Synthesis of Functional Polyethylenes with Soluble Metallocene/ Methylaluminoxane Catalyst

Päivi Aaltonen* and Barbro Löfgren

Helsinki University of Technology, Polymer Science Centre, P.O. Box 356,
FIN-02151 Espoo, Finland

Received December 20, 1994; Revised Manuscript Received April 27, 1995[⊗]

ABSTRACT: This paper describes an easy method for preparing functional polyolefin copolymers of ethylene and 10-undecen-1-ol with a soluble metallocene/methylaluminoxane catalyst. The GPC profiles of the samples showed a reduction in the molar mass and a marked broadening in the molar mass distributions of the polymers with the addition of the polar compound. The bimodal molar mass distribution curve obtained indicated the presence of two or more active sites in the catalyst. The same results were obtained in DSC analysis. Two transition temperatures can be taken as evidence of the presence of a macroscopic phase separation of the polymer and the nonuniformity of the catalyst. The melt flow indices of the polymers were dramatically increased with the addition of functionalities to the polyethylene backbone, providing marked improvement in the processability of the polymers.

Introduction

The chemical modification of polyolefins to enhance their chemical and physical properties is an area of keen interest. The incorporation of functional groups into hydrocarbon polymers can provide polymers with improved adhesion, dyeability, printability, and permeability. Furthermore, functional groups offer sites for initiating a graft copolymerization allowing compatibilization with other polymers.

Although the Ziegler−Natta process continues to be the most important method for preparing polyolefins, the conventional catalysts have major limitations in their intolerance to Lewis bases.[1] The Lewis acid components (Ti, V, Zr, and Al) of the catalyst tend to form complexes with the nonbonded electron pairs of heteroatoms in preference to reacting with the π electrons of the double bond of the monomer. The net result is the deactivation of the active polymerization sites by formation of stable complexes between catalysts and functional groups.[2]

The more the polar compound resembles an α-olefin, the more likely it is to polymerize at the centers that are active for olefins.[2] In practice, the undesirable interaction can be avoided by (a) insulating the double bond from the heteroatom by a spacer group, (b) increasing the steric hindrance about the heteroatom, (c) reducing the electron-donating character of the heteroatom (e.g. by attaching an electron-attracting group to it), or (d) choosing catalyst components that are inert to the functional groups.

A preferred current approach to the synthesis of functional polymers is the use of monomers possessing functionalities that do not interfere with polymerization and can easily be converted to functional polymers by postpolymerization chemical reactions. Recently, Chung and co-workers investigated borane-containing functional monomers in olefin copolymerization, successfully converting the borane group to polar functionalities.[3] A new approach to end-functionalized polypropylenes has been described by Mülhaupt et al.[4] and Shiono et al.[5] These authors synthesized terminally functionalized polypropylenes and block copolymers with stereospecific soluble metallocene/methylaluminoxane catalyst by making use of versatile chemical reactions of the vinylidene end groups of the polymer. Yet another route to functional polyolefins has been reported by Marathe et al.[6] Ethylene and 5-vinyl-2-norbornene are copolymerized with dicyclopentadienylzirconium dichloride/ methylaluminoxane catalyst, yielding polyolefins with a pendant vinyl double bond that can be functionalized to a hydroxy or epoxy group.

This paper describes a facile synthesis of functional polyolefins through direct copolymerization of ethylene and 10-undecen-1-ol with a soluble metallocene/methylaluminoxane catalyst. A detailed chemical analysis of the polymers is presented.

Experimental Section

Apparatus and Method of Polymerization. Polymerizations were performed in n-heptane in a 0.5 dm^3 stainless steel autoclave at 60 and 80 °C with 2.5 bar ethylene overpressure. The catalyst was $(n\text{-butCp})_2ZrCl_2$ with methylaluminoxane (MAO) as cocatalyst. The stirring speed, with a propeller-like stirrer, was 400 rpm.

n-Heptane (350 cm^3) was introduced into the evacuated and N_2-purged reactor. The comonomer was added batchwise under N_2 pressure, and the cocatalyst, with a pump. The ethylene feed was started at the polymerization temperature. Consumption of ethylene was followed with a mass flow controller connected to a computer with an acquisition frequency of 1 Hz. After equilibrium was reached, polymerization was initiated by pumping the toluene solution of $(n\text{-butCp})_2ZrCl_2$ catalyst into the reactor. The partial pressure of ethylene was maintained constant with an electronic pressure controller and a solenoid valve, and the reactor temperature was controlled with a thermostat connected to a Pt-100 resistance thermometer. The pressure control was accurate to within ±0.03 bar and the reactor temperature to within ±0.1 deg. The conversion of the monomer was low in order to keep the concentration in the reactor constant.

After the polymerization had run the full time (40 min), the reactor was degassed and the polymerization product was stirred with a mixture of ethanol and a small amount of concentrated hydrochloric acid for 6 h and filtered. The residual polymer was then rewashed with ethanol for 3 h with magnetic stirring and dried.

Chemicals. The $(n\text{-butCp})_2ZrCl_2$ catalyst and methylaluminoxane (10% MAO in toluene) were from Witco GmbH. The analytical grade n-heptane was from Merck, and ethylene (grade 3.5), from AGA. The 10-undecen-1-ol was analytical grade purchased from Fluka. n-Heptane and ethylene were further purified by passing them through columns containing

---

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1995.

0024-9297/95/2228-5353$09.00/0

Table 1. Copolymerization of Ethylene and 10-Undecen-1-ol at 60 °C[a]

run	amt of alcohol in feed, $\times 10^3$ mol	yield of polymer, g	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	T_m, °C	MFI, g/10 min
1	0	24.7	222 000	3.4	135.9	0.83[c]
2	1.0	15.4	203 400	3.3	134.7	1.46[c]
3	2.0	12.3	143 300	3.5	132.7	4.39[c]
4	3.0	7.8	120 700	5.2	132.4	0.40[d]
5	4.0	4.5	80 100	6.8	126.3	3.51[d]
6	5.0	2.7	60 700	bimodal	127.3	n.d.[e]
7	6.0	0.8	47 600	bimodal	126.0[b]	n.d.[e]

[a] t_p = 60 °C, $p(C_2H_4)$ = 2.5 bar, Zr = 4.94 × 10^{-6} mol, Al (as MAO) = 1.98 × 10^{-2} mol. [b] Heating rate 2 deg/min. [c] Weight 21.6 kg. [d] Weight 2.16 kg. [e] Not detected.

Table 2. Copolymerization of Ethylene and 10-Undecen-1-ol at 80 °C[a]

run	amt of alcohol in feed, $\times 10^3$ mol	yield of polymer, g	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	T_m, °C	MFI, g/10 min
8	0	35.6	42 900	2.4	134.8	17.8[c]
9	1.0	23.8	42 500	3.6	133.9	16.2[c]
10	2.0	16.0	47 100	3.9	134.3	11.7[c]
11	2.3	12.2	38 200	3.1	132.3	27.0[c]
12	2.8	8.4	32 900	4.6	132.0	33.9[c]
13	3.7	7.3	33 900	5.4	130.4	27.7[c]
14	5.8	6.0	35 400	bimodal	127.7	n.d.[d]
15	7.7	3.4	52 800	bimodal	128.8[b]	n.d.[d]
16	9.6	1.7	117 800	bimodal	131.7	n.d.[d]

[a] t_p = 80 °C, $p(C_2H_4)$ = 2.5 bar, Zr = 4.94 × 10^{-6} mol, Al (as MAO) = 1.98 × 10^{-2} mol. [b] Heating rate 2 deg/min. [c] Weight 2.16 kg. [d] Not detected.

molecular sieves, Cu, and Al_2O_3. The 10-undecen-1-ol was dried with molecular sieves and purged with N_2.

Polymer Characterization. Melting temperatures were recorded with a Perkin-Elmer DSC-7 differential scanning calorimeter. The melting endotherms were measured upon reheating the sample to 180 °C at heating rates of 2 and 10 deg/min.

Molar masses were investigated with a Waters high-temperature GPC device equipped with three Tosoh mixed bed columns with an exclusion limit for polystyrene of 4 × 10^8. Solvent 1,2,4-trichlorobenzene was applied at a flow rate of 1.0 cm^3/min. The columns were calibrated universally with linear low-density polyethylenes of broad molar mass distribution.

The NMR spectra were recorded on a JEOL NMR spectrometer. The monomer content of the polymers was calculated from the ^1H NMR spectrum.

The melt flow indices were measured with a Ceast MFI melt flow index device at 190 °C using 2.16 and 21.6 kg weights. The melt flow index was calculated in terms of grams of polymer made to flow in 10 min.

Results and Discussion

In the presence of metallocene catalyst, ethylene was copolymerized with 10-undecen-1-ol under mild conditions with good yield. Destructive poisoning of the catalyst was avoided through the use of functional monomers with long spacer groups. The copolymerizations were carried out in the presence of a catalytic system $(n\text{-butCp})_2ZrCl_2$/MAO (Cp = cyclopentadienyl) at the polymerization temperatures of 60 and 80 °C for 40 min. The reaction conditions and the results of the polymerizations are listed in Tables 1 and 2.

A typical ^1H NMR spectrum of the copolymer is shown in Figure 1. The composition of the copolymers was calculated from the intensities of the methylene protons and the hydroxyl group (δ = 3.5 ppm). The concentration of the polar groups in the polymer was greatest when the polymerizations were conducted at 60 °C and 9.9 weight % of alcohol was present in the polymer. At the polymerization temperature of 80 °C the highest alcohol concentration achieved in the product was 1.2 weight %.

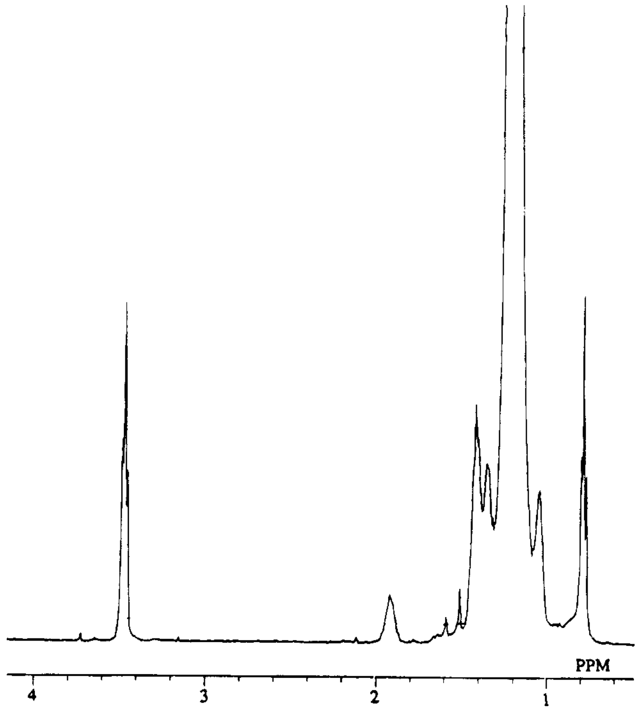

Figure 1. ^1H NMR spectrum of the ethylene–10-undecen-1-ol copolymer.

The activity of the catalyst rapidly decays when the concentration of the alcohol in the polymerization mixture is increased. Figures 2a illustrates the effect of the alcohol concentration in the monomer feed on the activity of the catalyst at the polymerization temperatures 60 °C, and Figure 2b shows the effect at 80 °C. The major difference is the more rapid deactivation of the catalyst at 60 °C as the amount of comonomer is increased. This may be due to the better incorporation of the functional monomer at lower polymerization temperatures or to the increase in the ethylene polymerization rate at high temperatures.

The deactivating effect of the alcohol is partly due to the complex formation between polar monomer and MAO. As the polymerization proceeds, the conversion of the alcohol increases and the complexed MAO is liberated. The net result is an activation of the catalyst and an increase in the consumption of ethylene (Figure 3). As can be seen, the complex formation between alcohol and MAO is not an irreversible process and the activity of the catalyst is preserved. More detailed studies concerning the reaction of alcohol with MAO are in progress, and the results will be reported later.

GPC Studies. The GPC chromatograms of the various copolymers showed a lowering of the molar mass and a broadening of the molar mass distributions with an increase in the mole amount of alcohol in the polymerization mixtures. A likely explanation for the decrease in the molar mass of the polymer is the greater probability of chain transfer reactions as the comonomer concentration increases. The GPC curves of the polymers are shown in Figure 4a,b.

The broadening of the molar mass distribution occurs even when only a small amount of alcohol is present in

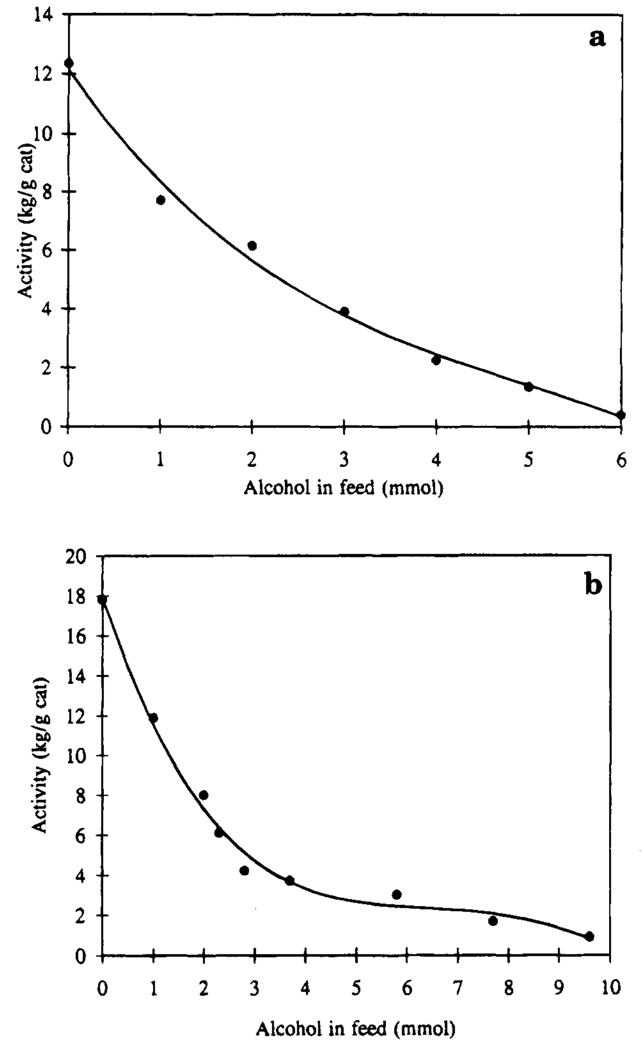

Figure 2. (a) Effect of 10-undecen-1-ol concentration on the activity of the catalyst. t_p = 60 °C, $p(C_2H_4)$ = 2.5 bar, Zr = 4.94×10^{-6} mol, Al (as MAO) = 1.98×10^{-2} mol. (b) Effect of 10-undecen-1-ol concentration on the activity of the catalyst. t_p = 80 °C, $p(C_2H_4)$ = 2.5 bar, Zr = 4.94×10^{-6} mol, Al (as MAO) = 1.98×10^{-2} mol.

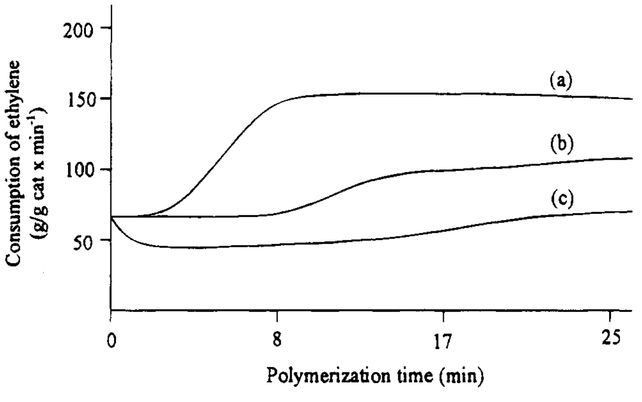

Figure 3. Dependence of ethylene consumption on 10-undecen-1-ol addition: (a) 2.0×10^{-3} mol, (b) 3.0×10^{-3} mol, and (c) 4.0×10^{-3} mol of alcohol in feed. t_p = 60 °C, $p(C_2H_4)$ = 2.5 bar, Zr = 4.94×10^{-6} mol, Al (as MAO) = 1.98×10^{-2} mol.

the polymerization mixture. With higher alcohol concentrations, a second peak appears in the GPC curve, indicating that the product is bimodal.

Interesting behavior was observed when the polymerizations were conducted at 80 °C. As illustrated in Figure 4b, an increase in the alcohol concentration caused the original low molar mass end of the curve to disappear and the high molar mass end to become predominant. We suggest that with no, or very low concentrations of, alcohol in the feed, the catalyst is a "single site" and the polymer shows narrow molecular weight distribution (curve a), but when the alcohol concentration is increased, an active site of a second type is formed. At moderate alcohol concentrations of the feed there are thus two active sites present in the catalyst producing ethylene copolymer of two different molar masses (curves b and c). However, when the alcohol concentration is increased still, active sites of the first type are transformed to active sites of the second type and the product shows a high molar mass and again a narrow molar mass distribution (curve d). However, the activity of the new sites is much lower than the activity of the original ones.

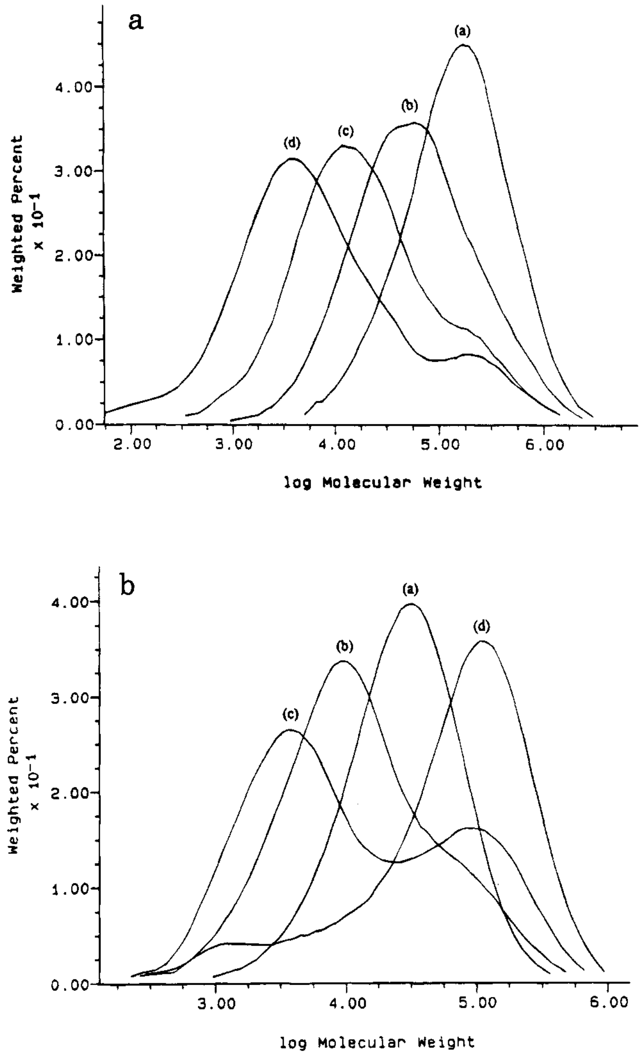

Figure 4. (a) GPC chromatograms of copolymers prepared at 60 °C: (a) 0 mol, (b) 3.0×10^{-3} mol, (c) 5.0×10^{-3} mol, and (d) 6.0×10^{-3} mol of alcohol in feed. (b)GPC chromatograms of copolymers prepared at 80 °C: (a) 0 mol, (b) 3.7×10^{-3} mol, (c) 7.7×10^{-3} mol, and (d) 9.6×10^{-3} mol of alcohol in feed.

Another possible explanation for the formation of only one molar mass fraction at high alcohol concentrations is the more rapid deactivation of the active centers of the first type with an increase in the amount of alcohol in the feed. The active sites of the second type are more stable against the destructive interference of the polar monomer, but they too will be deactivated if the alcohol concentration is increased still further.

Thermal Characterizations. The thermal properties of the copolymers were investigated by the DSC

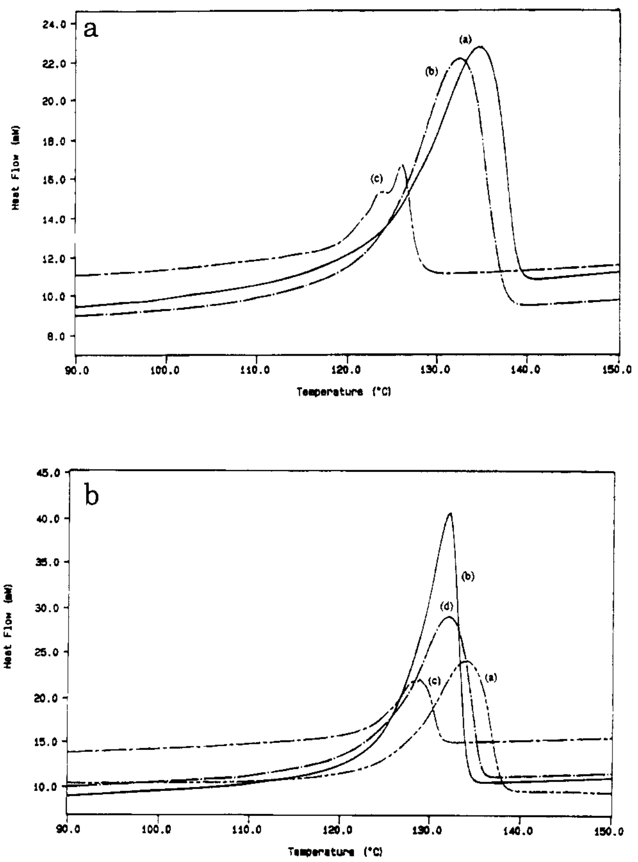

Figure 5. (a) DSC curves of copolymers prepared at 60 °C: (a) 1.0 × 10^{-3} mol, (b) 3.0 × 10^{-3} mol, and (c) 6.0 × 10^{-3} mol of alcohol in feed. (b) DSC curves of copolymers prepared at 80 °C: (a) 1 × 10^{-3} mol, (b) 2.8 × 10^{-3} mol, (c) 5.8 × 10^{-3} mol, and (d) 9.6 × 10^{-3} mol of alcohol in feed.

technique. The samples were first heated to 180 °C and then cooled to 0 °C (20 deg/min). The melting endotherms were measured upon reheating the sample at rates of 2 and 10 deg/min. The slower heating rate was used for the bimodal samples in order to separate the two melting temperatures of the sample. Figure 5a shows the DSC thermograms of copolymers prepared at 60 °C with different mole amounts of 10-undecen-1-ol in the monomer feed. It is clearly seen that the single exothermic melting peak continuously moves to lower temperatures with an increase in the hydroxyl group concentration in the polymer. The bimodal sample (curve c) shows two transition temperatures, which argue for the presence of a macroscopic phase separation of the polymer and the nonuniformity of the catalyst active sites. The polymerizations conducted at 80 °C show similar melting temperature depressions and peak separations, as described above. Surprisingly, the melting endotherm of the copolymer prepared at the highest alcohol concentration in the monomer feed appears again in the higher temperature range (Figure 5b, curve d), perhaps due to the high molar mass of the polymer.

Effect of Al/Zr Mole Ratio. The polymerization activity is strongly dependent on the Al/Zr mole ratio. At low Al/Zr mole ratios most of the aluminum alkyl is complexed with the polar monomer and there is no free MAO present in the system to form the active catalyst. With an increase in the amount of the cocatalyst the activity of the catalyst increases almost linearly. The results of the polymerizations are summarized in Table 3.

Table 3. Effect of Al/Zr Mole Ratio on the Copolymerization of Ethylene and 10-Undecen-1-ol[a]

run	Al/Zr, mol/mol	yield of polymer, g	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	T_m, °C
17	2000	1.6	107 800	bimodal	137.9
18	3000	3.2	53 600	bimodal	133.9
19	4000	6.6	61 200	bimodal	134.7
20	5000	8.8	44 100	bimodal	138.3

[a] t_p = 80 °C, $p(C_2H_4)$ = 2.5 bar, Zr = 4.94 × 10^{-6} mol, 10-undecen-1-ol = 3.0 × 10^{-3} mol.

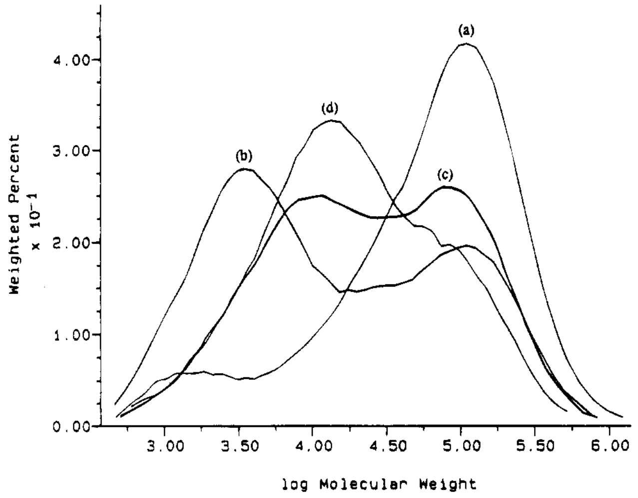

Figure 6. GPC curves of sampes prepared at Al/Zr mole ratios of (a) 2000, (b) 3000, (c) 4000, and (d) 5000.

The molar mass of the polymers decreases with the increase in the Al/Zr mole ratio. Figure 6 illustrates the molar mass distribution plots of samples prepared at different Al/Zr mole ratios. A high molar mass polymer fraction is observed at low Al/Zr mole ratios, and a bimodal molar mass distribution when the Al/Zr mole ratio increases. If the Al concentration is increased still, a low molar mass polymer fraction with a narrow molar mass distribution is obtained.

Melt Flow Indices. In general, it is difficult to process polymers prepared with homogeneous metallocene catalyst because their melt flow indices are low due to the narrow molar mass distribution of the material. The melt flow indices of the present polymers were measured at 190 °C using 2.16 and 21.6 kg weights. As can be seen from the results summarized in Tables 1 and 2, a small addition of the functional monomer causes a dramatic increase in the melt flow index of the polymer, improving the processability markedly.

Conclusions

Current interest in the functionalization of linear hydrocarbon polymers derives from the significant improvement that can be achieved in physical, mechanical, and rheological properties. Advances in metallocene catalysis chemistry are now providing a way to synthesize a broad range of functional polymers through the direct polymerization of polar compounds. In this study the method was applied to the synthesis of copolymers of ethylene and 10-undecen-1-ol. Characterization of the polymerization products revealed a marked broadening of the molar mass distributions of the polymers with the addition of the polar compound. At moderate alcohol concentrations the molar mass distribution curve became bimodal, indicating the presence of two or more active sites in the catalyst. A two-phase morphology was also evident in the DSC curves. Of major importance was the dramatic increase in the melt flow indices of the polymers with the addition of functionalities to the polyethylene backbone. A marked improvement in the processability of the polymers was thereby achieved.

References and Notes

(1) Kapur, S. L.; Deshpande, A. B. *Polym.Eng. Sci.* **1974**, *14*, 276.

(2) Boor, J., Jr. *Ziegler-Natta Catalysts and Polymerizations*; Academic Press: New York, 1979.

(3) (a) Chung, T. C. *Macromolecules* **1988**, *21*, 865. (b) Chung, T. C.; Raate, M.; Berluche, E.; Schulz, D. N. *Macromolecules* **1988**, *21*, 1903. (c) Ramakrishnan, S.; Berluche, E.; Chung, T. C. *Macromolecules* **1990**, *23*, 378. (d) Chung, T. C.; Rhubright, D. *Macromolecules* **1991**, *24*, 971. (e) Chung, T. C.; Ramakrishnan, S.; Kim, M. W. *Macromolecules* **1991**, *24*, 2675.

(4) Mülhaupt, R.; Duschek, T.; Rieger, B. *Makromol. Chem., Macromol. Symp.* 1991, *48/49*, 317.

(5) Shiono, T.; Kurosawa, H.; Ishida, O.; Soga, K. *Macromolecules* **1993**, *26*, 2085.

(6) Marathe, S.; Sivaram, S. *Macromolecules* **1994**, *27*, 1083.

MA946517A