Thermotropic polyesters: synthesis and properties of *t*-butyl-substituted poly(4-oxybenzoate)s

V. Kalyvas, Z. G. Li, J. E. McIntyre*, A. H. Milburn, J. G. Tomka and A. M. Voice

Department of Textile Industries and IRC in Polymer Science and Technology, University of Leeds, Leeds LS2 9JT, UK

(Received 18 August 1992)

Two series of novel *t*-butyl-substituted copolyesters, poly(3-*t*-butyl-4-oxybenzoate-*co*-4-oxybenzoate)s and poly(3,5-di-*t*-butyl-4-oxybenzoate-*co*-4-oxybenzoate)s, have been synthesized. The former were prepared by the conventional transesterification reaction via an acetolysis route and the latter were made from or via a novel monomer, 3,5-di-*t*-butyl-4-hydroxybenzoyl chloride. These polymers were characterized by solution viscometry, infra-red spectroscopy, wide angle X-ray scattering, hot-stage polarizing microscopy and thermal analysis (d.s.c., t.g.a. and t.m.a.). Both poly(3-*t*-butyl-4-oxybenzoate) and poly(3,5-di-*t*-butyl-4-oxybenzoate) were semicrystalline and did not melt before decomposing, although they were easily soluble in conventional solvents. Of the monosubstituted copolymers, only the 50:50 composition melted at a temperature substantially below decomposition, forming a nematic mesophase, which makes this copolymer the most promising for processing. None of the disubstituted copolymers melted below its decomposition temperature.

(Keywords: thermotropic; liquid crystalline; copolyester; *t*-butyl substituent)

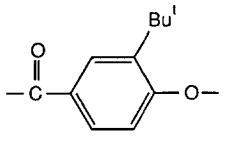
INTRODUCTION

In the past two decades, main-chain thermotropic liquid crystalline polymers have received much attention due to their importance as new engineering materials[1–3]. Rigid-rod-like polyesters consisting of wholly *para*-linked units, such as poly(4-oxybenzoate) (POB) and poly(1,4-phenylene terephthalate) (PPT), are highly crystalline and do not melt without decomposition. The objective of thermotropic liquid crystalline polymer design is to disrupt the regular structure of the intractable *para*-linked aromatic polymers so that processable nematic melts are obtained[4–6].

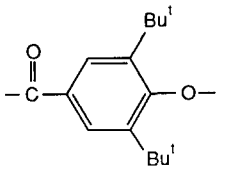
A method frequently used for this purpose is the introduction of substituents into the polymer backbones. Several polymer systems containing substituted oxybenzoyl units have been reported. Poly(3-chloro-4-oxybenzoate)[7] was highly crystalline and did not show any endothermic transitions below 450°C. Poly(3,5-di-chloro-4-oxybenzoate)[8], a semicrystalline polymer. did not melt below decomposition. Poly(3-chloro-4-oxybenzoate-*co*-4-oxybenzoate)[7] compositions rich in unsubstituted units possessed a first order transition between 200 and 340°C which was assigned as an orthorhombic to pseudo-hexagonal crystal transition rather than a melting. Compositions rich in substituted units melted between 360 and 400°C. The equimolar composition exhibited the lowest melting temperature, just above 330°C. Poly(3-methoxy-4-oxybenzoate) and poly(3,5-dimethoxy-4-oxybenzoate) were found to be insoluble and infusible[9].

The effect of substitution by *n*-alkyl has been reported[10] with poly(3-propyl-4-oxybenzoate) melting at 296°C to form a nematic phase from which highly oriented fibres could be drawn. Polymers with longer side chains ($n = 6$–18) exhibited even lower melting temperatures (between 0 and 100°C) with liquid crystalline to isotropic phase transitions between 200 and 290°C.

This paper is a continuation of our investigation of the effect of *t*-butyl substituents in rigid aromatic polyesters. Previous work has concentrated on PPT[11]. This paper is concerned with the synthesis and characterization of homopolymers composed of oxybenzoyl units bearing one (*I*) or two (*II*) *t*-butyl substituents, and with copolymers of either of these units with unsubstituted oxybenzoyl units.



I



II

EXPERIMENTAL

Monomer preparation

4-Acetoxybenzoic acid was made by acetylation of 4-hydroxybenzoic acid.

3-*t*-Butyl-4-acetoxybenzoic acid was prepared by heating 2-*t*-butyl-4-methylphenol with excess of acetic anhydride and a trace of concentrated sulfuric acid for 30 min under reflux. The solution was then cooled, poured

* To whom correspondence should be addressed

0032-3861/93/143076-07

into water, extracted with toluene, washed with dilute potassium hydroxide solution and water and dried over anhydrous magnesium sulfate. After distilling off the toluene, the oily product (56 g) was dissolved in propionic acid (350 ml) containing 0.8 g of cobalt(II) bromide hydrate (BDH) and 1.6 g of manganese(II) bromide tetrahydrate (BDH). Oxygen was passed through the vigorously refluxing solution for 2 h. After cooling to below 100°C, 350 ml of water was added, and the solution was allowed to cool to ambient temperature. The precipitate that formed was filtered off and recrystallized from 250 ml of 80% methanol to give 24 g (38% yield) of feathery needles (m.p. 188–190°C).

3,5-Di-*t*-butyl-4-acetoxybenzoic acid was made by acetylating 3,5-di-*t*-butyl-4-hydroxybenzoic acid (Aldrich, 98%), which had been recrystallized from 60% aqueous ethanol with acetic anhydride in acetic acid with concentrated sulfuric acid as catalyst. The acetylated product had a melting point of 191°C after recrystallization three times from 60% aqueous ethanol.

3,5-Di-*t*-butyl-4-hydroxybenzoyl chloride was prepared by refluxing 3,5-di-*t*-butyl-4-hydroxybenzoic acid with an excess of redistilled thionyl cloride in the presence of a few drops of *N,N*-dimethylformamide as catalyst. The product was recrystallized twice from *n*-heptane and dried at 60°C in vacuum overnight. Yield 56% (m.p. 76–77°C). Elemental analysis: calculated for $C_{15}H_{21}O_2Cl$, C 67.02%, H 7.89%, Cl 13.19%; found, C 66.85%, H 8.00%, Cl 12.40%. I.r. (KBr): 3580, 2980, 1747, 1602, 1580, 1366, 1195, 1050, 984, 822, 705, 696 cm^{-1}.

Polymer synthesis

Poly(3-t-butyl-4-oxybenzoate). This polymer and its copolymers, poly(3-*t*-butyl-4-oxybenzoate-*co*-4-oxybenzoate)s, were synthesized by melt polycondensation at 282°C of 3-*t*-butyl-4-acetoxybenzoic acid with 4-acetoxybenzoic acid in various molar ratios, using a method described previously[11]. The polymers were ground and washed with acetone and water successively, then dried in vacuum at 120°C overnight.

Poly(3,5-di-t-butyl-4-oxybenzoate). Attempts to synthesize this disubstituted polymer via the acetolysis route used for the monosubstituted polymers were not successful.

The polymer was synthesized by the melt polycondensation of 3,5-di-*t*-butyl-4-hydroxybenzoyl chloride at temperatures ranging from 242 to 350°C. About 0.5 g of the monomer was charged into a polymerization tube which had previously been heated and cooled in nitrogen to remove moisture and hence reduce the probability of hydrolysis during subsequent heating. The polycondensation was carried out in a vapour bath, except for temperatures higher than 330°C, where a sand bath was used. The polymers were ground and washed with acetone and water successively, then dried in vacuum at 120°C overnight.

The corresponding copolymers, poly(3,5-di-*t*-butyl-4-oxybenzoate-*co*-4-oxybenzoate)s, were prepared by solution polycondensation in pyridine using 10% excess of thionyl chloride, according to the method described by Imai *et al.*[12]. The polymers were precipitated in an excess of alcohol, washed in a blender twice with alcohol and once with acetone, and then dried at 40°C under vacuum for 12 h. A sample of the homopolymer (*II*) was prepared by the same method.

Polymer characterization

The inherent viscosities (η_{inh}) of the polymers were measured at 25°C either in chloroform (0.5 g dl^{-1}), or in a mixed solvent of trifluoroacetic acid and dichloromethane (1:3 by volume) at a concentration of 0.25 g dl^{-1}, as reported below.

Thermo-optical observations were made on a hot-stage polarizing microscope at a heating rate of 20°C min^{-1}. Differential scanning calorimetry (d.s.c.), was undertaken at 20°C min^{-1}. Thermogravimetric analysis (t.g.a.; 10°C min^{-1}) and thermomechanical analysis (t.m.a.; 20°C min^{-1}) were carried out under nitrogen. Wide angle X-ray scattering (WAXS) patterns were obtained using a curved position-sensitive detector and *FT*i.r. spectra were recorded using the potassium bromide technique. These procedures have been described previously in detail[11].

RESULTS AND DISCUSSION

Poly(3-t-butyl-4-oxybenzoate)

The as-made polymer was soluble in a mixture of trifluoroacetic acid and dichloromethane (1:3 by volume) and its η_{inh} in this solvent was 0.55 dl g^{-1}. It was found to soften and flow upon heating, but not below its decomposition temperature (*Table 1*, molar percentage of substituted units, $[s] = 100$). T.g.a. (*Figure 1*) showed 5% weight loss from this polymer at a temperature of 410°C (curve c) which is approximately 100°C lower than the corresponding weight loss temperature for POB (curve a). Thus it is evident that incorporation of a single *t*-butyl substituent in each repeat unit causes a substantial lowering of the thermal stability (*Figure 2*). A double endotherm between 400 and 450°C was obtained for poly(3-*t*-butyl-4-oxybenzoate) ($[s] = 100$) using d.s.c. The upper endotherm, apparently corresponding to melting on the basis of the hot-stage observations, was above the onset of decomposition and is therefore not shown in *Figure 3*.

WAXS analysis of poly(3-*t*-butyl-4-oxybenzoate) revealed this polymer to be semicrystalline (*Figure 4*, $[s] = 100$). *Table 2* shows the interplanar spacings calculated from the diffraction peaks. Although it is impossible to obtain a full structural analysis without highly crystalline oriented material, it is worth noting that the *d*-spacings of the prominent peaks, normally

Table 1 Characterization of mono-*t*-butyl-substituted copolymers

$[s]^a$	$\eta_{inh}{}^b$ (dl g^{-1})	$T_s{}^c$ (°C)		$T_f{}^d$ (°C)	$T_{5\%}{}^e$ (°C)
		T.m.a.	H.s.p.m.		
0	–	–	–	–	507
40	3.22	304	365	440	450
50	1.84	214	260	310	430
60	2.51	327	360	410	450
70	1.72	357	380	435	430
80	2.29	378	395	425	425
90	0.55	415	440	440	425
100	0.55	429	445	455	410

[a] Molar percentage of *t*-butyl-substituted units
[b] Inherent viscosity determined in trifloroacetic acid/dichloromethane
[c] Softening temperature, detected by t.m.a. and observed by hot-stage polarizing microscopy (h.s.p.m.)
[d] Flow temperature, observed by h.s.p.m.
[e] Temperature of 5% weight loss, determined by t.g.a.

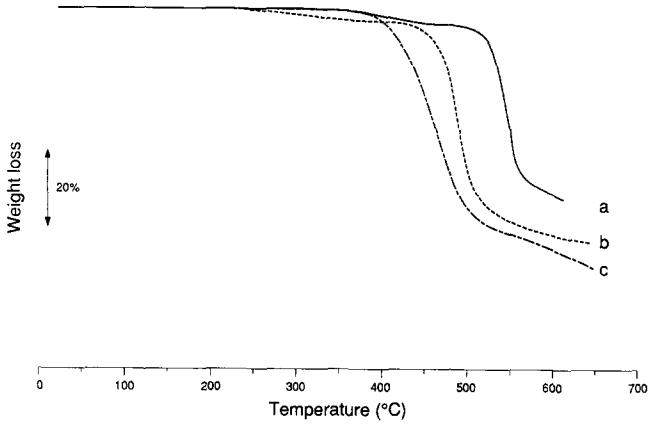


Figure 1 T.g.a. curves for polymers from the mono-*t*-butyl-substituted series. (a) $[s]=0$, (b) $[s]=50$ and (c) $[s]=100$ ($[s]$ = molar percentage of substituted units)

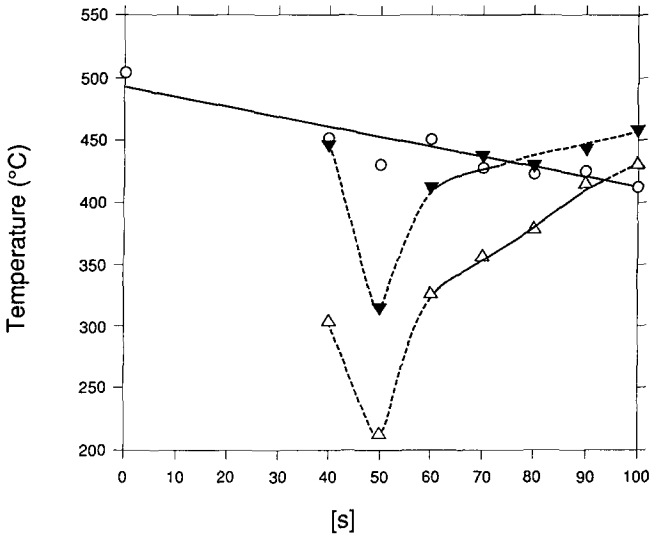


Figure 2 Thermal transitions of the mono-*t*-butyl-substituted series. △, Softening (from t.m.a.); ▼, flow (from hot-stage polarizing microscopy); ○, 5% weight loss (from t.g.a.)

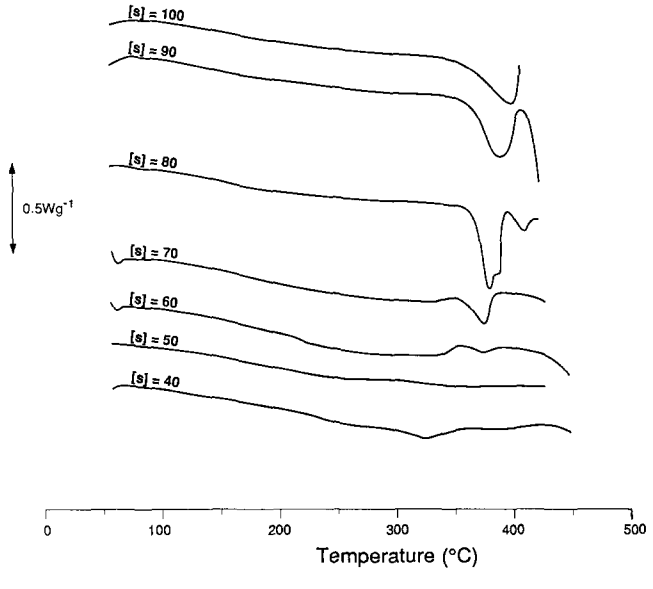


Figure 3 D.s.c. curves of the mono-*t*-butyl-substituted series, shown up to the respective temperatures of 5% weight loss ($[s]$ = molar percentage of substituted units)

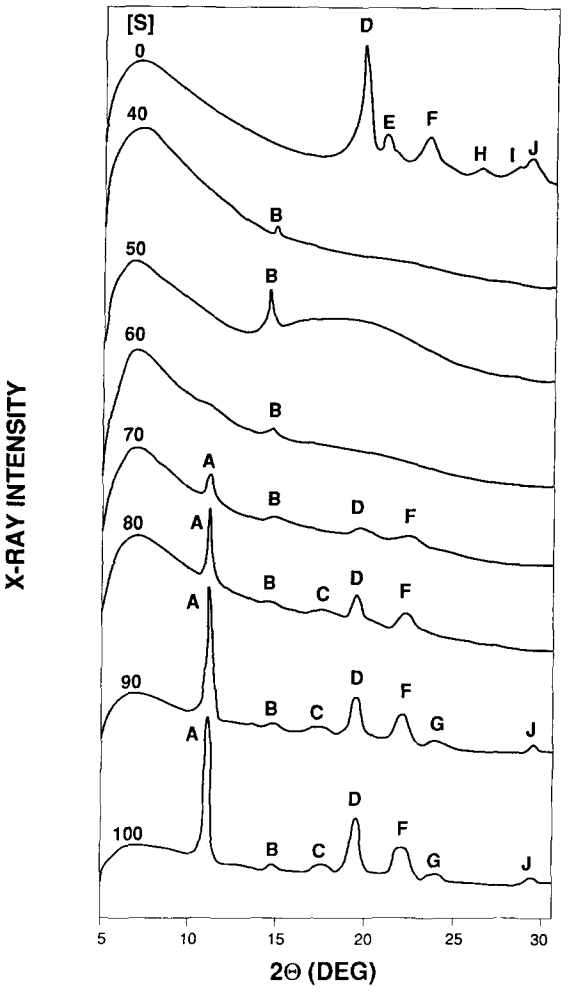


Figure 4 X-ray diffractograms of the mono-*t*-butyl-substituted series. *Table 2* gives the interplanar spacings of the peaks

Table 2 Interplanar spacings (nm) for mono-*t*-butyl-substituted copolymers

		[s]				
Peak[a]	*hkl*[b]	0	70	80	90	100
A			[c]	0.766(s)	0.766(vs)	0.770(vs)
B			[c]	0.588(vw)	0.587(w)	0.587(w)
C				0.492(vw)	0.494(w)	0.493(w)
D	110	0.441(vs)	[c]	0.444(m)	0.450(s)	0.451(s)
E	111	0.417(w)				
F	200	0.374(m)	[c]	0.391(m)	0.398(m)	0.399(m)
G					0.368(w)	0.368(w)
H	013	0.334(vw)				
I	004	0.307(vw)				
J	211	0.300(w)			0.302(vw)	0.303(w)

[a] Peaks as labelled in *Figure 4*
[b] Reflection for poly(4-oxybenzoate), $[s]=0$
[c] Peak present but too weak to be fitted
Peak intensities: vs = very strong, s = strong, m = medium, w = weak, vw = very weak

arising from lateral chain packing, are larger than those of the unsubstituted POB ($[s]=0$). This supports the expectation that a single *t*-butyl substituent in the repeat unit will result in a reduced chain-packing density compared with unsubstituted chains.

Poly(3-t-butyl-4-oxybenzoate-co-4-oxybenzoate)s

All copolymers synthesized ($[s]=40$, 50, 60, 70, 80 and 90) were opaque. With the exception of $[s]=40$, they

were completely soluble in a mixture of trifluoroacetic acid and dichloromethane and their viscosities in this solvent are given in *Table 1*. The insoluble fraction of $[s]=40$ is attributed to blocks of *p*-oxybenzoyl units, i.e. the copolymer is assumed to be inhomogeneous in composition, a common problem observed when the reactivities of the comonomers are unequal[7,13–15].

Figure 4 shows the WAXS patterns obtained for these copolymers and *Table 2* displays the calculated interplanar spacings of the dominant peaks. It can be seen that copolymer $[s]=90$ is crystalline and has the structure of the fully substituted homopolymer, $[s]=100$. Copolymers $[s]=80$ and 70 exhibit a small degree of crystallinity, again with the structure of $[s]=100$. Copolymers $[s]=60$, 50 and 40 are essentially non-crystalline according to WAXS. The peak B found in all copolymers was also present in the substituted monomer. From all these results it is evident that introduction of more than 30% of unsubstituted *p*-oxybenzoyl units causes a loss of crystal structure of the substituted polymer.

T.m.a. revealed that, with the exception of $[s]=90$, all the copolymers softened well below their decomposition temperature (determined by t.g.a.), with $[s]=50$ having the lowest softening temperature of 214°C (*Figure 2*, *Table 1*). Only $[s]=50$ was found to flow (at 310°C) sufficiently below decomposition to be melt-processable. This composition displayed a nematic mesophase and thus achieved the objective of thermotropic liquid crystalline polymer design. Copolymers with $[s]\geqslant 60$ also exhibited liquid crystallinity but only at temperatures close to, or above, decomposition.

The thermal stability of these copolymers (as determined by the temperature of 5% weight loss by t.g.a.) decreased with increasing percentage of substituted units (*Figures 1* and *2*).

Figure 3 shows the d.s.c. curves obtained for the copolymers. For $[s]\geqslant 70$ multiple endotherms were detected which decreased in temperature with decrease in concentration of substituted units. For $[s]=50$ no distinct endotherm was detected, in agreement with the non-crystalline nature of this sample determined by WAXS.

The peak seen in the thermogram of $[s]=40$ at 330°C is not due to melting, since no flow was seen for this copolymer by hot-stage microscopy. This endotherm is attributed to the crystal–crystal transition of POB[16,17], present in blocks in the insoluble fraction.

Since $[s]=50$ was the only composition to be processable from the liquid crystalline mesophase, the properties of this copolymer were investigated in more detail. Samples were held at 370°C (within the liquid crystalline region) for 30 s and quenched on a pre-cooled steel bar. They were then annealed for 30 min at temperatures of 280, 300 or 320°C. Their d.s.c. curves (*Figure 5*) show a weak glass transition at about 210°C, in good agreement with the softening temperature (*Figure 2*). Weak endotherms are also seen, indicating that this copolymer can crystallize to a small extent. The peak temperature increases with increasing annealing temperature.

Poly(3,5-di-t-butyl-4-oxybenzoate)

Initially, synthesis was attempted by the acetolysis route from 3,5-di-*t*-butyl-4-acetoxybenzoic acid, but at best only very low degrees of polymerization were achieved. This is attributed to the much reduced reactivity

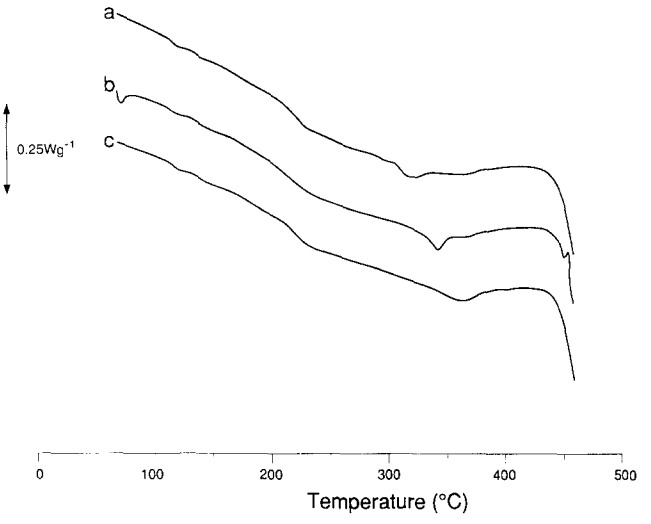


Figure 5 D.s.c. curves of $[s]=50$ in the mono-*t*-butyl-substituted series, after heating at (a) 280°C, (b) 300°C and (c) 320°C

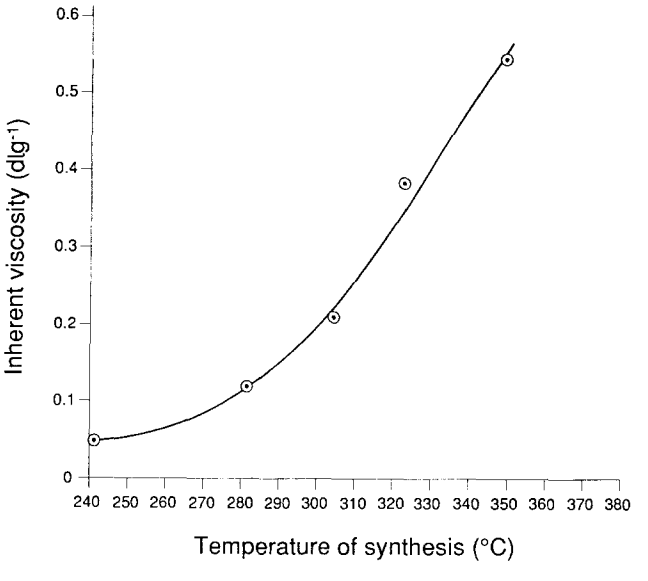


Figure 6 Inherent viscosity (measured in chloroform) *versus* synthesis temperature for poly(3,5-di-*t*-butyl-4-oxybenzoate) made from the monomer 3,5-di-*t*-butyl-4-hydroxybenzoyl chloride

of the acetoxy function due to steric hindrance by the two bulky *t*-butyl groups attached in *ortho*-positions. The ester group in this compound was also found to be very resistant to hydrolysis by boiling aqueous alkali.

The more reactive monomer 3,5-di-*t*-butyl-4-hydroxybenzoyl chloride was therefore synthesized, found to be stable at room temperature under dry conditions, and used for the melt-polymerization. The degree of polymerization was found to be greatly affected by the reaction temperature (*Figure 6*). For temperatures between 242 and 282°C the products were of very low viscosity ($\eta_{inh}\approx 0.1\ dl\ g^{-1}$ or less, measured in chloroform), exhibited softening and flow, and were non-crystalline, based on d.s.c. T.g.a. revealed a 5% weight loss at temperatures less than 360°C, which is attributed to the loss of oligomers. On the other hand, polymers prepared at temperatures between 305 and 350°C ($\eta_{inh}=0.21$–$0.54\ dl\ g^{-1}$) did not soften or melt before decomposing, as revealed by hot-stage microscopy and t.m.a. They were semicrystalline (WAXS) and 5% weight loss did not occur until approximately 415°C.

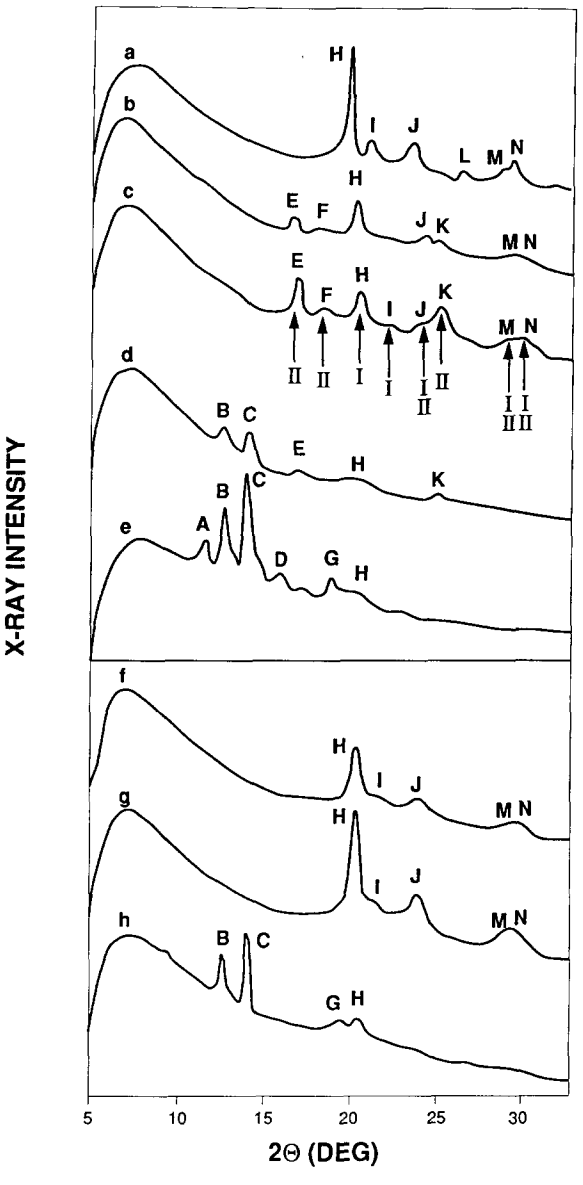


Figure 7 X-ray diffractograms for the di-*t*-butyl-substituted series. As-made: (a) $[s]=0$, (b) $[s]=40$, (c) $[s]=50$, (d) $[s]=60$ and (e) $[s]=100$. Heat treated: (f) $[s]=40$, (g) $[s]=50$ and (h) $[s]=60$

*F*Ti.r. analysis of these polymers showed that the lowest molecular weight material (synthesis temperature 242°C) possessed a peak at 1800 cm^{-1}, which was not present in the spectra of the higher-molecular-weight polymers. This peak was assigned to anhydride formed from the residual acid chloride end groups during polymer work-up.

X-ray analysis of polymer synthesized at 305°C ($\eta_{inh}=0.21$ dl g^{-1}) showed it to be semicrystalline, but to possess a different crystal structure from that of unsubstituted POB or monosubstituted POB (*Figure 7*, *Table 3*, for $[s]=100$). The dominant peaks were at 2θ positions corresponding to larger *d*-spacings than those present in POB or poly(3-*t*-butyl-4-oxybenzoate), as expected for such bulky substituents.

Although the polymers synthesized above 305°C were infusible, they could easily be dissolved in chloroform at room temperature, so there is a possibility of solution-processing this polymer. The enhanced solubility could result from the more loosely packed chain structure (shown by WAXS) together with the shielding of the polar ester groups by the aliphatic *t*-butyl groups. The infusibility may be due to the rigidity of the polymer chain accentuated by steric hindrance due to the two *t*-butyl groups.

Other bulky substituents such as phenylalkyl[18–20] and biphenyl[21] have also been reported to improve the solubility of aromatic polyesters, although in these cases the melting temperatures have also been reduced enough to make them melt-processable.

*Poly(3,5-di-*t*-butyl-4-oxybenzoate-*co*-4-oxybenzoate)s*

Copolymers of this type cannot be made by melt-polymerization of the pure acid chlorides as for the disubstituted homopolymer because 4-hydroxybenzoyl chloride is unstable at room temperature. These polymers can be made by forming the acid chloride *in situ* in a solution polymerization[12]. This method was applied to the synthesis of poly(3,5-di-*t*-butyl-4-oxybenzoate) and found to give only a low molecular weight ($\eta_{inh}=$ 0.08 dl g^{-1}). Nevertheless, it was applied to the formation of copolymers and slightly higher molecular weights were

Table 3 Interplanar spacings (nm) for the di-*t*-butyl-substituted copolymers

		[*s*]				
Peak[a]	*hkl*[b]	0	40	50	60	100
A						0.762(m)
B					0.696(m)	0.698(s)
C					0.628(m)	0.634(vs)
D						0.561(w)
E			0.532(w)	0.528(m)	0.530(w)	
F			0.491(w)	0.493(w)		
G						0.473(m)
H	110	0.441(vs)	0.438(w)	0.434(m)	[c]	
I	111	0.417(w)		[c]		
J	200	0.374(m)	0.367(vw)	0.367(vw)		
K			0.357(vw)	0.353(m)	0.355(vw)	
L	013	0.334(vw)				
M	004	0.307(vw)	0.310(vw)	0.308(vw)		
N	211	0.300(m)	0.302(vw)	0.300(vw)		

[a] Peaks as labelled in *Figure 7*
[b] Reflection for poly(4-oxybenzoate), $[s]=0$
[c] Peak present but too weak to be fitted
Peak intensities: vs = very strong, s = strong, m = medium, w = weak, vw = very weak

Table 4 Inherent viscosity and t.g.a. results for disubstituted copolymers made with the acid chloride *in situ*

$[s]^a$	$\eta_{inh}{}^b$ (dl g^{-1})	$T_{5\%}{}^c$ (°C)	$T_{max}{}^d$ (°C)
40	0.19	300	473
50	0.16	287	499
60	0.20	336	479
100	0.08	359	486

[a] Molar percentage of disubstituted units
[b] Inherent viscosity determined in trifluoroacetic acid/dichloromethane
[c] Temperature of 5% weight loss (t.g.a.)
[d] Temperature of maximum rate of weight loss (t.g.a.)

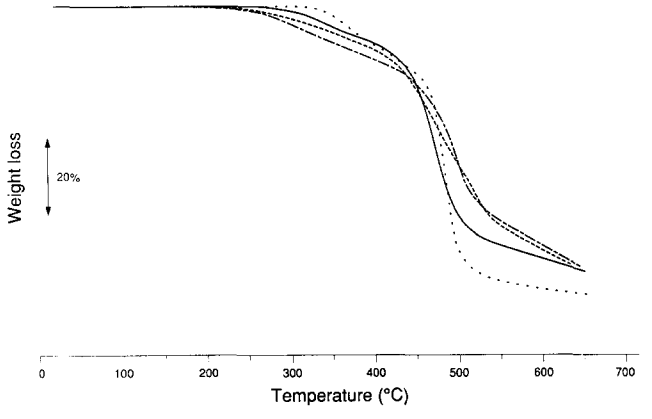


Figure 8 T.g.a. curves for the di-*t*-butyl-substituted series. ····, $[s]=40$; —·—·—, $[s]=50$; ———, $[s]=60$; - - - -, $[s]=100$

obtained for copolymers with $[s]=40$, 50 and 60 (*Table 4*). The copolymers, like the homopolymer $[s]=100$, were all readily soluble in chloroform.

T.g.a. revealed a gradual weight loss (up to about 20%) followed by rapid decomposition for all these polymers (*Figure 8*, *Table 4*). The initial weight loss can be attributed to post-polycondensation. Hot-stage polarizing microscopy showed no evidence of flow below decomposition for any of these polymers, even under shear.

X-ray analysis of the as-made copolymers showed $[s]=40$ and 50 to exhibit a crystal structure which may be assigned to a mixture of phases I and II of POB (*Figure 7*, *Table 3*). Copolymer $[s]=60$ was found to possess the same structure as the disubstituted homopolymer, $[s]=100$, with a hint of the phase II structure found in $[s]=40$ and 50.

Heat-treating these copolymers at temperatures between 250 and 270°C (i.e. in the region of a d.s.c. exotherm) overnight in capillary tubes immersed in an oil bath resulted in the following crystal structure modifications. The structures of $[s]=40$ and 50 were transformed from a mixture of phase I and II into phase I only. Heat-treatment of $[s]=60$ caused loss of peaks characteristic of $[s]=50$ and improved the crystal structure corresponding to $[s]=100$.

Comparison with t-butyl-substituted poly(phenylene terephthalate)

Work of a similar nature was carried out[11] to investigate the effect of mono-*t*-butyl substitution on PPT. It was found that crystallinity was maintained throughout the copolymer series, with copolymers having approximately equimolar ratios of substituted and unsubstituted phenylene terephthalate units, $[s]=50$ and 60, possessing two crystal structures — that of PPT and that of poly(*t*-butyl-1,4-phenylene terephthalate). This is in contrast with the present work, where essentially no crystalline order is present in the middle of the composition range for copolymers poly(3-*t*-butyl-4-oxybenzoate-*co*-4-oxybenzoate).

This can be understood if the consitution of the polymer chains is considered. The repeating unit of PPT possesses two benzene rings, only one of which bears a *t*-butyl substituent in the substituted polymer. The repeating unit of POB possesses only one benzene ring, hence poly(3-*t*-butyl-4-oxybenzoate) has every ring substituted. Thus the equimolar random copolymer poly(*t*-butyl-1,4-phenylene terephthalate-*co*-1,4-phenylene terephthalate) will possess longer sequences of the substituted and unsubstituted structures than present in the equimolar random copolymer poly(3-*t*-butyl-4-oxybenzoate-*co*-4-oxybenzoate), thus making it possible for crystals to be formed.

CONCLUSIONS

Two series of novel *t*-butyl-substituted copolyesters, poly(3-*t*-butyl-4-oxybenzoate-*co*-4-oxybenzoate)s and poly(3,5-di-*t*-butyl-4-oxybenzoate-*co*-4-oxybenzoate)s, were synthesized and characterized. Both homopolymers, poly(3-*t*-butyl-4-oxybenzoate) and poly(3,5-di-*t*-butyl-4-oxybenzoate), possessed different crystal structures from that of POB with the disubstituted polymer having interplanar spacings considerably larger than those for POB. Neither substituted homopolymer melted before it decomposed. In the monosubstituted series of copolymers only the 50:50 composition melted to a nematic mesophase far enough below decomposition for melt spinning and injection moulding to be possible. None of the disubstituted copolymers melted below decomposition but they all dissolved easily in chloroform and are therefore potentially processable from solution.

ACKNOWLEDGEMENT

Z.G.L. thanks the British Council and the Chinese government for financial support.

REFERENCES

1 Dobb, M. G. and McIntyre, J. E. in 'Advances in Polymer Science', Vol. 60/61, Springer-Verlag, Berling, 1984, pp. 61–98
2 Calundann, G. W. and Jaffe, M. Proceedings of the Robert A. Welch Foundation Conference on Chemical Research XXVI, Houston, TX, 15–17 November 1982, pp. 247–287
3 Jackson, W. J. Jr. *Mol. Cryst. Liq. Cryst.* 1989, **169**, 23
4 Griffin, B. P. and Cox, M. K. *Br. Polym. J.* 1980, **12**, 147
5 Brown, P. J., Karacan, I., Liu, J., McIntyre, J. E., Milburn, A. H. and Tomka, J. G. *Polym. Int.* 1991, **24**, 23
6 MacDonald, W. A. in 'High Value Polymers' (Ed. A. H. Fawcett), The Royal Society of Chemistry, Cambridge, 1991, p. 428
7 Schwarz, G. and Kricheldorf, H. R. *Macromolecules* 1990, **23**, 1568

8 Kricheldorf, H. R. and Schwarz, G. *Polymer* 1984, **25**, 520
9 Lenz, R. W. and Feichtinger, K. A. Papers presented at the Joint ACS/JCS Honolulu Meeting, April 1979, Vol. 20, No. 1, p. 114
10 Stern, R., Ballauf, M. and Wegner, G. *Makromol. Chem., Makromol. Symp.* 1989, **23**, 373
11 Li, Z. G., McIntyre, J. E., Tomka, J. G. and Voice, A. M. *Polymer* in press
12 Imai, Y., Aoyama, S., Nguyen, T.-Q. and Ueda, M. *Makromol. Chem., Rapid Commun.* 1980, **1**, 655
13 Jin, J. I., Lee, S. H., Park, H. J. and Kim, I. J. *Polym. J. (Japan)* 1989, **21**, 615
14 Joseph, E. G., Wilkes, G. L. and Baird, D. G. *Polym. Eng. Sic.* 1985, **25**, 377
15 Gilkey, R. and Caldwell, J. R. *J. Appl. Polym. Sci.* 1959, **2**(5), 198
16 Lieser, G. *J. Polym. Sci., Polym. Phys. Edn* 1983, **21**, 1611
17 Kricheldorf, H. R. and Schwarz, G. *Polymer* 1990, **31**, 481
18 Brugging, W., Kampschulte, U., Schmidt, H. W. and Heitz, W. *Makromol. Chem.* 1988, **189**, 2755
19 Heitz, W. and Niessner, N. *Makromol. Chem.* 1990, **191**, 225
20 Vogel, W. and Heitz, W. *Makromol. Chem.* 1990, **191**, 829
21 Hatke, W. and Schmidt, H. W. *Am. Chem. Soc. Polym. Prepr.* 1991, **32** (1), 214