Copolymerization of ethylene and propylene using catalysts based on titanium compounds modified with trimethylsilanol

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Copolymerization of ethylene and propylene was performed using a catalyst based on $TiCl_4$ modified with trimethylsilanol which is soluble in toluene (diluent used in the polymerization) even after cocatalyst addition. The copolymers were analysed and their structures were found to be very similar to those obtained with vanadium catalysts.

(Keywords: ethylene–propylene copolymer; chemical inversion; random copolymer)

Introduction

The physical properties of ethylene–propylene (EP) random copolymers are strongly dependent upon the monomer sequence distribution as well as on the number of chemically inverted propylene units (chemical inversion)[1,2]. In comparison to the common titanium catalysts, vanadium-based catalysts produce more random copolymers with much higher chemical inversion[3–6]. Thus, EP random copolymers are still produced mainly using vanadium catalyst, despite their low activity and stability.

The copolymers of ethylene with higher olefins are important commercial products, and industrial efforts have been directed towards finding novel and more efficient catalysts for the synthesis of desired copolymers. The copolymer composition and structure are assumed to depend on the catalyst characteristics, such as stereospecificity and homogeneity. We have recently found that $TiCl_4$ and $CpTiCl_3$ modified with trimethylsilanol (TML) combined with common trialkylaluminium are able to polymerize ethylene and propylene[7]. The catalyst was therefore employed in EP copolymerization in this work. Carrying out the olefin copolymerizations with these new homogeneous Ziegler–Natta catalysts based on $TiCl_4$ or $CpTiCl_3$ modified with TML, we have found that the copolymer structure is markedly dependent on the catalyst composition.

Experimental

Materials. Research grade ethylene, propylene and toluene (from Takachiho Chemical Co.) were further purified according to the usual procedures. Nitrogen of ultra-high purity (99.9989%, from Nippon Sarso Co.) was purified by passing through a 3 Å molecular sieve, P_2O_5 and $CaCl_2$ columns. $TiCl_4$ and $CpTiCl_3$ were purchased commercially and used without further purification.

EP copolymerization and analytical procedures. In a $100\,cm^3$ autoclave equipped with a magnetic stirrer were placed $20\,cm^3$ of toluene, 0.1 mmol of Ti in toluene solution and a given amount of $Si(CH_3)_3OH$ under nitrogen at room temperature. The mixture was then agitated for a certain time and a given amount of alkylaluminium was added. The reactor was cooled with liquid nitrogen, degassed *in vacuo*, and determined amounts of the purified monomers were introduced. The polymerization was conducted at 40°C for a certain time. The polymerization was terminated by adding dilute hydrochloric acid solution in methanol. The precipitated polymer was washed with methanol, followed by drying *in vacuo* at 60°C for 6 h. The ^{13}C n.m.r. spectrum of the copolymer was recorded at 120°C using a Jeol FX-100 spectrometer in the pulse Fourier transform mode. Sample solutions were made in 1,2,4-trichlorobenzene/d_6-benzene (9/1 v/v) up to 20 wt%. The d.s.c. curve was obtained with a Shimadzu Thermal Analyzer DT-30 at a heating rate of $10°C\,min^{-1}$. Molecular weight and molecular weight distribution of the polymer were determined by g.p.c. at 150°C by means of a Water Associates ALC/GPC using *o*-dichlorobenzene as solvent and a Shodex 80M column (AD-80M/S).

Results and discussion

As mentioned above, vanadium catalysts such as VCl_4 and $VOCl_3$, which produce highly random EP copolymers, are soluble in hydrocarbon solvents. On the other hand, titanium catalysts, such as $TiCl_3$ and $TiCl_3.\frac{1}{3}AlCl_3$, are solid and insoluble in those solvents, and have a low activity for random copolymerization. Seemingly, if a Ti^{3+} compound is soluble in hydrocarbon and/or halogenated hydrocarbon solvents, it would have an activity for random EP copolymerization higher than that of vanadium catalysts. Thus, we studied preparative methods for soluble Ti^{3+} compounds and their catalyst activities for EP copolymerization.

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The EP copolymerization was carried out using two catalyst systems: $TiCl_4$/TML and $CpTiCl_3$/TML combined with different kinds of cocatalyst. For comparison, copolymerization was also performed with unmodified catalysts ($TiCl_4$ or $CpTiCl_3$). The results are summarized in *Table 1*. The microstructures of copolymers are shown in *Table 2*. A large difference between the catalysts was observed in the $S_{\alpha\beta}$ peak, which is attributed to the chemical inversion of propylene units[3-6]. *Figures 1a* and *b* show the ^{13}C n.m.r. spectra of typical copolymers obtained with unmodified $TiCl_4$ and $TiCl_4$ modified with TML, respectively. The peak assignments were made according to the literature[8]. The product of monomer reactivity ratios ($r_E r_P$), shown in *Table 2*, indicates that the copolymers obtained with modified catalysts are statistically random copolymers whereas those obtained with the unmodified catalyst are poor in propylene units and have a somewhat blocky character.

The microstructures of copolymers, shown in *Table 2*, were analysed using ^{13}C n.m.r. spectra. The dyad sequence distributions were estimated using the following relationships[9]:

$$[PP] = I(S_{\alpha\alpha})$$

$$[EP] = I(S_{\alpha\gamma}) + I(S_{\alpha\delta})$$

$$[EE] = 1/2[I(S_{\beta\delta}) + I(S_{\delta\delta})] + 1/4 I(S_{\gamma\delta})$$

$$[P] = [PP] + 1/2[EP]$$

$$[E] = [EE] + 1/2[EP]$$

where $I(S_{xy})$ is the peak intensity of carbon[8].

By using the monomer sequence distributions in the copolymers, the product of the reactivity ratios ($r_E r_P$) and

Table 1 Results of ethylene–propylene copolymerization[a]

Run no.	Catalyst system	Type of cocatalyst	Propylene in feed (mol%)	Yield (g)	T_m[b] (°C)	$10^{-3} \times \bar{M}_n$[c]	$10^{-4} \times \bar{M}_w$[c]	$\bar{M}_w/\bar{M}_n$[c]
1	$TiCl_4$	$Al(i\text{-}Bu)_3$	50	0.89	120	–	–	–
2	$TiCl_4$	$Al(i\text{-}Bu)_3$	80	0.45	117	–	–	–
3	$TiCl_4$	MAO	50	0.45	119	–	–	–
4	$TiCl_4$	MAO	80	0.20	115	–	–	–
5	$TiCl_4$/TML[d]	$Al(i\text{-}Bu)_3$	50	0.86	119	–	–	–
6	$TiCl_4$/TML[d]	$Al(i\text{-}Bu)_3$	80	0.38	118	–	–	–
7	$TiCl_4$/TML[d]	$AlClEt_2$	50	0.80	120	–	–	–
8	$TiCl_4$/TML[d]	MAO	50	0.90	112	16.8	25.0	14.9
9	$TiCl_4$/TML[d]	MAO	80	0.43	–[f]	8.7	7.3	8.4
10	$CpTiCl_3$	$Al(i\text{-}Bu)_3$	50	0.04	118	–	–	–
11	$CpTiCl_3$	$Al(i\text{-}Bu)_3$	80	0.03	116	–	–	–
12	$CpTiCl_3$/TML[e]	$Al(i\text{-}Bu)_3$	50	0.73	118	–	–	–
13	$CpTiCl_3$/TML[e]	$Al(i\text{-}Bu)_3$	80	0.10	116	–	–	–

[a] Copolymerization of ethylene and propylene was conducted at 40°C in a stainless steel reactor for 15 min with 0.1 mmol of Ti and Al/Ti = 10 in toluene (20 ml)

[b] T_m, melting temperature obtained by d.s.c.

[c] Average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) and molecular weight distribution ($\bar{M}_w/\bar{M}_n$) obtained by g.p.c.

[d] $TiCl_4$/TML = 2

[e] $CpTiCl_3$/TML = 10

[f] No melting temperature was observed

TML, trimethylsilanol; MAO, methylaluminoxane

Table 2 Microstructure of copolymers[a]

Run no.	Catalyst system	Type of cocatalyst	Propylene in feed (mol%)	Dyad sequence distribution[b] [EE]	[EP]	[PP]	Monomer content[b] [E]	[P]	$r_E r_P$	ρ	$[S_{\alpha\beta}]/[S_{\beta\beta}]$
1	$TiCl_4$	MAO	80	0.78	0.21	0.01	0.88	0.12	0.79	0.98	0.78
2	$TiCl_4$	$Al(i\text{-}Bu)_3$	80	0.59	0.37	0.04	0.78	0.22	0.60	0.93	0.35
3	$TiCl_4$/TML[c]	MAO	50	0.70	0.29	0.01	0.84	0.16	0.39	0.91	0.85
4	$TiCl_4$/TML[c]	MAO	80	0.45	0.43	0.12	0.67	0.33	1.14	1.03	0.57
5	$TiCl_4$/TML[c]	$Al(i\text{-}Bu)_3$	80	0.63	0.34	0.03	0.80	0.20	0.64	0.94	0.30
6	$CpTiCl_3$/TML[d]	$Al(i\text{-}Bu)_3$	50	0.88	0.11	0.01	0.94	0.06	0.95	0.94	–

[a] Copolymerization conditions were the same as in *Table 1*

[b] Estimated from ^{13}C n.m.r. spectra of copolymers

[c] $TiCl_4$/TML = 2

[d] $CpTiCl_3$/TML = 10

TML, trimethylsilanol; MAO, methylaluminoxane

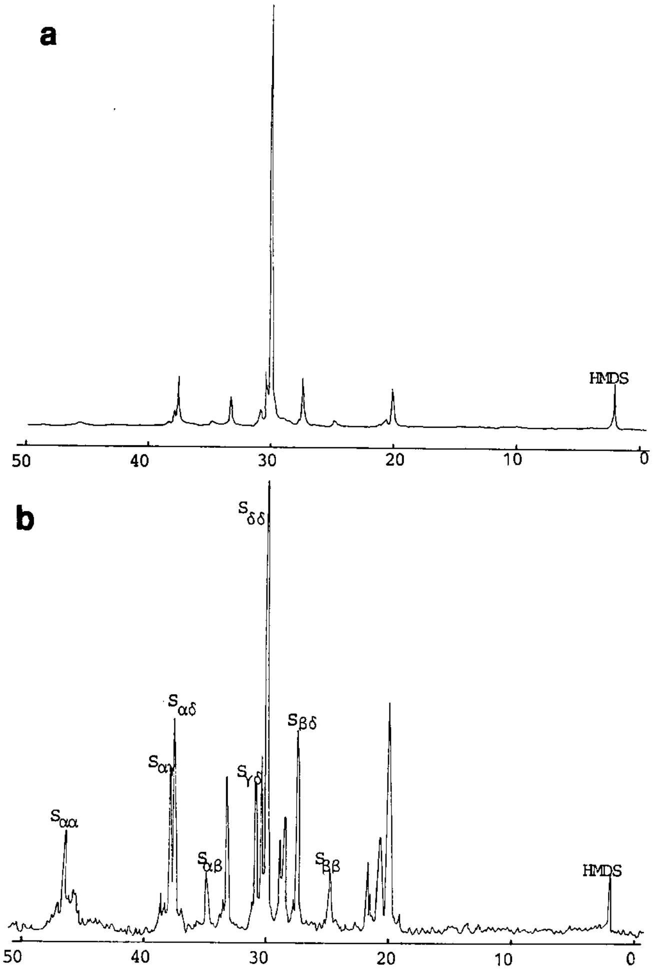

Figure 1 ^{13}C n.m.r. spectra of ethylene–propylene copolymers: (a) obtained by unmodified catalyst ($TiCl_4$) using methylaluminoxane as cocatalyst at Al/Ti = 10 (run no. 4 in *Table 1*); (b) obtained by $TiCl_4$ modified with TML using methylaluminoxane as cocatalyst at Al/Ti = 10 (run no. 9 in *Table 1*). Chemical shift assignments (in ppm) from hexamethyldisilane (HMDS)

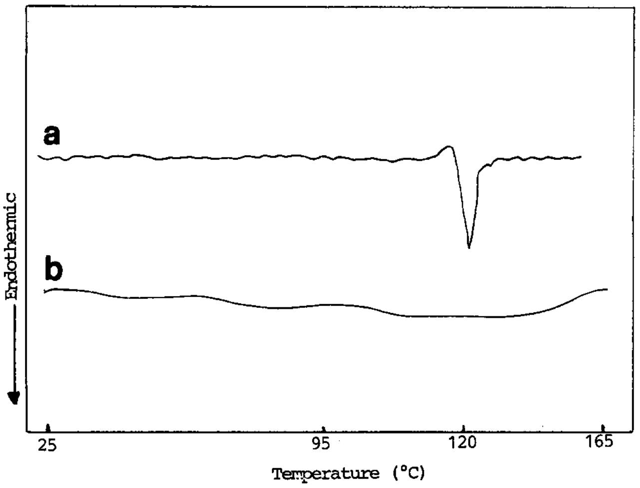

Figure 2 D.s.c. curves of ethylene–propylene copolymers: (a) obtained with unmodified catalyst ($TiCl_4$) using methylaluminoxane as cocatalyst at Al/Ti = 10 (run no. 4 in *Table 1*); (b) obtained with $TiCl_4$ modified catalyst using methylaluminoxane as cocatalyst at Al/Ti = 10 (run no. 9 in *Table 1*)

the persistence ratios $(\rho)^{10}$ were estimated according to the following equations:

$$r_E r_P = \frac{4[EE][PP]}{[EP]^2}$$

$$\rho = \frac{2[P][E]}{[EP]}$$

where [EE], [EP], [PP], [E] and [P] denote dyad sequence distributions and monomer contents in the copolymers. The persistence ratio is defined as the ratio of the actual mean length of closed ethylene (or propylene) sequence to the mean length of the Bernoullian process with the same ethylene (or propylene) content. Although some of the copolymers contained appreciable amounts of chemical inversion, for convenience $r_E r_P$ and ρ were estimated without considering it.

The sequence distribution can be considered to be more blocky than that anticipated by Bernoullian statistics when $r_E r_P$ or ρ are larger than unity. On the other hand, when they are less than unity the sequence distribution can be considered to be more alternating.

The d.s.c. curves of typical copolymers obtained with unmodified catalysts display a clear peak at approximately 120°C, corresponding to the melting temperature of a long sequence of ethylene units. Some copolymers obtained with modified catalysts did not present any melting peak, indicating a random distribution of ethylene and propylene units in the polymer chain. Some d.s.c. curves are shown in *Figure 2*.

In conclusion, it was found that the soluble $TiCl_4$ and $CpTiCl_3$ modified with $Si(CH_3)_3OH$ (TML) are able to produce EP copolymers with structures very similar to those produced with vanadium catalysts. A more detailed study is now being carried out and the precise results will be reported in another paper.

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