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Reaction Kinetics Analysis of Urethane Polymerization to Gelation

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Reaction Kinetics Analysis of Urethane Polymerization to Gelation

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ABSTRACT:

A chemical reaction analysis of a thermosetting, urethane resin formulated from a triol and a diisocyanate is reported. Population density distributions of oligomeric molecules, monomer concentration, the cumulative molar concentration of intramolecular bonds, the resin's average molecular weights, and extent of reaction were determined **as** a function of time. Rate expressions for intermolecular reactions were first order with respect to the concentration of each reactant and were proportional to the functionality of their respective chemical moieties. Rate expressions for intramolecular reactions were first order with respect to the concentration of the reactant and were proportional to the functionality of the limiting chemical moiety on the reactant. The initial ratio of the chemical equivalents and effects of dilution were incorporated into numerical simulations. Stanford and Stepto's experimental data were analyzed. Gel points and the concentration of intramolecular bonds were correlated as a function of conversion. Intramolecular reaction rate expressions derived with the aid of Gaussian chain statistics require the molar concentrations of **all** chemical isomers of a specified chemical composition. The present reaction rate expression allows chemical isomers to be lumped into a single population density distribution variable, substantially reducing the dimensions of the simulation. Numerical results demonstrate that the simplified rate expression is an excellent.

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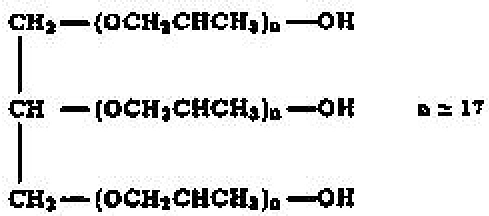

Figure 1. Niax triol a propylene oxide adduct of glycerol.

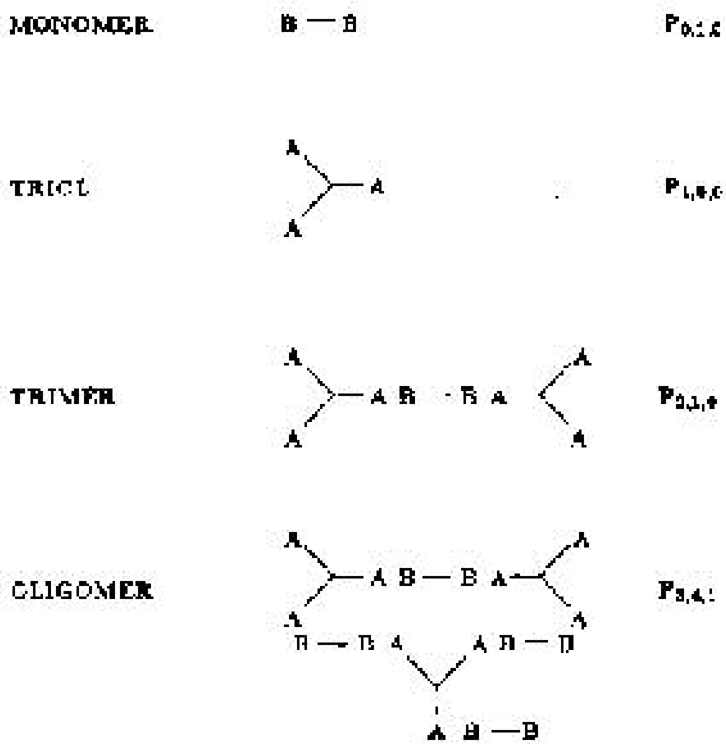

Figure 2. Examples of monomer and oligomeric molecules.

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Table I. Comparison of Population Density Distributions

t	i_A	i_B	$P_{i_A,i_B,0}$ [a]	$N(m_1,n_1)$ [b]
0.1	2	2	9.35E−03	9.30E−03
	3	5	1.36E−04	1.40E−04
	4	6	2.08E−06	2.11E−05
	5	5	5.98E−06	6.07E−06
0.2	2	2	1.86E−02	1.88E−02
	3	5	1.77E−03	1.77E−03
	4	6	5.79E−04	5.79E−04
	5	4	1.22E−04	1.22E−04
0.3	2	2	1.89E−02	1.89E−02
	3	5	4.06E−03	4.08E−03
	4	6	1.76E−03	1.76E−03
	5	5	2.85E−04	2.95E−04
0.4	2	2	1.55E−02	1.55E−02
	3	5	5.22E−03	5.22E−03
	4	6	2.50E−03	2.50E−03
	5	5	3.19E−04	3.19E−04

[a] $P_{i_A,i_B,0}$, Liu,[27] $A_{1,0,0} = 4$, $B_{0,1,0} = 2$, $k_1 = 1$, $k_2 = 0$, $r = 1$. [b] $N(m_1,n_1)$, Stockmayer,[27] $f_1 = 4$, $g_1 = 2$, $r = 1$, $m_1 = i_A$, $n_1 = i_B$.

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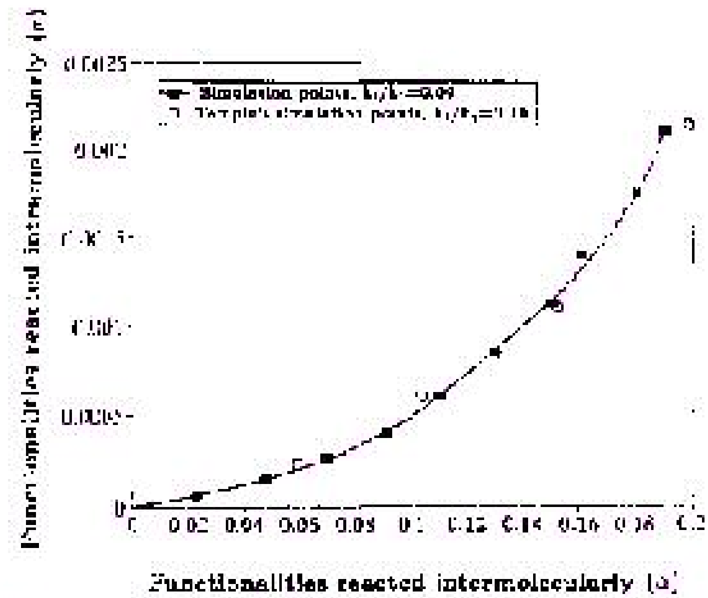

Figure 7. Fraction of functional groups reacted intramolecularly vs the fraction of functional groups reacted intermolecularly ($f_A = 2$, $f_B = 3$, $r = 1$).

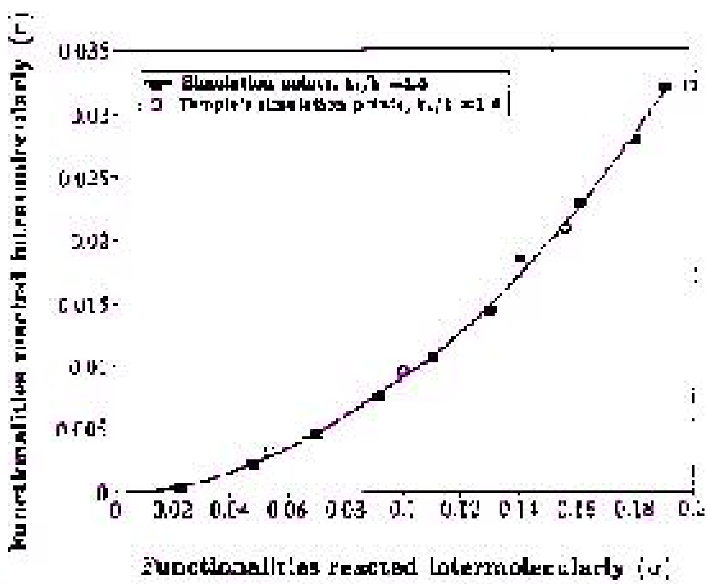

Figure 8. Fraction of functional groups reacted intramolecularly vs the fraction of functional groups reacted intermolecularly ($f_A = 2$, $f_B = 3$, $r = 1$).

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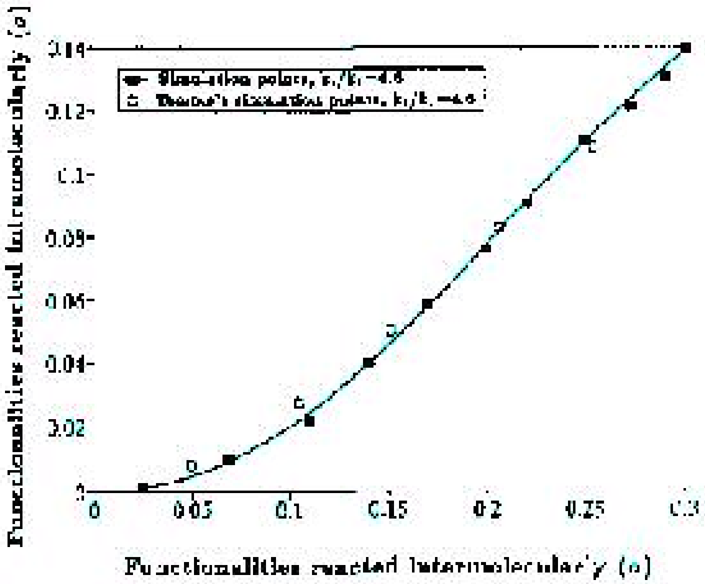

Figure 9. Fraction of functional groups reacted intramolecularly vs the fraction of functional groups reacted intermolecularly (f_A = 2, f_B = 3, r = 1)