

Copolymerization of ethylene and 1,5-hexadiene under high pressure catalyzed by a metallocene

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

University of Darmstadt, Institute of Chemical Engineering, Petersenstraße 20, D-64287 Darmstadt, Germany

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Abstract

The copolymerization of ethylene and 1,5-hexadiene was investigated under high pressure of 1500 bar using a zirconocene catalyst in the presence of methylaluminoxane. The concentration of the diene was varied over a wide range including the homopolymerization of both ethylene and 1,5-hexadiene. From the amount of polymer formed per unit of time and the catalyst feed the productivity was determined. The resulting polymers were analyzed by DSC, GPC, IR- and ^{13}C -NMR-spectroscopy to evaluate the average molecular weights together with the polydispersity, the crystallinity, the melting point and the structure. The catalyst exhibits a good ability for copolymerization and cyclopolymerization of 1,5-hexadiene in which a predominance of *trans* ring formation was observed.

Keywords: Copolymerization; Ethylene; 1,5-hexadiene; High pressure/temperature; Metallocene catalyst

1. Introduction

Polymers with cyclic groups often exhibit high glass transition temperatures and high molecular weights. These polymers are excellent materials for optical and medical applications [1]. They can be prepared by copolymerization of ethylene and cyclic olefins, like norbornene, by means of metallocene catalysts [2]. An other access to cyclic polymers is the cyclopolymerization of diolefins. A number of nonconjugated diolefins, like 1,5-hexadiene, 1,4-pentadiene or 1,7-octadiene is capable of

undergoing cyclopolymerization in presence of metallocene catalysts. The cyclopolymerization of 1,5-hexadiene was first reported by Marvel and Stille [3] and has been studied since with different catalyst systems using classical Ziegler–Natta catalysts and metallocene systems. An analysis concerning the ^{13}C -NMR spectra of the homopolymer of 1,5-hexadiene was performed by Cheng and Khasat [4] including the assignments of the measured peaks to *cis* and *trans* configuration. Further detailed investigations on the cyclopolymerization of the above mentioned monomers in solution at low temperatures of 0 to -25°C and ambient pressure were performed by Waymouth et al. [5–9] using different metallocene catalysts together with MAO as cocatalyst. The researchers suc-

* Corresponding author. Tel.: +49-6151-162315; fax: +49-6151-164214.

ceeded to evaluate the effect of catalyst structure on the stereochemistry of the insertion and the cyclization reaction at transition metal centers of different catalysts in the presence of MAO. Recently a paper has been published concerning the copolymerization of ethylene and 1,5-hexadiene under low pressure with a titanocene based catalyst system [10] in which the polymer structure was investigated as a function of reaction temperature and diene concentration as well as the ratio of aluminum to titanium.

It is well known that high pressure decreases the rate of reactions having a positive volume of activation [11]. For this reason high pressure can suppress the ring opening reaction which is highly undesired in the polymerization of cyclic olefins. On the other hand high pressure favors reactions in which a negative volume of activation results from the decrease of the volume in the transition state [12]. High pressures beyond 1000 bar were therefore applied in this work to accelerate the cyclopolymerization of 1,5-hexadiene in the copolymerization with ethylene.

2. Experimental

The polymerization experiments were performed in a continuously operated laboratory unit equipped with a stirred autoclave of 100 ml capacity. The apparatus and the technique of polymerization are described earlier [13]. A pressure of 1500 bar, a temperature of 180°C and a residence time of 240 s were maintained constant inside the autoclave during polymerization. The concentration of the comonomer in the feed was varied between 0 and 100 mol%. Thus also the homopolymerization of 1,5-hexadiene could be investigated. A C_2 -symmetric ansa metallocene, namely dimethylsilylbistetrahydroindenylzirconiumdichloride, was used as catalyst in concentrations of 0,01 to 1,0 mol ppm in the feed. Methylaluminumoxane (MAO), available in a solution of 10 wt% in toluene, was the cocatalyst. It was added to the feed of monomers

in an amount to adjust a high ratio of aluminum to zirconium of 22000 mol/mol.

After the reactor the pressure was released to normal. The polymer which separated from the unreacted monomers was collected to be analyzed.

3. Results

First the productivity of the catalyst was evaluated from the amount of polymer formed per unit of time and the amount of catalyst added to the stream of monomers. It is plotted in Fig. 1 versus the concentration of comonomer in the feed (full triangles). For comparison results from copolymerization tests of ethylene and 1-hexene performed earlier [14] under the same conditions have been incorporated into the diagram (open triangles). Both curves commence from a value of 4200 kg polymer/g Zr, the productivity found in the homopolymerization of ethylene. In the copolymerization the productivity decreased first steeply and then less steeply with increasing concentration of the comonomer. With 20 mol% 1,5-hexadiene in the feed a productivity of around 1000 kg PE/g Zr resulted. In the homopolymerization of the diene the productivity decreased further to 50 kg PE/g Zr. The productivity observed in the copolymerization of ethylene and more than 20

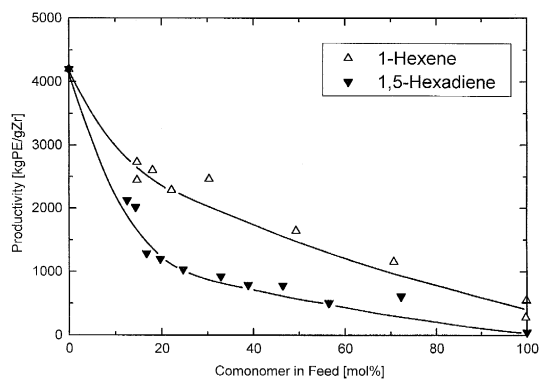


Fig. 1. Productivity pressure: 1500 bar, temperature: 180°C, residence time: 240 s.

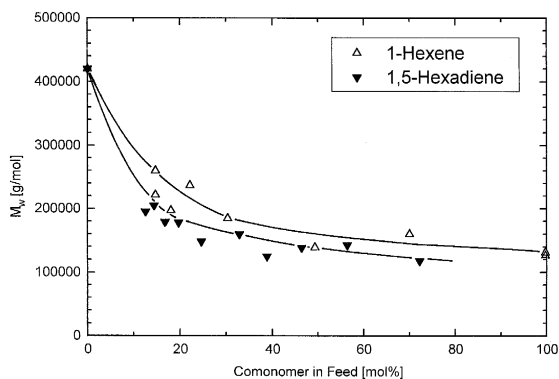


Fig. 2. Weight average molecular weight pressure: 1500 bar, temperature: 180°C, residence time: 240 s.

mol% 1-hexene was twice the productivity in the copolymerization with 1,5-hexadiene.

The copolymer samples were analyzed by GPC, DSC and IR spectroscopy. Selected samples were investigated by ¹³C-NMR. Furthermore density and melt index were measured.

The course of the weight average molecular weight versus comonomer concentration curves is very similar to the M_n curves (Fig. 2). Also M_w decreased steeply in the beginning to reach nearly constant values at comonomer concentrations of above 30 mol%. The weight average molecular weight of ethylene/1,5-hexadiene polymer samples was found to be always lower than that of ethylene/1-hexene copolymers.

The polydispersity was determined from the ratio of the weight average to number average molecular weights. It was between 2 and 3 for the copolymers of ethylene and diene. The samples from the copolymerization of ethylene and hexene showed polydispersities of around 2. Also by the polymerization under high pressure low polydispersities typical for polymers prepared with metallocenes resulted indicating that even under high pressure and temperature the metallocene catalyst system behaved like a single site catalyst.

The density was measured on films using the suspension method at 25°C in a mixture of isopropanol and water. The films 0.02 mm thick were heat treated before. The copolymers from

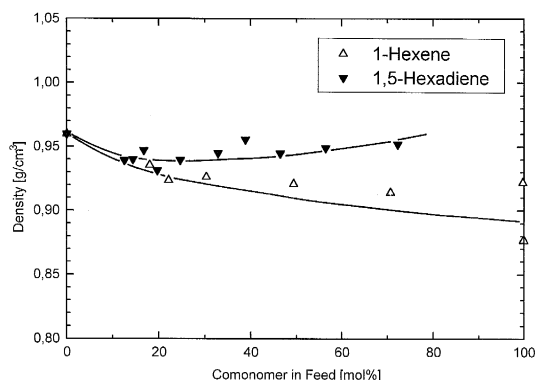


Fig. 3. Density pressure: 1500 bar, temperature: 180°C, residence time: 240 s.

ethylene and 1,5-hexadiene showed high densities in the range of 0.960 to 0.940 g/cm³. The densities of ethylene/1-hexene copolymers were lower. They decreased from 0.960 to 0.880 g/cm³ when the concentration of 1-hexene in the feed was high because of the increase of the short side chains by the incorporation of the comonomer (Fig. 3).

The crystallinity of the polymers determined by DSC is plotted in Fig. 4 versus the concentration of comonomer in the feed. Again also the data measured on samples from the copolymerization of ethylene and 1-hexene are presented for comparison. The shape of both curves is similar. The crystallinity of the ethylene homopolymer was 75%. It decreased to 30% in the homopolymerization of 1,5-hexadiene. The

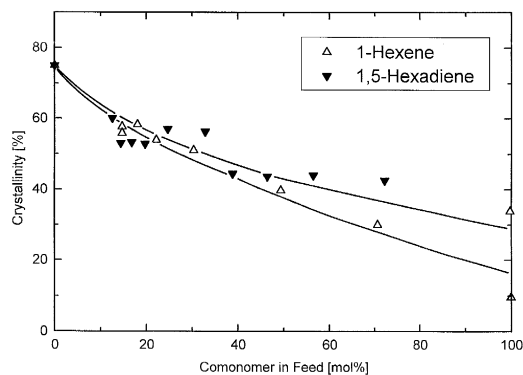


Fig. 4. Crystallinity pressure: 1500 bar, temperature: 180°C, residence time: 240 s.

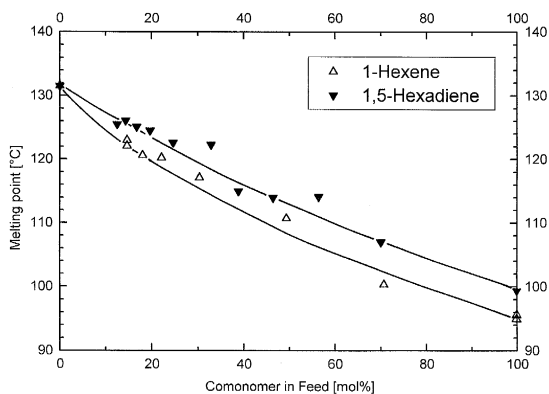


Fig. 5. Melting point pressure: 1500 bar, temperature: 180°C, residence time: 240 s.

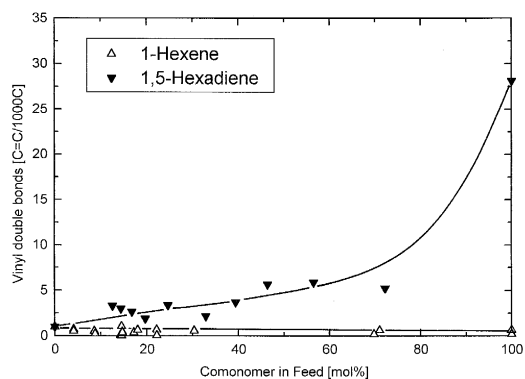


Fig. 6. Vinyl double bonds pressure: 1500 bar, temperature: 180°C, residence time: 240 s.

crystallinity of the ethylene/1-hexene samples was always higher than those of ethylene/1,5-hexadiene copolymers.

The melting point was also evaluated from the DSC-measurements. It decreased with both the concentration of 1,5-hexadiene and hexene in the feed. The ethylene homopolymer showed a melting point of 132°C. With the 1,5-hexadiene homopolymer a melting point of only 100°C was found (Fig. 5).

The number of vinyl double bonds was determined by IR-spectroscopy from the absorption at 910 cm^{-1} . The ethylene homopolymer contained only one double bond per 1000 C-atoms. This value remained practically unchanged in the copolymerization of ethylene and 1-hexene (Fig. 6). The number of vinyl double bonds in the copolymer with 1,5-hexadiene increased moderately up to a diene concentration of 50 mol% in the feed indicating that a high fraction

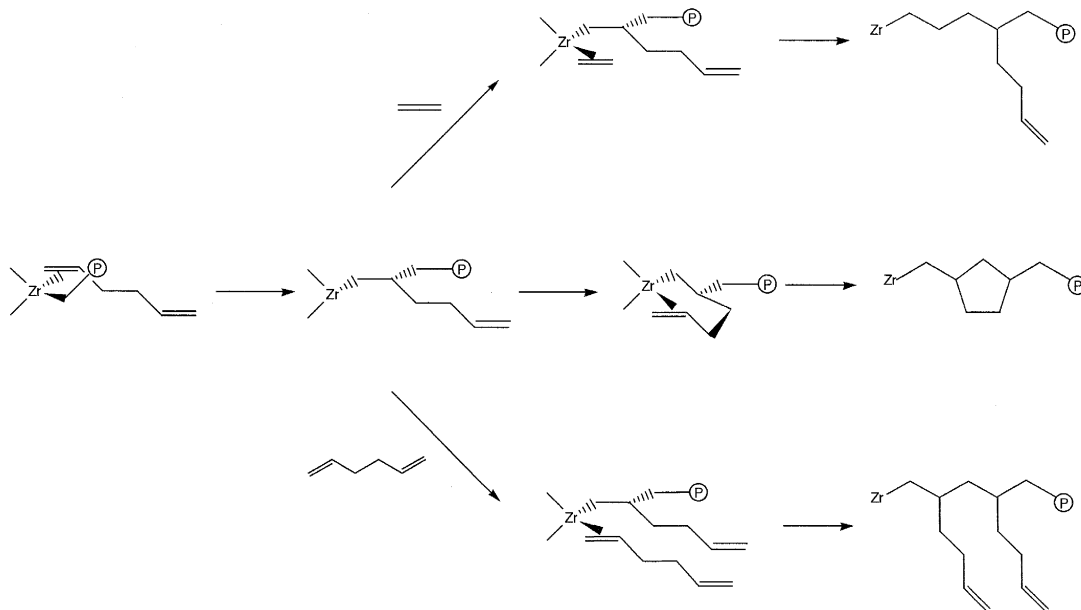


Fig. 7. Mechanism top: insertion of ethylene, middle: cyclopolymerization of 1,5-hexadiene, bottom: 1,2-polymerization of 1,5-hexadiene.

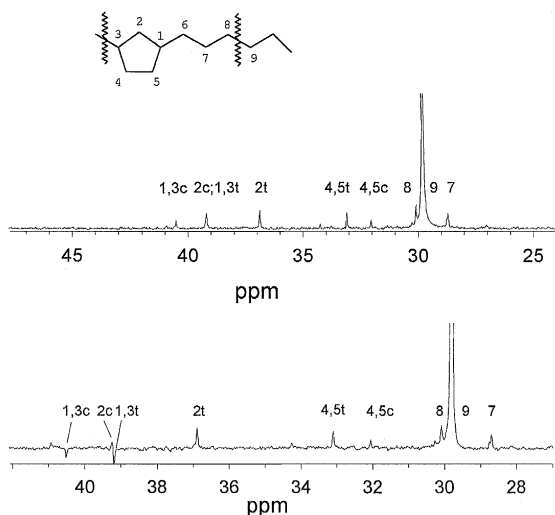


Fig. 8. ^{13}C -NMR spectrum (top) together with DEPT (bottom).

of 1,5-hexadiene reacts by cyclopolymerization. At higher diene concentrations the number of vinyl double bonds increased steeply. This means that the fraction of the second double bond of the diene which is not involved in the polymerization, increases.

Selected samples of the polymer were investigated by ^{13}C -NMR-spectroscopy. For this purpose the polymer was dissolved in a 1:1 (v/v) mixture of 1,2,4-trichlorobenzene and 1,1,2,2-tetrachlorodideuteroethane in a concentration of 100 mg polymer per ml. The spectra were obtained on a 300 MHz Bruker ARX 300 (400 K, 818 scans, 3.31 s delay time, 30° pulse angle). As an example the spectrum of a sample prepared with 72 mol% 1,5-hexadiene in the feed is presented in Fig. 8 together with the DEPT. In the range of 28 to 41 ppm in reference to TMS a number of peaks could be observed which were assigned using data from literature [15,16].

4. Conclusions

The polymerization tests performed under a pressure of 1500 bar show a good ability of the metallocene catalyst for the copolymerization of

ethylene and 1,5-hexadiene. Regarding also the high temperature of 180°C the polymerization is a high pressure, high temperature process. Under these conditions the polymerization takes place in a single phase meaning that the polymer is completely dissolved in the mixture of compressed monomers.

The productivity of the zirconocene/MAO catalyst system is high when the concentration of the unconjugated diene is below 20 mol% in the feed. But the productivity is lower than in the homopolymerization of ethylene and also lower than in the copolymerization of ethylene and 1-hexene or other 1-olefins. When the concentration of 1,5-hexadiene in the feed is above 20 mol% higher amounts of catalyst must be applied. The amount of catalyst required in the homopolymerization of 1,5-hexadiene is much more higher than in the homopolymerization of ethylene.

The analysis of the resulting ethylene/1,5-hexadiene copolymers shows a decrease of the molecular weight, the melting point and the crystallinity with increasing concentration of the comonomer in the feed which was expected. Also the low polydispersity is not surprising, when the GPC results gained on ethylene/1-olefin copolymers are taken into account for comparison.

Because the density practically does not change with the concentration of 1,5-hexadiene in the feed while the average molecular weights change drastically, ethylene/1,5-hexadiene copolymers with a high density and high or low average molecular weights can be produced by the high pressure process.

The most important result is the high effectiveness of the catalyst not only for copolymerization of ethylene and 1,5-hexadiene but also for cyclopolymerization of the diene under high pressure. During polymerization first a complexation of one of the double bonds of 1,5-hexadiene takes place at the vacant coordination side of the transition metal. After insertion into the polymer chain the complexation of the second double bond occurs followed by intra-

molecular cyclization to the 5-membered ring (Fig. 7). From IR spectroscopy it becomes obvious that the number of double bonds in the polymer is only small when the concentration of 1,5-hexadiene in the feed is below 50 mol%.

Analysis of the ^{13}C -NMR spectra of a sample with 72 mol% 1,5-hexadiene in the feed (Fig. 8) reveals both the selectivity of cyclopolymerization and the ratio of *cis* to *trans* rings as well as the amount of 1,5-hexadiene incorporated in the polymer. The integration of the resonance of the peak at 33.1 ppm assigned to 4.5 *trans*, the peak at 32.01 ppm assigned to 4.5 *cis*, and the peak at 29.8 ppm assigned to methylene group 9 reveals an incorporation of 1,5-hexadiene of 4.2 mol% and a predominance of *trans* rings determined by the diastereoselectivity of the cyclization step. We have analyzed a second sample of a copolymer of ethylene with 1,5-hexadiene and found that 2.3 mol% 1,5-hexadiene was incorporated in the copolymer (feed concentration was 33 mol%). A slight predominance of the formation of *trans* ring configuration was found for this copolymer too. For both samples we were not able to find a peak in the ^{13}C -NMR spectra corresponding to a vinyl-group. This could have many reasons. First the cyclopolymerization could be nearly complete, second the remaining double bonds could have reacted under the experimental conditions for ^{13}C -NMR (high temperature) or third a crosslinking could have taken place during the reaction.

For the example presented in Fig. 8 the calculation gives an amount of 60% *trans* rings resulting from the placement of the growing polymer chain in a pseudo-equatorial position.

The selectivity for cyclization depends on the polymerization conditions. It improves with decreasing concentration of 1,5-hexadiene. At high concentrations of the diene the competitive reaction, the 1,2-polymerization of 1,5-hexadiene, is favoured.

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