phase as the monomer. It is the nature of the active site which determines the final structure and the properties of the resulting polymer.

Kinetics of the Adiabatic Polymerization of Oligoester Acrylates

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The authors employed a thermometric technique to study the kinetics of adiabatic polymerization of oligoester acrylates, and found several specific properties of this reaction. Among them are an increase of the flexibility of the polymer matrix, and a decrease in the viscosity of the oligoester with temperature. These reaction features promote chain growth and radical termination, i.e., promote conditions approximating the steady state. This, in turn, gives polymers of higher molecular weight than those possible under isothermal conditions.

Quantitative Study on the Polar Effects of Substituents in Polymerization

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Attempts to account for the polarization effects induced by substituents on the energy of the polymerizing system gave a quantitative relationship between the rate constant for chain propagation and the polar properties of the substituents. When plotted on a Q–e diagram, this relationship contradicted the empirically derived relationships. For this reason, the author introduced a new parameter Q', which allows a more realistic separation of polar and resonance effects of the substituents on the reacting system. He then found a quantitative relationship between k_{ij} and P_i and Q_j, which allows calculation of rate constants for polymerization of all monomers from the rate constants for copolymerization (assuming that no steric effects are present).

Determination of Absolute Rate Constants for the Various Steps of a Chain Reaction by Means of Flash Photoinitiation

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The authors propose a new variant of the technique for determining the absolute rate constants of the constituent reactions of a chain process. This variant consists of measuring the rise in the temperature of the reactants (release of the heat of reaction) under adiabatic condition during flash photoinitiation. It was found that k_p/k_o for the polymerization of styrene at 20°C is 0.6×10^{-6}, while the k_p/k_o for the polymerization of acrylonitrile in dimethylformamide is 1.9×10^{-6}.

Heterolytic Rearrangement of Peresters. II. Effect of the Medium and of the Catalyst of the Reactivity of Cumyl Perbenzoate

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The rate of rearrangement of cumyl perbenzoate increases with the dielectric permittivity of the solvent. However, the permitivity effect is less pronounced than the specific solvation effect of the solvent. It is shown that in mixed solvent systems (methanol-water and ethanol-water) the log $k_{\text{rearr.}}$ increases proportionately to the ionizing power of the medium. The m_i coefficients in the Winstein-Gruwald equation are 0.39 and 0.49 for the two media, respectively. In benzene, carboxylic acids form complexes with cumyl perbenzoate. The instability constant for the cumyl perbenzoate-trichloroacetic acid complex is 0.026 at 6°C. Protonated acids and the Lewis acid $AlCl_3$ catalyze the rearrangement of this perester by increasing the polarity of the O — O bond.

Effect of the Medium on the Mechanism of the Reactions of Isocyanates with Alcohols. Part II.

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Kinetic data on the reactions of isocyanates with methanol in solvents of various polarity are compared with heats of mixing of these isocyanates and methanol with these solvents. The mechanism of addition of alcohols to isocyanates in inert solvents is different from that observed in solvents capable of specific solvation of the reagents.

Kinetics of Thermal Decomposition of Pentaerythritol tetranitrate Below the Melting Point

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The author derives an equation describing the kinetics of thermal decomposition of organic solids which melt progressively during the reaction. Specifically, he treats the case where the