Thermotropic polyesters: synthesis and properties of t-butyl substituted poly(1,4-phenylene terephthalate)s

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Copolyesters of poly(1,4-phenylene terephthalate) and poly(t-butyl-1,4-phenylene terephthalate) are synthesized by melt polycondensation using an acetolysis route. The products are characterized by solution viscometry, wide-angle X-ray scattering, hot-stage polarizing microscopy and thermal analysis (d.s.c., t.g.a. and t.m.a.). The copolymers are semicrystalline throughout the range, exhibit a minimum melting temperature at approximately equimolar proportions of the two components, and are melt-processable in the middle of the range.

(Keywords: liquid crystalline; thermotropic; copolyester)

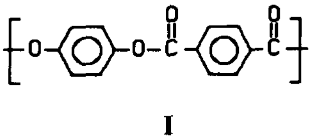
INTRODUCTION

Rigid-rod homopolyesters such as poly(4-oxybenzoate) (POB) and poly(1,4-phenylene terephthalate) (PPT) are highly crystalline, insoluble in all solvents other than a few very strong acids that appear to cause dissociation, and unsuitable for melt processing because they do not melt below their decomposition temperatures. POB has been reported$^{1-3}$ to melt at various temperatures from 445 to 610°C, and PPT at a temperature of 600°C, measured by d.s.c. at a heating rate of 80°C min^{-1} to minimize degradation[3]. Melt-processable thermotropic rigid-rod polyesters are generally obtained by disrupting the structure through copolymerization so as to reduce the crystal–mesophase transition to a temperature below that of decomposition. Such products can then be processed in fluid yet ordered states.

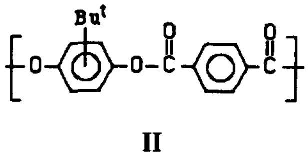
If oriented structures could be produced from the intractable homopolymers, their intractability should give the products superior chemical and thermal stability to those made from the copolymers, and their higher crystallinity should lead to superior mechanical properties. One possible approach to the production of such oriented structures is to form a polyester based upon the intractable homopolymer substituted by groups that can, in principle, be chemically eliminated after formation of the oriented structure. Groups that might be so eliminated include t-alkyl groups such as t-butyl, which can be removed from many aromatic rings by reverse Friedel–Crafts reactions using strong Lewis acid catalysts[4].

The polyester derived from t-butylhydroquinone (TBHQ) diacetate and terephthalic acid (TA), which contains appropriate chemical groups, was described by Jackson[5], who reported that it solidified during preparation at about 350°C and that it melted at too high a temperature, 444°C, to be melt-spun or injection moulded without thermally degrading. Jackson and Kuhfuss[6] also noted that copolyesters of TA, TBHQ, and phenylhydroquinone (PhHQ) had higher melting temperatures than those prepared from the same components but using chloro- or methyl-hydroquinone in place of TBHQ. Copolyesters of TA, TBHQ, and *p*-hydroxybenzoic acid (*p*-HBA) were disclosed by the same author[5]. The lowest melting temperature for those polymers was about 360°C when containing approximately 25 mol% *p*-HBA, based on the total moles of polymer. Connolly[7] added 4,4′-biphenol (BP) to the same copolymer to decrease the melting temperature further. As a result, a melting temperature of 332°C was obtained from the copolyester TA/TBHQ/BP/*p*-HBA (33.3/30.1/3.3/33.3 mol%).

This paper describes the synthesis and properties of copolyesters consisting of unsubstituted units (**I**) and substituted units (**II**).



I



II

The composition of these materials is expressed in terms of mol%, [*s*] of substituted units (**II**). Such copolymers may be suitable for chemical conversion by dealkylation into infusible PPT.

EXPERIMENTAL

Monomers

Terephthalic acid (TA) (Aldrich) was used as received. Hydroquinone diacetate (HQdiAc) (m.p. 123°C, lit.[8] 123–124°C) and t-butylhydroquinone

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diacetate (TBHQdiAc) (m.p. 67°C) were prepared from hydroquinone (HQ) and t-butylhydroquinone (TBHQ), respectively, by reacting with excess acetic anhydride using concentrated sulfuric acid as catalyst.

Polymer synthesis

The polyesters, $[s] = 0$ to 100, were made by melt transesterification without added catalyst using a procedure described previously[9]. The monomer mixture (about 2 g) was heated at 305°C for 2 h with passage of nitrogen and for 1 h further in vacuum (less than 0.2 mmHg). At the beginning of the heating, HQdiAc and TBHQdiAc rapidly melted, but the TA did not completely dissolve at this stage. As the polymerization progressed, the reaction mixture became homogeneous with an increase in viscosity, forming a turbid melt, and shear-induced opalescence was observed. This was noted to occur for all proportions of TBHQdiAc and was attributed to the liquid crystal nature of the intermediate materials produced. The reaction melt solidified within 50 min. The higher the proportion of HQdiAc the earlier solidification occurred, presumably due to easier crystallization of the polymers formed. The as-made polymers were ground, washed with acetone and water successively, and dried under reduced pressure at 120°C overnight.

Polymer characterization

Solution viscosities were determined at 25°C in a mixed solvent of *p*-chlorophenol (PCP) and 1,1,2,2-tetrachloroethane (TCE) (1:1 by volume) at a concentration of $0.1\ \mathrm{g\ dl^{-1}}$.

Infra-red and n.m.r. spectra were used to check the t-butyl content of the copolymers. Details are given elsewhere[10].

Optical observations were made on an Olympus polarizing microscope (Model BH-2) equipped with a Stanton–Redcroft hot-stage (type TH 600) at a heating rate of $20^{\circ}\mathrm{C\ min^{-1}}$. Each polymer powder sample was heated in nitrogen under a load of 0.03 N (about 3.0 g), as described previously[11]. Transition temperatures and enthalpies were measured with a DuPont 910 differential scanning calorimeter controlled by DuPont Thermal Analyst 2000 operating software (version 8), using 5–10 mg of polymer and a heating rate of $20^{\circ}\mathrm{C\ min^{-1}}$. The transition temperature was taken at the peak position. Thermogravimetric analysis (t.g.a.) was carried out on a DuPont 951 thermogravimetric analyser controlled by DuPont Thermal Analyst 2000 operating software (version 8) at a heating rate of $10^{\circ}\mathrm{C\ min^{-1}}$ under nitrogen. Thermomechanical analysis (t.m.a.) (penetration mode) was performed on a Mettler TA 3000 system equipped with a Mettler TMA 40 measuring cell and a Mettler TC 10 TA processor. The polymer powder (5–8 mg) was contained in an aluminium pan loosely covered by a lid, and was heated at a rate of $20^{\circ}\mathrm{C\ min^{-1}}$ under nitrogen ($100\ \mathrm{ml\ min^{-1}}$). A constant load of 0.04 N (about 4 g) was applied throughout the heating. The softening temperature was taken at the intersection point of the baseline before the transition and the tangent drawn along the signal curve through the maximum signal change point which corresponds to the peak position of the derivative curve.

Qualitative X-ray diffraction patterns were obtained for the as-made powdered polymer samples by use of a flat-plate camera. The powders were mounted in capillary tubes of 1 mm diameter. Quantitative wide-angle X-ray diffraction analysis was carried out on a Spectrolab Series 3000 diffractometer with Inel XRG-3000 X-ray generator and Inel CPS-120 curved position-sensitive detector. The maximum resolution of the detector allowed data points to be taken at 0.03° intervals. Slit collimated CuKα radiation of wavelength 0.15406 nm was generated by voltage and current settings of 40 kV and 16 mA respectively, and by use of a nickel filter and monochromator. The capillary tubes containing the powdered samples, together with silver foil used for calibration, were positioned at the centre of curvature of the detector and the diffraction patterns were obtained at room temperature. A microprocessor running Inel software was used to store the data. Each data set was transmitted to an Amdahl 5860 mainframe computer for analysis. Using methods described earlier[12], the positions and integral breadths of resolved peaks were obtained.

RESULTS AND DISCUSSION

All the polymers were solid at the end of the preparation. The values of inherent viscosity determined in PCP/TCE are given in *Table 1*. With the exception of the unsubstituted homopolymer, $[s] = 0$, the values indicate that the molecular weights of these materials are sufficient to warrant evaluation of the effect of substitution on their properties. The low viscosity of the unsubstituted homopolymer was probably due to early solidification during the polymerization, which limited further increase of molecular weight. Although the solubility of these materials has not been investigated systematically, it is worth noting that only copolymers with $[s] \geqslant 60$ mol% were soluble in a mixture of trifluoroacetic acid and dichloromethane (30/70, v/v). This indicates that the presence of t-butyl groups increases the polymer solubility, in agreement with other studies concerned with PPTs modified by bulky substitutents[13–15].

X-ray diffraction patterns

Figure 1 shows the diffractograms for the copolymers with $[s] = 0$, 40, 60 and 100. *Table 2* documents the interplanar spacings, integral breadths and relative intensities of the peaks found for all copolymers studied in this work. A study of these diffraction patterns led to the following conclusions. (i) The peak positions of the unsubstituted PPT, $[s] = 0$, are in agreement with those

Table 1 Effect of concentration of substituted units, $[s]$, on polymer properties[a]

$[s]$ (mol%)	η_{inh} ($\mathrm{dl\ g^{-1}}$)	T_s (°C)	T_f (°C)	T_d (°C)	$T_{2\%}$ (°C)	$T_{5\%}$ (°C)	T_r (°C)
0	0.18	389	[b]	490	385	430	580
10	0.44	390	[b]	500	400	440	569
20	0.36	380	[b]	490	395	430	565
40	0.54	352	[b]	470	390	410	503
50	0.85	356	355	480	385	410	497
60	1.14	360	370	490	390	435	514
80	1.32	404	445	460	395	440	500
100	1.16	431	470	470	405	435	500

[a] T_s, softening temperature determined by t.m.a.; T_f, onset flow temperature observed by optical microscopy; T_d, decomposition temperature observed by optical microscopy; $T_{2\%}$, $T_{5\%}$, temperature of 2% and 5% weight loss determined by t.g.a.; T_r, temperature at fastest rate of weight loss determined by t.g.a.

[b] No flow observed

Table 2 Interplanar spacings (nm), relative intensities[a] and integral breadths (degrees, values given in parentheses) of X-ray reflections

	[*s*] (mol%)							
Peak[b]	0	10	20	40	50	60	80	100
A					1.075w	1.084m	1.080s	1.122s
					(0.15)	(0.59)	(0.24)	(0.50)
B					0.557vw	0.559w	0.554m	0.579m
					(0.92)	(0.65)	(0.55)	(0.40)
C					0.503vw	0.509w	0.503m	0.503m
					(0.74)	(0.63)	(0.93)	(0.43)
D	0.486w	0.486w	0.490w	0.483w	0.477w	0.484w	0.481m	0.487m
	(1.16)	(1.04)	(1.11)	(1.04)	(1.31)	(0.71)	(0.76)	(0.41)
E	0.437vs	0.437vs	0.437vs	0.436vs	0.435vs	0.439s	0.443m	0.439m
	(0.29)	(0.36)	(0.35)	(0.49)	(0.22)	(0.77)	(1.56)	(0.81)
F					0.430m	0.412s	0.405m	0.408m
					(2.19)	(2.66)	(2.20)	(1.70)
G	0.390m	0.388m	0.387m	0.386m	0.384m	0.379m	0.377m	0.385m
	(1.04)	(1.17)	(1.16)	(1.65)	(1.65)	(0.96)	(0.72)	(0.73)
H	0.316m	0.315m	0.314m	0.314m	0.313m	0.315w		
	(0.75)	(0.99)	(1.19)	(0.93)	(1.02)	(0.81)		
I	0.297m	0.297m	0.296w	0.295w	0.296w	[c]		
	(0.87)	(0.86)	(0.87)	(0.81)	(0.98)			
J	0.269w	0.269w						
	(0.78)	(1.67)						

[a] vs, very strong; s, strong; m, medium; w, weak; vw, very weak
[b] See *Figure 1*
[c] Present, but too weak to be resolved

found by Coulter *et al.*[16]. Their analysis, involving molecular modelling, determined the unit cell to be monoclinic with lattice parameters of $a = 0.798$ nm, $b = 0.533$ nm and $c = 1.264$ nm, and with $\beta = 98.98°$. (ii) The peak positions of the polymer with [*s*] = 100 revealed that this composition has different interplanar spacings and hence a different crystal structure to that of the polymer [*s*] = 0, thus showing that t-butyl substitution does significantly affect the crystal structure of PPT. (iii) Copolymers with [*s*] = 10, 20 and 40 produced diffractograms with peak positions characteristic of PPT, revealing that a small amount of t-butyl substitution does not substantially disrupt the crystal structure of PPT. (iv) The diffractogram of the copolymer with [*s*] = 80 exhibited peaks in the same positions as those for the polymer with [*s*] = 100, indicating that t-butyl substitution of 80% and higher yields the crystal structure of the fully substituted polymer. (v) The copolymer with [*s*] = 60, and to a lesser degree that with [*s*] = 50, exhibited peaks characteristic of both homopolymer crystal structures (i.e. [*s*] = 0 and [*s*] = 100) and were therefore considered to contain regions of each crystal structure. (vi) A study of the relative peak intensities in the diffraction pattern of each copolymer revealed a gradual loss of crystal structure characteristic of PPT and a gradual increase of crystal structure characteristic of homopolymer of unit **II** with increasing t-butyl substitution.

No highly oriented fibres were made, and the small number of reflections from the powders made a simple structure determination impossible.

Cheng *et al.*[17] studied the copolymer TA/PhHQ/PEHQ with molar ratio 50/25/25 (where PhHQ is phenyl-

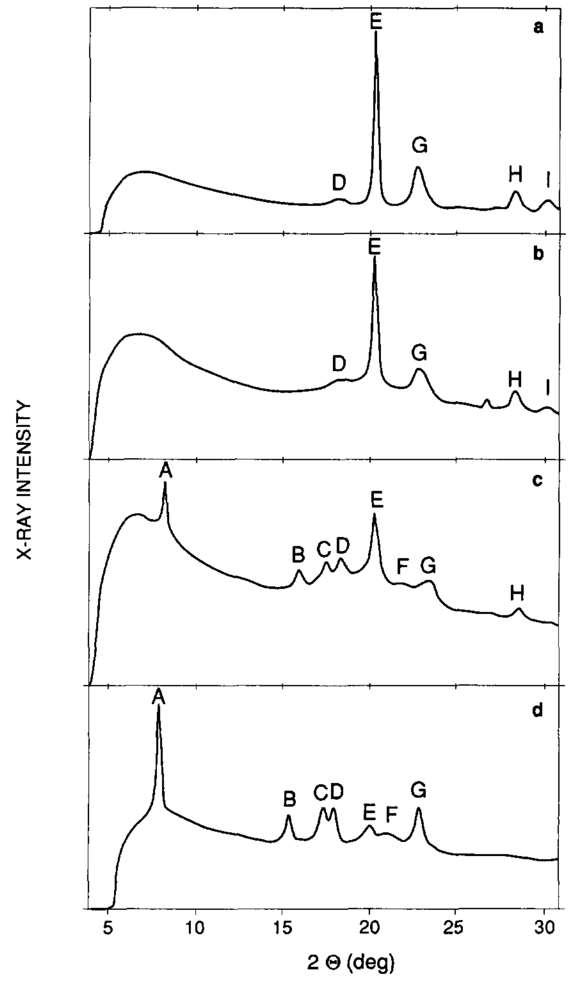

Figure 1 X-ray diffraction patterns of (a) [*s*] = 0, poly(1,4-phenylene terephthalate); (b) [*s*] = 40; (c) [*s*] = 60; (d) [*s*] = 100, poly(t-butyl-1,4-phenylene terephthalate). For labelling of peaks see *Table 2*

hydroquinone and PEHQ is (1-phenylethyl)hydroquinone), which is similar to those studied here although the phenyl and phenylethyl substituents are larger than the t-butyl group. They analysed the diffraction pattern of fibres from this copolymer and indexed the unit cell as monoclinic with $a = 1.330$ nm, $b = 0.9719$ nm, $c = 1.235$ nm and $\gamma = 78.0°$. This diffraction pattern exhibited a very strong reflection at 1.301 nm which was indexed as 1 0 0. Comparing Cheng's work with the work on t-butyl substitution reported here, allowed tentative assignment of the strong peak labelled A ($d = 1.08$ nm, see *Table 2*) as the 1 0 0 reflection, bearing in mind that the t-butyl group is smaller than the phenyl substituent used by Cheng. This assignment would result in the unit cell of the homopolymer of unit **II** having an a dimension of 1.08 nm.

Thermal transitions

Thermal transitions were investigated by hot-stage light microscopy, t.m.a. and d.s.c. and the results are summarized in *Tables 1* and *3*. A graphical summary of the microscopy results is given in *Figure 2*.

Hot-stage microscopy showed that, in spite of its low molecular weight, the unsubstituted homopolymer, $[s] = 0$, did not melt below the decomposition, manifested in discoloration, which took place around 490°C. This is in agreement with the literature[3]. The d.s.c. curve of this material showed a small broad endotherm between 300 and 420°C, whilst t.m.a. detected a softening point at 389°C. It is plausible that these effects are due to the changes of the monoclinic crystalline structure detected by Coulter *et al.*[16] by means of high-temperature X-ray diffraction. It is worth noting that the transformation of the orthorhombic crystalline structure of POB into the pseudohexagonal structure[18] also resulted in softening.

Table 3 Endotherms in as-made t-butyl-substituted PPT polymers

$[s]$ (mol%)	Range (°C)	Peak(s) (°C)	ΔH (J g^{-1})	Comment
0	300–460	382	26	[a]
10	368–458	412	23	[a]
20	345–450	405	26	[a]
40	326–405	378	21	[b]
50	335–397	370	17	[b]
60	325–391	375	19	[b]
80	369–437	405 428	28	[c]
100	384–454	411 446	33	[c]

[a] Solid–solid transition
[b] Crystal–nematic transition
[c] Double endotherm (see text)

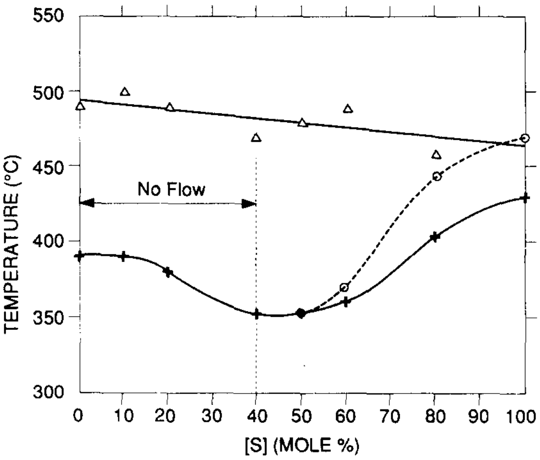

Figure 2 Effect of composition, $[s]$, on thermal properties: +, softening temperature, T_s; ○, flow temperature, T_f; △, decomposition temperature, T_d

Heating of the other homopolymer, poly(t-butyl-1,4-phenylene terephthalate), $[s] = 100$, resulted in the formation of a nematic mesophase, but the onset of flow at $T_f = 470°C$ coincided with decomposition. The softening, detected by t.m.a., took place at 431°C. The d.s.c. curve revealed a double endotherm with peak temperatures of 407°C and 441°C. The upper endotherm is ascribed to melting; its peak temperature is in good agreement with the values in the literature[5,19]. A similar double endotherm has also been observed in other nematogenic polymers[20–23], but the origin of the lower one is not yet adequately explained. Regardless of details, it is obvious that this polymer is not melt processable due to the absence of a temperature interval between the melting and decomposition temperatures (*Figure 2*).

The copolymers with $[s] = 10$, 20 and 40 exhibited similar phase transitions to those of the homopolymer with $[s] = 0$. No flow was seen with these copolymers and hence they were assumed not to be melt processable. Softening occurred, as revealed by t.m.a., at temperatures between 350°C and 390°C (*Table 1*); for the copolymer with $[s] = 40$, shear-induced birefringence was detected by hot-stage light microscopy from about 390°C. Decomposition for these copolymers was not observed on a hot-stage until about 490°C, a value similar to that for the whole series (*Figure 2*). As in the case of the homopolymer with $[s] = 0$, the d.s.c. traces from these copolymers showed only one broad indistinct endotherm (*Table 3*). This endotherm is again attributed to the monoclinic to orthorhombic transition of the PPT structure, whose X-ray diffraction peaks have been shown to be present in these copolymers (*Figure 1*).

The copolymer with $[s] = 80$ exhibited thermal transitions similar to those of the homopolymer with $[s] = 100$, albeit at lower temperatures. This is consistent with the X-ray data which revealed this copolymer to possess the crystal structure characteristic of this fully substituted homopolymer. The d.s.c. trace of copolymer with $[s] = 80$ showed a double endotherm with peak temperatures of 402°C and 427°C. The higher temperature endotherm was assigned to a crystal–nematic transition as revealed by hot-stage microscopy. This copolymer softened at 404°C with the onset of flow at 445°C. Hot-stage microscopy revealed the decomposition temperature to be 460°C, which is greater than the flow temperature, but the window between these two temperatures is not sufficient for melt processing.

Copolymers in the middle of the composition range, $[s] = 50$ and 60, exhibited slightly different thermal behaviour from that of either homopolymer. D.s.c. revealed both of these copolymers to possess only one endotherm (*Figure 3*) at peak temperatures of 369°C and 375°C, respectively. Hot-stage microscopy allowed this transition to be assigned to the formation of a nematic mesophase which lasted until decomposition at 480°C and 490°C, respectively. The onset of softening and flow at temperatures less than 370°C results in both these copolymers being melt-processable from a nematic mesophase (*Figure 2*).

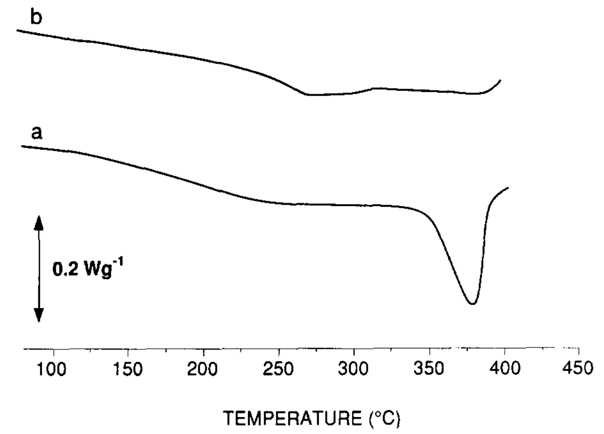

Figure 3 D.s.c. curves (20°C min^{-1}) for copolymer with $[s] = 60$: (a) as-made; (b) quenched from within nematic phase at 405°C

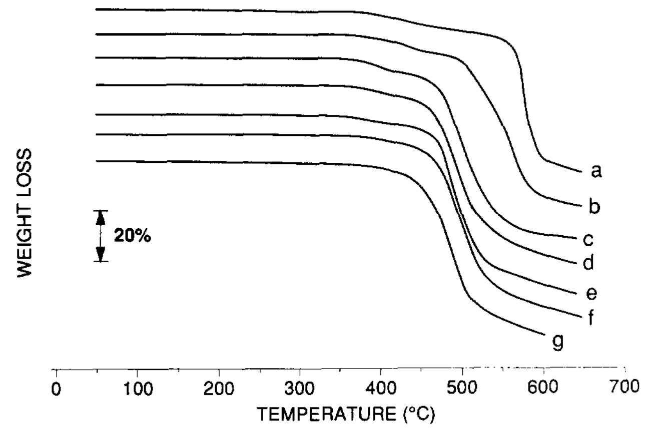

Figure 4 T.g.a. curves (10°C min^{-1}): (a) $[s] = 0$, poly(1,4-phenylene terephthalate); (b) $[s] = 20$; (c) $[s] = 40$; (d) $[s] = 50$; (e) $[s] = 60$; (f) $[s] = 80$; (g) $[s] = 100$, poly(t-butyl-1,4-phenylene terephthalate)

A spinning test showed that the copolymer with $[s] = 50$, made on a larger scale with a sand bath, could be melt extruded at about 390°C. Although the tensile strength and modulus of the as-spun fibre were not as good as expected, this indicated that this copolymer is melt-spinnable.

In an attempt to determine their structure in more detail, the copolymers with $[s] = 50$ and 60 were quenched from temperatures within the nematic region, and d.s.c. traces of their re-heats were recorded. This resulted in the melting endotherms being essentially absent (*Figure 3*). X-ray diffractograms of the quenched copolymer with $[s] = 60$ revealed that the quenching process had removed almost all the three-dimensional order.

None of the polymers showed evidence in the d.s.c. curve of a glass transition either before or after quenching. This is consistent with the results obtained for disubstituted PPT polymers by Heitz and Niessner[14].

Decomposition

The temperatures of 2% and 5% weight loss obtained from t.g.a. are lower than the temperatures of onset of decomposition observed by hot-stage microscopy. This difference may be due to early weight loss caused by further polymerization or loss of low-molecular-weight species. Indeed, a small step, which may correspond to further polymerization, is seen in the t.g.a. curves for $[s] = 0$, 20 and 40 at temperatures just above 400°C (see *Figure 4*).

The onset of major decomposition and the fastest rate of weight loss (T_r) both occur at substantially lower temperatures the higher the t-butyl content. Nevertheless, there is no sign for any of the polymers containing the t-butyl substitution of an initial stage in the t.g.a. curve corresponding to loss of t-butyl groups. For $[s] = 100$, loss of the t-butyl groups would correspond to a weight loss of 19.3%. Isothermal treatment of $[s] = 50$ at 330°C for 4 h also showed no sign of preferential loss of the t-butyl groups.

CONCLUSIONS

A series of novel copolyesters containing t-butyl substituents has been prepared from TA, HQdiAc and TBHQdiAc by melt polycondensation. Only copolymers with a mol% of substituted units **II**, $[s] \geqslant 50$ melted, the melt being nematic in nature. The lowest melt temperature was achieved for $[s] = 50$. Copolymers with $[s] \geqslant 80$ had no temperature window between melting and decomposition, leaving $[s] = 50$ and 60 as the only copolymers that were melt-processable from a nematic phase.

The initial objective, to preferentially remove the t-butyl groups from the structure, was found to be impossible by thermal treatment alone and thus it is necessary to find a catalytic method in order to encourage this removal[10,24].

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