a previous paper.[4] Relative peak areas were determined using a Du Pont analog curve resolver. The samples were examined in 1,2,4-trichlorobenzene (10-15 wt %) at 130° using a Varian XL-100 spectrometer operating at 25 MHz in the F.T. mode. d_6-Dimethyl sulfoxide was used as external standard and lock.

Conclusion

The results of the comparison of activation barriers for the syndiotactic polymerization of propylene are shown in Table II and may be summarized as follows. (i) Syndiotactic propagation should be favored over isotactic propagation and over the formation of tail-to-tail units (—● ●—) by differences in activation energy of 2.3 and 1.3 kcal/mol, respectively. Sterically disordered propagation should be favored over the formation of head-to-head units (●— —●) by a difference in activation energy of 1.6 kcal/mol. (ii) Formation of tail-to-tail units should be the necessary step for the restoration of syndiotactic steric control. (iii) The activation energies of steric control and head-to-head *vs.* head-to-tail arrangement forces are comparable. Preexponential factors are likewise important for steric control. (iv) The two catalyst systems employed, *i.e.*, with and without anisole, show essentially identical behavior. It may be noted that the interpretation of these experimental data is dependent on the hypotheses concerning chain growth outlined in the introductory section. These hypotheses are supported by previous studies[3-5] and by paper IX of this series.[9]

References and Notes

(1) Istituto di Chimica delle Macromolecole del CNR.
(2) Bell Laboratories.
(3) A. Zambelli, C. Tosi, and C. Sacchi, *Macromolecules*, **5**, 649 (1972).
(4) A. Zambelli, D. E. Dorman, A. I. R. Brewster, and F. A. Bovey, *Macromolecules*, **6**, 925 (1973).
(5) A. Zambelli and C. Tosi, *Advan. Polym. Sci.*, in press.
(6) The stereochemical *n*-ad notation is the one proposed by H. L. Frisch, C. L. Mallows, and F. A. Bovey, *J. Chem. Phys.*, **45**, 1965 (1966).
(7) See, for instance, G. E. Ham, "High Polymers," Vol. 18, Wiley-Interscience, New York, N. Y., 1964.
(8) A. Zambelli, G. Natta, and I. Pasquon, *J. Polym. Sci., Part C*, **4**, 411 (1963).
(9) F. A. Bovey, M. C. Sacchi, and A. Zambelli, *Macromolecules*, **7**, 752 (1974).

Polymerization of Propylene to Syndiotactic Polymer. IX. Ethylene Perturbation of Syndiotactic Propylene Polymerization

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ABSTRACT: The microstructure of ethylene-propylene copolymers, prepared in the presence of syndiospecific vanadium-based catalyst systems, has been examined by ^{13}C nmr. The decrease in the fraction of *rrrr* methyl pentads when a propylene unit is replaced by an ethylene unit is interpreted with regard to the mechanism of steric and arrangement control previously proposed.

In a previous paper[3] it was shown that the polymerization of propylene to syndiotactic polymer in the presence of homogeneous catalyst systems occurs mainly by *secondary* monomer insertion, that is, it gives rise to a growing chain ending in a substituted carbon

Me ●— ··· + C_3H_6 ⟶ Me ●— ●— ···

(Here —● and ●— mean $-CH_2CH(CH_3)-$ and $-CH(CH_3)CH_2-$ units, respectively; Me denotes the metal atom of the catalytic complex bonded to the growing chain end.) This conclusion was reached by consideration of the proportion of $(CH_2)_2$ sequences (*i.e.*, sequences of two methylenes bound on both sides to $CHCH_3$ groups[3]) in ethylene–propylene copolymers prepared with syndiotactic specific catalysts.

The aim of the present work is to determine whether such results are consistent with the perturbation of the steric pentads[4] as detected by ^{13}C nmr in such copolymers. The structure of a vinyl polymer chain can be described as a succession of steric *n*-ads[4] provided that the monomer units are regularly arranged in head-to-tail fashion. Syndiotactic polypropylene, obtained in the presence of homogeneous vanadium-based catalysts, also contains head-to-head and tail-to-tail monomer units.[3] A complete description of such chains, which probably consist of blocks of monomer units having different arrangements

··· ●— ●— ●— —● —● ··· —● ●— ●— ●— ···

is not possible in terms of steric *n*-ads only.

Clearly, the same considerations also apply to ethylene–propylene copolymers, making a detailed description of such chains rather complex. However, it is possible to compare the steric composition of such macromolecules by describing them in terms of blocks of equivalent, regularly arranged monomer units.

Results and Conclusions

We have determined the proportion of *rrrr* pentads[5] by measurements in the methyl region of the ^{13}C nmr spectra of a series of ethylene–propylene copolymers prepared using the syndiospecific catalyst VCl_4-$Al(C_2H_5)_2Cl$ and ranging in composition between 0 and 12 mol % ethylene (Table I). These measurements are based on the assumption that the reasonance at 172.5_9 ppm (from $^{13}CS_2$)[6] is always exclusively due to the methyl groups of *rrrr* pentads. Table I also shows the proportion of $(CH_2)_2$ sequences as detected by infrared analysis.[3] Such $(CH_2)_2$ sequences originate partly from ethylene units (—) in the arrangement —● — ●— and partly from propylene units in a head-to-head arrangement (●— —●). Part of the ethylene of such copolymers also gives rise to $(CH_2)_3$ sequences (●— — ●— or —● — —●), while longer sequences of methylenes are negligible due to the composition of the copolymers considered here. Table II gives the estimated proportion[3] of ethylene in the structures we are considering.

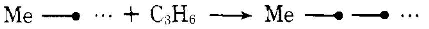
Because of the stereoblock structure of the syndiotactic propylene homopolymers, one could in principle distinguish a syndiotactic propagation process and a stereoirreg-

Table I
Ethylene-Propylene Copolymers

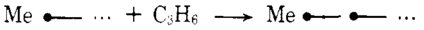
Run	$[C_2H_4]$, mol fraction	$[rrrr]$, mol fraction^a	$[(CH_2)_2]$, g/100 g polymer
a	0	0.51	1.4
b	0.016	0.43	3.5
c	0.027	0.37	4.3
d	0.054	0.28	7.9
e	0.119	0.07	11.2

^{a} Calculated on total monomer units (ethylene + propylene).

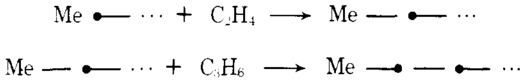
ular propagation process.[7] Therefore, one might assume that, contrary to what was previously stated,[3] syndiotactic propagation could occur through primary monomer insertion



and stereoirregular propagation through secondary insertion.



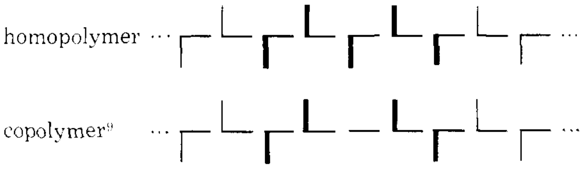
If this were the case, an ethylene could give rise to one $(CH_2)_2$ sequence only by addition during the stereoirregular propagation, followed by primary insertion of one propylene molecule; this primary insertion of propylene would probably initiate one syndiospecific propagation step



The $(CH_2)_3$ sequences could be generated in either syndiospecific or stereoirregular propagation processes.

It is evident that, under this hypothesis, the ethylene in $(CH_2)_2$ sequences would entail no decrease in the molar fraction of *rrrr* pentads in the copolymers and perhaps even an increase because of the switch from secondary (stereoirregular) to primary (syndiospecific) propylene insertion.[8]

Each ethylene in a $(CH_2)_3$ sequence should entail a maximum decrease of five *rrrr* pentads, provided that all such sequences are formed during syndiospecific propagation and that they all occur two or more positions from the ends of a block of syndiotactic propylene units. It can be readily seen that the ^{13}C nmr resonances of the four methyls marked with heavy lines below could be observably shifted from their normal positions when an ethylene unit is inserted as shown



In Figure 1, we have plotted the quantity $[rrrr] + 5E_{(CH_2)_3}$ against $[C_2H_4]$, where $[rrrr]$ is the mole fraction of this pentad, as measured at the unperturbed peak position, $E_{(CH_2)_3}$ is the mole fraction of ethylene involved in $(CH_2)_3$ sequences, and $[C_2H_4]$ is the total mole fraction of ethylene incorporated into the copolymer. If the presence of an isolated ethylene unit always causes the removal of just five *rrrr* methyl resonances from their normal positions, as suggested,[10] such a plot should correspond to the horizontal dotted line at 0.51. If the points fall below this line the ethylene units must be removing *more* than five methyls, while if they fall above it *less* than five are being removed. It will be observed that over the whole range examined the points are well *below* the line, so that the decrease in *rrrr* pentads cannot be caused only by $(CH_2)_3$ sequences but must be caused, at least partially and most probably entirely, by $(CH_2)_2$ ethylene sequences. This means that ethylene in $(CH_2)_2$ sequences is more effective in removing *rrrr* methyl pentads and can be most readily explained in terms of the following previously suggested hypotheses.

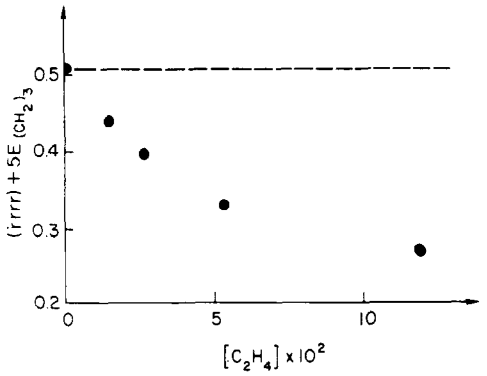


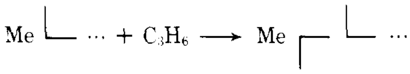
Figure 1. The quantity $(rrrr) + 5E_{(CH_2)_3}$, where $(rrrr)$ is the fraction of *rrrr* pentads observed at the homopolymer chemical shift position and $E_{(CH_2)_3}$ is the fraction of ethylene comonomer observed in $(CH_2)_3$ sequences, is plotted against $[C_2H_4]$, the total mole fraction of ethylene in the copolymers. As described in the text, the formation of $(CH_2)_3$ sequences is inadequate to explain the decrease in *rrrr* pentads.

Table II
Arrangements of Ethylene in the Copolymers

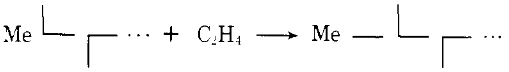
Run	$E_{(CH_2)_2}$,^{a} mol fraction	$E_{(CH_2)_3}$,^{b} mol fraction
a	0	0
b	0.014	0.002
c	0.021	0.006
d	0.040	0.014
e	0.079	0.040

^{a} $E(CH_2)_2 = C_2H_4$ in —•—•— arrangement. ^{b} $E(CH_2)_3 = C_2H_4$ in either —•——• or •——•— arrangement.

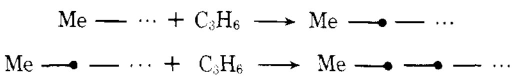
(1) Syndiotactic propylene addition occurs at a chain ending in a tail ($-CHCH_3$) unit.[3,8]



(2) Most ethylene units are added to tail-ending chains, so that they usually occur after a syndiotactic propylene block.[11]



(3) When a propylene is added to a methylene-ending (*i.e.*, head ending or ethylene ending) chain, a new methylene-ending chain is preferably but not invariably obtained.[12]



(4) Addition of propylene to a methylene-ending chain, giving a tail-ending chain (and a head-to-head junction), restores syndiotactic control thereafter.[11]

These findings are also in agreement with the fact that syndiotactic propylene homopolymers prepared in the presence of homogeneous vanadium catalysts consist of long syndiotactic blocks and shorter stereoirregular blocks.[11]

It might appear that a number of hypotheses could explain the observed experimental results and that our own conclusions are not rigorously based. This cannot be entirely denied. Nevertheless, one can easily convince oneself simply by drawing chain structures involving syndiotactic propagation occurring by primary insertion that it is not particularly easy to rationalize the observed experimental facts, *i.e.*, the proportion of $(CH_2)_2$ sequences in the copolymers,[3] the effect of ethylene on stereoregulation, and the stereoblock character of the syndiotactic homopolymers. A more detailed discussion of these hypotheses has been given in a previous review.[11]

Experimental Section

The ethylene–propylene copolymers and propylene homopolymer were prepared in liquid monomer at −78° using the VCl_4 (0.001 mol)-$Al(C_2H_5)Cl$ (0.01 mol) catalyst system described in a previous paper.[12] The polymer composition was evaluated by radiochemical analysis using ^{14}C-labeled ethylene. The $(CH_2)_2$ sequences were measured by infrared (13.30 μ band).[3] ^{13}C nmr analysis was carried out following the assignments of a previous paper[6] and under similar experimental conditions.[7]

References and Notes

(1) Bell Laboratories.

(2) Istituto di Chimica delle Macromolecole del CNR.

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

(4) H. L. Frisch, C. L. Mallows, and F. A. Bovey, *J. Chem. Phys.*, **45**, 1565 (1966).

(5) The stereochemical notation is that of Frisch, Mallows, and Bovey;[4] *m* = meso (isotactic dyad), *r* = racemic (syndiotactic dyad).

(6) A. Zambelli, D. E. Dorman, A. I. R. Brewster, and F. A. Bovey, *Macromolecules*, **6**, 925 (1973).

(7) A. Zambelli, C. Wolfsgruber, G. Zannoni, and F. A. Bovey, *Macromolecules*, **7**, 750 (1974).

(8) T. Suzuki and Y. Takegami, *Bull. Chem. Soc. Jap.*, **43**, 1848 (1970).

(9) Since steric control with syndiospecific catalysts does not bridge the intervening ethylene unit, the sequence

will also be generated. This does not affect our argument so long as one assumes a syndiotactic arrangement of propylene units on both sides of the ethylene unit.

(10) A referee has suggested that the effect of the central ethylene unit on the outer methyls of the pentad sequences shown may be less than an ϵ effect (nomenclature of D. M. Grant and E. G. Paul, *J. Amer. Chem. Soc.*, *86*, *2984 (1964)*) since in both homopolymer and copolymer they "see" the same number of carbon atoms within five bonds. If this were so, our conclusions would in fact be reinforced. The quantity plotted in Figure 1 would be $(rrrr) + 3E_{(CH_2)_3}$. It is not clear, however, that the argument from the Grant and Paul rules is conclusive. As an example of the incompleteness of these rules, it may be noted that they take no account of stereochemical configuration, the effects of which may be as large as 1.8–2.0 ppm.

(11) A. Zambelli and C. Tosi, *Advan. Polym. Sci.*, in press.

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

Dynamics of Poly(vinyl chloride). I. Infinite Perfect Model[1]

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ABSTRACT: A reanalysis of the dynamics and vibrational spectrum of poly(vinyl chloride) is presented in two papers one following the other. In paper I the dynamics of a translationally invariant infinite and isolated polymer chain is studied. Three most probable models of the polymer chain are considered. Dispersion curves and one-phonon density of states are calculated. $k = 0$ phonon frequencies are discussed in relation to the experimental spectrum. The problem of the force field and its influence on the results of the calculations is analyzed. The dynamical quantities calculated form the basis for a further analysis of the of the structure of PVC considered as conformationally and configurationally disordered material. This part of the problem is presented in paper II.

In the present paper (hereafter referred to as I) and in the following (hereafter referred to as II) the molecular dynamics of a single chain of poly(vinyl chloride) are considered. The dynamical properties of this material have already been the subject of several extensive investigations both from the experimental[3,4] and theoretical[5,6] viewpoints. In spite of the large amount of work, the dynamical properties as revealed from its vibrational spectrum and the corresponding structural features do not yet seem to be fully understood.

Practically all the previous authors have treated the normal modes of a translationally symmetrical, *i.e.*, structurally ordered, chain of PVC. The problem of the possible existence of different structures as revealed from the vibrational spectrum has been hinted and partially treated by several authors.[3-7] In the work we are reporting here we tackle the problem by treating the dynamics of a PVC chain containing configurational (tacticity) and conformational defects. When the concentration of such structural defects becomes large we deal with the dynamics of a disordered system.[8,9] It has already been shown that such an approach to polymer dynamics and polymer spectroscopy (infrared, Raman, and neutron scattering) provides the way to improve the interpretation of a few yet uninterpreted features of the experimental vibrational spectrum. Information on the structural properties of these materials can then be derived.[10-14]

In this paper (I) we briefly reanalyze the problem of a perfect PVC chain in order to determine some theoretical quantities which will be used in the analysis of the defect-containing or in the disordered chain. As already pointed out,[8] the vibrational analysis of a disordered material can be more easily performed if the vibrational spectrum of the ordered material is well known and is used as a reference point in the comparison. We have then calculated the phonon dispersion curves $\omega(k)$, the vibrational density of states $g(\omega)$, the $k = 0$ phonon frequencies, and the corresponding shape of the normal modes (from eigenvectors) for PVC in