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Articles

Studies on Comb-like Polymers. 1. Poly(octadecylethylene)

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ABSTRACT: The thermal properties of different samples of poly(octadecylethylene) were determined and their crystalline structures were studied by X-ray scattering. The atactic-rich, ether-soluble fraction melts sharply at 58 °C and has a structure characterized by disordered main chains and crystallized side chains. The isotactic-rich fraction, probably containing blocks of atactic polymer, can be obtained in different crystalline modifications according to the thermal treatment. A sample obtained by quenching from the melt shows an X-ray diffraction diagram very similar to that of the atactic material. It also melts at a temperature of ca. 58 °C. However, on further heating it undergoes a recrystallization which is followed by a second melting at ca. 83 °C. The samples subjected to thermal treatments capable of improving the crystallinity are of two main types. Both types have a structure characterized by main chains confined to planes regularly spaced. The melting point of the isotactic polymer varies slightly with thermal history (between about 75 and 85 °C) and is considerably higher than that of the atactic polymer (58 °C). The two materials form incompatible phases.

Since the early discovery by Rehberg and Fisher,[1] Kaufman et al.,[2] and Wiley and Brauer[3] that polymers containing long paraffinic side groups give rise to side-chain crystallization, many articles have appeared in the literature describing the structure, the properties, and the applications of these so-called comb-like polymers. The matter has been reviewed recently by Platê and Shibaev.[4]

However, as has been made evident in a recent publication by Morawetz and collaborators,[5] the principles governing side-chain crystallization in these materials are more complicated than thought before and are far from being fully understood. One of the problems is the influence (if any) exerted by the steric configuration of the backbone upon the crystalline structure and the properties of these polymers.[4] Moreover, there is no agreement on whether the main chains can participate in the crystal lattice.[6,7] Only for isotactic long side-chain poly(alkylethylenes) is there general agreement that the backbone chains may assume a regular conformation in the crystalline state.

Another point which has never been investigated is the dependence of the structure and the properties of comb-like polymers on the spacing of long side branches along the main chain. The only crystallographic study on comb-like polymers with side groups attached to every third atom of the main chain is the work of O'Donnell[8] on poly(alkylethylene sulfones).

In our laboratory, a study is being carried out on polymers containing long paraffinic side groups with various spacings along the backbone chain. Some of these polymers can be obtained with different stereochemical configurations, and this gives us the opportunity to evaluate the effect of this parameter on their structure and properties even though the quantitative determination of the degree of tacticity may be difficult or impossible in some instances.

A study of poly(octadecylethylene oxide) which contains one side group every third atom of the main chain and which can be obtained as an atactic as well as a stereoregular polymer will be dealt with in the second paper of this series. In this article we present, for comparison, data on the parent polyolefin, poly(octadecylethylene).

The previous studies by Reding,[9] Brownawell and Feng,[10] Turner Jones,[11] Fraser et al.,[12] and Holland-Moritz et al.[13-16] have given a sufficiently clear description of the structure of long side chain, isotactic polyolefins. In particular, the detailed X-ray diffraction study by Turner Jones[11] and the vibrational analysis by Fraser[12] and Holland-Moritz[13-16] have indicated that the packing of the side groups as well as their orientation with respect to the main chain direction is a function of the thermal history and of the temperature.

However, in none of these works[11-16] was any attempt to improve the tacticity of the samples through extraction or fractional precipitation described. Aubrey and Barnatt[17] showed that extraction of poly(hexadecylethylene) with hexane gives a soluble fraction melting at 41 °C and a residue which displays a DSC main endotherm at 68 °C plus a residual small peak near 41 °C. These authors also found that the insoluble fraction of the polymer, once quenched from the melt, shows a strong endothermic peak near 41 °C, followed by an exotherm and a second endotherm near 68 °C, thus demonstrating that recrystallization takes place during the heating cycle. Unfortunately, the lack of X-ray diffraction data on the crystalline forms of hexane-soluble and quenched hexane-insoluble polymers and their possible mutual transitions prevents comparing their crystalline structure with the two modifications described by Turner Jones[11] for isotactic polyolefins.

While the present work was in progress, Trafara et al.[18]

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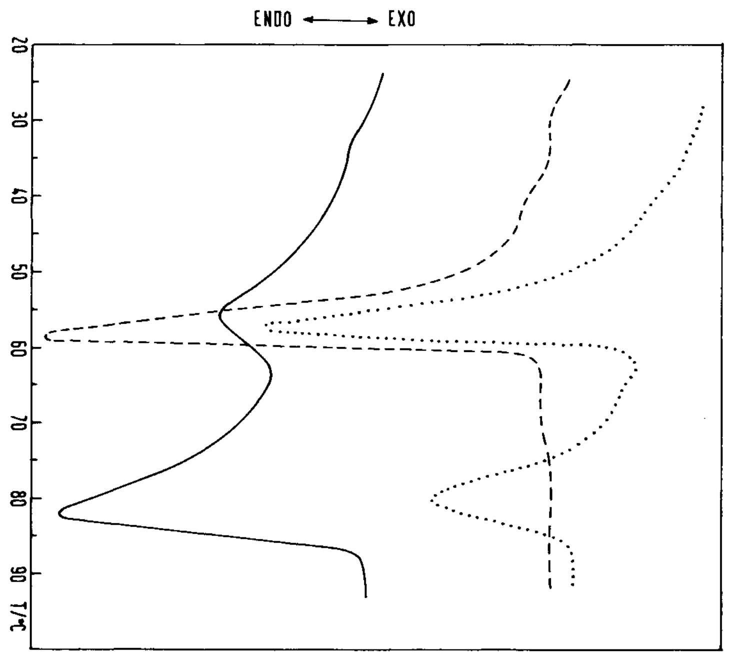

Figure 1. DSC traces of poly(octadecylethylene): heating rate 16 °C/min; (···) sample A, (- - -) sample B, (—) sample C_1 (cf. Table I).

published data which confirmed some of those previously described by Aubrey and Barnatt[17] and presented X-ray diffraction diagrams of some quenched poly(alkylethylenes). Unfortunately, in this study the finding by Aubrey and Barnatt that higher polyolefins can be separated into two fractions having different tacticity and properties seems to have been overlooked, and apparently unfractionated samples were considered.

In this paper we present the results of a study of poly(octadecylethylene). As expected, most of the data obtained confirm the results previously described by Turner Jones,[11] Aubrey and Barnatt,[17] and others for homologous polyolefins. However, the present results provide some refinement of previous knowledge on the structure and properties of these polymers.

Experimental Section

Poly(octadecylethylene) was prepared by polymerization of the purified commercial monomer (Aldrich) with $TiCl_3$–$Al(i\text{-}C_4H_9)_3$ in heptane under high vacuum. The product, after conventional purification, was precipitated three times from $CHCl_3$ solution into a 95/5 v/v mixture of methanol and ether to remove the monomer completely. It was then fractionated with boiling ethyl ether in a Kumagawa apparatus for 64 h. The yields of the fractions, their intrinsic viscosities (measured in toluene at 25 °C), and molecular weights, calculated by extrapolating to poly(octadecylethylene) the data obtained by Philippoff and Tornqvist[19] for lower homologous polyolefins, are give in Table I.

Results and Discussion

Thermal Properties. Figure 1 shows the DSC traces of samples A, B, and C_1 (see Table I for sample identification). All three samples had been melted and then cooled down to −20 °C at a rate of 16 °C/min just before measurement. The enthalpy of fusion is ca. 100 J/g for all samples. The polymer soluble in ether (sample B) shows a single melting at 58 °C whereas both the unfractionated sample A and the ether-insoluble fraction C_1 display two endotherms at ca. 57 and 80 °C. The area of the first peak decreases with an increase in the extraction

Table I

Intrinsic Viscosities, Molecular Weights, Melting and Crystallization Temperatures, and *d* Spacings of the Different Samples of Poly(octadecylethylene)

sample[b]	[η]	$\overline{M}_v \times 10^{-3}$	DSC heating traces, °C: endotherm(s)		DSC heating traces, °C: exotherm	DSC cooling traces, exotherm(s), °C		*d* spacings,[a] A							
A			57	80		37	52								
B	0.51	44	58			38		26.8 (m)						4.17 (vs)	
C_1	1.73	174	56	82		41	56								
C_2	1.73	174	59	86		41	56	39.1 (vs)	19.8 (m)	13.1 (s)		7.6 (m)	4.96 (m)	4.27 (vs)	3.75 (s)
C_3	1.73	174	58	82	63	41	56	46.0 (m, b)						4.13 (vs)	
C_4	1.73	174	58	78		41	56	49.0 (vs)	24.5 (w)	16.2 (s)	12.7 (w)	9.8 (w)	4.46 (m)	4.18 (vs)	3.7 (w)
C_5	1.73	174		75		41	56	49.1 (vs)	24.5 (m)	16.2 (s)	12.6 (m)	9.7 (w)	4.45 (s)	4.19 (vs)	3.8 (m)

[a] (vs) very strong, (s) strong, (m) medium, (w) weak, (b) broad. [b] Sample identification: (A) as obtained from polymerization, after precipitation and monomer removal (yield 61%); (B) fraction soluble in boiling ethyl ether (34% of A); (C) fraction insoluble in boiling ethyl ether (66% of A); (C_1) sample of C obtained from the melt at a cooling rate of 16 °C/min; (C_2) sample of C obtained from the melt at a cooling rate of 0.5 °C/h (type II, according to Turner Jones[11]); (C_3) sample of C quenched from the melt in liquid N_2 and brought to room temperature; (C_4) same as C_3, annealed 60 h at 55 °C (type I, according to Turner Jones[11]); (C_5) sample of C crystallized from toluene solution.

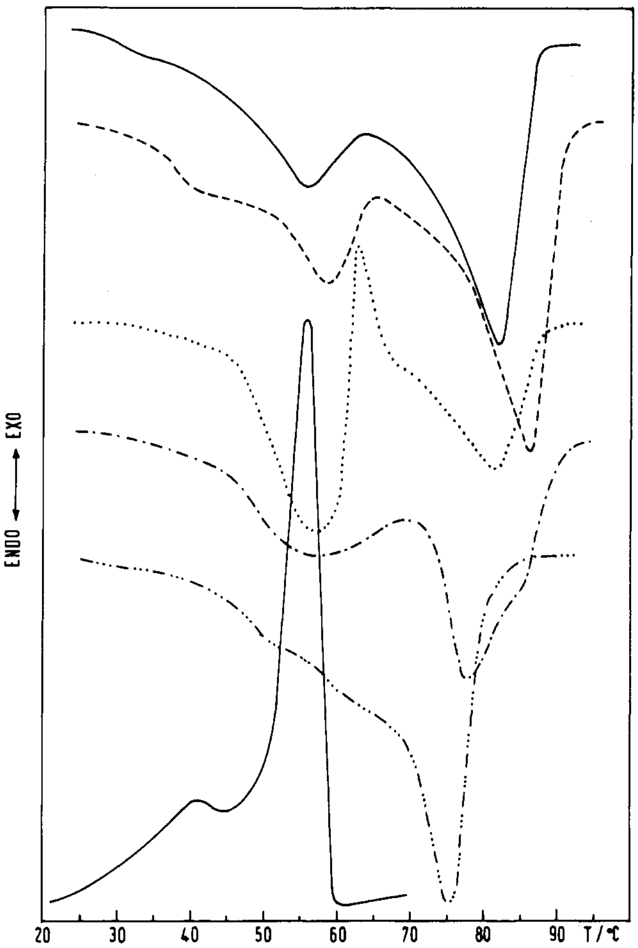

Figure 2. DSC traces of poly(octadecylethylene) sample C: heating and cooling rates 16 °C/min; (—) sample C$_1$, (- - -) sample C$_2$, (···) sample C$_3$, (-·-) sample C$_4$, and (-·····) sample C$_5$ (cf. Table I).

time, but no improved removal of the lower melting crystalline phase could be achieved by extending the extraction time beyond 64 h. We assume that the lower melting material is composed by atactic polymer and attribute the persistence of the residual low-temperature endotherm of the isotactic-rich fraction C to stereoblock structures.

Whereas the thermal treatments did not alter appreciably the DSC trace of sample B, their effect on the DSC trace of sample C is shown in Figure 2.

Sample C$_2$ was obtained following the procedure described by Turner Jones[11] to develop her type II modification (cf. Table I). The relevant DSC trace is similar to that of sample C$_1$ except for the slightly higher melting temperatures and for the low-temperature shoulder. The general similarity of the two DSC traces indicates that the structure of type II modification is thermodynamically and kinetically favored.

The trace of the quenched sample C$_3$ indicates that quenching gives rise to a crystalline structure which melts at a temperature very close to that of fusion of the atactic-rich sample B (cf. Figure 1 and Table I). After this melting, the formation of another crystalline phase becomes favored kinetically, and the isotactic-rich polymer undergoes a fairly rapid crystallization, as revealed by the exothermic peak at ca. 63 °C. The new crystalline phase melts at 82 °C, as does sample C$_1$.

Sample C$_4$ was obtained following the procedure indicated by Turner Jones[11] to obtain the type I modification, i.e., by annealing a quenched sample for 60 h at 55 °C (cf. Table I). We found that this was the best procedure for developing the type I structure of poly(octadecylethylene) by thermal treatments: in fact, if annealing was carried out at a lower temperature and/or for shorter times, the sample showed a stronger low-temperature endotherm and even an indication of an intermediate exotherm; if, conversely, annealing was carried out at a temperature too close to the main melting, the formation of the type II structure was favored and the high temperature shoulder increased or finally became a well-resolved peak. The main fusion of sample C$_4$ (78 °C) is lower than that of sample C$_2$ by 8 °C. This is much more than the difference observed by Turner Jones[11] between the melting points of types II and I modifications of homologous polyolefins (less than 2 °C). The apparent discrepancy may be due to the different techniques employed by Turner Jones and by us for the determination of the melting points (X-ray and DSC, respectively). Sample C$_5$ was obtained with a procedure followed by Holland-Moritz and co-workers,[15] i.e., by dissolving about 50 mg of sample C in 5 mL of boiling toluene, filtering off the liquid, and drying under vacuum the material crystallized on cooling. The low-temperature melting is not absent, as argued by Holland-Moritz, but is spread over a wide temperature range, thus failing to give rise to a well-resolved peak. This may be explained assuming that the atactic-rich blocks responsible for the formation of the lower melting phase, though not crystallized from toluene, were occluded in the crystallized material in the form of a solution which was evaporated later on, leaving a material with a very imperfect crystalline structure. However, the main crystalline phase of sample C$_5$ is composed of material with the type I structure, as revealed by the X-ray analysis.

The cooling trace of sample C, also shown in Figure 2, displays two exotherms, irrespective of the previous history of the sample. This is at variance with what was observed by Holland-Moritz[14] on homologous polymers. The reason of this discrepancy is unknown.

The spectroscopic studies by Fraser[12] and Holland-Moritz[13-16] have shown that, in agreement with Turner Jones's diffractometric results,[11] type II polyolefins are characterized by an orthorhombic unit cell of the side chain crystallites, whereas type I forms have the side chains closely packed but not in an orthorhombic lattice. The main difference between types II and I, as shown by their Raman and infrared spectra, seems to lie in the different types of packing of the essentially planar, all-trans, paraffinic side chains. Only in the type II form are these regularly packed in a three-dimensional lattice with the planes of the carbon atoms of two adjacent methylene sequences mutually perpendicular.

A detailed investigation of the influence of the temperature on the Raman and infrared spectra of isotactic polyolefins with long paraffinic side chains has led Holland-Moritz and co-workers[13-16] to conclude that the orthorhombic packing of the side chains of type II structures is lost in concomitance with the first endothermic transition observed by DTA and that a structure is formed in which the neighbouring CH$_2$ sequences are not contained in planes mutually perpendicular. Our data on the atactic-rich fraction I and on the quenched isotactic-rich fraction II of poly(octadecylethylene) indicate clearly that the low-temperature melting and crystallization peaks are due to a crystalline phase composed of atactic-rich material, although the change from the rhombic to the hexagonal lattice of the isotactic-rich polymer may occur in a close (but considerably broader) temperature range.

X-ray Analysis. The *d* spacings obtained by X-ray diffraction analysis of the samples of poly(octadecylethylene) are given in Table I. The atactic-rich sample B (ether-soluble fraction) is characterized by a very sharp reflection at $2\Theta = 21.3°$, corresponding to a spacing of 4.17 Å, similar to that found for most comb-like polymers studied so far and attributed to a hexagonal packing of the paraffinic side chains.[4] In the region of low angles, a reflection of medium intensity is observed for the same sample corresponding to a spacing of ca. 27 Å. This figure agrees with those found by Turner Jones[11] for homologous isotactic polyolefins examined in the molten state. This spacing is roughly half that displayed by the isotactic sample with type I structure (samples C_4 and C_5) and seems therefore to indicate that the atactic material forms an irregular one-layer structure, or is characterized by side-chain crystallites formed by intercalating side groups pointing in apposite directions, as has been proposed by Morawetz et al.[5] for poly(alkyl methacrylates).

The X-ray diffraction diagram of the quenched sample (C_3) of the isotactic-rich fraction of poly(octadecylethylene) is very similar to that of the atactic-rich material, except for the low-angle reflection which indicates an irregular two-layer structure. Both polymers are characterized mainly by side-chain crystallization with the paraffinic groups packed in a hexagonal lattice. This type of structure melts at ca. 58 °C as indicatd by the thermal analysis.

The crystalline structures of samples C_2 and C_4 or C_5 correspond closely to the modifications of types II and I discussed in detail by Turner Jones.[11]

Conclusions

Our data show that the stereospecific polymerization of octadecylethylene yields a product which is composed of two different crystalline phases. These can be separated to some extent by ether extraction. The atactic-rich fraction is characterized by a single, sharp melting endotherm at 58 °C. The ether-insoluble fraction is made up of isotactic-rich material but probably contains blocks of atactic polymer. Atactic and isotactic polymers give rise to different structures which form incompatible phases, as demonstrated by the two separate melting and crystallization processes shown by both the unfractionated polymer and sample C. The structure of the atactic-rich fraction is characterized by highly disordered main chains and side chains packed in a hexagonal lattice. The isotactic-rich fraction shows a crystalline structure which depends on the thermal history. The quenched sample exhibits only side-chain crystallinity.

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Studies on Comb-like Polymers. 2. Poly(octadecylethylene oxide)

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ABSTRACT: Different samples of poly(octadecylethylene oxide) were studied by thermal and X-ray analysis, and the results were compared with those found for poly(octadecylethylene). The sample prepared by cationic polymerization and the methylene chloride soluble fraction of that prepared by stereospecific polymerization present, on DSC analysis, a single melting endotherm at ca. 68 °C. The X-ray diagrams indicate that these two atactic-rich samples have a structure characterized by hexagonal packing of the side chains and irregular conformation of the main chains. However, the latter are probably confined to regularly spaced planes as shown by the sharp reflection at low angles. The fraction of the stereoregular polymer which is not soluble in methylene chloride displays an endothermic peak near 66 °C and a second endothermic effect at ca. 105 °C. The thermal analysis of the different samples of poly(octadecylethylene oxide) indicates that the atactic and the isotactic materials give rise to different, mutually incompatible, crystalline phases. However, the X-ray data obtained so far for the isotactic-rich sample are not sufficient for a detailed determination of its structure.

In the previous paper[1] we presented thermal and diffractometric data on poly(octadecylethylene) which confirm that the stereoregularity influences both the structure and the properties of long-side-chain polyolefins. In this paper we give a preliminary account of the results of a study of poly(octadecylethylene oxide) which contains one

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