Synthesis and characterization of comb-shaped polyesters based on 2-octadecyl-1,3-propanediol and phthalic acids

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Three isomeric poly(2-octadecyl-1,3-trimethylene phthalate)s were prepared by melt transesterification of the corresponding diphenyl ester and 2-octadecyl-1,3-propanediol. Intrinsic viscosity, size exclusion chromatography and light scattering determinations yielded weight-average molecular masses of 110000 and higher. High-resolution, solution ^{13}C n.m.r. spectroscopy analysis of both the diphenyl ester precursors and polyesters identified the main-chain units, the isomeric aromatic acid residue and glycol carbons, the linking and the terminal ends of the octadecyl side chain, and finally allowed detection of phenyl ester end groups at 1–2% level. No absorption band due to hydroxyl end groups was monitored in the i.r. polyester spectra. I.r. spectroscopy, d.s.c. and powder X-ray diffractometry provided a clear indication of the crystallinity of the prepared polyesters. The relevant melting enthalpy values and X-ray diffraction patterns were typical of comb-shaped polymers in which the paraffinic side chains crystallize independently with their characteristic hexagonal packing.

(Keywords: synthesis; characterization; comb-shaped polyesters)

INTRODUCTION

Comb-shaped polymers have been studied with increasing interest in the last two decades, owing to their peculiar properties and correlation with side-group liquid crystal polymers[1]. This has resulted in a better understanding of their structure–property relationships. Knowledge of molecular parameters such as length of the side chain and relative spacing, chemical nature, microstructure and flexibility of the main chain are of great importance in the study of comb-shaped polymers containing long linear hydrocarbon side chains. Indeed, they determine the structural principles governing the behaviour of the main and side chains upon which the polymer properties are dependent.

In the course of a previous investigation on comb-shaped polyesters from phthalic acids and racemic 1,2-icosanediol[2], we showed the ability of these polyesters to exist in the crystalline state due to exclusive crystallization of the octadecyl lateral groups. This result led us to conclude that the necessary condition for the side-chain crystallization in these polyesters is fulfilled despite the presence of rigid aromatic moieties in the polyester backbone and the considerable distance between the branching points of the paraffinic side chains.

In order to investigate the structure and the properties of the above-mentioned polyesters in further detail we considered it important to avoid loss of regular structure during the polyester preparation due to the occurrence of chemical isomerism of a tail-to-tail and head-to-head type. Therefore, we decided to use a symmetrical glycol instead of an asymmetrical one for the polycondensation reaction.

The present work deals with the synthesis, microstructure and thermal behaviour of comb-shaped polyesters of 2-octadecyl-1,3-propanediol and the three isomeric phthalic acids. Previously, we reported some preliminary results on the characterization of these polyesters; however, they are limited to samples of low molecular masses[3].

EXPERIMENTAL

Materials

The glycol 2-octadecyl-1,3-propanediol (OPD) was prepared and purified as described elsewhere[4]. The precursors diphenyl phthalate, isophthalate and tere-

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phthalate were synthesized and purified as described previously[2].

Polyester synthesis

The comb-shaped polyesters were prepared by melt polycondensation of the corresponding isomeric diphenyl phthalates with OPD according to the procedure reported for the synthesis of aliphatic comb-shaped polyesters[4].

Intrinsic viscosities

Limiting viscosity numbers of polyesters were measured in tetrahydrofuran (THF) at 303 K in an Ubbelohde viscometer, whereas the polystyrene standards were evaluated from the Mark–Houwink equation with $k = 1.4 \times 10^{-4}$ and $a = 0.75$[5].

Size exclusion chromatography (s.e.c.)

Polyester s.e.c. measurements were carried out on a Millipore-Waters II apparatus equipped with a set of three ultrastyragel columns (10^3, 10^4 and 10^5 Å pore size, respectively) using refractive index detection and THF as eluent at a flow rate of $1.0\,\mathrm{ml\,min^{-1}}$. Sample concentrations were in the range 0.20–0.30% (w/v). Absolute weight-average molecular masses ($M_{\mathrm{w,abs}}$) were determined by low-angle laser light scattering (l.a.l.l.s.) with a Chromatix KMX-6 photometer coupled to an Optilab 5902 refractometer using a light source operating at 632.8 nm and Knauer h.p.l.c. pump 64[6]. The necessary (d*n*/d*c*) determinations were performed on 3 ml of $\leq 0.15\%$ (w/v) THF solutions at a flow rate of $0.8\,\mathrm{ml\,min^{-1}}$.

^{13}C n.m.r. spectroscopy

^{13}C n.m.r. 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 5 mm (i.d.) tubes. Diphenyl ester spectra were recorded with a pulse width of 3.5 μs ($\sim 60°$); 0.92 s pulse acquisition and 2 s pulse repetition intervals were used to obtain normally 2000 scans. For polyesters a pulse width of 2.3 μs ($\sim 45°$) and up to 16 000 scans were employed. Chemical shifts were referenced to the central resonance of $CDCl_3$ (76.90 ppm from tetramethylsilane).

I.r. spectroscopy

I.r. polyester spectra were recorded on a Perkin–Elmer 283B spectrophotometer equipped with a Specac variable temperature cell. Suitable polyester samples in the form of films were obtained by melting a few milligrams of polyester powder between NaCl plates. The resulting molten polyester was squeezed to obtain a film of satisfactory thickness, and allowed to resolidify on cooling to room temperature.

Differential scanning calorimetry

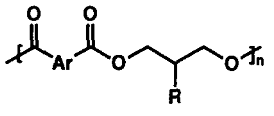
D.s.c. experiments were performed on a Perkin-Elmer DSC 4 instrument equipped with an Intracooler-I apparatus.

X-ray diffractometry

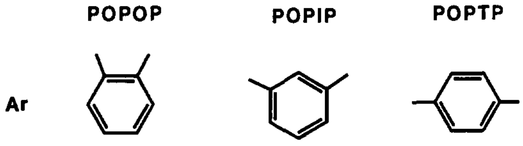
Powder X-ray diffraction patterns were obtained with Ni-filtered CuKα radiation employing a Philips PW 1010 wide-angle diffractometer. Measurements were performed at 20°C on matched polyester specimens.

RESULTS AND DISCUSSION

The polyesters described here are isomeric poly(octadecyltrimethylene phthalate)s of the general formula:

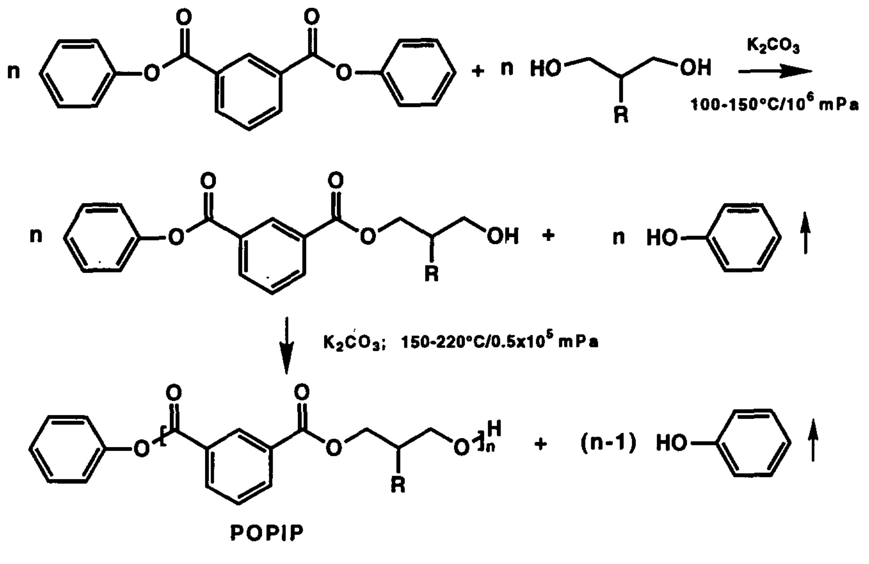


where



and

R = $(CH_2)_{17}CH_3$



Scheme 1

The polyesters were prepared by melt polycondensation of OPD with the required diphenyl ester in a 1:1 molar ratio. As an example, the synthesis of poly(2-octadecyl-1,3-trimethylene isophthalate) (POPIP) is shown in *Scheme 1*. The experimental details have been reported previously[4].

Molecular mass characteristics of the prepared polyesters recovered essentially in quantitative yields are given in *Table 1*. The peak molecular masses (M_p) determined by intrinsic viscosity and s.e.c. have been used to calculate the number-average degree of polymerization (*DP*), which in every case was found to be $\geqslant 120$. The calculated weight-average molecular masses ($M_{w,calc}$) compare well with the $M_{w,abs}$ values experimentally determined by light scattering. To our best knowledge these M_w values consistently >110000 are the highest reported[2-4,7-10] values for comb-shaped polyesters. These results demonstrate the significant improvements in the efficiency of the developed polytransesterification procedure as compared to the initial investigation[3] and strongly substantiate the superiority of the diphenyl ester precursor as already previously discussed in the case of the aliphatic comb-shaped polyesters[4]. It should be stressed, however, that alternative precursors such as acid dichlorides or dimethyl esters were not investigated in the present case in contrast to an earlier investigation[2]. Indeed, we reported in that investigation the homogeneous polycondensation via an acylation reaction of aromatic acid dichlorides with a long chain diol as a route to comb-shaped polyesters. However, products of limited molecular mass resulted due to the difficulty in assuring an exact stoichiometric ratio of the reactants. Similar results have recently been obtained by Yokota and co-workers[7,9] in the synthesis of aliphatic comb-shaped polyesters from alkanedioic acid dichlorides and long-chain-substituted propanediols. It is worth pointing out that interfacial polycondensation, normally an effective synthetic procedure for polyesters, is precluded in the present case due to the inability of 2-octadecyl-1,3-propanediol to dissolve in aqueous alkali.

Both polyesters and the diphenyl ester precursors were investigated by proton decoupled ^{13}C n.m.r. spectroscopy. ^{13}C spectral information has apparently not previously been reported on the precursor substances. Consequently, a thorough discussion of the precursor spectra and assignments will be given here because they can provide ^{13}C chemical shift information on possible end groups in the polyesters. As a representative example the spectrum of diphenyl isophthalate is shown in *Figure 1c*. Here the phenyl pattern (q, o, m, p) recently evaluated for the aliphatic analogues[11] is easily recognized and the corresponding chemical shifts are reported in *Table 2*.

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

Polyester	Acidic residue	[η] (dl g^{-1})	M_p[a]	*DP*[b]	$M_{w,calc}$[c]	$M_{w,abs}$[d]
POPOP	Phthalic	0.39	89000	137	126000	117000
POPIP	Isophthalic	0.38	78000	120	110000	110000
POPTP	Terephthalic	0.68	100000	154	141000	137000

[a] From s.e.c. peak position by use of a universal calibration with polystyrene standards

[b] Number average degree of polymerization calculated from $\bar{M}_n = M_p/\sqrt{2}$ as previously deduced[4]

[c] Calculated molecular masses using $\bar{M}_w = \sqrt{2}\,M_p$[4]

[d] Absolute molecular masses as determined by l.a.l.l.s.

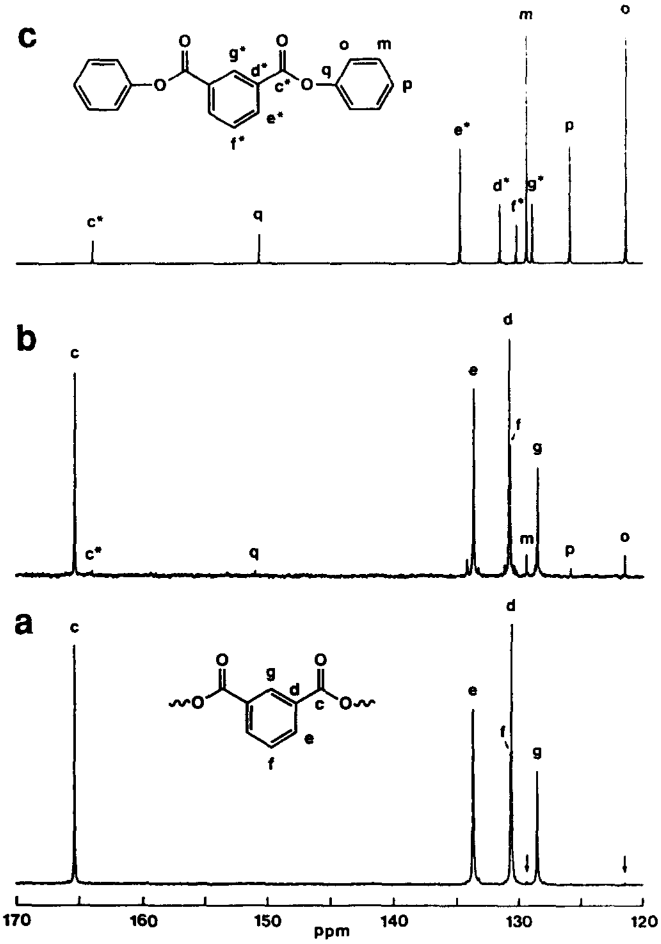


Figure 1 62.90 MHz ^{13}C n.m.r. spectra of the aromatic and carbonylic carbon region of: (a) POPIP, *DP* = 120 (this work, 16000 scans) phenyl end group; (b) POPIP, *DP* = 26[3] (2000 scans); (c) diphenyl isophthalate (17000 scans)

Table 2 62.90 MHz ^{13}C n.m.r. chemical shifts of aromatic diphenyl esters (ppm in CDCl$_3$)[a]

						Phenyl			
Ester	c*	d*	e*	f*	g*	q	o	m	p
Phthalic	165.60	131.54	131.54	129.29		150.59	121.33	129.29	125.89
Isophthalic	163.95	131.47	134.67	130.13	128.87	150.57	121.38	129.34	125.87
Terephthalic	164.16	133.86	130.17			150.67	121.46	129.48	126.06

[a] With reference to structures in *Figure 1c*

The assignments of the central isophthalate part are based partly upon the intensity differences of the two protonated carbons (e*) relative to the two non-protonated carbons (d*) and the single protonated carbons (f* and g*) in combination with previously published data[12] for model aliphatic isophthalates. The terephthalate moiety is easily assigned due to the high degree of symmetry present and the enormous difference between the four very intense protonated carbons (e*) and the two much less intense quaternary carbons (d*). The assignments of the d*, e*, f* and m (*meta*) carbons of diphenyl phthalate, on the other hand, are possible only when an additional n.m.r. experiment is performed where the proton-carbon coupling information was retained. This clearly revealed the overlap of the quaternary carbons (d*) (essentially a singlet with fine splitting due to long range proton coupling) and the tertiary carbons (e*) (a doublet in which fine splitting is also observed). In the same way the very intense m carbons of the phenyl rings (a doublet split in doublets) contained a small split doublet originating from the f* carbon of the orthophthalate moiety. Also in this latter case the previously published data[12] from phthalate models assisted the assignments. A closer inspection of *Table 2* reveals in fact only small differences (<0.2 ppm) between the phenyl carbon shifts in the three isomeric phthalates; also, compared to the phenyls of the aliphatic esters[11] only the p (*para*) carbons differ up to 0.6 ppm, whereas the rest show differences of 0.1–0.3 ppm.

The microstructure of the polyesters could then be investigated employing ^{13}C n.m.r. spectroscopy. Spectra of POPIP selected as characteristic polyesters representatives are shown in *Figures 1a* and *b*, featuring the acidic part, and *Figures 2a* and *b* exhibiting 2-octadecyl-1,3-oxytrimethylene, the glycol part. The detailed chemical shift information of all three polyesters is given in *Table 3*. *Table 3* shows the typical characteristics of the three isomeric phthalic acids detailed above. Small changes in both the carboxylic and aromatic carbon shifts, as compared to the diphenyl situation, exerted by the different shielding of the aliphatic glycol part can be observed. The assignments of the 2-octadecyl-1,3-oxytrimethylene part greatly benefit from the detailed analysis of the corresponding aliphatic comb-shaped polyesters[4] since only the glycol carbons a and b and the side-group linking carbon 1 and its neighbour 2 exhibit small deshieldings while the rest of the carbons are virtually insensitive to the change from aliphatic to aromatic acid. In fact only the deshielding on the oxymethylene carbons (a) is appreciable (up to 1.7 ppm), whereas the other deshieldings are only 0.5 ppm or less. In this context it should be mentioned that the introduction of a second side group on the 1,3-oxytrimethylene moiety[10] has considerably larger effects on the carbons just mentioned. Generally deshieldings on the order of 2 ppm were recorded, except for the 2 carbons which were shielded almost 4 ppm mainly due to the γ-effect exerted by the linking carbon in the second and new side group.

The information obtained from *Figure 1* confirms the results of the initial ^{13}C n.m.r. investigation of the stereochemistry of the low molar mass polyesters[3]. Here possible stereochemical evidences were rejected due to

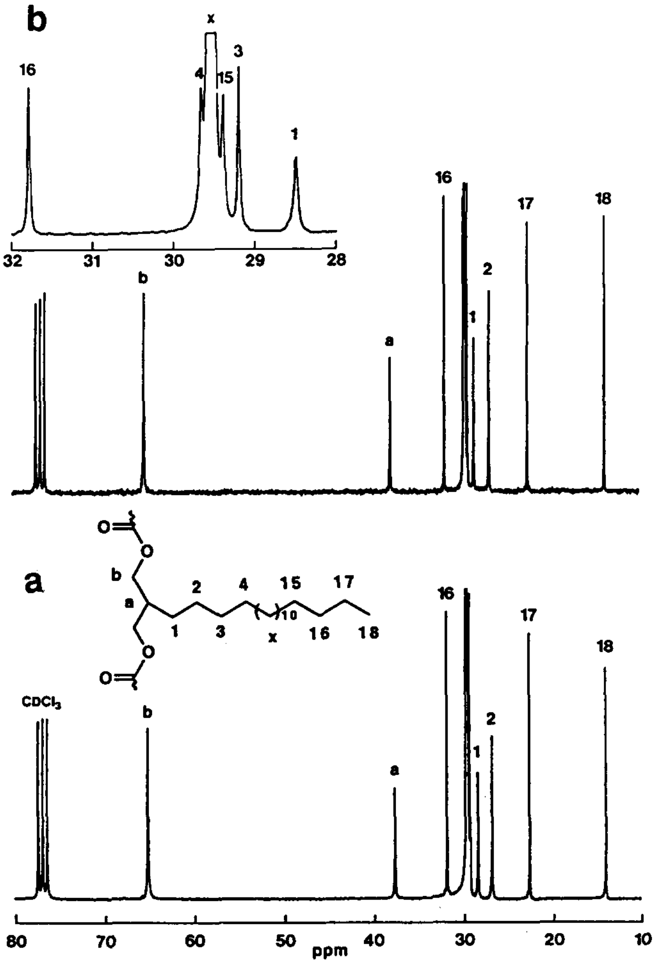
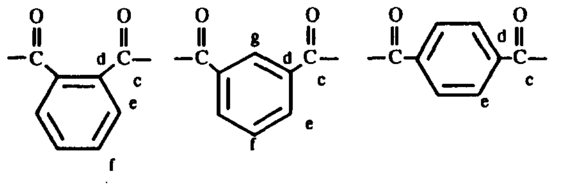
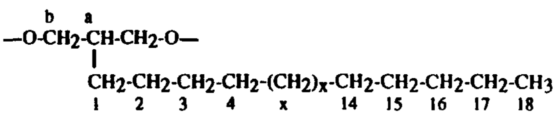


Figure 2 62.90 MHz ^{13}C n.m.r. spectra of aliphatic carbon region of POPIP: (a) sample with $DP=120$ (this work, 16 000 scans); (b) sample with $DP=26^3$ (2000 scans)

Table 3 62.90 MHz ^{13}C n.m.r. chemical shifts of polyesters from 2-octadecyl-1,3-propanediol and aromatic acids (ppm in CDCl$_3$)





$$\begin{array}{l} \overset{b}{-\text{O-CH}_2}\text{-}\overset{a}{\text{CH}}\text{-CH}_2\text{-O}- \\ \quad\quad\quad\;| \\ \underset{1}{\text{CH}_2}\text{-}\underset{2}{\text{CH}_2}\text{-}\underset{3}{\text{CH}_2}\text{-}\underset{4}{\text{CH}_2}\text{-}\underset{x}{(\text{CH}_2)_x}\text{-}\underset{14}{\text{CH}_2}\text{-}\underset{15}{\text{CH}_2}\text{-}\underset{16}{\text{CH}_2}\text{-}\underset{17}{\text{CH}_2}\text{-}\underset{18}{\text{CH}_3} \end{array}$$

Sample	Acid	a	b	c	d	e	f	g	1	2	3	4	x	14	15	16	17	18
POPOP	Phthalic	37.49	65.59	167.05	132.15	130.79	128.78	–	28.33	26.72	29.19		29.57		29.39	31.79	22.51	13.86
POPIP	Isophthalic	37.78	65.27	165.33	130.73	133.57	130.66	128.45	28.47	26.75	29.18	29.64	29.54		29.37	31.77	22.49	13.84
POPTP	Terephthalic	37.77	65.27	165.38	133.99	129.44	–	–	28.47	26.73	29.18	29.61	29.53	29.44	29.33	31.77	22.49	13.84

the absence of splitting of the carbonyl and aromatic carbons. However, no attention was paid to the small peaks (q, m, p, o) in *Figure 1b* which now can be identified as the carbons of the phenyl end group. The remaining small but unmarked peaks very likely stem from the isophthalate moiety linked to the phenyl end group. This ultimate isophthalate has two different ester groups resulting in six spectroscopically non-symmetrical aromatic carbons with the associated implications[13]. Since the POPIP sample of *Figure 1b* had a $M_n = 12\,000$ corresponding to $DP = 26$, it is not surprising that a corresponding phenyl end-group concentration of 4–8% can be detected by ^{13}C n.m.r. The concentration limits obviously depend on the presence of the phenyl end group in only one end of the polyester chain or in both ends. We have previously argued[4,10] that end groups in a concentration of <2–3% will be difficult to detect by ^{13}C n.m.r. Nevertheless, we present evidence in this paper that in the case of the phenyl ester end group it is possible to detect <2% (probably even <1% assuming only one phenyl end group in every chain) in the POPIP sample from this work, $DP = 120$ (*Figure 1a*). This detection, however, requires utilization of a considerable number of scans (in the actual case 16 000) resulting in a good signal-to-noise ratio of the final ^{13}C n.m.r. spectrum.

Surprisingly no evidence could be found for the other possible end group in the polyester, a hydroxyl-terminated 2-octadecyl-1,3-oxytrimethylene moiety. Both the oxymethylene (b) and the methine (a) carbons of structurally related propanediols have previously been shown to be shielded and deshielded 1–2 ppm, respectively, in a glycol end group in contrast to a glycol polyester triad[14,15]. Careful inspection, however, of the corresponding aliphatic part of the low molar mass POPIP in *Figure 2b* reveals no evidence of glycol end groups.

In agreement with the n.m.r. observation, no indication of characteristic absorption bands due to a detectable concentration of hydroxyl end groups was found in the i.r. spectra of the polyesters. As an example, the i.r. spectrum of POPTP is shown in *Figure 3*. It is clearly seen from the spectrum that only one rather weak band is observable in the 3700–3200 cm^{-1} region typical of the free and hydrogen-bonded stretching vibrations. However, this band has been unambiguously attributed to the first overtone at 3450 cm^{-1} of the ester carbonyl stretching (1725 cm^{-1}) in accordance with previous assignments[16].

In order to suggest a reasonable explanation for the above-mentioned results it is worth pointing out that recent ^{13}C n.m.r. measurements, from work in progress on polycondensation polyesters from aliphatic phenyl esters and mesogenic OPD derivatives, allowed us to confirm the presence of both phenyl and diol hydroxyl end groups in polyester samples having $DP = 15$–25. Most likely, hydroxyl end groups of OPD are also present in POPIP polyesters, and the apparent analytical insensitivity of the ^{13}C n.m.r. method to reveal them might be due in the present case to a fortuitous slight imbalance of stoichiometric ratio in favour of phenyl ester, thus allowing the detection of phenyl ends only.

Moreover, another potential source of loss of analytical detection of OPD hydroxyl ends might arise from the phenoxide ions, formed through the reaction of the acidic by-product phenol with K_2CO_3, and possibly involving OPD end groups in an exchange process (especially in the higher temperature stage of the polycondensation reaction) with formation of chemical equilibrium, and subsequent decrease of OPD hydroxyl ends in the polyester.

The changes in the physical states of polyesters POPOP, POPIP and POPTP with temperature were investigated by means of d.s.c. As an example, the heating and cooling d.s.c. scans of the polyester POPOP are presented in *Figure 4*. All of the thermograms in *Figure 4* display a similar feature: each of them shows a single sharp almost symmetrical peak. The endothermic peak in the heating trace of *Figure 4a* corresponds to the crystalline melting transition of the polyester as obtained from the purification procedure. This is confirmed by observing in the polarizing microscope the drastic softening of the sample at the corresponding peak temperature as well as the simultaneous disappearance of the diffuse opacity typical of crystalline comb-shaped polymers carrying long paraffinic side chains. Although in the synthesis of the phthalate polyesters a prochiral hydroxy compound such as 2-octadecyl-1,3-propanediol has been used, the polymers are stereoirregular due to the absence of steric control in the polycondensation process. Hence the structural requirements for main chain crystallization are lacking in these polyesters. Also, no evidence of a glass transition was obtained in the temperature range

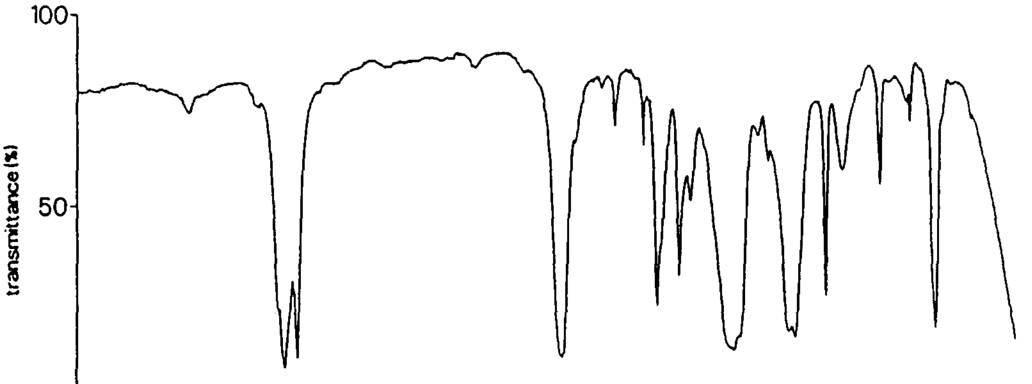


Figure 3 I.r. spectrum of polyester POPTP at 20°C. Solid film, recrystallized from the melt

examined. The polyester exhibits a sharp recrystallization exotherm when cooled from the melt; however, on cooling at 20°C min^{-1} this transition undergoes extensive supercooling (*Figure 4b*). *Figures 4c, d* and *e* are the heating scans started immediately after polyester recrystallization at different cooling rates. The traces clearly show a polyester thermal history dependence: the higher the cooling rate at which the polyester recrystallization is accomplished the more are the corresponding melting temperature and enthalpy shifted to lower values. However, when the polyester recrystallization is accomplished at a very slow cooling rate (0.1°C min^{-1}) the subsequent heating scan reproduces the thermal behaviour observed for the virgin polyester sample with improvement in the endotherm peak sharpness (cf. *Figures 4a* and *e*). The calorimetric data obtained from the d.s.c. measurements for all the examined polyesters are summarized in *Table 4*. As *Table 4* shows, the polyesters are characterized by relatively low temperatures and heats of fusion that are comparable with those reported for typical comb-shaped polymers whose octadecyl side chains crystallize with hexagonal packing[1,8]. Apparently, the same holds also for the number of crystallized side-chain methylenes calculated, assuming the heat of fusion per mole of CH_2 group corresponds to the average value found by Jordan *et al.*[8] for different comb-shaped polymers carrying paraffinic side chains crystallizing in the hexagonal modification. However, since the paraffinic side chains of the phthalate polyesters are much more widely spaced that those of the polymers studied by Jordan *et al.*, it should be expected in the present case that a lower number of methylenes were involved in the side chain crystallization. However, this is not the case and this can be reasonably explained by considering that phthalate polyester main chains are shortened by rotation around the C–O bonds. As a result, the main chains are no longer fully extended, thus allowing the hydrocarbon side chains to pack closely.

It is worth pointing out that the *ortho* polyester, POPOP, in the form of the virgin sample (namely recrystallized from dilute solution in the absence of external forces) exhibits the highest value of melting enthalpy as compared to the polyesters POPIP and POPTP. The enhanced tendency of the *ortho* polyester to develop crystallinity in comparison with the *meta* and *para* ones was previously observed for other aromatic comb-shaped polyesters[2,3] and recently for phthalate

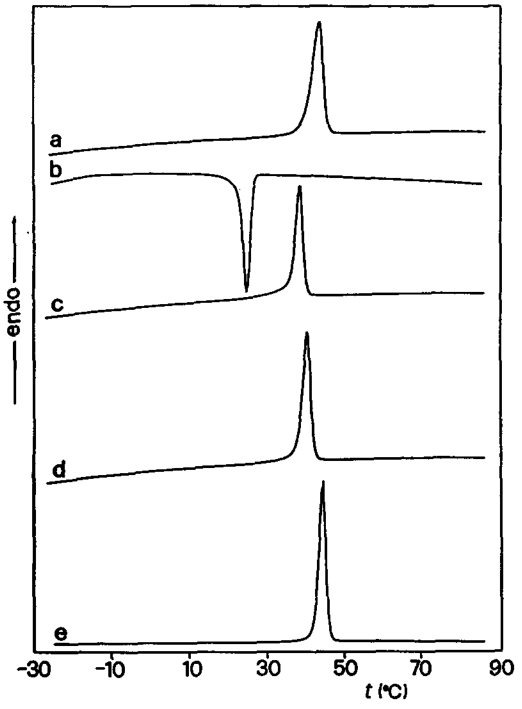


Figure 4 D.s.c. thermograms of polyester POPOP: (a) heating trace of virgin sample; (b) cooling trace at 20°C min^{-1}; (c), (d) and (e) reheating traces after cooling at 20, 1 and 0.1°C min^{-1}, respectively. Heating rate 20°C min^{-1}

Table 4 Calorimetric data of polyesters from diphenyl ester of phthalic acids with 2-octadecyl-1,3-propanediol

Polyester	D.s.c. run[a]	T_m (°C)	ΔH_m ($\mathrm{kJ\,mol^{-1}}$)	$n\mathrm{CH_2}$[b]
POPOP	I	43.4	29.7	9.1
(phthalic)	II	24.5	21.3	
	III	38.2	23.2	
	IV	40.0	24.9	
	V	44.2	27.0	
POPIP	I	42.2	23.5	7.2
(isophthalic)	II	16.0	16.3	
	III	32.1	17.7	
	IV	33.4	19.8	
	V	37.2	22.1	
POPTP	I	43.4	24.3	7.5
(terephthalic)	II	12.3	15.3	
	III	33.7	16.2	
	IV	34.7	19.7	
	V	37.6	22.3	

[a] I, first heating (virgin sample not subjected to any preliminary treatment); II, first cooling; III, second heating, after cooling the sample at 20°C min^{-1}; IV, third heating, after cooling the sample at 1°C min^{-1}; V, fourth heating, after cooling the sample at 0.1°C min^{-1}. The heating rate for all experiments was 20°C min^{-1}

[b] Number of crystallized methylene groups in the side chain

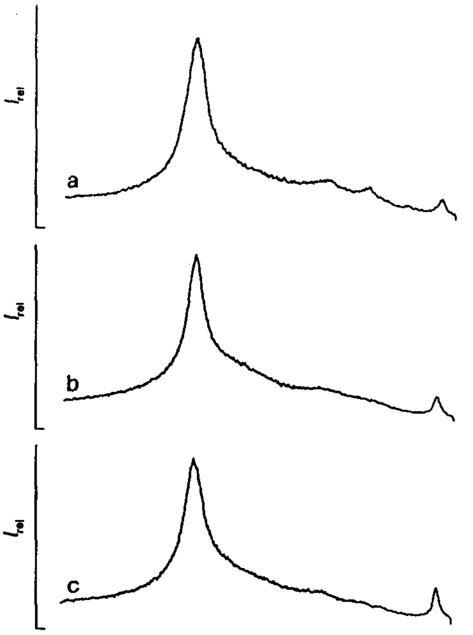


Figure 5 Powder X-ray diffraction diagrams at 20°C of virgin samples: (a) POPOP; (b) POPIP; (c) POPTP

polyesters bearing two geminal octadecyl side chains[10]. This trend for the polyesters POPOP, POPIP and POPTP is also reflected by the powder X-ray diffraction patterns shown in *Figure 5*. Each diffractogram is seen to consist mainly of a strong Bragg reflection at $2\Theta = 21.2°$, corresponding to an equivalent distance of almost 4.2 Å. This peak is normally considered to arise from recrystallization of the paraffinic chains with hexagonal packing[1]. This is also supported by the close similarity of the present X-ray patterns with those obtained in the previous investigation of comb-shaped polyesters based on phthalic acids and 1,2-icosanediol[2], as well as by the singlet character of the methylene rocking band[17] observed at $720\,\mathrm{cm}^{-1}$ in the i.r. spectra of crystalline samples of the three polyesters (*Figure 3*). An additional significant feature in the diffractograms of *Figure 5* is provided by the presence of a weak but distinct peak in the low-angle region at $2\Theta = 4.9°$. On the basis of previous assignments for similar polyesters[2], this could likely correspond to the second-order reflection (not reported here because of the limited goniometer low-angle sweep) arising from molecular arrangement of the polyester in layers in which conformationally disordered main chains lie on parallel planes with the side chains crystallized within them[2].

It should be observed that the relative intensity of the diffraction peak at $2\Theta = 21.2°$ in *Figure 5a* is higher than that of *Figures 5b* and *c*, indicating a higher crystallinity of POPOP in comparison to POPIP and POPTP. This result is consistent with the data of the d.s.c. analysis and might be explained by assuming the existence of more favourable main-chain conformations for the *ortho* polyester able to induce the crystallization of a larger number of methylene groups.

The results and conclusions presented here are in agreement with the conclusions drawn from previous investigations of a variety of aromatic comb-shaped polyesters containing n-octadecyl pendent groups[2,10], thus demonstrating the fundamental role of the alkyl side chains in determining the crystalline structure of this type of polyesters.

The applied preparative procedure results in aromatic comb-shaped polyesters with relatively high molecular masses and attractive mechanical properties. The study of the solid state behaviour of these polyesters is presently being extended to the measurement and investigation of their mechanical properties which will be reported elsewhere.

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