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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References and Notes

(1) C. E. Rehberg and C. H. Fisher, *J. Am. Chem. Soc.*, **66**, 1203 (1944).

(2) H. S. Kaufman, A. Sacher, T. Alfrey, Jr., and I. Fankuchen, *J. Am. Chem. Soc.*, **76**, 6280 (1948).

(3) R. H. Wiley and G. M. Brauer, *J. Polym. Sci.*, **3**, 647 (1948).

(4) N. A. Platé and V. P. Shibaev, *J. Polym. Sci., Macromol. Rev.*, 8, 117 (1974), and references therein.

(5) H. W. S. Hsieh, B. Post, and H. Morawetz, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 1241 (1976).

(6) N. A. Platé, V. P. Shibaev, B. S. Petrukhin, Yu. A. Zubov, and V. A. Kargin, *J. Polym. Sci., Part A-1*, **9**, 2291 (1971).

(7) E. F. Jordan, Jr., D. W. Feldeisen, and A. N. Wrigley, *J. Polym. Sci., Part A-1*, **9**, 1835 (1971).

(8) J. H. O'Donnell, Ph.D. Thesis, Leeds University, 1963.

(9) F. P. Reding, *J. Polym. Sci.*, **21**, 547 (1956).

(10) D. Brownawell and I-Ming Feng, *J. Polym. Sci.*, **60**, S 19 (1962).

(11) A. Turner Jones, *Makromol. Chem.*, **71**, 1 (1964).

(12) G. V. Fraser, P. J. Hendra, J. M. Chalmers, M. E. A. Cudby, and H. A. Willis, *Makromol. Chem.*, **173**, 195 (1973).

(13) K. Holland-Moritz, I. Modric, K. U. Heinen, and D. O. Hummel, *Kolloid Z. Z. Polym.*, **251**, 913 (1973).

(14) K. Holland-Moritz, *Colloid Polym. Sci.*, **253**, 922 (1975).

(15) K. Holland-Moritz, E. Sausen, and D. O. Hummel, *Colloid Polym. Sci.*, **254**, 976 (1976).

(16) I. Modric, K. Holland-Moritz, and D. O. Hummel, *Colloid Polym. Sci.*, **254**, 342 (1976).

(17) D. W. Aubrey and A. Barnatt, *J. Polym. Sci., Part A-2*, **6**, 241 (1968).

(18) G. Trafara, R. Koch, K. Blum, and D. Hummel, *Makromol. Chem.*, **177**, 1089 (1976).

(19) W. Philippoff and E. G. M. Tornqvist, *J. Polym. Sci., Part C*, **23**, 881 (1968).

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 oxygen atom per monomer unit in the main chain and, consequently, has the side chains attached to every third atom of the backbone.

The work of Vandenberg[2] has shown that the cationic polymerization of monosubstituted epoxides gives an atactic polymer with random head-to-tail and head-to-head, tail-to-tail linkages, whereas the polymerization with coordination catalysts produces an isotactic polymer with head-to-tail structure, together with an atactic fraction resulting from head-to-head, tail-to-tail polymerization. Thus, poly(octadecylethylene oxide) lends itself to a study of the effect of tacticity on its structure and properties, although a quantitative determination of the degree of stereoregularity is not possible with the common ^{1}H NMR technique.

The polyethers containing long paraffinic side groups have received comparatively little attention in the past. Allen et al.[3] and Lal and Trick[4] reported the transition temperatures of some poly(alkylethylene oxides) up to poly(decylethylene oxide), but no crystallographic study of these materials is available, to our knowledge.

The only crystallographic study on comb-like polymers containing one paraffinic branch every third atom of the backbone chain is the work of O'Donnell[5] on some poly(alkylethylene sulfones). The main features of the X-ray diffraction diagrams of the higher homologues of this class of polymers follow: (1) a rather broad diffraction band, with fine structure, corresponding to spacings of 4.5–4.9 Å, and (2) a sharp reflection with higher orders at low angles, corresponding to a spacing steadily increasing with the increase of the side-chain length. These features were interpreted as indicating poor regularity in the packing of the side chains but a fairly good lateral packing of the ribbon-like macromolecules. The values of the observed long spacings led O'Donnell to favor a model in which the side branches were inclined to the backbone axis as in isotactic polyolefins with the type II structure.[6] The results obtained by O'Donnell[5] would indicate that an increase of the spacing of the side chains along the main chain has the effect of reducing appreciably the ability of the long paraffinic branches to pack regularly, although the general behavior of a comb-like polymer seems preserved.

The work of Jordan et al.[7-9] and of Platé and Shibaev[10] on copolymers of long-chain monomers with different comonomers also has some relevance to the subject, since the copolymerization has the effect of increasing the average distance between successive long side groups along the main chain. All of the copolymers studied were shown to give rise to side-chain crystallinity over very wide ranges of composition, whatever the comonomer used. Moreover, the work of Jordan has demonstrated that the melting point of a comb-like polymer is only slightly depressed by increasing the comonomer content and, even more interesting, that the heat of fusion per unit weight of the long-side-chain component is almost invariant with copolymer composition. However, in these copolymers, the possibility of the presence of blocks of different length containing side groups linked to every second atom of the backbone cannot be ruled out completely.

Experimental Section

Octadecylethylene oxide was synthesized by epoxidation of purified octadecylethylene[1] with the procedure described by Emmons and Pagano[11] for the preparation of other olefin oxides. The pure monomer had mp 45 °C.

The cationic polymerization was carried out under vacuum, in 1,2-dichloroethane, at 20 °C for 1 h, using epichlorohydrin and a BF_3–THF complex as initiator. The residual monomer was removed by repeated precipitation into mixtures of methanol and methylene chloride (78/22 v/v). The polymer was finally washed

Table I
Intrinsic Viscosities, Melting and Crystallization Temperatures, and *d* Spacings of the Different Samples of Poly(octadecylethylene oxide)

sample[c]	[η]	DSC heating traces, endotherm(s), °C		DSC cooling traces, exotherm(s), °C		*d* spacings,[a] Å						
A	0.35	67		54		51.0 (vs)		17.3 (s)		10.5 (m)		4.13 (vs)
B		65	105[b]	48	73	50.0 (w)	45.0 (vs)	16.8 (w)	14.8 (s)		8.9 (w)	4.12 (vs)
C	0.50	65		48		50.5 (vs)		16.8 (s)		10.2 (w)		4.13 (vs)
D	4.17	65	103[b]	49	76		42.1 (vs)		14.7 (s)		8.9 (m)	4.10 (vs)
E		65	102	44	76							

[a] (vs) very strong, (s) strong, (m) medium, (w) weak. [b] This figure corresponds to the highest temperature endotherm. [c] Sample identification: (A) atactic polymer prepared by cationic polymerization; (B) unfractionated polymer prepared by stereospecific polymerization; (C) sample of B, soluble in boiling methylene chloride (30% of B); (D) sample of B, insoluble in boiling methylene chloride (70% of B); (E) sample of D added with 15% (w/w) hexanol.

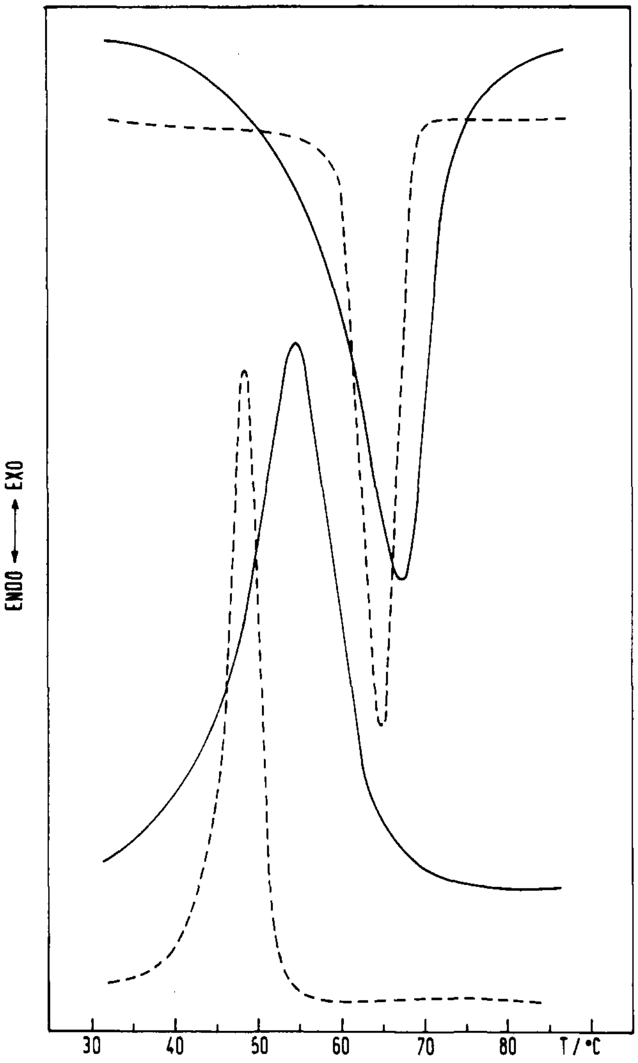

Figure 1. DSC traces of poly(octadecylethylene oxide): heating and cooling rate 16 °C/min; (—) sample A and (- - -) sample C (cf. Table I).

with cold diethyl ether. The yield was 69%.

The stereospecific polymerization was carried out under vacuum, in heptane, at 50 °C for 20 h, with a Ni-dimethylglyoxime-$Al(C_2H_5)_3$ catalyst. The product, washed repeatedly with boiling methanol containing 2% hydrochloric acid and with boiling distilled water, was precipitated into methanol from a hot toluene solution (5 g in 5 L of solvent). The yield was 65%.

The polymer was fractionated with boiling methylene chloride for 90 h. Previous attempts with different solvents such as acetone,[4] butanone, and ether failed to give appreciable results.

The yields of the fractions and their intrinsic viscosities measured in toluene at 25 °C are given in Table I.

Results and Discussion

Thermal Properties. In Figure 1 are reported the DSC heating and cooling traces of samples A and C (cf. Table I). It is evident that the cationic polymer as well as the CH_2Cl_2-soluble fraction of the polymer prepared with the stereospecific catalyst present a single melting and crystallization process, as does the atactic-rich fraction of the parent poly(octadecylethylene).[1]

Samples A and C are therefore assumed to be atactic and composed by a single, crystalline phase. This melts approximately 10 °C higher than atactic poly(octadecylethylene).

Figure 2 shows the DSC traces of samples B, D, and E. The heating traces of samples B and D display a sharp low-temperature endotherm, corresponding to that of samples A and C, plus an ill-resolved endothermic effect spread over a wide temperature range. The higher temperature effect is, on the contrary, very well visible on the cooling traces, where two distinct exotherms are visible. Jordan et al.[12] have shown that the addition of an appropriate nonsolvent to comb-like polymers can increase both crystallinity and crystal perfection. The traces obtained with a sample of polymer containing 15% (w/w) of hexanol (sample E) are also shown in Figure 2. Although the alcohol has caused a slight change in the transition temperatures and of the relative areas of the melting and crystallization peaks, it has also caused a much better resolution of the high temperature endotherm.

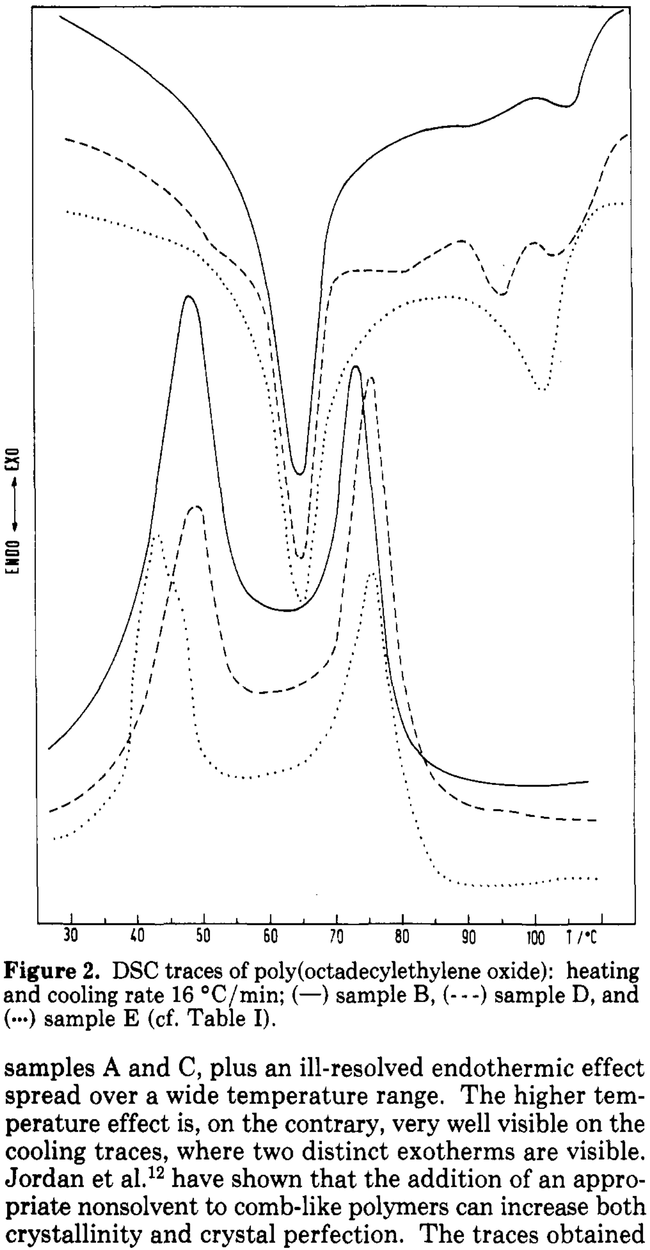

Figure 2. DSC traces of poly(octadecylethylene oxide): heating and cooling rate 16 °C/min; (—) sample B, (- - -) sample D, and (···) sample E (cf. Table I).

Figure 2 shows that all three samples, B, D, and E, are composed of two immiscible, crystalline phases. Comparison with Figure 1 demonstrates that only the lower melting crystalline phase is extractable with boiling CH_2Cl_2. However, as demonstrated by the trace of sample D in Figure 2, the extraction of the lower melting material is far from complete despite the long extraction time employed.

The results of the calorimetric study indicate that the stereoregular sample of poly(octadecylethylene oxide) is composed of two phases: the first appears identical with the atactic sample obtained via cationic polymerization; the second is probably composed of highly isotactic material. This finding demonstrates that stereoregularity has an appreciable effect on the structure and the properties of poly(alkylethylene oxides). In this respect, these polymers resemble closely the parent polyolefins.[1] The melt enthalpies measured for all samples of poly(octadecylethylene oxide) were of about 125 J/g, independent of tacticity. This figure is somewhat higher than that found for the corresponding polyolefin. This point will be discussed in more detail in a future paper.

X-ray Analysis. The *d* spacings of the powder X-ray diffraction diagrams obtained with the samples of poly(octadecylethylene oxide) are reported in Table I. All samples show a single, sharp reflection at wide angles plus a strong, very sharp reflection at low angles with several odd orders. In the wide-angle region, the diagrams differ appreciably from those obtained by O'Donnell[5] for poly(alkylethylene sulfones). For the latter polymers, a much broader diffraction band, with some fine structure, had been observed, corresponding to spacings in the range 4.5–4.9 Å, whereas for poly(octadecylethylene oxide), the single, sharp reflection corresponds to ca. 4.1 Å. We cannot offer any definite explanation for the apparent discrepancy. However, it must be noted that, although both types of polymers contain on the average one side chain on every third atom of the backbone, appreciable differences may arise from at least two factors: (1) the steric and polar character of the SO_2 groups of polysulfones is very different from that of the oxygen atoms of poly(octadecylethylene oxide) and therefore the main chains of the two polymers probably experience very different intra- and intermolecular interactions, which in turn influence the way of packing of the side groups; and (2) if the backbone chains are imagined in a planar all-trans conformation, a mean distance of 7.21 Å between two successive side groups on each side of the main chain can be calculated for poly(octadecylethylene oxide), whereas this distance becomes 8.45 Å for O'Donnell's polymers.

The wide-angle region of the diffraction diagrams of poly(octadecylethylene oxide) resembles closely that exhibited by most comb-like polymers, except for isotactic polyolefins. It is also very similar to the diagrams of atactic and quenched isotactic poly(octadecylethylene).[1] With respect to the latter polymers, a slightly lower spacing (4.10–4.13 vs. 4.17 Å) is observed in poly(octadecylethylene oxide), which indicates a slightly tighter packing of the paraffinic side groups in this polymer. By analogy with the X-ray diagrams of most comb-like polymers,[10] we assume that the paraffinic side chains of atactic poly(octadecylethylene oxide) are packed into a hexagonal lattice. The intensity and sharpness of the wide angle reflex, i.e., the extent and regularity of packing of the side groups, increase as a result of the annealing.

As for the low-angle reflection, it must be noted that, contrary to poly(octadecylethylene), poly(octadecylethylene oxide) displays a very sharp and intense diffraction peak also in its atactic samples A and C. The spacing corresponding to this reflection is of the order of 50 Å and is therefore very close to that which could be calculated assuming that the side groups were extended at right angles on both sides of the main chain.

The occurrence of the low-angle reflection in atactic poly(octadecylethylene oxide) indicates that, though the main chains possess an irregular conformation as a result of stereoirregularity and of random head-to-tail and head-to-head, tail-to-tail enchainments, they are most probably confined to regularly spaced parallel planes perpendicular to the direction of the side chains. Poly(octadecylethylene oxide), as well as many comb-like polymers having the paraffinic side chain linked to the backbone through polar groups, display a structure reminiscent of smectic liquid crystals, superimposed upon the crystalline packing of the side groups, probably because of the polar nature of the main chains (including the eventual bridging groups) with respect to the side groups which therefore undergo an easier segregation. This difference of polarity becomes very slight in polyolefins and this may explain the absence of strong low-angle reflections in atactic and quenched isotactic poly(octadecylethylene).[1]

The isotactic-rich sample D is characterized by a smaller spacing (ca. 42 Å) of the planes containing the backbone chains. If the side chains are imagined as fully extended in an all-trans conformation, they must be inclined with respect to these planes by about 120°. A structural model similar to that proposed by Turner Jones[6] for type II polyolefins could therefore be applicable to isotactic poly(octadecylethylene oxide).

Conclusions

The calorimetric data and the powder X-ray diffraction results indicate that atactic poly(octadecylethylene oxide) is composed of a single crystalline phase characterized by efficient hexagonal packing of the side groups and main chains confined to regularly spaced, parallel planes perpendicular to the direction of the side chain. The sample prepared by stereospecific polymerization is composed of two independent crystalline phases which may be separated to some extent by solvent extraction. The soluble fraction, probably atactic, is practically identical with the sample prepared by cationic polymerization. The insoluble fraction, composed mainly of isotactic material, is also characterized by closely packed side groups, but these are oriented at an angle of ca. 120° with respect to the planes of the main chains. The two structures have distinct melting and crystallization temperatures.

The results obtained by studying poly(octadecylethylene oxide) demonstrate that the increased spacing of the side groups of this polymer along the main chain, with respect to the usual spacing prevailing in most known comb-like polymers, has not impaired their ability to pack closely to give crystalline structures. Moreover, our data indicate that, as already observed for the polyolefins,[1,6] the stereoregularity influences strongly both the properties and the crystalline structure of poly(alkylethylene oxides).

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References and Notes

(1) P. L. Magagnini, F. Andruzzi, and G. F. Benetti, *Macromolecules*, accompanying paper.
(2) E. J. Vandenberg, *J. Polym. Sci., Part A-1*, **7**, 525 (1969).
(3) G. Allen, C. Booth, and C. Price, *Polymer*, **8**, 414 (1967).
(4) J. Lal and G. S. Trick, *J. Polym. Sci., Part A-1*, **8**, 2339 (1970).
(5) J. H. O'Donnell, Ph.D. Thesis, Leeds University, 1963.
(6) A. Turner Jones, *Makromol. Chem.*, **71**, 1 (1964).
(7) E. F. Jordan, Jr., B. Artymyshyn, A. Speca, and A. N. Wrigley, *J. Polym. Sci., Part A-1*, **9**, 3349 (1971).
(8) E. F. Jordan, Jr., *J. Polym. Sci., Part A-1*, **9**, 3367 (1971).
(9) E. F. Jordan, Jr., G. R. Riser, B. Artymyshyn, J. W. Pensabene, and A. N. Wrigley, *J. Polym. Sci., Part A-2*, **10**, 1657 (1972).
(10) N. A. Platé and V. P. Shibaev, *J. Polym. Sci., Macromol. Rev.*, **8**, 117 (1974), and references therein.
(11) W. D. Emmons and A. S. Pagano, *J. Am. Chem. Soc.*, **77**, 89 (1955).
(12) E. F. Jordan, Jr., D. W. Feldeisen, and A. N. Wrigley, *J. Polym. Sci., Part A-1*, **9**, 1835 (1971).