

Ethylene-Propene Copolymerization. Monomer Reactivity and Reaction Mechanism

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Received September 19, 1984

ABSTRACT: The relative reactivity of ethylene and propene in the first insertion steps of Ziegler-Natta copolymerization has been evaluated by analyzing via ¹³C NMR the ¹³C-enriched end groups of copolymer fractions of different stereoregularity. Some possible inferences concerning reaction mechanism are reported.

In a previous paper² we have shown that by copolymerization of ethylene and propene in the presence of the heterogeneous catalytic system δ -TiCl₃-Al(¹³CH₃)₃-Zn(¹³CH₃)₂ it is possible to determine the relative reactivity of ethylene and propene for the insertion steps reported in Scheme I. The relative reactivities $\rho_1 = k_1/k_2$, $\rho_2 = k_{11}/k_{12}$, $\rho_3 = k_{21}/k_{22}$, and $\rho_4 = k_{221}/k_{222}$ can be evaluated by means of the equations

$$\rho_1 = \frac{1}{F} \frac{[a] + [b]}{[c] + [d] + [e] + [f] + [g] + [h] + [i]} = \frac{1}{F} \frac{I_{11.9_5} + I_{12.3_4}}{I_{20.4-21.9}} \quad (1)$$

$$\rho_2 = \frac{1}{F} \frac{[a]}{[b]} = \frac{I_{11.9_5}}{I_{12.3_4}} \quad (2)$$

$$\rho_3 = \frac{1}{F} \frac{[c]}{[d] + [e] + [f] + [g] + [h] + [i]} = \frac{I_{20.4-20.9} - I_{21.3-21.9}}{2I_{21.3-21.9}} \quad (3)$$

$$\rho_4 = \frac{1}{F} \frac{[d] + [e]}{[f] + [g] + [h] + [i]} \approx \frac{1}{F} \frac{I_{21.6}}{I_{21.7_6}} \quad (4)$$

where the square brackets stand for the molar amount of the a, b, c, etc., end groups reported in Scheme I; I 's are the intensities of the nuclear magnetic resonances (see Figure 1) of the enriched methyls having chemical shift δ_i ; $I_{\delta_j-\delta_x}$ is the sum of the intensities of the resonances ranging between δ_j and δ_x , and F is the C₂H₄/C₃H₆ molar ratio in the comonomer solution used for the copolymerization.

These equations and the assignment of the ¹³C resonances have been justified in ref 2 and will not be discussed further.

The ρ 's here mentioned show the influence of the structure of the alkyl groups (methyl, *n*-propyl, isobutyl, 2,4-dimethylpentyl) bonded to the metal of the active sites on the relative reactivity of C₂H₄ and C₃H₆ in the insertion.

Of course, the values of the ρ 's are related to the reaction mechanism and to the structure of the active sites.^{3,4} This point was not developed at all in ref 2 because the catalytic system δ -TiCl₃-Al(CH₃)₃-Zn(CH₃)₂, when used for propene homopolymerization, gives rise to a mixture of macromolecules of different stereochemical structure, i.e., highly isotactic, stereoirregular, and stereoblock.⁵

Such behavior is diagnostic for the presence of at least two types of active sites of different structure and, possibly, acting through different reaction mechanisms.⁵ At least in principle, one could guess that the relative reactivity of ethylene and propene could be different on active sites of different structure (i.e., the stereospecific and the nonstereospecific ones). In that case the observed values of the ρ 's should be averaged for the copolymer macromolecules formed on different active sites and through

different copolymerization processes, and one could hardly attempt to make any unambiguous correlation with reaction mechanism.

Therefore, we have prepared a copolymer, similar to one of those reported in ref 2, at 50 °C in the presence of the catalytic system δ -TiCl₃-Al(¹³CH₃)₃-Zn(¹³CH₃)₂ and attempted to separate the macromolecules of different stereoregularity in order to evaluate the ρ 's belonging to the different sites.

The copolymer was fractionated by stepwise precipitation from toluene solution by gradual incremental addition of methanol. Six fractions were collected and analyzed by ¹³C NMR.

The degree of isotactic regularity of the propene homosequences of the two copolymers has been evaluated from the intensity ratio between the resonances of the mm stereochemical triads⁶ (between δ 19.3 and 19.9) and the resonances of the propene triad homosequences PPP⁷ (between δ 26.4 and 27) (see also ref 2).

For each fraction, the composition, the molecular weight,⁸ and the relative reactivities ρ_1 , ρ_2 , ρ_3 , ρ_4 (see eq 1-4) have been also evaluated by ¹³C NMR analysis as reported together with the assignment of the relevant resonances in ref 2 and in the Experimental Section. The results are summarized in Table I.

The spectrum of the methyl region of fraction IV and the assignment of the resonances of the enriched carbons of the end groups shown in Scheme I are reported, as an example, in Figure 1. Inspection of Table I shows that fractional precipitation only partially achieved the goal of separating the copolymer into highly stereoregular and stereoirregular fractions. In fact, the most stereoregular copolymer fractions of polypropene obtained under similar conditions have a mm/PPP ratio larger than 0.9.⁹

Even with this limitation it can be observed that (1) ρ_1 is considerably lower than ρ_2 , ρ_3 , and ρ_4 for all the fractions and that (2) the values of all the ρ 's do not seem to be strongly dependent on the stereoregularity of the fractions.

In order to justify the low value of ρ_1 , in comparison with ρ_2 , ρ_3 , and ρ_4 , found even for the most stereoregular fractions, it is important to realize that, as reported in previous papers,¹⁰ the insertion of propene into the metal-methyl bonds of the isotactic-specific sites is not enantioselective but only regioselective. Insertion becomes enantioselective only after the alkyl group bonded to the active sites becomes larger than CH₃.¹⁰ As a consequence, on these sites, propene has two kinetically equivalent modes of insertion into the active Mt-CH₃ bond, while it has only one mode into Mt-R bonds (R is an alkyl group larger than CH₃). Of course, ethylene always has four equivalent modes (see Figure 2).

By assuming that the preexponential factors of the kinetic rate constants are proportional to the modes of insertion we expect that

$$k_1/k_2 = \rho_1 \propto 2e^{(E_2-E_1)/RT}$$

Scheme I
Enriched End Groups Resulting from Initiation Steps of Ethylene-Propene Copolymerization in the Presence of $\delta\text{-TiCl}_3\text{-Al}(^{13}\text{CH}_3)_3\text{-Zn}(^{13}\text{CH}_3)_2$

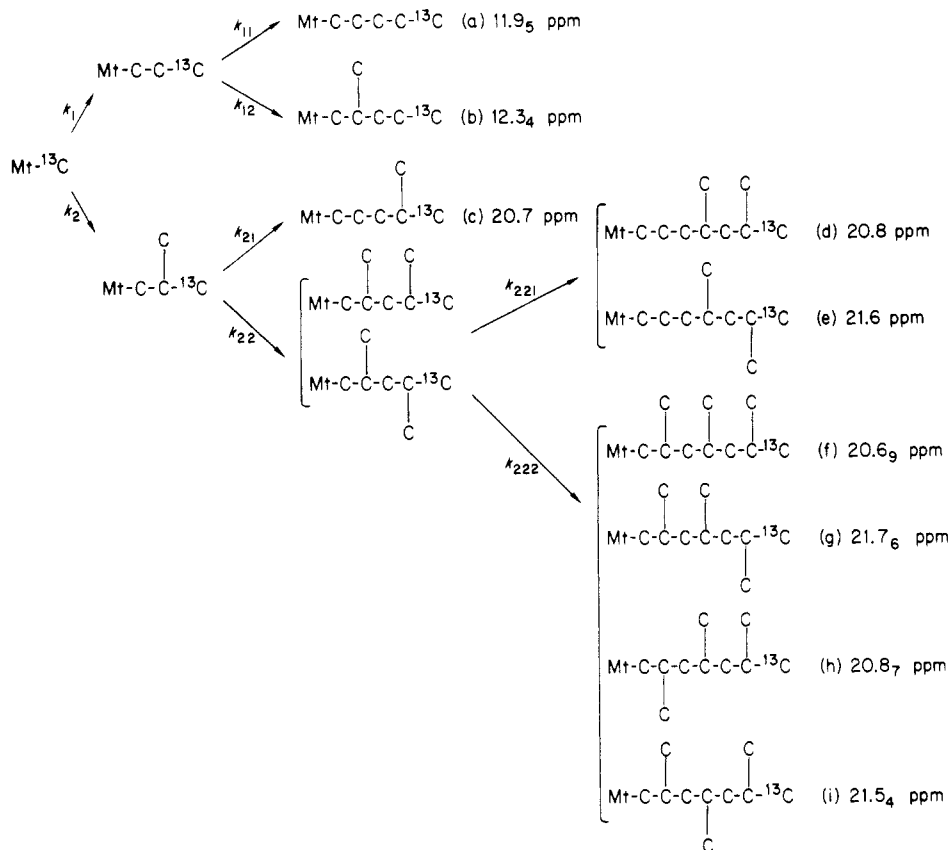


Table I
Fractionation of the Ethylene-Propene Copolymer

fraction concn,	wt %	mm/PPP	M_N	f^a	ρ_1	ρ_2	ρ_3	ρ_4
I	9.0	0.75	12000	1.10	4.6	35	24	$\cong 16$
II	9.8	0.78	12500	0.82	4.9	21	16	$\cong 17$
III	8.2	0.58	21000	0.85	3.5	23	25	$\cong 19$
IV	45.9	0.58	18000	0.70	3.8	22	23	$\cong 20$
V	6.6	0.57	8300	0.96	3.6	21	20	$\cong 24$
VI	20.5	0.64	2800	0.72	4.2	24	24	$\cong 23$

^a C₂H₄/C₃H₆ molar ratio in the copolymer fractions evaluated as reported in ref 2.

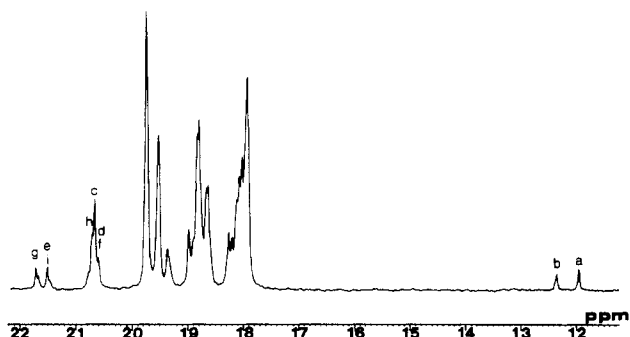


Figure 1. ¹³C NMR spectrum of fraction IV of Table I. Methyl region. Chemical shifts are referred to HMDS. The letters show the assignments of the resonances of the enriched carbons of the end groups reported in Scheme I.

From the values of ρ_1 reported in Table I for these fractions one can evaluate

$$E_2 - E_1 \cong 0.4 \text{ kcal/mol}$$

Such a positive $E_2 - E_1$ difference, in consideration of the I⁻ effect of the CH₃ substituent of propene, could mean that the insertion mechanism is a nucleophilic attack on

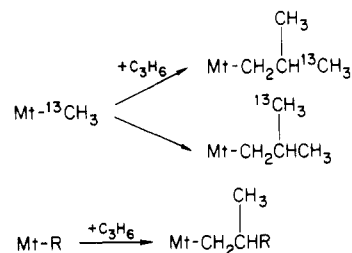


Figure 2. Two kinetically equivalent modes are available for regiospecific insertion of propene into Mt-CH₃ bonds. Insertion into Mt-R bonds is both regioselective and enantioselective so that only one mode is available. Because of the D_{2h} symmetry, four kinetically identical modes are always available for ethylene.

the double bond. An alternative explanation, however, could simply imply steric retardation by the CH₃.

Considering the unique allowed mode of insertion of propene into the Mt-R bonds of the isotactic sites, and under the same assumption as above concerning the preexponential factor of the kinetic rate constants, one expects that

$$k_{21}/k_{22} = \rho_3 \propto 4e^{(E_{22}-E_{21})/RT}$$

Again, the relative reactivity of ethylene (see Table I) is higher than that justified simply by considering the modes of insertion. In fact, $E_{22} - E_{21} = 1$ kcal/mol.

It is also worthwhile to note that $\rho_3/\rho_1 \cong 5$ instead of being $\rho_3/\rho_1 = 2$, as expected simply by considering the modes of attack. This fact can hardly involve any electronic effect and consequently suggests steric interactions between the methyl of the incoming propene and the growing chain end, in addition to those responsible for the steric control.

Concerning the values of the ρ 's belonging to the less stereoregular fractions, one can only observe that they are not too different from those of the most stereoregular fractions. This could possibly mean that the reaction mechanisms and the structures of the active sites causing, respectively, stereoregular and stereoirregular propagation, are rather similar to each other. For example, Corradini et al. suggested that the isotactic-specific sites are chiral octahedral titanium atoms on the surface of TiCl_3 crystals bearing an alkyl substituent.¹¹ The alkyl substituent should be constrained to a fixed conformation across the titanium-carbon bond and the enantioselectivity of the insertion should arise from the nonbonded interactions between the methyl substituent of the propene entering into the chain and the carbon of the growing chain end, β to the titanium.¹¹ This mechanism of steric control can readily explain the lack of enantioselectivity of the insertion of propene into Mt-CH_3 bonds.

Of course, similar octahedral sites should not be stereospecific, if, for some reason, the rotation around the titanium-carbon bond is not restricted. On the other hand, the number of modes of insertion of the two monomers should be the same on such sites as on those conformationally restricted.

Experimental Part

Ethylene-propene copolymerization was performed at 50 °C as previously described² by using the following: $\delta\text{-TiCl}_3$, 4×10^{-4} mol; $\text{Al}^{(13}\text{CH}_3)_3$, 1.2×10^{-3} mol; $\text{Zn}^{(13}\text{CH}_3)_2$, 1.7×10^{-3} mol; heptane, 125 cm³; polymerization time, 15 min; yield, 1.3 g. The enrichment of the organometallic cocatalysts was 47%; $F = 0.048$.

The synthesis of the enriched cocatalysts has been reported previously.¹⁰ Fractional precipitation has been performed by dissolving 1.3 g of copolymer in 180 mL of toluene at 30 °C. Some copolymer failed to dissolve and was filtered off (fraction I).

The other fractions were obtained by adding CH_3OH while stirring until turbidity developed. The temperature of the solution was raised until it again became clear. The solution was then cooled at 30 °C and let stand until phase separation was observed (usually 24 h). The precipitated polymer-rich phase was collected

and the previously described procedure was repeated. The last fraction (VI) was recovered by evaporation of the solvent under vacuum.

The ¹³C NMR analysis was performed on polymers dissolved in 1,2,4-trichlorobenzene/1,2-dideuteriotetrachloroethane at 135 °C on a Bruker AM300 spectrometer in the FT mode: pulse width, 45°; acquisition time, 1.081 s, without delay. The chemical shifts are relative to hexamethyldisiloxane (HMDS).

The number-average molecular weights of the fractions of Table I are evaluated from the NMR spectra by neglecting possible differences of the NOE and assuming that, because of the fast chain transfer with $\text{Zn}^{(13}\text{CH}_3)_2$, each macromolecule has one enriched methyl end group.^{10,12} In that case

$$\bar{M}_N = \frac{\sum I_u}{\sum I_e}(43)(14)$$

where $\sum I_u$ is the summation of the intensities of the resonances of all the unenriched carbons of the macromolecules (i.e., CH_3 , CH_2 , and CH); $\sum I_e$ is the summation of the intensities of the resonances of the enriched methyl carbons of the end groups; 43 is the ratio between the enrichment of the methyls (47%) and the natural abundance (1.1%); 14 is the molecular weight of the methylene group.

Acknowledgment. Italian CNR, Programma Finalizzato di Chimica Fine e Secondaria, and Ministero della Pubblica Istruzione are acknowledged for financial support.

Registry No. Ethylene, 74-85-1; propylene, 115-07-1.

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