Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Wood, J. S. , Negulescu, I. and Vogl, O.(1977) 'Higher Aliphatic Polyaldehydes. III. Crystal Structure, Crystallinity, and Melting Transitions of Isotactic Poly-n-hept aldehyde', Journal of Macromolecular Science, Part A, 11: 1, 171 — 194

To link to this Article: DOI: 10.1080/00222337708061260

URL: http://dx.doi.org/10.1080/00222337708061260

J. MACROMOL. SCI.–CHEM., A11(1), pp. 171-194 (1977)

Higher Aliphatic Polyaldehydes. III. Crystal Structure, Crystallinity, and Melting Transitions of Isotactic Poly-n-heptaldehyde*

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ABSTRACT

Anionically polymerized poly-n-heptaldehyde (PHA) has been studied by wide-angle x-ray diffraction, and a tetragonal unit cell is proposed. DSC studies reveal several endotherms due to side-chain melting with a pronounced dependence upon annealing.

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*For the preceding paper in this series, see I. Negulescu and O. Vogl, J. Polym. Sci. Polym. Chem. Ed., 14, 2415 (1976).

INTRODUCTION

Poly-n-heptaldehyde (PHA) has been prepared by low-temperature anionic polymerization of n-heptaldehyde which was then endcapped with an acetic anhydride–pyridine mixture at 130° C [1]. The polymer, which is insoluble in the capping mixture at 130° C, was identified by high-resolution NMR as isotactic PHA. It exhibits a dual melting behavior. The lower melting region of 75-105° C was assigned to the melting of the side chain and the melting point of 147° C to that of the main chain [2]. The polymer was found to be highly crystalline according to x-ray studies, but a more detailed study of the crystal structure, crystallinity, and the melting behavior in the region of 75-105° C was found desirable.

The properties of semicrystalline polymers are strongly influenced by their crystallization conditions [1-15]. In some cases, multiple endotherms have been observed for these polymers. It has been suggested that two interpretations could be used to explain this phenomenon. One explanation is that one endotherm corresponds to the melting of crystals in which the polymer chains within the crystal are extended and another endotherm may be caused by the melting of the crystalline phase in which the chains are folded [15]. Another interpretation indicates that multiple endotherms are caused by distribution of various discrete crystals which are different in size and/or perfection [10, 12, 16, 17]. It was suggested that the higher melting endotherm could be attributable to crystals which are obtained by dynamic crystallization during the melting of crystals of lower melting point.

The first interpretation may be valid only in the case of polymers in which the chain length is sufficiently large for polymer lamellae to form. If the chain is rather short, as in the case of comblike polymers where lamellar folding is not possible, the second consideration would be strongly favored. In the case of the crystallization of PHA [18, 19], the lower transition [20] is most likely the crystallization of the aliphatic side chain, whereas the higher transition appears to be the melting of the backbone of the polyoxymethylene backbone chain [10, 12, 16, 17, 21].

Jordan [20] recognized, in the case of homopolymers with a side-chain length of 12 to 22 carbon atoms, that the DSC curves qualitatively reflected the distribution of crystallite sizes and he calculated the crystallinity of side chains in poly(n-alkyl acrylates), poly(n-alkyl acrylamides) and poly(vinyl esters). It has also been shown that in the case of polyolefins with unbranched side chains or of poly(alkyl acrylates) of a minimum aliphatic side chain length, the crystallization of the side chains can prevent the formation of a crystalline lattice in which the polymer backbone is involved.

One of the most useful methods for the investigation of multiple endotherms in polymeric systems is the determination of the melting endotherm as a function of the heating rate.

Wunderlich [22, 23] has studied extensively the temperature of the melting endotherm as a function of the heating rate particularly in the case of crystalline polystyrene [14] and poly(vinylidine fluoride) [24]. The change of melting temperature as a function of the crystallization temperature was interpreted quantitatively by Hoffman and Weeks [25] in polymers which are capable of chain folding; he discussed the melting temperature as a function of the lamellar thickness which in turn was related to dynamic crystallization phenomena [10, 14, 16, 24].

The crystalline structure of isotactic higher polyaldehydes was described by Natta and Corradini [26, 27]. Isotactic polyacetaldehyde was extensively investigated, and the diffraction pattern obtained from oriented fibers of isotactic polyacetaldehyde has been used for the direct interpretation of the powder diagrams of polypropionaldehyde and poly-n-butyraldehyde. All isotactic aldehydes so far investigated have a crystal structure with a tetragonal unit cell containing 16 monomer units, which indicates a four-fold helix with four polymer chains in the unit cell and a repeat distance of approximately 4.8 Å.

EXPERIMENTAL

Isotactic PHA [1] was synthesized by anionic polymerization of n-heptaldehyde with lithium tertiary butoxide in methylcyclohexane at -60°C. The polymer was endcapped at 130°C in suspension. The polymer portion which is insoluble in the reaction mixture at 130°C and represents 95% of the total polymer, was isolated and identified by NMR as isotactic poly-n-heptaldehyde.

The x-ray data for the examination of the structure of PHA were obtained from powder patterns which were recorded with a Geiger counter using CuKα radiation. The x-ray patterns of PHA films were also recorded by use of CuKα radiation.

DSC measurements were carried out with a Perkin-Elmer differential scanning calorimeter (DSC 1B). The scanning speed and the chart speed were varied according to the desired investigation; the attenuation selector setting was 0.32 mcal/cm-sec. Temperature readings were regulated for direct dial read-out by adjusting the average calibration for the melting temperature of p-nitrotoluene (triple point, 51.5°C) and indium metal (mp 156.6°C). The heats of fusion were checked out with a sample of 6.2 mg indium metal. Peak areas were measured with a planimeter and the peak maxima of the endotherms were taken as the temperature of transition in all experiments. This procedure gave best agreement with values which were obtained by other methods [18]. Furthermore, the temperature of departure or of return of the endotherm to the baseline was very dependent on the sample geometry and was not used in our investigation. Polymer samples were annealed and quenched in the DSC sample holder.

Infrared spectra of PHA films were obtained on a Perkin-Elmer 180 IR spectrometer which provided the best facilities to expand the infra red bands in the region of interest. The polymer films were prepared by pressing PHA powder between NaCl plates.

For other purposes PHA was oriented by extrusion in an Instron rheometer at 100° C through a capillary of 0.5 mm diameter and 25.4 mm length.

The density of the polymers was determined by weighing a known volume of PHA. The flotation method for the determination of the density was not used because of the possibility of unusual swelling behavior of PHA samples.

RESULTS AND DISCUSSION

Crystal Structure of Isotactic PHA

PHA gave a highly crystalline x-ray pattern, a portion of which (from $2\theta = 10°$ to $35°$) is illustrated in Fig. 1. The d spacings for the reflections obtained from the diffractometer scans and from film are tabulated in Table 1 together with their relative F_{obs} values. Since the distribution of intensities in the pattern for crystalline PHA appeared similar to that reported for poly-n-butyraldehyde (PBA) by Natta, Corradini, and Bassi [27], it seemed reasonable to assume a tetragonal unit cell here also, with a c axis dimension closely related to the identity period along the polyacetalic backbone chain. In polyacetaldehyde the c axis is 4.79 Å [27]. The d spacings calculated for isotactic PHA with tetragonal cell dimensions a = 25.9 and c = 4.52 Å are listed in Table 1 and, apart from two weak lines ($2\theta = 12.1$ and $18.05°$), the agreement between observed and calculated d values is reasonable. Also included in Table 1 are the F_{obs} and F_{calc} values for PBA from Natta's study [27]. The relatively low value of 4.52 Å for the identity period is in agreement with the high crystallinity of PHA and the isomorphism of the monomer units of crystalline

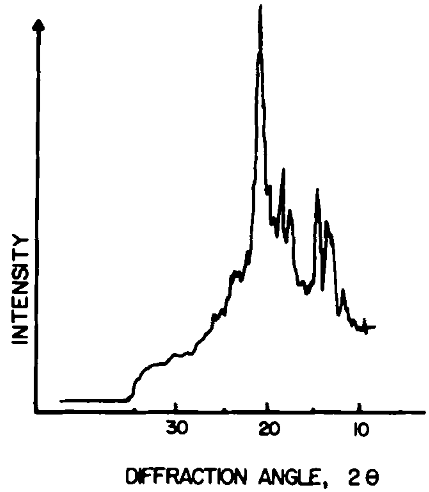

FIG. 1. X-Ray powder diagram for crystalline poly-n-heptaldehyde.

copolymers of n-heptaldehyde and n-butyraldehyde over the whole composition range [28]. The presence of the two additional lines in the diffraction pattern together with the observation of a doublet, rather than a single line centered at 6.42 Å, might allow an alternative interpretation of the pattern to be made in terms of a unit cell of lower symmetry, possibly orthorhombic, while maintaining the same basic arrangement of polymer chains. The flexibility of the long side chains in PHA might permit small deviations from tetragonal symmetry, so that reflections hk0 and kh0 would have slightly different d values. However, we have not attempted a structural interpretation in terms of such a unit cell.

The tetragonal unit cell of PHA contains 16 monomer units and the cell volume gives a calculated density of 0.995 g/cc. If one compares the crystalline density of various isotactic polymers of higher polyaldehydes, it can be seen that with increasing hydrocarbon side chain length the density of the higher polyaldehydes decreases. The density of polyacetaldehyde (PAA) is 1.14 g/cc, while that for polypropionaldehyde (PAA) is 1.050 g/cc. The density values for the higher homologs of isotactic higher polyaldehydes should be lower than 1.000 g/cc and a calculated density for poly-n-butyraldehyde (PBA) of 0.997 g/cc has been reported [27].

On assuming that PHA obtained with cationic initiators is a

TABLE 1. d-Spacings and Structure Factors for Isotactic Poly-n-heptaldehyde

hkl	d_{obs} (Å)	d_{calc} (Å)	F_{obs} (rel.)	F_{obs} (rel)[a]	F_{calc} (rel)[a]
200	12.6	12.95	>100	151	150
220	–	9.18	–	50	85
[b]	7.31		10.7		
400	6.51-6.32[c]	6.49	33.0	–	5
420	5.86	5.81	36.0	120	117
[b]	4.92		23.0		
440	4.64	4.59	34.0	–	32
101	–	4.44		–	15
211	4.15	4.20	100	137	138
620		4.11		–	8
301		4.07		73	75
640	3.59	3.60	–	–	34

[a] Data for poly-n-butyraldehyde from Corradini, Natta, and Bassi [27].

[b] Reflections unassigned in tetragonal symmetry.

[c] Doublet.

completely amorphous polymer and has an observed density of 0.880 g/cc, a minimum percentage crystallinity w_c for PHA may be estimated by using the specific volume relations [29] given in Eq. (1):

$$w_c = [(V_a - V)/(V_a - V_c)]\ 100 \qquad (1)$$

where V is the specific volume, V_c that of purely crystalline polymer, and V_a that of amorphous PHA.

The experimental density of isotactic PHA which was insoluble in the capping mixture and had $\overline{M}_w > 7000$ was 0.958 g/cc, which indicates a crystallinity of 70%. Isotactic polymer of lower molecular weight, ($\overline{M}_w$ = 3300) had a density of 0.933 and a crystallinity of 50%. These values for the percentage crystallinity are minimum values, because PHA obtained with cationic initiators is probably not entirely amorphous.

Chain Conformation and Side-Chain Packing of Isotactic PHA

Natta and co-workers [27] in their study of isotactic polyaldehydes, revealed that PAA, PPA, and PBA contain four polymer chains in the unit cell. Two of them have a right-handed conformation and the other two a left-handed conformation corresponding to 4_1 and 4_3 screw axis symmetry, respectively. This general picture has also been assumed to be correct for the unit cell of isotactic PHA, the space group being I $4_1/a$. The chain conformation is determined mainly by the identity period along the crystal c axis.

Figure 2 illustrates a possible mode of packing of the polymer chains in isotactic PHA on assuming the same conformation for the side chains, i.e., a planar C-C backbone skeleton as suggested by Natta [27] for the shorter side chains in PBA and as depicted in Fig. 3. In PPA and PBA, the side chain axes are inclined 45° to the a axis of the unit cell. As the length of the side chain is increased, however, maintenance of this angle would produce voids in the structure between the polymer chains and parallel to the c axis, and hence lead to a much less efficient packing of the chains. Rotation of the polymer chains around their axes by approximately 13° allows an "interlocking" of side chains and leads for PHA to a highly efficient packing arrangement in which the side chains on neighboring polymers are paired. They are separated by C/4 normal to the projection. This arrangement in the cell leads to a predicted a axis of 26.4 Å which is close to that obtained from the powder patterns.

Earlier x-ray work suggested that polymers with long aliphatic side chains have their side chains packed side by side in a lamellar structure similar to that of the hydrocarbon chains in the orthorhombic unit cells of higher paraffins or polyethylene. A very strong reflection at 4.2 Å has been found characteristic of such structures [30-32]. It was however shown later by Plate [33-35] that a strong reflection near 4.2 Å also appears in x-ray diagrams of polymers with side chains which are packed in hexagonal fashion. The presence of the strong reflection at 4.20 Å in the polyaldehydes indicates that yet a third arrangement is consistent with such a reflection.

In order to shed more light on this problem, additional information

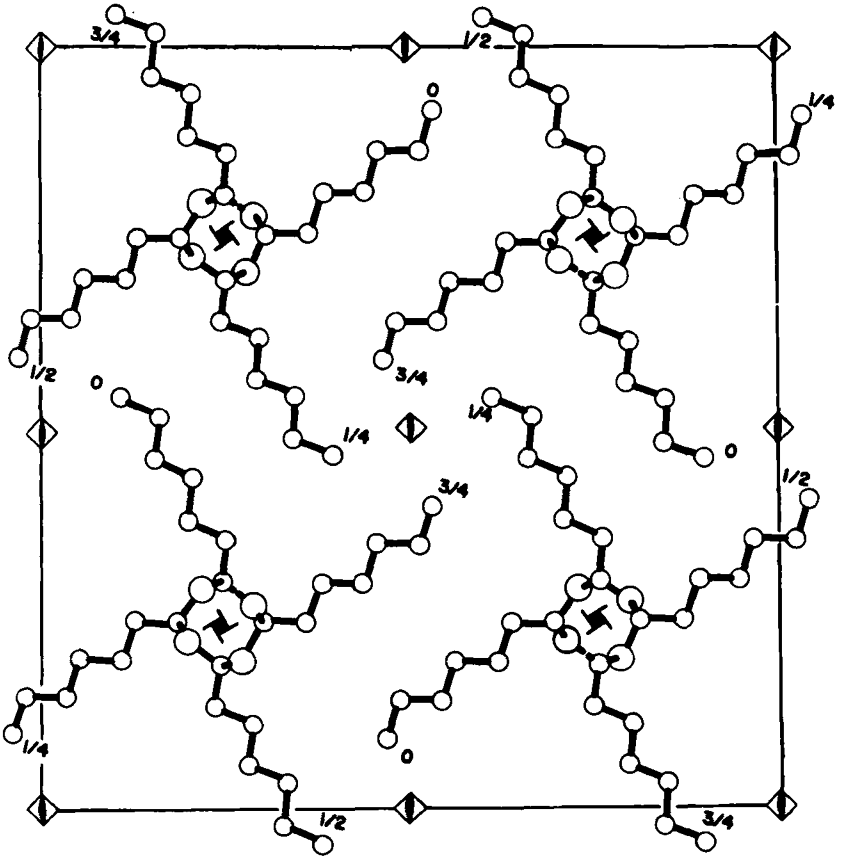

FIG. 2. Projection (001) of isotactic poly-n-heptaldehyde.

about the packing of normal aliphatic chains can be obtained by observing the infrared spectrum in the 700-750 cm^{-1} region. Chapman [36, 37] has shown that typical absorption bands in the infrared spectra correspond to different modifications in long-chain aliphatic compounds. A hexagonal crystal structure is characterized by strong absorption in the 720 cm^{-1} region which corresponds to the vibration of CH_2 groups in the methylene chain. A more stable rhombic form shows an absorption doublet in the 717 and 727 cm^{-1} region. If normal alkane chains crystallize in an orthorhombic packing, the

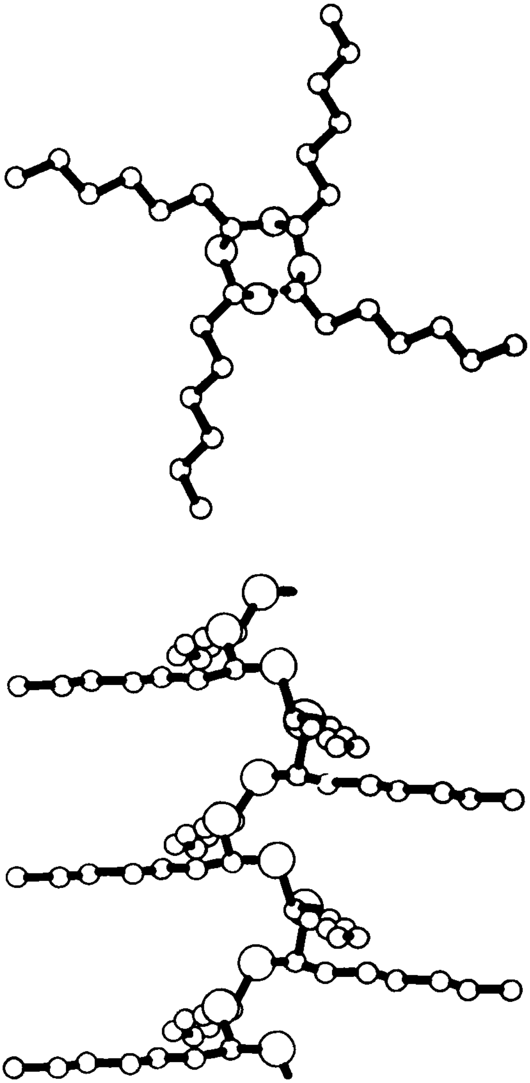

FIG. 3. Top and side views of isotactic poly-n-heptaldehyde chain.

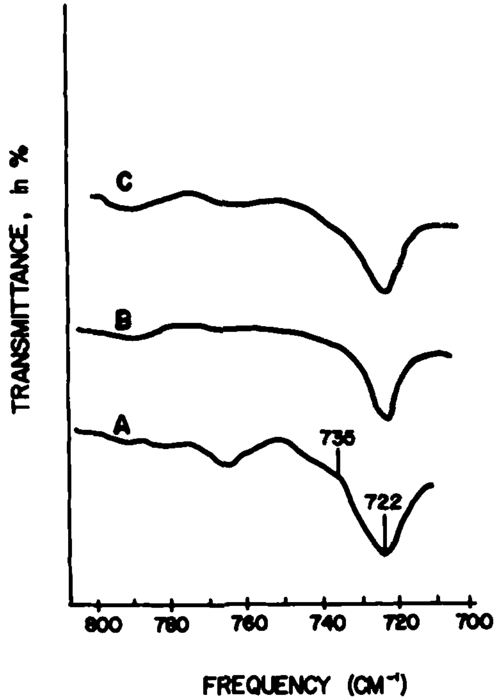

FIG. 4. Infrared spectra of isotactic poly-n-heptaldehyde: (A) $\overline{M}_n$ 3300; (B) $\overline{M}_n$ 5000; (C) $\overline{M}_n$ > 7000.

presence of a doublet at 720 and 730 cm^{-1} can be expected as in the case of long-chain paraffins and polyethylene.

The x-ray diagram of isotactic PHA exhibits a very strong reflection in the 4.2 A region, and the IR spectrum of the polymer shows a single peak at 722 cm^{-1} (Fig. 4). There is also a shoulder present at 735 cm^{-1}, but this absorption does not seem to be related to a crystalline absorption. It was noted that even in a rhombic lattice, a shoulder appears with a similar intensity to that of the band at 722 cm^{-1}, and this is believed to be due to the interaction of two paraffin chains in the crystal [36, 37]. Moreover, the shoulder appears to be sensitive to the molecular weight of the polymer because it was found that as the molecular weight increased, the intensity of the shoulder peak decreased [38, 39]. Therefore, it might be concluded that the strong diffraction pattern at 4.2 Å is related to the single peak at 722 cm^{-1} due to the CH_2 group and that this absorption may be interpreted as arising from the partial order of parallel hydrocarbon chains arranged side by side in the tetragonal crystal lattice of isotactic PHA. A similar type of partial order was suggested by Turner-Jones [40] in the case of isotactic polyolefins with unbranched side chains. When the polymers were quenched, the paraffinic side chains were arranged only in a limited degree of order.

A different packing arrangement to that depicted in Fig. 2 might be achieved if the side chains adopt an alternative conformation to the planar arrangement assumed here. For a helical conformation, Plate et al. [34] calculate an increment of 2.35 Å for each half-doubled step of the $(CH_2)_n$ chain as opposed to 2.75 Å for each doubled unit in the transconformation. This would lead to shorter side chains and presumably to different packing of the polymer chains in the crystal. The lengths of the side chains and their steric requirements obviously affect the unit cell symmetry and dimensions, and it is probable that an increase of the aliphatic side chain beyond 10 or 11 carbon atoms may prevent altogether the formation of a crystal lattice of the polyoxymethylene backbone chain; in other words, the paraffin groups will crystallize regardless of the tacticity of the polymer main chain. A suppression of main-chain crystallization has been observed in the case of isotactic polyolefins [40] with normal side chains or in poly(alkyl acrylates) of unknown stereoregularity [33].

Side-Chain Crystallinity

The crystallinity χ_c in polymers can be estimated by calorimetry when the relation (2) [41]

$$\chi_c = \Delta H_f/\Delta H_{f,0} \qquad (2)$$

is satisfied; ΔH_f is the enthalpy of fusion and $\Delta H_{f,0}$ is the enthalpy of fusion for a 100% crystalline phase. This relation was successfully utilized by Jordan [20] to calculate the crystallinity of the side-chain portions of poly(n-alkyl acrylates), poly(N-n-alkyl amides) and poly(vinyl esters). It was shown that the crystalline phase of these polymers did not include the whole side chain but only some fraction of the side chain.

It appears reasonable to assume that data for the enthalpy of fusion of the hexagonal modification of n-alkanes (the α-hexagonal-to-liquid transition, $\alpha_H - \ell$) [42] could represent the crystalline portion of the side chains of isotactic PHA. By use of the equation proposed by Jordan [20], the percentage crystallinity χ_c can be estimated as:

$$\chi_c = [\Delta H_f(n)\, 14.02]/[C + k(n)] \qquad (3)$$

where ΔH_f is in cal/g, 14.02 is the molecular weight of a single methylene unit, and n is the number of side chain methylene groups including the terminal methyl group. C, the contribution of the chain ends to the total heat of fusion, here is assumed to be zero because there are only short-chain enthalpy changes associated with the fusion of each methylene group; k represents ΔH_f(cal/mole) for a methylene group and was assumed to be 742 cal/mole for each CH_2 group [20]. This number was used for other polymers with long paraffinic side chains and is close to the value of 735 cal/mole CH_2 which was determined for the $\alpha_H - \ell$ transitions of n-alkanes near their melting point [42]. To estimate the percent crystallinity of the side chain χ_{cs} which is responsible for the polymer side-chain crystal lattice, we use Eq. (4):

$$\chi_{cs} = f\chi_c \qquad (4)$$

where f is defined as:

$$f = MW_{unit}/(MW_{side\ chain} - 1.008) \qquad (5)$$

Two well defined transition regions can be observed in crystalline PHA when the polymer is investigated by DSC [18]: one in the region of 75-101° C and one around 148° C, which normally is manifested as a shoulder on the endotherm degradation peak which has its maximum at 180° C. The low-temperature transition represents the "melting" of the side chain and requires a heat of fusion of 8.60 cal/g (Fig. 5A). When the appropriate values from Eqs. (3) and (4) are substituted, a percent crystallinity of $\chi_{cs} = 0.31$ is obtained, which indicates that 31% of the total methylene groups of the polymer side chains are present in the crystal lattice. The figures in Eqs. (3) and (4) are only

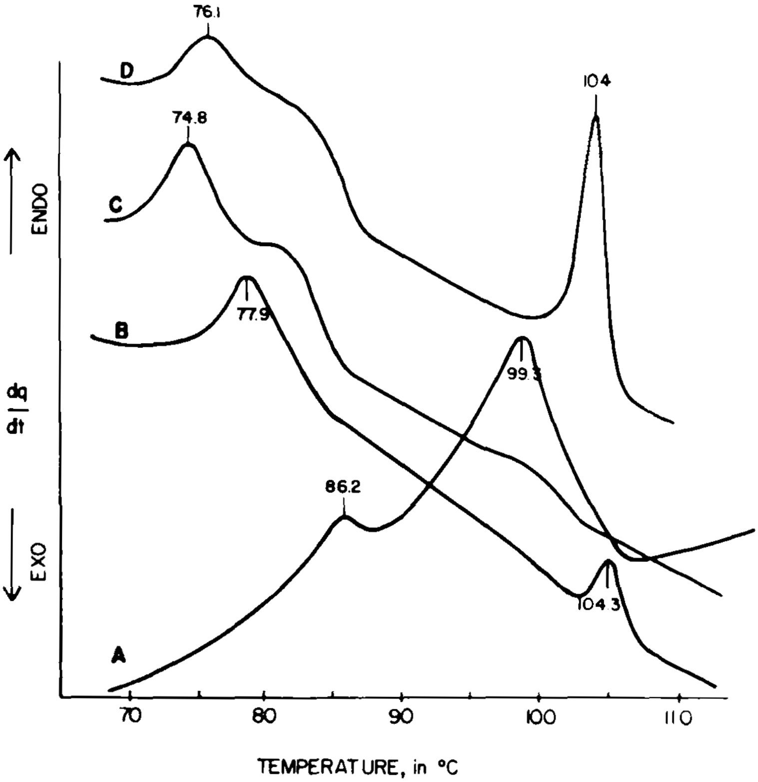

FIG. 5. DSC curves of isotactic poly-n-heptaldehyde: (A) scanning of reference polymer, 12.2 mg, $\Delta H_f = 8.6$ cal/g; (B) scanning of extruded polymer, 8.5 mg, $\Delta H_f = 3.3$ cal/g; (C) rescanning of extruded polymer, $\Delta H_f = 5.4$ cal/g; (D) scanning of samples B and C after annealing in DSC sample holder at 93° C for 10 hr, $\Delta H_f = 7.3$ cal/g. Scanning rate 10° C/min.

of relative value but they can be used to compare the amount of crystallinity of various samples of isotactic PHA of different thermal history or even of PHA of lower tacticity. Even in isotactic PHA of high crystallinity, where w_c is greater than 70%, the side-chain crystallization may be depressed or even prevented by mechanical work.

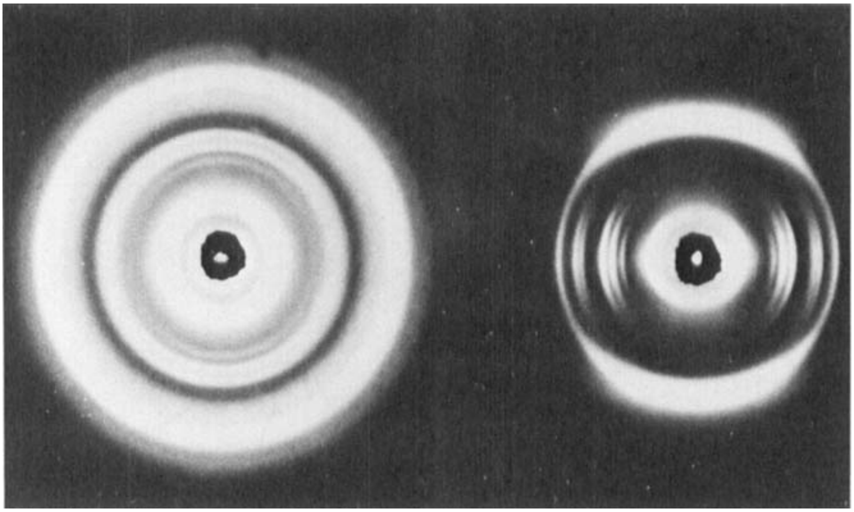

FIG. 6. X-Ray diffraction diagram of (A) oriented and (B) unoriented poly-n-heptaldehyde.

For example, if isotactic PHA was extruded at temperatures where the polymer side chains had already melted but the backbone had not, for example, at 100°C, the orientation of the polymer backbone (Fig. 6) during the extrusion process prevented the side-chain crystallization from occurring effectively, and a χ_{cs} for the extruded polymer from 0.31 to 0.11 was observed (Fig. 5B). This observation seems to be very reasonable, because the mechanical work under these extrusion conditions was similar to a quenching reaction. When the extruded samples were annealed under various conditions (Figs. 5C and 5D), the side chains developed a sufficient mobility for crystallization to occur (χ_{cs} increased from 0.11 to 0.27).

Influence of Thermal History on the Melting Behavior of Crystalline Side Chains in Isotactic PHA

Melting of crystalline PHA was studied by DSC in the region of 75-101°C, which corresponds to the side-chain transition. This region consisted of three melting endotherms, depending on the crystallization conditions and the thermal history of the sample (Fig. 7).

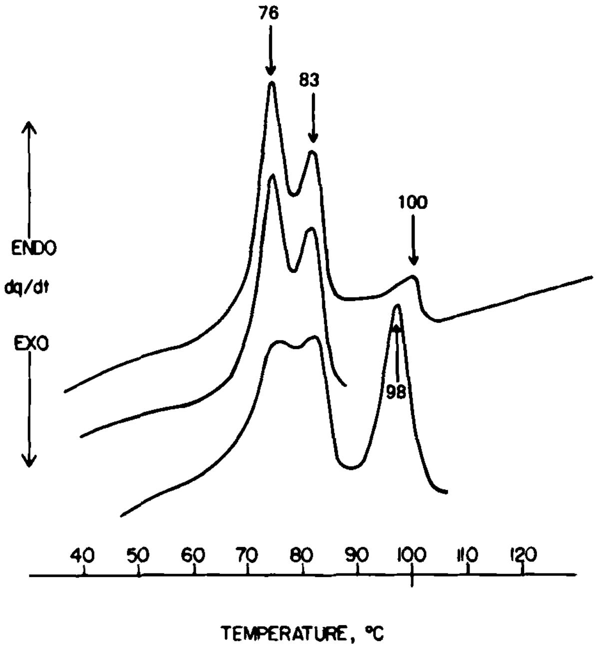

FIG. 7. DSC endotherms of poly-n-heptaldehyde: (A) first scanning of a recrystallized sample; (B) scanning was stopped at 88° C and the polymer was annealed at this temperature for 1 hr; (C) rescanning of sample B. Sample size 10 mg; heating rate 20° C/min.

When crystalline PHA was annealed at temperatures higher than 84° C (Fig. 7B), a high-temperature transition near or above 100° C was obtained. Annealing may mean keeping a partially crystalline polymer sample at constant temperature below the melting point but it also might mean isolation of the polymer from the endcapping reaction (130° C) [22, 43]. When the polymer sample was isolated from the capping reaction by slow cooling of the polymer sample or if the polymer was treated to increase its thermal stability [44] by boiling it in DMF (155° C) and slowly cooled to room temperature, the high temperature peak at 102° C (Fig. 8B) was readily observed. If, however, the polymer was cooled quickly from 130° C to room temperature as, for example, by hot filtration and washing the polymer after capping with cold acetone (which amounts to a quenching reaction), a DSC endotherm of 78° C (Fig. 8A) was observed.

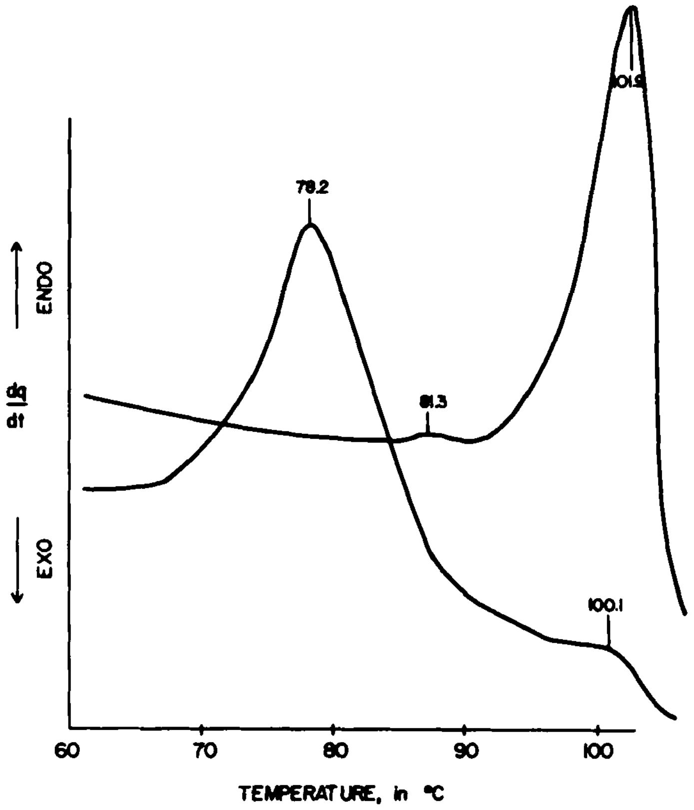

FIG. 8. DSC curves of poly-n-heptaldehyde subjected to different thermal conditions after polymer capping: (A) quickly cooled from 130° C to room temperature by washing with acetone; (B) aliquot polymer sample of same synthesis after boiling in DMF suspension and slowly cooling from 155° C to room temperature. Sample size 10 mg; heating rate: 20° C/min.

The sample of PHA was heated past the transition of side-chain crystallization, for example, to 110° C, and the sample was cooled in order to achieve the recrystallization of the side chain. Only one crystallization endotherm at 61° C was then noticed in the DSC thermograms of both samples, regardless of the previous thermal history of the sample. Upon rescanning under the same conditions after recrystallization had occurred, either sample had three endothermic peaks (Fig. 7A).

Crystalline PHA was also subjected to a thermal treatment during the extrusion process (Fig. 5). The shape of the DSC curves of the extruded material differed depending upon the thermal treatment of PHA after the extrusion process; however, the rescan of the oriented polymer (Fig. 5C) resembled that of nonextruded polymer (Fig. 7A). It appeared that under the annealing conditions the stress introduced by the mechanical treatment was released and regular crystallization had occurred.

The multiple DSC endotherms may represent multiple distributions of crystal sizes or crystal perfections [20]. Annealing or recrystallization caused probably the formation of larger and more perfect crystals. It is nevertheless interesting that three discrete peaks may be reproducibly obtained which indicates that the formation of discrete crystallites of uniform size might be observed rather than a random distribution of crystallite sizes.

Semicrystalline polymers generally melt over a broad temperature range due to a distribution of the thickness of crystallites and their varied perfection. Rapid crystallization [10] or reorganization [14] occurs only in the fused domain; consequently, the recrystallization must be fast enough to avoid complete melting of the sample. On the other hand, it is true that recrystallization rate depends on the crystal perfections or on the degree of order which is present in the side-chain packing, and only the less perfect part of the crystallites can recrystallize.

It was found that the highest endotherm in the region of side chain crystallization gave a higher temperature of fusion at a lower heating rate. Evidence for this explanation is presented in Fig. 9, where DSC curves were recorded at different scanning rates. At very slow heating rates such as 1-5°C/min (Fig. 9A, C), only one endotherm was noticeable in the DSC curve. At a heating rate of 10°C/min, a recrystallization phenomenon may be noticed at 84.5°C, while the maximum of the melting endotherm is similar to that observed at slower heating rates (Fig. 9D). At much higher scanning rates, for example, 40 and 80°C/min, the recrystallization phenomenon is retarded and the temperature of the main melting endotherm is lowered by 15-20°C (Figs. 9E and 7). Only the DSC curves obtained at heating rates greater than 10°C/min gave a picture of the thermal behavior of the initial polymer. Figure 10 shows the DSC curve of the side-chain crystallization of PHA. In the first sample, the scanning was carried out in the sequence, a-b-c-a, which shows essentially only the lower transition point. Rescanning of 10A after annealing at 102°C at 13 hr showed the development of a very significant peak near 110°C and the heat of fusion of the higher endotherm represents 48% of the total peak required for the melting of the side chain crystallization.

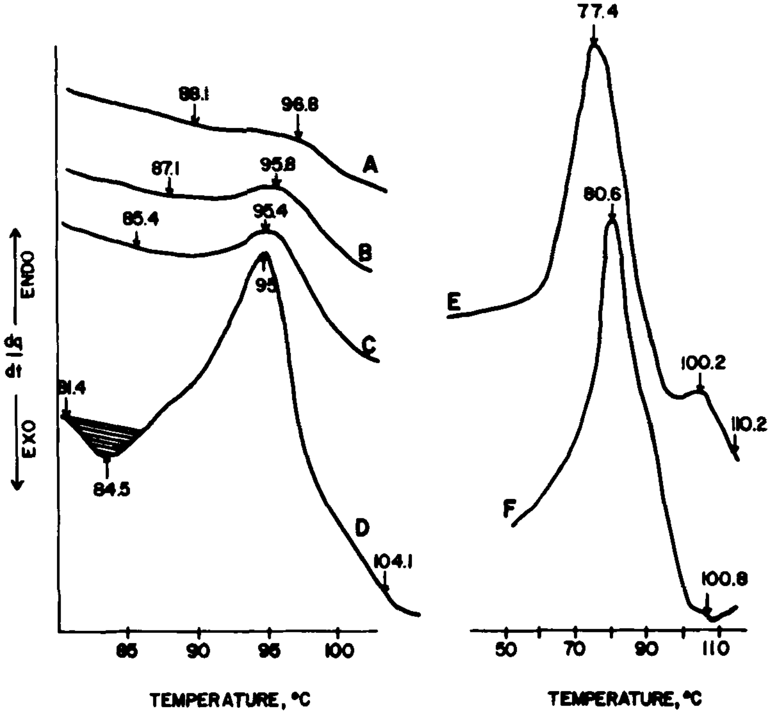

FIG. 9. Effect of heating rate on DSC thermograms of crystalline poly-n-heptaldehyde: (A) scanning rate 1.25° C/min, recorder speed 5 mm/min, sample size 13.5 mg; (B) scanning rate 2.5° C/min, recorder speed 10 mm/min, sample size 17.6 mg; (C) scanning rate 5.0° C/min, recorder speed 20 mm/min, sample size 10.1 mg; (D) scanning rate 10.0° C/min, recorder speed 40 mm/min, sample size 15.8 mg; (E) scanning rate 40.0° C/min, recorder speed 80 mm/min, sample size 12.8 mg; (F) scanning rate 80.0° C/min, recorder speed 160 mm/min, sample size 10.0 mg. Recorder voltage 10 mV.

The absence of this endotherm both in the original and rescanned DSC curve (Figs. 10A, C) indicates that recrystallization took place.

Long exposures of PHA to temperatures of 80-100° C could cause polymer degradation [1], and care must be taken to ascertain every time either that polymer degradation has not occurred or that the amount of degradation of polymer to monomer is known or at least can be estimated.

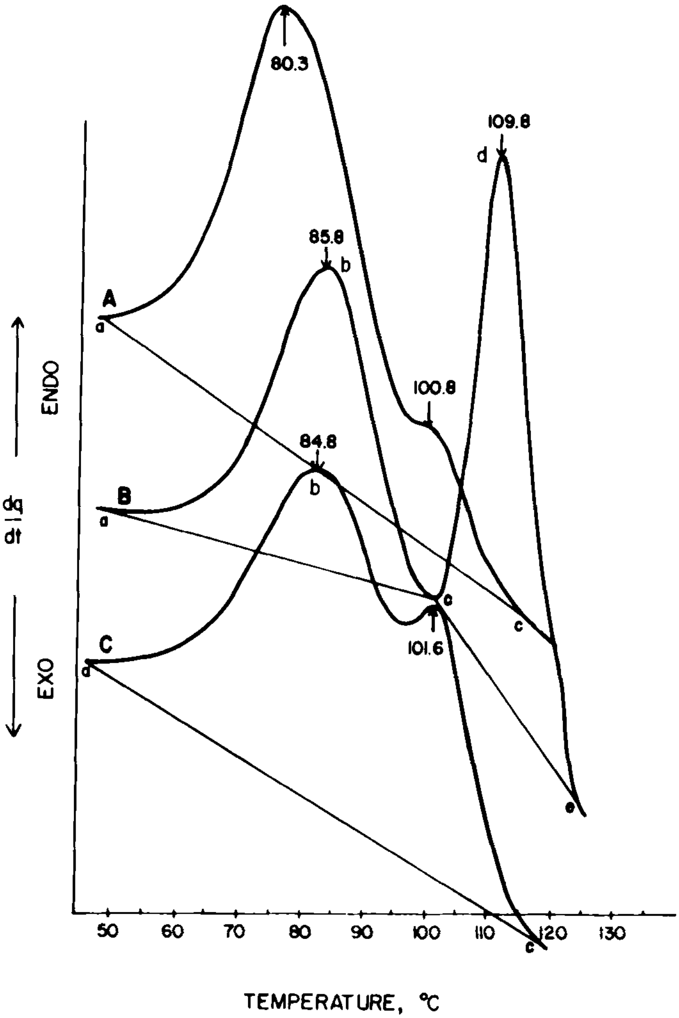

FIG. 10. DSC curves of poly-n-heptaldehyde side-chain crystallization: (A) rescanning of sample of Fig. 8F in sequence a-b-c-a; (B) rescanning of sample 10A after annealing at 102°C for 13 hr; (C) rescanning of sample 10B. Scanning rate 80°C/min, sample size 10 mg, recorder speed 160 mm/min.

The equilibrium melting temperature of a polymer T_m was defined by Hoffman and Weeks [25] as the melting point of an assembly of crystals in equilibrium with the polymer liquid. It has been shown on crystalline PHA that the so-called observed melting points T_m(obs.) of the side-chain melting can be obtained experimentally by plotting T_m as a function of isothermal crystallization temperature, when freed of secondary effects such as recrystallization. The data fit a straight line of positive slope on a plot of T_m(obs.) versus T_m flat. The most important assumptions in this theory were that the dimension of the growing crystal retained a size similar to the growth nucleus during isothermal crystallization which was justified on the basis of our knowledge of polymer crystal growth with polymers which are capable of chain folding.

The equation which describes the isothermal crystallization is [25]

$$T_m(\text{obs.}) = T_m[1-(\beta/2)] + (T_x/\beta) \qquad (6)$$

where β is a constant related to the r/v crystal dimension; for example, the mean step height ℓ of crystals which melt at T_m(obs.) is β times as large as the mean step height ℓ' of the primary nucleus. According to this theory, thinner lamellae or sections thereof will melt first, and the supercooled liquid produced by a melting crystal at T_m(obs.) during the warming process has the tendency to recrystallize at this temperature and form crystals with a larger volume and value of ℓ and hence a higher T_m(obs.) than the original crystal.

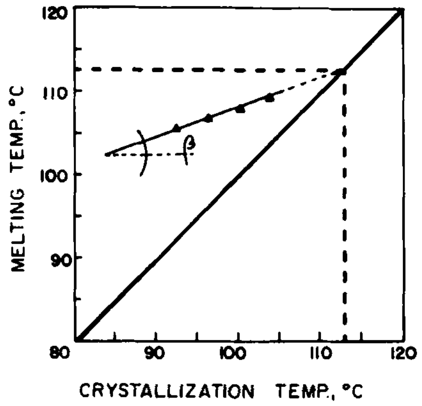

FIG. 11. Estimation of equilibrium melting point of side-chain crystallization of poly-n-heptaldehyde.

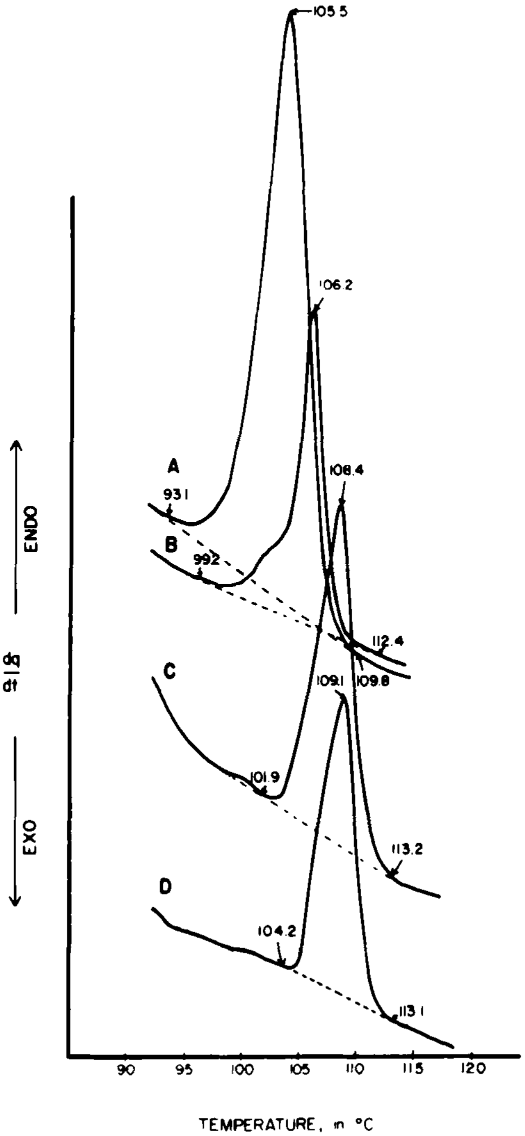

FIG. 12. Dependence of the side-chain crystallization temperature of poly-n-heptaldehyde on annealing conditions: (A) annealing temperature 90°C for 10 hr, relative area of higher temperature transition vs. total transition area = 59%; (B) annealing temperature 94°C for 3 hr, relative area = 28%; (C) annealing temperature 98°C for 1 hr, relative area = 28%; (D) annealing temperature 100°C for 44 hr, relative area = 65%. Scanning conditions: heating rate 20°C/min, recorder speed 80 mm/min, sample size 11.4 mg.

Polymer recrystallization was slower at higher crystallization temperatures where a nucleation mechanism was involved. As a consequence, for a specified heating rate, the T_m(obs.) values obtained for high T_x values were more correct than those obtained for low T_x values.

In this paper, we tried to relate side-chain crystallization of PHA with the above-mentioned theory of polymer crystallization. The paraffinic side chains are too short to form a chain fold upon crystallization, but they can be considered fixed because of their attachment to the polyoxymethylene backbone. The supercooled polymer liquid produced after the melting of the less perfect crystallites is already somewhat oriented due to the presence of the polymer crystal lattice even after side chains melt at T_m(obs.). The plot of the melting temperature which corresponds to the last DSC endotherm (Fig. 11), T_m(obs.), as a function of crystallization temperature, T_x, for crystalline PHA, is presented in Fig. 12. The effect of recrystallization after the melting of less perfect crystals was less pronounced when a heating rate of higher than 10° C/min was used for this scan.

The extrapolated equilibrium melting temperature of side chains in PHA, T_m, is 113.0° C, less than 4° C higher than the maximum of T_m(obs.) which was 109.5° C. The value of $\beta = 1.4$ showed that, during the recording of the DSC curves for the determination of T_m, recrystallization played a minor role; the β value of isotactic polystyrene was 2.0 when T_m(obs.) was plotted against the crystallization temperature, and it was 3.0 when it was taken as a function of reorganization temperature. Usually a β value obtained under conditions where recrystallization occurs during the warm-up process of the sample tends to be too large. The meaning of β and T_m of the crystalline side chains in crystallization of higher polyaldehydes such as PHA will become clearer when polyaldehydes with much longer paraffinic side chains become available and can be studied.

ACKNOWLEDGEMENTS

We would like to thank the Xerox Corporation for their partial support of this work. It was also supported from a grant of the National Science Foundation (Materials Research Laboratory). One of us (I.N.) would like to thank the Fulbright Commission for its support which permitted him to work at the University of Massachusetts and to the Institute P. Poni in Jassy, Romania, for granting him one year's leave of absence.

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Accepted by editor March 23, 1976
Received for publication May 5, 1976