polymer communications

Copolymerization of ethylene and 1-hexadecene with Cp_2ZrCl_2–methylaluminoxane catalyst

J. Koivumäki* and J. V. Seppälä
Department of Chemical Engineering, Helsinki University of Technology, SF-02150 Espoo, Finland
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The metallocene catalyst system Cp_2ZrCl_2–methylaluminoxane showed surprisingly high activity for 1-hexadecene, and high concentrations of comonomer could be incorporated into the copolymer compared with a heterogeneous titanium catalyst. A temperature rising elution fractionation (TREF) fractogram of the copolymer revealed it to have narrow branching distribution, much narrower than in commercial linear low density polyethylene, and to have features in common with a commercial low density polyethylene.

(Keywords: metallocene catalyst; copolymerization; ethylene; 1-hexadecene: TREF)

Introduction

Research in the field of homogeneous metallocene catalysts has increased dramatically during the past 5 years as these catalysts have considerable advantages over traditional catalysts. They polymerize ethylene with very high activity[1–3] and used in copolymerization with higher α-olefins and dienes they give highly random distribution of the comonomers[4–10]. In this work copolymers with high concentrations of 1-hexadecene were synthesized and the comonomer distribution was investigated.

Experimental

Materials. Cp_2ZrCl_2 was a commercial product (from Alrich-Chemie), methylaluminoxane (MAO) was 10 wt% in toluene (from Schering AG) and n-heptane was grade GR (from J. T. Baker). Ethylene was grade 3.5 (from AGA) and 1-hexadecene was for synthesis (from Merck). Ethylene, 1-hexadecene and n-heptane were further purified by passing them through columns containing molecular sieves, CuO and Al_2O_3 before their addition to the reactor.

Copolymerization. Copolymerization was performed in n-heptane in a $0.5\,dm^3$ reactor under a constant overpressure of 3.8×10^5 Pa. 1-Hexadecene was pumped into the reactor, which contained 300 ml n-heptane, and ethylene was added up to the polymerization pressure. Copolymerization was initiated by adding a premixed solution of catalyst and cocatalyst. The Al/Zr mole ratio was 1600. The reactor pressure was controlled automatically with a pressure transducer and a magnetic valve. Copolymerization was stopped by degassing the reactor, after which the organic layer was washed with a mixture of ethanol and dilute hydrochloric acid and water, and n-heptane was evaporated gently. The product was dried under vacuum at 80°C until no 1-hexadecene evaporation was observed.

Characterization. 1-Hexadecene content of the copolymers was determined with a Jeol GSX-400 n.m.r. spectrometer from the methylene, branching, α, β and γ carbons. Molecular weight distributions were investigated with a Waters high-temperature g.p.c. device equipped with three Tosoh mixed bed columns with an exclusion limit for polystyrene of 4×10^8. Solvent 1,2,4-trichlorobenzene was used at a flow rate of $1.0\,cm^3\,min^{-1}$. The columns were calibrated universally with broad molecular weight distribution low density polyethylenes (LDPE). Differential scanning calorimetry curves were obtained with a heating rate $10°C\,min^{-1}$ from -100 to 180°C. The same sample was heated to the end temperature twice and between the runs it was cooled back to -100°C in 15 min. Only the second heating curve was analysed.

Results and discussion

As shown in *Table 1*, the Cp_2ZrCl_2–MAO catalyst system showed high activity for 1-hexadecene, and high concentrations of the monomer were achieved; by contrast only traces of 1-hexadecene were found in the copolymer synthesized with the $MgCl_2/TiCl_4$–triethylaluminium (TEA) catalyst system. *Table 1* and *Figure 1* also confirm earlier findings[5,11,12] that when the concentration of the longer α-olefin in the reactor is increased, the molecular weight of the copolymer is decreased, and waxy, low melting copolymers are obtained. In order to get a suitable copolymer for a temperature rising elution fractionation (TREF) run, the polymerization temperature was decreased. *Figure 2* shows that the copolymer obtained in this work has a narrow comonomer distribution and that, except for the tail at the high-temperature end of the fractogram, the TREF fractogram closely resembles that run from a commercial LDPE. From the same figure one can see that the copolymer obtained here is evidently much more homogeneous than commercial linear LDPE (LLDPE). In the near future we intend to carry out a comprehensive study in the

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* To whom correspondence should be addressed

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Table 1 Properties of the copolymers

Run	Polymn temp. (°C)	Polymn time (min)	$[C_{16}H_{32}]$ in the reactor (mol dm^{-3})	$[C_{16}H_{32}]$ in the copolymer		ΔH_f (J g^{-1})	$\bar{M}_w$ (g mol^{-1})	$\bar{M}_w/\bar{M}_n$	Density (g cm^{-3})	Activity (kg(g cat h)$^{-1}$)	Yield (g)
				(mol%)	(wt%)						
1	70	10	0.6	4.7	28.4	46.4	3100	2.8	0.906	41.0	20.5
2	70	10	0.3	3.9	24.3	75.4	3900	2.8	0.930	33.5	21.2
3	70	10	0.1	1.9	13.5	126.2	8700	2.7	0.965	30.9	16.5
4	30	20	0.5	2.9	19.4	92.0	59 000	2.7	0.924	7.0	7.7
5	30	20	0.6	3.3	21.3	69.4	56 000	2.6	0.938	7.1	7.1
6	15	20	0.6	2.5	17.1	75.4	156 000	3.6	0.952	3.8	3.8
7[a]	60	20	0.5	0.1	0.9	147.9	n.d.	n.d.	0.926	0.7	2.0

[a] Catalyst: $MgCl_2/TiCl_4$ + TEA; titanium content 7 wt%; Al/Ti = 200

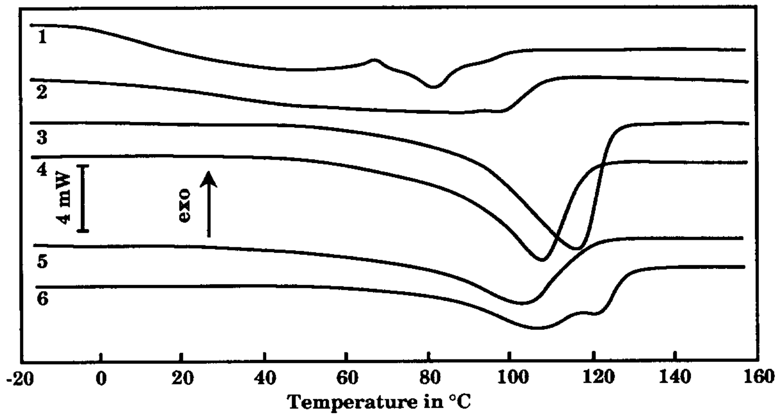

Figure 1 D.s.c. curves of the copolymers. Sample 10–11 mg, heating rate 10°C min^{-1}

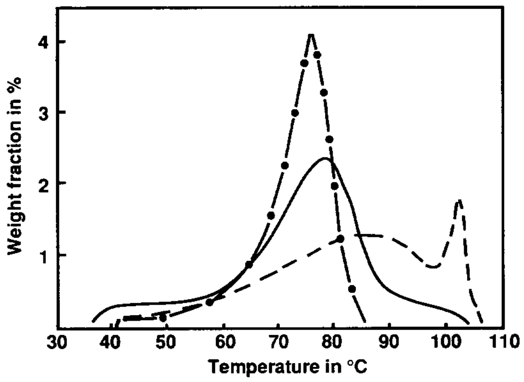

Figure 2 TREF fractograms of different polyethylenes. ——, Sample no. 4; – –, commercial LLDPE (ethylene/1-octene copolymer); –•–•–, commercial LDPE

linear α-olefin field; even longer α-olefins than 1-hexadecene will be polymerized with various metallocene catalysts, and the rheology of the copolymers will be checked.

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