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1-1-1992

# Kinetic Analysis of Competing Intramolecular and Intermolecular Polymerization Reactions

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Noureddini, Hossein and Timm, Delmar C., "Kinetic Analysis of Competing Intramolecular and Intermolecular Polymerization Reactions" (1992). *Papers in Molecular Chemistry*. Paper 5.

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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.**

## Kinetic Analysis of Competing Intramolecular and Intermolecular Polymerization Reactions

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Received August 21, 1990; Revised Manuscript Received December 8, 1991

Macromolecules; 1992; 25(6); 1725-1730.

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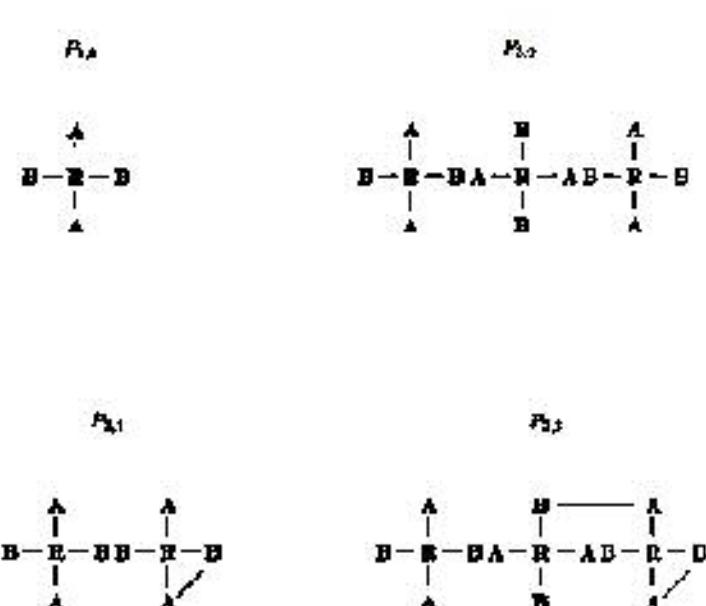
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**ABSTRACT:** Kinetic reaction theory was used to model a step-growth, the most polymerization of a monomer of even functionality  $j$ . Intermolecular additions were represented by second-order and intramolecular reactions were expressed by first-order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

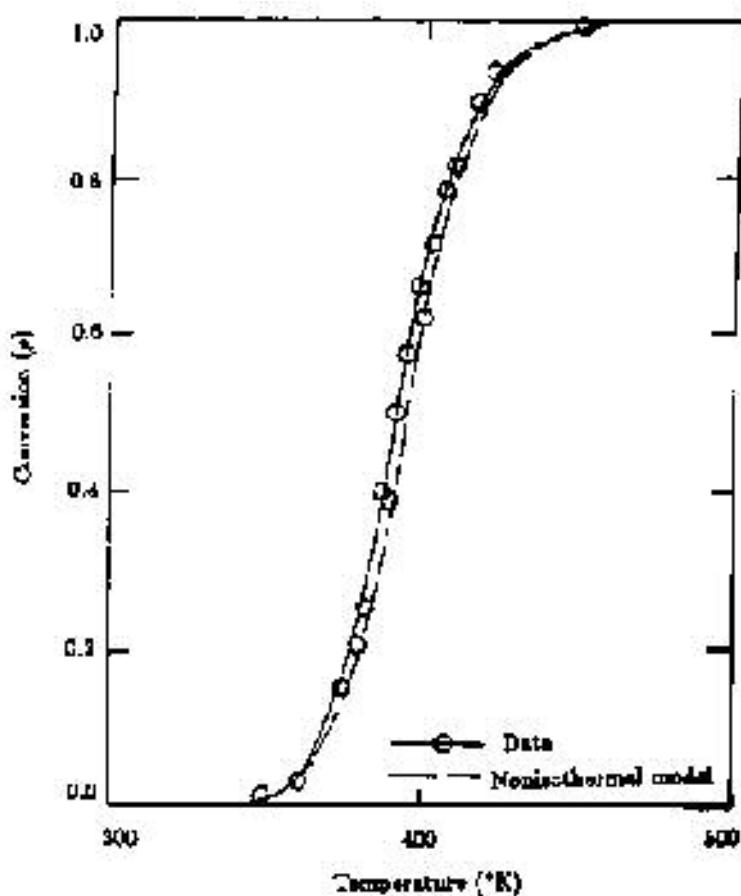
$$P_{ij} = \frac{j(j-1)\dots(j-2j+2)}{2(j-2)\ell-j+1} \cdot \frac{c^{\ell+j-1}(1-\rho+\rho)(1-\rho)^{1/\ell}}{(1+c)^{\ell+1}}$$

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



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

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