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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Imanishi, Yukio , Kohjiya, Shinzo and Okamura, Seizo(1968) 'Cationic Polymerization of Cyclic Dienes. IV. Polymerizations of Cyclopentadiene with Stannic Chloride-Trichloroacetic Acid and Borontrifluoride Etherate', *Journal of Macromolecular Science, Part A*, 2: 3, 471 – 487

To link to this Article: DOI: 10.1080/10601326808051425

URL: <http://dx.doi.org/10.1080/10601326808051425>

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Cationic Polymerization of Cyclic Dienes. IV. Polymerizations of Cyclopentadiene with Stannic Chloride-Trichloroacetic Acid and Borontrifluoride Etherate

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SUMMARY

Cyclopentadiene has been polymerized with $\text{SnCl}_4\text{-CCl}_3\text{CO}_2\text{H}$ or $\text{BF}_3\text{-O}(\text{C}_2\text{H}_5)_2$ in toluene solution at -78°C . In the polymerization induced by $\text{SnCl}_4\text{-CCl}_3\text{CO}_2\text{H}$, it was found that two different types of polymerizations coexisted. At first the polymerization was very rapid and of nonstationary state, but toward the end it was slow and of stationary state. As the majority of monomers initially present was consumed during the nonstationary-state polymerization, intrinsic viscosities of resultant polymer showed the behavior characteristic of nonstationary-state polymerization, such as (1) they decreased with increasing catalyst concentration, and (2) they were affected very little by the water concentration. The polymerization induced by $\text{BF}_3\text{-O}(\text{C}_2\text{H}_5)_2$ was much slower than that by $\text{SnCl}_4\text{-CCl}_3\text{CO}_2\text{H}$, but it was found to be of nonstationary state. However, it was nearly stationary-state polymerization, except for the very beginning of the polymerization. This was reflected in the behavior of polymer intrinsic viscosities—such as (1) they were unaffected by the catalyst concentration, and (2) they were lowered with increasing the water concentration. Taking into account these experimental findings as well as those found in the polymerization by $\text{TiCl}_4\text{-CCl}_3\text{CO}_2\text{H}$, a tentative mechanism was proposed for the initiation reaction of cyclopentadiene polymerization, in which a reaction order among a monomer, a catalyst, and a cocatalyst is important in determining the mechanism.

INTRODUCTION

In the 1920s Staudinger and Bruson [2] studied the polymerization of cyclopentadiene (CPD) with a number of metal halides and found that CPD was polymerized to a rubbery polymer under some selected conditions. Since then several investigations have been carried out on the polymerization of CPD, but few investigations have been made on the polymerization mechanism of CPD. We have made a series of investigations on the polymerization mechanism of cyclic dienes [1]. The polymerization of CPD with titanium tetrachloride (TiCl_4)-trichloroacetic acid (TCA) has been reported [3], and investigation of the cationic polymerization of methylcyclopentadiene [4] and cyclohexadiene [5] has been completed. Consequently, it was found that in the polymerizations of CPD with TiCl_4 -TCA and cyclohexadiene with stannic chloride (SnCl_4)-TCA, the initiation reaction was so fast that nonstationary-state polymerization was achieved, but that in the polymerization of cyclohexadiene with borontrifluoride etherate ($\text{BF}_3\text{-OEt}_2$) stationary-state concentration of the growing species was established. To elucidate the factor determining the stationary or nonstationary character of cyclic diene polymerization, we extended our work to the polymerizations of CPD with SnCl_4 -TCA and $\text{BF}_3\text{-OEt}_2$. This paper will describe about the interesting but complicated kinetic features observed in these polymerization systems and the importance of the catalyst to determine the stationary-state character of the polymerization system.

EXPERIMENTAL

Reagent

CPD was obtained by the pyrolysis of dicyclopentadiene. Dicyclopentadiene was washed with aqueous potassium carbonate solution, water, dilute hydrochloric acid, and finally water, dried overnight with anhydrous sodium sulfate, and distilled in vacuo several times. Dicyclopentadiene purified was heated to ca. 180°C under the nitrogen stream and CPD generated was collected and stored at -78°C . CPD was again distilled from calcium hydride just before use (b.p. $40\text{-}41^\circ\text{C}$).

SnCl_4 was distilled from phosphorous pentoxide into glass ampoules. Commercial TCA (guaranteed reagent) was used without further purification. The equimolar mixture of SnCl_4 and TCA was used to start the polymerization. $\text{BF}_3\text{-OEt}_2$ was distilled into glass ampoules and used.

Toluene was washed with sulfuric acid, water, aqueous sodium hydroxide solution, and water, dried with calcium chloride overnight,

refluxed over calcium hydride overnight, and distilled. It was again refluxed and distilled over calcium hydride just before use.

Procedures

Polymerizations were carried out in an all-glass apparatus submerged in a dry ice-methanol coolant (-78°C). The glass apparatus was equipped with a monomer inlet, an outlet, and a magnetic stirrer. Known amounts of toluene and catalyst were charged into the apparatus. After thermal equilibration, a known amount of precooled monomer was added to the catalyst solution with syringe through the self-sealing rubber cap of the inlet under the vigorous agitation to start the polymerization. After suitable time intervals, aliquot samples (usually 5 ml) of the polymerization solution were withdrawn through the self-sealing rubber cap of the outlet with a syringe and discharged into a large amount of methanol to stop the polymerization. The polymer precipitate was washed repeatedly with methanol, dried in vacuo, and weighed. Methanol used in the present experiments contained a small amount of 4, 4'-thiobis-(6-*t*-butyl-3-methylphenol), which served as an antioxidant.

Polymer molecular weights were compared in terms of intrinsic viscosity at 30°C of polymer solution either in toluene or in benzene.

RESULTS

Rate of Polymerization with Stannic Chloride-Trichloroacetic Acid

In Fig. 1 the effect of the initial concentration of catalyst $[C]_0$ on the time-conversion curves of CPD polymerization with SnCl_4 -TCA is demonstrated. From the initial slopes of the tangents of the time-conversion curves the initial rate of polymerization (R_p) was found to be proportional to $[C]_0^{1.0}$.

Time-conversion curves in Fig. 1 were replotted in Fig. 2 in the form of $\log [M]_0/[M]_t$ against t (the first-order plot), where $[M]_0$ and $[M]_t$ stand for the initial monomer concentration and the monomer concentration at time t , respectively. No simple linear relationship was observed between $\log [M]_0/[M]_t$ and t , which means that the stationary concentration of the growing species has not been established. Similarly, the zeroth- or second-order plot of Fig. 1 showed no linearity. The temperature rise during the polymerization was about 4°C . Therefore, the first rapid polymerization can hardly be accounted for by the large instantaneous temperature rise as a result of exothermic propagation reaction. TiCl_4 -TCA as an initiator, which gave much faster initial polymerization, did not show such behavior as SnCl_4 -TCA did.

However, it should be noted that the first-order plot in Fig. 2 can be divided into two steps, i.e., the first curved section (step I)

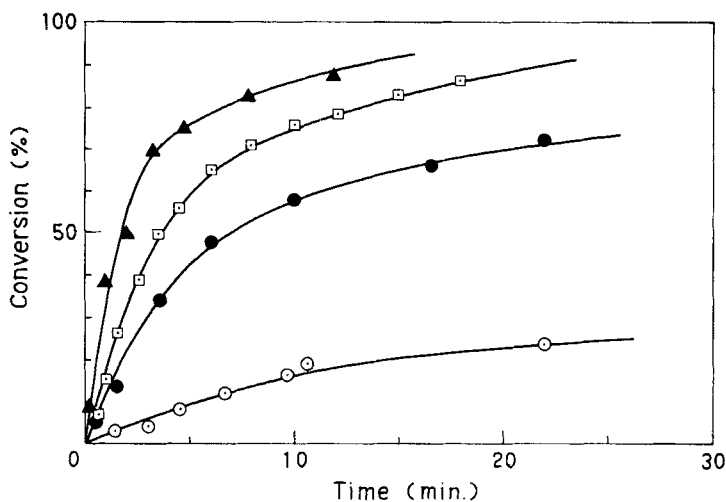


Fig. 1. Effect of $[C]_0$ on time-conversion curves for the polymerization of CPD with SnCl_4 -TCA at -78°C . $[M]_0$, 1.5 moles/liter. $[C]_0$: \blacktriangle , 5.0 mmoles/liter; \square , 2.5 mmoles/liter; \bullet , 2.0 mmoles/liter; \circ , 1.0 mmoles/liter. $[\text{H}_2\text{O}]_0$, ca. 3 mmoles/liter. Solvent, toluene.

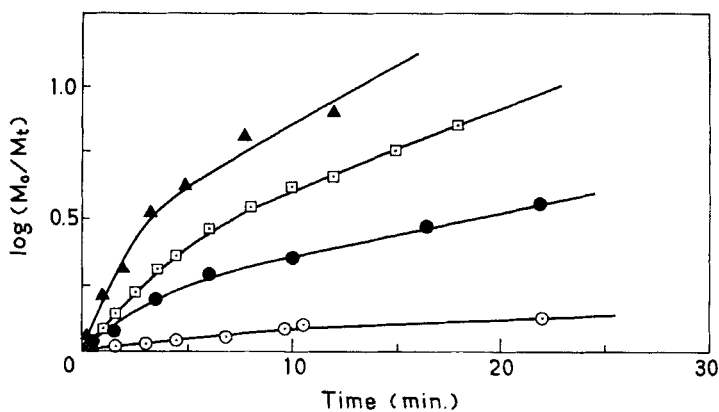


Fig. 2. Polymerization of CPD with SnCl_4 -TCA at -78°C . The first-order plot of Fig. 1.

and the straight section (step II). In step I the polymerization of CPD is started with a rapid initiation reaction and the propagation reaction follows with diminishing numbers of the growing species as a consequence of termination reaction (nonstationary-state polymerization). On the other hand, in step II the nonstationary-state polymerization has ceased and only stationary-state polymerization is observed. In the present paper quantities concerning step I and step II and the initial quantity are denoted by suffixes I, II, and 0, respectively. To know the effect of $[C]_0$ on the concentration of growing species at each polymerization step, the initial slopes of the tangents of the step I, $\{(\ln[M]_0/[M]_t)/t\}_{I_0}$, and the slopes of the step II, $\{\ln[M]_0/[M]_t\}/t\}_{II}$, were plotted against $[C]_0$, in Fig. 3. It was found that either the initial concentration of growing

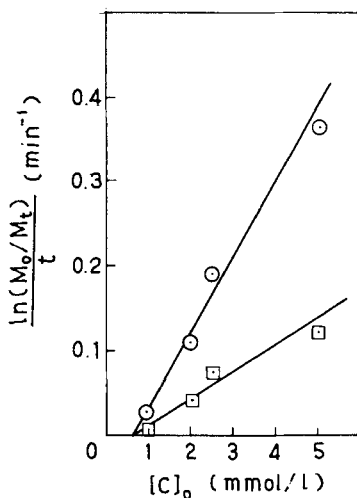


Fig. 3. Effect of $[C]_0$ on the concentration of active species at step I and step II. Polymerization conditions the same as in Fig. 1. ○, Initial slope of the first-order plot at step I. □, Slope of the first-order plot at step II.

species at step I or the concentration of growing species at step II was proportional to $[C]_0$.

Next, the effect of $[M]_0$ on the polymerization rate was investigated, and it was found that R_p was proportional to $[M]_0^{1.4}$. The first-order plot of the polymerization with varying monomer concentrations, which is not shown here, demonstrated the presence of two steps (step I and step II), in analogy with Fig. 2. Similarly to Fig. 3, the slope of the first-order plot at each step was plotted

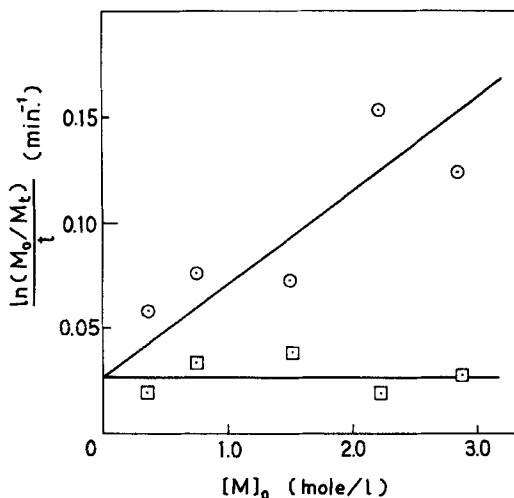


Fig. 4. Effect of $[M]_0$ on the concentration of active species at step I and step II. $[C]_0$, 2 mmoles/liter; $[H_2O]_0$, 4-6 mmoles/liter; solvent, toluene. ○, Initial slope of the first-order plot at step I. □, Slope of the first-order plot at step II.

against $[M]_0$ in Fig. 4. It can be said that the initial concentration of growing species at step I is proportional to $[M]_0$, while the concentration of the growing species at step II is independent of $[M]_0$.

From the experimental evidence mentioned above it has been made clear that the cationic polymerization of CPD with $SnCl_4$ -TCA occurs with either stationary- or nonstationary-state polymerization at the beginning, but that only the stationary-state polymerization survived toward the end. In nonstationary-state polymerization, $R_{p,I} = k_I [C]_0 [M]_0^2$, and in stationary-state polymerization rate, $R_{p,II} = k_{II} [C]_0 [M]_t$.

The effect of water on the polymerization rate was investigated. The time-conversion curves and their first-order plots for the polymerizations with varying water concentrations showed that the increase of water concentration lowered the polymerization rate a little, but that when water concentrations much exceeded the catalyst concentration the polymerization rate dropped sharply. The coexistence of steps I and II under the various water concentrations was again indicated.

Intrinsic Viscosity of Polycyclopentadiene Obtained with Stannic Chloride-Trichloroacetic Acid

Intrinsic viscosities of polycyclopentadiene (PCPD) produced with $SnCl_4$ -TCA were affected by $[C]_0$, as shown in Fig. 5. The

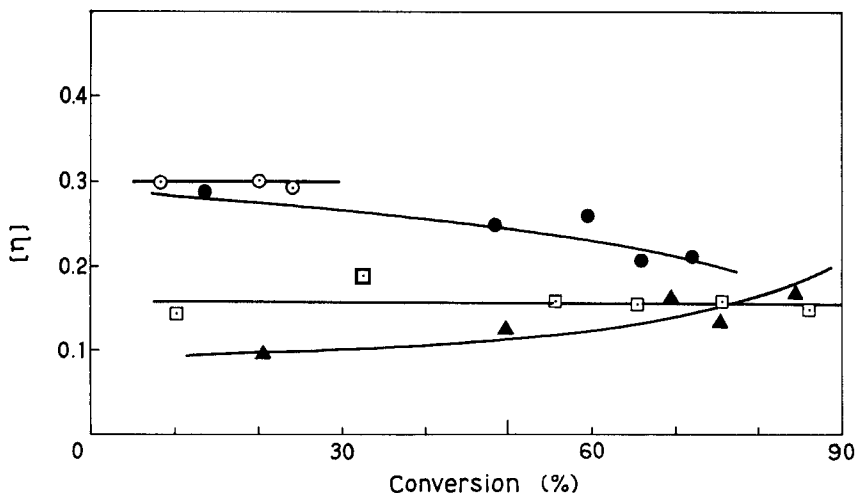


Fig. 5. Effect of $[C]_0$ on polymer intrinsic viscosity obtained with SnCl_4 -TCA. Symbols the same as in Fig. 1.

lower was $[C]_0$, the higher was the intrinsic viscosity of polymer. The effect of $[C]_0$ may be no doubt related to the nonstationary-state character of the polymerization system (step I). Intrinsic viscosities of PCPD increased with increasing $[M]_0$.

While water affected the rate of polymerization, the viscosity of polymer was little affected by water concentration. This fact may also be related to the nonstationary character of the polymerization system. With reference to the effects of $[C]_0$, $[M]_0$, and $[\text{H}_2\text{O}]_0$ on R_p and the intrinsic viscosity, a very similar situation has been met in the polymerization of CPD with TiCl_4 -TCA [3], which was found to be nonstationary-state polymerization. These findings will be discussed elsewhere.

Rate of Polymerization with Borontrifluoride Etherate

The polymerization of CPD catalyzed by $\text{BF}_3\text{-OEt}_2$ generally proceeded more slowly than that by SnCl_4 -TCA. The effect of catalyst concentration on time-conversion curves is shown in Fig. 6. Having determined the initial slope of the tangent for each time-conversion curve, it was found that R_p was proportional to $[C]_0^{4.0}$.

Next, the polymerization of CPD was carried out with varying concentrations of monomer, and the time-conversion curves are determined for each monomer concentration in Fig. 7. The determination of the initial slope of each time-conversion curve showed the relationship that R_p is proportional to $[M]_0^2$. As a consequence,

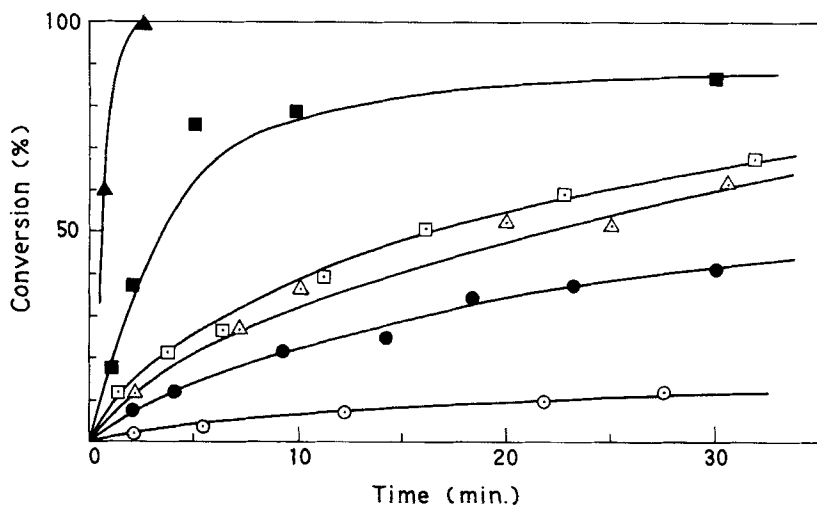


Fig. 6. Effect of $[C]_0$ on time-conversion curves for the polymerization of CPD with $\text{BF}_3\text{-OEt}_2$ at -78°C . $[M]_0$, 1.5 moles/liter. $[C]_0$: \blacktriangle , 30 mmoles/liter; \blacksquare , 13 mmoles/liter; \square , 10 mmoles/liter; \triangle , 8.0 mmoles/liter; \bullet , 7.5 mmoles/liter; \circ , 5.0 mmoles/liter. $[\text{H}_2\text{O}]_0$, ca. 5 mmoles/liter. Solvent, toluene.

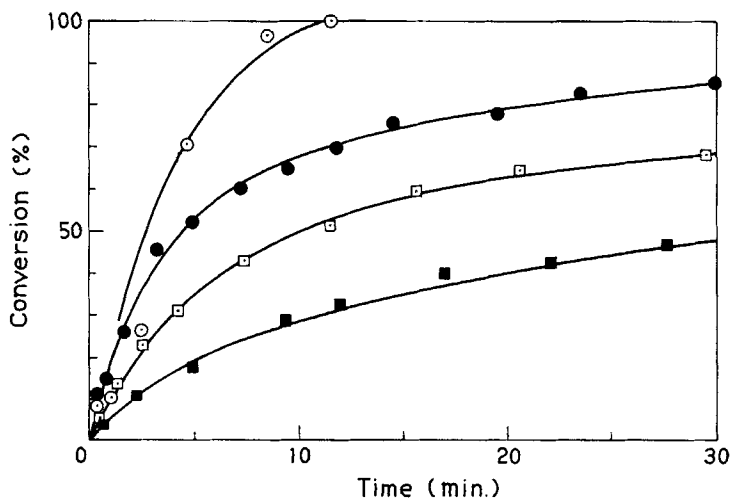


Fig. 7. Effect of $[M]_0$ on time-conversion curves for the polymerization of CPD with $\text{BF}_3\text{-OEt}_2$ at -78°C . $[C]_0$, 10 mmoles/liter. $[M]_0$: \circ , 1.5 mole/liter; \bullet , 1.0 mole/liter; \square , 0.59 mole/liter; \blacksquare , 0.29 mole/liter.

for the polymerization with $\text{BF}_3\text{-OEt}_2$, the kinetic relationship $R_p = k[M]_0^2[C]_0^4$ was established.

The first-order plots of the time-conversion curves in Fig. 7 became smooth convex curves instead of straight lines. Similar first-order plots were derived from Fig. 6. These experimental facts imply that the polymerization of CPD with $\text{BF}_3\text{-OEt}_2$ is a nonstationary one, but that the nonstationary character is much less marked than that in $\text{SnCl}_4\text{-TCA}$ -catalyzed polymerization because the curvature of the first-order plot was not so marked. In fact, it can be regarded as a stationary-state polymerization except for the very early stage of the polymerization (see below).

With increasing amount of water the rate of polymerization catalyzed by $\text{BF}_3\text{-OEt}_2$ decreased.

Intrinsic Viscosity of Polycyclopentadiene Obtained by Borontrifluoride Etherate

In general the intrinsic viscosity of PCPD produced by $\text{BF}_3\text{-OEt}_2$ was higher than that by $\text{SnCl}_4\text{-TCA}$. The most striking feature of the PCPD obtained with $\text{BF}_3\text{-OEt}_2$ was that it was only partly soluble in benzene at room temperature, while PCPD's obtained with $\text{TiCl}_4\text{-TCA}$ or $\text{SnCl}_4\text{-TCA}$ were soluble in benzene under the comparable conditions. The influences of the catalyst concentration and the water concentration on the formation of benzene-insoluble polymer were investigated at various conversions. Although the effect of reagent concentration was not clearly demonstrated, it was evident that under a given condition the benzene-insoluble fraction decreased with conversion (20-40% at lower conversions and 10-20% at higher conversions). To investigate the nature of the benzene-insoluble fraction, PCPD obtained with $\text{BF}_3\text{-OEt}_2$ was submerged in a variety of solvents and the change of the solubility was followed with suitable time intervals. It was found that PCPD produced with $\text{BF}_3\text{-OEt}_2$ was completely soluble in toluene and chloroform on standing at 30°C for 120 hr, but that the polymer was not completely soluble in cyclohexane, trichlorobenzene, decahydronaphthalene, and benzene on standing at 30°C for more than 200 hr. Next, PCPD produced with $\text{BF}_3\text{-OEt}_2$ (2 g, $[\eta]$ 0.720, 30°C , toluene) was extracted with benzene at 30°C for 50 hr and the intrinsic viscosity of toluene solution of benzene-soluble fraction (1.45 g, $[\eta]$ 0.592) was compared with that of benzene-insoluble fraction (0.55 g, $[\eta]$ 0.863). Furthermore, the viscosity of benzene-soluble fraction in toluene solution ($[\eta]$ 0.592) was compared with that in benzene solution ($[\eta]$ 0.585). These experimental results indicate that toluene is a better solvent than benzene for PCPD and toluene dissolves PCPD of higher molecular weight than benzene does.

On the basis of the experimental results mentioned above, toluene was used as the solvent for the viscosity measurement. The effect

of monomer concentration on the intrinsic viscosity of PCPD was investigated, while the concentrations of catalyst and water were kept constant. Consequently it was found that the molecular weight of PCPD increased with increasing monomer concentration. The influence of the catalyst concentration on the intrinsic viscosity of PCPD was investigated, while the concentrations of monomer and water were kept constant. The results shown in Fig. 8 indicated

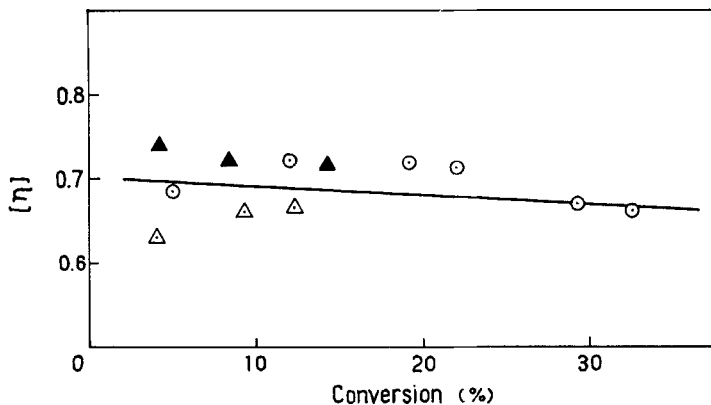


Fig. 8. Effect of $[C]_0$ on polymer intrinsic viscosity obtained with $\text{BF}_3\text{-OEt}_2$ at -78°C . $[M]_0$, 1.0 mole/liter. $[C]_0$: \blacktriangle , 10 mmoles/liter; Δ , 5.0 mmoles/liter; \circ , 3.0 mmoles/liter. $[\text{H}_2\text{O}]_0$, ca. 2.5 mmoles/liter.

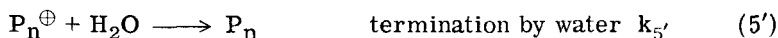
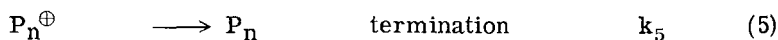
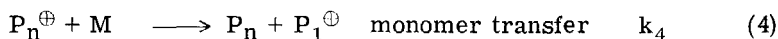
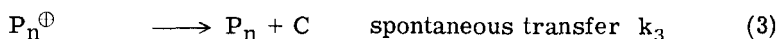
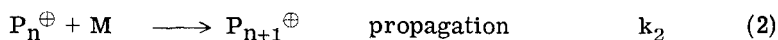
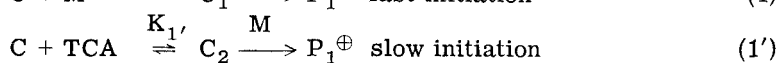
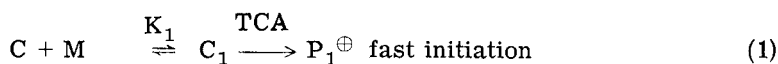
that the catalyst concentration affected little the intrinsic viscosity of polymer. This has been commonly observed in a stationary-state polymerization of vinyl monomers (ion-pair mechanism). For the last, the effect of water concentration on the intrinsic viscosity of PCPD was investigated, the concentrations of monomer and catalyst being kept constant. It was found that the intrinsic viscosity of PCPD was decreased with the increment of water concentration, in particular at low conversions, which is in marked contrast to the effect of water in SnCl_4 -TCA-catalyzed polymerization and admittedly interpreted in terms of conventional stationary-state kinetics.

DISCUSSION

Stationary or Nonstationary Character of the Cyclopentadiene Polymerization

The polymerization of CPD with SnCl_4 -TCA in toluene at -78°C was found to include concomitantly nonstationary- and stationary-

state polymerizations. The fast initiation reaction induced by a part of catalyst molecules added led to a nonstationary state, where the initial rate of polymerization R_{p, I_0} was expressed by the following equation: $R_{p, I_0} = k_1[C]_0[M]_0^2$. On the other hand, the slow initiation reaction induced by the rest of catalyst molecules brought about stationary-state polymerization, where the rate of polymerization $R_{p, II}$ was expressed by the following equation: $R_{p, II} = k_{II}[C]_0[M]_t$. In the early stage of the polymerization (step I) both mechanisms are operative, so the initial overall polymerization rate R_{p_0} appeared to be proportional to $[M]_0^{1.4}$. As the major amount of monomers is consumed in the nonstationary polymerization during step I, the molecular weight of polymer obtained with SnCl_4 -TCA was successfully explained on the basis of the nonstationary-state kinetics which are given below. According to Burton and Pepper [6] and our previous paper [3], several elementary reactions were put forward to explain the kinetic observations:



where M, C, and P represent monomer, catalyst, and polymer, respectively. The active species are marked by the superscript \oplus and the degree of polymerization of polymer is given by the suffix n. In the above reactions two possible initiation mechanisms are proposed. Provided the protonation of catalyst-monomer complex (C_1) by TCA [Eq. (1)] is rapid and the protonation of monomer by catalyst-cocatalyst complex (C_2) [Eq. (1')] is slow, the former leads to a fast initiation reaction and the latter to a slow initiation reaction.

To account for the nonstationary-state polymerization brought about by SnCl_4 -TCA (step I), elementary reactions (1) and (2) to (5') are employed and reaction (1) was assumed to be the fastest one among them, hence $[P_1^{\oplus}]_0 = K_1[C]_0[M]_0$. These elementary

reactions derive kinetic Eqs. (6) and (7) for the polymerization rate and the degree of polymerization (\bar{P}_n), respectively.

$$-dM/dt = K_1[C]_0[M]_0\{(k_2 + k_4)[M]_t + k_3\} \exp[-(k_5 + k_5'[\text{H}_2\text{O}])t] \quad (6)$$

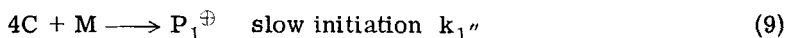
$$\begin{aligned} 1/\bar{P}_n &= \frac{k_4}{k_2 + k_4} + \frac{K_1[C]_0[M]_0}{[M]_0 - [M]_f} \\ &+ \frac{k_2 k_3 K_1 [C]_0 [M]_0 \{1 - \exp[-(k_5 + k_5'[\text{H}_2\text{O}])t]\}}{(k_2 + k_4)(k_5 + k_5'[\text{H}_2\text{O}])([M]_0 - [M]_t)} \quad (7) \end{aligned}$$

The observed effects of $[M]_0$, $[C]_0$, and $[\text{H}_2\text{O}]_0$ on the rate of polymerization ($R_{p, I} = k_1[M]_0^2[C]_0$) and \bar{P}_n of PCPD ($\bar{P}_n \propto 1/[C]_0$, $\bar{P}_n \propto [\text{H}_2\text{O}]_0^8$) can be satisfactorily explained on the basis of Eqs. (6) and (7). The increase of the molecular weight of PCPD with the increase of monomer concentration is not explainable by Eq. (7). However, this discrepancy can be ascribed to the fact that the stationary-state polymerization occurs simultaneously, which requires the rise of molecular weight of polymer with increasing the monomer concentration (see below).

To explain the stationary-state polymerization at step II, the elementary reactions (1') to (5') were taken into account and the stationary concentration of growing species was assumed. If in the slow initiation reaction (1') the equilibrium $C_2 + M \rightleftharpoons P^\oplus$ exists and is virtually complete, these elementary reactions derive the Eq. (8). Equation (8) explains the observed rate of polymerization at step II ($R_{p, II} = k_{II}[M]_t[C]_0$),

$$-dM/dt = \frac{k_1'[C]_0 [TCA] (k_2 + k_4) [M]_t}{k_5 + k_5'[\text{H}_2\text{O}]} \quad (8)$$

The polymerization of CPD with $\text{BF}_3\text{-OEt}_2$ in toluene at -78°C is, strictly speaking, a nonstationary-state polymerization in which the initiation reaction is rather fast. However, it is very close to stationary-state polymerization, and this is reflected in the molecular weight of PCPD obtained with $\text{BF}_3\text{-OEt}_2$. The effect of polymerization conditions on the molecular weight of PCPD can be explained in terms of stationary-state kinetics. If the initiation reaction (9) in place of reactions (1) or (1') is proposed and stationary concentration of growing species is assumed, the kinetic equations (10) and (11) are derived from Eq. (9) and (2) to (5');



$$-dM/dt = \frac{k_1'' (k_2 + k_4) [M]^2 [C]^4}{k_5 + k_5' [H_2O]} \quad (10)$$

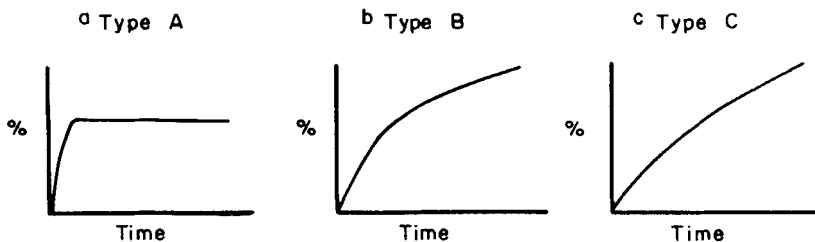
$$1/\bar{P}_n = \frac{k_4}{k_2} + \frac{k_3 + k_5 + k_5' [H_2O]}{k_2 [M]} \quad (11)$$

Equation (10) explains the observed overall polymerization rate in a BF_3 - OEt_2 -catalyzed system ($R_{p_0} = k[M]_0^2 [C]_0^4$). It is not known why four molecules of catalyst participate in the initiation reaction. It seems that three extra catalyst molecules are required to stabilize the ionic species by solvation. Equation (11) explains the experimental fact by the molecular weight of PCPD obtained with BF_3 - OEt_2 ($\bar{P}_n \propto [M]_0$, $\bar{P}_n \propto [C]_0$, $\bar{P}_n \propto 1/[H_2O]_0$). These are in marked contrast to the experimental findings in $SnCl_4$ -TCA-catalyzed polymerization, and the differences between the initiation mechanisms are clearly demonstrated.

The nature of catalyst is very important to determine the initiation mechanism. In Table 1 the experimental facts so far obtained in our laboratory on the cationic polymerization of CPD are summarized, particularly in connection with the initiation mechanism. Here again the importance of the nature of the catalyst is clearly

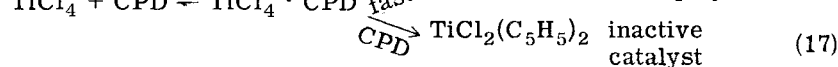
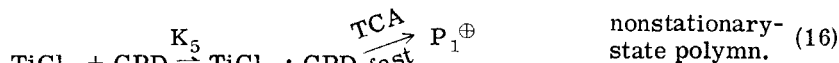
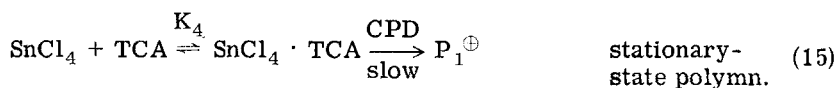
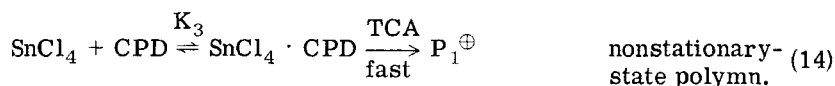
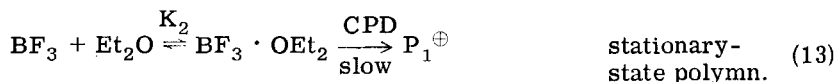
Table 1. Summary of Cationic Polymerization of Cyclopentadiene

TiCl ₄ -TCA catalyst	SnCl ₄ -TCA catalyst	BF ₃ -OEt ₂ catalyst
Time-conv. curve, Type A ^a	Time-conv. curve, Type B ^b	Time-conv. curve, Type C ^c
R_{p_0} : large $[\eta]$: 0.1-0.3	R_{p_0} : medial $[\eta]$: 0.2-0.5	R_{p_0} : small $[\eta]$: 0.4-0.7
The higher the $[C]_0$, the smaller the $[\eta]$	The higher the $[C]_0$, the smaller the $[\eta]$	$[\eta]$ is independent of $[C]_0$



revealed. Nonstationary character in cyclic diene polymerization is more enhanced in the order $\text{TiCl}_4\text{-CCl}_3\text{COOH} > \text{SnCl}_4\text{-CCl}_3\text{COOH} > \text{BF}_3\text{-OEt}_2$, which is in complete agreement with the order of the acidity of metal halide.

The reason nonstationary and stationary polymerizations coexist in stannic chloride-catalyzed polymerization is another point of interest. It is tentatively proposed that the order of the reaction in a termolecular reaction among a catalyst (BF_3 , SnCl_4 or TiCl_4), a co-catalyst (Et_2O or TCA), and a monomer (CPD) is important, i.e.,



In the postulated mechanism above, it is important that CPD is very susceptible to the complex formation with metal halide, and that TiCl_4 is most electrophilic, BF_3 is least electrophilic, and SnCl_4 is intermediately electrophilic. The above mechanism could roughly explain the experimental results mentioned in this paper and listed in Table 1. With BF_3 , $K_2 > K_1$, so that the initiation reaction proceeds almost entirely by the reaction of monomer with $\text{BF}_3\text{-OEt}_2$ complex. As the ionization of monomer by $\text{BF}_3\text{-OEt}_2$ complex is slow, the polymerization system assumes a stationary-state character. With TiCl_4 , $K_5 > K_6$, so that the initiation reaction proceeds virtually by the reaction of TCA with $\text{TiCl}_4\text{-CPD}$ complex. As the protonation of $\text{TiCl}_4\text{-CPD}$ complex by TCA is fast, the nonstationary-state character emerges. Furthermore, TiCl_4 is so electrophilic that $\text{TiCl}_4\text{-CPD}$ complex can react with another molecule of CPD to give dicyclopentadienyl dichloride. This reaction competes with the initiation reaction, thus leading to the leveling-off phenomenon of

the time-conversion curve and the inverse proportionality of the final conversion to the initial monomer concentration [3]. With SnCl_4 , K_3 competes with K_4 , so two initiation mechanisms are operative. The protonation of SnCl_4 -CPD complex by TCA is fast; hence the nonstationary-state polymerization $R_{p, I} = k_I[M]_0^2[C]_0$. On the other hand, if the protonation of monomer by SnCl_4 -TCA complex is slow, stationary-state polymerization, $R_{p, II} = k_{II}[C]_0[M]_t$, will result.

To confirm the proposed mechanism we attempted to investigate the effect on the time-conversion curve of the addition of monomer and catalyst in the course of the polymerization. The polymerization of CPD was started with SnCl_4 -TCA. When the polymerization came to about 80% conversion and only a stationary-state polymerization was operative, CPD was added. The change of the time-conversion curve is shown in Fig. 9 as a first-order plot. Non-

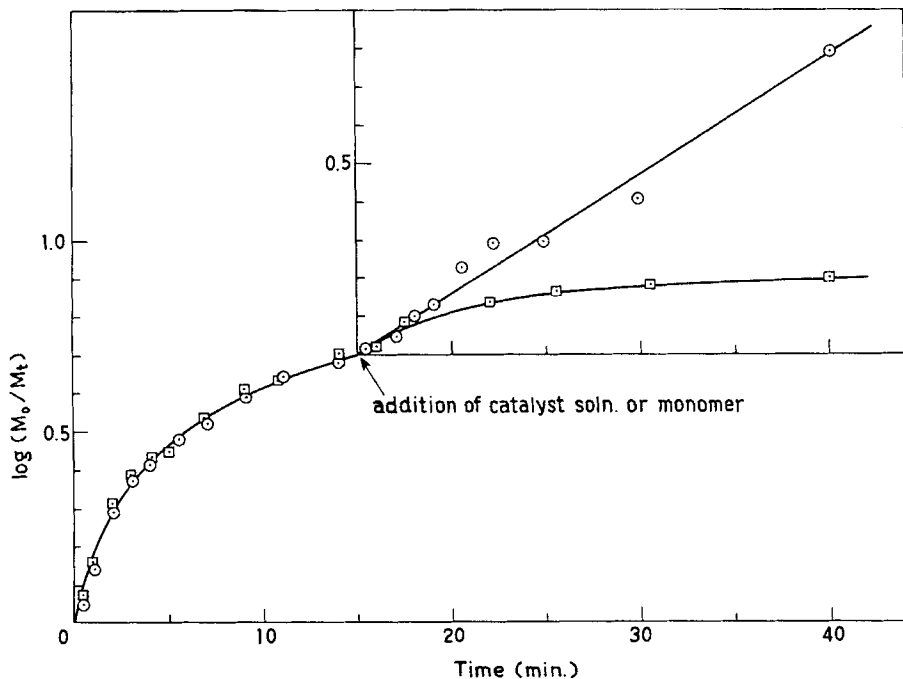


Fig. 9. Effect of the addition of catalyst or monomer on the polymerizing system of CPD with SnCl_4 -TCA. $[M]_0$, 1.5 moles/liter; $[C]_0$, 2.0 mmoles/liter. ○, Experiment of catalyst addition; added catalyst, 2.0 mmoles/liter. □, Experiment of monomer addition; $[M]$ after monomer addition, 1.6 moles/liter.

stationary-state polymerization was observed, as expected, as a consequence of the shift of the equilibrium (14) to the right. On the other hand, as is seen in Fig. 9, the addition of a small amount of SnCl_4 -TCA did not bring about nonstationary-state polymerization but stationary-state polymerization with increased concentrations of the active species. This is exactly what we expected, because the formation of SnCl_4 -CPD complex is unfavored when both the catalyst and the monomer concentrations are low. The effect of catalyst addition on polymerization was further studied in some details. When the polymerization of CPD catalyzed by SnCl_4 -TCA reached about 75% conversion, a fairly large amount of catalyst (SnCl_4 and TCA) was added. Although the concentration of residual monomer was low, a high catalyst concentration made the formation of SnCl_4 -CPD complex [Eq. (14)] rather important. Accordingly, the reproduction of the nonstationary state was observed a little. When the catalyst (SnCl_4 and TCA) was added at low conversion, the nonstationary-state character of the subsequent polymerization was very marked. This is what we expected from Eq. (14), because in this case both monomer and catalyst concentrations were high. These experimental results support the initiation mechanism postulated above. The coexistence of nonstationary and stationary polymerizations has been suggested also by Blake and Eley [7] with regard to the alkyl vinyl ether- BF_3 - OEt_2 system, in which very nucleophilic monomer is also involved.

Although the kinetic data can be interpreted in the present manner, it should be pointed out that the conclusions need to be supported by other data to be firm.

Properties of Polycyclopentadiene

PCPD obtained by BF_3 - OEt_2 was partly soluble in benzene at room temperature but completely soluble in toluene and chloroform under the same condition. Various reasons are considered for this phenomenon. A similar phenomenon was observed with poly(α -methylstyrene) [8], in which the entanglement of polymer chains was one of the most important reasons. However, the insolubility of the present polymer is not accounted for in terms of the entanglement of polymer chains or chain branching caused by the reaction of polymers, because the proportion of benzene-insoluble polymer decreased at higher conversions. Likewise, it is not explained by the partial oxidation of PCPD, because no difference was detected between infrared spectra of benzene soluble and insoluble fractions. The difference of molecular weight reasonably explains the solubility difference, as mentioned earlier. However, this cannot be an absolute reason for the experimental results, because PCPD having intrinsic viscosity (Benzene solution at 30°C) of about 2, which was produced with SbCl_3 or GeCl_4 , was soluble in benzene at room temperature

[9]. The crystallinity of PCPD and/or the relative abundance of 1, 2 and 1, 4 propagation units in PCPD may not be abandoned as a reason for the solubility difference.

The polymerization of CPD with TCA as a catalyst has received much attention from Wassermann's school [10]. They concluded that PCPD consisted of a conjugated-polyene-type structure as a result of hydrogen migration. However, under our conditions (low temperature and metal halide as catalyst) no indication was observed for the polyene-type structure [11].

ACKNOWLEDGMENT

The authors are very grateful for the helpful advice and discussions of Dr. T. Higashimura. The authors thank Mitsubishi Monsanto Chemical Co. for providing the dimer of CPD.

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Accepted by editor December 4, 1967

Submitted for publication January 23, 1968