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^{13}C NMR Analysis of Propene–Butene Copolymer. Steric Structure of Chain End Groups and Inhomogeneity of Isotactic Sites

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ABSTRACT: Propene and 1-butene have been copolymerized in the presence of the catalytic system $TiCl_3$/$Al(^{13}CH_2CH_3)_3$. The results of ^{13}C NMR analysis of chain end groups in isotactic fractions of different composition provide stereochemical evidences of the inhomogeneity of the isotactic sites.

In a recent paper,[1] we have reported the results of fractionation and of ^{13}C NMR analysis of a series of propene–butene copolymers. A broad compositional distribution in the fractions of copolymer samples obtained with a large range of feeding mixture compositions in the presence of $TiCl_3/Al(CH_2CH_3)_3$ as catalyst has been observed. This compositional distribution has also been found in the isotactic part of copolymers. Indeed, in each sample more than one essentially isotactic fraction characterized by decreasing 1-butene content, regardless of the feeding mixture composition adopted, has been isolated by fractionation. We interpreted the results in terms of the presence, on the catalyst surface, of different kinds of isotactic sites that show a partial selectivity toward the comonomers.

In an attempt to correlate the observed copolymer dispersity to structural characteristics of the isotactic sites, in this paper we have studied the configurational structure of ^{13}C-enriched chain end groups.

Experimental Section

Reagents. δ-$TiCl_3$ (HRA Stauffer) was purified by extraction with boiling toluene. $Al(^{13}CH_2CH_3)_3$ was prepared (starting from 90% ^{13}C-enriched $Ba^{13}CO_3$) by reaction of CH_3-$^{13}CH_2Li$ and $AlCl_3$.

Copolymerization. Copolymerization apparatus and reaction conditions have already been described.[1] To 100 cm^3 of toluene, containing 3 mmol of suspended $TiCl_3$ and saturated at 15 °C with the propene–butene mixture, were added 3 mmol of $Al(^{13}CH_2CH_3)_3$ (90% ^{13}C enriched). During the polymerization, a constant flow of gas mixture was maintained through the reaction medium by means of two computer-controlled mass flowmeters, coupled with flow control valves (MKS Intruments, Inc.). The rate of flow was ≈15 times higher than gas consumption. After 3 h the copolymerization was stopped with methanol and the copolymer was precipitated with acidified methanol, collected, and dried under vacuum (3.4 g).

Copolymer Fractionation. The propene–1-butene copolymer was fractionated in Kumagawa extractors with diethyl ether, *n*-hexane, *n*-heptane, and *n*-octane. Time of fractionation was 24 h.

^{13}C NMR Analysis. The ^{13}C NMR analysis of copolymer fractions was carried out at 125 °C on a AM-270 Bruker spectrometer operating at 67.89 MHz in the PFT mode. The copolymer samples were dissolved in 1,2,4-trichlorobenzene containing ≈1% of hexamethyldisiloxane (HMDS) and $C_2D_2Cl_4$ as internal standards. Copolymer composition and isotactic regularity were determined from ^{13}C NMR spectra, according to refs 2 and 3.

Molecular Weight Determination. Average molecular weights of propene–butene copolymer fractions were determined by GPC with a Waters 150-C apparatus at 135 °C using 1,2-dichlorobenzene as solvent.

Results

A propene–butene copolymer sample was prepared in the presence of δ-$TiCl_3/Al(^{13}CH_2CH_3)_3$ using a 3/1 propene/butene feeding mixture. The propene/butene ratio was chosen on the basis of the previously studied copolymers, in order to obtain a significant fractionation of the isotactic part. The copolymer was fractionated

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Table I
Chain and First-Step Isotactic Regularity of Fractionated Propene–Butene Copolymer

Fr[a]	wt %	% B[b]	[mm][c]	I_e/I_t[d]	$\bar{M}_w \times 10^{-3}$[e]
EE	36	19.9	nd	nd	nd
E6	16	17.5	0.58	1.6	400
E7	10	14.5	0.88	2.9	180
E8	11	14.0	0.94	4.6	960
R8	26	9.5	0.97	>8	640

[a] Fr = copolymer fractions: EE = diethyl ether soluble; E6 = diethyl ether insoluble–hexane soluble; E7 = hexane insoluble–heptane soluble; E8 = heptane insoluble–octane soluble; R8 = octane insoluble. [b] %B = mol % of butene units in the copolymer fraction, determined by ^{13}C NMR. [c] Molar fraction of isotactic triads determined by ^{13}C NMR.[14] [d] I_e/I_t = isotacticity of the first polymerization step. See text. [e] Determined by GPC.

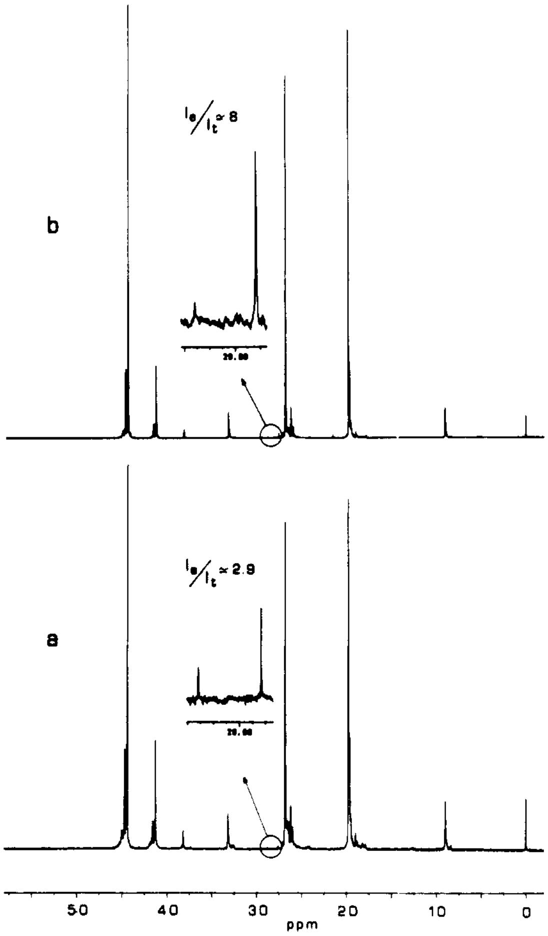
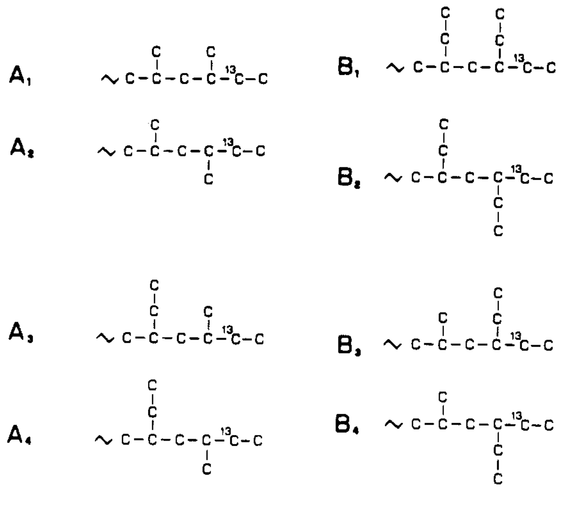


Figure 1. ^{13}C NMR spectra of propene–butene fractions: hexane insoluble–heptane soluble (a) and octane insoluble (b). Chemical shifts are in ppm downfield from hexamethyldisiloxane (HMDS).

with boiling diethyl ether, n-hexane, n-heptane, and n-octane.[1] Table I reports the fractionation results together with the fractional composition from the ^{13}C NMR analysis. Figure 1 shows the ^{13}C NMR spectra of two fractions, n-hexane insoluble–n-heptane soluble (a) and n-octane insoluble (b). The carbon resonances of inner monomeric units are assigned by comparison with the previously reported ^{13}C NMR analysis of propene–butene copolymers[2-4] and allow the quantitative evaluation of isotacticity and of comonomer composition, as previously shown by Randall.[2] Three smaller resonances at 24.1, 27.6, and 28.8 ppm are well detectable. Those at 27.6 and 28.8 ppm are shown in the expanded regions of spectra. These resonances, absent in copolymer samples prepared with naturally ^{13}C-enriched aluminum alkyl cocatalyst,[1] are due to ^{13}C-enriched methylene carbons of the copolymer end groups in different stereochemical arrangements.[5,6]

Chart I



In Chart I all the possible steric arrangements of the chain end groups of a propene–butene copolymer obtained with a 1–2 regiospecific isotactic catalyst are shown. Only the first and second inserted comonomer units are considered. Unfortunately the resonances of ^{13}C-enriched methylenes of chain end groups containing 1-butene as first monomer unit (Chart I, group B), expected between 24.2 and 24.7 ppm,[7] and that of groups A_3 and A_4 are too small to allow quantitative evaluations. The small resonance, detected at 24.1 ppm, was assigned to the enriched methylene of group B_3, by comparison with the resonance of group B_1 previously identified at 24.2 ppm in a polybutene homopolymer.[7,8] Considering the butene content of the fractions and assuming that in the copolymer fractions the overall comonomer composition is not different from that of the initiation steps, one would expect the enriched resonances corresponding to A_4, B_1, B_2, and B_4 steric arrangements to have very low intensity.[9] Therefore, in our spectra only the two enriched methylene resonances of chain end groups A_1 and A_2 having propene as first and second monomer units, detected at 27.6 and 28.8 ppm, are quantitatively significant. Despite this limited NMR analysis of chain end groups in the propene–butene copolymer under consideration, the detected ^{13}C-enriched resonances of copolymer chains having propene as first and second inserted units allow some important remarks about the inhomogeneity of isotactic active sites.

Discussion and Conclusions

As previously reported,[5,10] the enriched methylene resonance of end groups at higher field (27.6 ppm) is related to the e (erythro or isotactic) steric placement of the first propene inserted unit, with respect to the second one, while the resonance at 28.8 is related to the t (threo or syndiotactic) steric relationship between the same units (Figure 2). As a consequence, the intensity ratio, I_e/I_t, between the enriched resonances represents the isotactic regularity of the first polymerization step. Inspection of the spectra of Figure 1 and of the data of Table I shows the following: (i) the presence of more than one essentially isotactic fraction; (ii) a significant decrease of butene content in these fractions, from 14.5% in E7 to 9.5% in R8; (iii) a very large increase of isotactic regularity in the first polymerization step. Indeed I_e/I_t varies from 2.9 in E7 (corresponding to a first-step isotacticity of about 75%) to 8 in R8 (isotacticity of about 89%).

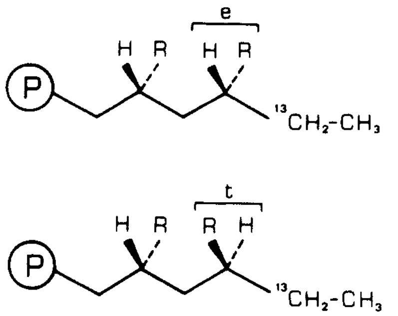


Figure 2. Stereochemical placement of e (erythro or isotactic) and t (threo or syndiotactic) first added monomeric unit in propene–butene copolymer chains. R = CH_3 or CH_2CH_3.

It was previously shown[5,11–13] that the I_e/I_t value is reproducible for a given catalytic system under the same experimental conditions but varies significantly with even small changes in the environment of the active site. The different I_e/I_t value in isotactic fractions of the propene–butene copolymer therefore indicates that active sites responsible for growing the isotactic copolymer chains are inhomogeneous. Indeed, while the overall isotacticity of copolymer chains increases by 9% from E7 to R8, the isotacticity of the first propene unit added increases by about 14% in the same fractions. This fact has to be related to different steric features of active sites. It is important to stress that the I_e/I_t ratio previously found in highly isotactic polypropene samples obtained with the same catalyst did not exceed the value of 3.3.[13] This means that the butene units present in different amount in the copolymer chains have changed their solubility features and allowed a further fractionation of the isotactic part of the sample. As a consequence, some significant isotactic fractions with different I_e/I_t medalues were collected. So in isotactic poly-α-olefins obtained in the presence of Ziegler–Natta heterogeneous catalysts, the I_e/I_t ratio reasonably represents the average value of the first-step stereoregulating capability of various active sites producing polymer chains of close overall isotacticity.

In the propene–butene copolymer under consideration, the decreasing butene content (by 5% from E7 to R8) that accompanies the increasing overall isotacticity and the more evident increasing first-step isotacticity is a further element showing that the relative selectivity of isotactic sites toward the comonomers derives from their dispersity. Indeed, the addition on the Mt–polymer bond of bulkier butene units is more difficult in active sites characterized by high isotactic control on propene addition. This can also be the reason why it is not possible to detect A_3, expected to have intensity comparable to B_3. This fact is in keeping with previously reported results of ^{13}C NMR analysis of chain end groups of linear poly-α-olefins prepared with δ-$TiCl_3$-based catalysts.[7] It was shown that, considering high isotactic homopolymer fractions obtained in the presence of $Al(CH_2CH_3)_3$, the addition of the first 1-butene or 1-pentene unit on the Ti–CH_2CH_3 bond is characterized by a lower isotactic regularity with respect to the addition of propene on the same Ti–alkyl bond. This means that the steric demand of bulkier monomers is more easily satisfied on more "open" isotactic sites, i.e., on sites probably showing a relatively large freedom of orientation of the ethyl group bonded to the Ti (Figure 3). As a matter of fact, a very high isotactic control on first propene addition has been previously observed with catalysts containing bulkier halogen ligands ($I_e/I_t > 8$ with the system $TiI_3/Al(CH_2CH_3)_3$).[12] The stronger nonbonded interactions among the Ti ligands (halogen atoms and alkyl group) of active sites in this system effect a more constrained orientation of the ethyl group (i.e., of the two first carbon atoms of growing polymer chain).

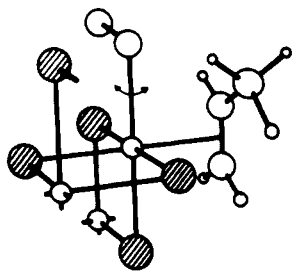


Figure 3. Model drawing of active site with a propene monomer complexed on Ti. Local structural conditions depending on the high disorder of δ-$TiCl_3$ can produce, also in isotactic sites, a relatively free orientation of ethyl group and consequently a partial comonomer selectivity.

The present results, obtained in the presence of $TiCl_3$ free from $AlCl_3$, seem to agree with a model of continuous distribution of isotactic sites characterized by very small differences in structure or environment. It is worthwhile to note that Kakugo and co-workers have recently observed, by means of a careful column fractionation of isotactic polypropene obtained with $TiCl_3 \cdot {}^1/_3AlCl_3/Al(CH_2CH_3)_2Cl$, the presence of two well-differentiated types of essentially isotactic sites.[15] On the other hand, the same authors did not observe any significant dispersion of 1-butene units in fractionated propene–butene copolymer samples with the same catalyst. However, this fact was probably due to the extremely low content of 1-butene units in the copolymer (0.2 mol %).[16]

Concerning the origin of the observed dispersity of isotactic sites, it seems reasonable to refer to the structural features of δ-$TiCl_3$. As it is well-known, the activation by grinding leads to extensive crystal fractures and to sliding between Cl–Ti–Cl layers.[17] As a consequence, various local structures can be formed on the $TiCl_3$ surface, different from those we can suppose by a simple rigid fracture. Of course, the possibility of different types of complexes with Al–alkyls in the proximity of active site cannot be ruled out. In conclusion, even in absence of a direct determination of active sites structure, the stereochemical ^{13}C NMR analysis of poly-α-olefins chain end groups provides strong evidences of isotactic site inhomogeneity. The comonomer dispersion in the propene–butene copolymer fractions is directly related to significant differences in steric control on first monomer addition.

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Registry No. $TiCl_3$, 7705-07-9; $Al(CH_2CH_3)_3$, 97-93-8; (propene)(1-butene) (copolymer), 29160-13-2.