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Polymerization in the Crystalline State. VII. A Crystallographic Study of the Radiation-Initiated Polymerization in Single Crystals of Vinyl Stearate[1,2]

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The crystal structure of vinyl stearate was determined and the nature of the radiation-induced solid-state polymerization of this monomer was studied by following changes in the X-ray diffraction patterns of single polymerized crystals. The monomer has a layer structure with vinyl groups lying in sheets separated by 25.4 Å. The chain propagation seems to proceed within these layers, and the parallel orientation of the stearate residues is preserved during this process. During polymerization, the side chains rotate around the b axis of the monoclinic crystal of the monomer and assume orientations almost perpendicular to the plane containing the monomer end groups; the packing of the side chains attains hexagonal symmetry in a manner similar to that characterizing allotropic phase transitions of paraffins in the neighborhood of their melting point. A discrete monomer phase is observed in crystals containing as much as 30% polymer but disappears at a 40% polymer content. Infrared spectral analysis indicates that poly(vinyl stearate) produced in the solid state is more isotactic than polymer prepared in a liquid phase. The manner in which the oriented side chains are attached to the chain backbone and the significance of low angle reflections observed with the polymer present problems which have not been resolved.

Introduction

The central question in the study of solid-state polymerizations is the definition of the extent to which the geometrical arrangement of the reactive functional groups in the monomer crystal determines the nature of the reaction product or the spatial orientation of the polymer chains. With a vinyl monomer, the disposition of the reactive double bonds allows, in general, many alternative ways in which the chain could propagate, and an evaluation of their relative probabilities would be exceedingly difficult, even if the monomer crystal structure were known in detail. The situation should be greatly simplified if the monomer crystal has a layer structure, so that the reactive vinyl groups lie in sheets widely separated from one another. In that case, it is reasonable to assume that the polymer chains can propagate only within these layers and the study of the geometry of the chain propagation is reduced from a three-dimensional to an effectively two-dimensional problem.

Molecules of vinyl stearate contain long paraffinic residues which tend to lie parallel to one another in the crystal, so that the crystals have a layer structure. A study of the solid-state polymerization of this substance[4] offers an additional advantage. It has been shown that vinyl polymers carrying long aliphatic hydrocarbon side chains exhibit the phenomenon of "side-chain crystallization," *i.e.*, the side chains pack into paraffin-like crystallites, even if the backbone of the

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(1) Abstracted from a Ph.D. thesis submitted by N. Morosoff to the Graduate School, Polytechnic Institute of Brooklyn, June 1965. Financial support of this investigation by the U. S. Atomic Energy Commission (Contract AT-(30-1)-1715) and by the National Science Foundation (Project 2271-NSF-7503) is gratefully acknowledged.

(2) For the preceding paper in this series and pertinent references, see J. H. O'Donnell, B. McGarvey, and H. Morawetz, *J. Am. Chem. Soc.*, **86**, 2322 (1964).

(3) To whom communications should be addressed.

(4) (a) A. J. Restaino, R. B. Mesrobian, H. Morawetz, D. S. Ballantine, G. J. Dienes, and D. J. Metz, *J. Am. Chem. Soc.*, **78**, 2939 (1956); (b) W. Burlant and A. Adicoff, *J. Polymer Sci.*, **27**, 269 (1958).

polymer to which they are attached is not stereoregular.[5–7] It is therefore possible to use crystallographic methods for ascertaining the extent to which the orientation of these side chains is preserved when vinyl stearate is polymerized in the solid state.

In the present work we have determined the crystal structure of vinyl stearate as a point of departure which would make it possible to consider in detail the nature of the solid-state polymerization of this monomer. The changes in the X-ray diffraction pattern of a single monomer crystal were then followed as a function of the degree of conversion to polymer. A spectroscopic method was employed to compare the stereoregularity of polymers obtained when the polymerization was carried out in the solid and the liquid state. The data show not only that the parallel arrangement of the long axes of the stearate residues is preserved during the polymerization, but also that the side-chain crystallites retain a considerable degree of mutual orientation in all crystallographic directions. Polymerization in the solid state seems to lead to a more isotactic product than the reaction of the molten monomer.

Experimental

Monomer Preparation. Commercial vinyl stearate was found to contain impurities which were difficult to remove even by repeated recrystallization. The monomer was, therefore, synthesized from stearic acid purified by crystallization from concentrated sulfuric acid, followed by three recrystallizations from glacial acetic acid. The vinyl stearate was then obtained by ester interchange of vinyl acetate with stearic acid using mercuric acetate and 100% sulfuric acid to catalyze the reaction.[8] The product was distilled at a pressure of 1 mm., collecting the fraction boiling at 147–155°. The monomer was recrystallized from acetone (m.p. 34.6–35.6°, lit.[8] 35–36°). Single crystals for crystallographic studies were grown by slow evaporation of solutions containing 2 g. of vinyl stearate in 35 ml. of acetone containing 3.5 ml. of water.

Monomer Crystal Structure Studies. Preliminary examinations of the crystals were carried out on Weissenberg and precession cameras using Ni-filtered Cu radiation. Lattice constants were obtained from a diffractometer trace of a polycrystalline sample. Intensity data for the crystal structure analysis were taken on crystals cooled to $-45°$, to prevent polymerization in the X-ray beam, using a General Electric Co. XRD-5 single crystal goniostat employing Ni-filtered Cu radiation, a proportional counter, and pulse height discriminator. A total of 222 independent reflections were measured. The structure was determined by use of structure factor–electron density section iterations using IBM-7040 and IBM-7094 computers. Analysis of the monomer on a differential scanning calorimeter over the temperature interval from $-55°$ to the melting point indicated no solid-phase transition up to the temperature at which polymerizations were carried out.

Polymerization. Vinyl stearate samples sealed *in vacuo* and pre-irradiated with γ-rays from a Co^{60} source at $-78°$ were polymerized at 20°. This procedure was found to lead to variable polymerization rates, presumably because of the high sensitivity of the polymerization to traces of oxygen (which was found to inhibit the reaction) and to a variable concentration of crystal imperfections. Crystallographic studies were carried out on single crystals post-polymerized for several days after irradiation with 200,000 rads. Crystals exposed to the atmosphere and placed before a collimated X-ray beam, so that only a portion of the crystal was irradiated (for 100 hr. at room temperature), were sometimes found to give diffraction spots typical of crystals post-polymerized after γ-irradiation, superimposed on the monomer diffraction pattern. (The assumption that X-ray irradiation in the atmosphere leads to polymerization was strengthened by the observation that this treatment produces an acetone-insoluble fraction.) Such crystals were used to characterize the relative orientation of the monomer and the polymer resulting from it.

Crystallographic Study and Characterization of Partially Polymerized Single Crystals. Partially polymerized single crystals of vinyl stearate were studied by the use of X-ray precession photographs and of rotation, oscillation, and Weissenberg photographs taken on a Weissenberg camera with a 5.73-cm. diameter. Accurate data for low angle reflections were obtained from oscillation photographs using a flat plate camera with a 9.94-cm. distance between sample and plate and by use of the single crystal goniostat. To obtain data on samples with a known polymer content, a number of similar single crystals contained in a vial were post-polymerized as described above. Some of the crystals were melted and their polymer content was estimated by comparing the infrared spectrum in the 1750- to 1650-cm.$^{-1}$ region with the spectra of synthetic mixtures of monomer and polymer. This region contains the C=O stretching vibration which lies at 1766 cm.$^{-1}$ for the monomer and at 1750 cm.$^{-1}$ for the polymer, as well as the C=C stretching vibration at 1650 cm.$^{-1}$. This analysis is relatively accurate ($\pm 2\%$) in samples containing more than 50% polymer; at lower polymer content the experimental error is considerably larger. It was assumed that this analysis is representative of the crystal taken from the vial for X-ray analysis.

Estimation of Tacticity of Poly(vinyl stearate). To determine the tacticity of poly(vinyl stearate), the polymer was converted to poly(vinyl alcohol) which may be analyzed by infrared spectroscopy.[9] The poly(vinyl stearate) was dissolved in butanol at 100° under a nitrogen atmosphere, and 0.25 equiv. of sodium butylate was added per base mole of the polymer. The mixture was maintained for 30 min. at 100° and for 6–16 hr. at 55°. A small amount of material precipitated within 5 min. after the addition of the sodium butylate. The reaction mixture was cooled and centrifuged. Water was added to the precipitate and the aqueous phase was separated, if possible. The system was vacuum dried and extracted with methanol to remove residual sodium stearate. After vacuum drying, the sample was incorporated into a KBr pellet for infrared spectral analysis. Commercial poly-

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[5] H. S. Kaufman, A. Sacher, T. Alfrey, Jr., and I. Fankuchen, *J. Am. Chem. Soc.*, **70**, 3147 (1948).

[6] S. A. Greenberg and T. Alfrey, Jr., *ibid.*, **76**, 6280 (1954).

[7] M. G. Broadhurst, E. R. Fitzgerald, and A. J. Bur, *J. Appl. Phys.*, **32**, 972 (1961).

[8] D. Swern and E. F. Jordan, *Org. Syn.*, **30**, 106 (1950).

[9] K. Fujii and J. Ukida, *Makromol. Chem.*, **65**, 74 (1963).

(vinyl alcohol) used for comparison was DuPont Elvanol, Grade 70-05, with a molecular weight of 14,000.

Results

Crystal Structure of the Monomer. The monomer crystal is monoclinic, space group Pa. At −45°, the unit cell dimensions are a = 5.57, b = 7.25, c = 28.8 Å., β = 118°. The crystals have the form of thin platelets with the large face parallel to the ab plane. At 20°, the dimensions of a and c are essentially unchanged from the low temperature values, but b is found to have increased in length to 7.4 Å. The details of the structure will be discussed in a separate publication.[10] The structure is similar to that of other esters of long-chain paraffinic acids with the paraffinic chains fitting into an orthorhombic subcell and the end groups lying in the 101 plane of the subcell. The subcell dimensions for vinyl stearate at −44° are a' = 4.99, b' = 7.25, c' = 2.55 Å. The arrangement of the molecules in the unit cell is represented in the projections shown in Figures 1a and b, which shows also the relation of the subcell to the unit cell. The structure is similar to that of ethyl stearate[11] except for the conformation of the ester groups (Figure 2). The monomer crystal has a layer structure with the vinyl groups lying in planes separated by 25.4 Å. The long axis of the molecules is parallel to the a–c plane and at an angle of 63° to the a–b plane. The disposition of the vinyl groups is shown in Figure 1b and their distances from each other are listed in Table I.

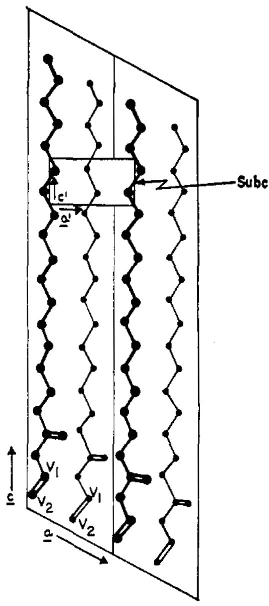

Figure 1a. Vinyl stearate structure: projection parallel to the b axis showing two unit cells and an orthorhombic subcell.

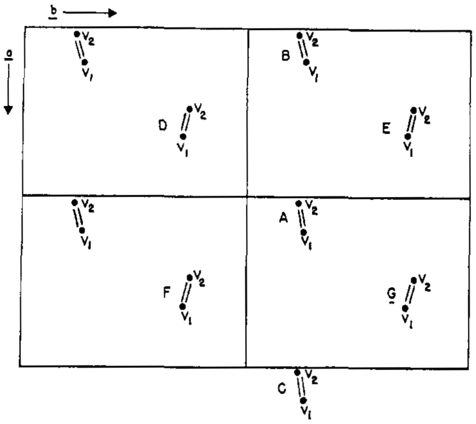

Figure 1b. Vinyl stearate structure: disposition of vinyl groups in a projection perpendicular to the ab plane.

Table I. Vinyl Contact Distances[a]

Designation	Distance, Å.	Designation	Distance, Å.
V_2(A)–V_2(C)	5.57	V_2(A)–V_1(B)	5.58
V_2(A)–V_2(D)	4.35	V_2(A)–V_1(C)	5.87
V_2(A)–V_2(E)	4.81	V_2(A)–V_1(D)	4.69
V_2(A)–V_2(F)	4.35	V_2(A)–V_1(E)	4.64
V_2(A)–V_2(G)	4.81	V_2(A)–V_1(F)	4.86
		V_2(A)–V_1(G)	4.82

[a] See Figure 1b for atomic designations.

X-Ray Observations on Post-Polymerized Single Crystals. The two most intense reflections in the powder pattern of vinyl stearate are the (110) reflections corresponding to a spacing of 4.1 Å. and the (020) reflection corresponding to a spacing of 3.7 Å. These intense reflections are typical of paraffins and paraffinic derivatives crystallizing with the paraffinic chains in an orthorhombic subcell. The powder pattern of poly(vinyl stearate), whether produced by solid-state polymerization or by more conventional methods, contains one intense line corresponding to a spacing of 4.2 Å.[12] Such a single intense reflection is common to many paraffins and paraffinic derivatives just below their melting points and is characteristic of a hexagonal crystal modification.[13]

Müller[14] showed that in some paraffins the b axis of the orthorhombic subcell increases on heating until the angle between the (110) and (1$\bar{1}$0) planes attains a value of 60°, thus transforming the originally orthorhombic subcell to a hexagonal subcell. The two are shown in Figure 3. In other paraffins the transition to hexagonal packing occurs discontinuously at a phase transition temperature. The hexagonal packing would be the result expected from rotation of paraffin chains around the long axis of the paraffins, which may be demonstrated by a variety of techniques.[15–17] It would be reasonable to assume that such a hexagonal subcell accounts also for the single 4.2-Å. reflection of poly(vinyl stearate). However, since it has been demonstrated that the side chains of the polymer do not rotate,[7] it is assumed that the axes of the side chains lie parallel to each other but with random orientations of the plane defined by the paraffinic zig-zag chain about the chain axis.

If the solid-state polymerization of vinyl stearate were to occur with retention of orientation and if the hexa-

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(10) N. Morosoff and B. Post, in preparation.

(11) S. Aleby, *Acta Cryst.*, **15**, 1248 (1962).

(12) D. A. Lutz and P. Witnauer, *J. Polymer Sci.*, **B2**, 31 (1964).

(13) A. A. Scheuer, G. G. Bayle, and W. M. Mazee, *Rec. trav. chim.*, **75**, 513 (1956).

(14) A. Müller, *Proc. Roy. Soc.* (London), **A138**, 514 (1932).

(15) A. M. King and W. E. Garner, *J. Chem. Soc.*, 1368 (1936).

(16) W. O. Baker and C. P. Smyth, *J. Am. Chem. Soc.*, **60**, 1229 (1938).

(17) R. F. Grant and D. L. Williams, *Can. J. Chem.*, **41**, 378 (1963).

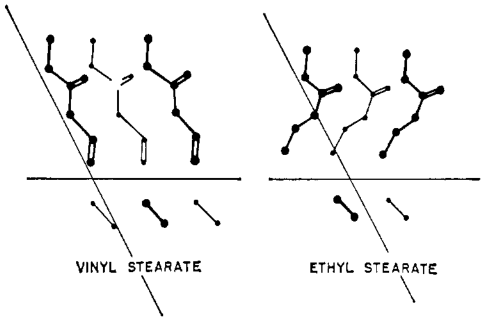

Figure 2. Projections parallel to the *b* axis showing the ester group regions of ethyl stearate[11] and vinyl stearate.

gonal unit cell described above were to be adopted, it would be expected that partially polymerized and properly oriented single crystals would give X-ray photographs showing six discrete reflections from planes at angles of 60° with respect to each other, these corresponding to a 4.2-Å. spacing. Moreover, it would be expected that two of these discrete reflections would be oriented in the same direction as the (020) reflection of the monomer. Both of these expectations were realized in the X-ray photographs of partially polymerized single crystals of vinyl stearate described below.

X-Ray photographs were taken of single crystals in which about 30, 40, 50, and 80% of the monomer had been converted to polymer. The crystals with a 30 and 40% conversion were studied in detail. The crystal containing 30% polymer was observed to have curled somewhat and under the microscope it gave a textured appearance as if the curled crystal were made of small subdivisions, held together loosely. An oscillation photograph taken on a Weissenberg camera with the crystal oscillating around the *a* axis, and with a mean orientation such that the X-ray beam was perpendicular to the large face of the crystal, showed two rings corresponding to spacings of 4.2 and 3.7 Å., respectively. Six discrete and intense spots were superimposed on the 4.2-Å. rings. These six reflections correspond to coplanar reciprocal lattice points; the reciprocal lattice plane contains the rotation axis and the six reciprocal lattice points which form a regular hexagon. In addition, two discrete spots having the same orientation as two of the 4.2-Å. reflections are superimposed on the 3.7-Å. ring. An oscillation photograph, with the mean orientation of the crystal relative to the X-ray beam displaced by 90°, revealed greatly decreased intensities for four of the 4.2-Å. reflections and no sign of the remaining two 4.2-Å. or of the 3.7-Å. reflections. This indicates a considerable degree of biaxial orientation. This oscillation photograph also revealed the presence of several low angle reflections of three types. One type consisted of arcs indicating a disorientation of at least 40°. These were found to correspond to orders of the 25.4-Å. (001) spacing of the monomer. The other two types of reflections were discrete spots indicating no disorientation and appeared to correspond to the long spacings discussed in detail for the 40% polymerized single crystal.

The single crystal converted to a 40% polymer content did not appear to have curled and had a smooth surface. It differed in appearance from unpolymerized crystals in that it was milky, as contrasted to the clear transparent monomer, and did not exhibit birefringence under the polarizing microscope. The aligned rotation photograph of this crystal showed only one spacing giving rise to intense reflections. Six spots corresponding to the 4.2-Å. hexagonal reflections were observed. Bernal chart readings showed that these reflections could be interpreted in terms of a reciprocal lattice plane containing both the axis of rotation and the six (100) hexagonal reciprocal lattice points. (A precession photograph taken on another crystal, with unknown conversion, substantiated this interpretation.) Additional spots in the rotation photograph corresponded to (110) and (200) reflections of the hexagonal lattice. A zero-layer and first-layer Weissenberg photograph of the 4.2-Å. reflections were taken to determine the extent of biaxial orientation. The zero-layer photograph shows a reflection extending over 14°. The first-layer photograph shows two adjacent reflections, whose centers are displaced by about 15°, each extending over about 10°. It is suggested that the zero layer, exhibiting only one orientation, corresponds to the orthorhombic (020) reflection, whereas the first-layer reflections which exhibit two orientations correspond to the orthorhombic (110) reflections of the monomer subcell.

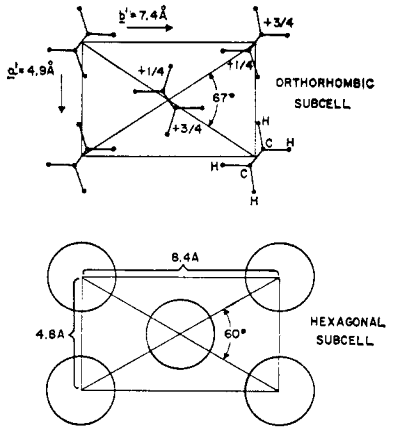

Figure 3. Expansion of the *b'* axis in the orthorhombic subcell of *n*-paraffins to form a hexagonal subcell. Projections of both subcells are parallel to the *c'* axis (circles in the hexagonal subcell projection trace loci of the centers of the hydrogen atoms).

Oscillation photographs taken on a Weissenberg camera, with the large face of the crystal approximately parallel to the X-ray beam, revealed the presence of two types of long spacings: one set consisted of extremely sharp diffraction peaks; the other consisted of relatively broad maxima. Data obtained with the Weissenberg and a flat plate camera as well as with a goniostat were within experimental error. The long spacings are listed in Table II. The 27-, 8.98-, and 6.7-Å. spacings are the first, third, and fourth orders of a 27-Å. spacing. The remaining three reflections, corresponding to 16.0-, 9.84-, and 7.06-Å. spacings, are not so easily interpreted. Similar spacings have been observed previously in powder diagrams of poly(vinyl stearate).[12] The goniostat readings indicated that the intensity of the reflection corresponding to the 27-Å. spacing was very sensitive to the relative orientation of the crystal and the X-ray beam. By contrast, the intensity of the diffuse 16-Å. reflection was found to remain constant (with stationary counter), while the crystal was rotated through an angle of 20°.

Table II. Long Spacings Observed in Vinyl Stearate Containing 40% Polymer

Spacings, Å.	Description
27.0 ± 0.1	Narrow
16.0 ± 0.3	Broad
9.84 ± 0.03	Broad
8.98 ± 0.02	Narrow
7.06 ± 0.06	Very weak
6.74 ± 0.05	Very weak

Rotation and oscillation photographs of crystals containing 50 and 80% of polymer indicated that both the 4.2-Å. hexagonal lateral spacings and the long spacings noted in the 40% polymerized crystals are retained. However, no careful measurements of the diffraction angles of the low angle reflections were carried out.

Insight into the reorientation process, induced by polymerization, was obtained by X-ray studies of a single crystal, a portion of which was polymerized in a collimated X-ray beam. The unpolymerized crystal was aligned and oriented on a precession camera so as to yield an (*hk*0) precession photograph. A second precession photograph taken with the crystal in the same orientation (after polymerizing a portion of the crystal) contained the two- (020) and the four- (110) type reflections of the monomer with the addition of two diffuse 4.2-Å. reflections on the (0*k*0) axis of the photograph. The six diffuse 4.2-Å. reflections in an hexagonal array, as well as two (020) monomer reflections were observed in a photograph taken with the large crystal face oriented from 70 to about 90° relative to the X-ray beam. A first-layer Weissenberg photograph with the crystal rotating about its *b* axis revealed that the additional four diffuse reflections had a 20° spread, indicating an orientation of the chains in the polymerized portion of the crystal ranging from 70 to 90° to the *ab* plane of the monomer.

Steric Configuration of Polymer. The infrared spectra of poly(vinyl alcohol) obtained by the alcoholysis of poly(vinyl stearate) samples prepared by polymerization in the melt or in the solid state were compared with the spectrum of commercial poly(vinyl alcohol). The ratio of the absorbance at 916 and 850 cm.$^{-1}$ was found to be 0.20 in the commercial poly(vinyl alcohol), as against 0.25 and 0.13 in poly(vinyl alcohol) derived from poly(vinyl stearate) polymerized in the melt and in the solid state, respectively. The ratio D_{916}/D_{850} was once believed to increase with increasing syndiotacticity,[9] but this analysis was recently shown to be unreliable.[18] Unfortunately, the samples at our disposal were insufficient for a determination of tacticity by nuclear magnetic resonance.[18]

Discussion

Solid-state reactions in which molecules of the reaction product are oriented with respect to crystallographic directions of the parent crystal ("topotactic" reactions) are fairly common in inorganic processes,[19a] but only a few organic reactions of this type have been reported. Among these, particular interest attaches to the conversion of single crystals of trioxane to polyoxymethylene whose crystallites are highly oriented with respect to crystallographic directions of the monomer.[19b] The retention of orientation during this polymerization process is probably favored by the very small heat of reaction,[20] and the question arises, therefore, whether the formation of an oriented polymer is also possible in the case of solid-state polymerizations of vinyl derivatives, which would be expected to evolve about 15 kcal./mole of monomer consumed.

E.s.r. studies in this laboratory have demonstrated that it is possible to add at least one molecule of a vinyl monomer to a radical imbedded in a monomer crystal without loss of orientation.[2] It has also been shown that *p*-benzamidostyrene, whose molecules form hydrogen-bonded sheets in the crystalline state, may be polymerized so as to retain the infrared dichroism of the monomer crystal.[21] In the present investigation, the phenomenon of side-chain crystallization made it possible to follow in detail changes in the orientation and packing of the stearate residues during the polymerization of vinyl stearate in the crystalline state. No direct information could, however, be obtained which would reveal whether the chain backbone propagates in a preferred crystallographic direction.

The results of this study show that the stearate residues of vinyl stearate remain parallel to each other during the polymerization process. The packing of the paraffinic chains changes from orthorhombic to hexagonal, and at conversions above 40% the diffraction pattern of the monomer disappears entirely, suggesting that the residual monomer also adopts the hexagonal mode of packing. This behavior is not surprising, since it is known that impurities stabilize the hexagonal structure of *n*-paraffins and their derivatives.[22,23] The polymer itself adopts this structure because of restraints imposed on the side chains by their attachment to the polymer backbone. Even in the case of a highly stereoregular polymer with long paraffinic side chains, the hexagonal side-chain packing is observed under conditions of rapid crystallization.[24] Such packing will, of course, be favored more highly if a chain backbone with a low degree of stereoregulation reduces the order of the system. The monomer adopts the hexagonal form presumably because of the disruption of its crystal structure by the polymerization process. It should be noted that the transition to the hexagonal subcell occurs during the polymerization in the same manner as during the phase transitions of paraffins studied by Müller,[14] *i.e.*, by an expansion of the *b* axis. This explains the identical orientation of the (020) orthorhombic and two (100) hexagonal spots in the rotation photograph of the crystal containing 30% polymer and in the precession photograph of the crystal which was partly polymerized by X-rays.

Once the chains behave as if they had cylindrical symmetry (either because of "rotation" around their

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(18) K. C. Ramey and N. D. Field, *J. Polymer Sci.*, **B3**, 63 (1965).

(19) (a) L. S. D. Glasser, F. P. Glasser, and H. F. W. Taylor, *Quart. Rev.* (London), **16**, 343 (1962); (b) G. Carazzolo, S. Leghissa, and M. Mammi, *Makromol. Chem.*, **60**, 171 (1963).

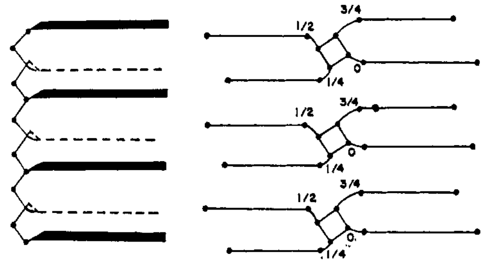
(20) H. Nauta, "Proceedings of the Fifth International Symposium on the Reactivity of Solids," R. Schwab, Ed., Elsevier Publishing Co., Amsterdam, in press.

(21) S. Z. Jakabhazy, H. Morawetz, and N. Morosoff, *J. Polymer Sci.*, **C4**, 805 (1964).

(22) M. G. Broadhurst, *J. Res. Natl. Bur. Std.*, **A66**, 241 (1962).

(23) Yu. V. Mnyukh, *Zh. Strukt. Khim.*, **1**, 370 (1960); *J. Struct. Chem.* (USSR), **1**, 346 (1960).

(24) A. T. Jones, *Makromol. Chem.*, **71**, 1 (1964).



a. SYNDIOTACTIC POLYMER

b. ISOTACTIC POLYMER

Figure 4. Schematic representations of packing expected for syndiotactic polymers with long side chains (view approximately perpendicular to planar main chain) and the packing suggested by Jones[24] for isotactic polymers with long side chains (view parallel to axis of main chain helix).

long axes or because of a random orientation of the planes defined by the zig-zag of the paraffinic chains) the preferred packing should require chain ends to lie in planes perpendicular to the chain axes. This principle is obeyed in, *e.g.*, ethyl stearate, for which a hexagonal phase with a long spacing of 26.6-Å. is stable within 8° of the melting point, while the stable phase at lower temperature is monoclinic with a spacing of 25.5 Å. between planes containing the end groups.[25] In the case of the polymerization of the vinyl stearate, the side chains seem to rotate around the *b* axis, but they remain parallel to the *ac* plane of the parent monomer. The failure of the side chains to attain fully an orientation perpendicular to the end group planes may be a consequence of limited mobility in the solid phase.

Let us now consider the manner in which the side chains are attached to the polymer backbones. If a syndiotactic polymer were produced, the chain backbone would tend to assume an all-*trans* conformation and the side chains could then lie along most of their length parallel to each other as indicated schematically in Figure 4a. Such an arrangement would also be in agreement with the observed long spacing of 27 Å., somewhat shorter than the 28.6-Å. spacing of the hexagonal ethyl stearate modification. The mode of attachment of paraffinic side chains to the backbone of an isotactic vinyl polymer has been discussed in detail by Jones.[24] She concluded that the backbone would have to assume the helical conformation characteristic of isotactic vinyl polymers and that the side chains should then extend in alternate directions as indicated in Figure 4b. This is the structure assumed apparently by isotactic poly(octadecene-1) and it might explain the broad low angle reflections observed in the present study, which can be interpreted as corresponding to higher orders of a 48–49.6-Å. spacing. This may be compared to long spacings of 52 Å. expected on the basis of Jones' data[24] for isotactic polymers with a 19-membered side chain oriented at right angles to the polymer backbone. However, it seems impossible to conceive of any way in which a vinyl stearate crystal, in which all the molecules point in the same direction, could be transformed into a polymer with such a geometry.

The geometric considerations outlined above led us to expect that the polymer produced in the solid state would be syndiotactic. However, the spectroscopic data suggest that this polymer is, in fact, characterized by a rather low degree of stereoregularity (and is less syndiotactic than polymers obtained by polymerization in the liquid state) although conclusive evidence by nuclear magnetic resonance spectroscopy is not available at this time. Although the backbone of an atactic polymer would not be spiralized like that of the isotactic species, it would also be prevented from assuming the all-*trans* conformation. This should make it very difficult for all the side chains to extend to the same side of the plane containing the backbones of the polymer chains and it is at present not clear how this dilemma can be resolved.

We can only speculate about the orientation of the chain backbone. Since the reactive vinyl groups lie within layers from which they cannot depart, it is difficult to see how polymerization could proceed to high conversion, if the chains propagated in random directions. The high degree of biaxial orientation of the side-chain crystallites also seem to imply some degree of order in the arrangement of the chain backbones. The question may then be raised whether the polymer chains formed in the solid state have a tendency to assume the folded form typical of chain molecules in single crystals.[26] Experimental techniques other than those used in the present study will have to be used to resolve this problem.

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(25) T. Malkin, *J. Chem. Soc.*, 2796 (1931).

(26) P. H. Geil, "Polymer Single Crystals," Interscience Division of John Wiley and Sons, Inc., New York, N. Y., 1963.