Polymerization of Propylene to Syndiotactic Polymer.
VI. Monomer Insertion

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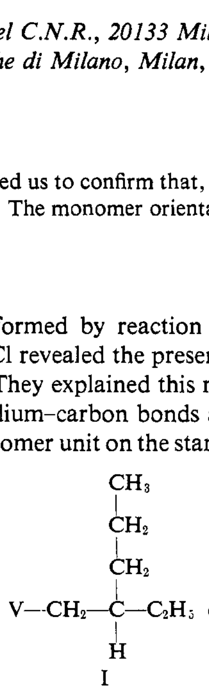
ABSTRACT: The infrared analysis of ethylene–propylene copolymers allowed us to confirm that, in the syndiospecific polymerization of propylene, insertion occurs on metal–secondary carbon bonds. The monomer orientation in the insertion is essentially due to steric effects.

The mechanism of the syndiospecific polymerization of propylene has been extensively studied.[1–12] In particular it is well established that, in the presence of the homogeneous vanadium-based syndiospecific catalyst systems, (1) the propagation occurs by monomer insertion on a vanadium-carbon bond,[1,2] (2) the mechanism of addition to the double bond is cis,[7] and (3) the syndiotactic propagation takes place only when proper ligands are bonded to the catalytic vanadium, and the driving force of the steric control consists in the asymmetric configuration of the last unit of the reactive chain end.[5,6,8,9]

Some kinetic studies on polymerization, and the spectroscopic examination of the catalytic systems, also suggest that the formal oxidation number of vanadium of the true syndiospecific catalyst complexes is three,[2–4] and that chain propagation proceeds through two steps, possibly represented by monomer coordination on the catalyst and insertion of the previously coordinated monomer into the metal–carbon bond.[6]

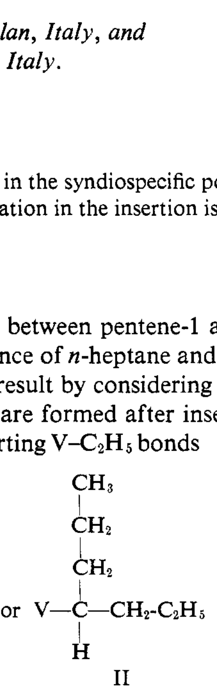
It was also shown that the molar amount of the catalytic complexes is only a small fraction of the total amount of vanadium present in the former syndiospecific catalyst systems; in the preparation of these systems, the vanadium salt reacts, *e.g.*, with $Al(C_2H_5)_2Cl$ and gives in addition to the true catalyst complexes some other inactive vanadium compounds.[2]

Takegami and Suzuki[10,11] tried to establish whether monomer insertion occurs on a vanadium-primary carbon bond (*primary insertion*) or on a vanadium–secondary carbon bond (*secondary insertion*).[13] They began by observing that, in the presence of vanadium-based syndiospecific catalyst systems such as VCl_4–$Al(C_2H_5)_2Cl$ at low temperature, α-olefins bulkier than propylene do not homopolymerize. However, glc examination of the mixture obtained by hydrolyzing the products formed by reaction between pentene-1 and VCl_4–$Al(C_2H_5)_2Cl$ revealed the presence of *n*-heptane and 3-methylhexane. They explained this result by considering that hindered vanadium–carbon bonds are formed after insertion of a bulky monomer unit on the starting V–C_2H_5 bonds


$\mathrm{V{-}CH_2{-}CH(CH_2CH_2CH_3){-}C_2H_5}$

I

or


$\mathrm{V{-}CH(CH_2CH_2CH_3){-}CH_2{-}C_2H_5}$

II

No further insertion of bulky monomer molecules could occur on such hindered vanadium–carbon bonds. Accordingly, 3-methylhexane is obtained after hydrolysis of I and *n*-heptane after hydrolysis of II. Since, in the hydrolysis products, *n*-heptane was in strong excess over 3-methylhexane, formation of II should be preferred over formation of I. Extrapolation of these conclusions would thus indicate that the secondary insertion instead of the primary one also occurs in the syndiospecific polymerization of propylene.

In our opinion, the data of Takegami and Suzuki show that in some cases the formation of a vanadium–secondary carbon bond is preferred to that of a vanadium–primary carbon bond. However, we believe that further data are required to reach the conclusion that the secondary insertion actually occurs in the syndiospecific polymerization of propylene. First it should be checked whether I and/or II forms exclusively in the reaction between pentene-1 and the catalytic complexes, or even in the reaction between pentene-1 and the aforementioned compounds present in the catalyst systems and containing the largest amount of vanadium, but

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[1] A. Zambelli, G. Natta, and I. Pasquon, *J. Polym. Sci., Part C*, No. **4**, 411 (1963).

[2] G. Natta, A. Zambelli, G. Lanzi, I. Pasquon, E. R. Mognaschi, A. L. Segre, and P. Centola, *Makromol. Chem.*, **81**, 161 (1965).

[3] M. H. Lehr, *Macromolecules*, **1**, 178 (1968).

[4] M. H. Lehr and C. J. Carman, *ibid.*, **2**, 217 (1969).

[5] A. Zambelli, G. Natta, I. Pasquon, and R. Signorini, *J. Polym. Sci., Part C*, No. **16**, 2485 (1967).

[6] A. Zambelli, I. Pasquon, R. Signorini, and G. Natta, *Makromol. Chem.*, **112**, 160 (1968).

[7] A. Zambelli, M. G. Giongo, and G. Natta, *ibid.*, **112**, 183 (1968).

[8] A. Zambelli, A. Léty, C. Tosi, and I. Pasquon, *ibid.*, **115**, 73 (1968).

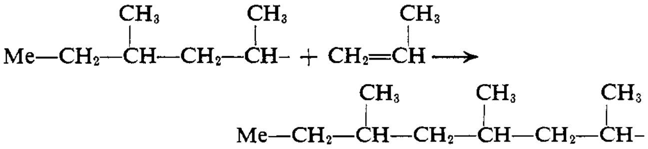
[9] A. Zambelli, G. Gatti, C. Sacchi, W. O. Crain, Jr., and J. D. Roberts, *Macromolecules*, **4**, 475 (1971).

[10] Y. Takegami and T. Suzuki, *Bull. Chem. Soc. Jap.*, **42**, 848 (1969).

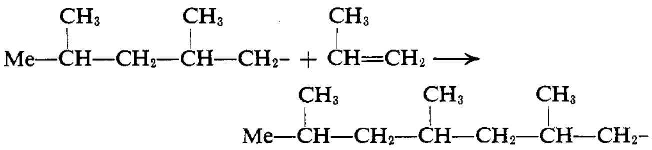
[11] T. Suzuki and Y. Takegami, *ibid.*, **43**, 1848 (1970).

[12] J. Boor, Jr., and E. A. Youngman, *J. Polym. Sci., Part A*, **1**, 1861 (1966).

(13) By *primary insertion* we mean the formation of the bond between the metal and the propylene *head* (*i.e.*, the $-CH_2-$ group)


$$\mathrm{Me{-}CH_2{-}CH(CH_3){-}CH_2{-}CH(CH_3){-} + CH_2{=}CH(CH_3) \longrightarrow Me{-}CH_2{-}CH(CH_3){-}CH_2{-}CH(CH_3){-}CH_2{-}CH(CH_3){-}}$$

whereas by *secondary insertion* we mean the formation of the bond between the metal and the propylene *tail* (*i.e.*, the $-CH(CH_3)-$ group)


$$\mathrm{Me{-}CH(CH_3){-}CH_2{-}CH(CH_3){-}CH_2{-} + CH(CH_3){=}CH_2 \longrightarrow Me{-}CH(CH_3){-}CH_2{-}CH(CH_3){-}CH_2{-}CH(CH_3){-}CH_2{-}}$$

inactive in polymerization. Secondly, it should be shown that substitution of propylene for a monomer, which is so bulky as to prevent polymerization, does not exceedingly perturb the behavior of the syndiospecific catalytic complexes.

Therefore, this work aims at establishing, by an independent method, to what extent propylene insertion during the chain propagation yields metal-secondary carbon rather than metal-primary carbon bonds.

We have tackled the problem essentially on the basis of the infrared analysis of the chemical constitution of the copolymerization products of propylene with ethylene.

In this way we have avoided all hypotheses on (1) the possible reactions with propylene of compounds other than the true catalytic complexes and (2) the possible reactions of substances that are unable to polymerize. Furthermore, the only hypothesis introduced, *viz.*, that the presence of ethylene does not modify the reaction mechanism, had already been experimentally proved.[8,9]

Experimental Section

Ethylene–Propylene Copolymerization. Copolymer samples 1–10 were prepared by condensing C_3H_6 (50 g) in a glass reactor thermostated at $-78°$. After completing this operation, a precooled gaseous mixture of N_2, C_3H_6, and ^{14}C-labeled C_2H_4 was bubbled through liquefied propylene. The reactor was kept at atmospheric pressure by discharging undissolved gases. After saturation of liquefied propylene with ethylene from the gaseous phase, the components of the catalyst system, VCl_4 (0.5×10^{-3} mol) and $Al(C_2H_5)_2Cl$ (5×10^{-3} mol), diluted in anhydrous *n*-heptane (1–2 ml), were introduced separately. Bubbling of the N_2, C_3H_6, and C_2H_4 mixture was continued until the end of the runs.[14] To ascertain complete saturation of propylene before introducing the catalysts, the gaseous phase leaving the reactor was analyzed by glc, and the copolymerization was started only when the ratio of the partial pressures of nitrogen and ethylene was equal to that of the feed mixture. Analogous controls were done at intervals on the off gas during the copolymerization. A ratio of ~10 between the amount of ethylene passed through the reactor and that of converted ethylene was always maintained. Ethylene bubbled through during saturation was not taken into account.

Samples 11, 12, and 13 were prepared in a similar way in *n*-heptane (70 ml); the solution in *n*-heptane was saturated by bubbling ethylene–propylene–nitrogen mixtures of different compositions. C_3H_6–C_2D_4 copolymers were prepared in *n*-heptane at low monomer conversion without adding monomers during the runs.

Copolymerizations were stopped by introduction of butyl alcohol in the system. The copolymers were then coagulated with methanol (previously cooled in order to avoid a vigorous boiling of propylene) and purified by dissolving in toluene, washing the solution first with aqueous hydrochloric acid then with water until neutralization, and reprecipitating with methanol. The copolymers were dried *in vacuo* at 80–100°. Their compositions were determined radiochemically.

X-Ray Analysis of the Amorphous Copolymers. X-Ray measurements were performed on a Philips diffractometer equipped with pulse discriminator and proportional counter, by using nickel-filtered copper radiation.

Particular care was taken in order to obtain specimens with very smooth surfaces. As for polymers showing syndiotactic crystallinity (those containing 0–6 mol % ethylene), the samples were quenched from the melt and examined before occurrence of crystallization.

Infrared Spectra of Ethylene–Propylene Copolymers. The infrared examination of ethylene–propylene copolymers may effectively elucidate the monomer insertion in syndiospecific polymerization: actually the ir spectrum reveals the presence of bands originating from propylene and ethylene sequences of different lengths, *i.e.*, 12.25 μ, characteristic of the rocking vibration of $-(CH_2)_1-$ groups (hence of propylene sequences containing two or more units); 13.30 μ, characteristic of the rocking vibration of $-(CH_2)_2-$ groups which arise either from two head-to-head propylene units or from one ethylene unit inserted between two tail-to-tail propylene units; 13.64 μ, characteristic of the rocking vibration of $-(CH_2)_3-$ groups (hence of one ethylene unit lying between two head-to-tail propylene units); and 13.85 μ, characteristic of the rocking vibration of $-(CH_2)_n-$ groups with $n \geqslant 5$ (hence of long ethylene sequences).

In view of the purposes of the present work, only the second and the third of these bands have been utilized; furthermore, the numbers of units present in sequences containing two and three methylene groups have been deduced from the corresponding absorptivities by the method of Bucci and Simonazzi.[15] This method is based on a three-component analysis of the complex band between 13 and 14 μ, and consists in the solution of the set of simultaneous equations

$$A(_{13.30\ \mu})/S = A_2 + 0.2A_3 + 0.12A_5$$

$$A(_{13.64\ \mu})/S = 0.1A_2 + A_3 + 0.35A_5$$

$$A(_{13.85\ \mu})/S = 0.5A_3 + A_5$$

where S is the sample thickness in centimeters. The coefficients were determined from the spectra of atactic polypropylene with head-to-head linking, of hydrogenated natural rubber, and of *n*-nonadecane. The absorbances per unit thickness, A_2, A_3, and A_5, obtained from these equations were then converted to percentages of methylene groups by dividing them by the respective absorptivities for 1% CH_2, which were 1.0/cm (13.30 μ), 1.2/cm (13.64 μ), and 1.2/cm (13.85 μ). As will be seen later, many ethylene–propylene copolymers examined in this work exhibited the bands at 13.30 and 13.64 μ only. We have observed that for these copolymers the absorbance at 13.85 μ is always less than one-half that at 13.64 μ, as would result from the last equation of the foregoing system. In other words, the half-width of the 13.64-μ band in these copolymers is smaller than in hydrogenated natural rubber. Instead of calculating a new set of standard absorptivities, we have considered the results obtained by solving the two-equation system resulting from elimination of both third row and column in the preceding one, as sufficiently accurate.

The presence of tail-to-tail enchained propylene units, *i.e.*, of methyl branches on adjacent carbon atoms, is also revealed by a band near 9 μ. Hydrogenated poly(2,3-dimethylbutadiene)[16] or alternating ethylene–*cis*-2-butene copolymer[17] can be used as a model compound. The former shows a sharp peak at 9.0 μ, which is broadened toward the low-wavelength side, with a pronounced shoulder between 8.7 and 8.8 μ. From Figure 3 of ref 15, the absorbance of this peak turns out to be about twice that of the 13.30-μ band. The latter compound shows a band at 8.85 μ in the crystalline state; in the molten state this band broadens and shifts to 8.80 μ. The spectrum reported in Figure 7 of ref 16 concerns a much too thin sample to enable an accurate measurement of band absorptivities. Therefore, our quantitative measurements were based on a low molecular weight model compound, *viz.*, 3,4-dimethylhexane, which shows a peak at 8.90 μ with absorbance 240 g^{-1} cm^2 (referred to the group $-CH(CH_3)-CH(CH_3)-$). Both in polypropylene and in low ethylene copolymers prepared with the syndiospecific catalyst described in this work, the vibration yielded by vicinal methyls gives rise to a weak shoulder at 8.83 μ on the long-wavelength side of the propylene band at 8.65 μ.

As discussed below, we also determined the so-called "syndiotacticity index"[1] of these copolymers (IS). This index is given by

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[14] The partial pressure of C_3H_6 in the feed mixture was always equal to the vapor tension of propylene at $-78°$. The partial pressures of the other components were variable.

[15] G. Bucci and T. Simonazzi, *J. Polym. Sci., Part C*, **No. 7**, 203 (1964).

[16] J. van Schooten and S. Mostert, *Polymer (London)*, **4**, 135 (1963).

[17] G. Natta, G. Dall'Asta, G. Mazzanti, and F. Ciampelli, *Kolloid-Z. Z. Polym.*, **182**, 50 (1962).

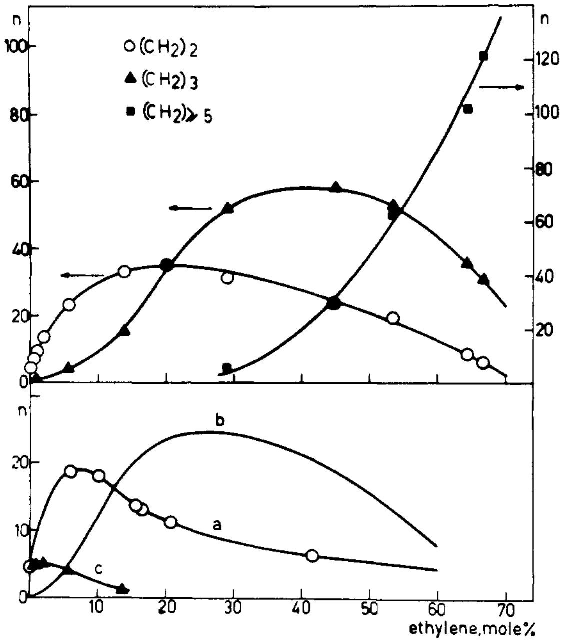

Figure 1. (Upper) Distribution of methylene groups (expressed as the number *n* of CH_2's per 100 monomer units) over sequences of different length. (Lower) (a) Methylene groups in $(CH_2)_2$ sequences originated from two head-to-head propylene units (deduced from the spectra of C_2D_4–C_3H_6 copolymers), (b) methylene groups in $(CH_2)_2$ sequences originated by insertion of one ethylene unit between two tail-to-tail propylene units (obtained by subtracting the number of methylenes in $(CH_2)_2$ sequences of type **1** from the total number of methylenes in $(CH_2)_2$ sequences plotted in the upper part of the diagram), (c) vicinal methyls.

the absorbance ratio $A_{11.54\,\mu}/0.5(A_{2.32\,\mu} + A_{2.35\,\mu})$. Reproducible values for IS were only obtained by annealing samples at 80° for 12 hr.

Results and Discussion

Monomer Insertion. Both the catalyst system and the reaction temperature chosen for the preparation of the copolymers described in this work are typically syndiospecific. It is to be expected that the infrared analysis of the constitution of these copolymers will reveal some peculiar features of this polymerization. A plot of the numbers of $(CH_2)_2$, $(CH_2)_3$, and $-CH(CH_3)-CH(CH_3)-$ groups in the copolymers and in a sample of syndiotactic polypropylene prepared in the same conditions (Figure 1) shows four main properties: (a) both the propylene homopolymer and the copolymers contain $(CH_2)_2$ and $-CH(CH_3)-CH(CH_3)-$ groups; (b) the maximum number of $(CH_2)_2$ groups found in copolymers is much higher than twice that in the corresponding homopolymer; (c) at low ethylene concentration, almost all ethylene units give rise to $(CH_2)_2$ groups, *i.e.*, they lie between two tail-to-tail propylene units, while $(CH_2)_3$ sequences begin appearing in noticeable amounts only at higher ethylene content; (d) the vicinal methyls do not appreciably decrease on introducing ethylene until $(CH_2)_3$ sequences become detectable. Any satisfactory mechanism assumed for propylene insertion must account for these four properties.

In the propylene homopolymer, the $(CH_2)_2$ groups instead of the usual $-CH_2-CH(CH_3)-$ groups only originate from inversion of the chemical arrangement of two subsequent monomer units (*i.e.*, when head-to-head arrangement occurs).

In the copolymers, the $(CH_2)_2$ groups can form either as in the propylene homopolymer or by insertion of one ethylene unit on a vanadium–propylene secondary carbon bond, followed by primary insertion of a propylene unit.

The two mechanisms of formation of $(CH_2)_2$ group are shown by the two schemes

$$\mathrm{Me}\ \lrcorner \xrightarrow{+\llcorner} \underset{\mathbf{1}}{\mathrm{Me}\ \llcorner\ \lrcorner} \qquad (1)$$

$$\mathrm{Me}\ \llcorner \xrightarrow{+\_} \mathrm{Me}\ \_\ \llcorner \xrightarrow{+\lrcorner} \underset{\mathbf{2}}{\mathrm{Me}\ \lrcorner\ \_\ \llcorner} \qquad (2)$$

where Me = catalyst metal atom, $\_$ = ethylene unit, $\llcorner$ = tail–head propylene unit, and $\lrcorner$ = head-tail propylene unit.

In order to distinguish the sequences of two methylenes formed according to mechanism 1 from those formed according to mechanism 2, propylene–ethylene-d_4 copolymers have been examined: in these copolymers, the $(CH_2)_2$ groups originating from propylene still absorb at 13.30 μ, while the band characteristic of $(CD_2)_2$ groups originated from ethylene is displaced toward higher wavelengths.

Figure 1 also shows the $(CH_2)_2$ groups of type **1** observed in C_3H_6–C_2D_4 copolymers. The data plotted in Figure 1 can be correlated with the kind of propylene insertion, on the condition that the presence of ethylene does not modify the behavior of the catalytic complexes. This possibility was considered in a previous paper,[8] where it was shown that stereospecificity of both iso- and syndiospecific catalysts with respect to propylene was retained in the presence of ethylene.

This being so, we can now examine which consequences on the reaction mechanism and which properties of the copolymers are brought about by the data of Figure 1, whether the *primary* insertion is assumed as *normal* and the *secondary* insertion as *wrong*, or *vice versa.*

The data of Figure 1 show that $(CH_2)_2$ groups of type **1** increase when passing from the homopolymer to copolymers containing up to about 10 mol % ethylene.

Were the primary insertion the normal one, this would mean that the kinetics of the event

$$\mathrm{Me}\ \lrcorner\ \_ \xrightarrow{+\llcorner} \mathrm{Me}\ \llcorner\ \lrcorner\ \_$$

is faster than the kinetics of the event

$$\mathrm{Me}\ \lrcorner\ \lrcorner \xrightarrow{+\llcorner} \mathrm{Me}\ \llcorner\ \lrcorner\ \lrcorner$$

Most ethylene units in copolymers containing less than 10 mol % ethylene give rise to $(CH_2)_2$ groups of type **2** instead of $(CH_2)_3$ groups (Figure 1). Accordingly, the assumption that the primary insertion is the normal one would also entail that once the event

$$\mathrm{Me}\ \lrcorner \longrightarrow \mathrm{Me}\ \llcorner\ \lrcorner$$

favored, as seen, by the preceding occurrence of the event

$$\mathrm{Me}\ \_ \longrightarrow \mathrm{Me}\ \lrcorner\ \_$$

has taken place, the event

$$\mathrm{Me}\ \urcorner \longrightarrow \mathrm{Me}\ \_\ \llcorner$$

will probably take place.[18] These assumptions would thus suggest rather strange effects of the penultimate unit.

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(18) By probable and inprobable we mean a higher and respectively lower probability than the bernoullian one (*i.e.*, the probability predictable by exclusively considering the concentration of the reacting monomers and by assuming the absence of any effect of units already entered in the chains).

TABLE I

CONSTITUTION OF THE ETHYLENE–PROPYLENE COPOLYMERS PREPARED WITH THE SYNDIOSPECIFIC CATALYST SYSTEM VCl_4 (0.5×10^{-3} MOL)–$Al(C_2H_5)_2Cl$ (5×10^{-3} MOL) AT −78°

(A) C_2H_4–C_3H_6 Copolymers

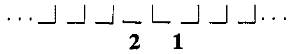
Sample	C_2H_4, mol %[a]	No.[b] (per 100 monomer units) CH₂'s organized in sequences of length 2[c]	3	≥5	Vicinal CH_3's	2ϑ(Cu Kα)	IS[d]
1	0	4.5			4.4	16.18	1.52
2	0.6	7.2			4.6	16.22	1.37
3	1.0	9.4			4.7	16.17	1.26
4	1.9	13.8	1.2		5.0	16.30	1.19
5	5.6	25.3	4.5		4.0	16.55	0.27
6	13.8	33.0	15.2		1.2	16.90	0.11
7	20	35.4	35.6			17.27	
8	29	31.3	52	6.3		17.68	
9	45	24.6	58	35.2		18.02	
10	53	19.5	54	66		18.23	
11	64	8.7	36.8	104		18.53	
12	67	6.2	31.3	123		18.63	
13	78	4.6	8.9	163		n.d.	

(B) C_2D_4–C_3H_6 Copolymers

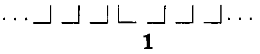
Sample	C_2D_4, mol %[a]	No.[b] (per 100 monomer units) of CH₂'s organized in sequences $(CH_2)_2$[e]
14	6.0	18.6
15	10.2	18.1
16	15.6	13.6
17	16.5	13.0
18	21	11.1
19	42	6.2

[a] Determined by radiochemical analysis using ^{14}C-labeled ethylene. [b] Determined by ir analysis of the bands at 13.30, 13.64, 13.85, and 8.83 μ, respectively. [c] This column lists the total number of $(CH_2)_2$ groups, *i.e.*, of both type **1** and **2**. [c] The index of syndiotacticity, as defined in a previous paper,[1] is proportional to the propylene crystallinity. [e] These $(CH_2)_2$ groups are only of type **1**, *i.e.*, they are yielded by two head-to-head propylene units. After fitting a smooth curve both to them (lower part of Figure 1) and to the total $(CH_2)_2$ groups (upper part of Figure 1), it becomes possible to obtain by difference the $(CH_2)_2$ groups of type **2** (lower part of Figure 1).

Moreover, as to the copolymer properties, when polymerization occurs in the presence of a very low ethylene concentration ($\lesssim 2\%$), ethylenic units would almost exclusively occupy the positions immediately after a defect in the chemical arrangement of the propylene molecule placed at the end of a block of syndiotactic polypropylene; the resulting copolymers would be then formed by syndiotactic blocks, each separated from the other by a $(CH_2)_2$ group of type **1** and a $(CH_2)_2$ group of type **2**



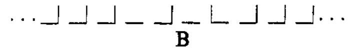
On the other hand, propylene homopolymers prepared under the same conditions would be formed by syndiotactic blocks separated by one $(CH_2)_2$ group of type **1** and by two substituted vicinal carbons



Since the amount of $(CH_2)_2$ sequences in the homopolymer is about 2%, the degree of crystallinity of copolymers with an ethylene content up to $\sim 2\%$ would not be appreciably lower than that of the homopolymer. Actually, the two chains would contain the same number of defects, or in other words the lengths of the chemically and sterically regular blocks would be the same.

On increasing ethylene concentration in the feed mixture so as to obtain copolymers with an ethylene content up to $\sim 10\%$, a different type of defect would be observed prior to an actual decrease of the length of the chemically and sterically regular propylene blocks. The copolymers would be formed by chemically and sterically regular propylene blocks separated by more than one $(CH_2)_2$ group of type **1** and more than one $(CH_2)_2$ group of type **2** separated by $-CH(CH_3)-$ (A), or by $(CH_2)_2$ groups of types **1** and **2** and by $(CH_2)_5$ groups separated by $-CH(CH_3)-$ (B).

A



B

Thus the degree of crystallinity should initially decrease to a low extent when passing from homopolymer to copolymers containing increasing amounts of ethylene.

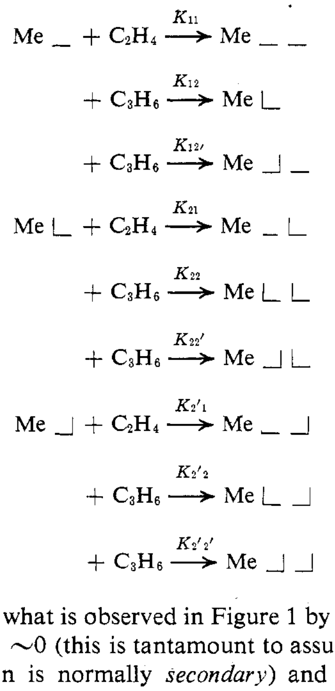
Instead, it has been experimentally found (Table I) that the syndiotactic crystallinity index decreases quickly on increasing the ethylene concentration in the copolymers; furthermore, even copolymers with a content of 7 mol % ethylene look completely amorphous by X-ray examination at room temperature.

More significant are the variations of the maximum diffracted intensity angle (2ϑ) of copolymers in the amorphous state (either because incapable of crystallization or because quenched) at different compositions (Figure 2). The value of such an angle is related to the structure of the amorphous material and ultimately to the bulkiness and the conformation of the macromolecules. The highest slope of the curve shown in Figure 2 corresponding to ethylene content near 0% leads to the conclusion that the first ethylene units introduced in a syndiotactic chain during copolymerization cause strong variations in the arrangement of the macromolecules; therefore, such units do not show any clustering tendency, as would be expected were propylene insertion normally primary.

Furthermore, direct evidence against the primary insertion is given by the fact that increase of $(CH_2)_2$ groups of type **2** in the copolymers is not accompanied by an equal decrease of vicinal methyls. It may be easily seen that if the normal insertion in the syndiospecific polymerization of propylene is the primary one, the formation of a $(CH_2)_2$ of type **2** requires the disappearance of two vicinal methyls. By contrast, Figure 1 shows that in a series of copolymers with increasing ethylene contents, the amount of vicinal methyls remains initially unaltered, in spite of the formation of increasing amounts of $(CH_2)_2$ of type **2**, and decreases only for higher ethylene contents, when considerable amounts of $(CH_2)_3$ groups begin appearing.

These difficulties are overcome by admitting that the normal propylene insertion is *secondary*. In that case $(CH_2)_2$ groups of type **1** would increase (see Figure 1) simply because the *primary* propylene insertion takes place when the last unit of the growing chain is ethylene instead of propylene, and because the relative reactivity of propylene *vs.* ethylene is higher when the last unit of the growing chain is a propylene unit inserted in primary way rather than a propylene unit inserted in the secondary one.

In other words, if we represent the copolymerization through the following steps



we can explain what is observed in Figure 1 by admitting that (1) $K_{2'2} \gg K_{2'2'} \sim 0$ (this is tantamount to assuming that propylene insertion is normally *secondary*) and (2) $K_{22}/K_{22'} > K_{12}/K_{12'}$, $K_{12}/K_{12'} < 1$ (these inequalities are due to the increase of type **1** $(CH_2)_2$ on passing from homopolymer to copolymers with an ethylene content up to about 10%; furthermore, they explain why in copolymers with lower ethylene contents, most ethylene gives $(CH_2)_2$ sequences, while the $(CH_2)_3$ group appears at higher ethylene contents.

Ionicity of the Catalytically Active Vanadium–Carbon Bond. Syndiospecific polymerization of propylene was often regarded as being ionic coordinated. Kinetic evidence shows that polymerization occurs through two steps, probably consisting of the coordination of monomer and the insertion. However, no direct data exist concerning the ionicity of the vanadium–carbon bond.[6]

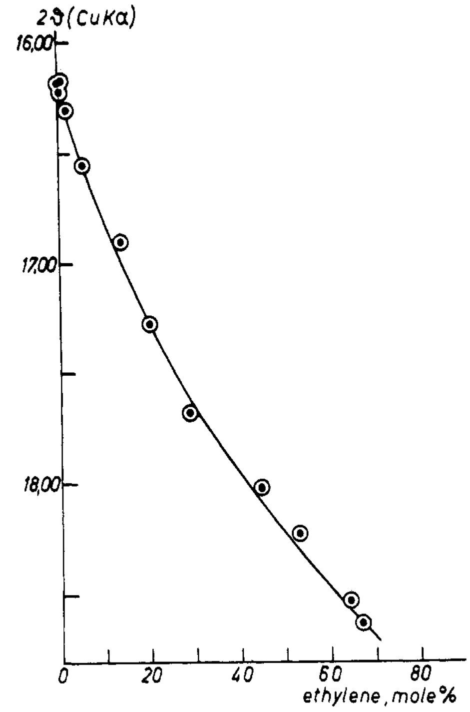


Figure 2. Maximum diffracted intensity angle of the amorphous ethylene–propylene copolymers.

TABLE II
MECHANISM OF PROPYLENE INSERTION

Last unit of the growing chain	Catalytic Me–C bond	New formed catalytic Me–C bond	
Propylene	Secondary	$+C_3H_6$	Secondary
	Primary	$+C_3H_6$	Secondary
Ethylene	Primary	$+C_3H_6$	Primary

Boor and Youngman found radioactivity in polypropylenes terminated with tritium-labeled methanol (CH_3OT).[12]

However, such radioactivity was rather low and of doubtful significance: methanol does not necessarily react with the catalyst directly and simply causing a methanolysis reaction.

Appreciable radioactivity was detected by us in syndiotactic polypropylenes obtained by polymerizations broken with ^{14}C-labeled methanol.[19]

As previously remarked, propylene can very easily pass from primary to secondary insertion or *vice versa* depending on the last unit of the growing chain. Table II shows the preferred behavior of propylene in the insertion as a function of the last unit of the growing chain and the type of the metal–carbon bond on which the insertion occurs. That means that this type of insertion depends more on steric effects than on the polarity of the catalytic metal–carbon bond and on the propylene dipole moment.

Conclusions

Four main conclusions may be drawn from this work. (1) The constitution and the properties of the ethylene–propylene copolymers obtained with vanadium-based syndiospecific catalysts seem to confirm Takegami and Suzuki's belief[10,11]

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(19) Unpublished data from our laboratory.

that propylene insertion preferably yields *secondary* metal–carbon bonds. The word "preferably" is used to indicate the type of insertion characteristic of the propylene sequences. (2) The ease with which propylene can pass from the secondary to the primary insertion by effect of the last-entered unit of the growing chain shows that the polarity of the catalytic metal–carbon bond has little or no effect on the monomer orientation and its influence on insertion is in any case lower than that of steric factors. (3) Termination reactions with radioactive methanol at present do not allow any deduction on the reaction mechanism. (4) Experimental data available so far seem only to enable the classifying of propylene syndiospecific polymerization as a coordinated nonradical reaction.

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