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Effect of phenyltriethoxysilane as external donor on the microstructure of ethylene-propylene copolymers*

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SUMMARY

The effect of an external electron donor, namely, phenyltriethoxysilane (PES) on the compositional heterogeneity and the microstructure of ethylene-propylene copolymers prepared using a titanium-magnesium catalyst has been investigated. Addition of PES causes an increase in the average sequence length of ethylene and propylene. The products of reactivity ratios of ethylene and propylene indicate that the copolymer is blocky in nature. The external donor produces a propylene sequence in the copolymer which is richer in mmmm pentads.

INTRODUCTION

High efficiency olefin polymerization catalysts based on titanium-magnesium compounds generally consist of an internal electron donor and an external electron donor(1). The internal electron donor (typically ethyl benzoate, dibutyl phthalate, etc.) are added during the catalyst preparation stage and are presumed to stabilize the high energy surfaces of the magnesium chloride support generated during the process of milling. The external electron donor, generally added alongwith the organoaluminum compound, is believed to improve the stereospecificity of the catalyst without adversely affecting its activity. The complex role of internal and external donor on the activity, stereospecificity and molecular weight distribution of the polymers has been extensively discussed in the literature(2).

External electron donors are generally used in the polymerization of α-olefins to improve isotacticity of the homopolymer. However, their role in the copolymerization of ethylene with higher α-olefins has been far less studied. The role of ethyl benzoate as an external donor on the composition, reactivity ratios and microstructure of ethylene-propylene copolymers has been reported(3). Based on a comparison of observed and calculated triad sequence distribuution, it was concluded that ethyl benzoate blocks active Ti(III) species having two chlorine ligand vacancies. Copolymerization was proposed to occur on a Ti(III) species having one chlorine ligand vacancy.

This paper reports the results of our studies on the effect of an external donor namely, phenyltriethoxysilane (PES), on the compositional heterogeneity and microstructure of ethylene-propylene copolymers prepared using a titanium-magnesium catalyst.

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EXPERIMENTAL

Preparation of Catalyst : Titanium-magnesium catalyst was prepared by reacting a complex of magnesium chloride and 2-ethylhexanol with titanium tetrachloride followed by introduction of dibutyl phthalate. The catalyst contained 2.4% Ti by weight.

Copolymerization : Ethylene and propylene were copolymerized in a 0.7 L reactor in hexane medium at 70°C in the presence and absence of PES as an external electron donor. The pressure and composition of the reaction medium were held constant by continuous introduction of a mixture of gaseous monomers. The copolymers were fractionated by sequential extraction in refluxing diethylether, pentane, hexane and heptane.

Analysis : Carbon 13 NMR spectra were recorded at 120°C on a Bruker MSL 300 model NMR spectrometer operating at 75.5 MHz for ^{13}C nuclei. The solutions for analysis were prepared by dissolving about 150 mg of the copolymer in about 2 mL of o-dichlorobenzene containing about 15% by volume of deuterated benzene for internal lock. The spectra were obtained under conditions permitting quantitative analysis by allowing pulse delay of 10 seconds, and analyzed according to the method of Randall(4).

RESULTS AND DISCUSSION

The copolymer samples used in the study are described in Table 1. Conditions for polymerization with and without PES were adjusted to obtain a copolymer of identical copolymer composition. Copolymer samples 1 and 2 were sequentially extracted in boiling ether, pentane, hexane and heptane. The weight fraction soluble in each of the solvent and the content of propylene contained in the fraction is shown in Table 2. It is observed that the addition of PES to $AlEt_3$ causes a marked decrease in the ether soluble fraction and a concomitant increase in the heptane soluble and insoluble fractions (Table 2). These results indicate that PES predominantly blocks those active sites which produce copolymers with high propylene content and presumably low degrees of crystallinity. It is evident from the extraction data that both copolymers are heterogeneous in composition. This indicates that both catalysts have broad distribution of active sites with respect to copolymerization reactivity.

Table 1 : Ethylene-Propylene Copolymers Used in the Study[a]

Sample No.	Pressure atm	Time min	Yield kg/g Ti	$[C_2H_4]/C_3H_6]$ in hexane	Mole % C_3H_6 in copolymer
1[b]	4	60	63	0.27	41.4
2[c]	2	100	70	0.18	42.4

a Polymerization was conducted with triethylaluminum as cocatalyst at 70°C

b Phenyltriethoxysilane was used as the external donor. TEAL/PES mole ratio = 4

c No external donor was used

Table 2 : Solvent Extraction Data of Ethylene-Propylene Copolymers

Sample Number	1		2	
Copolymer fraction	Amount Wt %	Propylene content[1], Mol. %	Amount Wt %	Propylene content, Mol. %
Ether	13.2	56.0	32.6	45.5
Pentane	13.7	52.0	15.4	52
Hexane	9.3	50.3	13.2	39
Heptane	32.0	37.0	16.6	38
Residue	31.8	28.0	22	23

1 Determined by IR spectroscopy

The carbon 13 NMR spectra of copolymers 1 and 2 are shown in Figures 1 and 2. The results of analysis of the spectra according to the method of Randall are shown in Table 3. Sequence numbers were determined independently from ethylene and propylene centered triads and were found to be in close agreement indicating excellent internal consistency of the quantitative data generated from the spectrum. It is clear from the results that the addition of PES increases the average sequence lengths of ethylene and propylene (n_E and n_p) as compared to a catalyst containing no external donor, for both the whole polymer and its fraction soluble in ether or pentane. The insoluble fraction of copolymer 1 is richer in ethylene and has a higher n_E.

The reactivity ratios of ethylene and propylene (r_E and r_p) for the whole polymer and fractions with and without PES are also shown in Table 3. The product of $r_E.r_p$ is greater than one in most cases indicating the blocky nature of the copolymer. The values of $r_E.r_p$ for copolymer 1, prepared by using a catalyst containing PES is greater than copolymer 2, prepared by using a catalyst without PES.

The triad sequences observed experimentally are compared with those calculated based on first order Markovian propagation. The agreement is far from satisfactory indicating multiplicity of active sites even in the catalyst modified by PES. Soga and coworkers reported good agreement between observed and calculated triad distribution for EP copolymers prepared using a Mg-Ti catalyst and ethylbenzoate as an external donor(3a).

The tacticity of the propylene sequences for copolymers 1 and 2 and one of its fractions is shown in Table 4. The results confirm the heterogeneous nature of copolymers. The use of an external electron donor produces a propylene sequence in the copolymer which is richer in mmmm pentads. However, the % mmmm pentad is lower in the soluble fraction compared to the whole polymer. Thus, even in copolymerization, PES causes an enhancement of isospecific propagation of the propylene sequences.

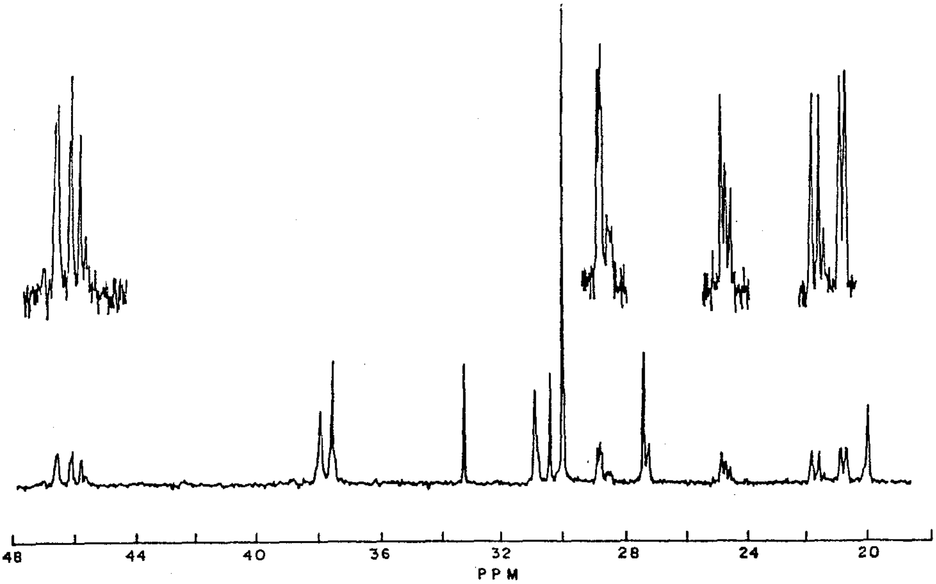

FIG.1 : CARBON-13 NMR SPECTRUM OF E-P COPOLYMER 1 PREPARED IN THE PRESENCE OF PES

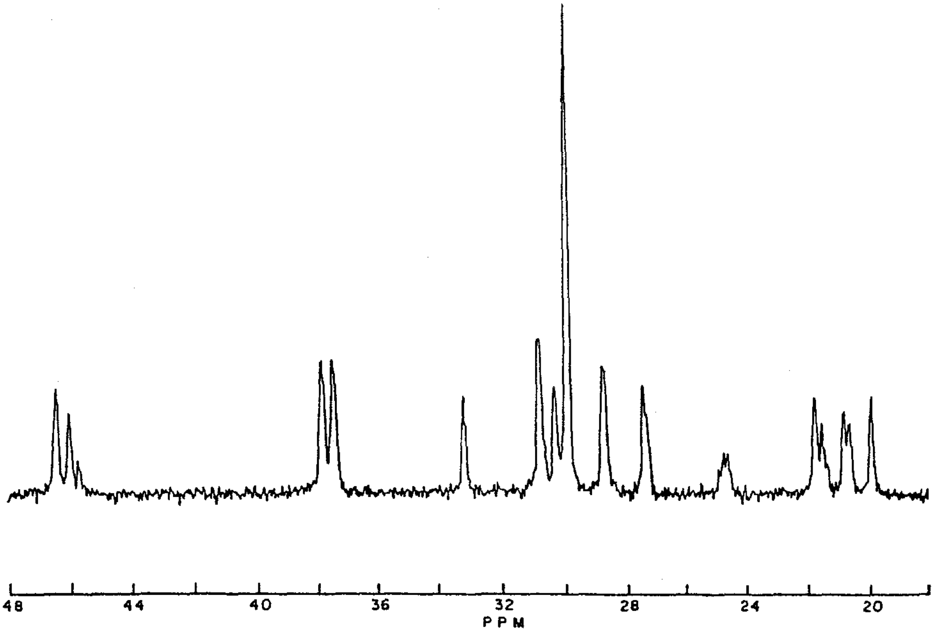

FIG.2 : CARBON-13 NMR SPECTRUM OF E-P COPOLYMER 2 PREPARED IN THE ABSENCE OF PES

Table 3 : Results of ^{13}C Analysis of E-P Copolymers

,Sample No.	Composition		Diad & Triad Sequence Distribution(a)									Average seq. length		Sequence Nos. from triads		r_E	r_P	Reac. Ratio $r_E.r_P$
	%E	%P	EE	PP	EP	EEE	EEP	PEP	EPE	EPP	PPP	E	P	E-centered	P-centered			
1	57.63	42.36	39.43	24.16	36.40	29.8 (22.0)	19.3 (24.0)	8.6 (6.6)	5.6 (7.3)	25.2 (22.6)	11.6 (17.5)	3.17	2.33	18.200	18.200	8.15	0.353	2.88
C_5 soluble fraction	44.65	55.35	25.44	36.15	38.41	18.9 (14.5)	13.1 (21.9)	12.7 (8.3)	11.4 (6.7)	15.5 (25.1)	28.4 (23.6)	2.33	2.88	19.205	19.205	4.98	0.501	2.50
Residue	63.60	36.40	49.80	22.65	27.60	44.4 (38.9)	10.8 (21.6)	8.4 (3.0)	8.4 (5.2)	10.7 (17.1)	17.3 (14.1)	4.61	2.65	13.800	13.750	13.57	0.437	5.92
2	58.59	41.41	38.16	20.98	40.87	27.2 (24.2)	22.0 (26.6)	9.4 (7.1)	11.4 (10.1)	18.1 (20.7	11.9 (10.6)	2.87	2.03	20.435	20.435	10.37	0.185	1.92
Ether soluble fraction	49.62	50.38	23.45	24.22	52.34	8.4 (11.1)	30.1 (24.7)	11.1 (13.8)	12.6 (13.6)	27.1 (25.1)	10.7 (11.7)	1.90	1.93	26.170	26.165	3.37	0.246	0.83

(a) Triad distribution calculated according to Markovian distribution ( )

Table 4: Microtacticity of Propylene Sequences in Ethylene-Propylene Copolymers

	Sample Number			
Pentad	1	1a	2	2a
mmmm	22	17	13	14
mmmr	21	14	10	12
mmr	21	5	3	3
mmrr	0	0	0	
mrmm+rmrr	19	23	18	24
mrmr	16	16	16	12
rrrr	0	0	0	0
rrrm	0	0	0	3
mrrm	22	25	40	32

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REFERENCES

1. Barbe PC, Cecchin G, Noristi L (1986) Adv. Polym. Sci. 81 : 1
2. For some representative discussion on the subject, see
   a) Sergeev SA, Bukatov GD, Zakharov VA, Moroz EM (1983) Makromol. Chem. 184 : 2421.
   b) Sergeev SA, Bukatov GD, Zakharov VA (1984) Makromol. Chem. 185 : 2377.
   c) Kissin YV, Sivak AJ (1984) J. Polym. Sci. Polymer Chem. Ed. 22 : 3747.
   d) Pino P, Rotzinger B, Achenbach EV (1985) Makromol. Chem. Suppl. 13 : 105.
   e) Soga K, Shiono T, Doi Y (1988) Makromol. Chem. 189 : 1531.
   f) Seppala JV, Harkonen M, Luciani L (1989) Makromol. Chem. 190 : 2535.
3. a) Soga K, Shiono T, Doi Y (1983), Polym. Bull., 10 : 168.
   b) Kashiwa N, Mizuno A, Minami S (1984) Polym. Bull. 12 : 105.
   c) Wu Q, Yang N-L, Lin S (1990) Makromol. Chem. 191 : 89.
4. Randall JC (1989), J. Makromol. Sci., Rev. Makromol. Chem. Phys., C29 : 201.

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