Polymer Bulletin 11, 85-88 (1984)

Polymer Bulletin

Vinyl Polymerization by Ziegler Catalysts

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SUMMARY

Methylmethacrylate and styrene were polymerized with $Co(acac)_3$-$AlEt_2Br$ catalyst system in benzene at 40°C. Rate of polymerization is linear to monomer concentrations. Maximum percent conversion of polymer was obtained when $Al/Co \geqslant 2$ with styrene and $Al/Co \geqslant 3$ with methylmethacrylate. With increase in aging time catalytic activity decreases. Activation energy was found to be 60 KJ $mol.^{-1}$ with styrene and 49 KJ $mol.^{-1}$ with methylmethacrylate.

INTRODUCTION

Ziegler catalysts containing metal acetylacetonates and aluminum alkyls polymerize olefins and vinyl monomers (1,2). A literature study reveals that there is no detailed kinetic investigation on Ziegler catalysts containing metal acetylacetonates and aluminum alkyls. Although there are a few kinetic details with titanium catalysts (3-5) and aluminum alkyls, detailed study with cobalt salts and aluminum alkyls on the polymerization of vinyl monomers are very few. The present system is homogenious and is a convenient one to follow the kinetics of vinyl polymerization. In this article the results of kinetic studies on methylmethacrylate and styrene by $Co(acac)_3$-$AlEt_2Br$ catalyst are reported.

EXPERIMENTAL DETAILS

Inhibitors in styrene and methylmethacrylate were removed by washing with 10% alkali solution followed by distilled water. After drying over calcium chloride, the monomers were distilled at reduced pressure under nitrogen atmosphere. The middle fractions were detained and stored under nitrogen atmosphere.

Cobalt acetylacetonate was prepared by the standard procedure (6) and stored under nitrogen. Diethylaluminumbromide was prepared by procedures given in the literature (7,8) and stored under nitrogen. 0.25 M solution of $Co(acac)_3$ and 0.5 M solution of $AlEt_2Br$ were freshly prepared in benzene before use.

Benzene was freed from unsaturated compounds by repeated washings with concentrated sulfuric acid followed by water and dried over anhydrous calcium chloride. It was then filtered, refluxed with sodium shavings under nitrogen and distilled to collect the middle fraction. Ethanol was

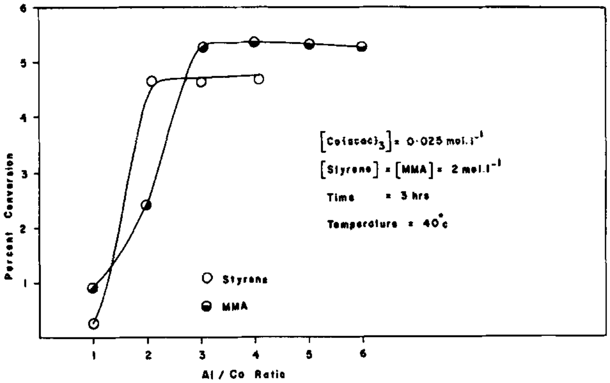

FIG.1. Effect of Al/Co ratio on Percent Conversion of Polymerization by $Co(acac)_3 - AlEt_2Br$ System.

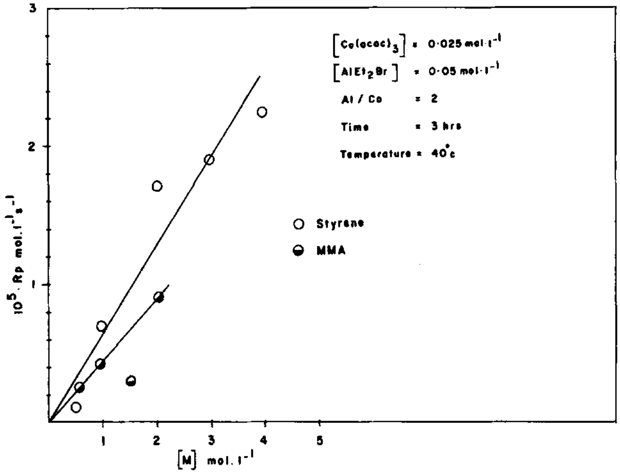

FIG.2. Effect of Monomer Concentration on Polymerization by $Co(acac)_3$-$AlEt_2Br$ System.

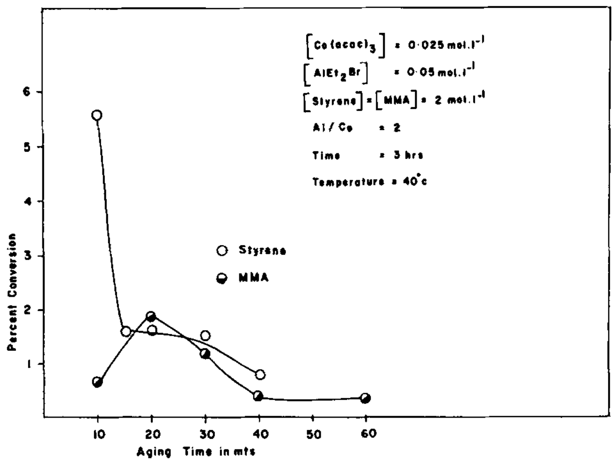

FIG.3. Effect of Aging Time on Percent Conversion of Polymerization by $Co(acac)_3 - AlEt_2Br$ System.

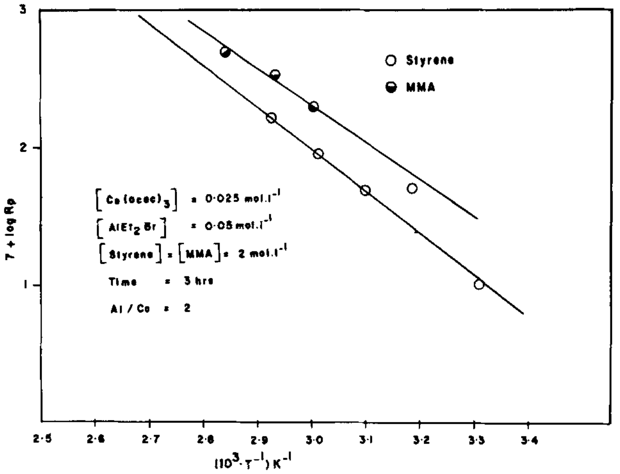

FIG.4. Effect of Temperature on log Rp of Polymerization by Co(acac)$_3$-AlEt$_2$Br System.

refluxed over calcium oxide and distilled to collect the middle fraction.

All operations such as preparation of the catalyst, addition of monomers etc., were carried out inside a dry box, which was continuously flushed with ultrapure nitrogen. In the particular experiment, benzene was added as a solvent to a 75 ml. Erlenmeyer flask followed by Co(acac)$_3$ solution, AlEt$_2$Br solution and finally monomer. After addition of all reactants, the reaction flask was lightly stoppered and kept in a thermostat adjusted to 40°C. After a definite reaction time, the resultant mixture was poured into acidified ethanol. The precipitate was filtered through a sintered glass funnel, dried at 40°C/10 mm Hg and weighed.

RESULTS AND DISCUSSION

The order of addition of the catalyst components and monomers has a great influence on the polymerization (5). The addition of cobalt-acetylacetonate to the benzene solvent followed by diethylaluminumbromide changes the green colour to light brown, and there was no solid formation indicating the homogeneous nature of the catalyst system. Further addition of monomer to the catalyst did not change its colour indicating that there was no complex formation with the monomer.

The Al/Co ratio was varied from 1 to 6 in methylmethacrylate and from 1 to 4 in styrene polymerization, keeping the Co(acac)$_3$ concentration constant and changing the concentration of diethylaluminumbromide. It is seen in Fig.1 that maximum conversion to polymer was obtained when Al/Co = 2 in styrene and Al/Co = 3 in methylmethacrylate, and increasing the Al/Co ratio beyond that had no effect on precent conversion. It is believed that the reactive species are formed by the exchange of acac groups by ethyl groups in the metal complex. At relatively high Al/Co ratios ($\geqslant 2$) activity of the catalyst is high. In homogeneous catalyst systems, stoichiometric complex (1:2 or 1:3) will give the maximum percent conversion (2), which was found to be the case in previous studies also (9).

The kinetics of the reaction shows that the rate of polymerization is linearly propotional to increase in monomer concentration (Fig.2). For methylmethacrylate polymerization, maximum efficiency of the catalyst was observed when the aging time was 20 minutes. For styrene polymerization maximum effeciency was reached at the aging time 10 minutes. Further increase of aging time decreases the effeciency of the catalyst (Fig.3). There is general agreement that too much of aging of the catalyst decreases the catalytic activity (10,11). The activation energy was calculated to be 60 KJ $mol.^{-1}$ for styrene and 49 KJ $mol.^{-1}$ for methylmethacrylate (Fig.4). The activation energies for propylene and styrene polymerizations are reported (12-14) to be in the range 14 K.Cals and 9 K.Cals respectively indicating coordinating-anionic mechanism for the polymerization. In the present system involving $Co(acac)_3$ and $AlEt_2Br$ also a coordinating-anionic mechanism can be assumed to take place.

The authors are thankful to the UGC, INDIA for the financial support.

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Accepted July 25, 1983