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Cationic Polymerization of Cyclic Dienes. VII.* The Kinetic Observations on the Polymerization of 1,3-Cyclohexadiene

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SUMMARY

1, 3-Cyclohexadiene was polymerized at 0°C in methylene chloride or benzene using boron trifluoride etherate or stannic chloride-trichloroacetic acid as catalyst. The former catalyst led to a stationary-state polymerization but the latter brought about a nonstationary-state polymerization in which the initiation reaction was very fast. The very fast initiation reaction is a consequence of a strong interaction between the monomer and the metal halide. Part of the added catalysts was made inactive by the interaction with the excess monomers.

1, 3-Cyclohexadiene was polymerized more slowly than cyclopentadiene under comparable conditions. This was accounted for mainly by the different stabilities of the cycloalkenyl cations.

Poly(1, 3-cyclohexadiene) was of low molecular weight ($[\eta] = 0.04 \sim 0.12$). The effect of the polymerization condition on the molecular weight was studied and was explained in terms of a stationary-state kinetics with the boron trifluoride etherate system and in terms of a nonstationary-state kinetics with the stannic chloride-trichloroacetic acid system.

INTRODUCTION

During the course of our study on the cationic polymerization of cyclic dienes, kinetic investigations on the homopolymerization

*For the previous paper of this series, see Ref. [1].

and the copolymerization of cyclopentadiene (CPD) [1, 2] and methylcyclopentadiene [3] have been performed. These five-membered cyclic dienes were found to be very reactive in cationic polymerization, and their high reactivity was explained in terms of the high stability of cyclopentenyl cations [2c]. Here, the work was extended to 1, 3-cyclohexadiene (CHD) to study the effect of ring size on the reactivity of cyclic diene. This paper describes the kinetics of the cationic polymerization of CHD.

EXPERIMENTAL

Materials

CHD was synthesized according to the method of Marvel and Hartzell [4]. Crude CHD was washed with 3N HCl and water, dried with anhydrous MgSO_4 , and distilled twice from metal sodium. It was redistilled from CaH_2 just before use (bp = 79.2 ~ 79.5°C, $n_D^{27} = 1.4740$). The purity of CHD was proved to be 96.9% by gas chromatography (conditions: dinonyl phthalate, 1.5 m; plus polyethylene glycol 400, 1.5 m; 60°C). It contained cyclohexene (1.7%) and benzene (1.4%) as impurities. It was found that the composition of CHD prepared by the present method changed with time when stored at 0°C. After 12 days the composition was CHD 94.4%, cyclohexene 2.6%, and benzene 3.0%. It seems that a certain disproportionation reaction takes place. Therefore, CHD was used for the polymerization soon after the preparation.

Benzene, methylene chloride, stannic chloride (SnCl_4), and boron trifluoride etherate ($\text{BF}_3 \cdot \text{OEt}_2$) were purified as usual. Trichloroacetic acid (TCA) (guaranteed reagent) was used without further purification.

Procedures

Polymerizations were performed in a glass apparatus as described in earlier papers [2, 3]. The conversion of monomer to polymer was determined either by the weight of polymer formed or by the amount of the residual monomer measured by gas chromatography (conditions the same as for the purity of CHD).

The intrinsic viscosities of polycyclohexadiene (PCHD) were measured in toluene solution at 30°C. Molecular weights of a few samples were determined with an ebulliometer.

RESULTS

Kinetic Measurements on the Polymerization Rate of CHD

The polymerization of CHD in benzene proceeded completely homogeneously. In methylene chloride, however, the polymerization

solution was not completely homogeneous because the polymer produced was dissolved into methylene chloride only with difficulty. All polymerization systems studied turned yellow upon the addition of monomer to the catalyst solution. The color deepened until it became dark red at higher conversions. When the polymerization solution was discharged to a large amount of methanol, the color disappeared immediately and white, fine powder of PCHD was obtained. PCHD was soluble in common organic solvents but insoluble in methanol, acetone, and ether.

The conversion of monomer into polymer determined by gravimetry was in good agreement with that determined by gas chromatography, as illustrated in Table 1. In the present investigation the conversion was determined by gravimetry, unless otherwise stated.

Polymerization with SnCl_4 -TCA. Polymerizations of CHD with SnCl_4 -TCA were carried out in benzene or in methylene chloride at 0°C . Figure 1 shows the effect of the catalyst concentration on the rate of polymerization in methylene chloride, while the concentration of monomer was kept constant. As shown in the figure, the polymerization rate increased with increasing catalyst concentration, but the rate of polymerization was quite large only at the start of polymerization and fell off quickly toward the end. Sometimes the polymerization stopped before all monomers were consumed. A very similar situation occurred in polymerization in benzene except that polymerization was much slower in benzene than in methylene chloride.

The effects of monomer concentration on the rate of polymerization were investigated, keeping the catalyst concentration constant. Figure 2 shows the results observed in methylene chloride. Here again, the leveling-off phenomenon of the conversion-time curve was observed. Very similar conversion-time curves also were observed in benzene.

The first-order plot of the conversion-time curve, which is not shown here, showed that the polymerization of CHD by SnCl_4 -TCA was a nonstationary-state polymerization, in which the polymerization was started with a very rapid initiation reaction.

The leveling-off phenomenon of the conversion-time curve is not due to the consumption of monomer or cocatalyst, but rather

Table 1. Conversions of Monomer Determined by Gravimetry and Gas Chromatography^a

Polymerization time, min	1	5	10	20	30	60	98	232
Conversion by gravimetry, %	1	13	31	44	49	54	56	60
Conversion by gas chromatography, %	1	14	32	45	50	54	56	59

^aPolymerization condition: Solvent, benzene; temperature, 0°C , $[\text{M}]_0$, 1.05 mole/liter; $[\text{SnCl}_4]_0 = 1.54$ mmole/liter; $[\text{SnCl}_4]_0/[\text{TCA}]_0 = 1.0$.

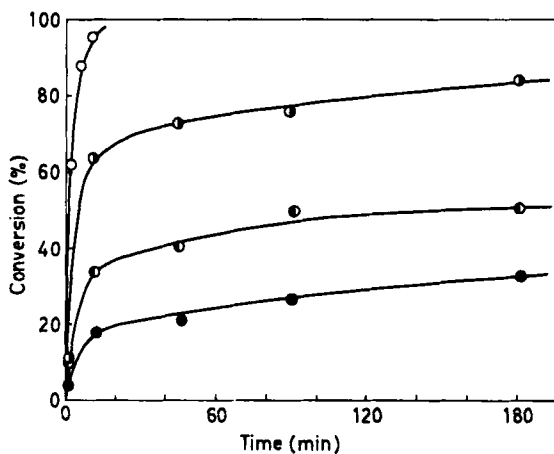


Fig. 1. Time-conversion curves for the polymerization of cyclohexadiene by stannic chloride-trichloroacetic acid in methylene chloride at 0°C. The effect of catalyst concentration. $[M]_0$, 1.05 mole/liter; $[H_2O]_0$, 4.5 mmole/liter; $[C]_0$, ○: 11.5 mmole/liter, ●: 5.8 mmole/liter, ◐: 3.8 mmole/liter, ◑: 1.9 mmole/liter.

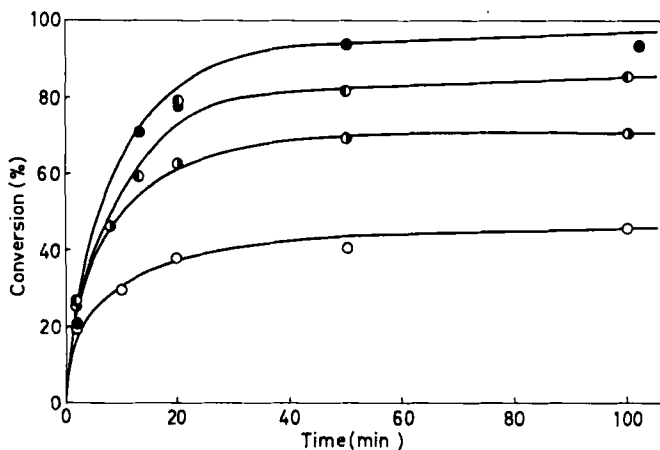


Fig. 2. Time-conversion curves for the polymerization of cyclohexadiene by stannic chloride-trichloroacetic acid in methylene chloride at 0°C. The effect of monomer concentration. $[C]_0$, 5.8 mmole/liter; $[H_2O]_0$, 2.8-3.1 mmole/liter; $[M]_0$, ○: 2.63 mole/liter, ◐: 1.58 mole/liter, ◑: 1.05 mole/liter, ●: 0.53 mole/liter.

to the consumption of SnCl_4 . The following experimental results support this conclusion. (i) The presence of CHD in the dormant polymerization solution was confirmed by gas chromatography (see, for example, Table 1). In every case the sum of the monomer reacted (weight of polymer) and the residual monomer (gas chromatography) was exactly equal to the initial monomer concentration. (ii) When a relatively large amount of SnCl_4 was used, the polymerization went to completion (see Fig. 1). The addition of SnCl_4 to the dormant solution reinitiated the polymerization, while the addition of TCA had no effect (see Fig. 3).

Another interesting point should be noted in Fig. 2. The final conversion was lower, as the initial monomer concentration was higher. As will be seen later, this inversion phenomenon was not observed with $\text{BF}_3 \cdot \text{OEt}_2$. Therefore, some of the SnCl_4 initially added must have reacted with CHD and been converted into inactive species. To test this possibility, CHD was treated with an equimolar amount of SnCl_4 under several conditions. From the reaction product a fraction boiling at 107°C was collected. It showed a single peak at $t_R = 23$ min in gas chromatography, while CHD showed a peak at $t_R = 8$ min. This product was recovered only when SnCl_4 was used, and it may be related to the catalyst deactivation. It contained a fairly high percentage of chlorine (20-30%) and Sn, but the elemental analysis for chlorine was scattered because of the instability of the substance and the presence of Sn. It was proved to be acidic, that is, 1 ml was equivalent to 5.89 mmoles NaOH. At 0°C it polymerized *n*-butyl vinyl ether, but it was inactive for the polymerization of CHD.

To conclude, SnCl_4 , but not $\text{BF}_3 \cdot \text{OEt}_2$, reacts with CHD to give an acidic substance. It is less acidic than SnCl_4 itself and incapable

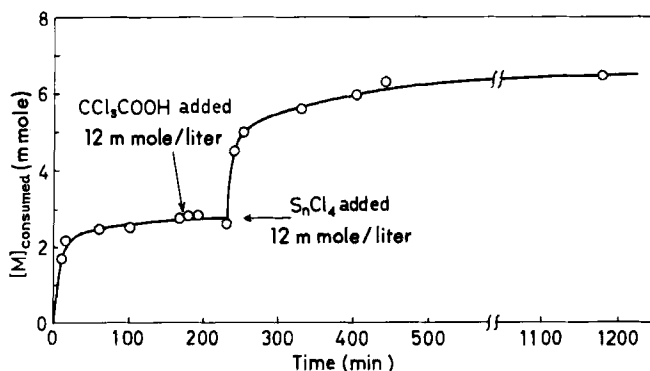


Fig. 3. Effect of the addition of catalyst or cocatalyst on the polymerization of cyclohexadiene by stannic chloride-trichloroacetic acid in benzene at 0°C . $[\text{M}]_0$, 2.1 mole/liter; $[\text{C}]_0$, 8.0 mmole/liter.

of polymerizing CHD. The higher the concentration of CHD, the more SnCl_4 is converted into the less acidic species, thus lowering the final conversion.

In the present investigation, the mole ratio of TCA against SnCl_4 was kept at unity. To check the effect of the TCA/ SnCl_4 ratio on the polymerization, polymerizations were carried out at several TCA/ SnCl_4 ratios ranging from 0 to 2. The conversion-time curves are shown in Fig. 4. It is obvious that the rate of polymerization increases sharply with increasing TCA/ SnCl_4 mole ratio. The intrinsic viscosities of PCHD, however, were independent of the concentration of TCA. The conversion-time curve for 1:1 SnCl_4 /TCA catalyst system is indicative, in particular, of a nonstationary-state polymerization mentioned above.

It was found that water has a deleterious effect on the polymerization rate, although only a few experiments were made on the effect of water.

Polymerization with $\text{BF}_3 \cdot \text{OEt}_2$. Polymerizations of CHD with $\text{BF}_3 \cdot \text{OEt}_2$ were carried out in benzene or methylene chloride at 0°C . Figure 5 shows the conversion-time curves for the polymerization in benzene, in which the monomer concentration was kept constant and the catalyst concentration was varied. In methylene chloride, very similar conversion-time curves were obtained except that polymerization was much faster. In $\text{BF}_3 \cdot \text{OEt}_2$ -catalyzed polymerization, the conversion-time curve approached 100% conversion without leveling off as in SnCl_4 -TCA-catalyzed polymerization.

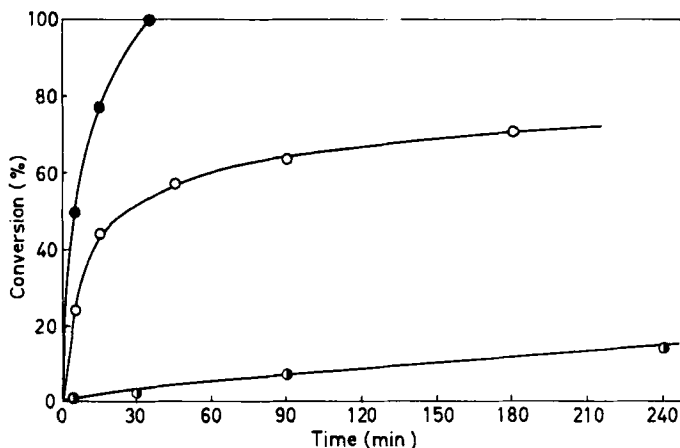


Fig. 4. Effect of the composition of catalyst on the polymerization of cyclohexadiene by stannic chloride-trichloroacetic acid in benzene at 0°C . $[\text{M}]_0$, 1.05 mole/liter; $[\text{C}]_0$, 15.4 mmole/liter; $[\text{H}_2\text{O}]_0$, 1.2 mmole/liter; $[\text{SnCl}_4]_0/[\text{CCl}_3\text{COOH}]_0$, ●: 1/0, ○: 1/1, ◐: 1/2. $[\eta]$ at the highest conversions are: ●: 0.051, ○: 0.057, ◐: 0.059.

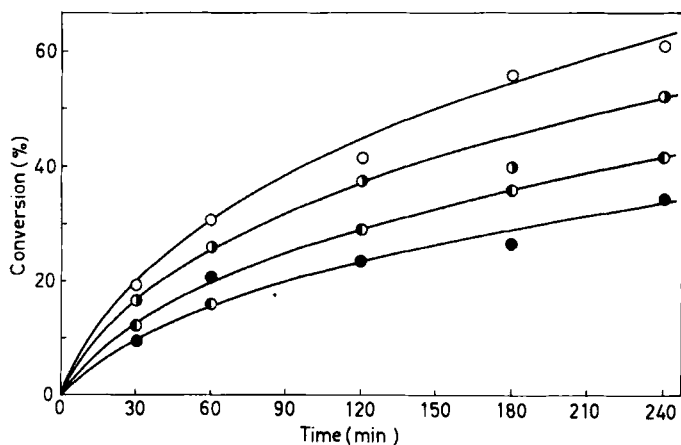


Fig. 5. Time-conversion curves for the polymerization of cyclohexadiene by boron trifluoride etherate in benzene at 0°C. The effect of catalyst concentration. $[M]_0$, 1.05 mole/liter; $[H_2O]_0$, 3.4 mmole/liter; $[C]_0$, ○, 58.7 mmole/liter, ○●, 46.9 mmole/liter, ●●, 35.2 mmole/liter, ●, 23.5 mmole/liter.

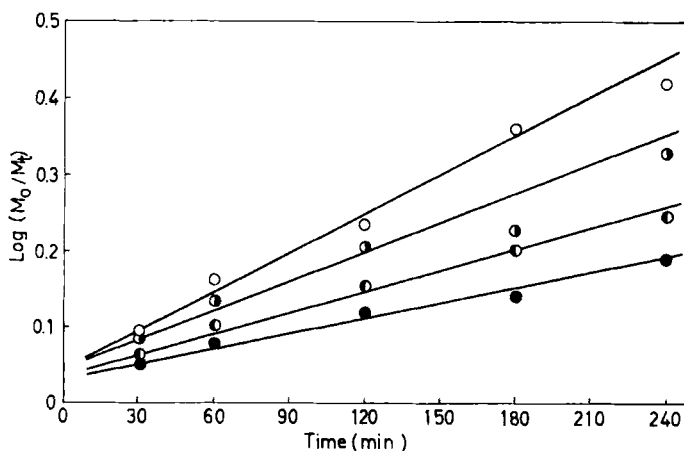


Fig. 6. First-order plot of the overall rate of polymerization by boron trifluoride etherate in benzene at 0°C. Notation is the same as in Fig. 5.

The first-order plot of Fig. 5 is shown in Fig. 6. A linear relationship was found between $\log ([M]_0/[M]_t)$ and time, and this implies that the stationary-state concentration of the growing species is established over a wide range of conversion except at the very beginning of polymerization. This is in marked contrast to SnCl_4 -TCA-catalyzed polymerization.

The slopes of the straight lines in Fig. 6 were plotted against the catalyst concentrations. Figure 7 shows that the overall rate of polymerization (R_p) is proportional to the catalyst concentration. In methylene chloride the same relationship as in benzene was found, as shown in Fig. 7.

The effect of varying monomer concentration on the conversion-time curve was investigated, keeping the catalyst concentration constant. Figure 8 shows the results in benzene. A single conversion-time curve was drawn for different initial monomer concentrations. This means that the overall rate of polymerization is proportional to monomer concentration. In methylene chloride the same relationship was also observed, as shown in Fig. 8. From Figs. 7 and 8, the kinetic equation for the overall rate of polymerization catalysed by $\text{BF}_3 \cdot \text{OEt}_2$ can be expressed as $R_p = k[M][C]$.

$$k = 0.2 \pm 0.05 \text{ liter/mole min, in } \text{CH}_2\text{Cl}_2, 0^\circ\text{C}$$

$$k = 0.03 \pm 0.003 \text{ liter/mole min, in benzene, } 0^\circ\text{C}$$

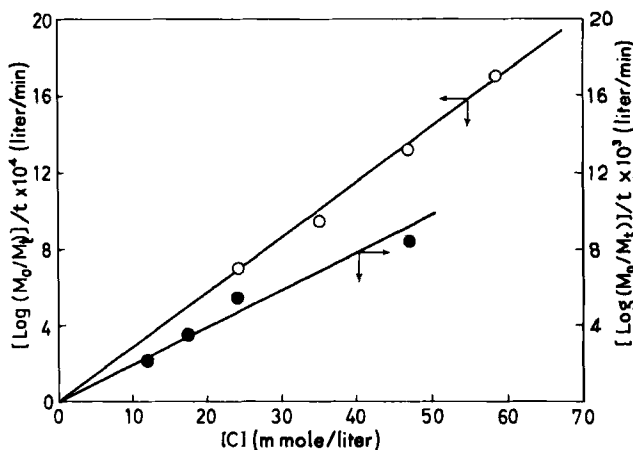


Fig. 7. Plot of $\log (M_0/M_t)/t$ vs catalyst concentration. \circ : Boron trifluoride etherate-benzene- 0°C system. $[M]_0$, 1.05 mole/liter. Slope = $k = 0.03 \pm 0.003$ liter mole⁻¹ min⁻¹. \bullet : Boron trifluoride etherate-methylene chloride- 0°C system. $[M]_0$, 1.05 mole/liter. Slope = $k = 0.2 \pm 0.05$ liter mole⁻¹ min⁻¹.

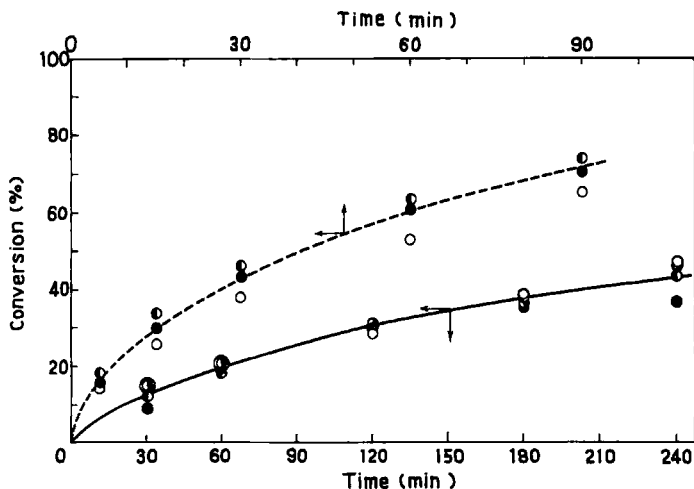


Fig. 8. Time-conversion curve for the polymerization of cyclohexadiene by boron trifluoride etherate at 0°C . The effect of monomer concentration. $[\text{M}]_0$, mole/liter: \circ , 2.10; \bullet , 1.58; \odot , 1.05; \ominus , 0.53. —: Benzene as solvent. $[\text{C}]_0$, 35.2 mmole/liter; $[\text{H}_2\text{O}]_0$, 3.2-3.4 mmole/liter. ----: Methylene chloride as solvent. $[\text{C}]_0$, 23.5 mmole/liter; $[\text{H}_2\text{O}]_0$, 2.6-2.7 mmole/liter.

It was found that water has a deleterious effect on the polymerization rate, although only a few experiments were made on the effect of water.

Molecular Weight of Polycyclohexadiene

The influence of the polymerization condition on the polymer intrinsic viscosity was investigated. It was established at first that in $\text{BF}_3 \cdot \text{OEt}_2$ -catalyzed polymerization the intrinsic viscosity of polymer was almost independent of conversion. In SnCl_4 -TCA-catalyzed polymerization the intrinsic viscosity of polymer, which was recovered from the polymerization solution after the final conversion was reached, was measured. The effect of the initial monomer concentration on the intrinsic viscosity of polymer was investigated, and the experimental data are shown in Fig. 9. It was found that the intrinsic viscosity of polymer increased with the increment of the initial monomer concentration, that in methylene chloride solution polymers of higher viscosity were produced than in benzene solution, and that apart from the effect of catalyst concentration (see below) $\text{BF}_3 \cdot \text{OEt}_2$ produced PCHD of higher viscosity than SnCl_4 -TCA.

The effect of catalyst concentration on polymer viscosity is noteworthy. The experimental results are shown in Fig. 10, where the

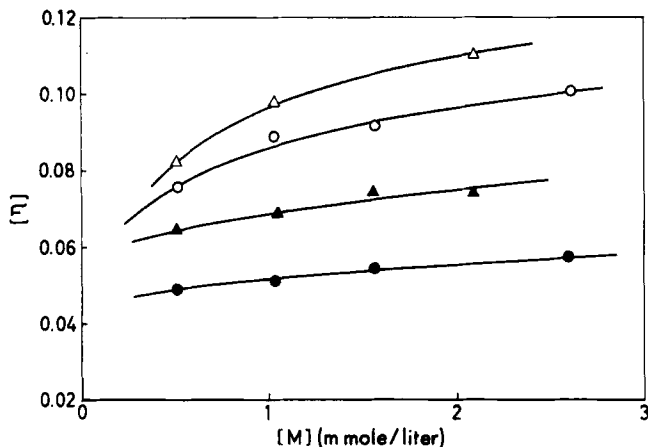


Fig. 9. Effect of monomer concentration on the intrinsic viscosities of polycyclohexadiene. O: $\text{SnCl}_4 \cdot \text{CCl}_3\text{COOH}-\text{CH}_2\text{Cl}_2-0^\circ\text{C}$, $[\text{C}]_0 = 5.8$ mmole/liter. ●: $\text{SnCl}_4 \cdot \text{CCl}_3\text{COOH}-\text{C}_6\text{H}_6-0^\circ\text{C}$, $[\text{C}]_0 = 15.4$ mmole/liter. Δ: $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2-\text{CH}_2\text{Cl}_2-0^\circ\text{C}$, $[\text{C}]_0 = 23.5$ mmole/liter. ▲: $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2-\text{C}_6\text{H}_6-0^\circ\text{C}$, $[\text{C}]_0 = 35.2$ mmole/liter.

viscosity of polymer produced with $\text{BF}_3 \cdot \text{OEt}_2$ is found to increase slightly with the increment of the catalyst concentration, while that with SnCl_4 -TCA is found to decrease with the increment of the catalyst concentration.

In the $\text{BF}_3 \cdot \text{OEt}_2$ -catalyzed system the polymer viscosity decreased with increasing water concentration. In SnCl_4 -TCA-catalyzed polymerization, however, water had very little effect on the polymer viscosity.

The intrinsic viscosity of polymer increased with lower polymerization temperature. The polymer prepared in SnCl_4 -TCA-methylene chloride system at -78°C had an intrinsic viscosity of 0.12.

DISCUSSION

CHD has been said to be a less reactive monomer in cationic polymerization [5]. In fact, only a low molecular weight PCHD has been synthesized in cationic and anionic polymerizations, with the exception that *n*-butyl lithium gives PCHD having $[\eta] = 0.2$ [5]. However, the present investigation on the cationic polymerization of CHD demonstrated that CHD is so reactive that it brings about a fast initiation reaction with SnCl_4 -TCA, although the molecular weight of polymer remained low. Cationic copolymerization of CHD indicated that CHD was almost as reactive as isobutene [2b]. The high reactivity of CHD may be ascribed to the stability of a cyclo-

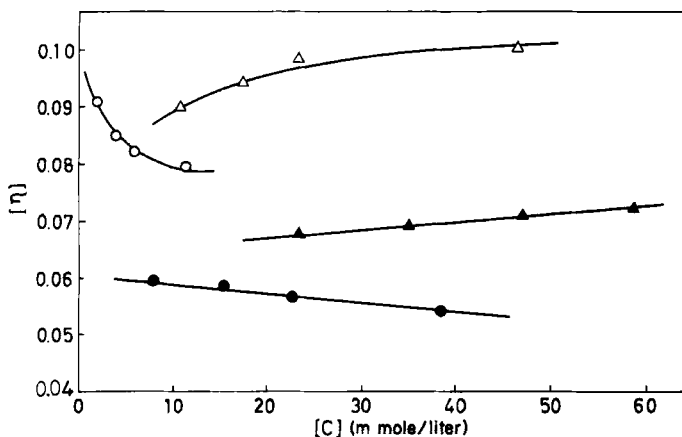


Fig. 10. Effect of catalyst concentration on the intrinsic viscosities of polycyclohexadiene. $[M]_0$, 1.05 mole/liter. ○: $\text{SnCl}_4 \cdot \text{CCl}_3\text{COOH}-\text{CH}_2\text{Cl}_2-0^\circ\text{C}$. ●: $\text{SnCl}_4 \cdot \text{CCl}_3\text{COOH}-\text{C}_6\text{H}_6-0^\circ\text{C}$. △: $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2-\text{CH}_2\text{Cl}_2-0^\circ\text{C}$. ▲: $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2-\text{C}_6\text{H}_6-0^\circ\text{C}$.

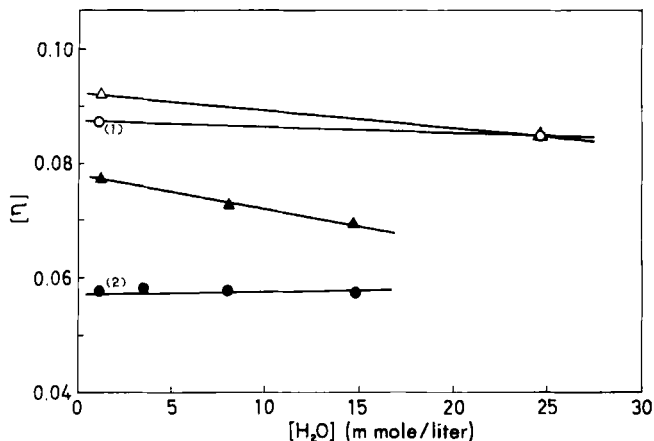


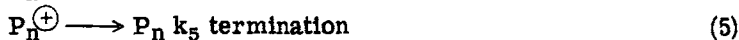
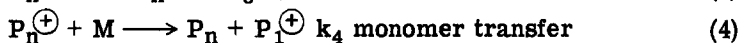
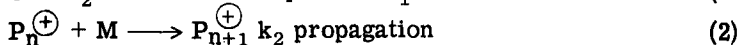
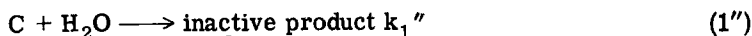
Fig. 11. Effect of water concentration on the intrinsic viscosities of polycyclohexadiene. $[M]_0$, 1.05 mole/liter. ○: $\text{SnCl}_4 \cdot \text{CCl}_3\text{COOH}-\text{CH}_2\text{Cl}_2-0^\circ\text{C}$, $[C]_0 = 5.8$ mmole/liter. ●: $\text{SnCl}_4 \cdot \text{CCl}_3\text{COOH}-\text{C}_6\text{H}_6-0^\circ\text{C}$, $[C]_0 = 15.4$ mmole/liter. △: $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2-\text{CH}_2\text{Cl}_2-0^\circ\text{C}$, $[C]_0 = 23.5$ mmole/liter. ▲: $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2-\text{C}_6\text{H}_6-0^\circ\text{C}$, $[C]_0 = 35.2$ mmole/liter. Polymer (1): $\bar{M}_n = 3000$ by ebulliometer, Polymer (2): $\bar{M}_n = 2200$ by ebulliometer.

hexenyl cation. The pK_a value of a cyclohexenyl cation could be -10.2 [6, 7], which is much larger than -15.5 for a *t*-butyl cation [6].

On the other hand, the reactivity of CHD is much lower than that of CPD. This difference may be explained partly in terms of the cation stability. A higher stability of cycloopenyl cation as compared with cyclohexenyl cation has been shown by Deno et al. [7-9]. The monomer reactivity difference may be partly due to a steric factor. In a cyclohexene unit, C_4 and C_5 atoms deviate from a plane [10], and an enchainment of a CHD monomer into a PCHD chain may suffer much steric hindrance. A similar explanation has been given for the polymerization of internal olefins [11].

Since an NMR study of PCHD showed that polymerization conditions had little influence on the structure of polymer [12], we can discuss the effect of polymerization conditions on the polymerization kinetics without distinguishing 1, 2-type and 1, 4-type propagation reactions. The most interesting feature found in the cationic polymerization of CHD is the fact that $SnCl_4$ -TCA gives rise to a non-stationary-state polymerization and the final conversion was inversely proportional to the initial monomer concentration, while $BF_3 \cdot OEt_2$ caused a stationary-state polymerization.

To explain the kinetic observations, we put forward the following elementary reactions:



In the above, the notations are those usually employed. x in Eq. (1) represents the molecularity of the initiation reaction with reference to monomer. Attempts to determine x in the $SnCl_4$ -TCA-catalyzed system have been unsuccessful.

In the $SnCl_4$ -TCA-catalyzed system, it was stipulated that reactions (1), (1'), and (1'') are fastest among the elementary reactions and compete with each other. Thus we can derive Eqs. (6) and (7) for the final conversion Y and the degree of polymerization (\bar{P}_n). The mathematical derivation was made similarly to that reported for the polymerization of CPD [2c].

$$Y = 1 - \frac{[M]_{\infty}}{[M]_0} = \left\{ 1 + \frac{k_3}{(k_2 + k_4)[M]_0} \right\} \left\{ 1 - \exp \frac{-(k_2 + k_4)[C]_e}{k_5 + k_5' [H_2O]} \right\} \quad (6)$$

$$\frac{1}{\bar{P}_n} = \frac{k_4}{k_2 + k_4} + \frac{k_2 k_3 + (k_2 + k_4)(k_5 + k_5' [H_2O])}{(k_2 + k_4)(k_5 + k_5' [H_2O])([M]_0 - [M]_{\infty})} [C]_e \quad (7)$$

where $[M]_{\infty}$ represents the residual monomer concentration at a final conversion, and $[C]_e$ stands for the real concentration of catalyst available for the initiation reaction and is given by Eq. (8).

$$[C]_e = \frac{k_1 [M]_0^x}{k_1 [M]_0^x + k_1' [M]_0^{x+1} + k_1'' [H_2O]} [C]_0 \quad (8)$$

Equations (6) and (7) explain the effects of polymerization conditions on Y and \bar{P}_n satisfactorily.

When highly electrophilic Lewis acids such as SnCl_4 and TiCl_4 are used in combination with very nucleophilic cyclic dienes such as CPD and CHD, the time-conversion curves seem peculiar. However, they are explained on the same basis that cyclic dienes interact strongly with metal halides and a very fast initiation reaction and some catalyst deactivation takes place. This is the most distinguished feature in the cationic polymerization of cyclic dienes by strong catalysts.

To explain the experimental results observed in the $\text{BF}_3 \cdot \text{OEt}_2$ -catalyzed system, the establishment of the stationary concentration of the chain carrier was assumed. If the initiation reaction, Eq. (1), does not involve monomer, we can derive the following equations for the rate of polymerization and \bar{P}_n ,

$$\frac{-d[M]}{dt} = \frac{k_1(k_2 + k_4)[M][C]}{k_5 + k_5' [H_2O]} \quad (9)$$

$$\frac{1}{\bar{P}_n} = \frac{k_4}{k_2} + \frac{k_3 + k_5 + k_5' [H_2O]}{k_2[M]} \quad (10)$$

where reactions (1') and (1'') were ignored.

Equations (9) and (10) explain the effects of polymerization conditions on the rate and \bar{P}_n . As was described in the preceding section, polymer viscosity increased with catalyst concentration in the $\text{BF}_3 \cdot \text{OEt}_2$ -catalyzed system. This could be explained in terms of chain branching. However, as will be seen in a subsequent paper [12], catalyst concentration does not seem to affect the chain branching. So this problem is left to be solved.

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