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Preparation and characterization of comb-shaped polyesters from 2,2-dioctadecyl-1,3-propanediol and phthalic acids

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Summary

New types of comb-shaped polyesters have been prepared by transesterification of 2,2-dioctadecyl-1,3-propanediol and the three isomeric diphenyl phthalates. Intrinsic viscosity and SEC analyses allowed determination of DPs (60-89) and molar masses; results compare well with absolute average weight molar masses (56,000-118,000) determined by low-angle laser light scattering. High-resolution ^{13}C NMR reveals the characteristic aromatic and glycol polyester patterns; it resolves many side-chain methylene carbons, but shows no evidence of end-groups. All the polyesters are crystalline as shown by X-ray diffractometry and DSC, the crystallinity being exclusively due to the octadecyl side-group crystallization in the hexagonal form. The results indicate that the crystallinity decreases substantially when going from the ortho- to the terephthalate polyester.

Introduction

Polyesters carrying long paraffinic side-groups are attractive members of the comb-shaped polymer family because their polyester nature offers extensive flexibility in the choice of building blocks and hence, at least in principle, wide possibilities of governing the properties. We have previously been interested in the study of aromatic comb-shaped polyesters with octadecyl side-groups on the glycols, 1,2-icosanediol and 2-octadecyl-1,3-propanediol (1-4). Very recently we initiated a programme (5-7) aiming at a detailed understanding of the relationship between structure and properties of well defined and characterized aliphatic and aromatic comb-shaped polyesters.

In this communication we report on the preparation and characterization of new types of aromatic comb-shaped polyesters with two octadecyl side-groups on every glycol unit. To our best knowledge, only one other account describes the preparation of polyesters with two long side-groups in every repeat unit; recently Ballauff (8) has reported on poly(1,4-phenylene-2,5-dialkoxyterephthalate)s with two hexadecyl groups. In this case, however, the side-groups are positioned on the acidic part of these all aromatic main-chain, and hence rigid-chain, polyesters.

Experimental

Materials

2,2-Dioctadecyl-1,3-propanediol (BOPD)

The glycol was prepared by $LiAlH_4$ reduction of the corresponding diethyl 2,2-dioctadecyl-malonate (m.p. 51.7 °C, by DSC) which was obtained by alkylation of diethyl 2-octadecyl-malonate prepared and purified as described recently (6). After recrystallization from methanol, BOPD has m.p. 74.8 °C.

Diphenyl phthalate, isophthalate, and terephthalate

These precursors were synthesized and purified as described previously (2).

Polyester synthesis

The polyesters are prepared according to the polytransesterification procedure newly developed for comb-shaped polyesters based on aliphatic diphenyl esters (6).

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Polyester characterization

Intrinsic viscosities

Limiting viscosity numbers of polyesters were measured in THF at 303.15 K in an Ubbelohde viscometer, whereas for the polystyrene standards were evaluated from the Mark-Houwink equation with $k = 1.4 \cdot 10^{-4}$ and $\alpha = 0.70$ (9).

Size exclusion chromatography (SEC)

Polyester SEC measurements were carried out on a Millipore-Waters II apparatus equipped with a set of three ultrastyragel columns with 10^3, 10^4 and 10^5 Å pore size, respectively, using refractive index detection and tetrahydrofuran as eluent at a flow rate of 1.0 ml min^{-1}. Sample concentrations were in the range 0.20-0.30% (w/v). Absolute weight average molar masses were determined by low-angle laser light scattering (LALLS) with a Chromatix KMX-6 Photometer coupled to a Optilab 5902 Refractometer using a light source operating at 632.8 nm and a Knauer HPLC Pump 64 (10). The necessary (dn/dc) determinations were performed on 3 ml 0.15% and lower (w/v) THF solutions at a flow rate of 0.8 ml min^{-1}.

^{13}C nuclear magnetic resonance (NMR) spectroscopy

Polymer spectra were recorded at 62.896 MHz on a Bruker AC 250 spectrometer. The spectra were obtained at 300 K on 20% (w/v) solutions in $CDCl_3$ in 5mm I.D. tubes. Spectra were recorded with a pulse width of 2.3 μs (≈ 45°); a 0.92 s pulse acquisition and 2 s pulse repetition were used to obtain ≈1000 scans. Chemical shifts are referenced to the central resonance of $CDCl_3$ (76.90 ppm from tetramethylsilane).

Differential scanning calorimetry (DSC)

DSC experiments were performed on a Perkin-Elmer DSC-4 instrument equipped with an Intracooler-I apparatus.

X-ray diffraction

The powder X-ray diffractograms were obtained on a Siemens D-500 diffractometer employing the CuK_α radiation.

Results and Discussion

Poly(2,2-dioctadecyl-1,3-propylene phthalate) (PBOPOP), poly(2,2-dioctadecyl-1,3-propylene isophthalate) (PBOPIP), and poly(2,2-dioctadecyl-1,3-propylene terephthalate) (PBOPTP) were prepared by the newly developed two-stage ester-interchange reaction which proved to be very effective in obtaining high molar masses for a series of comb-shaped polyesters based on medium-to-long aliphatic diphenyl esters and 2-octadecyl-1,3-propanediol (6). The SEC traces in all instances revealed single symmetrically shaped peaks indicating a uniform molar mass distribution. The indicative molar masses, $\overline{M}_p$, listed in Table 1, were determined at the peak maximum by means of a universal calibration plot obtained from polystyrene standards. These molar masses have been used to estimate the number average degree of polymerization, $\overline{DP}$, of this new class of comb-shaped aromatic polyesters employing the relationship: $\overline{M}_n = \overline{M}_p / \sqrt{2}$

Table 1 Intrinsic viscosities, molecular masses, and degrees of polymerization for polyesters from 2,2-dioctadecyl-1,3-propanediol and the phthalic acids.

Polyester	Acid	$[\eta]$ / dl g^{-1}	$\overline{M}_p$[a]	DP[b]	$\overline{M}_{w,\,cal}$[c]	$\overline{M}_{w,\,abs}$[d]
PBOPOP	Orthophthalic	0.25	60,000	60	89,000	56,000
PBOPIP	Isophthalic	0.31	69,000	69	98,000	93,000
PBOPTP	Terephthalic	0.41	89,000	89	126,000	118,000

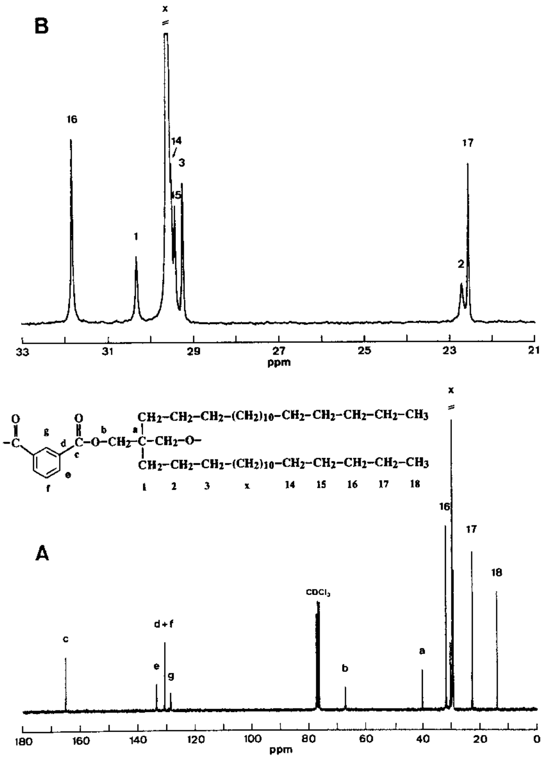
[a] From SEC peak position by use of a universal calibration with PS standards.

[b] Number average degree of polymerization calculated from $\overline{M}_n = \overline{M}_p / \sqrt{2}$ as previously deduced (6).

[c] Molar masses calculated employing $\overline{M}_w = \sqrt{2}\ \overline{M}_p$ (6).

[d] Absolute molar masses determined by LALLS.

Figure 1 62.90 MHz ^{13}C NMR spectrum of the polyester based on isophthalic acid (PBOPIP) (A); expansion of part of aliphatic region (B).

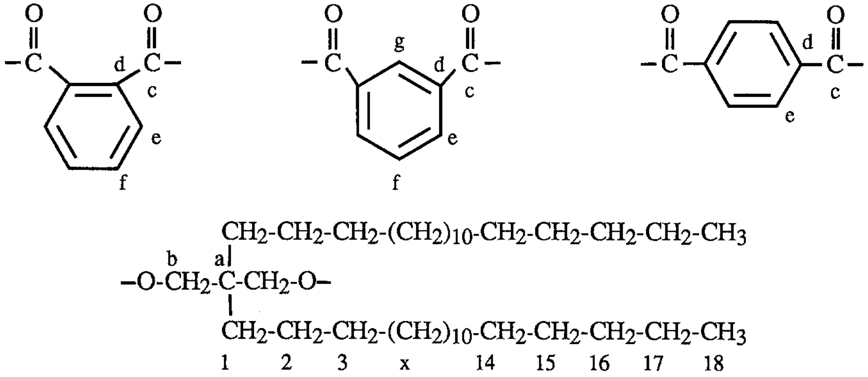


deduced previously (6) for this kind of polycondensation system. The calculated DPs, listed in Table 1, range from 60-89 and fulfill the intrinsic requirements for obtaining polyesters with attractive mechanical properties. The absolute weight average molar masses, $\overline{M}_{w,abs}$, also listed in Table 1, determined by LALLS, compare (except for PBOPOP) well with the calculated molar masses, $\overline{M}_{w,cal}$, lending confidence to the argument leading to the DP estimate.

In an attempt to investigate the microstructure, the polyesters were characterized by high-resolution ^{13}C NMR in $CDCl_3$ solution. A representative spectrum of PBOPIP is shown in detail in Fig.1. The ^{13}C chemical shifts of all three polyesters are listed in Table 2. The aromatic carbons (d-g) of the the three polyesters are identified by the characteristic pattern previously assigned in other comb-shaped polyesters (3,4). However, in this case only three of the usually four peaks are resolved for the isophthalic unit, whereas the typical three and two peaks are seen for the orthophthalic and terephthalic units, respectively. In fact, the chemical shifts of the aromatic carbons are virtually insensitive to influences from the second octadecyl side-chain. Also, the carbonyl shifts (c) are only marginally influenced by the introduction of the second side-chain into the glycol units. All glycol carbon assignments are facilitated by previous NMR investigations on 2-octadecyl-1,3-propanediol based aromatic (4) and aliphatic (6) polyesters. The glycol main-chain carbons, (a) and (b), both experience deshieldings in contrast to corresponding carbons in the octadecyl monosubstituted series as a result of the second octadecyl side-chain. Also the side-chain methylene carbons closest to the branching points, (1) and (2) (of Fig. 1 and Table 2), in a similar manner are deshielded and shielded, respectively. However, the chemical shifts of both glycol main-chain and methylene side-chain carbons are only marginally influenced by the structurally different aromatic acids. These observations are consistent with those of the corresponding monosubstituted series (7).

Careful inspection of the ^{13}C NMR spectra of the polyesters in the aromatic and glycol main-chain regions does not reveal any peaks which could originate from phenyl ester (5,7) or glycol end-groups (11,12), respectively. The phenyl resonances are clearly separated from the aromatic acid resonances (7), but are only slightly dependant on the type of adjoining aromatic acid. The oxymethylene and the quaternary glycol carbon atoms will be shielded and deshielded 1-2 ppm, respectively, in a glycol end-group in contrast to a glycol triad. We predict these resonances to be observable by ^{13}C NMR if end-groups are present in >2-3%.

Table 2 62.90 MHz ^{13}C NMR chemical shifts of polyesters from 2,2-dioctadecyl-1,3-propanediol and aromatic acids, ppm in $CDCl_3$.



Sample	Acid	a	b	c	d	e	f	g
PBOPOP	Orthophthalic	39.65	67.79	167.00	132.14	130.82	128.71	-
PBOPIP	Isophthalic	40.11	67.20	165.22	130.74	133.58	130.74	128.58
PBOPTP	Terephthalic	40.04	67.06	165.31	133.97	129.49	-	-

Sample	Acid	1	2	3	x	14	15	16	17	18
PBOPOP	Orthophthalic	30.37	22.67	29.25	29.65	29.58	29.51	31.83	22.56	13.94
PBOPIP	Isophthalic	30.34	22.73	29.26	29.62	29.53	29.44	31.83	22.57	13.96
PBOPTP	Terephthalic	30.27	22.59	29.27	29.61	29.48	29.39	31.83	22.59	13.99

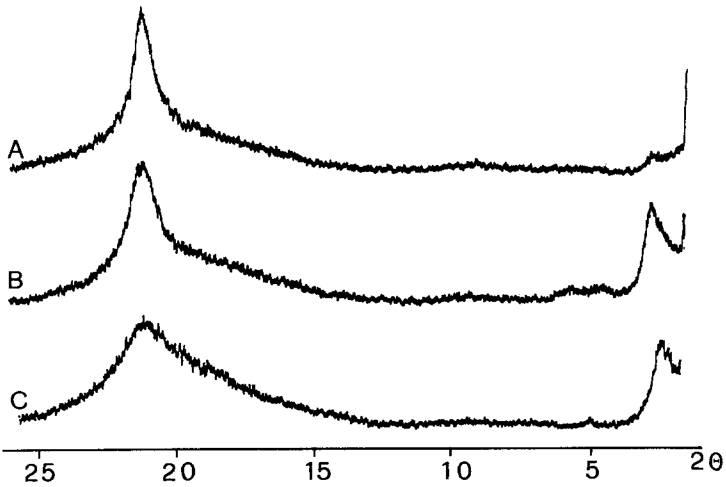


Figure 2 Powder X-ray diagrams of virgin samples of polyesters: PBOPOP (A), PBOPIP (B), and PBOPTP (C).

The powder X-ray diffractograms of samples of polyesters BPOPOP, PBOPIP, and BPOPTP as isolated from precipitation in methanol are shown in Fig. 2. The presence of a strong reflection in the wide-angle region at $2\Theta \approx 21.1°$, corresponding to a spacing of 4.20Å, is typical of paraffinic side-chain crystallization with hexagonal packing. This is in agreement with previous X-ray observations of other crystallizable polyesters based on phthalic acids and the octadecyl monosubstituted diol (4), as well as with the observed relatively low values of melting temperatures and enthalpies to be discussed below. A comparison of the patterns in Fig. 2 shows a decrease of intensity and peak broadening of the wide-angle reflection on going from (A) to (C), thus indicating a decrease of crystallinity of the same order from PBOPOP to PBOPTP. This trend is consistent with the results of the calorimetric measurements.

The reflection in the low angle region, corresponding to a spacing of 29-34Å, is attributable to the arrangement of the main-chains in parallel planes. The otherwise more ordered polyester PBOPOP shows a very weak low-angle reflection. At present, we cannot offer an explanation for this finding.

The thermal behaviour of the polyesters measured by DSC is shown in Figs. 3-5. The relevant calorimetric data are collected in Table 3. Inspection of Figs. 3-5 shows that the virgin samples of all the polyesters are characterized, on the first heating run, by similar thermograms featuring a single endothermic peak (traces a), with small changes (not exceeding 3°C) in the melting point values. However, more conspicuous differences are observed from the corresponding values of the melting enthalpies, as is clearly seen from Table 3. This trend is attributed to a decrease of crystallinity on going from PBOPOP to PBOPTP, in agreement with the X-ray observations. Figures 3 and 4 show that the thermal history influences the melting temperatures of PBOPOP and PBOPIP, whereas the peak shape remains almost unaffected. A more complex behaviour with peak broadening and dual melting is displayed by the sample of PBOPTP cooled from the melt as shown by traces (b) and (c) of Fig. 5. From a structural point of view the different thermal behaviours observed for the PBOPTP samples crystallized from the melt might be due to a different combination of side- and main-chain properties, that is to say, to the occurrence of conformations less favourable to the side-chain crystallization with respect to PBOPOP and PBOPIP. However, polyester annealing is effective in restoring the single peak behaviour. In particular, the prolonged annealing leads to an improvement of peak sharpness for all three polymers.

Table 3 DSC[a] data of polyesters from 2,2-dioctadecyl-1,3-propanediol and the phthalic acids

Polyester	Sample pretreatment	T_m (°C)	ΔH_m (kJ/mol)
PBOPOP (orthophthalic)	virgin sample without thermal history	44.7	40.5
	cooled from the melt at 20°C/min	39.4	32.0
	cooled from the melt at 1°C/min	38.0	31.4
	annealed at 27°C for 170h	41.4	36.8
PBOPIP (isophthalic)	virgin sample without thermal history	41.5	37.0
	cooled from the melt at 20°C/min	34.4	31.7
	cooled from the melt at 1°C/min	33.0	30.3
	annealed at 27°C for 170h	38.9	32.3
PBOPTP (terephthalic)	virgin sample without thermal history	42.8	28.9
	cooled from the melt at 20°C/min	30.1 (38.7)	30.4
	cooled from the melt at 1°C/min	24.1 (38.9)	31.4
	annealed at 27°C for 170h	40.0	23.2

[a] DSC (heating rates 20°C/min) traces from Figs. 3-5.

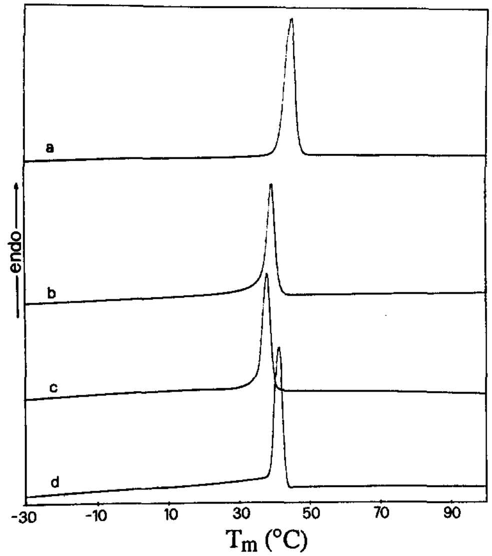


Figure 3 DSC traces of polyester PBOPOP; (a) heating trace of virgin sample; (b) & (c) heating traces of the same sample cooled from the melt at 20 & 1 °C/min., respectively; (d) trace of the sample annealed at 27°C for 170h. Heating rates: 20°C/min.

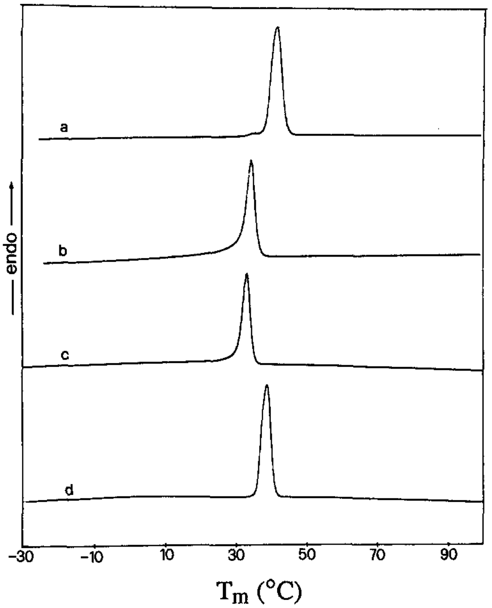


Figure 4 DSC traces of polyester PBOPIP. Conditions as in Figure 3.

The data in Table 3 show that the highest values of the melting enthalpy, ΔH_m, are recorded for the ortho polyester (PBOPOP), whereas the para isomer (PBOPTP) exhibits the lowest ones. This difference is apparently due to the occurrence of more favourable main-chain conformations which induce the crystallization of a larger number of methylene units in the ortho polyester. A comparison of the melting enthalpies referred to one mole of side-chain with those previously measured for analogous octadecyl monosubstituted aromatic polyesters exhibiting crystallinity merely due to side-group hexagonal packing (4) shows substantially higher values for the latter group. Accordingly, it can be concluded that the geminal introduction of a second octadecyl pendant group in the polyester diol unit results in a decrease of the tendency towards crystallization of the side-chains.

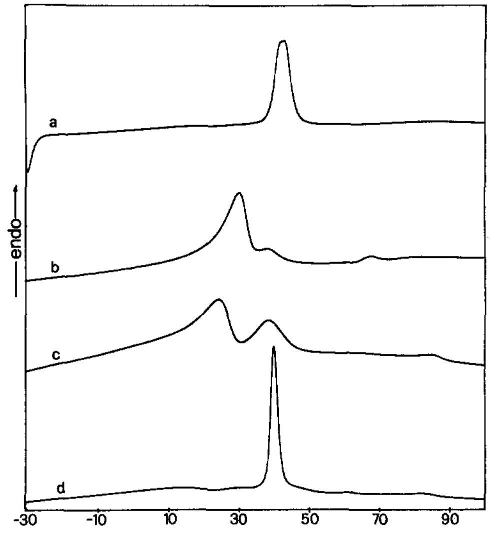


Figure 5 DSC traces of polyester PBOPTP. Conditions as in Figure 3.

The results presented in this paper confirm that all the investigated polyesters are true comb-shaped polymers in structure and behaviour. A more detailed investigation of these polyesters including the study of their mechanical properties is in progress, and will be the subject of a subsequent communication.

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References

(1) Andruzzi, F., Lupinacci, D., Magagnini, P.L., and Segre, A.L., *Polym. Bull.*. **11**, 241 (1984)

(2) Andruzzi, F., Barone, C., Lupinacci, D., and Magagnini, P.L., *Makromol. Chem., Rapid Comm.* **5**, 603 (1984)

(3) Segre, A.L., Andruzzi, F., Barone, C., Paci, M., and Magagnini, P.L., *J. Polym. Sci., Polym. Phys. Ed.* **23**, 2611 (1985)

(4) Andruzzi, F., Cerrai, P., Lupinacci, D., Tricoli, M., and Hvilsted, S., *Proc. VIII Ital. Meeting Macromol. Sci.*, Milan, 1987, 367

(5) Hvilsted, S., Andruzzi, F. Cerrai, P., and Tricoli, M., *Polymer* **32**, 127 (1991)

(6) Andruzzi, F. and Hvilsted, S., *Polymer*, accepted for publication (1990)

(7) Andruzzi, F., Paci, M., and Hvilsted, S., in preparation for publication (1990)

(8) Ballauff, M., *Makromol. Chem., Rapid Commun.* **7**, 407 (1986)

(9) Collins, E.A., Bares, J., and Billmeyer, F.W. in "Experiments in Polymer Science", Wiley, New York, 1973, Chap. 7, p. 151

(10) Almdal, K., Ph.D. thesis (Risø-M-2787), Risø National Laboratory, Denmark (1989)

(11) Hvilsted, S. in "Organic Coatings, Science and Technology" (Eds. G.D. Parfitt and A.V. Patsis) Marcel Dekker, New York, 1986, Vol 8, pp. 79-108

(12) Hvilsted, S. in "Biological and Synthetic Polymer Networks", (Ed. O. Kramer), Elsevier Appl. Sci. Publ., England, 1988, Chap. 15, pp. 243-254

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