Polymer Bulletin 25, 567–570 (1991)

Polymer Bulletin

Preparation of syndiotactic polyolefins by using metallocene catalysts

T. Asanuma, Y. Nishimori, M. Ito, N. Uchikawa, and T. Shiomura

Mitsui Toatsu Chemicals, Inc., Osaka Research Laboratory, Takaishi, Osaka, Japan

Summary

Polyolefins having syndiotactic structure were obtained by using 1-methyl-1-ethylidene-(cyclopentadienyl-1'-fluorenyl)zirconium dichloride and methylaluminoxane as a catalyst. 1-Butene and 4-methyl-1-pentene gave crystalline polymers having syndiotactic structure, while 1-pentene, 1-hexene and 1-octene gave noncrystalline polymers having syndiotactic structure.

The identification of syndiotactic and isotactic polyolefins was made by ^{13}C-NMR, X-ray diffraction, and differential scanning calorimetry.

Introduction

Syndiotactic polypropylene has been prepared by using Ziegler type catalyst since 1960, but the stereospecificity of the polymer was rather poor. Recently it was reported that by using metallocene catalyst, highly syndiotactic polypropylene was prepared (1). It was also reported that syndiotactic poly(4-methyl-1-pentene) was obtained by hydrogenation of poly(4-methyl-1,3- pentadiene)(2). We tried to produce other syndiotactic polyolefins such as poly-(1-butene), poly(1-pentene), poly(1-hexene) and poly(1-octene) directly from the monomers.

Experimental

1-Butene, 1-pentene, 1-hexene and 1-octene were purchased from Wako Pure Chemicals Ind. and 4-methyl-1-pentene(4MPT) was purchased from Tokyo Kasei Kogyo Co. All these monomers were distilled on calcium hydride and then dried by using molecular sieves 3A. Toluene was purchased from Wako Pure Chemicals Ind. and purified by the same procedure. 1-Methyl-1-ethyliden-(cyclopentadienyl-1'-fluorenyl)zirconium dichloride(cat.2) was prepared according to the literature(1), and 1,2-ethylenebis(tetrahydroindenyl)zirconium dichloride(cat.1) was prepared according to the literature(3). Methyl-aluminoxane(MAO) was purchased from Tosoh Akzo Co.

1-Butene was polymerized in 300 ml autoclave and other olefins were polymerized in 200 ml flask under the condition as shown in table 1. After polymerization, methanol and toluene were added to the polymerization product and the mixture was warmed to 70 °C and was washed with acidic water to remove the catalyst residues.

^{13}C-NMR spectra were measured on JEOL GX-400 operating in the FT mode. Polymers(ca. 30mg) were dissolved in 1,2,4-trichlorobenzene(0.4mL) and tetrachloro-1,2-dideuterioethane (ca. 0.05mL) in 5-mm-i.d. tubes. Tetramethylsilane was used as an internal reference. The X-ray powder diffraction spectra were taken with Cu-K α radiation.

The molecular mass distributions of polymers were determined at 135°C with a Waters Associates ALC/GPC(model 150C) equipped with a Shodex AD80 MS column by using standard polystyrene and by using 1,2,4-trichlorobenzene as solvent.

The melting point and crystallization temperature of polymers were measured by differential scanning calorimetry(Perkin Elmer model 4) at a heating and cooling rate of 10 K/min under nitrogen atmosphere.

The limiting viscocity of polymers was measured at 135 °C in tetrahydronaphthalene solution.

Table 1. Polymerization conditions and results

catalyst (mmol×10^3)	monomer (g)	MAO mmol	Temp °C	Yield * g	Activity kg/mol·hr	[η] dℓ/g	Mn ×10^{-4}	Mw ×10^{-4}	Mw/Mn
cat.1(3.0)	1-butene(80.9)	2.97	30	13.8	4600	0.26	1.1	2.0	1.8
cat.2(2.9)	1-butene(80.1)	2.97	30	15.4	5310	0.49	2.0	5.0	2.5
cat.1(4.5)	1-pentene(9.6)	2.97	8	2.3	511	0.11	0.6	1.0	1.7
cat.2(5.2)	1-pentene(12.7)	2.97	8	2.6	500	0.52	2.5	5.0	2.0
cat.1(12.1)	1-hexene (33.5)	5.94	30	25.9	2140	0.13	0.6	1.0	1.7
cat.2(11.9)	1-hexene (54.0)	5.94	30	40.0	3361	0.26	1.3	3.0	2.3
cat.1(6.0)	4MPT (27.0)	2.97	30	2.3	383	0.21	0.8	2.0	2.5
cat.2(11.9)	4MPT (98.0)	5.94	30	10.9	916	0.30	1.8	3.0	1.7
cat.1(11.9)	1-octene (54.0)	5.94	30	33.2	2790	0.10	0.5	1.0	2.0
cat.2(11.9)	1-octene (71.5)	5.94	30	47.7	4008	0.23	1.3	3.0	2.3

*Polymerized for 1 hr.

Results and Discussion.

The results of polymerization are shown in table 1. In all cases polymerization proceeded smoothly and polymers with narrow molecular weight distribution were obtained. Cat.2 always gave polymers of higher molecular weight compared to cat.1.

Fig.1 to 5 show the ^{13}C-NMR spectra of the polymers. ^{13}C-NMR analysis of predominantly isotactic polyolefins have been reported (polypropylene and poly(1-butene) (4), poly(1-pentene), poly(1-hexene), poly(1-octene) and poly(4-methyl-1-pentene)(5)). These authors predicted chemical shifts for several stereoconfigurations. The peak observed at 26.9 ppm(in Fig.1b) is assigned to the side chain methylene carbon directly bonded to the main chain of the syndiotactic structure. The isotactic pentad fraction is about 0.89 for the polymer obtained by using cat.1, while the syndiotactic pentad fraction is about 0.91 for the polymer obtained by using cat.2. The peak observed at 38.1 ppm(in Fig.2a) is assigned to the side chain methylene carbon directly bonded to the main chain of the isotactic structure and the peak observed at 37.5ppm(in Fig.2b) is assigned to that of the syndiotactic structure. The mm triad of the side chain methylene carbon directly bonded to the main chain of poly(1-hexene) is observed at 35.3 ppm(in Fig.3a) and the rr triad is observed at 34.4 ppm(in Fig.3b). The peak observed at 42.5 ppm(in Fig.4a) is assigned to the methylene carbon of the main chain of isotactic structure of poly(4-methyl-1-pentene) and the peak observed at 43.1 ppm(in Fig.4b) is assigned to that of syndiotactic structure. These data correspond to the results reported by A.Zambelli(2). The mm triad of the side chain methylene carbon directly bonded to the main chain of poly-(1-octene) is observed at 35.7 ppm(in Fig.5a) and the rr triad is observed at 35.1 ppm (in Fig.5b).

Fig.6 shows the DSC diagram of poly(1-butene), the curve(a) shows isotactic polymer and (b) shows syndiotactic one. Fig.7 illustrates the DSC diagram of poly(4-methyl-1-pentene), curve(a) shows isotactic polymer, and (b) shows syndisotactic one. Fig.8 illustrates the DSC diagram of poly(1-pentene), curve(a) shows the isotactic polymer and (b) shows syndiotactic one. Syndiotactic poly(1-butene) and poly(4-methyl-1-pentene) are crystalline at room temperature, though poly(1-pentene) fails to give crystalline polymer . The melting point of syndiotactic poly(1-butene) is lower than that of isotactic one. Syndiotactic poly(4-methyl-1-pentene) has 3 melting peaks, and the highest peak is lower than that of isotactic one.

Fig.9,10 and 11 show the the X-ray powder diffraction spectrum of poly(1-butene), poly(4-methyl-1-pentene), and poly(1-pentene), respectively. These results are consistent with that of DSC.

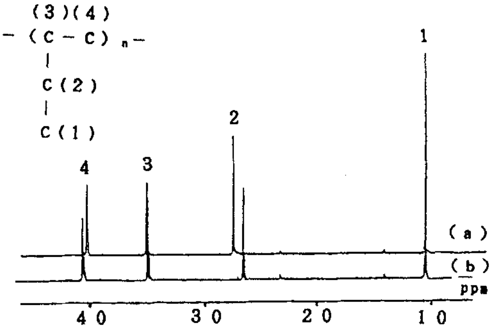

Fig.1 ^{13}C-NMR spectra of isotactic(a) and syndiotactic(b) poly(1-butene)

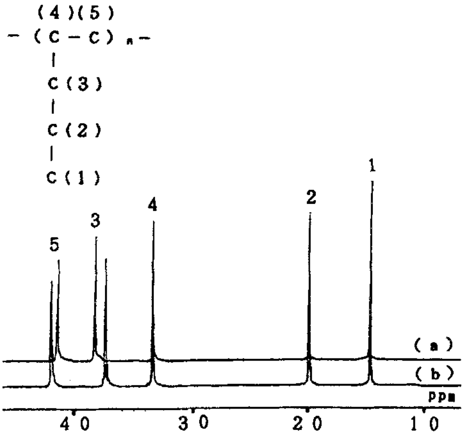

Fig.2 ^{13}C-NMR spectra of isotactic(a) and syndiotactic(b) poly(1-pentene)

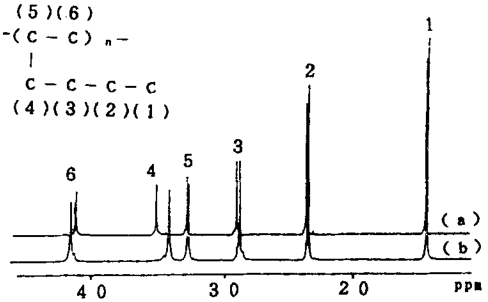

Fig.3 ^{13}C-NMR spectra of isotactic(a) and syndiotactic(b) poly(1-hexene)

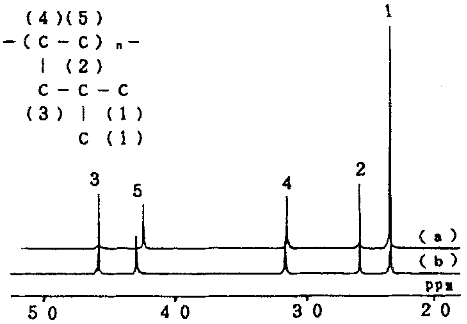

Fig.4 ^{13}C-NMR spectra of isotactic(a) and syndiotactic(b) poly(4-methyl-1-pentene)

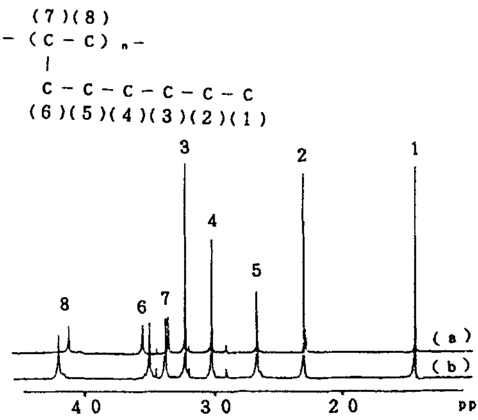

Fig.5 ^{13}C-NMR spectra of isotactic(a) and syndiotactic(b) poly(1-octene)

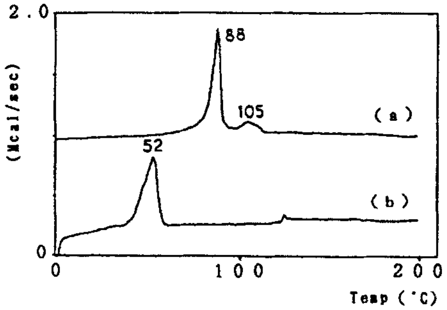

Fig.6 DSC diagram of isotactic(a) and syndiotactic(b) poly(1-butene)

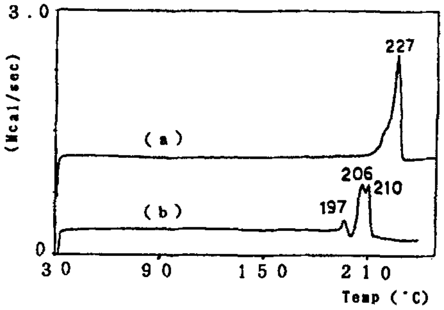

Fig.7 DSC diagram of isotactic(a) and syndiotactic(b) poly(4-methyl-1-pentene)

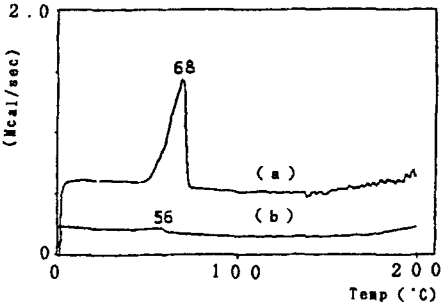

Fig.8 DSC diagram of isotactic(a) and syndiotactic(b) poly(1-pentene)

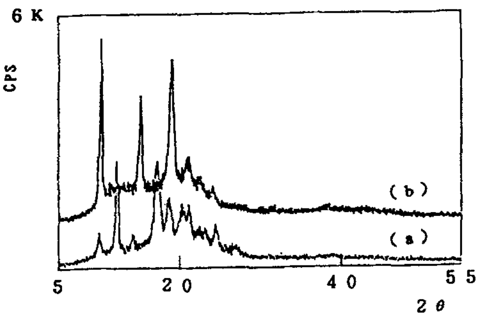

Fig.9 X-ray powder diffraction spectrum of isotactic(a) and syndiotactic(b) poly-(1-butene)

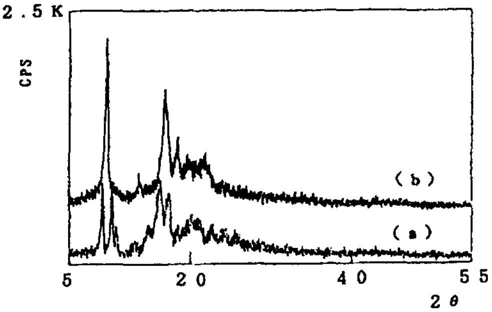

Fig.10 X-ray powder diffraction spectrum of isotactic(a) and syndiotactic(b) poly-(4-methyl-1-pentene)

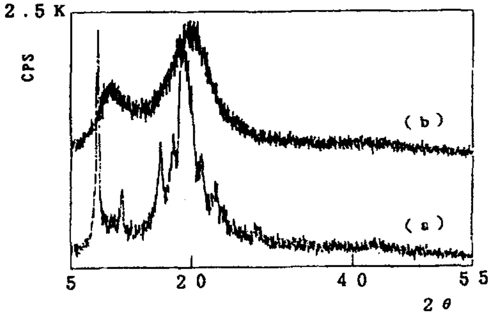

Fig.11 X-ray powder diffraction spectrum of isotactic(a) and syndiotactic(b) poly-(1-pentene)

References
1.J.A.Ewen, R.I.Jones, and A.Razavi, J.Am.Chem.Soc., 110, 6255(1988)
2.A.Zambelli, P.Ammendola, and A.Proto, Macromolecules, 22, 2126(1989)
3.F.R.W.P.Wild,M.Wasiucionek,G.Huttner, and H.H.Brintzinger, J.Organomet.Chem., 288, 63(1985)
4.T.Asakura, and Y.Doi, Macromolrcules, 16, 786(1983);
T.Asakura,K.Omaki,S-N.Zhu, and R.Chujo, Polym. J.,16, 717(1984);
S-N.Zhu,T.Asakura, and R.Chujo, Polym.J., 16, 895(1984)
5.T.Asakura,K.Yamamoto, and Y.Doi, Polym.Prepr.Jpn. 34, 2153(1985);
Y.Nishiyama, and T.Asakura, Polym.Prepr.Jpn., 36, 2408(1987);
K.Soga, and H.Yanagihara, Makromol.Chem., 189, 2839(1988)

Accepted December 28, 1990 S