

Versatile Laboratory-Scale Polymerization Reactor System: Metallocene/MAO-Based Ethylene/Cycloolefin Copolymerizations

HARRI LASAROV, KARI MÖNKKÖNEN, TUULA T. PAKKANEN

University of Joensuu, Department of Chemistry, P.O. Box 111, FIN-80101 Joensuu, Finland

Received 26 May 1999; accepted 10 September 1999

ABSTRACT: A novel lab-scale reactor system designed for investigation of olefin polymerization reactions using homo- and heterogeneous catalysts is introduced. The high inert atmosphere level of the system is based on stainless-steel lines and cylinders, a nitrogen/vacuum technique, and removable reactants chambers which are packed in a glove-box. The solvent is transferred straight from the distiller through the reagents' containers into the reactor. The reactor is equipped with an ethylene pressure/mass flow and two temperature-control systems. Data acquisition is based on a personal computer and software for monitoring and data storage. The results of versatile ethylene copolymerization with cyclopentene, cyclooctene, and cyclododecene with this reactor system are discussed. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2921–2928, 2000

Key words: reactor design; metallocene/MAO catalyst; cycloolefin copolymers

INTRODUCTION

Since the discovery of transition-metal catalysts for olefin polymerization, much effort has been paid to understand the structure and the behavior of these catalysts. The trend in the development of the single-site metallocene catalysts is shifting from an emphasis on improving the stereospecificity and activity toward improving the polymer physical properties, processability, and morphology. Recently, late transition-metal complexes expand the range of obtained olefin (co)polymers by polymerizing polar monomers.¹ On the other hand, modern industrial polymerization processes require a heterogeneous catalyst system.

Polymerization of cycloolefins has been investigated commercially over 40 years.^{2–7} These

early processes based on heterogeneous Ti or V catalyst had disadvantages including low activities and varying product properties that were difficult to control. A breakthrough was finally achieved with the metallocene catalyst technology,⁸ which was first developed for ethylene and propylene polymerization.^{9–12} Currently, the properties of metallocene-based cycloolefin copolymers (COC), for example, a glass transition temperature of poly(ethylene-co-norbornene) can be tailored from 20 to 260°C by varying the content and distribution of norbornene units in a polymer chain.^{13–16}

Both catalyst and new polymer material investigations pose a challenging problem to construct the reactor systems with high inertness and purity levels as well as precision to control temperature, pressure, and monomer composition in the reactions. In this work, a lab-scale reactor system was designed and constructed to study olefin (co)polymerizations using both homo- and heterogeneous catalyst systems. The reactor system and

Correspondence to: T. T. Pakkanen.

Journal of Applied Polymer Science, Vol. 77, 2921–2928 (2000)
© 2000 John Wiley & Sons, Inc.

the effects of polymerization conditions on metallocene/MAO-based various ethylene/cycloolefin copolymers are presented.

EXPERIMENTAL

Materials

The catalyst used was bis(cyclopentadienyl)zirconium dichloride, Cp_2ZrCl_2 , obtained from Aldrich (Steinheim, Germany). Methylaluminoxane (MAO) was purchased from Witco (Bergamen, Germany) as a 10 wt % toluene solution. The Al content of the cocatalyst was 4.97 wt %. The toluene (Lab-Scan, Dublin, Ireland) used as a solvent was purified by refluxing over sodium benzophenone after which it was distilled under a nitrogen atmosphere. Nitrogen (99.999%, AGA, Espoo, Finland) was used without further purification. The ethylene (99.5%, from AGA) was purified using two columns containing molecular sieves and a Cu catalyst on a Al_2O_3 carrier before entering the reactor. Cyclopentene (Aldrich) was distilled under nitrogen prior to use. Cyclooctene (Aldrich) and cyclododecene (Aldrich) were dried with molecular sieves, then deoxygenated with bubbling of nitrogen.

Product Characterization

Melting temperatures and crystallization of the copolymers were measured with a Mettler Toledo DSC 821 system. The samples were heated first to 150°C (20°C/min), cooled to -50°C (10°C/min), then heated again to 250°C (10°C/min) and the second curve was analyzed.

The molar mass (M_w and M_n) and molar mass distribution (M_w/M_n) were determined on a Waters 150C ALC/GPC. The GPC was calibrated with NMWD PS and BMWD PE standards. A 10^7 Å and two TSK-Gel mixed-bed columns were used for GPC analysis at 135°C with trichlorobenzene (0.7 mL/min) as the eluent.

FTIR measurements were carried out using a Nicolet Magna 750 FTIR spectrometer. Measurements were done using melt-pressed thin films.

The ^{13}C -NMR spectra were recorded at 100°C on an AMX-400 NMR spectrometer operating at 100.62 MHz for ^{13}C . The copolymers were dissolved in *d*-toluene, $\text{C}_6\text{D}_5\text{CD}_3$, which was used as an internal reference (δ 21.4 ppm) and for lock purposes. A 30° pulse of 3.83 μs , a pulse repeti-

tion time of 20 s, and complete decoupling were used to collect 1000 scans.

Polymerization Procedure

The reactor system was evacuated and back-filled with nitrogen three times prior to use. The catalyst Cp_2ZrCl_2 was preactivated (30 min) by packing it together with a cocatalyst, MAO. Ethylene homopolymerization was carried out using a catalyst concentration of 2.04×10^{-6} mol/L [Zr] with an Al/Zr ratio of 2000. In the ethylene/cycloolefin copolymerizations [Zr] of 8.4×10^{-6} mol/L, the Al/Zr ratio of 3200 was used. First, an appropriate amount of cycloolefin and most of the toluene were injected into the evacuated reactor using a slight nitrogen overpressure. After the polymerization temperature had stabilized, the ethylene was introduced into the reactor via a semiflow- or a mass-flow-controlled inlet. When using a batch-type reaction, the appropriate amount of ethylene was measured during the filling of the reactor by a mass flow meter. All the polymerizations were initiated by injecting a mixture of the catalyst/MAO and the rest of the toluene into the reactor using nitrogen overpressure. The polymerizations were terminated by venting the reactor and adding 10 mL of ethanol immediately into the reactor medium (250 mL). The reaction mixture was stirred with 4 mL of concentrated HCl overnight, after which the separated toluene phase was evaporated under a vacuum. Finally, the polymer product was dried in an oven at 60°C.

REACTOR SYSTEM

The reactor system with a 0.5- or 1.0-L stainless-steel autoclave (Büchi AG, BEP 280, type III) and a magnetic stirrer (Büchi AG, BMA 220) is presented in Figure 1. The diameters of the cylinder type vessels are 66 mm (0.5 L) and 84 mm (1.0 L), respectively. The turbine impeller with three vertical curved blades has a diameter of 30 mm and is positioned at 15 mm from the bottom in the both reactors. The high level of the inert atmosphere and the possibility to pressurize the system are achieved by using stainless-steel tubes and chambers equipped with leak-proof fittings (Swagelock) and valves (Whitey).

Reagent injection is based on three removable chambers, each of which can be packed in a glove-box. Two of these are Büchi AG's pressure burettes (0.05 and 0.1 L) and are mostly used

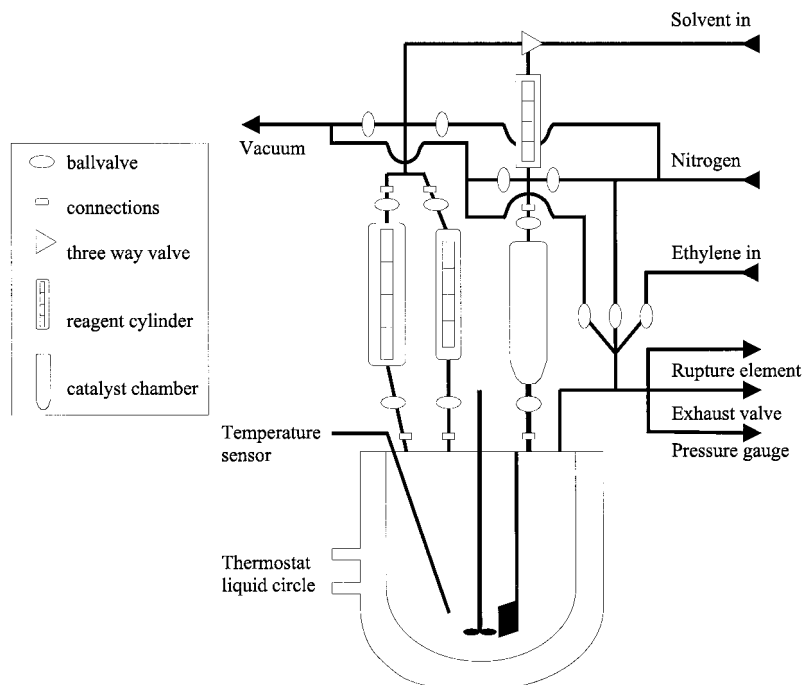


Figure 1 Feed system of the polymerization reactor.

for liquid injection since they have a flat bottom and a 1/4-in. outlet of the burette, whereas the third self-designed chamber (0.15 L) with a 1/2-in. outlet and the conelike bottom is designed mainly for introduction of the catalyst or solid materials. The reactant containers are placed on a coverplate of the reactor via O-ring face-seal connectors and are connected to the injection line with Swagelok's quick-connects. The valves of the vacuum and the nitrogen lines are installed both to the reactor and to each place in the injection lines where the line is opened for filling the chambers. Reagents are injected using nitrogen overpressure and/or a solvent, which also allows rinsing residues of reagents on the walls of the chambers such as the injection of the heterogeneous catalyst in a slurry form.¹⁷ The three-chamber design makes it possible to vary polymerizations conditions, for example, part of the MAO can be introduced before the catalyst to destroy possible oxygen and moisture residues in the reactor.

The purification of the solvent may be performed using two different methods, which makes it easier to vary the solvent for each studied system (Fig. 2). However, both systems make the transfer of the diluent possible through the desired reagent chamber. A removable quick-hose-connected cylinder (1.0 L) is designed to fill with

distilled solvent using standard inert atmosphere techniques. The ball valve on top makes it possible to fill the container by a needle, whereas the needle valve in the bottom end makes it easier to manually control the solvent flow to the reactor.

The main on-line constructed system consists of a fixed distiller (3.0 L) in which the mostly used solvent, toluene, is distilled freshly over sodium and benzophenone prior the polymerization. Before charging into the distiller, the solvent is deoxygenated by bubbling with nitrogen gas, after which it is stored over molecular sieves in a reservoir. Following the distillation, toluene is transferred via a stainless-steel line to a pressure burette (2.0 L) which is at this stage under a static vacuum. After pressurizing the burette, the solvent is transferred into the reactor via reagent chambers using a needle valve and moderate nitrogen pressure.

Purified ethylene is flowed first through a mass flowmeter (F-111C, Bronkhorst) (Fig. 3), after which the ethylene feed into the reactor is controlled by either a pressure meter/controller (P-602C, Bronkhorst) or a mass flow meter/controller (F-201C, Bronkhorst). These meters and controllers are connected to Bronkhorst's serie E-7000 unit which is used for digital readout and control of the ethylene supply. Consequently, the pressure (up to 10 bar) or the continuous flow

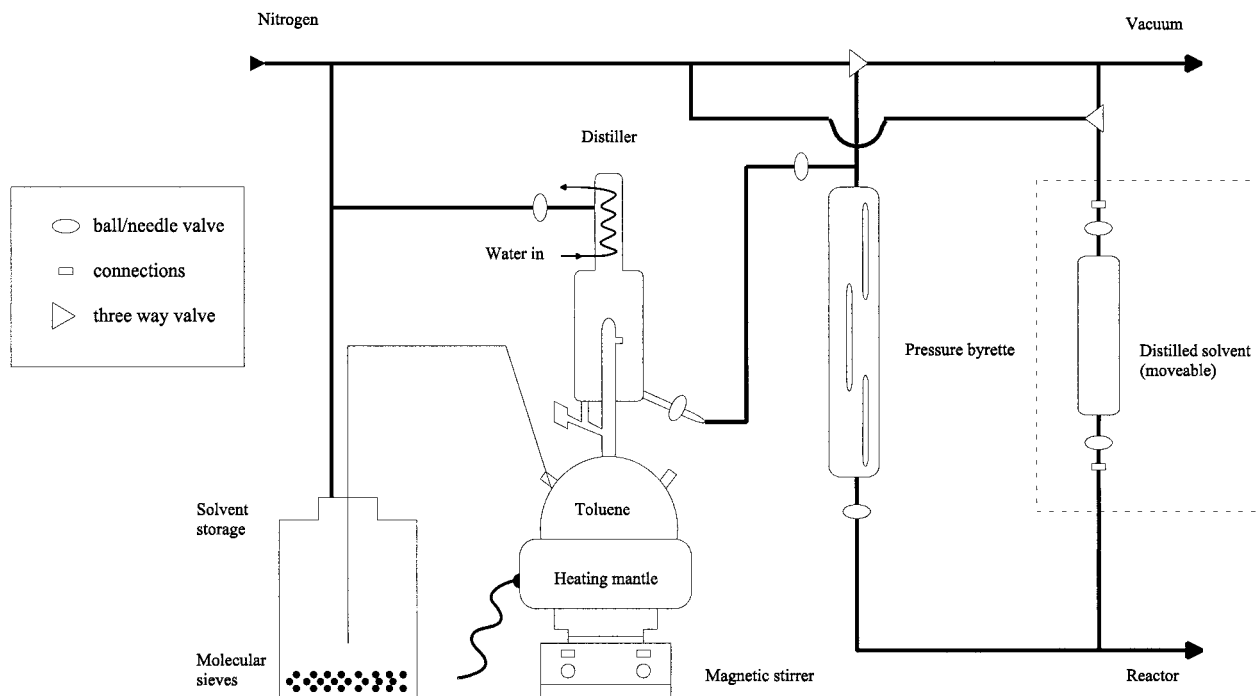


Figure 2 Solvent-purification systems.

(5–500 mL/min) of the ethylene can be set and kept constant during the polymerization.

Temperature Control

The reactor temperature was controlled automatically by a Julabo ATS3 or by self-constructed thermostat systems (Fig. 4). The Julabo ATS3 thermostat employs a cascade control unit with adjustable P, I, and D control parameters. Precise temperature control is obtained when the PID parameters are optimized for the investigated po-

lymerization system. However, room temperature is the lowest working temperature of the Julabo ATS3 due to the air-cooling of the heat-transfer liquid.

To achieve low polymerization temperatures from 30°C below to –40°C, the combination of heating and cooling systems shown in Figure 4 was used. The temperature of the heat-transfer liquid (mixture of glycol/water) in a Lauda M3 thermostat is adjusted by its heating device and a probe of a cryocooler (Neslab CC 100). The cooling energy of the cryocooler is manipulated

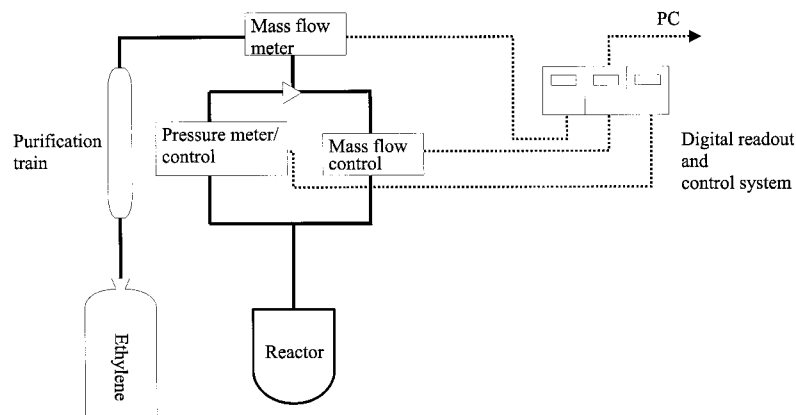


Figure 3 Control system for ethylene feed.

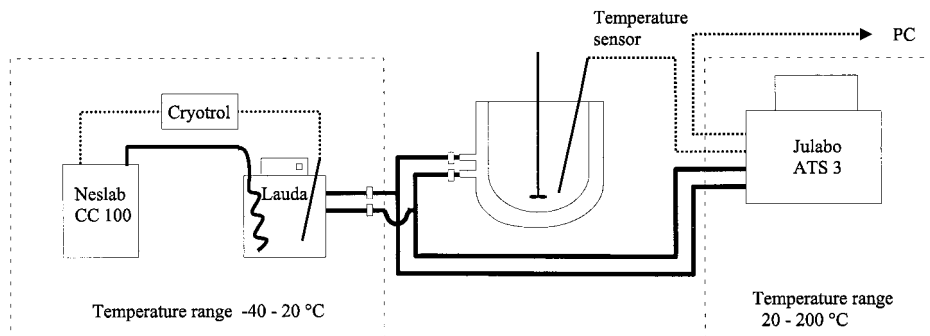


Figure 4 Temperature-control systems.

by a Cryotrol control unit. The balance between the heating and the cooling during the polymerization can be maintained since activity of the catalyst normally decreases at low temperatures. Accuracy of the temperature control system was $\pm 0.3^\circ\text{C}$.

Data Acquisition

The microcomputer-based data acquisition and collection system presented in Figure 5 was constructed using a Genie software (Advantech). The reactor temperature is measured by a Pt-100-double sensor and the total pressure is determined by a Trofag gauge. The meters of ethylene pressure and mass flow are connected first to the ethylene digital readout and control unit and then connected to the data acquisition card (PC-Multilab PCL-7115). With this system, the mass flow, total consumption (mL at NTP), and pressure of ethylene as well as the polymerization temperature and total pressure in the reactor are moni-

tored on-line on a display of the PC. After storing, the data can be processed for, for example, kinetic studies using standard PC programs.

RESULTS AND DISCUSSION

Ethylene Homopolymerization

To determine the capacity of the system, ethylene was polymerized with $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$, which is generally used as a reference catalyst. The activity of 41,000 (kg PE/mol Zr h) was obtained at 80°C using an ethylene overpressure of 1.0 bar and a polymerization time of 20 min. The data of ethylene consumption and the well-balanced temperature control during polymerization are presented in Figure 6.

Testing the polymerization activity of a new catalyst is generally done with ethylene as a monomer.¹⁷ The kinetics studies of catalysts are able to be performed using data of the ethylene

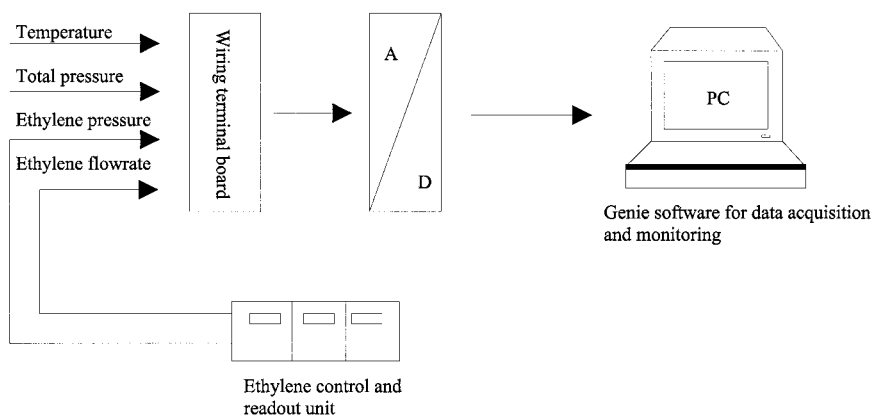


Figure 5 Data acquisition and monitoring system.

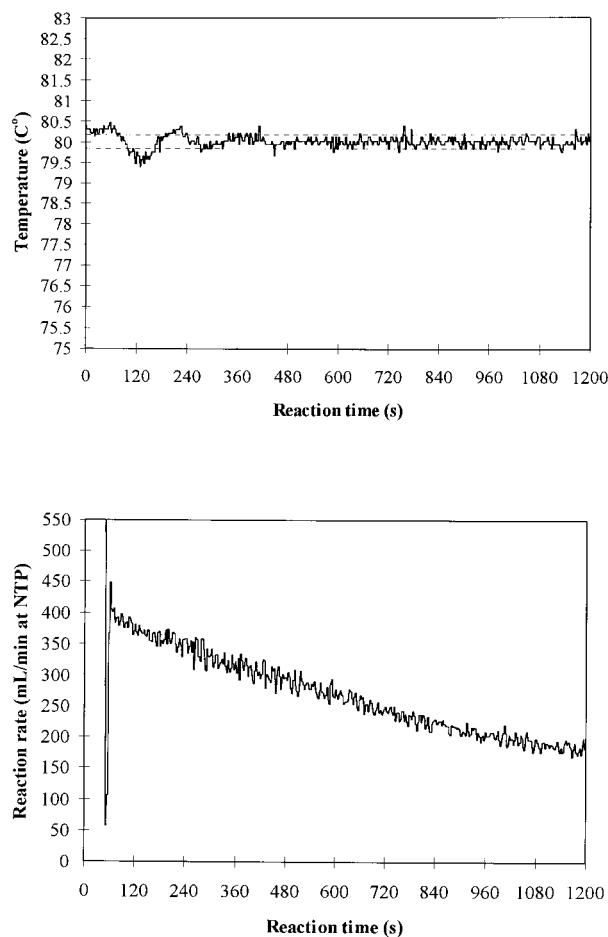


Figure 6 (Top) Temperature and (bottom) mass flow of ethylene during ethylene homopolymerization.

mass flow (mL/min at NTP). The remarkable decrease in ethylene consumption seen in Figure 6 indicates the increasing mass-transfer effect present in the reaction medium.

Ethylene Cycloolefin Copolymers

The polycycloolefins are not processable due to their high melting points and their insolubility in common organic solvents. By incorporating of these cyclic olefins with ethylene or α -olefins, cycloolefin copolymers (COC) can be produced, representing a new class of thermoplastic amorphous materials.¹⁸

Cycloolefins were copolymerized with ethylene at 30°C using a $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ catalyst and polymerization time of 60 min. The results of versatile ethylene/cycloolefin copolymerizations are presented in Table I. The amount of cyclic olefin in the copolymer was determined from the peak area of the ^{13}C -NMR spectrum and the molar mass analysis was performed using gel permeation chromatography (GPC).

According to Gupta et al., the $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ catalyst system is not able to polymerize cyclopentene.¹⁹ We found that this catalyst system catalyzed the copolymerization of cyclopentene with ethylene. This can be confirmed by NMR analysis. Figure 7 presents the ^{13}C -NMR spectrum of the cyclopentene/ethylene copolymer. Based on the NMR results, incorporation of cyclopentene into the copolymer occurs statistically by 1,2 insertion without ring-opening reactions.⁷ With this catalyst and under used polymerization conditions, no homopolymer of cyclopentene was detected.

While homopolymerization of cyclopentene results in 1,3 enchainment of the monomer units, isolated cyclopentene units are incorporated into ethylene copolymer chain by 1,2 insertion. Ethylene is able to compensate the steric hindrance at the α -carbon of the growing chain after and before the insertion of cyclopentene.⁷

Table I Results of Ethylene/Cycloolefin Copolymerization

Run	Comonomer	Cycloalkene/ Ethylene ^a (mol/mol)	Activity (kg/mol Zr h)	Cycloalkene in Copolymer (mol %)	T_m (°C)	Crystallinity ^b (%)	M_n (g/mol)	M_w (g/mol)	M_v (g/mol)	M_w/M_n
1	Cyclopentene	7.7	610	0.3	129.3	58.3	16,900	89,900	73,500	3.4
2	Cyclopentene	15.8	260	0.8	124.9	54.2	9,900	33,600	28,800	5.3
3	Cyclooctene	2.7	1600	<0.1	138.3	62.7	75,400	271,000	234,000	3.6
4	Cyclooctene	5.6	870	0.1	135.8	55.4	34,700	137,000	120,000	4.0
5	Cyclooctene	11.2	510	0.2	133.4	43.0	17,200	76,100	66,300	4.4
6	Cyclooctene	15.6	270	0.3	131.7	38.5	—	—	—	—
7	Cyclododecene	5.6	770	0	133.0	67.8	—	—	—	—

^a Cycloolefin/ethylene ratio in the reaction medium.

^b Calculated using $\Delta H_f = 290$ g/J as a reference.

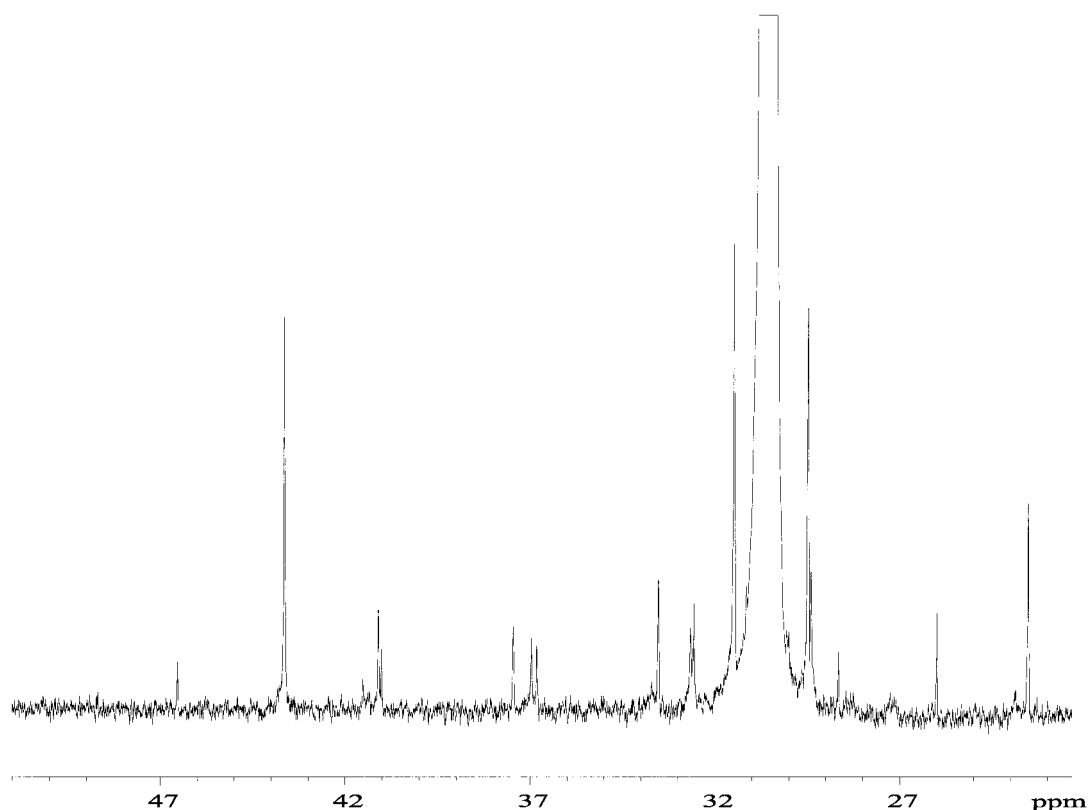


Figure 7 ^{13}C -NMR spectra of poly(ethylene-co-cyclopentene) produced by $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ at 30°C (run 2).

The highest monomeric content of cyclopentene in the polymer was 0.8 mol % under the used conditions. The increasing mol ratios of cyclopentene/ethylene in the reaction mixture increased the amount of cyclopentene incorporated into the copolymer. The influence of the monomer on the melting behavior and crystallinity was analyzed using DSC measurements. The DSC diagram shows only one sharp melting point. Incorporation of 0.8 mol % cyclopentene into the polymer chain led to a decline of melting point to 124°C . The crystallinity of poly(ethylene-co-cyclopentene) decreased when incorporation of cyclopentene increased.

The amount of cyclopentene incorporated in poly(ethylene-co-cyclopentene) has a weak influence on the molar mass, whereas the use of other comonomers, for example, cyclooctene, leads to copolymers for which a higher decrease in molar mass with increasing monomer incorporation is found. Poly(ethylene-co-cyclopentene) showed M_w/M_n values between 3.4 and 5.3. The molar mass distributions are broader than for ethylene

homopolymers ($M_w/M_n = 2$), which are produced with the same catalyst system.

Cyclooctene causes a considerable drop in molar mass. Number-average molar mass decreases from 75,400 g/mol (run 3 in Table I) to 17,200 g/mol (run 5 in Table I) when the cyclooctene feed level increased under investigated conditions. The molar mass distribution of the ethylene/cyclooctene copolymer was relatively broad. The DSC method proved that the amount of the crystalline phase and melting temperature in the copolymer decreased when incorporation of cyclooctene increased. The amount of cyclooctene incorporated was lower than that of cyclopentene.

Cyclododecene was not copolymerized with ethylene by the used catalyst system, $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$. The reason might be in the steric interactions of the Cp_2ZrCl_2 catalyst with the large cyclododecene ring. This result was already expected from the decreasing incorporation with the increasing ring size of the comonomer. However, the ring size has only a weak influence on the activities (Table I).

According to NMR, IR, and DSC measurements, the smallest cycloolefin used, cyclopentene, was the easiest monomer to incorporate and the amount of cyclopentene in the polymer chain was the highest with the observed catalyst system, whereas the 12-membered ring cyclododecene was not copolymerized. The $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ catalyst system shows limited activities and incorporation for monocyclic olefins, but it copolymerizes bicycloolefins, for example, norbornene with a moderate activity and a relatively high incorporation of norbornene into the copolymer chain.²⁰

CONCLUSIONS

With the described polymerization reactor system, both homogeneous and heterogeneous catalyst testing can be carried out reliably due to the high inertness level and the controlled ethylene supply of the present system. The data collection during the polymerization allows, for example, kinetic studies. Moreover, the feed of reagents, which is based on the three-chamber design, makes it possible to vary reactions conditions over a wide range when the synthesis of new copolymer materials are studied.

REFERENCES

1. Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew Chem Int Ed* 1999, 38, 429.
2. DuPont, U.S. Patent 2721189, 1954.
3. Montecatini, DE 1520259, 1961.
4. Montecatini, GB 951022, 1961.
5. Leuna, DD 109224, 1973.
6. Leuna, DD 222317, 1984.
7. Mitsui Petrochemicals, Eur Patent 156464, 1984.
8. Kaminsky, W.; Sphiel, R. *Makromol Chem* 1989, 190, 515.
9. Sinn, H.; Kaminsky, W. *Adv Organomet Chem* 1980, 18, 99.
10. Wild, F. R. W. P.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J Organomet Chem* 1982, 232, 233.
11. Ewen, J. A. *J Am Chem Soc* 1984, 106, 6355.
12. Kaminsky, W.; Külper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew Chem Int Ed Engl* 1985, 24, 507.
13. Mitsui Petrochemicals, Eur Patent 283164, 1987.
14. Hoechst AG, Eur Patent 407870, 1989.
15. Hoechst AG, Eur Patent 485893, 1990.
16. Hoechst AG, Eur. Patent 503422, 1991.
17. Timonen, S.; Pakkanen, T. T.; Iiskola, E. *J Organomet Chem* 1999, 582, 273.
18. Kaminsky, W. *Macromol Chem Phys* 1996, 197, 3907.
19. Gupta, V. K.; Satish, S.; Bhardwaj, I. S. *Macromol Chem Phys* 1994, 34, 439.
20. Lasarov, H.; Mönkkönen, K.; Pakkanen, T. T. *Macromol Chem Phys* 1998, 199, 1939.