Cationic Polymerization of Cyclic Dienes. VIII. The Kinetic Observations on the Polymerization of cis, cis-1,3-Cycloöctadiene

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The Kinetic Observations on the Polymerization
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SUMMARY

Cis, cis-1, 3-cyclooctadiene was polymerized by titanium tetra-
chloride-trichloroacetic acid in methylene chloride or toluene at
−78°C. The polymerization was very fast at first but slowed down
toward the end. When the polymerization was conducted in methy-
lene chloride, it stopped completely after the fast polymerization
ceased, and a portion of monomers was left unreacted. On the other
hand, when toluene was used as a solvent, a slow polymerization
was observed after the fast polymerization finished, and the poly-
merization went to completion. The conversion reached during the
fast polymerization was lower as the initial monomer concentration
was higher. These experimental findings were interpreted in terms
of a strong interaction between the excess monomers and the cata-
lyst to form an inactive monomer-metal halide adduct, which has
been commonly observed with other cyclic dienes studied so far,
such as cyclopentadiene and 1, 3-cyclohexadiene. To explain the
effect of solvent, a reactivation of the initially formed monomer-
metal halide adduct was invoked in the case of toluene as solvent,
which has not been observed with other cyclic dienes.

The reactivities of cyclic dienes in the homopolymerization were
found to be in the order: cyclopentadiene > cyclohexadiene > cyclo-
öctadiene. Polycyclooctadiene obtained under the present conditions
was of low molecular weight (DP: 15-18). The monomer transfer
reaction was presumed to be a predominant chain-breaking reaction.

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

INTRODUCTION

A series of investigations have been made on the cationic poly-
merization of cyclic dienes. In particular, cyclopentadiene (CPD) [2]
and 1, 3-cyclohexadiene (CHD) [3], which are the cyclic dienes of
normal-membered ring, have been investigated in detail. Many
interesting aspects have been encountered with these monomers,
which have not been observed with other vinyl monomers.

The investigation of the effect of the ring size on the polymeriza-
tion of cyclic dienes will help elucidate the behavior of cyclic dienes
in cationic polymerization. In this connection, cis, cis-1, 3-cyclo-
öctadiene (COD), which is a cyclic diene with a medium-membered
ring, was chosen as the next monomer to investigate. The kinetic
features in the polymerization of COD are reported and discussed
in this paper in comparison with those of CPD and CHD.

EXPERIMENTAL

Materials

COD can assume two types of configurations, i.e., cis, cis and
cis, trans. Commercially available COD was used in this investiga-
tion. The infrared spectrum of COD showed absorptions at 11.0 and
8.65 μ [3], the nuclear magnetic resonance spectrum (NMR) showed
peaks at τ = 4.45, 7.90, and 8.60 ppm [4], and n_D^{20} was 1.4938 [3].
All these physical values indicate that the present COD assumes a
cis, cis configuration.

COD was distilled twice from calcium hydride through packed
column under nitrogen stream (bp = 75.0°C/100 mm Hg). The
purity of COD checked by gas chromatography was higher than
99.9%.

Toluene and methylene chloride, as solvent, and titanium tetra-
chloride (TiCl$_4$), as catalyst, were purified as reported in earlier
papers. Trichloroacetic acid (TCA) (guaranteed reagent) was used
without further purification as cocatalyst.

Procedure

All polymerizations were carried out at —78°C using an equi-
molar mixture of TiCl$_4$ and TCA as a catalyst. The polymerization
procedure was almost the same as described in earlier papers.
The conversion of monomer was determined by the weight of
methanol-insoluble polymer formed. The water content of the poly-
merization system was determined by the Karl Fischer method.

The molecular weight of polymer was determined by ebullio-
meter. Intrinsic viscosities of toluene solution were also measured
at 30°C.

RESULTS

In all systems studied, the polymerization started immediately upon addition of the catalyst. The polymerization solution was not completely homogeneous and was colored red, but the purified polymer was white. Very little methanol-soluble product was formed.

Effect of Catalyst Concentration

The time-conversion curves for the polymerizations catalyzed by $TiCl_4$-TCA in toluene and in methylene chloride are shown in Figs. 1 and 2, respectively.
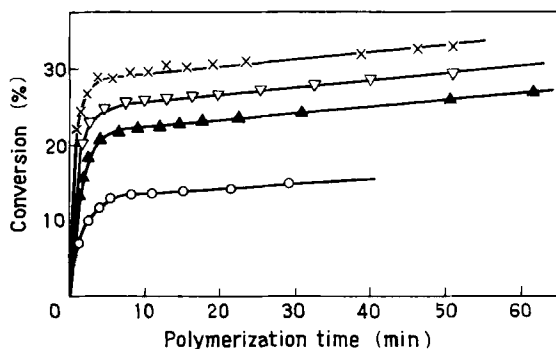

Fig. 1. Time-conversion curves of polymerization of cis, cis-1, 3-cyclooctadiene catalyzed by $TiCl_4$-TCA in toluene at −78°C. $[M]_0$, 0.73 mole/liter. $[C]_0$, mmole/liter: ×, 50.0; ▽, 45.0; ▲, 35.0; ○, 20.0. $[H_2O]_0$, 2.80 mmole/liter.

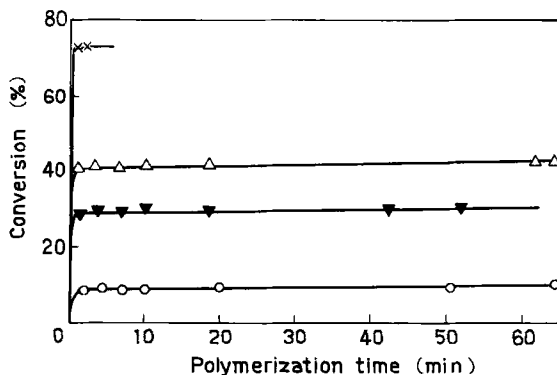**Fig. 2.** Time-conversion curves of polymerization of cis, cis-1, 3-cyclooctadiene catalyzed by $TiCl_4$-TCA in methylene chloride at −78°C. $[M]_0$, 0.73 mole/liter. $[C]_0$, mmole/liter: ×, 80.0; △, 20.0; ▼, 10.0; ○, 5.0.

As is seen in Fig. 1, the polymerization in toluene is very fast at first but slows down toward the end. The same situation has been encountered in the polymerization of CPD initiated by $SnCl_4$-TCA in toluene at —78°C [2c].

Figure 2 shows that the polymerization in methylene chloride is faster at first than that in toluene, but that it almost completely stops before it goes to completion. The same situation has been encountered in the polymerization of CPD inititiated by $TiCl_4$-TCA in toluene at —78°C [2a], or in the polymerization of CHD initiated by $SnCl_4$-TCA in benzene or methylene chloride at 0°C [1].

It should be noted here that the polymerization rate of CPD is larger than that of COD, as judged by the comparison of the time-conversion curves in toluene at —78°C [2a]. On the other hand, the polymerization of CHD by $TiCl_4$-TCA was investigated only at 0°C [1], so a precise comparison of the polymerization rate of COD with that of CHD is difficult. However, the polymerization of CHD in methylene chloride at —78°C reached a much higher conversion than that of COD even when catalyzed by a less acidic catalyst, $SnCl_4$-TCA, in a smaller concentration [1]. This would mean that CHD is polymerized faster than COD in the cationic polymerization. It follows, therefore, that the reactivity of cyclic dienes in the cationic polymerization decreases as the ring size increases; that is, in the order CPD > CHD > COD.

As pointed out above, the shape of time-conversion curves of the polymerization of COD in toluene is very similar to that of the polymerization of CPD in toluene initiated by $SnCl_4$-TCA, where the polymerization was explained in terms of the coexistence of the first nonstationary-state polymerization and the later stationary-state polymerization [2c].

Likewise, the polymerization of COD in toluene initiated by $TiCl_4$-TCA was divided into two parts; that is, the first, fast polymerization and the later, slow polymerization. The intercept given by the extrapolation of time 0 of the time-conversion curve for the later, slow polymerization would represent approximately the final conversion reached by the first, fast polymerization. The effects of initial catalyst concentration $[C]_0$ on the final conversion reached in the fast polymerization and the later, slow polymerization are shown in Fig. 3.

Figure 3 shows that the final conversion in the fast polymerization is proportional to $[C]_0^{1.0}$, but that the later, slow polymerization is almost independent of $[C]_0$.

With polymers obtained in toluene, the relationships between the intrinsic viscosity and $[C]_0$, the intrinsic viscosity and the conversion, and the number-average molecular weight and the conversion were investigated. The results are shown in Figs. 4-6. The number-average molecular weights of polymers produced in toluene were found to range from 1500 to 1800 and were almost unaffected by
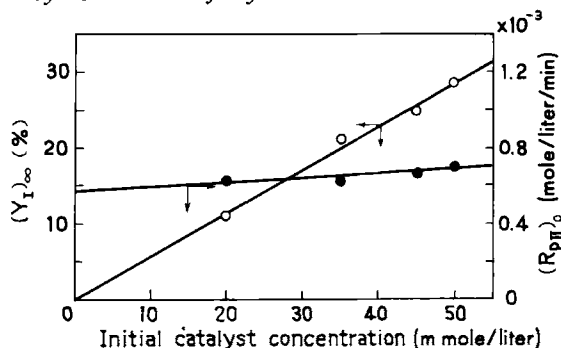
Fig. 3. Effect of initial catalyst concentration on final conversion of first-step polymerization $(Y_I)_\infty$ (○) and initial rate of second-step polymerization $(R_{pII})_0$ (●). Conditions the same as in Fig. 1.
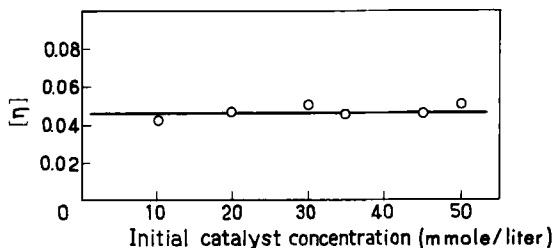
Fig. 4. Relationship between initial catalyst concentration and $[\eta]$ of polymer obtained by $TiCl_4$-TCA in toluene at $-78°C$. Conditions the same as in Fig. 1.

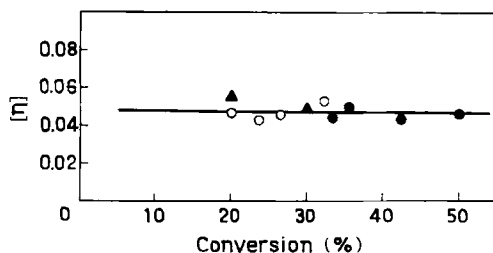**Fig. 5.** Relationship between conversion and $[\eta]$ of polymer obtained by $TiCl_4$-TCA in toluene at $-78°C$. $[M]_0$, 0.73 mole/liter. $[C]_0$, mmole/liter: ▲, 30.0; ○, 34.8; ●, 50.0.
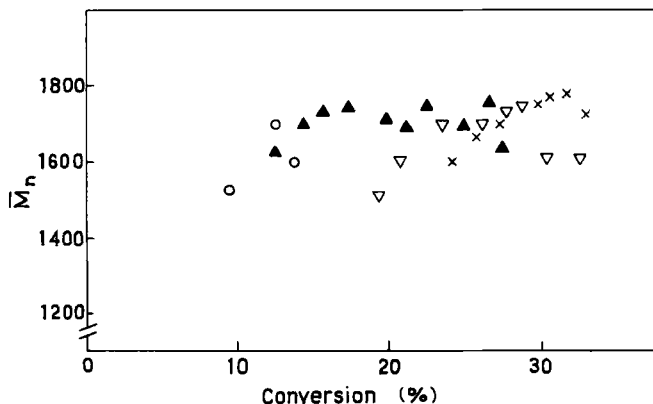
Fig. 6. Relationship between conversion and number-average molecular weight of polymer obtained by $TiCl_4$-TCA in toluene at $-78°C$. Conditions the same as in Fig. 1.

the changes of $[C]_0$ and conversion. This is in contrast to the fact that the intrinsic viscosity of polycyclopentadiene produced in toluene by $TiCl_4$-TCA or $SnCl_4$-TCA decreased with $[C]_0$ [2a, 2c].

The dependence on $[C]_0$ of the intrinsic viscosity of polycyclo-öctadiene obtained in methylene chloride by $TiCl_4$-TCA is shown in Fig. 7. The intrinsic viscosity seems to increase slightly with increasing $[C]_0$.

Effect of Monomer Concentration

Polymerizations were carried out in toluene by $TiCl_4$-TCA at various initial monomer concentrations ($[M]_0$). The time-conversion curves are shown in Fig. 8. Similarly to the case shown in
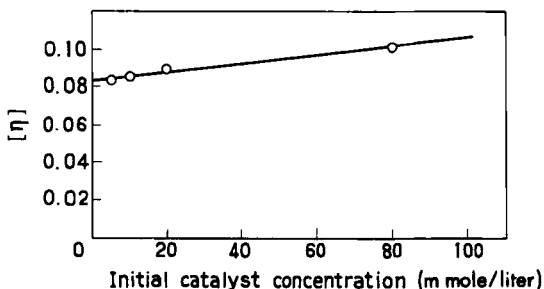

Fig. 7. Relationship between initial catalyst concentration and $[\eta]$ of polymer obtained by $TiCl_4$-TCA in methylene chloride at $-78°C$. Conditions the same as in Fig. 2.
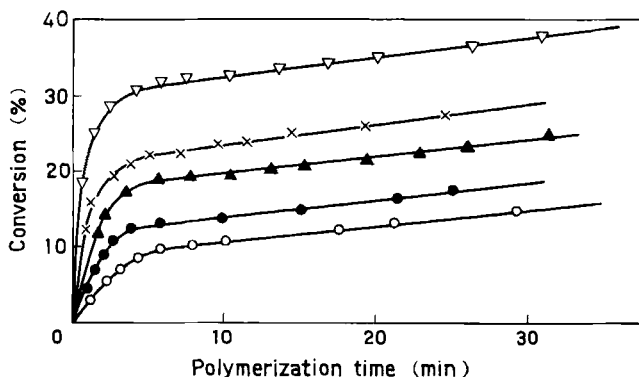
Fig. 8. Time-conversion curves of polymerization of cis, cis-1, 3-cyclooctadiene catalyzed by $TiCl_4$-TCA in toluene at $-78°C$. $[M]_0$, mole/liter: ∇, 0. 365; $\times$, 0. 548; $\blacktriangle$, 0. 730; $\bullet$, 0. 913; $\bigcirc$, 1. 10. $[C]_0$, 33. 6 mmole/liter. $[H_2O]_0$, 2. 3-2. 4 mmole/liter.

Fig. 1, the time-conversion curve was divided into two stages; that is, the first, fast polymerization and the later, slow polymerization. The effects of $[M]_0$ on the final conversion of the fast polymerization and on the rate of the slow polymerization were investigated and are shown in Fig. 9.

As can be seen in Fig. 9, the rate of the slow polymerization was proportional to $[M]_0^{1.0}$. On the other hand, the final conversion of the fast polymerization decreased as $[M]_0$ increased. This inversion phenomenon has been found in some cases, e.g., CPD-$TiCl_4$-
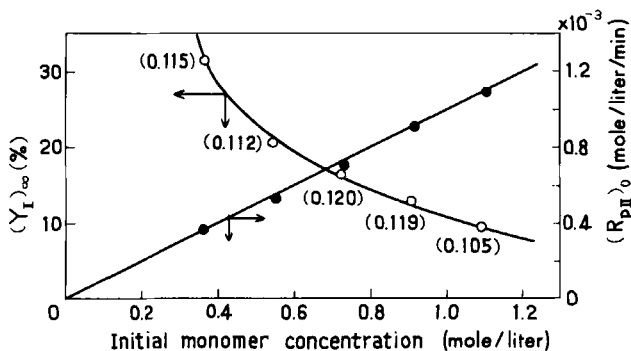

Fig. 9. Effect of initial monomer concentration on final conversion of first-step polymerization $(Y_I)_\infty$ ($\bigcirc$) and initial rate of second-step polymerization $(R_pII)_0$ ($\bullet$). Conditions the same as in Fig. 8. Figures in parentheses represent the amount of monomer consumed (mole/liter) during first-step polymerization.

TCA-toluene [2a], CHD-SnCl$_4$-TCA-benzene, methylene chloride systems [1]. However, it should be noted in Fig. 9 that the amount of monomer consumed (conversion X[M]$_0$, mole/liter) during the fast polymerization is almost unchanged with variation of [M]$_0$. Since the fast polymerization lasts for about 5 min regardless of [M]$_0$ (cf. Fig. 8), the polymerization rate (mole/liter/min) of the fast polymerization is nearly independent of [M]$_0$.

The effect of [M]$_0$ on the number-average molecular weight of polymer was investigated. As seen in Fig. 10, the polymer molecular weight increased a little as [M]$_0$ increased. When [M]$_0$ was larger than 0.73 mole/liter, the polymer molecular weight tended to increase with increasing conversion.

DISCUSSION

The rate behavior is discussed here, particularly in connection with initiation mechanism.

As stated above, the polymerization in toluene was divided into two steps. The initial rate of the first step is represented by $(R_{PI})_0$ and that of the second step by $(R_{PII})_0$. The kinetic investigations above are summarized in the following equations:

$$(R_{PI})_0 = K_I [C]_0^{1.0} [M]_0^0 \text{ nonstationary state} \qquad (1)$$

$$(R_{PII})_0 = K_{II} [C]_0^0 [M]_0^{1.0}, \text{ possibly stationary state} \qquad (2)$$

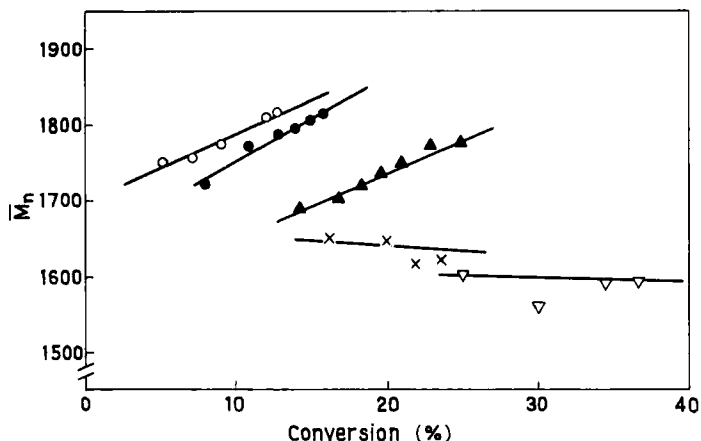where K_I and K_{II} represent the overall rate constant for each step.

Fig. 10. Relationship between conversion and number-average molecular weight of polymer obtained by TiCl$_4$-TCA in toluene at −78°C. Conditions the same as in Fig. 8.

A strong interaction between metal halide and monomer, and a catalyst inactivation by a reaction having higher order with respect to monomer concentration, have been observed in the cationic polymerizations of CPD [2a] and CHD [1] and seem to be common with other cyclic dienes. The same idea was incorporated into the kinetic interpretation of the present results.

A strongly electrophilic $TiCl_4$ (C) reacts quickly with a nucleophilic COD (M) to form a complex (MC).

$$M + C \xrightarrow{\text{fast}} MC \qquad (3)$$

In view of much higher concentration of monomer than catalyst,

$$[MC]_0 = [C]_0 \qquad (4)$$

where the subscript o represents the initial concentration. At the beginning of the polymerization no stationary state about MC is established, but TCA (Co) and COD compete for MC, leading to the formation of active species of polymerization (P*) and inactive complex (M_2C).

$$M_2C \xleftarrow{+M, k_1} MC \xrightarrow{+Co, k_2} P^* \qquad (5)$$
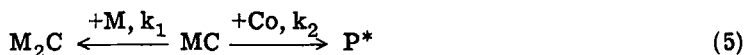
Therefore,

$$[P^*]_0 = \frac{k_2[Co]_0[C]_0}{k_1[M]_0 + k_2[Co]_0} \qquad (6)$$

Thus,

$$(R_{PI})_0 = \frac{k_p k_2[C]_0[Co]_0[M]_0}{k_1[M]_0 + k_2[Co]_0} \qquad (7)$$

where k_p represents the propagation rate constant. The effects of $[M]_0$ and $[Co]_0$ on R_{PI} may be of minor importance. Thus, Eq. (7) coincides with Eq. (1) qualitatively.

When the fast polymerization induced by the initially formed complex MC is finished, the polymerizations are carried out by the complex MC formed by a slow decomposition of the complex M_2C.

$$M_2C \xrightarrow[\text{slow}]{k_3} M + MC \xrightarrow[\text{fast}]{+Co, k_2} P^* \qquad (8)$$
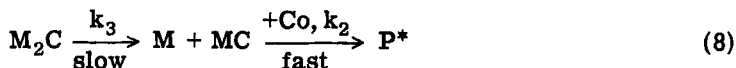
The initial concentration of M_2C is

$$[M_2C]_0 = \frac{k_1[M]_0[C]_0}{k_1[M]_0 + k_2[Co]_0} \tag{9}$$

Then the rate of initiation is

$$(R_i)_0 = k_3[M_2C]_0 = \frac{k_1k_3[M]_0[C]_0}{k_1[M]_0 + k_2[Co]_0} \tag{10}$$

If the unimolecular termination reaction occurs, and the stationary concentration of P^* is established,

$$R_i = R_t = k_t[P^*] \tag{11}$$

$$[P^*] = \frac{k_1k_3}{k_t} \frac{[M]_0[C]_0}{k_1[M]_0 + k_2[Co]_0} \tag{12}$$

Thus,

$$(R_{PII})_0 = \frac{k_pk_1k_3}{k_t} \frac{[M]_0^2[C]_0}{k_1[M]_0 + k_2[Co]_0} \tag{13}$$

Since $[C]_0 = [Co]_0$ always, $(R_{PII})_0$ would be almost unaffected by $[C]_0$. Equation (13) is in qualitative agreement with Eq. (2).

The second-stage polymerization was not observed in methylene chloride. This may be because the decomposition of the complex M_2C is unfavored in methylene chloride. In CPD-$TiCl_4$-TCA system [2a], the second-stage polymerization was not observed even in toluene. In view of much stronger nucleophilicity of CPD than COD, the decomposition of $(CPD)_2$-$TiCl_4$ complex would be highly prohibited.

The molecular weight of polycyclooctadiene was low, while the polymerization rate was quite high. This would mean that the monomer transfer reaction predonominates over other chain-breaking reactions.

As stated above, the fast initiation reaction and the catalyst deactivation by excess monomers, which are based on the strong interactions between a metal halide and a cyclic diene, were common to CPD, CHD, and COD. But the reactivation of cyclic diene-metal halide adduct to give an initiating species was suggested first with COD. On that basis, the kinetic observations were interpreted.

The present investigation showed that the reactivity of cyclic dienes decreased in the order CPD > CHD > COD. Clearly, they are in the sequence of increasing steric interference. It is reasonable to assume that the reactivity of cyclic dienes is governed by

the steric factor. The stability of cycloalkenyl cations may be another important factor in determining the reactivity of dienes, as suggested in the previous papers [1, 2]. However, no data are available concerning the stability of cycloöctenyl cation. In this connection, more research on the properties of cycloöctenyl cation is desirable.

ACKNOWLEDGMENT

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