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Investigation of the Mechanism of Cationic Polymerization of ϵ-Caprolactone

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ABSTRACT

In the present study the kinetics of the cationic polymerization of lactones has been considered. The differences in basicities of a monomer and a polymer in various systems have been taken into account. The kinetic data on ϵ-caprolactone polymerization obtained have been discussed on the basis of the mechanism including the following reactions: 1) chain propagation; 2) reversible combination of the active centers by the carbonyl group of the monomer; and 3) reversible combination of the active centers by the carbonyl group of the polymer.

Despite the amount of data published in recent years, the mechanism of the cationic polymerization of lactons is far from clear. In particular, this is also true of the polymerization of ϵ-caprolactone (CL). The few works dealing with the mechanism of the polymerization of CL [1-3]*

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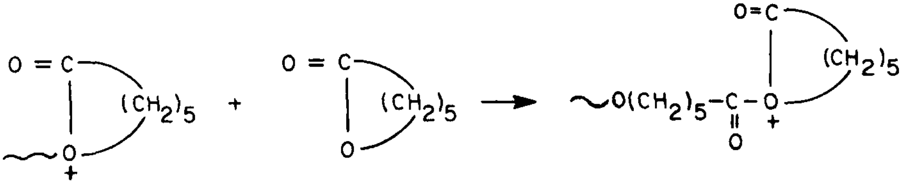
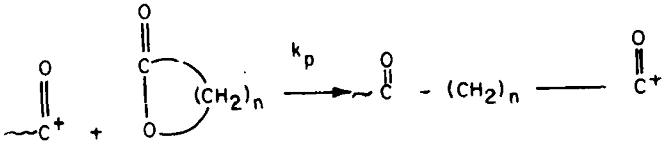
*After this paper had been prepared for publication, another paper on this subject appeared [7].

are chiefly devoted to the ability of CL to polymerize under the action of various initiators and to the molecular weights of polymers. The mechanism of the propagation reaction according to the S_N2 type, suggested by the authors,



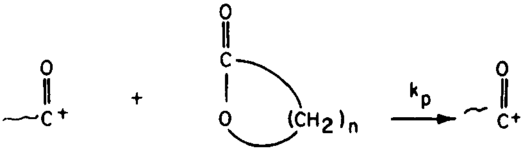
is based on its presumed analogy with that of the tetrahydrofuran polymerization.

The first papers in which the mechanism of the cationic polymerization of lactones were studied in detail by the kinetic method deal with the cationic polymerization of β-propiolactone (PL) [4-6]. Proceeding from the kinetic data, the authors came to the conclusion that polymerization is propagated by the acyl ion according to the reaction



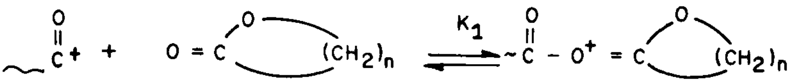
and that along with the propagation reaction there occurs in the system a reversible reaction that combines the active centers by carbonyl groups of the monomer and polymer molecules. The basic conclusions of the work, which amount to postulating these reactions, appear to be general in character. Taking into consideration the data in Refs. 4-6, the present paper gives a general analysis of possible cases of the polymerization of individual lactones with different ratios of basicity of the monomer and of the polymer chain, and investigates in detail the kinetics and mechanism of the polymerization of CL. In a system with rapid initiation, in which no kinetic chain termination reaction takes place, the major processes on the basis of the data obtained in Ref. 4 can be represented as follows (the counterion has been omitted for simplicity):

(1) Propagation:



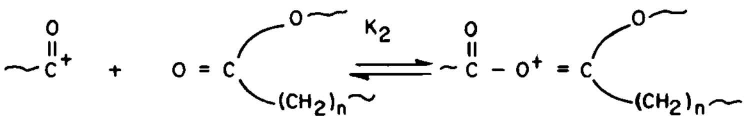
I

(2) Reversible combining of the active centers by the monomer molecules:



II

(3) Reversible combining of the active centers by the polymer molecules:



III

The equilibrium constants K_1 and K_2 equal P/xM and $Q/x(M_0 - M)$ respectively, where x is the concentration of the centers, M_0 and M are the initial and current concentrations of the monomer, respectively, and P and Q are the concentrations of the inactive ions formed according to Reactions II and III, respectively. Assuming that $x + P + Q = C$, where C is the initial concentration of the initiator, we find that

$$P + Q = K_1xM + K_2x(M_0 - M) = C - x$$

Hence

$$x = \frac{C}{K_1M + K_2(M_0 - M) + 1}$$

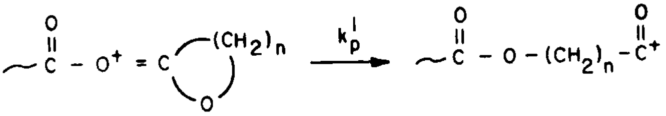
or, with sufficiently great values of constants K_1 and K_2,

$$x = \frac{C}{K_1M + K_2(M_0 - M)}$$

The rate of the process will be expressed as

$$-\frac{dM}{dt} = \frac{k_pCM}{K_1M + K_2(M_0 - M)} \qquad (1)$$

Equation (1) is a general one for the polymerization of lactones with different ratios of constants K_1 and K_2. It should be noted that the kinetic dependencies of lactone polymerization under the above conditions may also be described by a somewhat different scheme of reactions, namely, by Reactions II and III along with slow monomolecular reaction IV



IV

However, the schemes of processes I + II + III and II + III + IV are kinetically identical. Until new data are available, we shall follow the scheme I + II + III. Let us consider some possible cases.

1. $K_1 = K_2$ (the basicity of the monomer is equal to that of the polymer chain).

In this case, the polymerization rate will be expressed as

$$-\frac{dM}{dt} = \frac{k_p CM}{K_1 M_0} \tag{2}$$

It follows that in this case the initial rates are zero order in the monomer. In the course of the process, the rates are first order in the monomer. The concentration of the active centers remains unchanged during the polymerization. This is precisely the case in the polymerization of β-propiolactone [4-6].

2. $K_1 > K_2$ (the basicity of the monomer is greater than that of the polymer chain).

In this case the concentration of the active centers will rise in the course of the polymerization (substitution of a polymer for a monomer). The initial rates will be zero order, and the rates in the course of the process will be an order lower than the first one in the monomer. This corresponds to the theoretical case a in Fig. 1. In the extreme case ($K_1 \gg K_2$), the rate will be practically independent of the monomer concentration throughout the process:

$$-\frac{dM}{dt} = \frac{k_p C}{K_1} \tag{3}$$

3. $K_1 < K_2$ (the basicity of the monomer is smaller than that of the polymer chain).

In this case the concentration of the active centers will become lower in the course of polymerization. The initial rates will be zero order, and rates in the course of the process will be an order larger than the first one in the monomer. This corresponds to the theoretical

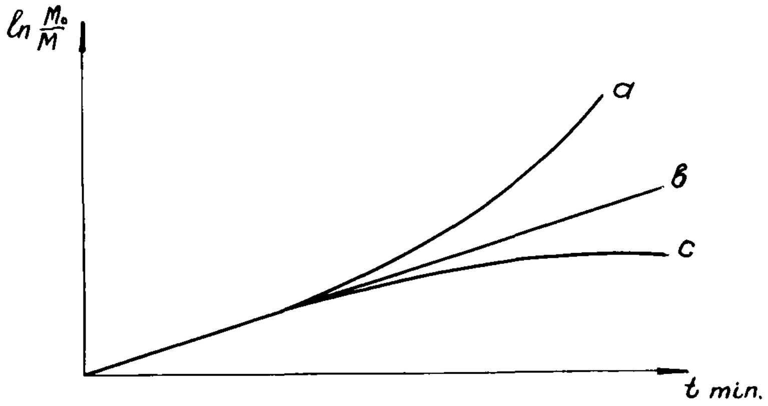


FIG. 1. Theoretical kinetic curves of lactone polymerization. (a) $K_1 > K_2$. (b) $K_1 = K_2$. (c) $K_1 < K_2$.

case c in Fig. 1. In the extreme case ($K_1 \ll K_2$), the rate will be directly proportional to the monomer/polymer ratio in the course of the process (from the moment when the first batch of the polymer is formed):

$$= \frac{dM}{dt} = \frac{k_pCM}{K_2(M_0 - M)} \qquad (4)$$

With the above in view, we will now consider the kinetics and the mechanism of the cationic polymerization of CL.

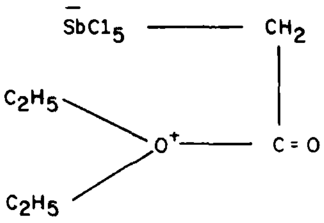
EXPERIMENTAL

CL was purified by long storage over calcium hydride, fractionally distilled under vacuum, and stored with 4,4-diphenylmethyldiisocyanate. Then it was redistilled under vacuum into dosing phials with thin-walled glass membranes, and from there it was vacuum-dosed into a dilatometer. The purity was chromatographically controlled.

Methylene chloride was shaken with concentrated sulfuric acid, washed off first with water and then with a 5% solution of NaOH, dried, and stored over CaH_2. It was condensed into the dilatometer through tubes with a metallic sodium wire.

The catalyst was synthesized according to the method described in Ref. 6 and vacuum dosed into thin-walled glass balls.

The kinetics of the process was studied dilatometrically. The



contraction determined in this work during the polymerization of CL amounted to 2.5%. The dilatometer was vacuum filled. The process proceeded up to 100% conversion. The polymer was dissolved in moist chloroform and precipitated by heptane.

KINETICS AND MECHANISM OF CATIONIC POLYMERIZATION OF CL

Figure 2 shows the kinetic curves of the polymerization of CL in semilogarithmic coordinates with the monomer concentration varying from 3 to 9.4 (bulk) mole/liter. As can be seen from Fig. 2, the initial rates do not depend on the monomer concentration, and in the course of the process the kinetic curves go upward from the straight line which corresponds to first order in monomer. Such a conversion curve shape corresponds to the case under examination (2) (Curve a, Fig. 1) and indicates that during polymerization the concentration of active centers rises owing to the more basic monomer replacement by a less basic polymer. In this case, the initial rates, according to formula I, are of zero order in monomer and can be determined from the expression

$$-\frac{dM_0}{dt} = \frac{k_pC}{K_1}$$

The ratio k_p/K_1 was found from this expression. Arrenius plots of these ratios, obtained at various temperatures (Fig. 3), give an effective activation energy of 22 ± 1 kcal/mole.

To determine the other parameters of the process, Eq. I, which describes the process, is put into integral form:

$$\ln\frac{M_0}{M} = \frac{K_1 - K_2}{K_2M_0}(M_0 - M) + \frac{k_pC}{K_2M_0}t$$

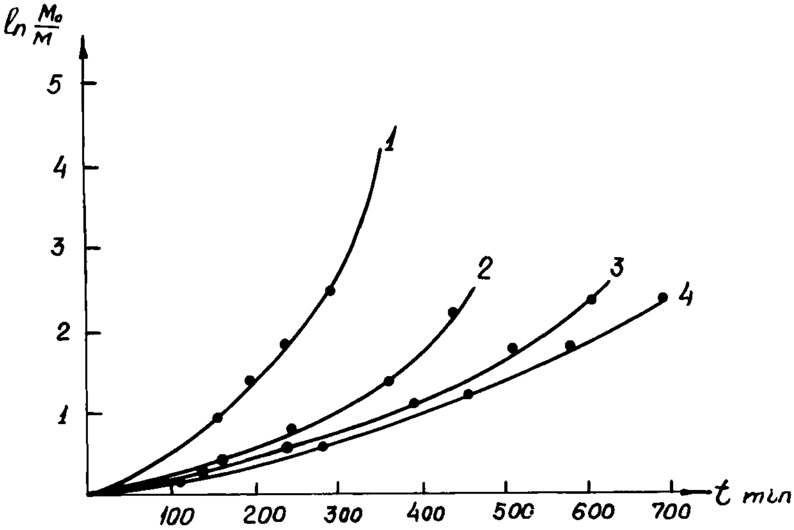


FIG. 2. Kinetic curves of ε-CL polymerization at various monomer concentrations; t = 50°C; C = 0.04 mole/liter. M_0: (1) 3 moles/liter; (2) 4.36 moles/liter; (3) 6.35 moles/liter; (4) 7.52 moles/liter.

or

$$\frac{M_0}{Ct}\ln\frac{M_0}{M} = \frac{k_p}{K_2} - \frac{K_1 - K_2}{K_2}\,\frac{M_0 - M}{Ct} \tag{5}$$

According to Eq. (5), when the above mechanism is valid, the process in coordinates

$$\frac{M_0}{Ct}\ln\frac{M_0}{M} - \frac{M_0 - M}{Ct}$$

will be characterized by straight lines with a negative slope toward the abscissa. The kinetic data of the polymerization of CL at 50°C are given in Fig. 4 in the above coordinates (the points obtained both in one run and in various runs are plotted). The appearance of the anticipated linear dependence is indicative that the suggested mechanism is correct. The slope and intersept of this straight line (Fig. 4) makes it possible to determine the ratio of constants K_1/K_2 as 3.6 ± 0.3 (50°C).

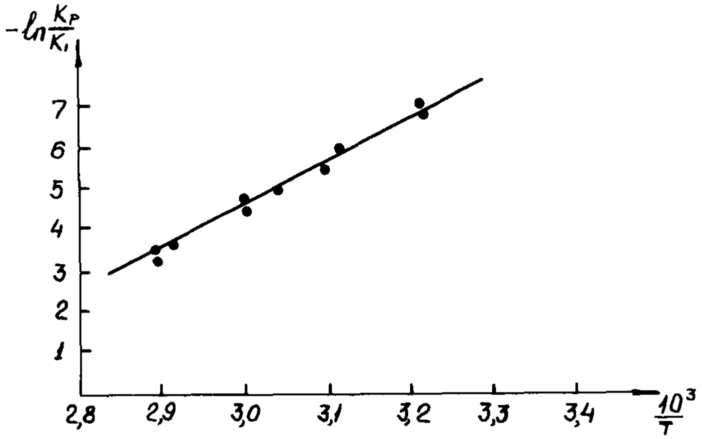


FIG. 3. Temperature dependence of $\ln(k_p/K_1)$.

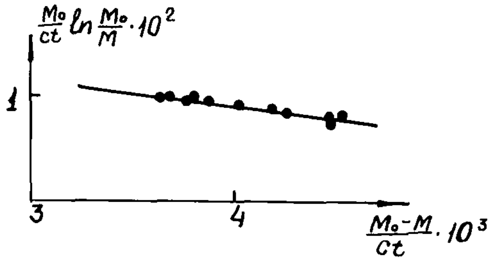


FIG. 4. Kinetic data of ϵ-CL polymerization calculated from Eq. (5) at 50°C.

The above kinetic regularities of CL polymerization were derived by varying the monomer concentration from 3 to 9.4 mole/liter. From the results obtained in this range of concentrations, it becomes obvious that the initial rates do not depend on the initial monomer concentration. This agrees well with the mechanism proposed. However, such a dependence does appear at monomer concentrations lower than 3 mole/liter. Figure 5 gives the initial rates of the process as a function of the monomer concentration. The increase in the rate with a rise in the concentration of the monomer thus observed may be due to the change in the dielectric constant of the medium with that of the monomer concentration. A similar phenomenon was recorded in the polymerization

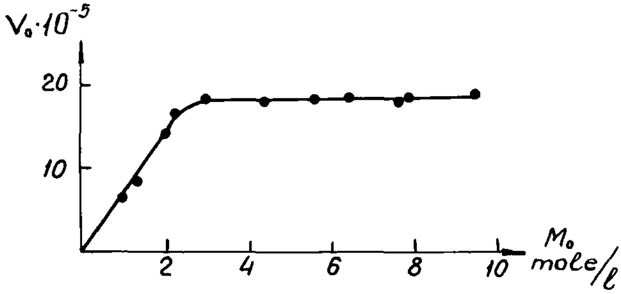
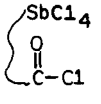


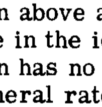
FIG. 5. Dependence of initial rate of ϵ-CL polymerization on the monomer concentration. C = 0.04 mole/liter; t = 50°C.

of PL, the bend observed on the curve of the initial rates dependence on M_0 being in the region of 2 mole/liter at 20°C [6]. As shown in the instance of PL [6], the replacement of methylene chloride by a more polar solvent, nitrobenzene (with a quantitative record of its donor properties), leads to the elimination of the rate dependence on M_0 in the range of low monomer concentrations. As in the case of PL, it may be assumed that the effect of the dielectric constant of the medium on the process is related to the possible existence of a growing end of the chain in two forms: ionic (active)



$$\mathrm{SbCl_5^-}\quad \mathrm{CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{}^{+}}$$

and nonionic (inactive)



$$\mathrm{SbCl_4}\quad \mathrm{\overset{\overset{\displaystyle O}{\|}}{C}{-}Cl}$$

the relationship between them being determined by the dielectric constant of the medium. It is evident that in the case of a polar monomer and a solvent of a medium polarity, with the monomer concentration above a certain limit, practically all the growing ends of the chain are in the ionic form, and a further change in the monomer concentration has no effect on their concentration and, consequently, on the general rate of the process.

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