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POLYMERIZATION OF CYCLOPENTADIENE WITH PERCHLORIC ACID*

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Cyclopentadiene was polymerized in toluene or in methylene chloride with perchloric acid. Kinetic features seemed to be very simple and propagation rate constants were estimated according to the kinetics of Pepper et al. The values of k_p were 6.7 l/mol sec. in methylene chloride and 0.83 l/mol sec. in toluene.

For long time, inorganic protonic acids have been known to initiate the cationic polymerization of vinyl momonomers, though only a few papers have been published. Pepper et al. reported the polymerization of styrene (St) with sulfuric acid$^{1)}$ and with perchloric acid$^{2)}$. Both acids are very active to initiate the polymerization rapidly. The termination reaction occurs in the St-H_2SO_4 system, but does not occur in the St-$HClO_4$ and the latter is a transfer dominated living polymerization system. The kinetics of these polymerizations is rather simple and is believed to propagate via carbonium ions, while Plesch et al.$^{3)}$ claimed that the polymerization of styrene with perchloric acid was not cationic and the perchlorate ester was an active species.

In our previous paper$^{4)}$ the propagation rate constant (k_p) was measured for the polymerization of cyclopentadiene (CPD) with $TiCl_4 \cdot CCl_3COOH$, and the present work was undertaken to determine k_p for the polymerization of CPD with $HClO_4$.

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* Part II of a series of papers concerned with propagation rate constant in cationic polymerization of cyclic dienes. For the previous paper in this series, see reference 4).

Experimental

Purifications of polymerization solvent and CPD were already described$^{5)}$. Preperation of perchloric acid solutions was essentially the same as that of Pepper et al.$^{6)}$ Polymerizations were started by addition of the precooled monomer solution to the catalyst solvent mixture at a dry ice-methanol temperature under dry nitrogen atomosphere. Methanol insoluble products were recovered and dried under vacuum.

Results

In Fig. 1 is shown the conversion-time curves for polymerization of CPD with perchloric acid in toluene at -78°C. At first, polymerization rate was very large and decreased progressively, soon attaining zero, that is, no more polymerization occurring then. This behavior could be reasonably explained by assuming very rapid initiation and rather active termination, as indicated for the St-H_2SO_4 system. The relationship between the asymptotic yield (Y_∞) and the initial catalyst concentration (C_0) or the initial monomer concentration (M_0) is illustrated in Fig. 2 or in Fig. 3 respectively. From Fig. 2, it can be seen that Y_∞ increased monotonously with increasing C_0. The curve falls into the axis of abscissa at C_0 = 1.0 m mol/l, the reason of which would be owing to the presence of impurities such as water inactivating the catalyst. Y_∞ is independent of M_0 as demonstrated in Fig. 3, which is different from the result obtained in the polymerization of CPD with $TiCl_4 \cdot CCl_3COOH$$^{4)}$. The NMR spectra of the polymer indicated that about 15 % of olefinic protons disappeared, which is larger than the values obtained by using Friedel-Crafts catalysts. Consequently a small part of the recovered polymer was insoluble in common organic solvents. It is estimated that the crosslinking may occur more actively than other catalyst systems in both solvents. Nevertheless, the ratios of 1,2 structure and 1,4 structure determined by NMR spectroscopy were almost the same as those with Friedel-Crafts catalysis$^{7)}$.

Limiting viscosity numbers of the polymers ranged from 0.1 to 0.4.

Discussion

The kinetic equations derived by Pepper et al. for St-H_2SO_4 system are as

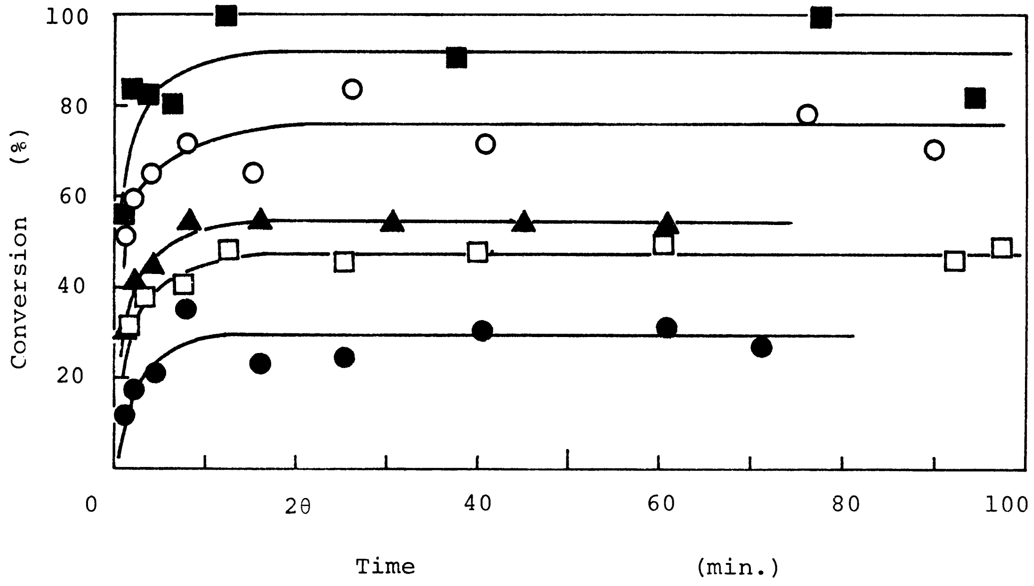

Fig. 1 Conversion-time curves for polymerization of cyclopentadiene with perchloric acid.

Solvent : toluene, Temp. : -78°C, M_0 = 1.3 mol/l

C_0 : ● 5.0 □ 8.6 ▲ 8.8 ○ 11 ■ 14 m mol/l

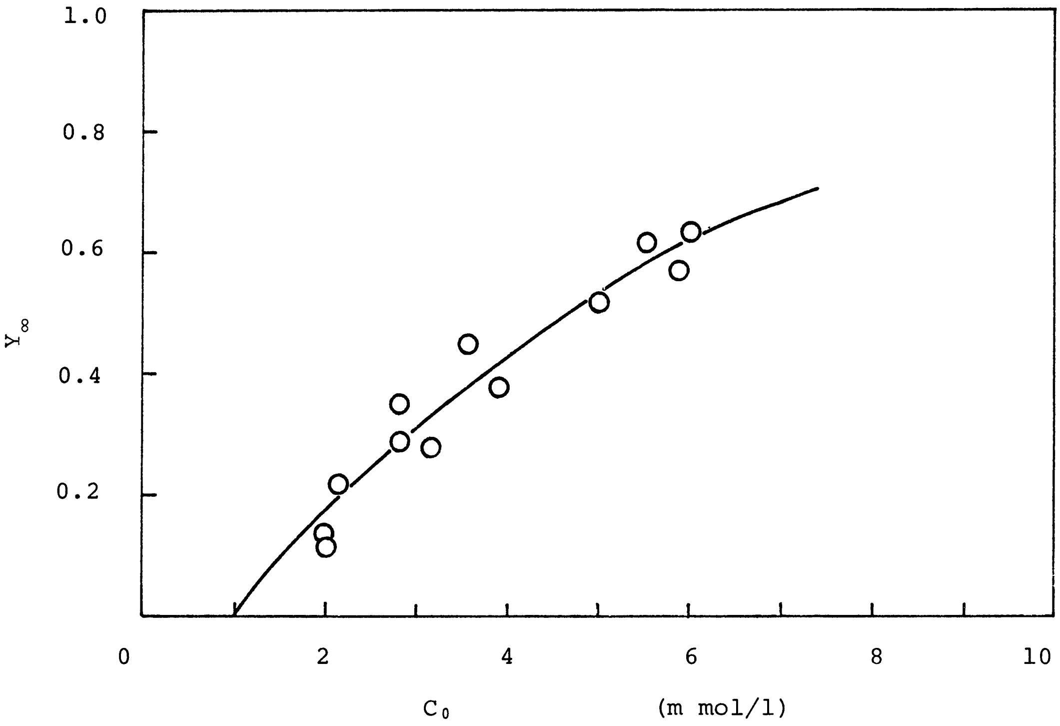

Fig. 2 Relationship between Y_∞ and C_0.

Polymerization Solvent : methylene chloride, Temp. : -78°C, M_0 = 1.3 m mol/l

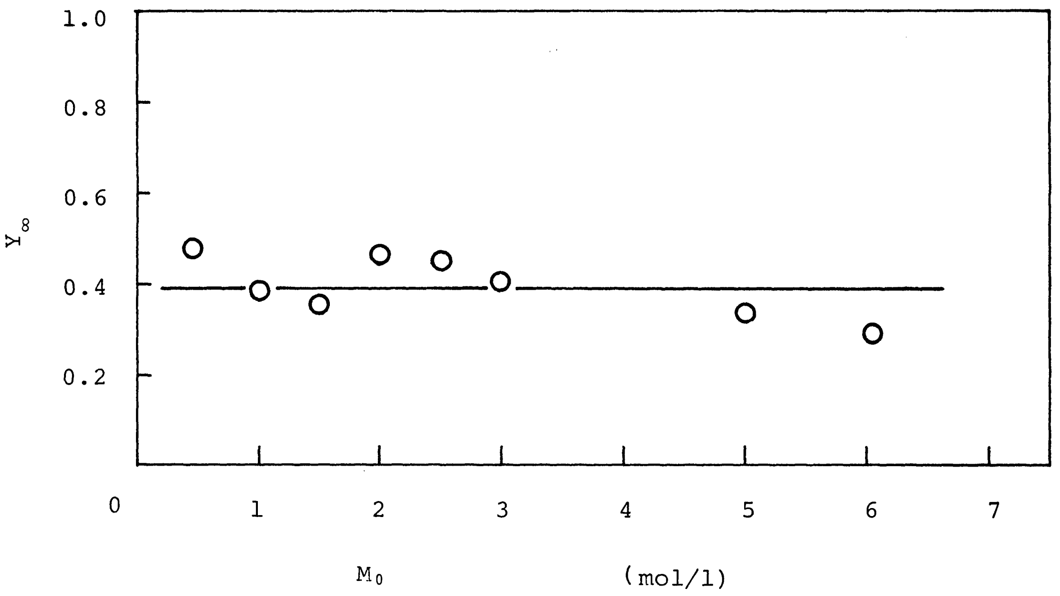

Fig. 3 Relationship between Y_∞ and M_0.

Polymerization Solvent : toluene, Temp. : -78°C, C_0 = 13 m mol/l

Table 1. Propagation and Termination Rate Constants

Monomer	Catalyst	Solvent	Temp. °C	k_p l/mol sec	k_t $sec.^{-1}$	Reference
CPD	$HClO_4$	methylene chloride	-78°	6.7	0.057	This work
"	"	toluene	"	0.83	0.008	"
"	$TiCl_4 \cdot CCl_3COOH$	"	-75°	350	0.11	4
styrene	$HClO_4$	ethylene dichloride	30°	17.0	———	2
"	H_2SO_4	"	25°	7.6	0.0067	1
"	$SnCl_4$	"	30°	0.42	———	8

follows[1],

$$\ln\left(\frac{1}{1 - Y_\infty}\right) = \frac{k_p}{k_t} \cdot C_0 \qquad (1)$$

$$\ln\left(\frac{1}{1 - Y_t}\right) = \frac{k_p}{k_t} \cdot C_0(1 - e^{-k_t t}) \qquad (2)$$

where Y_t means the yield at time t. According to these equations, rate constants could be calculated as shown in Table 1. Theoretical lines employing these values were shown in Figs. 1 and 2. The agreement of the experimental with the theoretical is rather satisfactory, taking the experimental defect (not the perfectly closed system) into account. Fig. 3 depicts the independence of Y_∞ on M_0 which is claimed by equation (1). All these facts indicate that the kinetics of Pepper et al. is applicable to the present system, and the calculated rate constants can be compared with those of the other related systems. As shown in Table 1, the values of k_p of the CPD-$HClO_4$ systems are much smaller than that of the CPD-$TiCl_4 \cdot CCl_3COOH$ system, and comparable to the k_p of styrene. For the cationic polymerization of styrene monomer, protonic acids seem to be more active than Friedel-Crafts metal, but the situation apparently reverses for CPD. The reason of this behavior is not clear, and the difference of polymerization temperature may cause the change of active species (for example, drift of the equiliblium of free ions and ion pairs). More detailed study is needed to clarify this point.

There are no termination reactions in the styrene-$HClO_4$ system, whereas there are in CPD-$HClO_4$ system, though it is considered that counter ions are identical in both systems. Moreover the k_t values of the CPD-$HClO_4$ systems are rather large, comparable to that of the styrene-H_2SO_4 system. This may also be caused by the change of temperature, as suggested from the results of Pepper et al.[9] They stated that at a lower temperature the termination reaction do exist though at a room temperature the polymerization of styrene with perchloric acid is a transfer dominated living polymerization. More experiments are necessary to clarify these phenomena. Furthermore these points are concerned with the problem of the nature of active species in cationic polymerization, and we are now preparing the more detailed experiments under rigorous conditions.

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