Polymer Bulletin 2, 637–642 (1980)

Polymer Bulletin

Kinetics of Polymerization of Styrene

The Catalyst System $CuCl_2$+ $AlEt_2Br$ in N-Hexane

M. V. Pandya*, D. D. Deshpande and N. M. Desai

Department of Chemistry, Indian Institute of Technology, Bombay, Powai,
Bombay-400 076, India

Summary

This paper presents the kinetic study of polymerisation of styrene with Ziegler-Nutta type catalyst system. The components of the catalyst are $CuCl_2$ and Diethyl aluminium bromide (DEAB). Out standing observations of the study are as follows.

i) The minimum aging period of the catalyst system is 4 hours.

ii) The optimum ratio of [Al]/[Cu] is observed to be 2.5.

iii) Polymerisation rate is found directly proportional to monomer concentration but inversely proportional to catalyst concentration.

iv) Energy of activation obtained is 5.47 K.cal/mole, within the range usually observed in anionic coordinated type mechanism.

v) Mol. wt. is of the order of 10^4 and the polystyrene obtained is partly soluble in acetone.

Introduction

Polymerization by Ziegler-Natta type of catalysts generally results in a product with increased proportion of stereoregular polymer. Titanium, vanadium and chromium are widely used as transition element component of Ziegler-Natta type catalysts. But copper compounds, which are less expensive are not studied extensively as catalyst components in these systems. A few patents (CROWFORD, 1959; CLAFF, 1960) and a publication (WASABURO, 1971) are reported on the use of copper as one of the components of Ziegler-Natta type catalysts. CLAFF (1960) has reported crystalline polyethylene resulting from cupric chloride and triethyl aluminium in methylene chloride as solvent.

---

* To whom correspondence should be made

0170-0839/80/0002/0637/$01.20

We have used the catalyst system cupric chloride in combination with diethylaluminium bromide in n-hexane to polymerize styreme at 20°, 30° and 40°C. The kinetic features of this system are reported here.

Experimental

Solvent n-hexane was treated with concentrated sulfuric acid, subsequently with small amount of alkali and finally with distilled water and dried over anhydrous calcium chloride. It was distilled and stored over sodium. Before use it was refluxed over sodium for a long time and distilled. Purity of the solvent was assessed by chromatographic method.

Anhydrous cupric chloride was prepared by heating $CuCl_2.2H_2O$ at 110°C under vacuum.

Diethylaluminium bromide (DEAB) was synthesized according to the method of GROSSEE (1940). It was distilled under nitrogen atmosphere at 80°C and 2 mm pressure and stored in dry-box. A solution of required normality was prepared in n-hexane and concentration was verified by EDTA titration for aluminium.

Styrene was freed from inhibitor by alkali treatment, washed with distilled water, and dried over anhydrous sodium carbonate. Before use it was distilled at 55°C under vacuum and stored over molecular sieves.

All polymerization reactions were carried out in a 50 ml specially designed flasks fitted with B-19 standard joints. Inside the dry-box, in an atmosphere of oxygen free dry nitrogen, a calculated amount of solvent and DEAB was added by means of syringes to a weighed amount of $CuCl_2$ in the flask. Catalyst so formed was aged in a thermostat at 30 ± 0.05°C for required time and monomer was added. After specific time of polymerization, the reaction was stopped by addition of acidic methanol. The polymer was precipitated by addition of excess of methanol, and was removed on a sintered crucible. It was washed with acidic methanol and subsequently with pure methanol. It was dried under vacuum to constant weight.

Results and discussions

Within a few minutes of addition of organometallic compounds, the color of $CuCl_2$ changed from black-brown to white. The catalyst system so formed was aged for a time ranging from 1 hr to 6 hrs. The percentage conversion of monomer to polymer decreases from 1 hr to

4 hrs of aging period and then remains constant upto 6 hrs as can be seen from Fig.1.

This behaviour can be attributed to the large number of catalyst sites formed in the initial period, some of which are long living and some short living. Over a period of 4 hrs the short living sites decay. The constant conversion from 4 hrs to 6 hrs is due to long living sites.

A very important factor in this type of catalysts is the [Al]/[Cu] ratio. To determine the optimum ratio experiments were carried out at varying [Al]/[Cu] ratio from 1.0 to 5.0. From Fig. 2 it can be seen that the conversion decreases upto a ratio of [Al]/[Cu] = 2.0 and then increases upto a maximum of 2.5 and again decreases.

ASHIKARI (1961), has explained this behaviour, that at low concentration of organometallic compound the reaction may be predominantly cationic in nature, but with increasing concentration of organometallic compound the mechanism changes from cationic to anionic type. The maxima of [Al]/[Cu] ratio of 2.5 is selected for our studies.

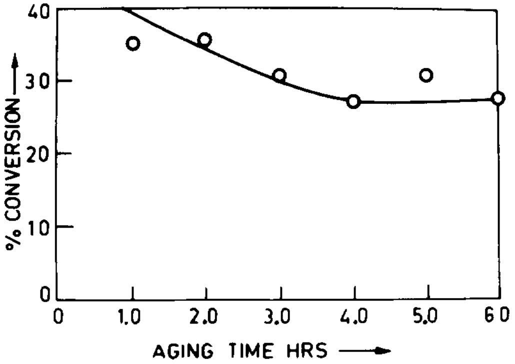

Fig.1: Plot of % conversion vs aging time.

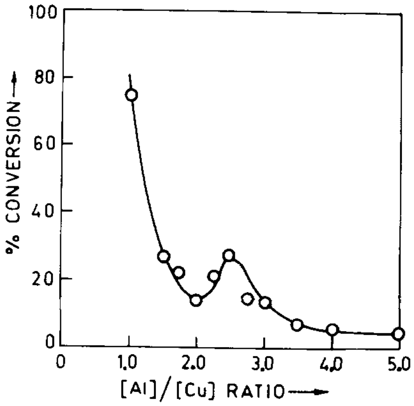

Fig.2: Plot of % conversion vs [Al]/[Cu] ratio.

With these two parameters namely [Al]/[Cu] ratio and aging time fixed at 2.5 and 4 hrs respectively kinetic studies were carried out at varying catalyst and monomer concentrations.

As the time of reaction increases the rate falls and shows a steady state, (Fig. 3). Initially the rate is high and the precipitated polymer (due to non-solvent medium) in this period traps the catalyst sites. And hence the passage of monomer to the catalyst site becomes diffusion controlled. This is the reason for steady state in the later period.

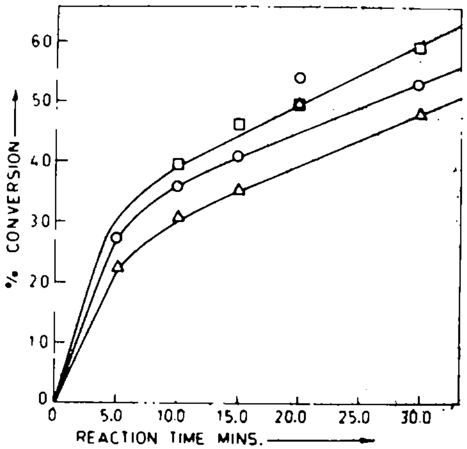

Fig.3: Effect of reaction time on % conversion.

It was observed that the conversion decreases with catalyst concentration and increases with monomer concentration linearly (Figs. 4 and 5).

The behaviour in Fig. 4 can be attributed to a large amount of chain transfer due to catalyst. REICH (1963) has explained this due to surface reaction where alkyl and monomer are adsorbed on the sites, but unadsorbed monomer may be sufficiently reactive for the initiation step.

The rate of polymerization can be given as

$$R_p = K_p \times [\text{catalyst}]^{-1} [\text{monomer}].$$

An activation energy of 5.47 KCal/mole for steady state polymerization was obtained by plotting log R_p vs 1/T as shown in Fig. 6.

The activation energy for conventional and modified Ziegler-Natta type catalyst system lies between 5-12 KCal/mole for anionic co-ordinated mechanism (FUKUI, 1962; KODAMA, 1960). The mechanism of this system may be of similar nature.

The polymers formed are of the molecular weight of the order of 10^4. These were soluble in methyl ethyl ketone but were only partly soluble in acetone. NATTA (1955) has shown that polystyrene of the molecular weight of 10^4 order of magnitude and of crystalline nature is insoluble in acetone. So the polymer formed may be at least in part stereoregular.

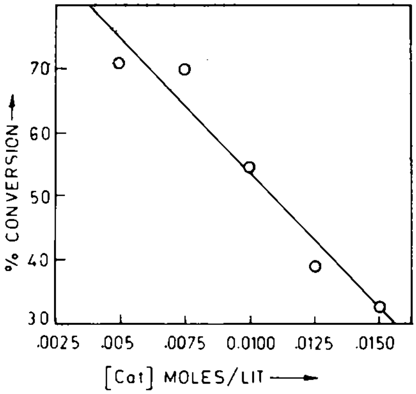

Fig.4 : Effect of catalyst concentration on % conversion.

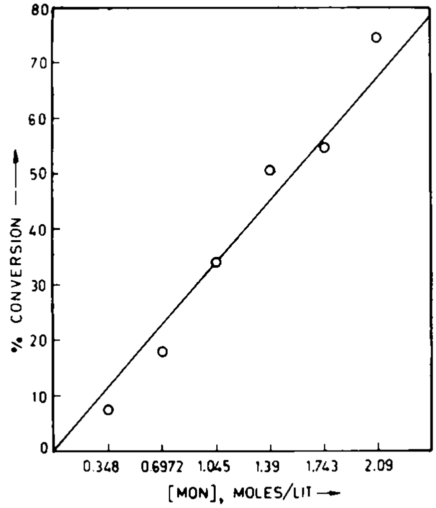

Fig.5 : Effect of monomer concentration of % conversion.

Conclusions

The catalyst systems seem to be having higher activity than those of conventional Ziegler-Natta type catalysts. It is usually observed that with higher rates of polymerizations, the stereoregularity of polymers is low. In this particular system we suspect some cationic overtones, as can be seen from lower molecular weights of polymer.

Further studies on these type of systems is in progress.

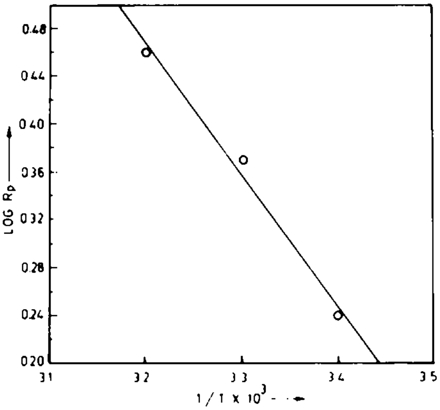

Fig.6 : Plot of log R_p vs 1/T

References

1. ASHIKARI N. et al., Bull.Chem.Soc.Japan, 34, 767 (1961)
2. CLAFF C.E. Jr., Brit. 828, 973, Feb.24 (1960)
3. CROWFORD J.W.C. et al., Brit. 812, 176 (1959)
4. FUKUI K., et al., Bull.Chem.Soc.Japan, 35, 303 (1962)
5. GROSSEE A. et al., J.Org.Chem., 5, 106 (1940)
6. KODAMA S. et al., J.Appl.Polymer.Sci., 3, 20 (1960)
7. NATTA G. et al., Proceedings of 4th World Petroleum Congress, Rome (Italy), Section IV/C; Repr. 13 (1955)
8. REICH L. et al., J.Polymer Sci., A1, 203 (1963)
9. WASABURO K. et al., J.Polymer Sci., A1, 9, 1599 (1971)

Received April 18, 198o