Copolymerization of ethylene and linear 1-olefins with a metallocene catalyst system under high pressure. Part II [1]. Comparison of propene, 1-butene, 1-hexene and 1-decene [2]

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

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

Abstract

The copolymerization of ethylene and linear 1-olefins under high pressure and high temperature was examined using a metallocene/methylaluminoxane system. The reactivity ratios of copolymerization as well as the physical properties of the resulting copolymers were determined. The polymerization was performed in a continuously operated stirred autoclave at 150 MPa and in the temperature range between 393 K and 493 K. A ratio of 22000 mol Al/mol Zr was applied based upon a metallocene concentration of 6×10^{-3} mol-ppm.

1. Introduction

The main aim of this research work was to evaluate the behavior of different linear 1-olefins in the copolymerization with ethylene using a metallocene/methylaluminoxane catalyst system under high pressure. The comonomers were 1-butene, 1-hexene and 1-decene besides propene, which was used earlier [1]. For this purpose the productivity and the reactivity ratios should be considered. Furthermore the physical properties of the resulting copolymers like average molecular weights, density, melting temperature and their dependency on the polymerization conditions, especially on the concentration of the comonomer in the feed, should be compared.

---

* Corresponding author.
[1] For Part I see ref. [1].
[2] Dedicated to the 65th anniversary of Prof. Dr.rer.nat. Dr.-Ing. E.h. H. Sinn.

2. Experimental

The continuously operated pilot unit used for polymerization was described earlier together with the experimental technique [1]. The liquid comonomers 1-hexene and 1-decene were fed by means of the high pressure membrane pump which was used also to meter condensed propene and 1-butene.

The polymerization tests were performed at a pressure of 150 MPa, with temperatures in the range of 393 to 493 K and a residence time of 240 s. Again the same silyl-bridged bis(tetrahydroindenyl)zirconocene was used in a concentration of 0.006 mol-ppm in the feed gas [1]. Cocatalyst was methylaluminoxane (MAO). The ratio of cocatalyst to catalyst metal was 22000 mol Al/mol Zr. The concentration of the comonomer in the feed was varied up to 100 mol%.

3. Results

The copolymerization diagram for the different comonomers is shown in Fig. 1. In the diagram the molar ratio of ethylene to comonomer in the polymer is plotted versus the ratio of the components in the reactor.

For this purpose the concentrations of ethylene and comonomer in the reactor were first calculated from the feed rates of all components and the composition of the polymer by means of a total mass balance. In the range of concentrations which were investigated the ratio of comonomer to ethylene incorporated into the polymer increased linearly with the ratio of the components present in the reactor. The highest rate of incorporation of the comonomer was obtained with propene. At a ratio of 0.5 mol propene to mol ethylene in the reactor the ratio of propene to ethylene in the copolymer was 0.04. It decreased to around 0.01 when 1-butene was the comonomer. Lower incorporation ratios were found when 1-hexene or 1-decene were used as the comonomer.

From the composition of the copolymer and the ratio of comonomer to monomer in the reactor the reactivity ratios were determined using the methods of Finemann and Ross [2] as well as that of Kissin and Böhm [3,4]. The reactivity ratios evaluated are collected in Table 1, in which 1 stands for ethylene and 2 for the comonomer. The reactivity ratio r_1 was found in the range of 12.43 (propene) to 80.02 (1-decene) whereas r_2 decreased from 0.08 with propene to 0.01 with 1-decene.

The other results will be discussed from a chemical engineer's point of view. Therefore in the following diagrams all results were plotted versus the comonomer concentration in the feed. When the concentration of the comonomer in the reactor is considered the curves are shifted to the right and to the left when the amount of comonomer incorporated into the polymer is considered. The shift is more steep with 1-decene and less steep with propene.

With each comonomer around 20 polymerization tests were performed. Because of this large
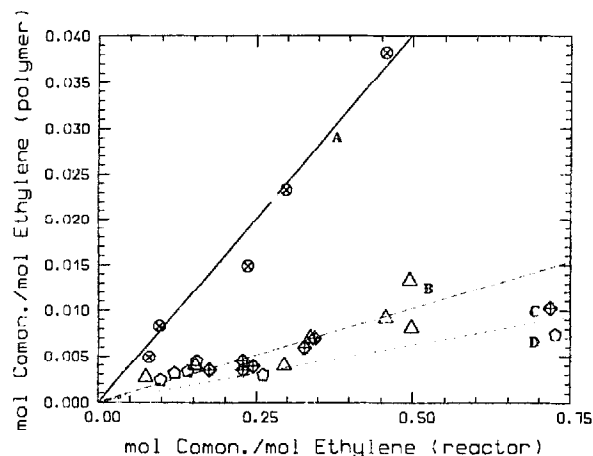

Fig. 1. Copolymerization diagram. Pressure = 150 MPa, Temperature = 453 K, Residence time = 240 s. Curve: A = propene, B = 1-butene, C = 1-hexene, D = 1-decene.

Table 1
Reactivity ratios for 150 MPa and 453 K

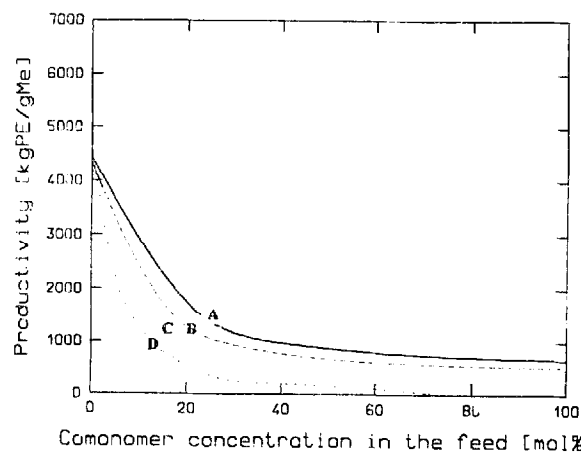|	r_1	r_2
Propene	12.43	0.08
1-Butene	53.45	0.02
1-Hexene	62.7	0.02
1-Decene	80.02	0.01

Fig. 2. Productivity of the catalyst system used with different comonomers. Pressure = 150 MPa, temperature = 453 K, residence time = 240 s. Curve: A = propene, B = 1-butene, C = 1-hexene, D = 1-decene.

amount of experiments the resulting data points were omitted in the following diagrams.

The productivity of the catalyst used in the copolymerization with different comonomers is shown in Fig. 2. It was determined from the amount of polymer formed and the amount of catalyst metal metered into the reactor. Compared
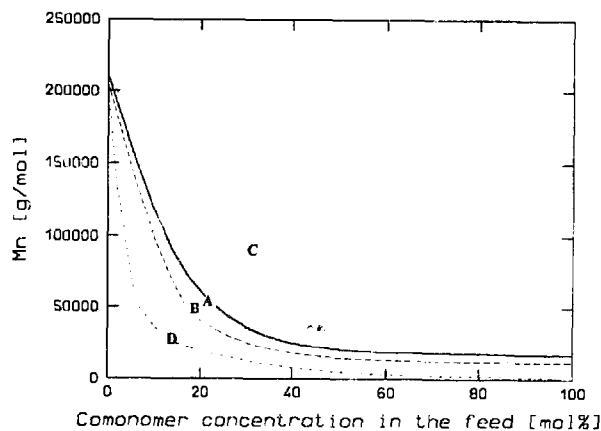
Fig. 3. Number average molecular weight M_n. Pressure = 150 MPa, temperature = 453 K, residence time = 240 s. Curve A = propene, B = 1-butene, C = 1-hexene, D = 1-decene.
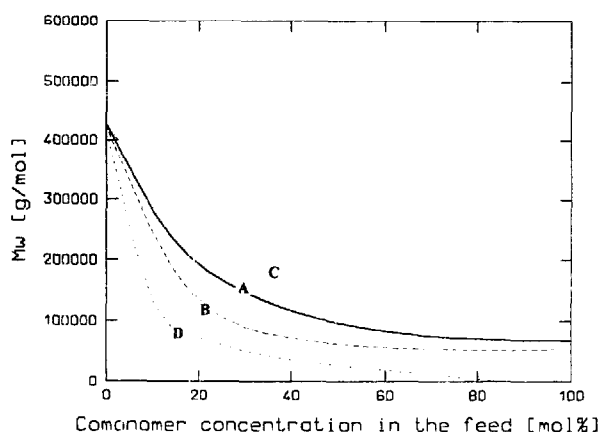

Fig. 4. Weight average molecular weight M_w. Pressure = 150 MPa, temperature = 453 K, residence time = 240 s. Curve A = propene, B = 1-butene, C = 1-hexene, D = 1-decene.
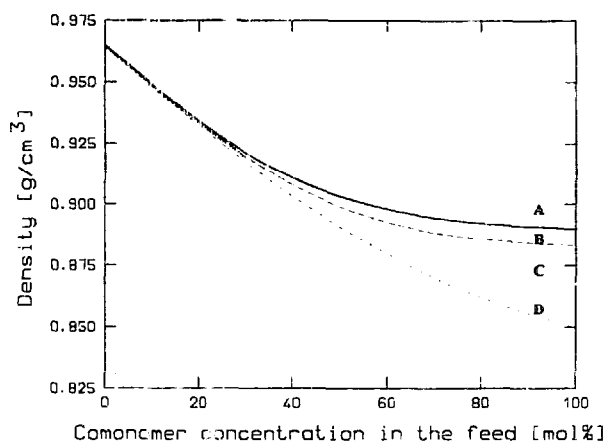

Fig. 5. Density. Pressure = 150 MPa, temperature = 453 K, residence time = 240 s. Curve A = propene, B = 1-butene, C = 1-hexene, D = 1-decene.

with the behaviour of propene the productivity of the catalyst used in the copolymerization with the other comonomers decreased also with increasing comonomer concentration in the feed. The productivity decreased in the order propene, 1-butene, 1-hexene to 1-decene.

The average molecular weights M_n and M_w, measured by means of GPC at 135°C in 1,2,4-trichlorobenzene using styrene polymers as references, showed a steep decrease up to a comonomer concentration of 10 to 20 mol% in the feed and remained then nearly constant at higher comonomer concentrations as shown in Fig. 3 and Fig. 4.

The lowest values of M_n were measured on samples with 1-decene. They increased when 1-butene and propene were used. The highest number average molecular weights were obtained with 1-hexene.

The weight average molecular weights of the copolymers prepared with different comonomers are compared in Fig. 4. M_w decreased with increasing concentration of the comonomer in the feed. Again the lowest values of M_w resulted with 1-decene whereas the copolymers with 1-hexene were found with the highest weight average molecular weights.

The density of the copolymers decreased with the comonomer concentration in the feed as shown in Fig. 5. The density of the ethylene homopolymer was 0.965 g/cm^3, whereas the density of the propene homopolymer was only 0.885 g/cm^3. The homopolymer formed using 1-decene showed the lowest density.

The melting temperatures of the various copolymers are plotted in Fig. 6 again versus the concentrations of the comonomer in the feed together with the melting temperature of the homopolymers. The ethylene homopolymer showed the highest melting temperature of 132°C. When propene was added to the ethylene feed the melting temperature decreased. With the propene homopolymer a melting temperature of 100°C was observed. The lowest melting temperature showed the homopolymer of 1-decene.
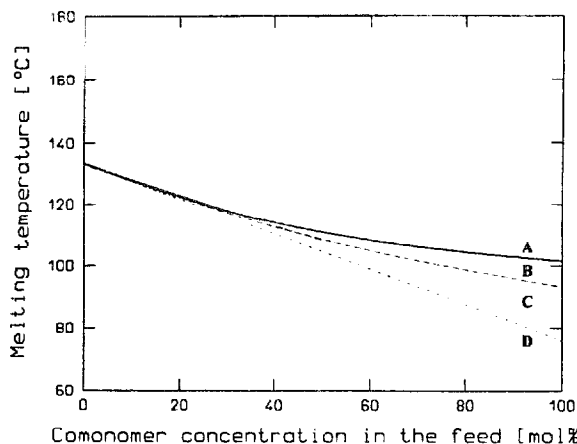
Fig. 6. Melting temperature. Pressure = 150 MPa, temperature = 453 K, residence time = 240 s. Curve A = propene, B = 1-butene, C = 1-hexene, D = 1-decene.
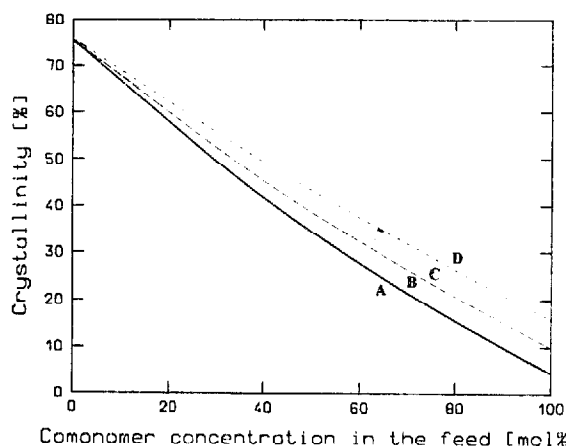

Fig. 7. Crystallinity. Pressure = 150 MPa, temperature = 453 K, residence time = 240 s. Curve A = propene, B = 1-butene, C = 1-hexene, D = 1-decene.

Also the crystallinity of the copolymers decreased with increasing concentration of the comonomer in the feed as presented in Fig. 7. The ethylene homopolymer showed the highest crystallinity. The lowest crystallinity was found for the homopolymer of 1-decene.

4. Conclusion

The most interesting result is the good ability of the metallocene/MAO system in the copolymerization of ethylene not only with propene but also with 1-olefins of higher chain length. Up to a ratio of 0.04 mol propene/mol ethylene could be incorporated into the polymer at a ratio of 0.5 mol propene/mol ethylene present in the reactor. At the same ratio of comonomer to ethylene in the

reactor the ratio of comonomer to monomer in the copolymer was in the range of 0.01.

The high performance of the zirconocene catalyst became obvious when its productivity was considered. The productivity was 4500 kg PE/g Zr in the homopolymerization of ethylene. It decreased only to half this value when the feed gas contained 20 mol% propene.

At the same level of 1-decene the productivity was reasonable high and was around 500 kg PE/g Zr. The lower reactivity in the polymerization with 1-olefins of greater chain length can be attributed to steric effects.

All physical properties of the copolymers depend on the comonomer and its concentration in the feed gas. As it is known from the polymerization with heterogeneous Ziegler catalysts under low pressure the density of the copolymers prepared with metallocenes can be controlled by the addition of 1-olefins.

The decrease of the average molecular weight with increasing concentration of the comonomer in the feed results from lower reactivity of the comonomer especially of 1-decene and the higher rate of chain transfer to these comonomers which give rise of termination of the growing chains.

Concerning the polydispersity, which can be calculated from the weight average molecular weight and the number average molecular weight, all polymer samples showed a small polydispersity in the range from 2 to 3, so it can be concluded that only one active site is present under the high pressure/high temperature conditions using this type of metallocene/MAO catalyst system.

Incorporation of propene, 1-butene etc. led to the formation of short side chains in the copolymer which hinder the close arrangement of polymer chains and decrease the density. Copolymers with a density in the range of 0.965 to 0.85 g/cm³ can be prepared using this type of catalyst system depending on the comonomer which was used.

For the same reason the melting temperature is lowered using higher comonomer concentrations in the feed.

By the copolymerization of ethylene with the α-olefins copolymers having melting temperatures of 80 to 132°C could be prepared.

Simultaneously the formation of crystalline areas is depressed which explains the decrease in crystallinity observed.

References

[1] C. Bergemann, R. Cropp and G. Luft, J. Mol. Catal. A, 102 (1995) 1.

[2] M. Fineman and S.D. Ross, J. Polym. Sci., 5 (1979) 129.

[3] Y.V. Kissin and D.L. Beach, J. Appl. Polym. Sci., 29, (1984) 1171.

[4] L.L. Böhm, J. Appl. Polym. Sci., 29 (1984) 279.