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Application of a cationic activated metallocene catalyst system in the copolymerization of ethylene and 1-butene under high pressure

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Abstract

The activation of metallocene catalyst by a cationic activator in the presence of triisobutylaluminium was examined in the copolymerization of ethylene and 1-butene under high pressure of 150 MPa and temperatures of 463 to 473 K. A continuously operated micro-pilot plant unit equipped with a stirred autoclave was used. The catalyst productivity determined from the amount of polymer and the catalyst feed was in the range of 100 to 300 kg polymer/g zirconium. The resulting copolymers were analyzed for their physical properties and the amount of 1-butene incorporated. The results of the polymerization with the metallocene/cationic activator system were compared to the data obtained earlier using methyl aluminoxane as the activator. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Cationic activated metallocene catalyst system; Copolymerization of ethylene with 1-butene; High pressure; High temperature

1. Introduction

Metallocene catalysts are now introduced in gas phase, solution and emulsion processes to manufacture linear low density and high density polyethylene or isotactic polypropylene. An excess of methyl aluminoxane (MAO) is required to activate the metallocene.

In previous years, a number of MAO-free catalyst systems have been developed. These are cationic metallocenes which can be obtained from conventional metallocenes and an ion exchange component containing a cation and a non-coordinating anion. Appropriate alkylated metallocenes were used together with $[(C_6H_5)_3C][B(C_6F_5)_4]$ [1], $B(C_6F_5)_3$ [2] or $[PhNMe_2H][B(C_6F_5)_4]$ [3]. The cation reacts with one alkyl ligand [1–5] of the metallocene, whereas the anion is stabilizing the cationic metallocene [5]. Another way leading to cationic metallocenes was examined starting from group 4 metallocenes and a mixture of trimethyl aluminium and dimethyl aluminium [4]. Whereas, the structure of MAO is up to now not accurately known, different methods, like ^{13}C-NMR spectroscopy, are available to characterize cationic activators.

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Up to now, less research was performed into the polymerization with metallocene/cationic activator systems under high pressures. Therefore, it was the aim of this work to investigate the use of a cationic activated zirconocene catalyst in the high pressure copolymerization of ethylene and 1-butene.

2. Experimental

The polymerization experiments were performed in a micro-pilot unit described earlier [6,7]. Temperatures of 463 to 473 K were applied. The pressure was 150 MPa. The stirred autoclave reactor was run at a residence time of 250 s. The comonomer concentration in the feed was varied between 5 and 55 mol%. Diphenylmethylen (1-cyclopentadienyl) 9-(2,7-di-*tert*-butyl) fluorenyl) zirconiumdichloride was used as catalyst together with the cationic activator *N*,*N*′-Dimethylanilinium-tetrakis(pentafluorophenyl)borate ($[PhNMe_2H][B(C_6F_5)_4]$).

The catalyst system was prepared by dissolving first the metallocene in toluene. Triisobutylaluminium (98 wt.% with 13.1 wt.% aluminium from Witco, Bergkamen) was then added under argon to obtain a ratio of 2100 mol aluminium/mol zirconium. The cationic activator was also dissolved in toluene and mixed to the metallocene/triisobutylaluminium solution in a ratio of 1.3 mol activator/mol metallocene.

The productivity of the catalyst was determined from the amount of polymer obtained in unit of time and the feed rate of the zirconocene. The resulting copolymers were analyzed by ^{13}CENMR for their 1-butene content. The average molecular weight was obtained from gel permeation chromatography (GPC). Melting point and crystallinity were determined by differential scanning calorimetry (DSC). Infrared spectroscopy (IR) was applied to evaluate the number of vinyl double bonds and the short chain branching frequency. Furthermore, the density was measured by the suspension method in a mixture of water and *i*-propanol.

3. Results

In Fig. 1, the productivity of the catalyst system is plotted vs. the concentration of 1-butene in the feed. The data were evaluated from tests performed at a polymerization temperature of 468 K. In the range of 5 to 55 wt.% 1-butene in the feed, the productivity decreased linearly with increasing concentration of the comonomer. With 5 mol% of 1-butene in the feed, a productivity of 300 kg polymer/g Zr was obtained. Only the half of this value resulted with 55 mol% comonomer in the feed. When the data are extrapolated to a feed without 1-butene, a productivity of 310 kg polymer/g Zr results for the homopolymerization of ethylene.

In order to show the influence of the concentration of 1-butene on the properties of the resulting copolymer, the data of samples gained at 468 K are presented. First, the weight average molecular weight is plotted vs. the concentration of the comonomer in the feed in Fig. 2. A weight average molecular weight of 175 000 g/mol resulted at a feed concentration of 5 mol% 1-butene. It decreased linearly to 130 000 g/mol when the comonomer concentration was increased to 55 mol%. This is due to the fact that 1-butene is not only incorporated into the polymer but also acts as a modifier which terminates the growth of the polymeric chains.

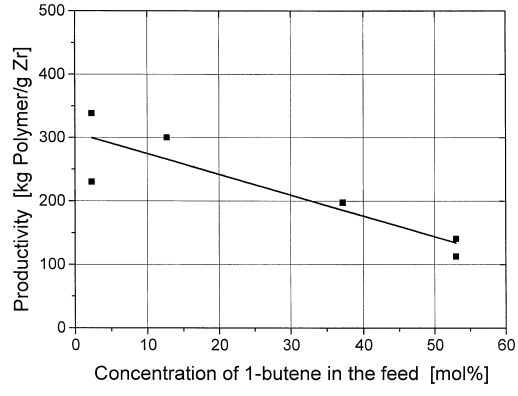

Fig. 1. Productivity. Pressure: 150 MPa, temperature: 468 K, residence time: 250 s.

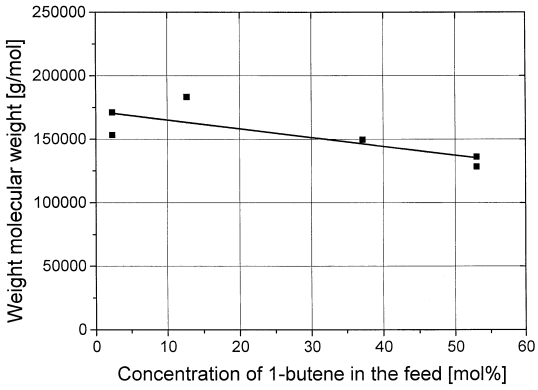

Fig. 2. Average of the molecular weight. Pressure: 150 MPa, temperature: 468 K, residence time: 250 s.

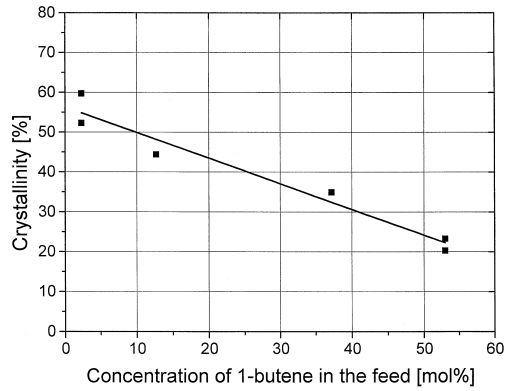

Fig. 4. Crystallinity. Pressure: 150 MPa, temperature: 468 K, residence time: 250 s.

From the ratio of the weight average and the number average molecular weight, the polydispersity was calculated. Values of around 1.5 were obtained, remaining constant when the concentration of the comonomer was varied.

The results of the analysis of the copolymer samples by DSC are shown in Figs. 3 and 4. A moderately high melting point of 403 K was measured on samples prepared with 5 mol% of 1-butene in the feed (Fig. 3). When the feed contained a high concentration of 55 mol% 1-butene, a significantly lower melting point of 379 K resulted.

Simultaneously, the crystallinity decreased from 55 to 23% when the comonomer concentration in the feed was increased from 5 to 55 mol% (Fig. 4). This indicates that an increasing amount of 1-butene is incorporated into the polymer.

As a result of the increasing comonomer incorporation, the number of short chain branches increases. This is shown in Fig. 5, in which the short chain frequency is plotted vs. the concentration of 1-butene in the feed. A low number of short chain branches was evaluated from IR spectroscopy on samples from polymerization runs with low concentration of 1-butene in the feed. Whereas the samples prepared with the high concentration of 1-butene exhibit a moderately high number of short chain branches per 1000 C-atoms.

The density of the copolymer samples varied in a wide range. This becomes evident from the plot of density vs. 1-butene concentration

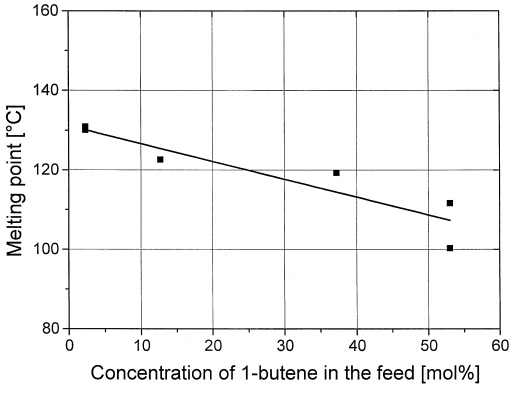

Fig. 3. Melting point. Pressure: 150 MPa, temperature: 468 K, residence time: 250 s.

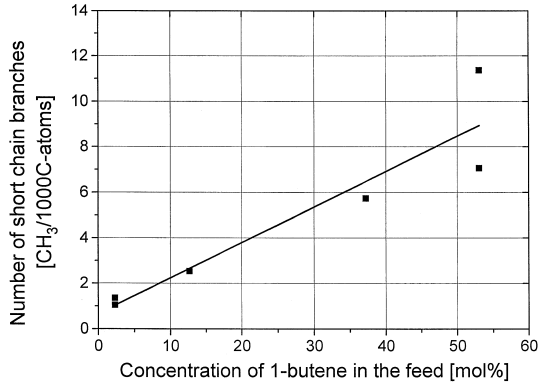

Fig. 5. Short chain branching. Pressure: 150 MPa, temperature: 468 K, residence time: 250 s.

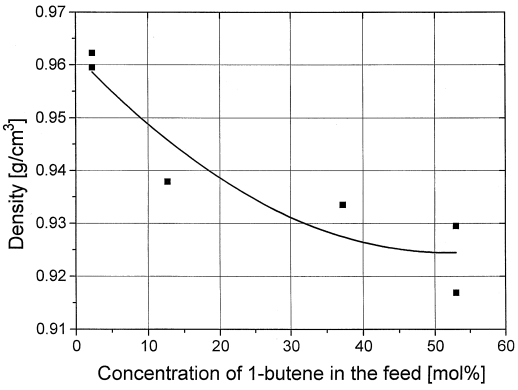

Fig. 6. Density. Pressure: 150 MPa, temperature: 468 K, residence time: 250 s.

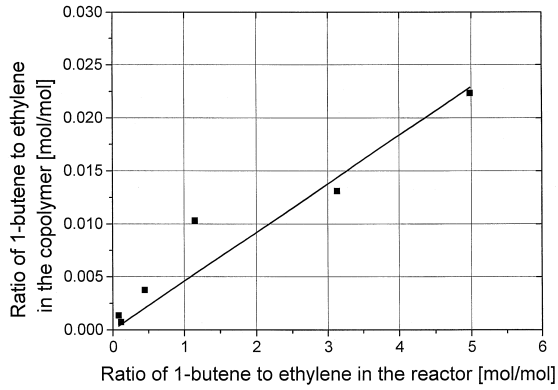

Fig. 8. Copolymerization diagram. Pressure: 150 MPa, temperature: 468 K, residence time: 250 s.

(Fig. 6). A high density of 0.960 g/cm^3 was measured on the samples from tests in which only a low amount of 1-butene was added. The density decreased first steeply and then less steeply when the concentration of 1-butene was increased in the feed. A lower density of 0.922 g/cm^3 was obtained when the polymerization was run with 55 mol% 1-butene.

The number of vinyl double bonds remained constant within the accuracy of the measurement when the concentration of 1-butene was changed. As can be seen from Fig. 7, the polymer contained around three double bonds of vinyl type per 1000 C-atoms of the polymer chain.

At least, a copolymerization diagram was designed from the results of IR analysis of the copolymer samples. In Fig. 8, the molar ratio of 1-butene to ethylene in the copolymer is plotted vs. the molar ratio of both monomers in the polymerization reactor. For this purpose, the concentration of ethylene and 1-butene of the reacting mixture in the polymerization autoclave was calculated from the composition of the feed and the conversion of the components. As was to be expected, the ratio of 1-butene and ethylene in the polymer increased with increasing ratio of the components in the reactor. At the highest ratio of 5 mol 1-butene to 1 mol ethylene in the reactor, which resulted when the feed contained 55 mol% 1-butene, a ratio of 0.025 mol 1-butene/mol ethylene in the polymer was obtained.

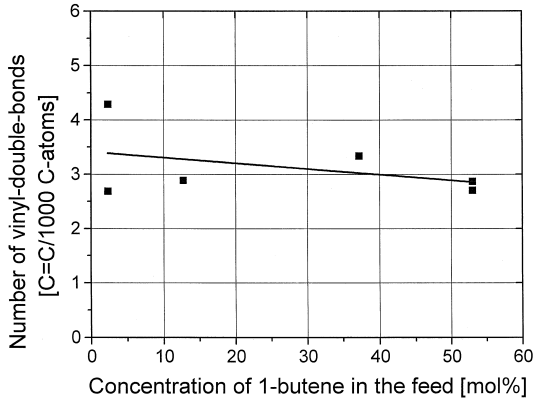

Fig. 7. Vinyl double bonds. Pressure: 150 MPa, temperature: 468 K, residence time: 250 s.

The reactivity ratios $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$, where the index 1 refers to ethylene and 2 to 1-butene, were calculated from the copolymerization diagram using the methods of Böhm [8] and Kissin and Beach [9]. Values of 220 for r_1 and 0.0045 for r_2 were obtained, meaning, that ethylene is preferentially incorporated into the polymer.

4. Conclusions

A reasonable high productivity of 310 kg polymer/g zirconium could be obtained in the metallocene catalyzed homopolymerization of

ethylene under high pressure using a cationic activator together with triisobutylaluminium in a ratio of 2100 mol Al/mol Zr. Under the same conditions of pressure and temperature, a productivity of around 4000 kg polymer/g Zr resulted in the polymerization with a different metallocene/MAO catalyst system when a ratio of 22 000 mol Al/mol Zr was applied [10,11].

Adding 55 mol% 1-butene to the feed, the productivity of the cationic activated catalyst decreased to one third of the value obtained in the homopolymerization of ethylene. The same behavior was observed in the polymerization using the metallocene/MAO-catalyst system. In this case, the productivity in the copolymerization with 55 mol% 1-butene decreased to 25% of the value of homopolymerization [11].

As can be seen from the copolymerization diagram the cationic activated zirconocene, catalyst exhibits a good ability for copolymerization. The reactivity ratios were found in the same range as those for the polymerization using MAO.

The low polydispersity of the polymer samples found in this work is a hint to a single site catalyst behaviour also in the presence of a cationic activator.

If, instead of MAO, a cationic activator together with a alkylaluminium compound as co-catalyst is used, a much lower amount of aluminiumalkyl is required to generate an active catalytic system. This gives benefits in the industrial polymerization process. On the other hand, it must be taken into account that cationic activators are more difficult to handle and are expensive up to now.

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