

Copolymerization of ethylene and linear 1-olefins with a metallocene catalyst system under high pressure. Part I. Copolymerization of ethylene and propene¹

C. Bergemann, R. Cropp, G. Luft *

University of Darmstadt, Institute of Chemical Engineering, Petersenstr. 20, 64287 Darmstadt, Germany

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Abstract

The copolymerization of ethylene and propene under high-pressure and high temperature was examined using a metallocene/methylaluminoxane catalyst system. The polymerization was performed in a continuously operated stirred autoclave at 150 MPa and in the temperature range between 393 K and 493 K. The ratio of aluminium to catalyst metal used was 22000 mol Al/mol Zr based upon a metallocene concentration of 6×10^{-3} mol-ppm in the feed. The reactivity ratios and the productivity as well as the physical properties of the resulting polymers were determined.

Keywords: Copolymerization; Ethylene; High pressure/temperature; Metallocene catalyst; Methylaluminoxane; Propene

1. Introduction

At present, Ziegler–Natta catalysts are used in different polymerization processes. One of them is the polymerization of ethylene under high pressure. The main advantage of this process is that no solvent is required. Furthermore a high pressure plant for the production of low density polyethylene can be used with only minor changes.

This was one reason to investigate the homo- and copolymerization of ethylene with a soluble homogeneous metallocene/methylaluminoxane catalyst under these reaction conditions.

Up to now only few papers have been published on the performance of Ziegler–Natta catalysts

under high pressure and high temperature. Mostly the use of titanium-based catalysts (e.g. α -TiCl₃) on a carrier like MgCl₂, together with trialkylaluminium compounds, e.g. AlEt₃, AlEt₂Cl, were reported [1–11]. Only very few papers deal with the use of metallocene catalysts under high pressure and high temperature [12,13].

The main purpose of this work was to describe the dependence of the productivity on the polymerization conditions and to evaluate the reactivity ratios. Furthermore the resulting polymers prepared under different reaction conditions were analyzed for their physical properties like average molecular weights, density, melt temperature etc.

The discussion of the results will be done mainly from a point of view of a chemical engineer.

* Corresponding author. Tel: (+49-6151)162315, fax: (+49-6151)164214.

¹ Dedicated to the 65th anniversary of Prof. Dr.rer.nat. Dr.Ing. E.h. H. Sinn.

2. Experimental

The polymerization experiments were performed in a 100 ml autoclave equipped with a fast running stirrer at 100 to 150 MPa and 393 to 493 K [14,15].

Ethylene was an industrial polymerization grade, which was taken from bombs and further purified by molecular sieves and a copper catalyst. It was fed continuously together with propene into the reactor (Fig. 1). The mixture of ethylene and propene entered the reactor from the top through the stirrer. The ethylene feed was controlled by a mass-flow-controller. A two stage compressor was used to pressurize the ethylene. Propene, with a high purity of 99.6%, was first condensed in a cooler and then metered by a high pressure membrane pump as a liquid. The pressure was maintained by means of an outlet valve controlled by the process computer. The residence time in the reactor was 240 s.

The concentration of the comonomer was varied up to 100 mol% in the feed. As catalyst a modified silyl-bridged bis(tetrahydroindenyl) zirconocene in toluene as the solvent was used. Its concentration in the feed was 0.006 mol-ppm. A solution of 10 wt.% of methylaluminoxane (MAO) in toluene (from Schering AG) was used without any purification as cocatalyst. The ratio of MAO to metallocene catalysts was 22000 mol Al/mol Zr. This high ratio was

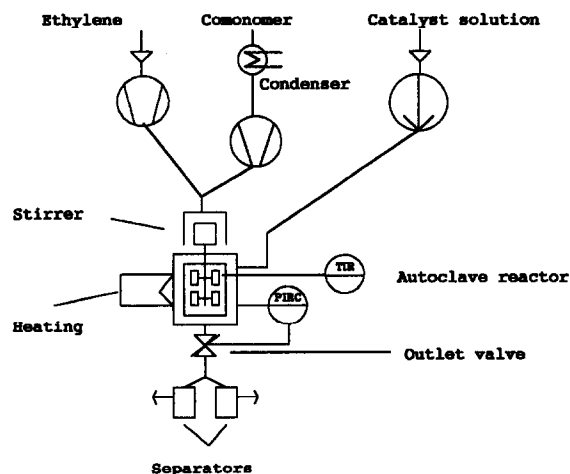


Fig. 1. Polymerization unit

required to achieve a conversion of ethylene and propene of 5–15%. This is in line with the observation of Fink et al. [16] in the polymerization of ethylene and propene under low pressure using a similar catalyst.

The catalyst solution was metered by a syringe type pump. Before any polymerization experiment could proceed, the entire apparatus was carefully evacuated. The stirred autoclave was heated and flushed with ethylene and the comonomer. When feeding of the catalyst solution was commenced, the temperature inside the reactor increased and reached a constant level within 5 min. After the reactor the pressure was released to ambient pressure. The polymer, which separated from the unreacted ethylene and comonomer was collected in different separators, one of which received the product until a steady state was attained. This polymer was wasted. Samples of 10–20 g of the polymer formed under steady state conditions were collected in the other separators to be analyzed later.

3. Results

The copolymers prepared were analyzed by IR spectroscopy for their composition. In Fig. 2 the ratio of the concentration of propene/ethylene in the polymer is shown as a function of the ratio of propene/ethylene in the reactor. The ratio of comonomer to monomer measured on the copolymer increased linearly with increasing ratios of the components in the reactor. But ethylene was preferentially incorporated into the polymer.

At a ratio of 1 mol propene/mol ethylene in the reactor the molar ratio of propene to ethylene in the polymer was only in the range of 0.08.

The reactivity ratios were determined from the concentration of ethylene, propene and polymer in the autoclave reactor and the composition of the resulting copolymer. For this purpose the concentration of the components in the reactor were first calculated from the feed rates and the conversion by means of the mass balance for each component. The method of Fineman and Ross I

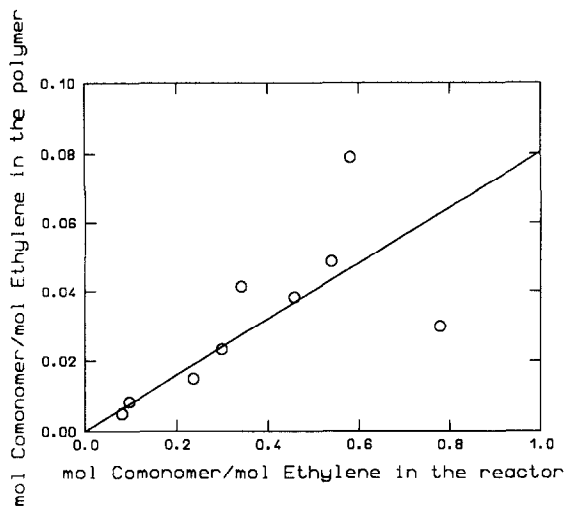


Fig. 2. Copolymerization diagram for the copolymerization of ethylene and propene. Pressure = 150 MPa, temperature = 453 K, residence time = 240 s.

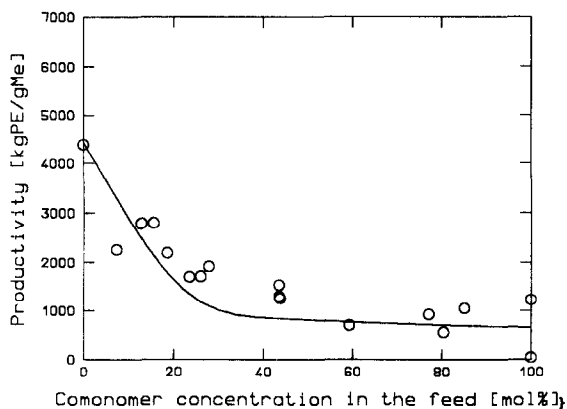


Fig. 3. Productivity as a function of comonomer concentration in the feed. Pressure = 150 MPa, temperature = 453 K, residence time = 240 s.

[17] and the method of Kissin and Böhm [18,19] were then applied to evaluate the reactivity ratios. The data obtained with both methods agreed within experimental error. The reactivity ratios were calculated to $r_1 = 12.43$ and $r_2 = 0.08$.

The productivity was determined from the yield of polymer and the amount of catalyst metal fed into the reactor. The productivity in the homopolymerization of ethylene under high pressure was 4400 kgPE/gMetal. It decreased first steeply with increasing concentration of propene in the feed (Fig. 3) and remained then nearly constant at higher propene concentrations.

This can be explained by the greater steric hindrance of propene compared with ethylene so that the diffusion of propene to the active centre is slower than that of ethylene. The productivity of the catalyst system with propene is therefore lower than with ethylene. No rate enhancement of propene on the reaction rate of ethylene was observed for this metallocene system (e.g. [20,21]) (Fig. 4). On the opposite the reaction rate of ethylene decreased steeply with increasing comonomer concentration in the reactor.

The average molecular weights M_n and M_w were measured by means of GPC at 135°C in

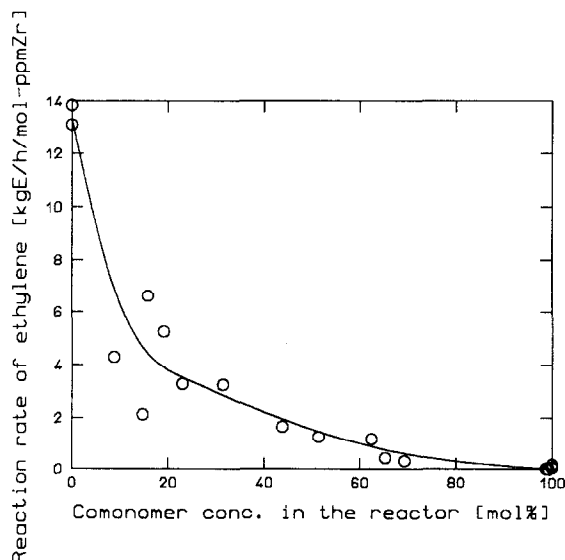


Fig. 4. Reaction rate of ethylene as a function of comonomer concentration in the reactor. Pressure = 150 MPa, temperature = 453 K, residence time = 240 s.

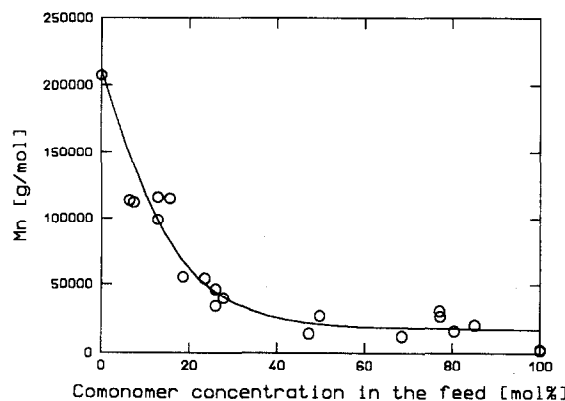


Fig. 5. Number average molecular weight as a function of comonomer concentration in the feed. Pressure = 150 MPa, temperature = 453 K, residence time = 240 s.

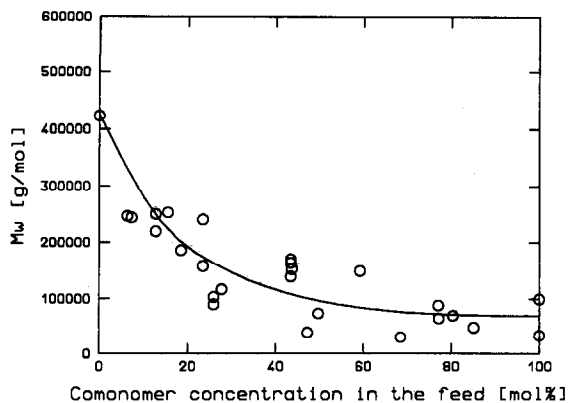


Fig. 6. Weight average molecular weight as a function of the comonomer concentration in the feed. Pressure = 150 MPa, temperature = 453 K, residence time = 240 s.

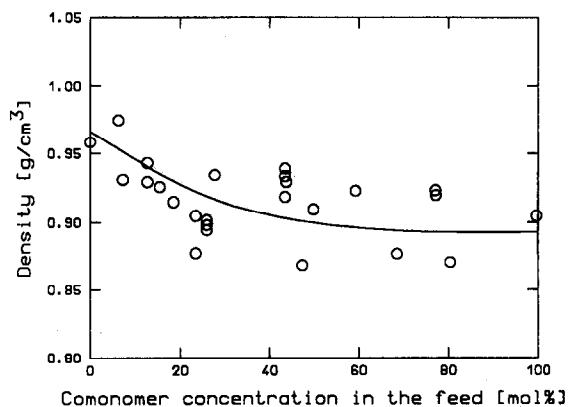


Fig. 7. Density as a function of comonomer concentration in the feed. Pressure = 150 MPa, temperature = 453 K, residence time = 240 s.

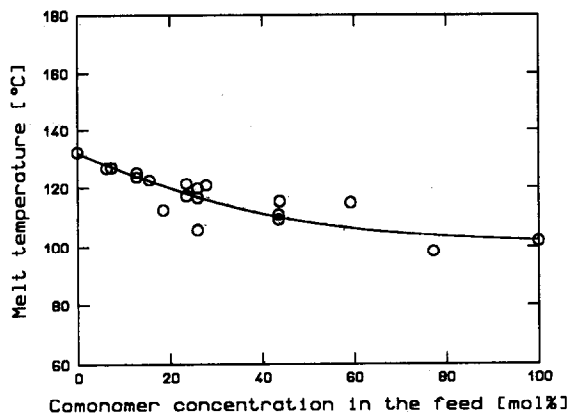


Fig. 8. Melt temperature as a function of comonomer concentration in the feed. Pressure = 150 MPa, temperature = 453 K, residence time = 240 s.

1,2,4-trichlorobenzene. They were plotted in Fig. 4 and Fig. 5 versus the concentration of propene in the feed. The number average as well as the weight average molecular weight showed a

steep decrease up to a comonomer concentration of 10 mol% in the feed. M_n and M_w remained nearly constant at higher propene concentrations.

The density was measured on pressed polymer films using the suspension method at 25°C. It was found in the range 0.946 to 0.940 g/cm³.

In the whole range of comonomer concentration, the density of the polymer decreased with concentration of the propene in the feed (Fig. 6). This can be explained by the incorporation of propene into the polymer chain which gives rise to short chain branches.

The melt temperature of the polymers was measured together with melt enthalpy by DSC. As shown in Fig. 7 the melt temperature decreased slowly with increasing propene concentration from 136°C of the ethylene homopolymer to 100°C of the propene homopolymer. This can be also attributed to the incorporation of propene and the formation of short chains in the polymer.

The crystallinity determined from melt enthalpy showed a nearly linear decrease with increasing propene concentration in the feed (Fig. 8). The effect of the propene incorporation into the polymer chain on the crystallinity is higher compared to changes of the density and the melting temperature with the concentration of the comonomer.

The crystallinity of the ethylene homopolymer was found high in the range of 70 to 80%. The

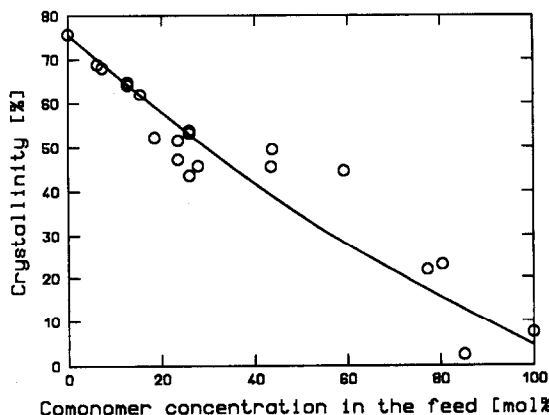


Fig. 9. Crystallinity as a function of comonomer concentration in the feed. Pressure = 150 MPa, temperature = 453 K, residence time = 240 s.

propene homopolymer showed an amorphous structure. The crystallinity was only 5% (Fig. 9).

4. Conclusion

The metallocene catalyst which we have used showed a good ability for copolymerization of ethylene with propene under the reaction conditions. The copolymerization experiments could be run in the whole range of comonomer concentration up to 100 mol% propene in the feed with reasonable high yield. The productivity was high and only small amounts of the catalyst (0.006 mol-ppm metallocene in the feed) were necessary.

The high ratio 22000 mol Al/mol Zr, which had to be used, results from wall effects and from traces of impurities in the small autoclave reactor.

The physical properties of the copolymers depend steeply on the concentration of the comonomer.

The propene incorporation into the polymer chain lowers the polymer chain length partly because propene as the last unit is not as reactive as ethylene and partly because of an increase of the transfer reaction to propene. This explains the decrease of both number and weight average molecular weight with increasing concentration of propene in the feed gas.

Due to the incorporation of propene, polymers differing in density, melt temperature and crystallinity, could be prepared.

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