(11) N. R. Mayne, *CHEMTECH*, 728 (1972).
(12) W. Fowells, C. Schuerch, F. A. Bovey, and F. P. Hood, *J. Am. Chem. Soc.*, **89**, 1396 (1967).
(13) R. Kraft, A. H. E. Muller, V. Warzelhan, H. Hocker, and G. V. Schultz, *Macromolecules*, **11**, 1093 (1978).
(14) H. K. Hall, Jr., *Macromolecules*, **2**, 488 (1969).
(15) C. D. Eisenbach and R. W. Lenz, *Makromol. Chem.*, 177, 2539 (1976).

Syndiotactic Specific Polymerization of Propene: Some Evidence for Insertion of the Monomer on the Metal–Carbon Bond

A. Zambelli,* M. C. Sacchi, and P. Locatelli

Istituto di Chimica delle Macromolecole del C.N.R., 20133 Milano, Italy.
Received June 7, 1979

ABSTRACT: ^{13}C NMR analysis of selectively enriched polypropylene seems to support, at least for syndiotactic polymerization, the traditional mechanism involving insertion of the monomer on the σ metal–carbon bond vs. the more recently proposed mechanism involving carbene intermediate, in analogy with olefin metathesis.

In previous papers we devoted considerable effort to the interpretation of the stereochemistry of polymerization of α-olefins in the presence of Ziegler–Natta catalytic systems.[1-11]

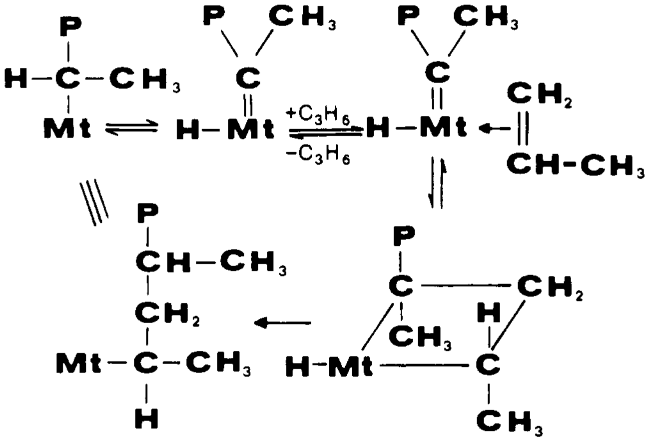
In our reasoning concerning the reaction mechanism, we assumed that polymerization involved insertion of the monomer on σ metal–carbon bonds. Actually, this belief was generally accepted in the literature.[12]

More recently, Ivin and co-workers[13] suggested a different picture of the insertion reaction involving α-hydrogen reversible shift, carbene, and metallocyclobutane intermediates (Scheme I).

The stereospecificity should depend on the relative configuration of the substituted carbons of the metallocyclobutane ring, and the H transfer from the metal to the more substituted carbon should exclude branching.[13] The evidence put forward by these authors are: (i) there are no unambiguous examples where a characterized metal–alkylolefin compound may be induced to react, giving the expected insertion product; and, (ii) there is a close identity between catalysts which cause Ziegler–Natta polymerization and those which give rise to olefin metathesis. On the other hand, it is generally accepted that metathesis involves metallocyclobutane and metal–olefin–carbene interconversion as the key steps in breaking and forming carbon–carbon bonds, and there is also evidence that transition metal alkyls can give rise to the reversible elimination of α-hydrogen.

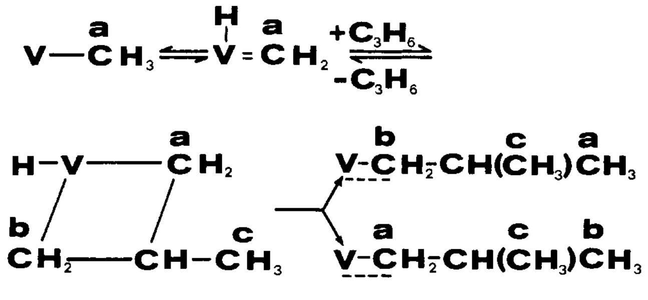
The mechanism proposed by these authors is oversimplified[13a] because it ignores the experimentally observed regiospecificity of propene polymerization,[4,6,10,14] in spite of the fact that it cannot be disregarded. On the contrary, when the correct regiospecificity of the monomer is accounted for by the isotactic and syndiotactic propagation steps, the different energies of the steric control could be qualitatively explained by the Ivin mechanism by simply considering the different distances between the substituted carbons of the cyclobutane ring depending on the regiospecificity (Figure 1). This fact prompted us to look for more direct evidence on the matter. In this paper, only syndiotactic polymerization of propene is considered, while the study of isotactic polymerization is still in progress.

Scheme I[a]



[a] P = polymer; Mt = metal atom of the catalytic complex.

Scheme II



Results

Syndiotactic polymerization of propene is only partially regiospecific.[6,7,15,16] Consequently, four propagation steps are possible:

$$\mathrm{Mt}{\vdash}\!\!-\!\!\bullet\mathrm{P} \xrightarrow{k_{11}} \mathrm{Mt}{\vdash}\!\!-\!\!\bullet \quad {\vdash}\!\!-\!\!\bullet\mathrm{P}$$

$$\mathrm{Mt}{\vdash}\!\!-\!\!\bullet\mathrm{P} \xrightarrow{k_{12}} \mathrm{Mt}\bullet\!\!-\!\!{\dashv} \quad {\vdash}\!\!-\!\!\bullet\mathrm{P}$$

$$\mathrm{Mt}\bullet\!\!-\!\!{\dashv}\mathrm{P} \xrightarrow{k_{22}} \mathrm{Mt}\bullet\!\!-\!\!{\dashv} \quad \bullet\!\!-\!\!{\dashv}\mathrm{P}$$

$$\mathrm{Mt}\bullet\!\!-\!\!{\dashv}\mathrm{P} \xrightarrow{k_{21}} \mathrm{Mt}{\vdash}\!\!-\!\!\bullet \quad \bullet\!\!-\!\!{\dashv}\mathrm{P}$$

---

* Address correspondence to this author at the Gulf Research and Development Co., Pittsburgh, Pa. 15230

0024-9297/79/2212-1051$01.00/0

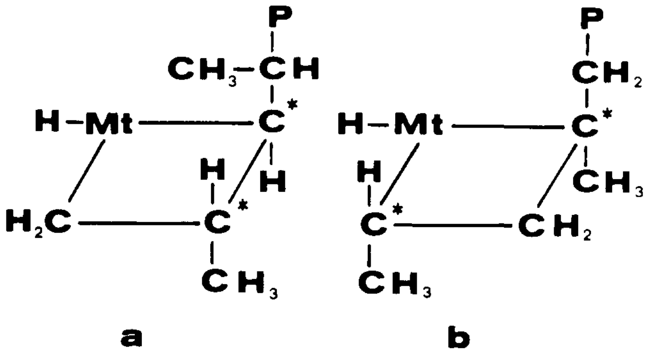


Figure 1. Metallocyclobutane intermediates for: (a) "primary insertion"; (b) "secondary insertion". Note the different distances of the chiral carbon atoms (starred) depending on the regiospecificity. Isotactic propagation occurs via primary insertion and syndiotactic propagation via secondary insertion.[10,14]

where $\vdash\!\!\bullet$ = CH_2CHCH_3 and $\bullet\!\!\dashv$ = $CH(CH_3)CH_2$.

It has also been previously observed that only step 22 is syndiotactic specific and that $k_{22}/k_{21} \gg k_{11}/k_{12} > 1$.[7,10] This means that the insertion of the monomer to be added to the reactive chain end is prevailingly primary when it occurs on a metal-unsubstituted carbon bond, while the secondary insertion is preferred on a metal-substituted carbon bond. As a consequence, when polymerization is initiated on a Mt–CH_3 bond, primary insertion of the monomer is expected, and the isopropyl end group should be detected in the polymer. Actually isopropyl end groups have been detected by ^{13}C NMR[10] in polypropylene prepared in the presence of the syndiotactic specific catalytic system VCl_4–$Al(CH_3)_2Cl$–anisole. It has also been shown that such groups are formed exclusively in the initiation step, while other end groups are formed in the termination of the chain.[10]

According to the mechanism proposed by Ivin and coworkers, the whole insertion process should be as shown in Scheme II.

Note that both carbons α to the V atom in the cyclobutane intermediate are unsubstituted (methylene carbons labeled a and b). Consequently, the α elimination should occur via H migration on either ^aC or ^bC. As a consequence, ^{13}C enriched methyl carbons should be observed in the isopropyl end groups when either 1-^{13}C-enriched propene or 3-^{13}C-enriched propene are polymerized in the presence of the previously mentioned catalytic system.

In Figure 2 are reported the ^{13}C NMR spectra of low molecular weight poly([3-^{13}C]propylene) and poly([1-^{13}C]propylene) obtained in the same reaction conditions (see Experimental Section).

It may be observed that enriched methyl carbons of isopropyl groups are detected centered at ~20.5 and 21.6 ppm, respectively, only in the spectrum of poly([3-^{13}C]propylene) (Figure 2a).

The presence of enriched carbons on both diastereotopic positions shows that initiation is not stereospecific. The fine structure of the above resonances also shows that chain propagation does not become stereospecific until insertion turns from primary to secondary, thus confirming the conclusion of previous papers where the assignment of the considered resonances was reported.[9,10] The different shifts here observed, in comparison with those reported previously,[9,10] depend on the different temperature (100 instead of 140 °C).

Obviously, this fact is an evidence disfavoring the mechanism proposed by Ivin and co-workers.[13] In the spectrum of poly([1-^{13}C]propene) (Figure 2b), the absence of any resonance at ~22.6 and 35–37 ppm can be observed (ethylene comonomer units inserted between propene units having the same orientation $\ldots CH_2CH(CH_3)$–$CH_2CH_2CH_2CH(_3CH_3)CH_2\ldots$).[7]

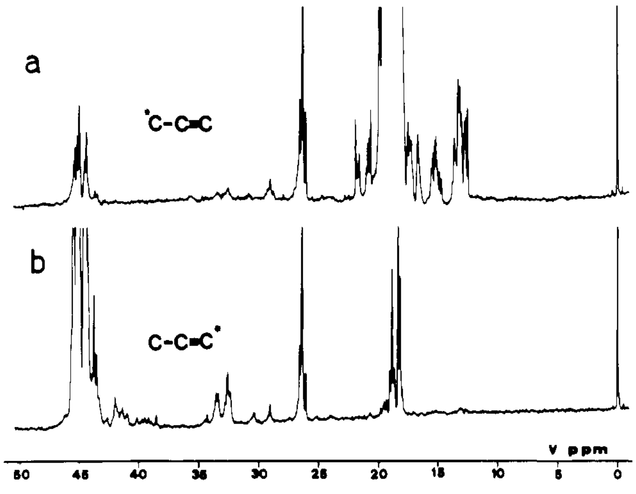


Figure 2. ^{13}C NMR spectra of prevailingly syndiotactic low molecular weight (a) poly([3-^{13}C]enriched propylene) and (b) poly([1-^{13}C]enriched propylene). The polymerization is started on metal–CH_3 bonds (see Experimental Section).

Due to the enrichment of the methylene carbons of the monomer, this fact shows the complete absence of productive metathesis during the polymerization.

Actually, ethylene copolymerizes vary rapidly with propene, and even traces of enriched ethylene arising from metathesis of [1-^{13}C]propene would be observed as ^{13}C-enriched comonomer units. The resonances between 32 and 34.5 ppm are due to head-to-head arranged propylene units ($\ldots CH(CH_3)CH_2CH_2CH(CH_3)\ldots$). Here again the assignment is according to the previously quoted papers.[1,7,17] The other observed resonances are not discussed here because they are irrelevant to the matter of the paper.

Conclusion

^{13}C-enriched methyls are observed in the isopropyl end groups when 3-^{13}C-enriched propene is polymerized in the presence of the syndiotactic specific catalytic system VCl_4–$Al(CH_3)_2Cl$–anisole. A similar ^{13}C enrichment is not observed when 1-^{13}C-enriched propene is polymerized in the same conditions. This fact seems to favor the hypothesis that at least in the case considered here polymerization occurs via insertion of the monomer on a σ metal–carbon bond without involving hydrogen shift and metallocyclobutane intermediates.

The absence of ethylene monomer units in the polymerization products seems also to show that in the reaction conditions reported here metathesis is absent, and therefore it does not seem justified to consider α-olefin polymerization and olefin metathesis as necessarily related reactions.[19]

Experimental Section

All of the solvents were purified by treatment with $LiAlH_4$ and distillation, and the reactions were performed in an inert atmosphere (nitrogen or helium).

VCl_4 and $Al(CH_3)_2Cl$ were commercial products.

90% Enriched [1-^{13}C]Propene. Triphenylphosphine (0.036 mol) dissolved in 100 mL of anhydrous tetrahydrofuran was introduced under a helium atmosphere into a 250-mL three-necked flask provided with a magnetic stirrer, a dropping funnel, and a reflux condenser. $^{13}CH_3I$ (0.035 mol, 90% ^{13}C enrichment) was added, and immediately a white solid was formed. The suspension was gently warmed and then stirred for 12 h at room temperature. Lithiophenyl (0.0355 mol) dissolved in 80 mL of THF was rapidly dropped and the yellow suspension stirred for 4 h. Half of the solvent was distilled off in order to eliminate

C_2H_4 arising from a trace amount of water. The flask was cooled at −78 °C and CH_3CHO (0.053 mol) added. The temperature was raised until evolution of propene was observed. Propene was passed through the reflux condenser at −30 °C and collected in a trap cooled at liquid-nitrogen temperature. Reaction was continued 4 h by warming at reflux temperature while stirring and stripping with a helium stream. The yield of [1-^{13}C]propene was 35% (based on $^{13}CH_3I$).

Enriched [3-^{13}C]propene (90%) was prepared as previously described.[10]

The ^{13}C-enriched monomers, after isotopic dilution, were purified by fractional distillation and subsequent treatment with $Al(C_2H_5)_3$. The monomer's purity which was checked by GLC on a Poropak Q column at 100 °C was higher than 99.9%.

Polymerization Runs. Soluble catalytic systems were prepared by mixing reagents (VCl_4, 5×10^{-4} mol; anisole, 5×10^{-4} mol; $Al(CH_3)_2Cl$,[18] 5×10^{-3} mol in 15 mL of toluene at −78 °C under nitrogen atmosphere). Reaction vessels were then cooled at liquid nitrogen temperature and evacuated at 10^{-4} mmHg. Subsequently, the proper amount of 10% enriched [1-^{13}C]propene or 30% enriched [3-^{13}C]propene was admitted and the temperature raised to −78 °C. After 24 h, the polymerizations were stopped by adding dropwise, under nitrogen atmosphere, HCl-acidified methanol. Care was taken to exclude air in order to prevent oxidation of reactive metal–carbon bonds from occurring instead of hydrolysis. The reaction mixture was left to stand at room temperature for 3 h. Finally, polymers were precipitated with excess methanol, purified by being dissolved in hot toluene and reprecipitated with methanol, and dried in high vacuum at 70 °C. The polymer yield was 0.4 g.

NMR Analysis of Polymers. Samples were prepared by dissolving the polymers in 1,2,4-trichlorobenzene and by adding 1% of hexamethyldisiloxane (HMDS) as an internal reference. Samples were placed in 10-mm o.d. tubes containing a coaxial capillary of deuterated dimethyl sulfoxide for field-frequency stabilization. Spectra were measured with an HX270 Bruker spectrometer operating at 67.88 MHz in the PFT mode. The temperature of the probe was 100 °C. A dwell time of 66 s was used with 16K of computer memory for the interferogram, corresponding to an acquisition time of 1.081 s and to a digital resolution of 0.0136 ppm/point. The pulse width was 10 s (the pulse width for a 90° pulse for the nucleus being examined is 30 s).

Acknowledgment. Thanks are due to Mr. G. Zannoni for technical assistance in performing NMR spectra.

References and Notes

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

(2) A. Zambelli, A. Lēty, C. Tosi, and I. Pasquon, *Makromol. Chem.*, **115**, 73 (1968).

(3) A. Zambelli, M. G. Giongo, and G. Natta, *Makromol. Chem.*, **112**, 183 (1968).

(4) A. Zambelli, C. Tosi, and M. C. Sacchi, *Macromolecules*, **5**, 649 (1972).

(5) A. Zambelli, "NMR Basic Principles and Progress", Vol. 4, Springer, New York, 1971; A. Zambelli, C. Wolfsgrüber, G. Zannoni, and F. A. Bovey, *Macromolecules*, **7**, 750 (1974).

(6) F. A. Bovey, M. C. Sacchi, and A. Zambelli, *Macromolecules*, **7**, 752 (1974).

(7) A. Zambelli, G. Bajo, and E. Rigamonti, *Makromol. Chem.*, **179**, 1249 (1978).

(8) A. Zambelli, P. Locatelli, G. Bajo, and F. A. Bovey, *Macromolecules*, **8**, 687 (1975).

(9) A. Zambelli, P. Locatelli, and G. Bajo, *Macromolecules*, **12**, 154 (1979).

(10) A. Zambelli, P. Locatelli, and E. Rigamonti, *Macromolecules*, **12**, 156 (1979).

(11) A. Zambelli and C. Tosi, *Adv. Polym. Sci.*, **15**, 38 (1974).

(12) See, e.g., J. Boor, Jr., *J. Polym. Sci., Part D*, **2**, 115 (1967).

(13) K. J. Ivin, J. J. Rooney, C. D. Stewart, M. L. H. Green, and R. Mahtab, *J. Chem. Soc., Chem. Commun.*, 604 (1978); K. J. Iving, *Proc. Eur. Symp. Poly. Spectrosc.*, **11**, 267 (1978).

(14) G. Natta, P. Pino, E. Mantica, F. Danusso, G. Mazzanti, and M. Peraldo, *Chim. Ind. (Milan)*, **38**, 124 (1956).

(15) T. Asakura, I. Ando, A. Nishioka, Y. Doi, and T. Keii, *Makromol. Chem.*, **178**, 791 (1977).

(16) Y. Doi, *Macromolecules*, **12**, 248 (1979).

(17) W. O. Crain, Jr., A. Zambelli, and J. D. Roberts, *Macromolecules*, **4**, 330 (1971).

(18) As shown in a preceding paper,[10] use of catalytic systems based on Al–methyl derivatives is required in order to obtain isopropyl end groups in the polymer chain. In fact, these are formed during the first primary monomer insertion on an Mt–methyl bond.

(19) After this paper was submitted for publication, a paper appeared in the literature where converging evidences are achieved by a different approach: E. R. Evitt and R. G. Bergman, *J. Am. Chem. Soc.* **101**, 3973, (1979).

Epitaxial Polymerization of $(SN)_x$. 1. Structure and Morphology of Single Crystals on Alkali Halide Substrates

S. E. Rickert, J. B. Lando,* A. J. Hopfinger, and E. Baer

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio.
Received June 25, 1979

ABSTRACT: S_2N_2 vapor was epitaxially crystallized on a variety of alkali halide substrates. The resulting platelet crystals were allowed to polymerize in the solid state while on the substrates to form $(SN)_x$ single crystals. The polymer chains were always parallel to the ⟨110⟩ directions on the surface, but only one chain direction was observed from each monomer crystal. While the usual α form of $(SN)_x$ was the structure obtained on KCl, a novel γ form was discovered from growth on NaF and KI. Lattice matching between the polymer chains and the ⟨110⟩ substrate spacings can explain these structures. Two projections of each structure were observed and explained by proposing two independent nucleation mechanisms.

Much interest has been generated in the past several years regarding the inorganic polymer, polythiazyl (better known as poly(sulfur nitride) or $(SN)_x$). Burt first reported synthesizing this polymer in 1910,[1] but for many years it was relatively ignored. In 1956, Goehring reported that the polymer could conduct electricity,[2] and the work was further developed by Kronick et al.[3] in 1962. Kronick also reported that S_2N_2, the cyclic dimer of sulfur nitride which is the reactive species, was highly unstable in its crystalline form. There the studies remained until intense work was initiated into the electrical conductivity of the polymer by groups at IBM,[4,5] the University of Pennsylvania,[6,7,11] Temple University,[8,9] and others.[10] Concurrently, various groups in France[12] and at Allied Chemical[13-15] studied the poly(sulfur nitride) crystal structure and polymerization mechanism of the solid state reaction.

We became interested in polythiazyl when it became apparent that increased crystal perfection in $(SN)_x$ would

0024-9297/79/2212-1053$01.00/0