

Polymerization Kinetics of Styrene Using Coordination Catalysts Containing Rare Earth Compounds

H. KOTHANDARAMAN,¹ D. SANGEETHA,¹ A. A. SRIRAMULU,¹ M. P. M. NAYAGAM,¹ AND T. M. AMINABHAVI,²

¹ Department of Polymer Science, University of Madras, Chennai 600 025, India

² Department of Chemistry, Polymer Research Group, Karnatak University, Dharwad 580 003, India

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ABSTRACT: Polymerization reactions of styrene in toluene at 60°C have been carried out using Ziegler–Natta catalysts containing praseodymium trichloroacetate–triethyl aluminum [Pr(OCOCCl₃)₃-Et₃Al] (system I) and praseodymium trichloroacetate–diethyl aluminum bromide [Pr(OCOCCl₃)₃-Et₂AlBr] (system II). The reaction was of first order with respect to both monomer and catalyst concentrations. At a stoichiometric ratio of Al/Pr = 8, an optimum catalytic activity was observed. The activation energies for systems I and II ranged between 21.06 kJ/mol and 13.79 kJ/mol, respectively. System I was white in color and system II is waxy. Molar masses of systems I and II were 9.1×10^5 and 2.2×10^4 , respectively. The polymers were characterized by viscometry and ¹H NMR methods. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 995–1002, 2001

Key words: praseodymium trichloroacetate; styrene; kinetics; polymerization; Ziegler and Natta

INTRODUCTION

Several studies^{1–4} have been conducted in the earlier literature on the kinetics of styrene polymerization using homogeneous Ziegler–Natta catalysts. Recently, Zhing and Shen⁵ have studied the homo- and copolymerization of styrene in solution using a calixarene–neodymium catalyst along with dibutyl magnesium as a cocatalyst. The neodymium-based catalysts have been used earlier for the homopolymerization of styrene.^{6–9} Other reports in the literature^{10–13} describe the use of gadolinium-based catalysts for the homo- and copolymerization of sty-

rene, butadiene, methylmethacrylate, methylacrylate, methylacrylonitrile, acrylonitrile, etc., yielding nearly 97% of *cis* content. This article reports the polymerization of styrene using praseodymium-based catalyst, Pr(OCOCCl₃)₃ along with triethyl aluminum and diethylaluminum bromide as cocatalysts. The polymers have been characterized by viscometry and ¹H-NMR. Kinetic schemes have been proposed based on experimental parameters such as reaction time, aging time, monomer concentration, catalyst concentration, stoichiometric ratio, and temperature.

EXPERIMENTAL

Materials

Nitrogen (IOL, Chennai) was purified by passing through Fieser solution, sulfuric acid, calcium chlo-

Correspondence to: H. Kothandaraman, Department of Polymer Science, University of Madras, Chennai 600 025, India.

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Table I Variation of Reaction Time

RT (h)	AlEt ₃			AlEt ₂ Br		
	R_p ($\times 10^4$) (mol/L/s)	Percent Conversion	Molar Mass ($\times 10^{-5}$)	R_p ($\times 10^4$) (mol/L/s)	Percent Conversion	Molar Mass ($\times 10^{-4}$)
1	2.46	31.2	7.0	2.56	46.1	1.1
2	1.98	59.0	7.9	2.04	73.4	1.2
3	1.28	75.9	8.1	1.62	87.6	1.6
4	1.16	91.6	8.8	1.30	93.5	1.9
5	1.01	99.6	9.1	1.07	96.1	2.2

RT, reaction time.

Experimental variables are set at: [Sy] = 2 mol/L⁻¹; Al/Pr = 8; temperature = 60°C; [Al] = 0.06 mol/L⁻¹; aging time = 0 min; [Pr] = 0.0075 mol/L⁻¹.

ride and finally a tube containing molecular sieves (3 Å). Analytical reagent-grade toluene was dried using activated alumina. Styrene was purified by washing with 10% alkali solution, followed by distilled water and dried over calcium chloride. The monomer was then distilled at reduced pressure under nitrogen atmosphere. The middle fractions were detained and stored under nitrogen atmosphere. Catalyst, praseodymium trichloroacetate, and the cocatalysts triethyl aluminum and diethyl aluminum bromide were prepared as per the published procedures.^{14,15} The catalysts and cocatalysts thus prepared were distilled under reduced pressure (2 mm) at 69°C and 82°C, respectively.

Polymerization

The polymerization reactor consists of a two-necked round-bottomed flask fitted with a rubber septum and a nitrogen inlet/outlet tube. The nitrogen gas was purged for a short time and then the inlet/outlet tube was closed. Required amounts of solvent, catalyst, and cocatalyst were injected through the septum. Monomer was added, and the reactor was kept in a specially fabricated constant temperature bath having the capacity to accommodate six reactors with the magnetic stirrers in all the reactors individually. After a specific reaction time, the reaction was arrested by the addition of methanol containing 5% HCl. The contents of the flask were then poured into a large excess of acidified methanol and kept overnight, during which time the polymer settled down. The solid was washed with methanol, dried in a vacuum oven at 50°C for 24 h, and weighed to a constant mass. The rate of polymerization, R_p was calculated on the basis of gravimet-

rically determined conversions using the following equation^{16,17}:

$$R_p = 1000 w/(v \times t \times M) \text{ mol L}^{-1} \text{ s}^{-1} \quad (1)$$

where w is mass (g) of the polymer, v is total volume (mL) of the reactor, t is time in seconds, and M is molar mass of the monomer.

Molar Mass

Molar mass of the polymer was determined by measuring viscosity of the polymer solution in

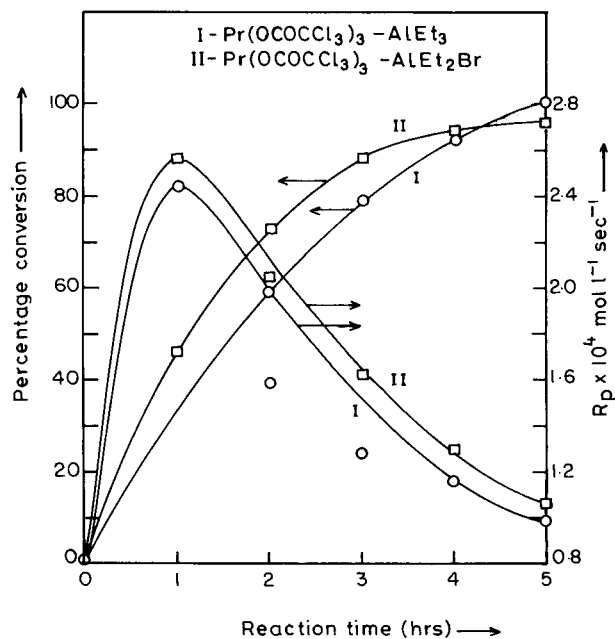


Figure 1 Percent conversion vs. reaction time for system I (○) and system II (□).

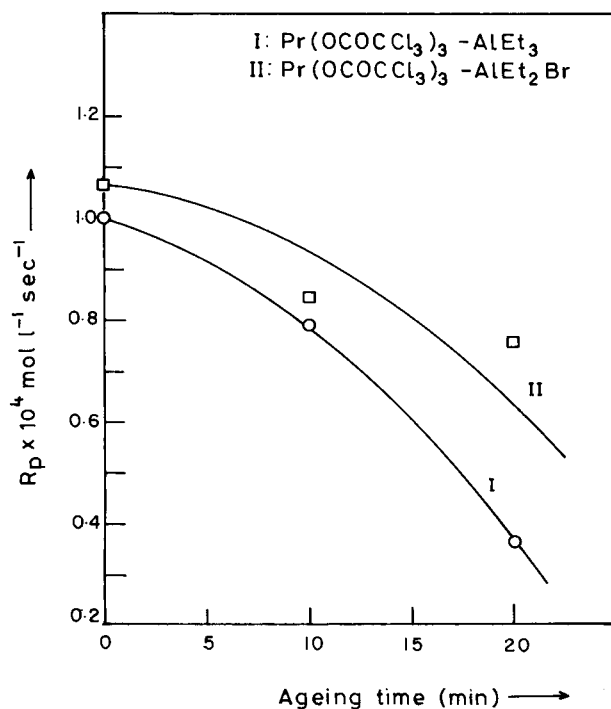


Figure 2 Rate of polymerization vs. ageing time for system I (O) and system II (□).

toluene at 30°C using an Ubbelohde suspended level dilution viscometer. The Huggins¹⁸-Kraemer¹⁹ procedure was used to calculate the intrinsic viscosity, $[\eta]$. The viscosity average molar mass, M_η was then calculated as²⁰

$$[\eta] = 1.10 \times 10^{-4} M_\eta^{0.725} \quad (2)$$

Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance (NMR) spectra were collected on a Varian 400-MHz NMR spectrome-

ter equipped with a Sun workstation. Chemical shifts are reported in ppm relative to TMS. A 40–50-mg portion of the sample was dissolved in 1 mL of CDCl_3 (Aldrich, Milwaukee, WI), and spectra were scanned.

RESULTS

The mechanism of polymerization was studied by varying reaction time, aging time, monomer concentration, catalyst concentration, Al/Pr ratio, and temperature. When the reaction time was varied from 1 to 5 h (Table I and Fig. 1), we observe a maximum rate at 1 h, which later declined with time. Such a behavior is typical of coordination anionic polymerization. By contrast, percentage conversion and molar mass values increase with an increase in reaction time.

Aging time is an important parameter in polymerization kinetics. It is the time allowed between addition of catalyst, cocatalyst, and monomer. The behavior of a catalyst depends upon the order in which the catalyst components are mixed. With an increase in aging time, the rate of polymerization decreases (Fig. 2), and the polymer yield as well as molar mass decrease. These data are presented in Table II.

The variation of monomer concentration on the rate of polymerization was investigated at Al/Pr = 8 and at 60°C for 5 h of reaction time. The results of R_p displayed in Figure 3 and numerical data given in Table III indicate that R_p as well as percentage conversion and molar mass of the polymer increase linearly with monomer concentration, suggesting no chain transfer reactions taking place during polymerization. The polymerization follows the first-

Table II Variation of Aging Time

AT (min)	AlEt ₃			AlEt ₂ Br		
	R_p ($\times 10^4$) (mol/L/s)	Percent Conversion	Molar Mass ($\times 10^{-5}$)	R_p ($\times 10^4$) (mol/L/s)	Percent Conversion	Molar Mass ($\times 10^{-4}$)
0	1.01	99.8	9.1	1.07	96.0	2.3
10	0.79	78.0	7.6	0.82	75.7	1.9
20	0.36	35.8	3.6	0.75	67.7	1.6

AT, aging time.

Experimental variables are set at: $[\text{Sy}] = 2 \text{ mol/L}^{-1}$; Al/Pr = 8; reaction time = 5 h; $[\text{Al}] = 0.06 \text{ mol/L}^{-1}$; temperature = 60°C; $[\text{Pr}] = 0.0075 \text{ mol/L}^{-1}$.

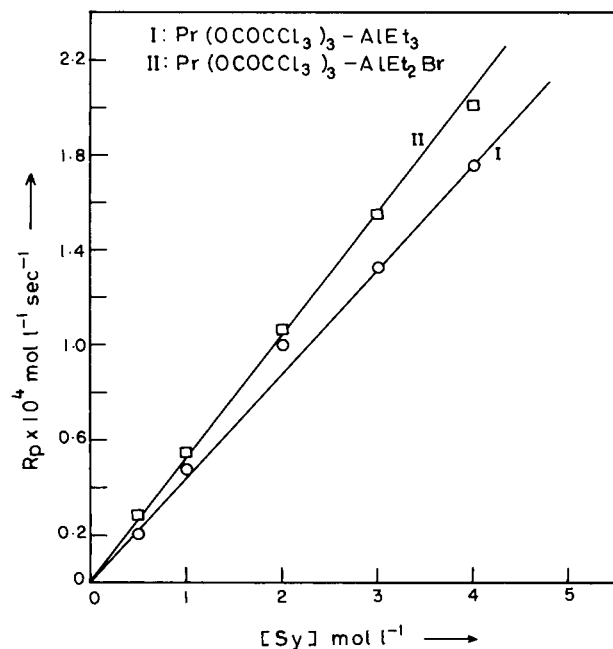


Figure 3 Rate of polymerization vs. styrene concentration for system I (○) and system II (□).

order kinetics with respect to monomer concentration $[Sy]$ in both the systems.

The dependencies of catalyst concentration on R_p (Fig. 4), percentage conversion, and molar mass are presented in Table IV. The polymerization reaction follows the first-order kinetics with respect to catalyst concentration $[Pr]$ for both the systems and the values of R_p as well as percentage conversion increase with increasing catalyst concentration, while molar mass decrease.

The effect of Al/Pr ratio on the rate of polymerization is presented in Figure 5. It is observed

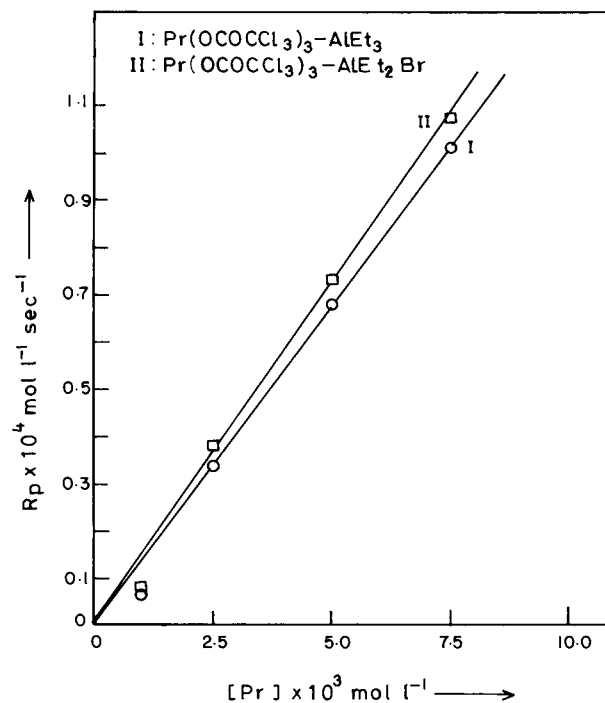


Figure 4 Rate of polymerization vs. catalyst concentration for system I (○) and system II (□).

that at the ratio value of 8, a maximum rate is observed for both the systems, which later showed a decline. The results presented in Table V indicate that the percentage conversion and molar mass increase considerably with increasing values of the Al/Pr ratio.

Effect of temperature on the rate of polymerization was not significant, but the percentage conversion increases considerably in both the systems (Table VI). Similarly, R_p values increase

Table III Variation of Monomer Concentration

$[M]$ (mol/L ⁻¹)	AlEt ₃			AlEt ₂ Br		
	R_p ($\times 10^4$) (mol/L/s)	Percent Conversion	Molar Mass ($\times 10^{-5}$)	R_p (mol/L/s)	Percent Conversion	Molar Mass ($\times 10^{-4}$)
0.5	0.20	79.2	6.2	0.24	86.0	0.88
1.0	0.49	97.8	7.7	0.52	93.4	1.25
2.0	1.02	99.9	9.1	1.07	96.1	2.24
3.0	1.33	87.7	10.8	1.55	93.0	3.49
4.0	1.74	86.5	12.6	1.99	90.0	4.16

Experimental variables are set at: temperature = 60°C; Al/Pr = 8; reaction time = 5 h; $[Al]$ = 0.06 mol L⁻¹; aging time = 0 min; $[Pr]$ = 0.0075 mol/L⁻¹.

Table IV Variation of Catalyst Concentration

[cat] ($\times 10^{-3}$) (mol/L)	AlEt ₃			AlEt ₂ Br		
	R_p ($\times 10^4$) (mol/L/s)	Percent Conversion	Molar Mass ($\times 10^{-5}$)	R_p ($\times 10^4$) (mol/L/s)	Percent Conversion	Molar Mass ($\times 10^{-4}$)
0.5	0.06	6.1	12.8	0.07	6.4	2.8
2.5	0.34	33.2	11.6	0.37	33.0	2.7
5.0	0.68	66.5	9.9	0.72	64.3	2.4
7.5	1.01	99.7	9.1	1.07	96.4	2.2

Experimental variables are set at: [Sy] = 2 mol/L⁻¹; Al/Pr = 8; reaction time = 5 h; [Al] = 0.06 mol/L⁻¹; aging time = 0 min; temperature = 60°C.

with an increase in temperature. The activation energies for system I and system II calculated from the slopes of the straight line plots of $\log R_p$ vs $1/T$ shown in Figure 6 are 21.6 and 13.8 kJ/mol, respectively. This falls within the range expected of coordination polymers, further supporting the coordination/anionic-type mechanism for the systems of this study.

DISCUSSION

To check the presence of free radicals after polymerization, hydroquinone was added to the reac-

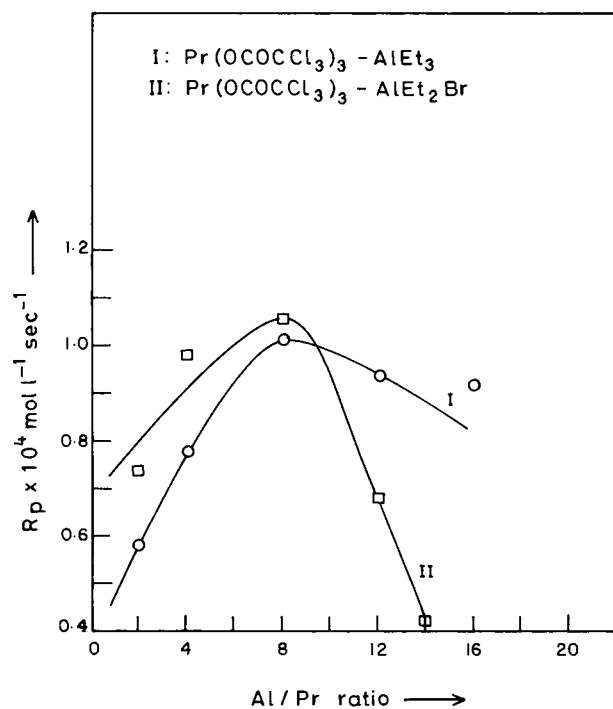
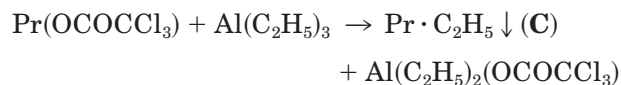
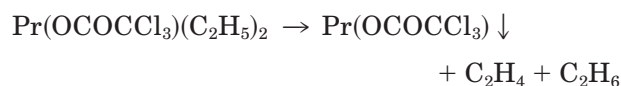
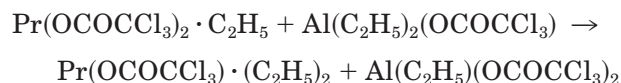
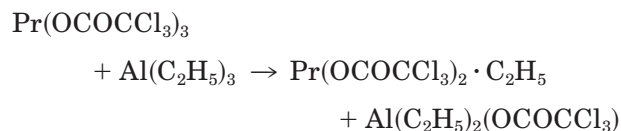


Figure 5 Rate of polymerization vs. the ratio of Al/Pr for system I (○) and system II (□).

tion medium and this did not affect either the rate of polymerization or the molar mass of the polymers. On the basis of the present results, the following mechanisms are proposed.

The active center is first formed through alkylation followed by reduction and further alkylation of the metal compound by the alkyl aluminum:



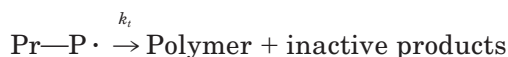
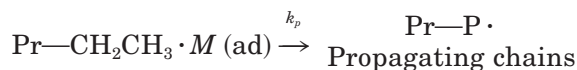
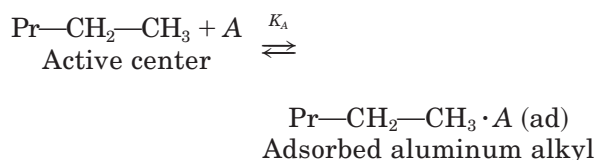
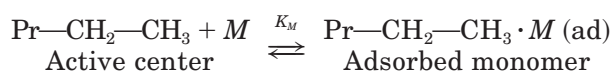
where (C) is the active center.

A two-step propagation reaction based on the Langmuir and Hinshelwood mechanism²¹ is proposed. The first step is the coordination of the monomer on the alkylated metal and the second step is the insertion of the coordinated monomer into the growing metal-carbon bond. Both the monomer and the aluminum alkyl molecules compete for adsorption on the catalyst surface and the polymerization will occur only if both are adsorbed appreciably. However, propagation proceeds by repeated insertions of a large number of monomer molecules. A unimolecular decay termination is thus proposed:

Table V Variation of Al/Pr Ratio

Al/Pr Ratio	AlEt ₃			AlEt ₂ Br		
	R_p ($\times 10^4$) (mol/L/s)	Percent Conversion	Molar Mass ($\times 10^{-5}$)	R_p ($\times 10^4$) (mol/L/s)	Percent Conversion	Molar Mass ($\times 10^{-4}$)
2	0.58	09.2	8.4	0.743	66.7	1.9
4	0.78	76.9	8.8	0.982	88.3	1.5
8	1.01	99.7	9.1	1.068	96.0	2.2
12	0.94	92.9	9.8	0.678	61.0	3.0
16	0.92	90.7	10.3	0.423	38.0	4.1

Experimental variables are set at: [Sy] = 2M; Al/Pr = 8; reaction time = 5 h; [Pr] = 0.0075 mol L⁻¹; aging time = 0 min; temperature = 60°C.



fractions of the surface covered by the monomer and the aluminum alkyl (θ_M and θ_A) are expressed by the Langmuir and Hinshelwood²¹ isotherms of the type:

$$\theta_M = \frac{K_M[M]}{1 + K_M[M] + K_A[A]} \quad (3)$$

$$\theta_A = \frac{K_A[A]}{1 + K_M[M] + K_A[A]} \quad (4)$$

where K_M is the rate constant for the adsorption of the monomer and K_A is the rate constant for the adsorption of the aluminum alkyl.

The rate of polymerization, R_p is then expressed as:

$$R_p = k_p C^* \theta_A \theta_M \quad (5)$$

where M is the monomer and A is aluminum alkyl, k_t is rate constant for termination. The

Table VI Variation of Temperature

Temp (°C)	AlEt ₃			AlEt ₂ Br		
	R_p ($\times 10^4$) (mol/L/s)	Percent Conversion	Molar Mass ($\times 10^{-5}$)	R_p ($\times 10^4$) (mol/L/s)	Percent Conversion	Molar Mass ($\times 10^{-4}$)
30	0.56	54.7	10.4	0.60	54.0	2.7
40	0.74	73.4	9.1	0.75	67.8	2.5
50	0.96	94.8	8.3	0.97	87.5	2.1
60	1.0132	99.84	9.100	1.070	96.23	2.3

Experimental variables are set at: [Sy] = 2 mol/L⁻¹; Al/Pr = 8; reaction time = 5 h; [Al] = 0.06 mol/L⁻¹; aging time = 0 min; [Pr] = 0.0075 mol/L⁻¹.

where k_p is the rate constant for polymerization and C^* is the concentration of the active centers.

Substituting the values of θ_A and θ_M from eqs. 3 and 4 into eq. 5, the R_p becomes

$$R_p = \frac{k_p K_M K_A C^* [M][A]}{(1 + K_M [M] + K_A [A])^2} \quad (6)$$

It may be inferred from eq. 6 that (1) the order of reaction with respect to monomer is one, and (2) the order of reaction with respect to catalyst is also one, since $c^* \propto [\text{catalyst}]$.²² When the concentration of monomer is constant and at concentration of aluminum alkyl sufficiently large, $K_A [A] \rightarrow K_M [M]$ and eq. 6 becomes

$$R_p = \frac{K_p K_A C^* [A]}{(1 + K_A [A])^2} \quad (7)$$

The validity of the above mechanism was checked from the plot of $([A]/R_p)$ vs. $[A]$, for which a straight line was obtained (see Fig. 7). Further experimental proofs supporting this mechanism are that the reaction is first order with respect to

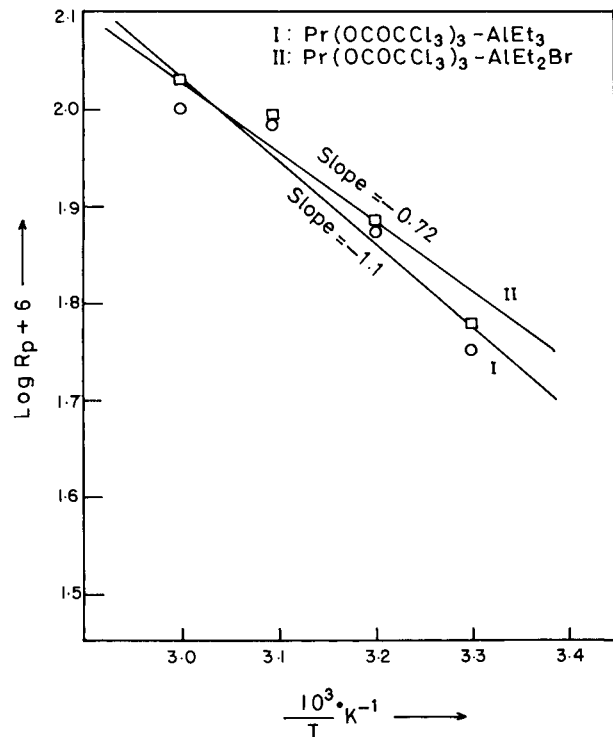


Figure 6 Arrhenius plot for system I (○) and system II (□).

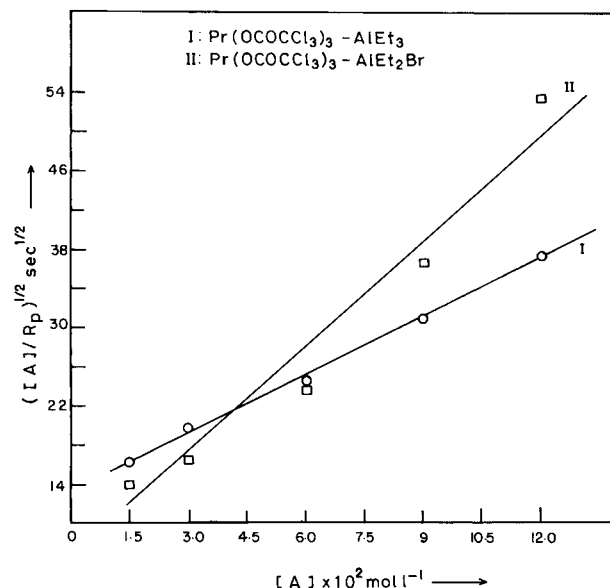


Figure 7 Plot of $([A]/R_p)^{1/2}$ vs. $[A]$ for system I (○) and system II (□).

monomer and catalyst and that the reaction shows maximum conversion with an increasing concentration of aluminum alkyl. A similar mechanism is possible for the polymerization involving AlEt_2Br .

Furthermore, proton NMR gave characteristic signals of polystyrene.

In conclusion, it may be noted that for system I, the molar masses are higher by an order of magnitude than observed for system II, indicating that praseodymium trichloroacetate-triethyl aluminum is a more efficient catalyst than praseodymium trichloroacetate-diethyl aluminum bromide.

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