Synthesis and properties of copolyesters having an ordered comonomer sequence: copolyesters prepared from naphthylene bis(4-hydroxybenzoate)s and α,ω-bis(4-carboxyphenoxy)alkanes

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A series of sequentially ordered copolyesters were prepared from isomeric naphthylene bis(4-hydroxybenzoate)s (NBHBs) and α,ω-bis(4-carboxyphenoxy)alkanes (BCPAs) with varying length of α,ω-alkylene units. All of the copolyesters were composed of naphthalenediol (NAPH), BCPA and *p*-hydroxybenzoic acid (POB) (1:1:2 molar ratio). The polymer chains were made up of –POB–NAPH–POB–BCPA– segments. The naphthalene units were derived from 1,5-, 1,6-, 2,6- and 2,7-naphthalenediols. The BCPAs employed were 1,4-butane, 1,5-pentane and 1,10-decane derivatives. The melting points and crystallizability of these copolyesters were found to be much higher than those of the corresponding random copolyesters having the same overall compositions. All of the polymers, with the exception of the polyester derived from 2,7-naphthalenediol and 1,5-pentane spacers, formed nematic phases in melts. The ordered sequence copolyesters were found to undergo a rapid sequence randomization at temperatures higher than their melting points. A model compound of a copolyester, 2,7-naphthylene bis[4-(4-n-butoxybenzoyloxy)-benzoate], was also synthesized and its thermal behaviour and liquid crystal properties were studied.

(Keywords: ordered sequence copolyesters; naphthalenediol-oxybenzoate copolymers; liquid crystalline polyesters; sequence randomization; triad monomer)

INTRODUCTION

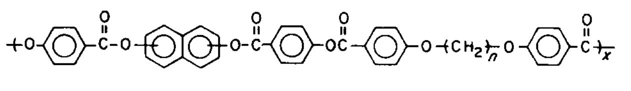
A wide variety of main chain, thermotropic polyesters has been reported by us[1–5] and others[6–10] in recent years. The structural variables taken into consideration in the synthesis of such polymers include the structure of the rigid rod-like units, the presence and the nature of substituents, length of flexible spacers, presence of rigid kinks, molecular weight, thermal history, etc. In addition to the ordinary thermotropic polyesters containing aromatic ester type mesogenic units, other novel thermotropic polymers have been reported. Some of the examples described recently are all hydrocarbon compositions[11], polyethers[12], hydrogen-bonded poly(ester amide)s[13], and polyurethanes[14].

It was recently found that the properties of copolyesters, including liquid crystallinity, are highly dependent not only on their chemical composition, but also on the comonomer sequence[15–22]. However, the ordered sequence copolyesters undergo a rather rapid sequence randomization above their melting points[16,17], although they seem to be fairly resistant to such a randomization below their melting points[3]. In order to synthesize copolyesters having regular sequences, one first has to prepare a symmetric, precursor trimeric compound with a predesigned monomer sequence and polymerize it with a second monomer:

$$\text{A–B–A} + \text{C} \rightarrow \cdots\text{–A–B–A–C–A–B–A–C–}\cdots$$
$$1:1 \text{ alternating copolyester}$$

Polymerization should be carried out under mild conditions so that the predesigned sequence is not disturbed during the final polymerization. Intermolecular ester exchange reactions can destroy the designed comonomer sequence order. Therefore, ordinary melt polymerization methods are not acceptable and a low temperature solution or interfacial polymerization is preferred. Several earlier reports describe the synthesis of ordered or alternating poly(ester amide)s[23–25], copolycarbonates[26,27], and poly(ester carbonate)s[28].

In this paper we describe the synthesis of a series of sequentially ordered copolyesters from isomeric naphthylene bis(4-hydroxybenzoate)s (NBHBs) and α,ω-bis(4-carboxyphenoxy)alkanes (BCPAs). The polymer chains are made up of *p*-oxybenzoyl (POB)-naphthalene (NAPH)-POB-BCPA- units:



OS-*X*,*Y*-*n*

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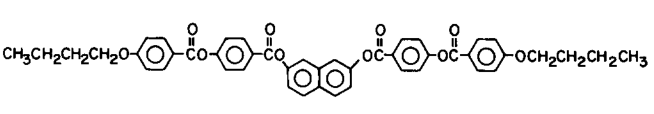
The naphthalene structures included in this study are 1,5-, 1,6-, 2,6- and 2,7-naphthylene units and *n* in the formula is 4, 5 or 10. For simplicity, the copolyesters will be described as OS-*X*,*Y*-*n*, where OS stands for 'ordered sequence' and *X* and *Y* are the substituent positions on the naphthalene ring. The number *n* signifies the number of methylene groups consecutively linked in the polymethylene spacer. The copolyesters included in this paper are OS-1,5-4, OS-1,6-4, OS-2,6-4, OS-2,7-4, OS-2,7-5 and OS-2,7-10.

We compare their basic properties such as glass transition temperatures (T_gs), melting points, isotropization temperatures (T_is), mesophase temperature ranges and crystallizing tendency with those of the corresponding random copolyesters, whose preparaton and properties were previously reported by us[2].

In order to utilize a supplementary compound in the structural analysis of the copolyesters, the following model compound, 2,7-naphthylenebis[4-(4-n-butoxybenzoyloxy)benzoate], was synthesized. Thermal transitions and the liquid crystalline properties of this compound were also examined:



III

EXPERIMENTAL

Synthesis of monomers

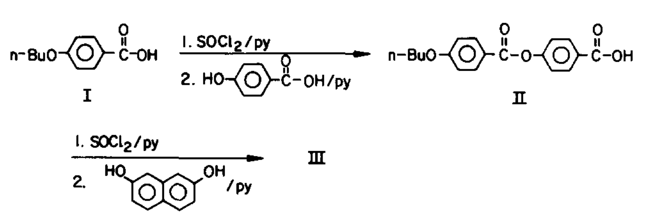
Isomeric naphthylene bis(4-hydroxybenzoate)s were synthesized via a multistep route as described in one of our earlier reports[18]. The BCPA[3] were also prepared following a literature method[29].

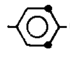
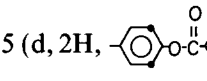
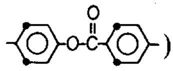
Preparation of polymers

All of the polymers were prepared in solution by direct polycondensation of equimolar amounts of an appropriate NBHB and a BCPA in the presence of thionyl chloride and pyridine[18].

Synthesis of model compound III

Compound III was prepared via the following route:



4-n-Butoxybenzoic acid, I (4.00 g, 2.05×10^{-2} mol) was dissolved in a mixture of dry pyridine (20 ml) and freshly purified thionyl chloride (1.5 ml). The mixture was stirred at room temperature for 30 min. To this mixture was added a solution of 4-hydroxybenzoic acid (2.84 g, 2.05×10^{-2} mol) dissolved in pyridine (10 ml). After the mixture was stirred at 80°C for 24 h, it was poured into distilled water. The precipitate was thoroughly washed with water and recrystallized from an ethanol–water (1:1 v/v) mixture. The yield of compound II, 4-(4-n-butoxybenzoyloxy)benzoic acid, was 2.91 g (83%) and its melting point was 167°C. This compound formed a nematic phase upon melting and underwent isotropization at 275°C. ^{1}H n.m.r. spectrum (CF_3COOD/TMS); δ 1.01 (t, 3H, $-CH_3$), 1.53 (m, 2H, $-CH_2-$), 1.85 (m, 2H, $-CH_2-$), 4.19 (t, 2H, $-OCH_2-$), 7.10 (d, 2H, OCH_2-), 7.35 (d, 2H, ), 8.25 (m, 4H, ). I.r. spectrum (KBr): >C=O stretchings at 1725 and 1690 cm^{-1}, aromatic C=C stretching at 1600 cm^{-1}, C–O stretchings at 1260, 1200 and 1155 cm^{-1}.

Compound II (0.80 g, 2.54×10^{-3} mol) was dissolved in dry pyridine (10 ml) and thionyl chloride (0.20 ml). The mixture was stirred at room temperature for 30 min. 2,7-Dihydroxynaphthalene (0.17 g, 1.02×10^{-3} mol) dissolved in pyridine (10 ml) was added to the above mixture. The mixture was then heated to and maintained at 80°C for 24 h. The mixture was then poured into methanol. The precipitate was thoroughly washed with water and then with boiling ethanol. The product thus obtained was found to be pure by t.l.c. and n.m.r. analysis. The yield was 0.66 g (86%). Compound III was found to be mesomorphic and melted at 185°C to a nematic phase. It showed isotropization at 229°C. Analysis: found C 73.25, H 5.57%; calc. C 73.39, H 5.36%. ^{1}H n.m.r. spectrum (CF_3COOD/TMS) δ 1.02 (t, 6H, $-CH_3$), 1.55 (sec, 4H, $-CH_2-$), 1.88 (quint, 4H, $-CH_2-$), 4.21 (t, 4H, $-OCH_2-$), 7.05–8.45 (m, 22H, Ar). I.r. spectrum (KBr): >C=O stretching at 1730 cm^{-1}, aromatic C=C stretching at 1600 cm^{-1}, C–O stretchings at 1255, 1190 and 1155 cm^{-1}.

Characterization of polymers

Elemental analyses were performed by the Analytical Laboratory of the Korea Research Institute of Chemical Technology. Inherent viscosity values were measured at 25°C using a Cannon-Ubbelohde type viscometer. Viscosity measurements were made on 0.1 g dl^{-1} solutions in a pentafluorophenol/*p*-chlorophenol/chloroform (3/3/4 v/v) mixture or in a trifluoroacetic acid/chloroform (1/1 v/v) mixture. ^{13}C n.m.r. spectra of the polymers were recorded on a Bruker AM-300 in a mixture of CF_3COOD and $CDCl_3$ (1/1 v/v). Thermograms were obtained under a N_2 atmosphere on a DuPont 910 DSC at a heating rate of 10°C min^{-1}. Indium was used as reference for temperature and enthalpy changes. Wide-angle X-ray diffractograms were recorded on a Jeol JDX-80 instrument using Ni-filtered Cu Kα radiation. The approximate degree of crystallinity was calculated from the areas of the crystalline and amorphous reflections in the diffractograms. Thermal behaviour and the optical textures of the melts were also examined on a hot stage (Mettler FP-2) attached to a polarizing microscope (Leitz, Ortholux).

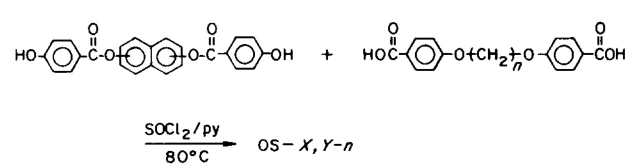
Thermal reorganization

A powdered sample of OS-2,7-4 was placed at 280°C under a N_2 atmosphere. Accompanying changes in its structure after varying the period of thermal treatment was followed by ^{13}C n.m.r. spectral analysis.

RESULTS AND DISCUSSION

Synthesis of copolyesters

All of the copolyesters were prepared by direct polycondensation of NBHB and BCPA at 80°C under a N_2 atmosphere in the presence of a mixture of thionyl chloride and pyridine, which is known to be an excellent condensing agent for reactions between dicarboxylic acids and diols[30]:



This method was previously found satisfactory for the preparation of wholly aromatic copolyesters having ordered sequences[18]. We could confirm by ^{13}C n.m.r. analysis that the present copolyesters indeed are of a predesigned sequence, i.e. in the order POB–NAPH–POB–BCPA along the chain. For example, in the ^{13}C n.m.r. spectrum of OS-2,7-4 shown in *Figure 1a*, we observe only singlet resonance peaks for carbons 1–5. The same resonance characters are also observed for the corresponding carbons in the model compound (*Figure 1b*). The corresponding random copolymer prepared in the melt from *p*-acetoxybenzoic acid, 2,7-diacetoxynaphthalene and BCPA, however, exhibits much more complicated ^{13}C n.m.r. spectral features (*Figure 1c*). Since *p*-acetoxybenzoic acid can undergo homocondensation, POB units in the random copolymer can be present in the monomeric as well as in the dimeric and longer POB blocks. In OS-2,7-4 only monomeric POB units are possible. A broad distribution in the length of oligomeric POB blocks in the random copolymer should result in multiplet n.m.r. peaks for carbons 1–5. In contrast, absence of dimeric and longer POB blocks in OS-2,7-4 makes the ^{13}C n.m.r. spectrum much simpler as described above. Therefore, we can conclude that the polymerization conditions utilized in this study are satisfactory for the preparation of sequentially ordered copolyesters. The results of the elemental analyses (*Table 1*) are in good agreement with computed values.

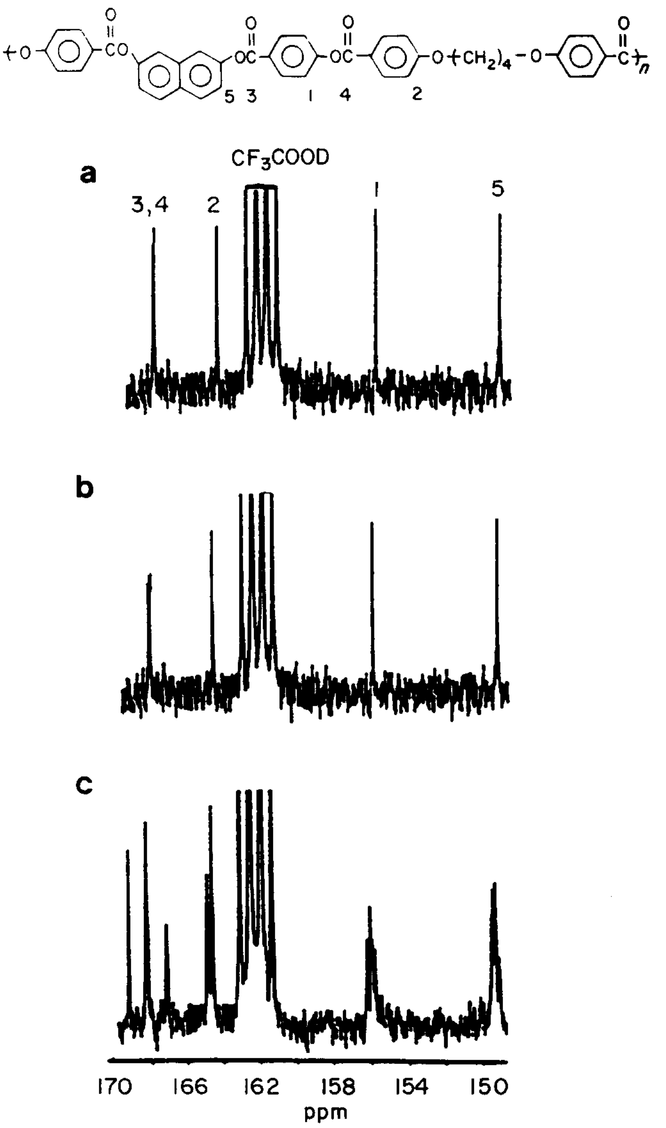


Figure 1 ^{13}C n.m.r. spectra obtained at room temperature ($CDCl_3$/CF_3COOD (1/1 v/v)): (a) for OS-2,7-4, (b) for compound III and (c) for the random copolyester

Table 1 Results of elemental analyses

Polymer	Elemental content (wt%)[a]	
	C	H
OS-1,5-4	71.9 (72.6)	4.47 (4.36)
OS-1,6-4	71.8 (72.6)	4.53 (4.36)
OS-2,6-4	71.7 (72.6)	4.45 (4.36)
OS-2,7-4	71.8 (72.6)	4.34 (4.36)
OS-2,7-5	72.1 (72.9)	4.67 (4.56)
OS-2,7-10	73.2 (74.1)	5.67 (5.45)

[a] Values in parentheses are those calculated for the chemical formulae

General properties

The inherent viscosity values (0.42–0.67, *Table 2*) of the present polymers are not very high, which most probably arises from the fact that they precipitate out of the reaction mixture as they are formed. The polymer yields are reasonably high and range from 83 to 91% (*Table 2*). The solubilities of the copolyesters were very poor and they were only slightly soluble in mixed solvents such as $CF_3COOH/CHCl_3$ and pentafluorophenol/*p*-chlorophenol/chloroform. They were, however, slowly soluble in pentafluorophenol.

The T_gs of the OS-*X*,*Y*-4 polymers range from 80 to 98°C depending on the substituent position on the naphthalene ring. In general, the T_g values of the ordered sequence copolyesters are significantly higher than those of the corresponding random sequence ones[2]. For example, the T_g value of OS-2,7-4 is 98°C, while that of the random copolymer is 71°C. Certainly, a regular sequence of comonomers along the chains lessens segmental mobility. Comparing the data shown in *Table 2* for OS-2,7-4, OS-2,7-5 and OS-2,7-10, as expected, it is evident that the T_g value drops with the length of the polymethylene spacer in the chain. The melting temperatures, T_ms, of the polymers range from ~220 to 290°C depending on the structure of the naphthalene moiety and the length of the polymethylene spacer. Some of the values are higher by as much as ~100°C than those of the corresponding random copolyesters[16,17]. For example, the T_m value of OS-2,7-5 is 259°C, whereas

Table 2 Properties of the copolyesters[a]

Polymer	Yield (%)	η_{inh}	T_g (°C)	T_m (°C)	T_i (°C)[b]	Degree of crystallinity (%)	LC
OS-1,5-4	88.1	0.44	80	289	d (>325)	39	Nematic
		(1.07)	(84)	(274)	(–)	(5)	(Nematic)
OS-1,6-4	84.3	0.52	89	229	281	13	Nematic
		(0.60)	(75)	(–)	(312)	(0)	(Nematic)
OS-2,6-4	91.2	0.52	83	259	d (>355)	33	Nematic
		(0.92)	(68)	(202)	(312)	(13)	(Nematic)
OS-2,6-4	86.8	0.49	98	272	352	23	Nematic
		(0.85)	(71)	(175)	(285)	(9)	(Nematic)
OS-2,7-5	83.2	0.67	87	259	–	16	Non-LC
		(0.62)	(72)	(161)	(295)	(<3)	(Nematic)
OS-2,7-10	89.3	0.42	57	219	250	22	Nematic
		(0.62)	(74)	(155)	(298)	(14)	(Nematic)

[a] Data in parentheses are those for the corresponding random copolyesters reported earlier by us in reference 2

[b] 'd' means that the polymer underwent thermal decomposition before reaching T_i

the value of the random counterpart is only 161°C. It is clear that the regular sequence of comonomers along the chain facilitates more efficient molecular packing in the crystal structure, which, in turn, raises the T_m value in comparison with random sequence copolymers.

Wide angle X-ray diffractograms of the OS-X,Y-4 series are shown in *Figure 2*. They reveal that the polymers are semicrystalline, which is consistent with the observation that melting endotherms appear for them all in d.s.c. analysis (*Figure 3*). The approximate degrees of crystallinity estimated from the diffractograms are shown in *Table 2*. It is noticeable that OS-1,6-4 and OS-2,7-5 exhibit comparably low degrees of crystallinity, 13 and 16%, respectively, whereas others have a degree of crystallinity of 22–39% depending on the symmetry of the naphthalene moiety and the length of the spacers. In contrast to the others, the OS-1,6-4 polymer contains asymmetrically disubstituted 1,6-naphthalenediyl units. In other words, the 1 and 6 positions are not identical. Therefore, the polymer chain is not of ordered sequence in a strict sense, although each comonomer unit appears regularly along the chain. This structural feature appears to be the reason for the low degree of crystallinity for OS-1,6-4. Poor crystallizing behaviour of OS-2,7-5 may be attributed to the odd number of methylene groups in the spacer. Very similar phenomena were earlier observed by us for the wholly aromatic copolyesters[18] prepared using terephthalic acid in place of BCPA and for the corresponding random copolyesters[2] containing the same pentamethylene spacer.

Another interesting point to be noted is the fact that X-ray diffractograms of the OS-X,Y-4 polymers are very different from each other indicating that their crystal structures are very much dependent on the substitution positions on the naphthalene units (*Figure 2*). In addition, comparison of diffractograms (*Figure 4*) for the OS-2,7-n series reveals that the length of spacers also causes changes in the crystal structures.

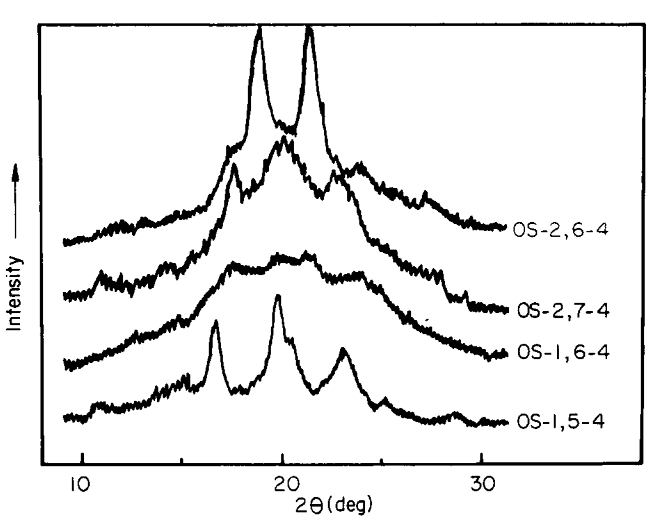


Figure 2 Wide angle X-ray diffractograms of the OS-X,Y-4 copolyesters

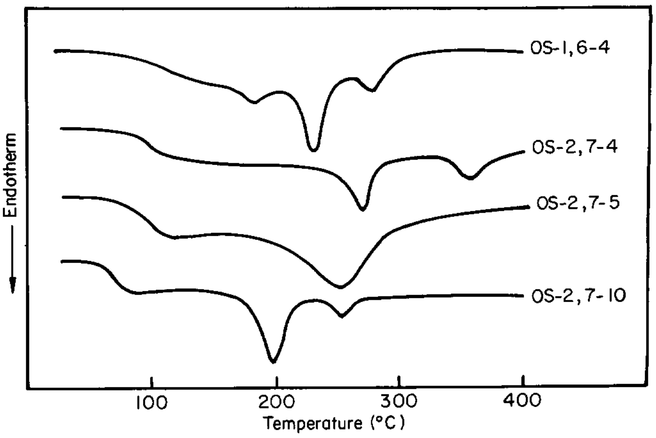


Figure 3 D.s.c. thermograms of copolyesters (heating rate 10°C min^{-1})

Liquid crystallinity and isotropization

All of the present copolyesters with the exception of OS-2,7-5 are liquid crystalline and form nematic melts. They exhibited either threaded Schlieren or polished marble textures (*Figure 5*) when their melts were observed using a polarizing microscope. It is rather surprising that even OS-1,6-4 is mesomorphic. Previously we[18] reported that the corresponding ordered sequence copolyester without a spacer prepared from 1,6-NBHB

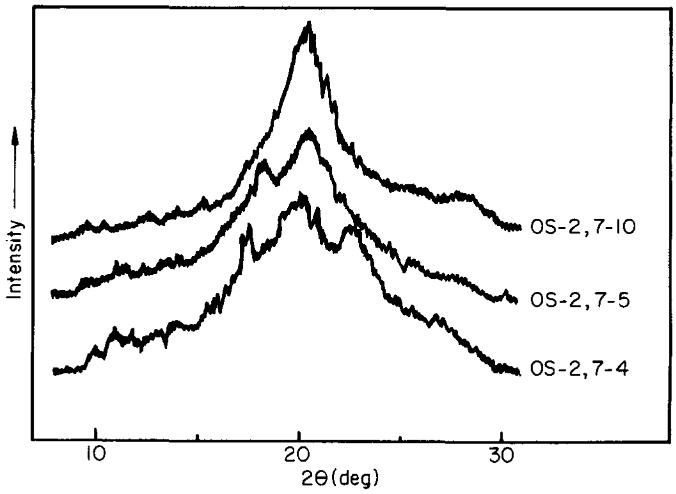


Figure 4 Wide angle X-ray diffractograms of the OS-2,7-*n* copolyesters

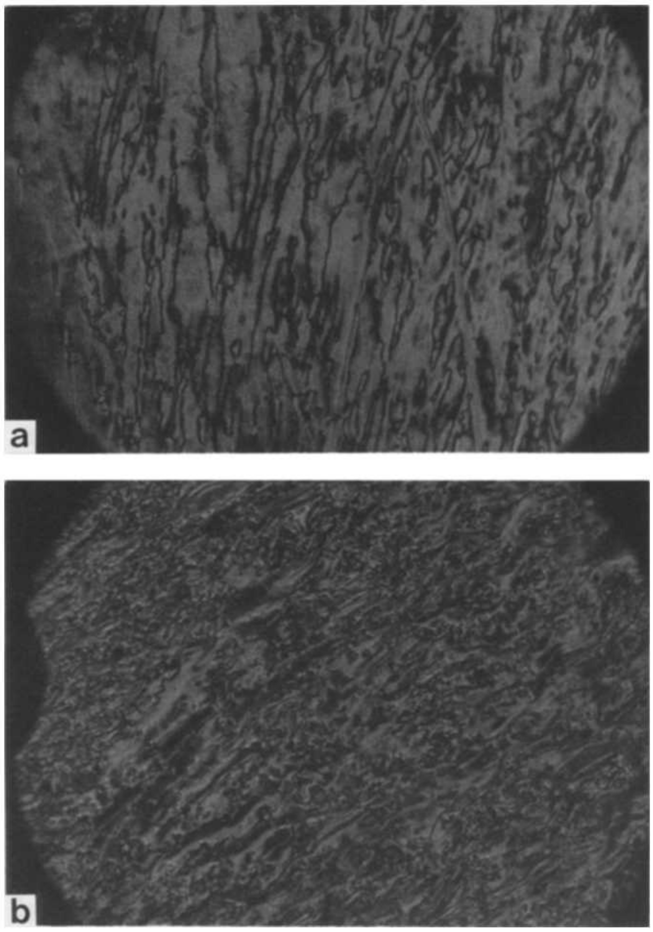
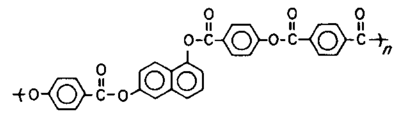


Figure 5 Photomicrographs for (a) OS-2,7-4 taken at 300°C and (b) OS-2,7-10 taken at 220°C. Magnification ×132

and terephthalic acid was not thermotropic:



In this structure every 1,6-naphthalenediol moiety destroys the linear shape of the polymer chain and makes the polymer unable to spontaneously form an ordered phase in the melt. The presence of the oxytetramethyleneoxy spacer ($-O-(-CH_2-)_4-O-$) in OS-1,6-4, however, gives the composition mesophase-forming capability. This clearly demonstrates that the spacer enables conformation adjustments to be made, to a certain extent, to mitigate the bent shape of the rigid structure. Such a conformational adjustment will make the molecules possess enough linear segments to be mesomorphic[31–33]. At the same time, the fact that OS-2,7-5 is not liquid crystalline suggests that there is a restriction in the degree of conformational freedom for a spacer. As a result, the odd number of methylene groups in OS-2,7-5 does not give the compound mesophase-forming capacity. The random counterpart of OS-2,7-5, however, was reported to be thermotropic[2]. This difference can be ascribed to the existence of dimeric or longer repeated POB structures along the chain in the random copolyester, which provides sufficiently long linear segments to give the copolymer a mesophase-forming capability.

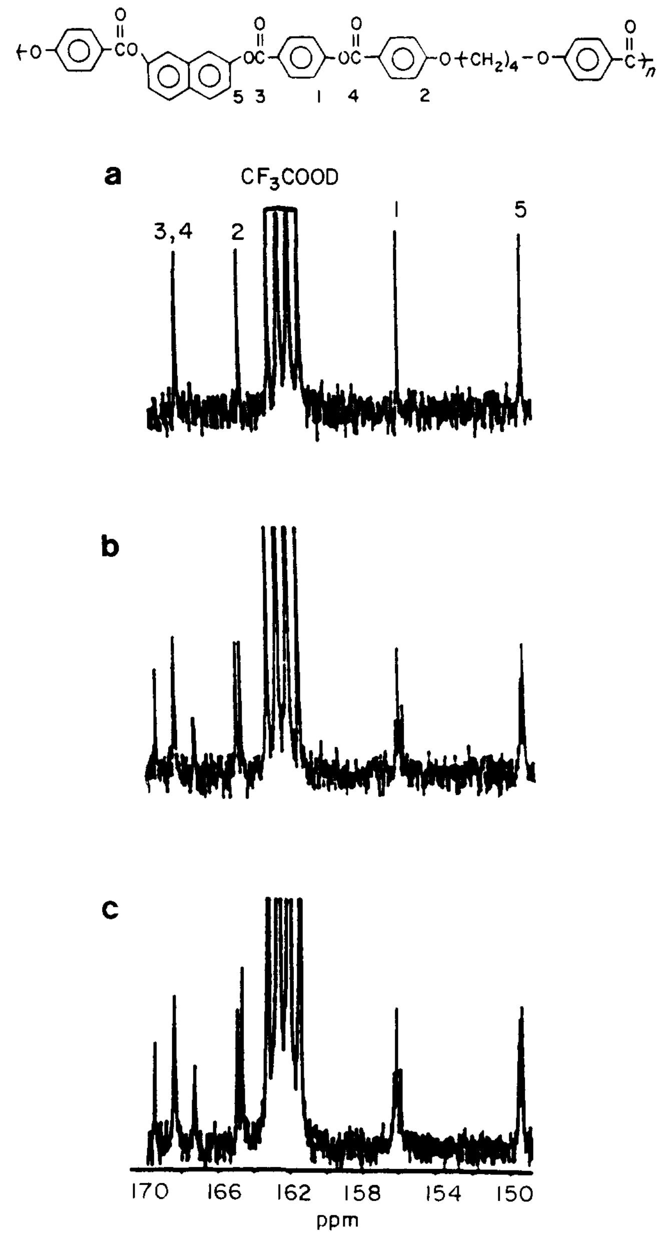
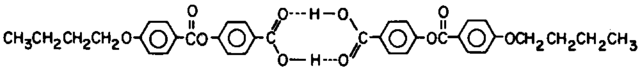


Figure 6 Changes in the ^{13}C n.m.r. spectrum of OS-2,7-4 after heat treatment at 280°C ($CDCl_3/CF_3COOD$ (1/1 v/v)): (a) as-polymerized; (b) 2 min at 280°C; (c) 4 min at 280°C

As far as isotropization is concerned, the copolyesters of OS-1,6-4, OS-2,7-4 and OS-2,7-10 exhibit clearing transition endotherms on their d.s.c. thermograms (*Figure 3*), but other compositions suffered thermal degradation before reaching their T_is. The OS-2,6-4 polymer, having a longer linear rigid structure as the mesogenic unit, maintained the nematic phase up to a temperature of ~350°C where it started to undergo thermal degradation. In contrast, the presence of the 1,6-naphthalenediyl unit in OS-1,6-4 reduces the thermal stability of the mesophase and, as a result, its T_i is only 281°C. In the case of OS-2,7-10 the long oxydecamethyleneoxy spacer destabilizes the mesophase and brings about isotropization at a lower temperature (250°C)[5].

As far as the liquid crystalline properties of II and III are concerned, they both formed a nematic phase upon melting, as described in the Experimental section. The particularly high T_i (275°C) for II can be ascribed to the thermal stability of the hydrogen-bonded dimeric structure:



Sequence changes

The sequence randomization of OS-2,7-4 was followed qualitatively by observing changes in the ^{13}C n.m.r. spectrum after heat treatment at 280°C for a varying period of time. *Figure 6* shows the spectral changes for OS-2,7-4. The ^{13}C n.m.r. spectrum of the sample heat-treated only for 2 min at 280°C reveals many changes in the resonance peaks for carbons 1–5*. It is very possible that a small amount of unidentified catalytic residue exists in the sample and causes the fast sequence randomization. Further work is in progress to study this point. The general profile of the spectra obtained for the heat-treated samples is quite similar to that for the corresponding random counterparts separately prepared in the melt[2].

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* There are typographic mistakes in the peak assignments in reference 16