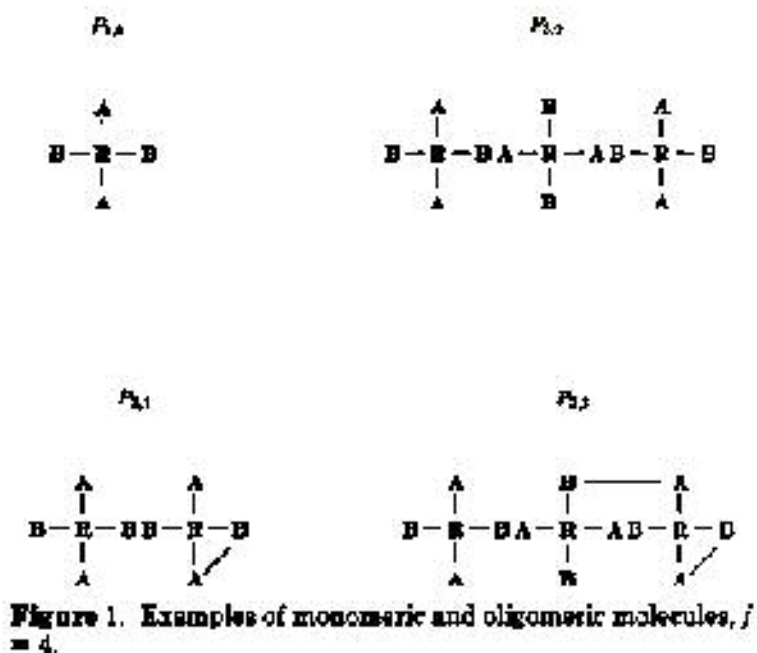
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ABSTRACT: Kinetic reaction theory was used to model a step-growth, the most polymerization of a monomer of f functional groups. Intermolecular additions were represented by second-order and intramolecular reactions were expressed by first-order rate 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 c . The solution for the normalized population density distribution is

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

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



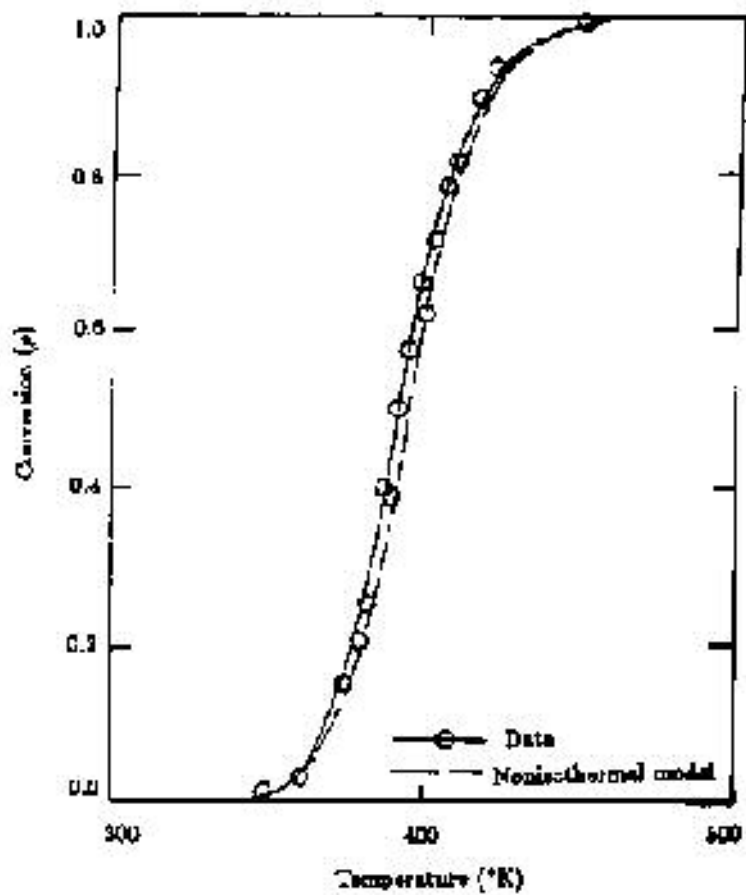


Figure 2. Calculated vs actual degree of cure for a 2 K/min scan by DSC analysis.