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Comblike Polymers

8. Synthesis and Characterization of an Alternate Copolymer of Phthalic Anhydride and Octadecyloxirane

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Summary

A new comblike polyester has been synthesized by the alternate copolymerization of phthalic anhydride and octadecyloxirane and has been separated from the octadecyloxirane homopolymer by ether extraction. The chemical structure of the polyester has been proved by IR and NMR analysis. The X-ray analysis and the differential scanning calorimetry have shown that the polyester is characterized by side-chain crystallinity despite of the considerable distance between adjacent paraffinic groups along the main chains. A long range order arising from the organization of the main chains on parallel planes is also shown by a low angle X-ray reflection.

Introduction

In the previous papers of this series (1) we have described the structure-properties relations of two families of comblike polymers, namely polyolefins and polyoxiranes with long, unbranched paraffinic side-chains. One of the most interesting results coming out from a comparison of the data obtained for these two polymer families is that the ability of the side-chains to become arranged into crystalline structures is not imparted if they are bonded to every third atom of the backbone (as in the polyoxiranes) rather than to every second main chain atom (as in the polyolefins and in all other common comblike polymers).

The conclusion that the side paraffinic chains of comblike polymers are still able to crystallize even if displaced to a longer distance from each other along the main chain has found a striking demonstration with the study of octadecyloxirane-oxirane copolymers (2). It has been found, in fact, that a copolymer with only 18% mole octadecyloxirane (A) and 82% mole oxirane (B) and containing a concentration of BAB triads much higher than expected for a random copolymer of this composition, still shows side-chain crys-

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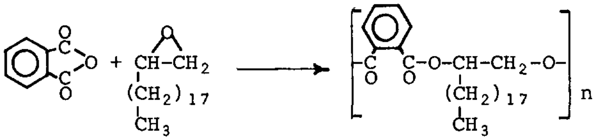
† Part 7: A.L. Segre, F. Andruzzi, D. Lupinacci, and P.L. Magagnini, Macromolecules 16, 1207 (1983)

tallinity. The enthalpy of fusion of this copolymer is of 36.4 kJ per mole of octadecyloxirane unit.

On the other hand, Corradini et al. (3) had already demonstrated that side-chain crystallization occurs even in poly(alkylmalonamides) with the C_{14}-C_{18} branches bonded to every 8th-14th main chain atom.

In the present note we describe the synthesis and the characterization of a new comblike polyester containing octadecyl side groups bonded to every 7th-9th main-chain atom. The polyester has been prepared through the alternate copolymerization of phthalic anhydride and octadecyloxirane (eq. 1) according to a procedure set up recently (4).

(Eq. 1)



Experimental

Phthalic anhydride (Aldrich) has been purified by double sublimation on the vacuum line (m.p. 405 K).

Octadecyloxirane has been prepared and purified as described in a previous paper of this series (5).

Toluene has been refluxed over sodium and fractionated.

Et_3Al-$Ni(dmg)_2$ has been prepared and used as described (5).

$(i\text{-}Bu)_3Al$ (Stauffer Chem. Co.) has been distilled on the vacuum line just before use.

Equimolar amounts (10^{-2} mole) of phthalic anhydride and octadecyloxirane have been introduced in a pyrex ampoule connected to the vacuum line. The latter has been evacuated and toluene (40 ml) has been run in the ampoule from a burette. After the addition of the catalyst (1.5-$2 \cdot 10^{-4}$ mole), the ampoule has been sealed off and immersed in a thermostatic bath at 80 ^{o}C for 24h. The viscous polymer solution has been diluted with sufficient toluene and poured with stirring into excess methanol-ether mixture (90/10 v/v). The white polymer has been reprecipitated from $CHCl_3$ solution into methanol and dried in vacuo. The crude polymer has been fractionated by extraction with boiling ether in a Kumagawa apparatus.

The IR analysis of the polymers, as films on KBr discs, has been made with a Perkin Elmer Mod. 283 instrument.

^{1}H NMR spectra have been measured with a X-L 100 Varian spectrometer at 100 MHz. The samples were 2% w/v $CDCl_3$ solutions in 5 mm tubes.

The ^{13}C NMR spectra have been taken on a Brucker WP 200 apparatus at 50.28 MHz on $CDCl_3$ solutions (8% w/v) in 10 mm tubes, with an accumulation of 17400 transients.

The DSC traces have been obtained with a Perkin Elmer DSC-1B instrument.

Powder X-ray diffractograms have been obtained with a Siemens D-500 apparatus.

Results

The polymer yields obtained with either of the catalyst systems {Et_3Al-$Ni(dmg)_2$ and $(i\text{-}Bu)_3Al$} were in the range 70-80%. However, the DSC traces of the polymers obtained with the two catalysts differ markedly. The DSC trace of the polymer produced with Et_3Al-$Ni(dmg)_2$ shows three well defined endotherms at ca. 315, 335 and 375 K. The last two endotherms correspond to the fusion of the atactic and stereoregular octadecyloxirane homopolymers, respectively (1), whereas that at ca. 315 K might be tentatively assigned to the copolymer. Thus, the copolymerization initiated by Et_3Al-$Ni(dmg)_2$ is accompanied by extensive homopolymerization of octadecyloxirane which leads, as it is usual with this catalyst, to both atactic and stereoregular polymer (5).

On the contrary, the DSC trace of the polymer obtained with $(i\text{-}Bu)_3Al$ shows only a small endotherm at ca. 335 K (atactic homopolymer) besides the main endotherm at 316 K.

The fraction soluble in hot ethyl ether, as obtained by extraction of the crude polymers in a Kumagawa apparatus, consists of low-melting material, contaminated by traces of atactic homopolymer. The DSC trace of this material is shown in Fig. 1. The melting temperature of 316 K is ca. 20 K lower than that of the atactic octadecyloxirane homopolymer (1). The enthalpy of fusion is also lower: 19.8 $KJ \cdot mole^{-1}$.

The chemical structure of the alleged copolymer has been determined by IR and NMR analysis. The IR spectrum (Fig. 2) shows the

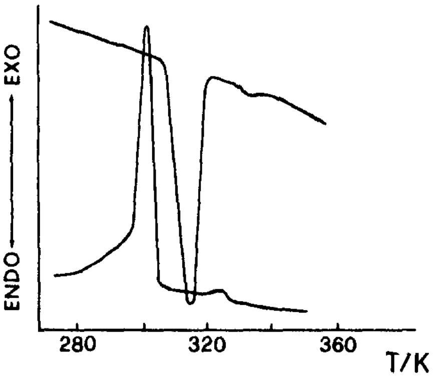


Fig. 1
DSC traces of the ether-soluble polymer.

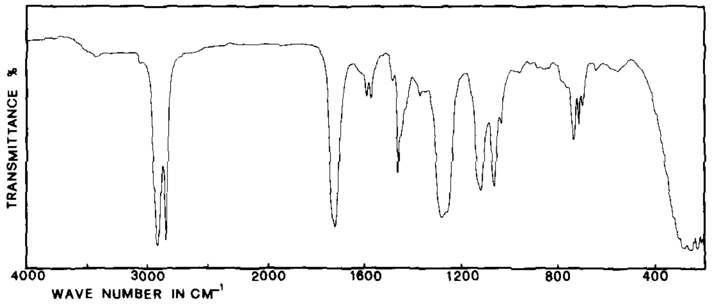


Fig. 2
IR spectrum of the ether-soluble polymer.

absorption bands typical of the ester group (1725 and 1275 cm^{-1}) as well as those due to the aromatic ring (3030, 1600-1425, and 735-700 cm^{-1}) besides those of the aliphatic groups of the octadecyloxirane unit. The IR spectrum is, therefore, a demonstration that both phthalic anhydride and octadecyloxirane have been incorporated into the polymer chain to give rise to an ester structure.

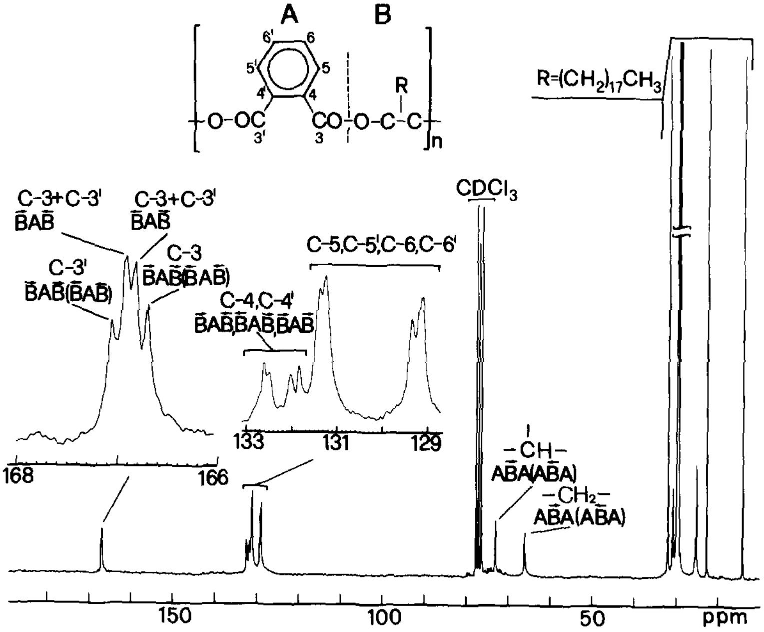


Fig. 3
50.28 MHz ^{13}C NMR spectrum of the copolymer.
The small shaded peaks at 72,74, and 79 ppm are attributed to octadecyloxirane homopolymer.
Arrows denote the orientation of the B units:
$\overleftarrow{B}$ = -O-CH(R)-CH$_2$- and $\overrightarrow{B}$ = -O-CH$_2$-CH(R)-

The ^1H NMR analysis has shown that the ratio of aromatic to aliphatic protons is consistent with a 1:1 ratio of phthalic anhydride to octadecyloxirane units in the macromolecular compound.

Fig. 3 shows the ^{13}C NMR spectrum of this polymer sample. The assignments are indicated in the same figure. The resonances at ca. 167 ppm and those in the region between 128 and 133 ppm have been assigned, respectively, to the carbonyl and to the ring carbons of the structural unit A. The peaks at 73 and 66 ppm, and the group of signals in the aliphatic resonance region between 13 and 33 ppm, have been attributed, in the order, to the main-chain methine and methylene carbons and to the side-chain carbons of the octadecyloxirane unit B. The assignments are based either on ^{13}C chemical shift values of carbonyl carbons in aromatic carboxylic esters (6) or on the spectral characteristics of closely related poly(alkylene esters) of aromatic dicarboxylic acids (7,8), and also on previous NMR data on octadecyloxirane polymers (9). The discrimination between protonated and unprotonated ring carbons has been aided by the consideration that these latter carbons generally give less intense signals due to reduced Overhauser enhancement.

The assignment of carbonyl and unprotonated ring carbons to different triads centered on A may be reasonably interpreted in terms of substitution effects due to the different possible orientations of the two adjacent B units. The sequence assignments are consistent with the number of the observed resonances, as well as with an approximate calculation of the peak areas.

As far as the protonated ring carbons are concerned, however, their resonance pattern cannot be explained with the same considerations because they are probably insensitive to these substitution effects. Their four-resonances pattern might be better explained in terms of cis vs. trans conformation of the carbonyl groups bonded to the ring (6).

All these observations, together with the fact that the resonances of the methine and methylene carbons appear as single peaks, demonstrate that the polymer under study has a polyester structure originated by an alternation of A units and randomly oriented B units.

The powder X-ray diffraction pattern of the copolymer is shown in Fig 4. The sharp reflection at $2\theta = 21.2$, corresponding to a 4.19 Å spacing, is typical of the crystalline packing of the polymethylene side-chains in a hexagonal lattice. The hexagonal packing of the paraffinic side-groups is also proved by the unsplitted rocking band at 720 cm^{-1} in the IR spectrum (10). The information obtained from the calorimetric analysis indicates that the enthalpy of fusion and, therefore, the degree of crystallinity of the copolymer are appreciably lower than expected for a comblike polymer with octadecyl side-groups (1). Nevertheless, it is noteworthy that side

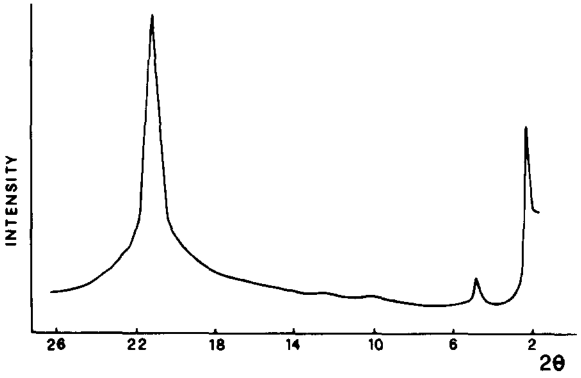


Fig. 4
Powder X-ray diffraction diagram of the copolymer.

chain crystallization can take place even in this macromolecular compound, in which the side-groups are spaced by 7-9 main-chain atoms. Moreover, the sharp low angle reflection at 2Θ = 2.3 (Fig.4) demonstrates that a long range order attributable to some kind of organization of the main chains in layers takes place in this copolymer.

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