Studies in Polymerization by Ring Scission

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While polymerization by ring opening is not novel and indeed is applied industrially, e.g. to ethylene oxide and caprolactam, it has been little studied in comparison to vinyl polymerization. The kinetics of copolymerization of some cyclic monomers have recently been studied (Dermer and Ames, 1963). This paper reports further observations that were made.

The rate of disappearance of β-propiolactone in acetonitrile containing 0.0024 *M* diethylamine (catalyst) was measured at 55 C. The lactone was determined by addition to excess standard sodium thiosulfate solution and backtitration after 30 minutes with standard iodine solution. The reaction was of first order in lactone, as might be expected, with $k = 6.9 \times 10^{-4}$

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min.$^{-1}$. Under nearly the same conditions in dimethyl sulfoxide, but with 0.0017 *M* catalyst, the reaction was faster, $k = 6.0 \times 10^{-3}$ min.$^{-1}$. In anisole the rate was too low to be measured conveniently. In these solvents under the same conditions the polymerization of 4-isopropyloxazolidine-2,5-dione (valine *N*-carboxy anhydride, or valine-NCA), prepared according to Bailey (1950), did not proceed according to a kinetic equation of integral order in monomer, possibly because the polymeric product precipitated throughout the reaction.

A mixture of 0.06 mole DL-alanine-NCA (prepared like the valine compound; mp 44-47 C (Bailey, 1950, Ben-Ishai and Katchalski, 1952), 0.06 mole propiolactone, 250 ml of anisole, and 0.5 ml of diethylamine catalyst was stirred at room temperature for 5 days. The solution was poured into excess ethyl ether and the solid product was collected, washed, and dried. It contained 12.2% nitrogen and its infrared spectrum showed the presence of both ester and amide groups. Further evidence for the copolymeric nature of such products has already been given (Dermer and Ames, 1964). A block copolymer of propiolactone on poly-DL-alanine was made similarly but without added catalyst; it softened at 75 C and contained 3.7% nitrogen. Isatoic anhydride could not be polymerized with basic catalysts even at the boiling point of dioxane.

3,3-Bis(chloromethyl)oxetane (BCMO), supplied by courtesy of the Hercules Powder Company, was vacuum-distilled and then polymerized. In chloroform solution with boron trifluoride catalyst, polymer began to precipitate soon after the reaction had started. Kinetic measurements could be made at 100 C in *o*-dichlorobenzene containing 0.02 *M* boron trifluoride etherate; the rate proved to be of second order in BCMO, $k = 2.5 \times 10^{-2}$ 1. mole^{-1} min.$^{-1}$. A similar dependence on monomer concentration has been found for 3,3-dimethyloxetane, which is similar in structure, when boron trifluoride and water are present (Rose, 1956). It was shown that BCMO can be determined much like epoxides by reaction with excess dioxane-hydrobromic acid, etc. (*cf.* Jungnickel *et al.,* 1953) provided that reaction time before back-titration is at least eight hours. 2,2-Bis(iodomethyl)oxetane, prepared as described by Campbell (1957), was polymerized in *o*-dichlorobenzene by boron trifluoride etherate at room temperature. The product was a white powder melting at 252-55 C (Campbell observed 290 C). The reaction mixture was heterogeneous and no kinetic data were obtained.

2,2,4-Trimethyl-3-hydroxy-3-pentenoic β-lactone, supplied by the courtesy of Tennessee Eastman Corporation, could not be polymerized at the boiling point of acetonitrile by either triethylamine or triphenylmethylammonium methoxide catalyst.

Propylene sulfide was prepared according to a literature method (Dermer, 1956), and a method for determining it was developed. The sample was dissolved in an inert solvent and treated with excess acetyl chloride and a little BF_3 etherate in toluene for 8 hours or more; then the mixture was titrated with standard sodium methoxide in methanol and compared with an appropriate blank. Acid-catalyzed polymerization of propylene sulfide in methylene chloride did not proceed by rate-law of integral order, again presumably because of precipitation of polymer.

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