

# Kinetics of Polymerization of Styrene. The Catalyst System $\text{Cu}_2\text{Cl}_2 + \text{AlEt}_3$ in *n*-Hexane

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## Synopsis

Studies on polymerization of styrene by the heterogeneous catalyst system  $\text{Cu}_2\text{Cl}_2 + \text{AlEt}_3$  are reported. Kinetic studies carried out at an optimum catalyst composition  $[\text{Al}]/[\text{Cu}] = 0.8$  and aging time of 4 h give a value of 55 kJ/mol for the activation energy. The rate law can be presented as  $R = K [\text{cat}] [\text{mon}]^2$ . A radical mechanism is proposed on the basis of the effect of hydroquinone and ESR spectra. The mechanism of polymerization with this catalyst system is different than that of  $\text{CuCl}_2 + \text{AlEt}_2\text{X}$  ( $\text{X} = \text{Br}, \text{Cl}$ ), which was reported earlier.

## INTRODUCTION

We have reported on the catalyst systems  $\text{CuCl}_2 + \text{AlEt}_2\text{Br}$ ,<sup>1</sup>  $\text{CuCl}_2 + \text{AlEt}_2\text{Cl}$ ,<sup>2,3</sup> and  $\text{CuCl}_2 + \text{AlEt}_3$ .<sup>4</sup> It is found that the first two systems polymerize styrene by ionic coordinated-type mechanism, whereas the third behaves as a radical initiator. Ziegler–Natta types of catalyst systems can be formed by combination of halides as well as subhalides of transition metals with organo-aluminum compounds. As an extension of our work with the  $\text{CuCl}_2 + \text{AlEt}_3$  system, we have studied the present catalyst system  $\text{Cu}_2\text{Cl}_2 + \text{AlEt}_3$ .

Wasaburo et al.<sup>5</sup> studied the same catalyst system for the polymerization of methyl methacrylate. They proposed a free-radical mechanism based on their studies of copolymerization of methyl methacrylate with styrene, acrylonitrile, and ESR studies.

## EXPERIMENTAL

Cuprous chloride (BDH, LR grade) was purified as reported by Keller et al.<sup>6</sup> Triethylaluminum was obtained as solution in *n*-hexane and was diluted to the required concentration with dry *n*-hexane. Purification of solvent, the monomer, and the procedure of polymerization were described earlier.<sup>1–4</sup> ESR spectra of catalyst in presence and absence of monomer were scanned on a 100-MHz Varian spectrometer using TCNE as standard.

## RESULTS AND DISCUSSION

Mixing the two catalyst components resulted in a black precipitate and metallic copper, along with gas evolution.

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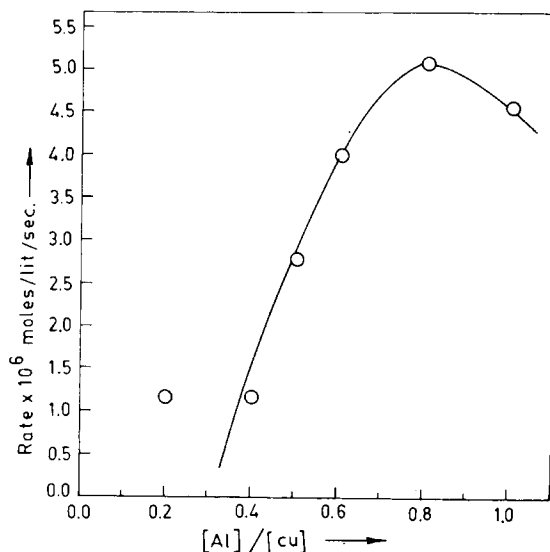


Fig. 1. Optimization of catalyst composition;  $[\text{Cu}_2\text{Cl}_2] = 0.025 \text{ M}$ ,  $[\text{Sty}] = 4.33 \text{ M}$ , aging time = 20 min, reaction time = 180 min, temperature =  $30^\circ\text{C}$ .

The variation in rate of polymerization with increasing  $[\text{Al}]/[\text{Cu}]$  is presented in Figure 1. The rate increases up to  $[\text{Al}]/[\text{Cu}] = 0.8$  and then decreases steeply. The phenomenon is attributed to the reduction in the valence state of the transition metal compound with increasing amounts of  $\text{AlEt}_3$ . At a composition of  $[\text{Al}]/[\text{Cu}] = 0.8$ , a complex having maximum activity for the polymerization might have been formed. In case of methyl methacrylate, a ratio of 1.23 was used by Wasaburo et al.<sup>5</sup> The catalyst system  $\text{CuCl}_2 + \text{AlEt}_3$  which polymerizes styrene at an optimum depends on the nature of the components of the catalyst and also on the nature of the monomer.<sup>4</sup> If the transition metal element is in the higher valance state, the ratio will be higher.

An optimum aging time of 20 min was observed, and the variation in rate with aging time is presented in Table I.

Kinetic studies were carried out at the above optimum conditions. Figure 2 shows variation of the percent conversion of monomer with time of polymerization. Steady rates of polymerization observed are  $3.6 \times 10^{-6}$ ,  $2.0 \times 10^{-6}$ , and  $1.1 \times 10^{-6}$  mol/L·s at 40, 30 and  $20^\circ\text{C}$ , respectively.

An activation energy of 55 kJ/mol is calculated using the Arrhenius plot pre-

TABLE I  
Aging Time Optimization<sup>a</sup>

Aging time, min	Rate $\times 10^6$ , mol/L·s
10	1.40
20	5.10
30	1.20
45	2.68
60	0.72

<sup>a</sup> Reaction conditions:  $[\text{Cu}_2\text{Cl}_2] = 0.025 \text{ M}$ ,  $[\text{Al}]/[\text{Cu}] = 0.8$ ,  $[\text{Sty}] = 4.33 \text{ M}$ , temperature =  $30^\circ\text{C}$ , reactin time = 180 min.

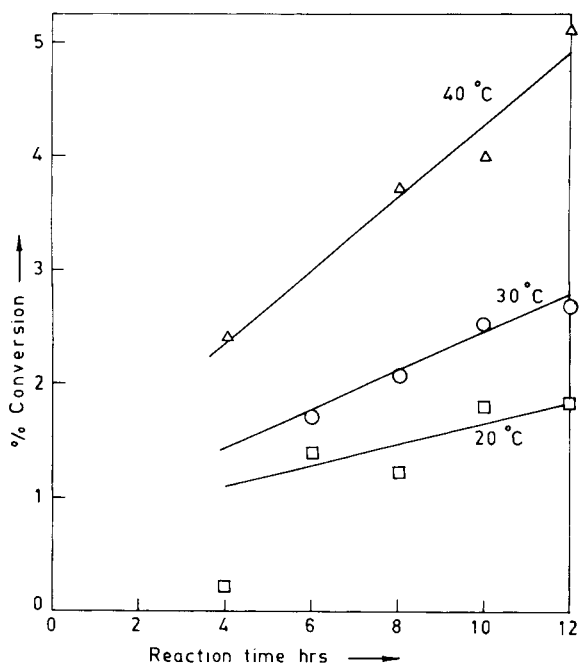


Fig. 2. Percent conversion vs. time at 40, 30, and 20°C; [Al]/[Cu] = 0.8. Other conditions same as in Fig. 1.

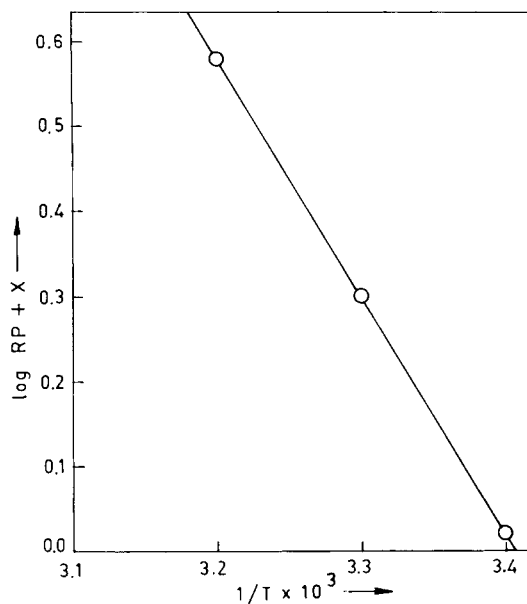


Fig. 3. Arrhenius plot;  $R = K[\text{cat}][\text{mon}]^2$ ;  $\log K = \log R - \log[\text{cat}] - 2 \log[\text{mon}] = \log R + \chi \dots$  ( $\chi = 6$ ).

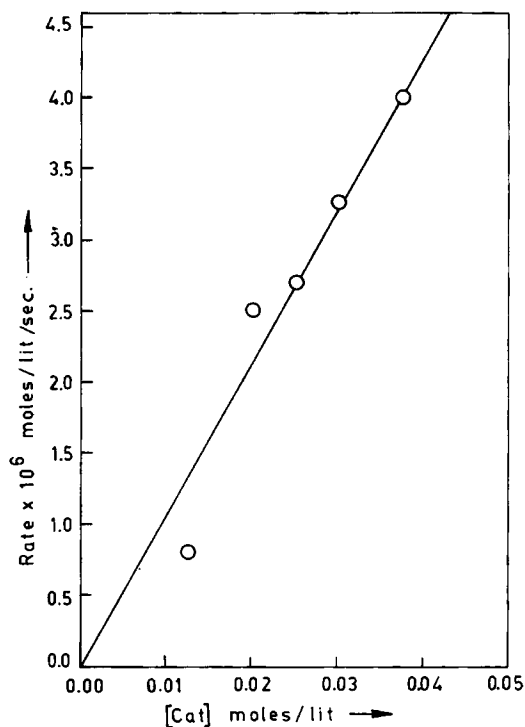


Fig. 4. Rate vs. catalyst concentrations at 30°C; [Sty] = 4.33 *M*, aging time = 20 min, reaction time = 180 min.

sented (Fig. 3). This is near the range of Ziegler-type polymerizations (21.0–50.4 kJ/mol).<sup>7</sup> Figures 4 and 5, presenting rate variation with [cat] and [mon], suggest the following rate law for polymerization:

$$R = K[\text{cat}][\text{mon}]^2$$

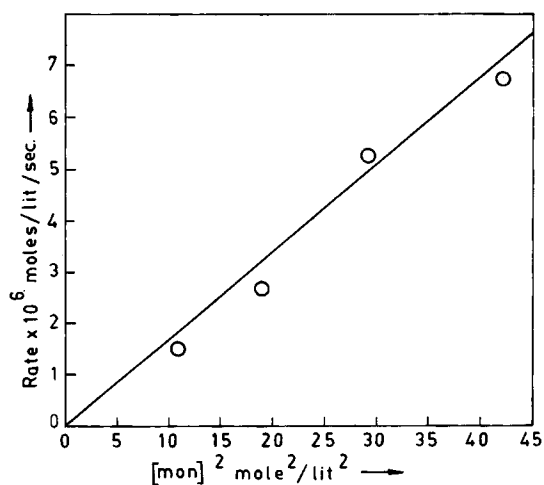


Fig. 5. Rate vs. monomer concentrations at 30°C; [Cu<sub>2</sub>Cl<sub>2</sub>] = 0.025 *M*, aging time = 20 min, reaction time = 180 min.

TABLE II  
Effect of Addition of Hydroquinone<sup>a</sup>

[HQ], M	Rate $\times 10^6$ , mol/L·s
0.00	3.34
0.03	2.71
0.06	2.29

<sup>a</sup> Reaction temperature = 30°C, aging time = 20 min, reaction time = 24 h, [Cu] = 0.025 M, [Sty] = 4.33 M, [Al]/[Cu] = 0.8.

Initial addition of hydroquinone, as a radical scavenger, before commencement of polymerization decreases the rate of polymerization (Table II). This suggests radical-type propagation as proposed by Wasaburo et al.<sup>5</sup>

The proportionality of rate to the first power of catalyst concentration is usually observed in Ziegler–Natta-type polymerizations. The second-order dependence of rate on monomer concentrations has been observed by many research workers for ionic coordinated mechanisms.<sup>8–13</sup> A few attempts based on theoretical relationships have been reported to explain this second-order dependence. Tait et al. have reported this dependence as due to the nonequilibrium nature of initiation process.<sup>11</sup> Reich and Stivala have explained the kinetics based on adsorption of monomer on an active dual site and worked out a few explicit formulas.<sup>14</sup> Gaylord et al. have proposed a scheme for second-order kinetics with respect to monomer.<sup>10</sup> However, rigorous testing of the above theoretical approaches has not been done.

In the case of radical mechanism for Ziegler-type polymerization, as discussed below, it is not a free-radical mechanism but a bound-radical mechanism emerging out of absorption of monomers on catalyst surfaces; and so the approach of Reich and Stivala may be considered in the present case.

In the absence of monomer, the ESR spectrum of the catalyst does not show any signal for radicals. In the presence of styrene, a signal is obtained which persists even up to 24 h (Fig. 6), indicating the presence of radicals. The  $g$  value calculated is 2.0022, compared to 2.00277 for TCNE.

In a normal free-radical polymerization, the rate increases in the beginning and remains steady. In the present case, the rate decreases and remains steady.

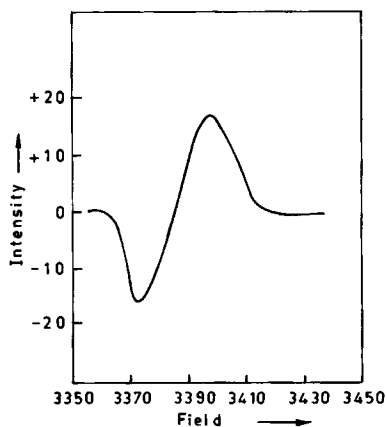


Fig. 6. ESR spectrum of catalyst mixture in the presence of styrene.

This is due to the necessity of the monomer unit to interact with the catalyst prior to formation of polymer. As suggested by Vollmert<sup>15</sup> and Mark and Gaylord,<sup>16</sup> the chain radical is not a free radical but remains as a ligand, bound to the transition metal during the entire chain growth. At a later stage, the rate becomes diffusion controlled due to the collection and precipitation of polymer at the catalyst sites.

## CONCLUSIONS

The system cuprous chloride + triethylaluminum in *n*-hexane polymerizes styrene by a bound radical mechanism.

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