Comb-shaped polyesters of aliphatic dicarboxylic acids and 2-octadecyl-1,3-propanediol: 1. Synthesis and microstructure

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Comb-shaped polyesters are prepared by polytransesterification of 2-octadecyl-1,3-propanediol and diphenyl suberate, sebacate, dodecanedioate, tetradecanedioate and hexadecanedioate in turn. The developed melt polycondensation procedure generally results in polyesters with intrinsic viscosities in the range 0.76–1.28 dl g^{-1}. High performance size exclusion chromatography reveals symmetrically shaped traces with peak maxima corresponding to molecular masses in the range 48 000–65 000 by use of the universal calibration. These molecular masses equivalent to degrees of polymerization, 97–124, can be shown to result from total functional group conversions >98.5%. Detailed ^{13}C nuclear magnetic resonance investigations of polyester solutions reveal many structural features originating from both main- and side-chain carbons and point to lack of stereoregularity. Infra-red spectra of polyesters reveal characteristic polyester absorption bands including bands indicative of the existence of a crystalline phase.

(Keywords: comb-shaped polyesters; aliphatic; preparation; intrinsic viscosity; size exclusion chromatography; ^{13}C nuclear magnetic resonance; infra-red)

INTRODUCTION

Polymers containing long side-chains, also called comb-shaped polymers, have received increasing attention over the last two decades. The interest in this special type of polymer stems from the possibility of crystallization of the side-chains, which will introduce physical properties other than those arising from an ordinary polymer structure. This unique combination of side- and main-chain behaviour is the factor responsible for the dual character of these polymers. Early and up-to-date studies on the resulting structure–property relationships of these polymers have been extensively reviewed[1,2].

Our previous work on polyesters carrying long alkyl side-chains was concerned with rigid chain polyesters consisting of isomeric phthalic residues and diol units bearing long paraffinic substituents[3–5]. These studies showed that the side-group crystallization takes place in spite of both the main-chain stiffness and the considerable distance between the branching points on the polyester main-chains. The extent of the observed side-chain crystallization was found to be related to the main-chain isomerism due to the disubstituted benzene ring. As a further step in this study it was desirable to extend it to wholly aliphatic polyesters, with the aim of investigating the influence of the flexible hydrocarbon segments of the polyester backbone on the ability of the lateral alkyl chains to give ordered structures. A primary goal was the development of a polymerization procedure ensuring polyesters of acceptable molecular masses, that is polyesters with average degrees of polymerization in the range 75–100. This range is considered to be adequate in order to warrant polyesters with sufficient physical strength to be useful while retaining ease of processing.

In this paper we report on a two-step melt polycondensation procedure involving, in turn, diphenyl esters of suberic, sebacic, dodecanedioc, tetradecanedioc and hexadecanedioc acid and 2-octadecyl-1,3-propanediol (OPD) resulting in polyesters of sufficiently high molecular masses. The prepared polyesters are characterized by intrinsic viscosity, size exclusion chromatography (s.e.c.), and high resolution ^{13}C nuclear magnetic resonance (n.m.r.) spectroscopy. Indications on crystallization as observed by infra-red (i.r.) spectroscopy are also reported. Results on the crystallization of some of the polyesters of this class, having rather low molecular mass and prepared by an acylation reaction, have recently been reported[6,7].

EXPERIMENTAL

Materials

Diethyl octadecylmalonate. A solution of sodium ethoxide (0.162 mol) in absolute ethanol (100 ml) was added dropwise to diethyl malonate (0.162 mol, Janssen Chimica). Monoalkylation of the sodium ester produced was performed by adding *n*-octadecyl bromide (0.162 mol, Fluka) in absolute ethanol (150 ml) to the above mixture. After refluxing for 1 h most of the solvent was distilled off and the residual oil washed with water until a white crystalline solid was obtained. The crude

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product was recrystallized from methanol (yield 72%, m.p. 35°C). The i.r. and n.m.r. spectra were consistent with the expected structure.

2-Octadecyl-1,3-propanediol. The compound was obtained from the reduction of diethyl octadecylmalonate. This ester (0.114 mol) in 200 ml of dry ethyl ether was added, under nitrogen and stirring, to a solution of lithium aluminium hydride (0.184 mol) in 200 ml of dry ethyl ether. After refluxing for 1 h and cooling to room temperature, the mixture was very slowly added to water to destroy excess hydride and then neutralized with hydrochloric acid. Solvent removal from the separated ethereal phase left a white precipitate of crude OPD (0.104 mol, yield 91%). The crude diol was washed several times with boiling ethyl ether, giving a white crystalline solid consisting of OPD and some residual inorganic salts, and an ethereal extract containing OPD and variable amounts of organic impurities. The extract was concentrated and OPD precipitated on cooling to room temperature. Recrystallization from ethyl ether followed by distillation in vacuum (200°C, 0.5×10^5 mPa) gave highly pure OPD melting sharply at 89°C (m.p. 86–89°C)[8]; OPD of the same purity was also recovered from direct vacuum distillation of the extraction solid residue.

Diphenyl suberate, sebacate, dodecanedioate, tetradecanedioate and hexadecanedioate. These compounds were synthesized and purified as described previously[9].

Polyester synthesis

This was carried out by an ester-interchange reaction. This step is similar to that previously reported for other polyesters[4], except for some substantial improvements concerning equipment and conditions. A typical polymerization was as follows: stoichiometric amounts (2.5×10^{-3} mol) of selected diphenyl ester and OPD were placed in a 20 ml flask, which was then weighed and potassium carbonate (7.5×10^{-5} mol) was added as catalyst. A pressure of 10×10^5 mPa was established in the flask by means of a nitrogen flow, under moderate pumping, and heating was started to melt the mixture (80–110°C). Phenol formation was indicated by its bubbling from the mixture and sublimation along the cold neck of the flask. After 20 min the temperature was raised to 140–150°C for 1 h to effect condensation of the low molecular mass polyester formed, while the pressure was reduced to 0.5×10^5 mPa to remove phenol effectively. During this stage the viscosity of the melt increases substantially with the conversion. The reaction was then temporarily interrupted to measure the phenol produced by weighing the flask and to recover the mixture splashed on the walls of the neck of the flask by rinsing with anhydrous benzene. Once the solvent was removed by careful distillation the polymerization was restarted by heating the viscous reaction product at a working temperature usually in the range 180–220°C while maintaining the 0.5×10^5 mPa pressure. The yield of polymer is substantially quantitative if no reactants are lost in the early stages of the polymerization. The crude polymer was purified by precipitating it from benzene: chloroform (80:20 v/v) solution into excess methanol and dried under vacuum.

Polyester characterization

Size exclusion chromatography. Polyester s.e.c. 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 (THF) as eluent at a flow rate of 1.0 ml min^{-1}. Sample concentrations were in the range 0.20–0.30% (w/v).

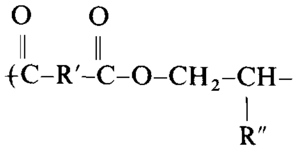
Intrinsic viscosities. Limiting viscosity numbers of polyesters were measured in THF at 303.15 K in an Ubbelohde viscometer, whereas the polystyrene standards were evaluated[10] from the Mark–Houwink equation with $k = 1.4 \times 10^{-4}$ and $\alpha = 0.7$.

^{13}C n.m.r. 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 5 mm i.d. tubes. A pulse width of 2.3 μs ($\approx 45°$), a 0.92 s pulse acquisition, and a 2 s pulse repetition were used to obtain ≈ 1000 scans. Chemical shifts were referenced to the central resonance of $CDCl_3$ (76.90 ppm from tetramethylsilane).

Infra-red spectroscopy. The i.r. polyester analysis was carried out using a 283 B Perkin Elmer spectrophotometer. Spectra were taken on solid film samples supported by KBr discs and prepared by melting the polymer between glass slides. For measurements above room temperature the sample holder was placed in a thermostatically controlled oven at the desired temperature. After appropriate insulation the sample holder was placed again in the sample housing and the temperature monitored by a thermocouple.

RESULTS AND DISCUSSION

The comb-shaped polyesters prepared in this study are poly(2-octadecyl-1,3-propylene suberate) (POPSU), poly(2-octadecyl-1,3-propylene sebacate) (POPSE), poly(2-octadecyl-1,3-propylene dodecanedioate) (POPDD), poly(2-octadecyl-1,3-propylene tetradecanedioate) (POPTD) and poly(2-octadecyl-1,3-propylene hexadecanedioate) (POPHD). These polyesters belong to the group of the fully aliphatic polyesters with the general structure:



$$\left[\overset{\displaystyle O}{\overset{\|}{C}} - R' - \overset{\displaystyle O}{\overset{\|}{C}} - O - CH_2 - \underset{\displaystyle R''}{\underset{|}{CH}} - CH_2 - O \right]_n$$

where R′ and R″ are the hydrocarbon part and the side-chain of the acid and oxyalkylene residues, respectively:

	POPSU	POPSE	POPDD	POPTD	POPHD
R′ =	$(CH_2)_6$	$(CH_2)_8$	$(CH_2)_{10}$	$(CH_2)_{12}$	$(CH_2)_{14}$
R″ =	$(CH_2)_{17}CH_3$				

The use of diphenyl esters in the polycondensation procedure is primarily based on their more tractable physical properties with respect to those of other potential precursors such as acid chlorides or dimethyl esters. Previous investigations dealing with the synthesis of comb-shaped polyesters based on a diol with a long side-chain and acid chlorides, dimethyl esters and diphenyl esters of the three isomeric aromatic dicarboxylic acids unanimously revealed that the best results were obtained using the latter[4]. This can be seen as a result either due to the superior leaving group character of the phenoxide group, as compared with the alkoxide group, or to the low volatility of the diphenyl ester (comparable to that of the diol) which avoids fortuitous loss of functionality with subsequent unwanted variation of the stoichiometric ratio of the reactants.

The purified polyesters were all investigated by s.e.c. in order to obtain a qualitative impression of the nature of the molecular mass distributions. The s.e.c. traces revealed single symmetrically shaped peaks for all the examined polyesters indicating uniform molecular mass distribution. Examples of s.e.c. curves of POPDD showing changes in peak breadth and position due to the different reaction temperature in the final step of polymerization are shown in *Figure 1*.

Careful temperature control close to 220°C proved necessary to obtain the product with the lowest elution volume. Similar results were obtained for the other polyesters. The elution volumes, V_e, of the peak maximum of representative samples of all polyesters are shown in *Table 1* together with the intrinsic viscosities.

The actual average molecular masses were not determined due to the lack of standards based on the same experimental polymers. However, the indicative molecular masses, M_p (*Table 1*) were determined at the peak maximum by means of a universal calibration plot obtained from polystyrene standards. The average degrees of polymerization, DP_p (*Table 1*) are calculated from the M_p values. The length of the methylene chain of the diphenyl esters in the range suberate to hexadecanedioate has no apparent influence on the achievable DP_p since in all the reported instances DP_p varies from 97 to 124 provided the described optimal reaction conditions are used.

In order to evaluate the effectiveness of the polytransesterification developed we consider the factors governing DP as proposed by Flory[11] and shown in a rearranged form:

$$DP = \frac{1+r}{1+r-2rp} \tag{1}$$

where p is the fractional conversion and r expresses the stoichiometric imbalance ($r \leqslant 1$). Thus $r = 1$ when the two bifunctional monomers/precursors are present in stoichiometric amounts and reduces equation (1) to the original equation developed by Carothers. The DP in equation (1) is the number average degree of polymerization which we compared with our value experimentally determined based on M_p. *Figure 2* depicts the evolution of DP (equation (1)) for different values of r as a function of p in the very high conversion range, >97%, which is normally an excellent conversion for a small molecule reaction.

Visual inspection of all the s.e.c. traces of polyester samples resulting from high conversions strongly suggests these molecular mass distributions to be Gaussian in shape. A Gaussian chromatogram is characterized by a so-called logarithmic-normal distribution of molecular

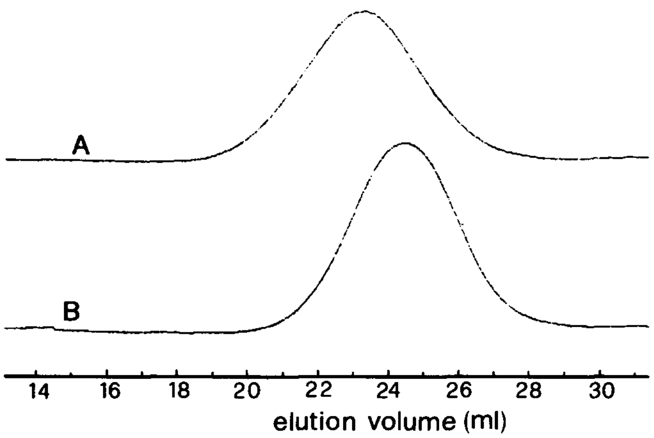


Figure 1 Size exclusion chromatography traces of POPDD samples prepared with different final polymerization temperatures: (A) 220°C; (B) 180°C. Solute concentration = 2 mg ml^{-1}; mobile phase THF; flow rate 1 ml min^{-1}; detection refractive index

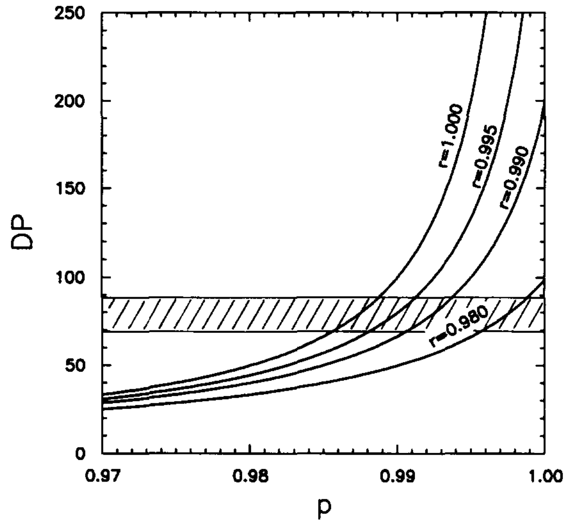


Figure 2 Number-average degree of step polymerization, DP, in the high conversion range, p, for different values of stoichiometric imbalance, r. The hatched area indicates the range of the experimentally obtained results in the polytransesterification in the present study

Table 1 Intrinsic viscosities, molecular masses, and degrees of polymerization for polyesters from diphenyl esters and OPD

Polyester	Acidic residue	$[\eta]^a$ (dl g^{-1})	V_e^b (ml)	M_p^c	DP_p^d
POPSU	Suberic	0.76	23.7	50000	107
POPSE	Sebacic	0.82	23.7	48000	97
POPDD	Dodecanedioic	1.28	23.0	65000	124
POPTD	Tetradecanedioic	1.12	23.3	58000	105
POPHD	Hexadecanedioic	0.89	23.5	56000	97

[a] Solvent: THF; temperature: 303 K
[b] Elution volume of s.e.c. peak
[c] From s.e.c. peak position by use of a universal calibration with polystyrene standards
[d] Average degree of polymerization calculated from the M_p value

masses. Berger and Schultz[12] have derived relationships between M_p and $\bar{M}_w$, weight average, and $\bar{M}_n$, number average molecular masses, respectively, for polydisperse polymers governed by a logarithmic-normal distribution and demonstrated that:

$$M_p = \sqrt{\bar{M}_w \bar{M}_n} \qquad (2)$$

At the very high conversions considered in these polycondensations, where p is close to 1, the ratio of weight average to number average molecular masses[13] will approach a value of 2. Introducing this ratio into equation (2) results in:

$$M_p = \sqrt{2}\bar{M}_n \qquad (3)$$

The experimentally found DP_p values listed in *Table 1* can now be converted according to equation (3). This conversion results in a range (hatched area in *Figure 2*) which illustrates the number average degrees of polymerization obtainable by the developed melt polycondensation procedure. A closer inspection of the hatched area reveals that for all polymerizations, conversions of functional groups $>98.5\%$ are achieved. Moreover a $DP > 100$ is impossible to obtain with a r value $\leqslant 0.98$. However, with the small amounts of reactants employed $r = 1$ is probably difficult to achieve. More likely $r = 0.995$ appears to be realistic. With this value the DP obtained can only be the result of conversions $>98.8\%$. The traces in *Figure 2* inevitably substantiate not only the necessity for extremely pure reactants and a quasi stoichiometric balance with no loss of functionality or any side reactions but also the almost ultimate conversions necessary in order to produce polyesters with a $DP > 100$.

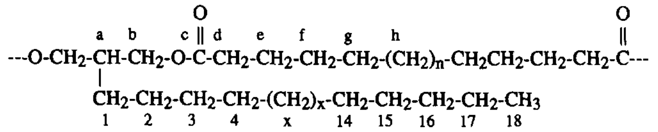
As far as the microstructure of these polyesters is concerned, it is opportune to observe that no chemical isomerism of head-to-head and tail-to-tail type should be expected on the basis of the structural symmetry of both the monomeric precursors. In further stereochemical considerations it is also useful to remember that the OPD molecule is prochiral, like monosubstituted vinyl monomers and other hydroxy compounds. Accordingly the methine carbons of OPD units incorporated into the polyester chain are still stereogenic, regardless of whether these carbons are essentially chirotopic or achirotopic. Therefore one should expect the occurrence of basic configurational arrangements such as iso, syndio and atactic sequences, depending on the experimental conditions. Since no stereospecific control of the relevant polycondensation reaction has been carried out, it seems reasonable to suppose that the whole polyester stereogenicity may be better described in terms of stereoirregular (atactic) structure, with the side chains randomly distributed along the backbone, rather than in terms of stereoregular (iso and syndiotactic) structures.

To obtain insight into the structure, the polyesters were subjected to solution n.m.r. investigations. *Figure 3* shows a high resolution ^{13}C n.m.r. spectrum of POPDD together with the structural assignments, while the corresponding chemical shift information is given in *Table 2*, which also includes ^{13}C n.m.r. information on POPSU, POPSE, POPTD and POPHD.

The assignments and chemical shifts of the oxymethylene (b) and methine (a) carbons are in close agreement with observations of other 2-substituted 1,3-propanediols in aliphatic polyesters[14,15]. The assignments of the methylene carbons of the acid part of the polyesters, (d–h), are based on the comprehensive data collection from the corresponding diphenyl esters[9]. The expected three resonances from the different non-symmetrical methylene carbons, (d–f), are found in POPSU. Surprisingly however, the central methylene carbons, (f) and (g), in POPSE resonate in one peak with an intensity of approximately twice that of the (d) and (e) peaks and in contrast to the corresponding four peaks visible in the diphenyl sebacate spectrum. While all five methylene carbons (d–h) of POPDD are resolved, as seen in *Figure 3b*, the resonances of the central methylene carbons (h) of POPTD and POPHD merge into the large resonance from the central methylene carbons (x) of the octadecyl side group. In the diphenyl analogue corresponding to POPTD and POPHD all six and seven non-symmetrical methylene carbon resonances, respectively, were resolved[9]. These observations were explained as resulting from a rotational isomeric equilibrium state leading to a type of macrocyclic order which does not seem to be possible in these extended macromolecules. The observed resolutions of the methylene carbons in the main chain, on the other hand, are in line with the normal ^{13}C spectral sensitivity to substitution at distances of up to four bonds in polymer main chains as observed in polymers in general[16], and in polyesters in particular[15].

The octadecyl side chain in all cases exhibits at least eight distinguishable resonances, one of which (x) is very intensive resulting from 9–11 paraffinic methylene carbons. The methyl terminal end with generally at least five carbons resolved and the (x) methylene carbons show a remarkable shift consistency in all polyesters. The assignments of the methyl terminal end are based on information from hexadecane and poly(octadecyloxirane)[17]. The striking similarity with the previously published octadecyl chain chemical shifts makes the assignments unequivocal. The methylene carbons (1–4)

Table 2 ^{13}C n.m.r. (62.9 MHz) chemical shifts of polyesters from OPD and aliphatic acids (ppm in $CDCl_3$)



$$\text{---O-}CH_2\text{-}\underset{\displaystyle CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}(CH_2)_x\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3}{\underset{|}{CH}}\text{-}CH_2\text{-O-}\overset{O}{\overset{\|}{C}}\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}(CH_2)_n\text{-}CH_2CH_2\text{-}CH_2\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{---}$$

Sample	Acid	n	a	b	c	d	e	f	g	h	1	2	3	4	x	14	15	16	17	18
POPSU	Suberic		37.19	63.89	173.31	33.95	24.57	28.62	–	–	28.06	26.56	29.16		29.51	29.42	29.32	31.74	22.49	13.89
POPSE	Sebacic		37.21	63.90	173.45	34.07	24.76	28.94	28.94	–	28.08	26.58	29.19		29.53		29.34	31.76	22.51	13.92
POPDD	Dodecanedioic	2	37.20	63.94	173.62	34.15	24.84	29.05	29.14	29.31	28.08	26.61	29.23	29.62	29.57	29.48	29.37	31.79	22.55	13.96
POPTD	Tetradecanedioic	4	37.20	63.94	173.65	34.17	24.86	29.07	29.18	29.57	28.09	26.61	29.23		29.57	29.49	29.37	31.80	22.56	13.97
POPHD	Hexadecanedioic	6	37.21	63.94	173.63	34.17	24.86	29.07	29.17	29.55	28.09	26.60	29.21		29.55		29.37	31.79	22.54	13.96

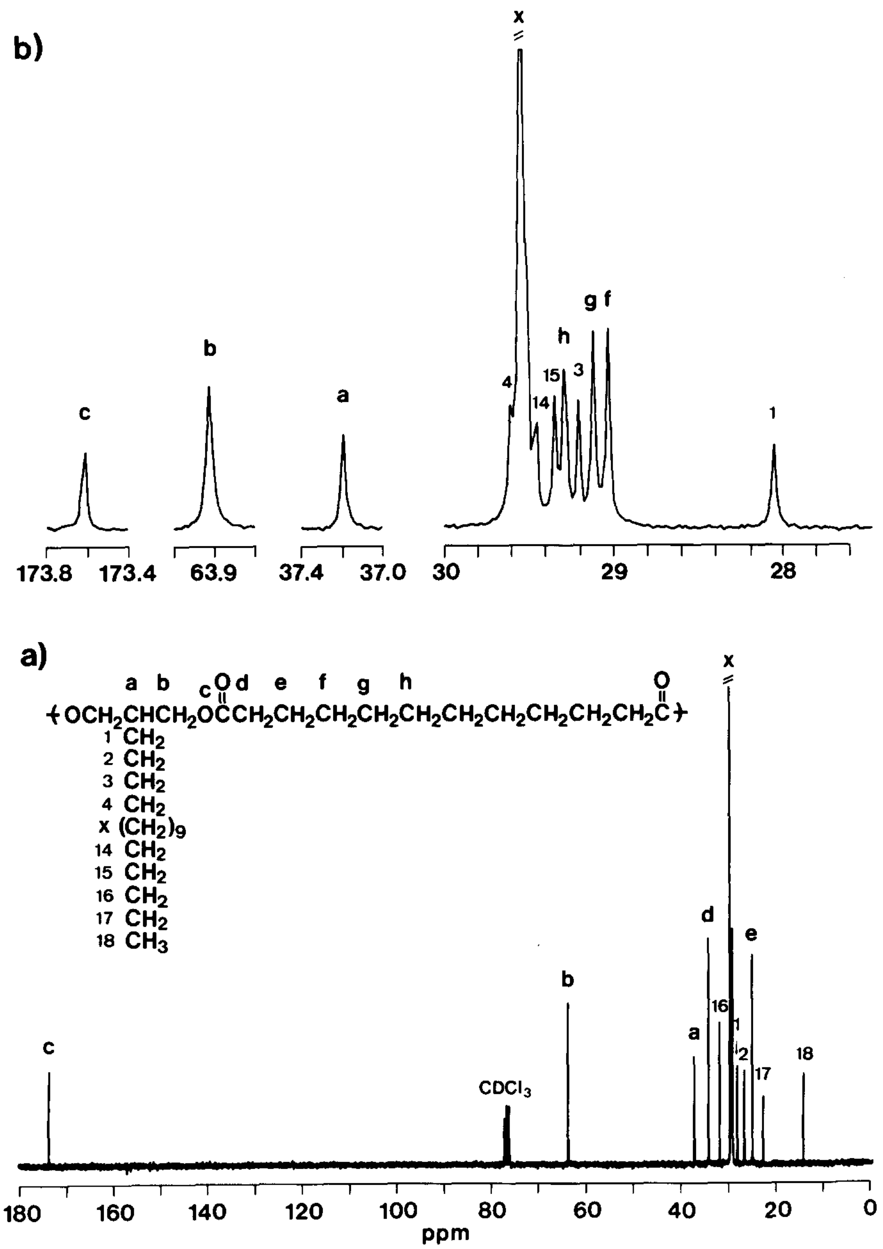


Figure 3 ^{13}C n.m.r. (62.90 MHz) of POPDD in $CDCl_3$: (a) full spectrum; (b) expansions of carbonyl, methylene and methine glycol and side- and main-chain methylene carbon regions

are assigned by calculation of the effects from the main-chain components by use of conventional substitution parameters[18] with the paraffinic methylene chemical shift as the starting value. The calculated values are close to the observed ones. Moreover, substantial support for these assignments comes from spectral information (not reported here) on similar polyesters containing a smaller number of methylene carbons in the acid part.

The expansions of the carbonyl and glycol main-chain carbon resonances (*Figure 3b*) do not reveal any splitting of the carbon resonances in question. This behaviour is interpreted as lack of stereoregularity in this polyester. The absence of any detectable peaks in the glycol main-chain range, and in a like manner the aromatic (phenyl) carbon range, also points to the very low concentration of end groups resulting from the achieved degrees of polymerization. Polyester end groups from 2-substituted 1,3-propanediols can be easily detected by ^{13}C n.m.r. provided the concentration is sufficient[15]; a qualitative estimation suggests 3–5% to be necessary.

The i.r. spectra of all the polyesters, in the form of films, have been analysed at different temperatures. As an example the i.r. spectra of POPTD are shown in *Figure 4*.

The aliphatic ester structure of POPTD is recognizable in both spectra through the absorption bands arising from ν_{CH_2} (2925–2850 cm^{-1}), ω_{CH_2} (1350–1150 cm^{-1}), ρ_{CH_2} (720 cm^{-1}), $\nu_{C=O}$ (1730 cm^{-1}), and ν_{C-O} (1175 cm^{-1}) vibrations. It is worth noting that on going from *Figure 4b* to *a* (by cooling the sample from 70 to 20°C) the spectral pattern becomes more complex, especially in the region from ~1300 to 700 cm^{-1}, due to band splitting and sharpening, as well as to the appearance of additional absorption bands. In particular the absorptions at 1250, 1200 and 1175 cm^{-1}, the latter being the strongest, are attributable to the C–O stretching mode

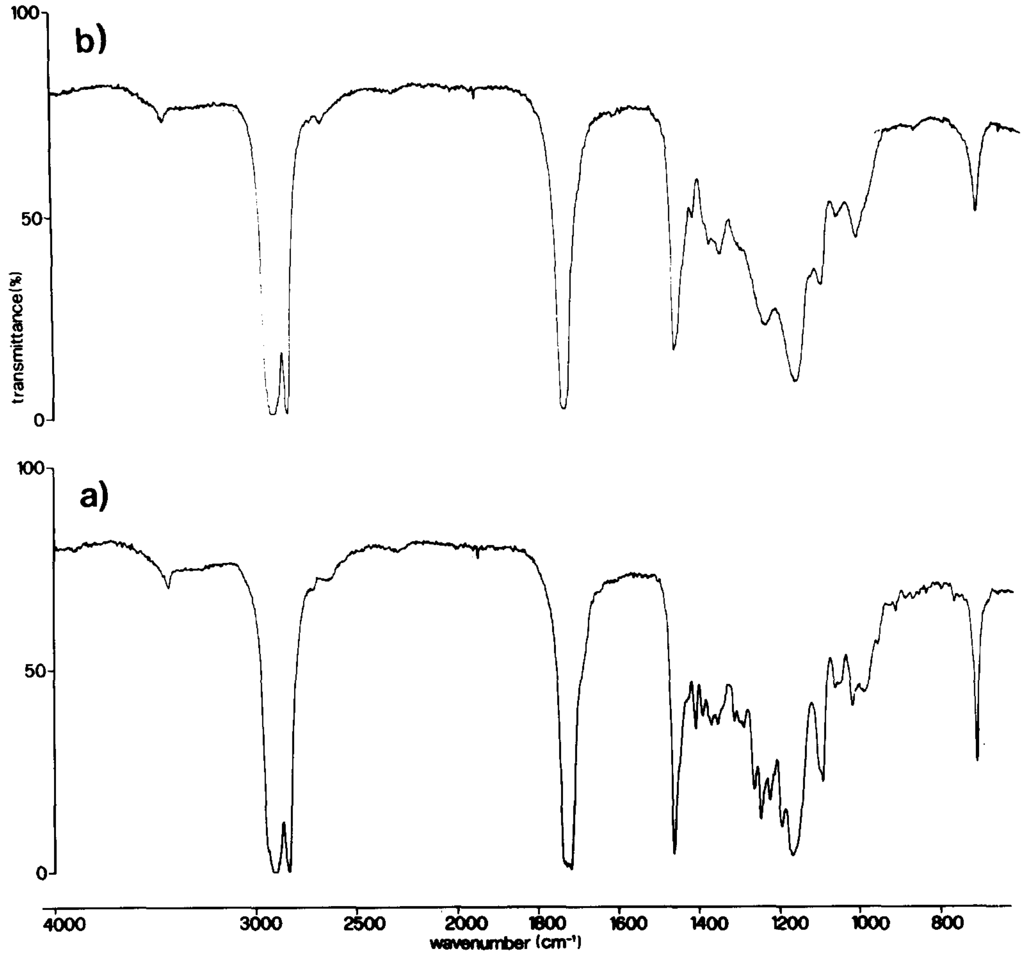


Figure 4 Infra-red spectrum of film of POPTD at: (a) 20°C; (b) 70°C

of the ester band, whereas the sharp characteristic band at 720 cm^{-1} is assigned to the CH_2 rocking mode of the methylene chains. Such a pattern reflects the existence of a crystalline phase in the solid film of POPTD at 20°C involving the packing of the side-chain, or of the main-chains, or of both. The fact that the rocking band of the methylene groups appears as a single peak would moreover suggest that the methylene chains of POPTD crystallize in a hexagonal form[19,20]. The observed spectral differences disappear on reheating the sample to 70°C (*Figure 4b*), and this was taken as an effective indication that the melting of the crystalline regions of POPTD takes place in the temperature range examined.

It is worth noting that when the polyester films are observed under polarized light at temperatures lower than the melting points they behave like unoriented material. However, when stretched the films display a deep birefringence and this was taken as a clear indication of the orientation of the crystalline regions.

The study of the thermal and mechanical properties of these polyesters, as well as of their structural organization, is in progress and will be the subject of a future paper.

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