

COPOLYMERIZATION OF ETHYLENE WITH 1-OCTENE USING $\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ CATALYST

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Abstract Copolymerization of ethylene/1-octene was carried out in toluene with various concentrations of comonomer in the feed using $\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ (methyl aluminoxane) as catalyst. It was found that with the increase of 1-octene concentration in the feed the content of 1-octene in the copolymer increases, while the density, melting point, crystallinity and intrinsic viscosity of copolymer decrease. A copolymer with very low density, containing 11.5 mol% of 1-octene (VLLDPE) can be produced with this catalyst system. The effect of temperature and zirconium aluminum mole ratio of the catalyst on the copolymerization was also investigated. The results of ^{13}C NMR determination of the copolymer showed that the 1-octene units in the copolymer are principally isolated.

Keywords Copolymerization; Ethylene; 1-Octene; Methylaluminoxane; $\text{Et}(\text{Ind})_2\text{ZrCl}_2$

INTRODUCTION

Copolymers of ethylene and higher α -olefins produced with homogeneous metallocene/MAO (methylaluminoxane) catalyst systems have unique and competitive properties (highly uniform distribution of comonomer incorporation and very narrow MWD) in comparison with those obtained by heterogeneous catalysts. The properties of copolymer are dependent on the type of catalyst^[1] and type of comonomer^[2]. Higher α -olefins such as 1-butene, 1-hexene and 1-octene are being used as comonomer. $\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ have been employed as catalyst to copolymerize ethylene with comonomer 1-butene^[3], 1-hexene^[2,4,5] into copolymer (LLDPE). Ethylene and 1-octene copolymerization have been reported by using zirconocene catalyst systems $(\text{CH}_3)_2\text{SiCp}_2\text{ZrCl}_2/\text{MAO}$ and $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ ^[2].

In the present study, we have prepared $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ compound as the catalyst for the copolymerization of ethylene and 1-octene, and the influences of incorporation of 1-octene on properties, density and molar mass of the copolymer were investigated.

EXPERIMENTAL

Materials

Toluene was purified by refluxing for 24 h over sodium metal, followed by fractional distillation. Polymerization grade ethylene and nitrogen (99.99%) were used

after purification by passing through columns of activated molecular sieve (4A). 1-octene was available from Aldrich Co. and was purified by distilling over metallic sodium.

$\text{Et(Ind)}_2\text{ZrCl}_2$ [6] and MAO [7] were prepared respectively according to the literature reported (Ind: η^5 -indenyl).

Copolymerization procedure

Copolymerizations were carried out in a 0.5 L glass reactor equipped with a stirrer. Toluene was used as solvent. For every experiment, the reactor was purged with nitrogen and replaced with ethylene at reaction temperature. 100 ml toluene, 1-octene and a solution of MAO were added consecutively, copolymerization was initiated by the addition of the solution of $\text{Et(Ind)}_2\text{ZrCl}_2$ in toluene at 50°C. Ethylene was continuously supplied to the reactor and the copolymerization was carried out at 10.06×10^5 Pa and 50°C for 1 h. Then it was quenched by adding ethanol containing hydrochloric acid. The copolymer product was washed with ethanol and dried in vacuum at 60°C.

Polymer characterization

The density of the polymer was measured by density gradient column techniques. A mixture of anhydrous ethanol and H_2O was used to prepare the density gradient at 25.0°C covering a density range of 0.82–0.95 g·ml⁻¹.

The melting points (T_m) of the copolymer were determined with a Perkin-Elmer Model DSC-7 instrument at a heating rate of 10°C/min. The crystallinity was calculated from the heat of fusion (ΔH_f^0) [8].

The intrinsic viscosity was measured by an AVS 300 viscometer in dilute decahydronaphthalene solution at 135°C.

The ^{13}C NMR spectra were recorded on a JNM-FX100 instrument. The polymer solutions for the ^{13}C NMR measurements were prepared in *o*-dichlorobenzene- d_4 . The 1-octene content and the triad sequence distribution were calculated from the intensity of the signals according to the method reported by Hsieh [9] and Nozaki [10].

RESULTS AND DISCUSSION

The copolymerization was conducted at 50°C under atmospheric pressure by changing the comonomer concentration in the feed. The results obtained are summarized in Table 1.

Table 1 shows that the activity of the catalyst increased markedly when a small amount of 1-octene was introduced in ethylene polymerization. An increase in the comonomer concentration in the feed does not enhance the activity further. For this phenomenon there are several possible explanations [2,10–11]. We have reported the

activity enhancement of copolymerization of ethylene with 1-butene for $\text{SiO}_2/\text{MgCl}_2$ bisupported Ti catalyst and explained by the formation of new active centers and/or the diffusion of the monomer^[12]. The copolymer produced in $\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ catalyst system during polymerization can be completely dissolved in toluene. In this case, we consider that the enhancement of catalyst activity in this system can hardly be attributed to the monomer diffusion. The formation of new active centers due to comonomer taken part in the activation of catalytic centers is a possible reason. With an increase in the comonomer concentration in the feed, the catalyst exhibits little or no enhancement in the copolymerization activity.

Table 1 Effect results of copolymerization of ethylene/1-octene

1-Octene in feed mol/L	[1-Octene] in copolymer mol%	Activity $\times 10^{-6}$ g polymer/molZr $\cdot$ h	Density (g/cm ³)	T_m (°C)	Crystallinity (%)	$[\eta]$ (ml/g)
0	0	3.1	0.9407	136.2	76.7	4.89
0.1	3.5	6.0	0.9093	113.4	52.6	1.69
0.2	5.9	7.5	0.9060	—	—	1.37
0.3	9.5	6.0	0.8940	91.4	—	1.01
0.4	11.5	7.5	0.8835	77.1	—	0.93

Copolymerization conditions: 50°C; $[\text{Zr}]=40\text{ }\mu\text{M}$; $\text{Al}/\text{Zr}=1250$; time=15 min

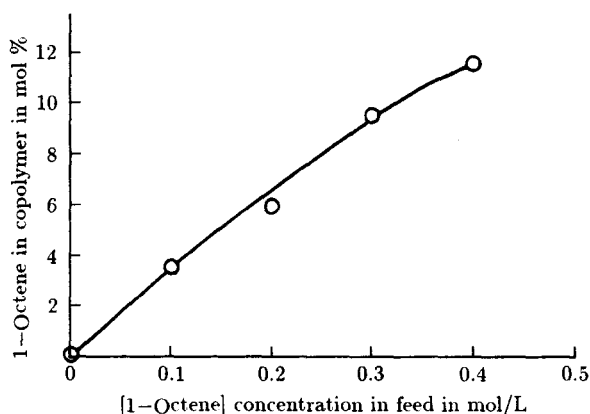


Fig. 1 Variation of 1-octene content in copolymer with 1-octene concentration in the feed

Fig. 1 shows an increasing incorporation of 1-octene in the copolymer with increasing 1-octene concentration in the feed. When the 1-octene concentration was 0.4 mol/L, the content of 1-octene in the copolymer reached 11.5 mole%. The monomer reactivity ratios estimated with Fineman-Ross method^[13] are $r_E = 27.78$ $r_O = 0.02$ (E =ethylene, O =1-octene). The value of $r_E \cdot r_O$ was estimated to be less than unity. It may be said that incorporation of 1-octene has an aleatory tendency similar to that of 1-hexene^[2].

With the increase in 1-octene comonomer in the feed, the density, melting point and crystallinity of the copolymer decrease. The copolymers show a broad range

of density. A copolymer with very low density (VLLDPE) can be produced with Et(Ind)₂ZrCl₂/MAO catalyst system. The DSC curves in Fig.2 show that, as the comonomer content increases, the melting range broadens.

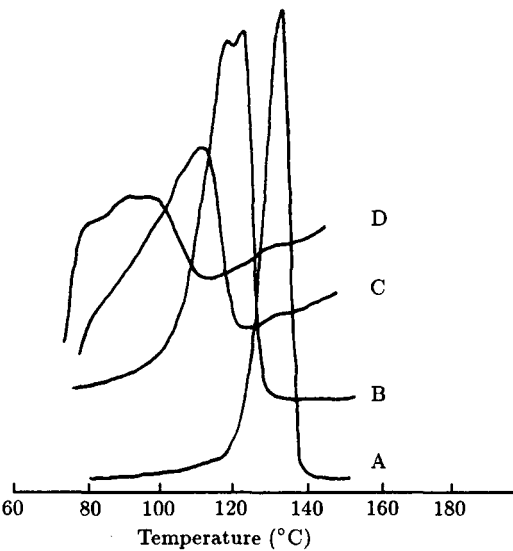


Fig. 2 DSC curves of copolymer with different 1-octene concentrations in feed: A: 0.1 mol/L; B: 0.2 mol/L; C: 0.3 mol/L; D: 0.4 mol/L
Copolymn conditions: the same as Table 1

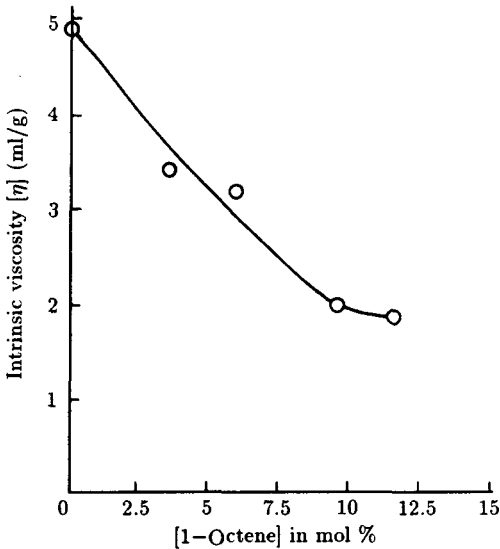


Fig. 3 Variation of intrinsic viscosities [η] of copolymer with 1-octene contents

Table 2 Monomer sequence distributions, average sequence lengths of copolymer obtained with various 1-octene concentration in the feed

1-Octene in feed (mol/L)	0.1	0.2	0.3	0.4
OO	0	0	0	0
OE	0.070	0.117	0.190	0.233
EE	0.930	0.883	0.809	0.767
OOO	0	0	0	0
OOE	0	0	0	0
EOE	0.035	0.059	0.095	0.071
OEO	0	0	0	0.024
OEE	0.070	0.117	0.190	0.273
EEE	0.895	0.824	0.715	0.672
$\bar{n}_0$	1	1	1	1
$\bar{n}_E$	27.6	16.1	9.5	6.6

The intrinsic viscosities [η] of ethylene/1-octene copolymers decrease with the increase of 1-octene content (Fig. 3). This intrinsic viscosity decrease could be the

consequence of the chain transfer to the comonomer.

The monomer sequence distribution and the number sequence lengths were obtained according to Ref. [14]. The results are given in Table 2, where $[1-O]$ and $[E]$ are the mole fractions of 1-octene and ethylene monomer units in the copolymers; $[1-O]=[EOE]+[EOO]+[OOO]$ and $[E]=[OEO]+[OEE]+[EEE]$.

Table 3 Effect of copolymerization temperature on catalytic activity and polymer properties

Temp (°C)	Activity $\times 10^{-6}$ g polymer/mol Zr·h	Density (g/cm ³)	T_m (°C)	Crystallinity (%)	$[\eta]$ (ml/g)
40	14	0.8976	103.5	39.8	1.48
50	25	0.9019	107.4	38.5	1.37
60	22	0.9050	101.0	30.2	1.17
70	16	—	—	—	—

Copolymer conditions: $[1\text{-octene}]=0.2$ mol/L, $[Zr]=20\mu\text{M}$, $Al/Zr=2500$, time=30 min

Table 4 Effect of Al/Zr on catalytic activity and polymer properties

Al/Zr mol/mol	Activity $\times 10^{-6}$ g polymer/mol Zr·h	Density (g/cm ³)	T_m (°C)	Crystallinity (%)	$[\eta]$ (ml/g)
750	4	0.9015	98.4	31.7	1.12
1250	10	0.9002	105.6	35.5	1.10
2500	25	0.9019	107.4	38.5	1.37
5000	27.2	—	—	—	—

Copolymer conditions: $[1\text{-octene}]=0.2$ mol/L, $[Zr]=20\mu\text{M}$, time=30 min

With the increase in mol% of 1-octene in the feed, the sequence distribution containing 1-octene units increases, while $[EEE]$ sequence decrease. The values of $n_0 = 1$ suggests that the 1-octene units in the copolymer are nearly isolated.

The effect of temperature and of zirconium/aluminum mole ratio on the copolymerization are shown in Table 3 and Table 4, respectively. It is observed that the optimum copolymerization temperature range for maximum catalytic activity is 50 to 60°C. With increasing copolymerization temperature, the density of the copolymer increases, while melting point, crystallinity and intrinsic viscosity of the copolymer decrease. The catalytic activity of the copolymerization is strongly dependent on the Al/Zr mole ratio. By varying the Al/Zr mole ratio from 750 to 2500 the catalytic activity may increase about 6 times. Moreover, the melting point and crystallinity of the copolymer increased with increasing Al/Zr ratio.

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