Aromatic and heteroaromatic polyesters: 1. The 1,3,4-oxadiazole unit as an angular spacer in polyesters based on phenylene and naphthylene groups*

Donald L. Brydon† and Ian S. Fisher
Department of Technology, Scottish College of Textiles, Netherdale, Galashiels TD1 3HF, UK

John Emans and David M. Smith†
Department of Chemistry, University of St Andrews, Purdie Building, St Andrews, Fife KY16 9ST, UK

and William A. MacDonald
I.C.I. Wilton Materials Research Centre, PO Box 90, Wilton, Middlesbrough, Cleveland TS6 8JE, UK

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Polyesters synthesized (by a melt-phase transesterification route) from terephthalic acid, hydroquinone diacetate, 6-acetoxy-2-naphthoic acid, 2,5-bis(acetoxyaryl)-1,3,4-oxadiazoles and (1,3,4-oxadiazole-2,5-diyl)dibenzoic acids have been studied by differential scanning calorimetry, hot-stage polarized light microscopy and thermal gravimetric analysis. Their fibre-forming properties have also been explored. Many of these polyesters have high thermal stability (>400°C), a liquid-crystalline melt phase and a light colour. Some also yield strong, stiff fibres.

(Keywords: aromatic polyesters; 1,3,4-oxadiazole; 6-acetoxy-2-naphthoic acid; terephthalic acid; liquid crystal; fibre)

INTRODUCTION

Thermotropic polymers, which owe their thermotropic character to the constitution of their main chain, have been known for some time. The early work in this field has been reviewed by Dobb and McIntyre[2], and it was McIntyre and his colleagues in I.C.I. who were responsible in the 1960s for some of the first studies of this type of polymer[3,4]. The relationship between thermotropic behaviour and main-chain constitution, however, was not set out until some 10 years later[5–7].

Polyesters with an 'all-aromatic' main chain have been extensively investigated, since the aromatic units constitute 'rigid-rod' segments of the chain which might be expected to produce liquid-crystalline characteristics. Both lyotropic and thermotropic systems are highly desirable for the production of fibre of high tenacity and high initial modulus, because high orientation of the liquid-crystalline phase can be achieved by shear at a spinneret. Thermotropic polymers, however, offer processing advantages over lyotropic polymers, in terms of both cost (no solvent is involved) and the range of fabricated items that can be produced.

Much of the work in this area has been directed towards the preparation of a polymer with a liquid-crystalline melt that is formed at a processable temperature (<350°C) and is stable over a broad temperature range. The melting points of the simple homopolyesters **P1**, **P2** and **P3** are much too high (610°C[8], 596°C and 577°C[9], respectively) to permit the formation of stable nematic phases. Modification of these polymers, however, by introducing some disorder into the chain, can bring about a substantial reduction in the melting point: thus, for example, the 50:50 random copolyester of *p*-oxybenzoyl and *p*-phenyleneterephthalate units (**P4**) melts at 510°C[8], and the 60:40 copolyester of *p*-oxybenzoyl and 6-oxy-2-naphthoyl units (**P5**) melts at only 265°C[10]. Dobb and McIntyre[2] draw attention, indeed, to the particular effectiveness of the 2,6-naphthylene unit in lowering the melting point of polyesters to reveal nematic behaviour: this unit is itself mesogenic, but has non-collinear bonds which produce a lateral disruption in the polymer chain.

Units that introduce an angle into the polymer chain (angular disruptors, e.g. *meta*-substituted aromatic rings) are also effective in reducing the melting points, but their usage has hitherto been kept to a minimum, or avoided altogether, since these units are non-mesogenic[11] and are reported to have an adverse effect on the mechanical properties of the resulting polymers[12].

In this paper and the three which follow, we examine the effect of introducing various types of disruption into a standard liquid-crystalline copolyester. The chosen reference ($\mathbf{P_R}$) is constituted from *p*-phenylenedioxy, terephthaloyl and 6-oxy-2-naphthoyl units in the ratio 25:25:50, and has already been described in the patent literature[13]. We first describe the effect on this polymer of introducing a unit containing a 1,3,4-oxadiazole ring system: this serves as an angular disruptor in the polymer chain, the deviation from linearity (*Figure 1* and *Table 1*)

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† To either of whom correspondence should be addressed

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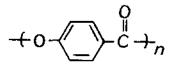
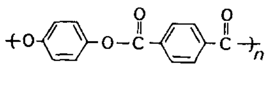
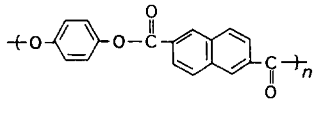


P1



P2



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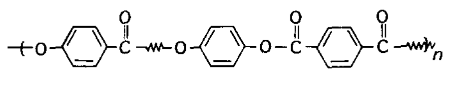
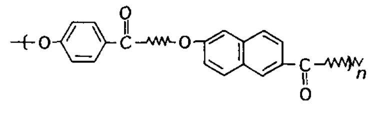
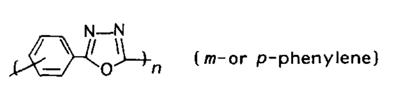


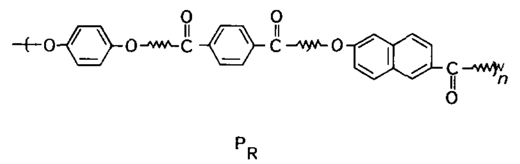
P4



P5



P6



P$_R$

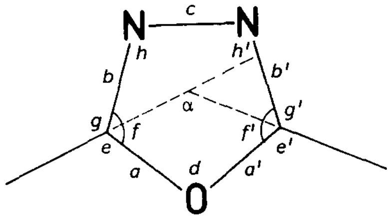


Figure 1 Dimensions of the 1,3,4-oxadiazole-2,5-diyl unit (see also *Table 1*)

being ~47°[14] (cf. the deviation of 60° arising from a *meta*-disubstituted ring).

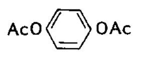
The choice of the 1,3,4-oxadiazole system is significant in several respects.

(i) 2,5-Diaryl-1,3,4-oxadiazoles bearing a wide range of substituents can be readily prepared by cyclization of suitably functionalized 1,2-diaroylhydrazines[15] (cf. Schemes 1 and 2).

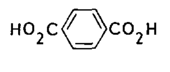
(ii) The oxadiazole ring is relatively resistant to thermal degradation: 2,5-diphenyl-1,3,4-oxadiazole undergoes retro-1,3-dipolar cycloaddition to benzonitrile and (via the Hofmann rearrangement) phenyl isocyanate only by flash vacuum pyrolysis at 775°C[16], and poly(phenylene-1,3,4-oxadiazole) (**P6**) also has excellent thermal stability[17].

(iii) Poly(phenylene-1,3,4-oxadiazoles), in which a proportion of the phenylene groups bear substituents, can be hot-drawn to fibres of high tenacity and high initial modulus[18].

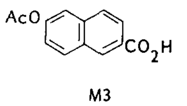
The oxadiazole-containing monomers used in this study are of two types, viz. diacetates (**M4**–**M6** and **M9**) and dicarboxylic acids (**M7** and **M8**), and they have been used in the general polymerization method as total or partial replacement for the standard monomers (**M1**–**M3**) that are used to prepare the reference polyester $\mathbf{P_R}$. Compounds **M4**–**M8** are obtained according to Schemes 1–3, and **M9** by a modification of Scheme 1 (see later).



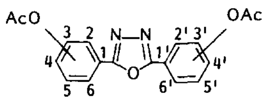
M1



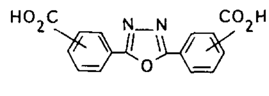
M2



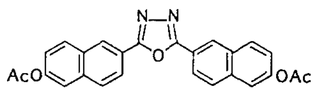
M3



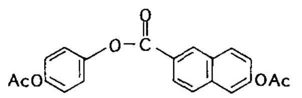
M4: 4,4'-(OAc)$_2$
M5: 3,3'-(OAc)$_2$
M6: 3,4'-(OAc)$_2$



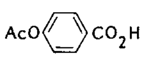
M7: 4,4'-(CO$_2$H)$_2$
M8: 3,3'-(CO$_2$H)$_2$



M9



M10



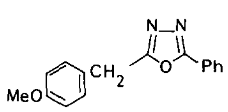
M11

Table 1 Dimensions of the 1,3,4-oxadiazole-2,5-diyl unit (see also *Figure 1*)

(a) Data based on *ab initio* molecular-orbital calculations by Dr C. M. Edge, to whom we express our thanks

Bond lengths (Å)	Interbond angles (deg)
$a, a'=1.36$	$d=102$
$b, b'=1.27$	$e, e'=117$
$c=1.43$	$f, f'=113$
	$g, g'=130$
	$h, h'=106$
	$\alpha=132$

(b) X-ray crystallographic data[14] for



Bond lengths (Å)		Interbond angles (deg)	
$a=1.365$	$a'=1.366$	$d=102.5$	
$b=1.279$	$b'=1.289$	$e=117.6$	$e'=118.7$
$c=1.412$		$f=112.9$	$f'=112.1$
		$g=129.5$	$g'=129.2$
		$h=106.1$	$h'=106.4$
		$\alpha=133.8$	

EXPERIMENTAL

Infra-red spectra are those of Nujol mulls, and ^1H n.m.r. spectra are those of solutions in d_6-dimethyl sulphoxide unless otherwise stated. 'Petroleum' refers to the fraction of b.p. 40–60°C.

PREPARATION OF MONOMERS

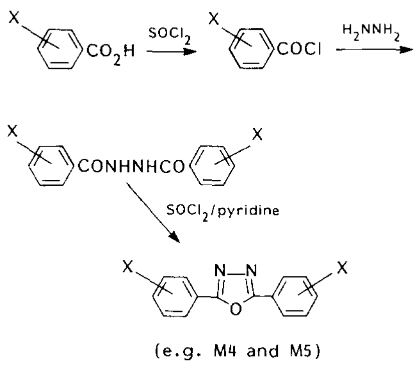
*The standard monomers **M1–M3***

Hydroquinone diacetate (**M1**) was obtained by acetylation of hydroquinone with acetic anhydride in aqueous sodium hydroxide; the diacetate had m.p. 123–124°C (from ethanol; lit.[19] 123–124°C). Terephthalic acid (**M2**) was standard (Aldrich) reagent-grade, and 6-acetoxy-2-naphthoic acid (**M3**) was generously donated by I.C.I.

*The symmetrical diacetates **M4** and **M5** (Scheme 1)*

p-*Acetoxybenzoic acid* (***M11***). *p*-Hydroxybenzoic acid (100 g) and acetic anhydride (300 ml) were heated under reflux for 4 h; the product that crystallized from the cooled solution was recrystallized twice from chloroform. It had m.p. 194°C (lit.[20] 191–192°C); yield, 123.7 g, 95%.

Scheme 1



m-*Acetoxybenzoic acid*, m.p. 128°C (from benzene/petroleum (70:30); lit.[20] 128°C), was similarly obtained (yield 108.3 g, 83%) from *m*-hydroxybenzoic acid (100 g), except that the product did not crystallize directly from the reaction mixture, and was obtained by pouring the latter into water (1 litre).

p-*Acetoxybenzoyl chloride.* This was prepared by heating *p*-acetoxybenzoic acid (100 g) and thionyl chloride (300 ml) under reflux until evolution of SO_2 and HCl ceased (2 h). The excess of thionyl chloride was distilled off, the last portion being co-distilled with benzene, and the resulting white slurry distilled *in vacuo* to separate the acid chloride from poly(*p*-oxybenzoyl). The acid chloride (89.9 g, 83%; b.p. 77°C/0.05 mmHg) crystallized on cooling. It had m.p. 30°C (lit.[21] 30°C).

m-*Acetoxybenzoyl chloride*, b.p. 102°C/1.5 mmHg (lit.[22] 155°C/16 mmHg), was similarly prepared (yield 84%) from *m*-acetoxybenzoic acid (100 g).

1,2-Bis(p-*acetoxybenzoyl*)*hydrazine.* A solution of *p*-acetoxybenzoyl chloride (79.4 g, 0.4 mol) in dioxan (100 ml) was added dropwise, with cooling and vigorous mechanical stirring, to a mixture of hydrazine monohydrate (10.0 g, 0.2 mol) and sodium carbonate (21.2 g, 0.2 mol) in dioxan (50 ml), so that the temperature of the mixture was maintained between 3 and 7°C. When addition was complete, stirring was continued for a further 3 h at this temperature, and 3 h more at room temperature. The mixture was then added to water (1 litre) and the product filtered off, washed (saturated aqueous $NaHCO_3$, then water) and recrystallized from methanol. It had m.p. 245–246°C (lit.[23] 247.5–248.5°C); yield, 40.1 g, 56%.

1,2-Bis(m-*acetoxybenzoyl*)*hydrazine*, m.p. 147–148°C (from methanol; lit.[23] 149.5–150°C), was similarly obtained (yield, 49%).

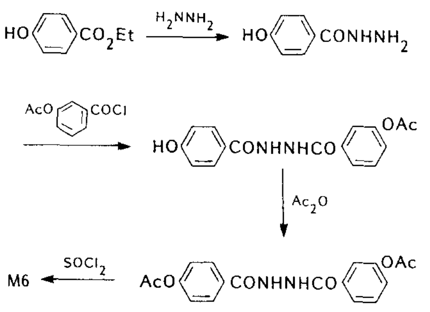
2,5-Bis(p-*acetoxyphenyl*)*-1,3,4-oxadiazole* (***M4***). 1,2-Bis(*p*-acetoxybenzoyl)hydrazine (30 g) was heated under reflux with a mixture of thionyl chloride and pyridine (98:2; 100 ml) for 2 h. The excess of thionyl chloride and pyridine were removed by distillation at reduced pressure and the residue recrystallized (twice) from acetone. Yield, 21.5 g, 75%; m.p. 206°C (lit.[23] 206.5–207°C).

2,5-Bis(m-*acetoxyphenyl*)*-1,3,4-oxadiazole* (***M5***), m.p. 159–160°C (from acetone; lit.[23] 159.5–160.5°C), was similarly obtained (yield, 47%).

*The unsymmetrical diacetate **M6** (Scheme 2)*

p-*Hydroxybenzoylhydrazine.* This was prepared by heating ethyl *p*-hydroxybenzoate (33.2 g, 0.2 mol) with hydrazine hydrate (15 g, 0.3 mol) directly, under reflux, for 2 h. By this stage the mixture was almost totally solid; it was washed with water and the product recrystallized from dimethylformamide. Yield, 26.3 g, 87%; m.p. 257°C (lit.[24] 260°C).

Scheme 2



1-(m-*Acetoxybenzoyl*)*-2-*(p-*hydroxybenzoyl*)*hydrazine.* This was prepared by the dropwise addition of a solution of *m*-acetoxybenzoyl chloride (19.9 g, 0.1 mol) in dioxan (30 ml), at room temperature, to a well-stirred suspension of *p*-hydroxybenzoylhydrazine (15.2 g, 0.1 mol) and sodium carbonate (5.3 g, 0.05 mol) in dioxane (60 ml). Stirring was continued for 4 h, after which the product was collected as for 1,2-bis(*p*-acetoxybenzoyl)hydrazine, above, and recrystallized from dimethylformamide; m.p. 160°C; yield, 16.3 g, 52%. It was converted without further purification into 1-(*m*-acetoxybenzoyl)-2-(*p*-acetoxybenzoyl)hydrazine, m.p. 160°C (from methanol); yield 84%. Found: C, 60.4; H, 4.4; N, 7.8. $C_{18}H_{16}N_2O_6$ requires C, 60.7; H, 4.5; N, 7.9%. ν_{max} (cm^{-1}) 3170 (NH), 1745 (ester CO), 1595 (amide CO), and 1565 (NH bend). δ_H ($(CD_3)_2CO$) 2.38 (6H, s, 2 × Me), 7.50–8.50 (8H, m, Ar–H). *m/z* 356 ($M^{+\cdot}$).

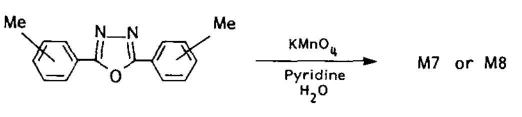
2-(m-*Acetoxyphenyl*)*-5-*(p-*acetoxyphenyl*)*-1,3,4-oxadiazole* (***M6***). This was prepared (yield, 69%) from 1-(*m*-acetoxybenzoyl)-2-(*p*-acetoxybenzoyl)hydrazine and thionyl chloride/pyridine by the method described for

M4, above, and had m.p. 195°C (from acetone). Found: C, 63.6; H, 4.1; N, 8.3. $C_{18}H_{14}N_2O_5$ requires C, 63.9; H, 4.2; N, 8.3%. ν_{max} 1745 cm^{-1} (CO). δ_H 2.38 (6H, s, 2 × Me), 7.50–8.50 (8H, m, Ar–H). *m/z* 338 ($M^{+\cdot}$).

The dicarboxylic acids M7 and M8 (Scheme 3)

The syntheses of these monomers are fully described in an earlier paper[25] (Scheme 3).

Scheme 3



2,5-Bis(6-acetoxy-2-naphthyl)-1,3,4-oxadiazole (M9)

This monomer was prepared from 6-acetoxy-2-naphthoic acid (**M3**) by the same general method as the other symmetrical diacetates **M4** and **M5**, above.

6-Acetoxy-2-naphthoyl chloride was obtained from the acid in 82% yield, and had m.p. 121°C (from carbon tetrachloride; lit.[26] 120–121°C).

1,2-Bis(6-acetoxy-2-naphthoyl)hydrazine (yield, 51%) had m.p. 246–248°C (from dimethylformamide). Found: C, 68.2; H, 4.3; N, 6.0. $C_{26}H_{20}N_2O_6$ requires C, 68.4; H, 4.4; N, 6.1%. ν_{max} (cm^{-1}) 3220 (NH), 1755 (ester CO), 1590 (amide CO). δ_H 2.35 (6H, s, 2 × Me), 7.25–8.75 (12H, m, Ar–H), 10.70 (2H, br s, 2 × NH). *m/z* 456 ($M^{+\cdot}$).

2,5-Bis(6-acetoxy-2-naphthyl)-1,3,4-oxadiazole (*M9*) (yield, 47%) had m.p. 229–230°C (from dimethylformamide). Found: C, 71.0; H, 4.2; N, 6.5. $C_{26}H_{18}N_2O_5$ requires C, 71.2; H, 4.1; N, 6.4%. ν_{max} 1755 cm^{-1} (CO). δ_H ($CDCl_3$) 2.38 (6H, s, 2 × Me), 7.25–8.75 (12H, m, Ar–H). *m/z* 438 ($M^{+\cdot}$).

p-*Acetoxyphenyl 6-acetoxy-2-naphthoate (M10)*

6-Acetoxy-2-naphthoyl chloride (24.9 g, 0.1 mol) was added in portions to a well-stirred solution of hydroquinone (11.0 g, 0.1 mol) in pyridine (50 ml). Stirring was continued for 4 h and the slurry was then added to water (250 ml). The product (*p*-hydroxyphenyl 6-acetoxy-2-naphthoate) was filtered off and recrystallized from dimethylformamide; it had m.p. 204–206°C. Found: C, 70.5; H, 4.2. $C_{19}H_{14}O_5$ requires C, 70.8; H, 4.4%. Acetylation (cf. section on acetoxybenzoic acid, above) gave compound **M10**, m.p. 154°C (from acetic acid). Found: C, 69.1; H, 4.4. $C_{21}H_{16}O_6$ requires C, 69.2; H, 4.4%. ν_{max} 1755, 1730, and 1715 cm^{-1} (CO). δ_H ($CDCl_3$) 2.53 (6H, s, 2 × Me), 7.25–8.50 (10H, m, Ar–H). *m/z* 364 ($M^{+\cdot}$).

PREPARATION OF POLYMERS

Apparatus

The apparatus (*Figure 2*) consisted of two components, the reaction flask (a Quickfit 100 ml long-neck, round-bottom flask) and a special stillhead. The latter had two inlets above the reaction flask (one fitted with a screw adapter to permit the entry of a stirrer and the other connected to a nitrogen supply) and a built-in condenser, which led to two other apertures, one for the collection of by-products and the other connected via cold traps to a vacuum pump. The pressure of the system was measured by a Vacustat connected in parallel to the vacuum line. The paddle-shaped stainless-steel stirrer bar was driven by a Heidolph RZR50 high-torque stirrer.

The reaction flask was heated using a silicone oil bath and electric hot-plate.

Procedure

For the preparation of $\mathbf{P_R}$, the reaction flask was charged with **M1** (0.025 mol), **M2** (0.025 mol) and **M3** (0.05 mol). The apparatus was purged with nitrogen for 5 min, and was maintained under a constant flow of nitrogen during the initial stage of the polymerization. The temperature was raised at 10°C min^{-1} up to a predetermined final temperature of 320°C. At 180°C **M1** melted, followed by **M2** at 210°C; **M3** slowly dissolved, giving a dark brown liquid. At 250°C, acetic acid began to distil, and by 285°C the distillation was proceeding vigorously. A small amount of crystalline material appeared on the cooler parts of the stillhead, although the majority of this was washed back into the reaction flask by the acetic acid.

As the acetic acid distilled off, the reaction mixture slowly turned turbid, and within 5 min became a thin, cream-coloured, opaque melt. The viscosity of the melt increased as the quantity of distillate increased. When the maximum temperature (320°C) was reached, it was maintained for 15 min, to ensure that all the by-product had been collected. The temperature was then allowed to drop to 260°C, the nitrogen flow was stopped and a vacuum applied gradually, to prevent the polymer rising and smearing on the reaction flask. A pressure of approximately 0.1 mmHg was maintained during the second stage of the polymerization. The temperature was then raised again to 320°C quickly, and the melt was stirred for a further 30 min. After this period, the polymer was allowed to cool quite rapidly in air.

The resulting polymer was smooth in texture, light cream in colour, and moderately tough.

The white crystals that had been deposited on the stillhead were identified (i.r. spectrum) as hydroquinone diacetate (**M1**) and corresponded to 2% of the total amount of **M1** added. Thus a stoichiometric imbalance was occurring, and amendments to the procedure were therefore sought.

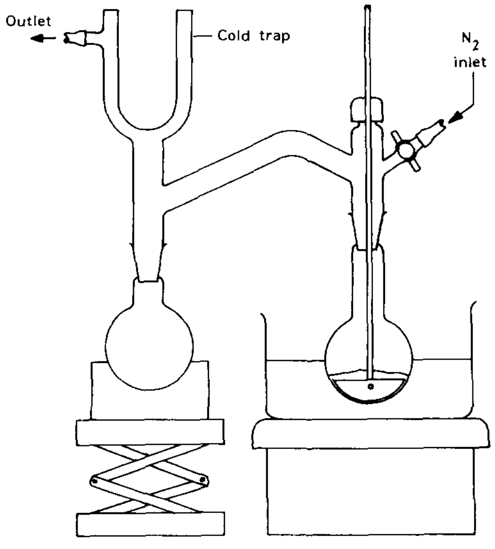


Figure 2 Polymerization apparatus

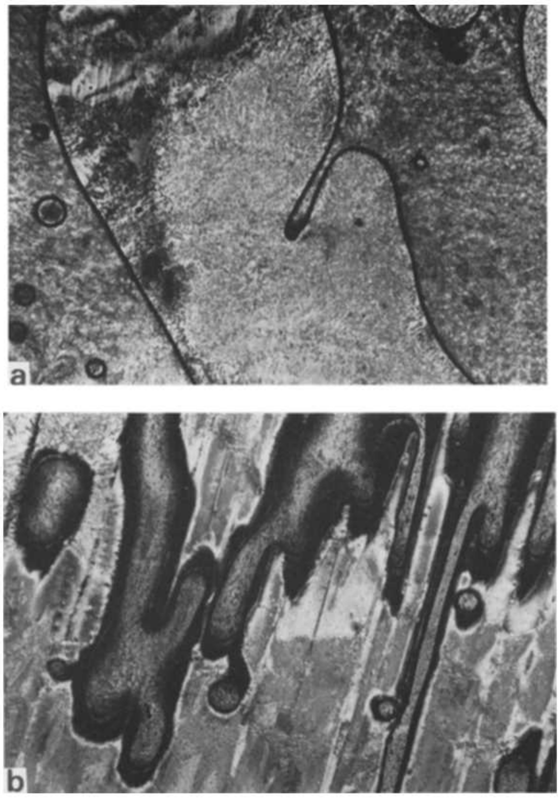


Figure 3 (a) The nematic phase of **P14**. (b) The nematic phase of **P14** after shearing

(i) The use of the preformed ester **M10** in place of **M1** and **M3** once again led to the production of **M1** (presumably by a transesterification route).

(ii) A 'slurry polymerization' technique, in which acetic acid (20 ml) was added to the monomers (**M1** and **M3** are soluble in acetic acid, but **M2** is only sparingly soluble), prevented the deposition of **M1** on the stillhead, but the acetic acid distillate was found to contain almost 4% of the original quantity of **M1**.

(iii) A 2% excess of **M1** was added, to compensate for loss of **M1** during the process. (Under these conditions, the quantity of **M1** collected corresponded to the excess added.)

Procedure (iii) was adopted for all subsequent preparations involving hydroquinone diacetate (**M1**).

Further modifications were attempted in order to increase the molecular weight of the polymers (as evidenced by melt viscosity). These attempts were made on the oxadiazole-containing polymer **P7** (in which **M4** totally replaces the **M1** of the reference polymer $\mathbf{P_R}$), and resulted as follows:

(iv) The use of a higher end temperature (340°C) for the polymerization produced a very dark brown polymer, indicative of degradation and/or side-reactions.

(v) The addition of catalytic amounts of potassium acetate and acetic anhydride (in an attempt to minimize thermal deacetylation of the diacetates) produced no significant difference in the polymer.

(vi) Increasing the duration of the final stage of polymerization, by maintaining the temperature at 320°C until the mixture could no longer be stirred, produced a final polymer that was little darker than the original, but much tougher and exceedingly fibrous in character.

Modification (vi) was adopted for subsequent polymer preparations: the stirring of the polymer under vacuum at 320°C was sustained until this became impracticable due to the viscosity of the melt, or until 2 h had passed. In several of the polymerizations, the end temperature was lowered when melts were believed to be isotropic at 320°C, and in other cases, the melt solidified on the application of the vacuum and could not be further processed.

POLYMER CHARACTERIZATION

Differential scanning calorimetry

This was carried out using a Mettler TC10 differential calorimeter cell coupled to a Mettler TA3000 processor. The calorimeter was calibrated using high-purity metal standards (In, Zn, Pb). The samples were contained in sealed aluminium pans, normally under an atmosphere of nitrogen, and were scanned up to 590°C, using different heating rates, with an empty pan and lid as a reference. All characterizations were carried out using the 'as-made' polymers; when various samples were annealed, their d.s.c. thermograms were unchanged.

Optical microscopy

Optical microscopy at temperatures up to 350°C was carried out using a Leitz Dialux 20 microscope fitted with a Leitz heating stage (model 350). Samples were observed using polarized light, and colour photographs were taken at 40 × magnification. A representative set of photographs is shown in *Figure 3*.

Thermal gravimetric analysis

T.g.a. was performed, using a Stanton automatic thermo-recording balance, on polymer samples in the form of 10 mm diameter pressed discs. Determinations were carried out in air, and the temperatures at which 2%, 5% and 10% weight loss had occurred were recorded. The second of those temperatures is taken to be the limit of thermal stability.

Solubility

This was investigated by shaking flasks containing polymer and solvent (0.1–0.15 g per 100 ml) for up to 72 h.

RESULTS AND DISCUSSION

The new polymers

Some 17 new polymers are described here, and are considered in groups according to their compositional relationship to the reference polymer, $\mathbf{P_R}$. Since the primary objective at this stage was to identify those polymers with the potential for fibre formation from a liquid-crystalline melt, and since all the polymers showed only restricted solubility in the normal range of solvents, no attempt was made to determine molecular weights or the nature of end-groups. Visual inspection of the melt at the final stage of the polymerization, and of the solid polymer obtained, was used to identify suitable candidates for further investigation. In particular, polymers were sought which formed a low-viscosity melt and produced a light-coloured solid with a tough fibrous texture.

$\mathbf{P_R}$ was produced from hydroquinone diacetate (**M1**), terephthalic acid (**M2**) and two equivalents of 6-acetoxy-

2-naphthoic acid (**M3**):

$\mathbf{P_R}$: $(\mathbf{M1})_1$ $(\mathbf{M2})_1$ $(\mathbf{M3})_2$

The groups of modified polymers were designed as follows:

*Replacement of **M1** by an oxadiazole-containing diacetate*

P7: $(\mathbf{M4})_1$ $(\mathbf{M2})_1$ $(\mathbf{M3})_2$
P8: $(\mathbf{M5})_1$ $(\mathbf{M2})_1$ $(\mathbf{M3})_2$
P9: $(\mathbf{M6})_1$ $(\mathbf{M2})_1$ $(\mathbf{M3})_2$

Initial evaluation indicated that **P7** was the most promising of these in respect of fibre formation from a melt; **P8** and **P9** were not therefore investigated further in this study, and attention was concentrated on **P7**. Increased melt viscosity was achieved (cf. 'Experimental') by increasing the time of the final heating stage, and further refinements to the composition were then made.

*Partial replacement of **M1** by the oxadiazole-containing diacetate **M4***

P10: $(\mathbf{M1})_{0.25}$ $(\mathbf{M4})_{0.75}$ $(\mathbf{M2})_1$ $(\mathbf{M3})_2$
P11: $(\mathbf{M1})_{0.5}$ $(\mathbf{M4})_{0.5}$ $(\mathbf{M2})_1$ $(\mathbf{M3})_2$
P12: $(\mathbf{M1})_{0.75}$ $(\mathbf{M4})_{0.25}$ $(\mathbf{M2})_1$ $(\mathbf{M3})_2$

All three were tough and fibrous, and very similar in appearance to **P7** prepared under the same conditions.

*The homopolymer of **M4** and **M2**.* Since polymers containing **M4** appeared promising, the effect of omitting altogether the laterally disrupting mesogenic unit (from **M3**) was explored.

P13: $(\mathbf{M4})_1$ $(\mathbf{M2})_1$

Only a grey powder was obtained, which decomposed below the melting point and could not therefore be processed further.

*Change in proportion of the **M3**-derived unit*

P14: $(\mathbf{M4})_1$ $(\mathbf{M2})_1$ $(\mathbf{M3})_1$
P15: $(\mathbf{M4})_1$ $(\mathbf{M2})_1$ $(\mathbf{M3})_3$

Both were sufficiently promising to warrant further investigation, although, visually at least, they offered no obvious advantage over **P7**.

*Replacement of **M1** and **M2** by oxadiazole-containing units*

P16: $(\mathbf{M4})_1$ $(\mathbf{M7})_1$ $(\mathbf{M3})_2$

This was light in colour, but a hard, brittle, compacted material.

*Replacement of **M2** by an oxadiazole-containing diacid*

P17: $(\mathbf{M1})_1$ $(\mathbf{M2})_{0.5}$ $(\mathbf{M7})_{0.5}$ $(\mathbf{M3})_2$

Even with only half of the terephthalic acid in $\mathbf{P_R}$ replaced by **M7**, the polymer was glassy rather than fibrous in character; and when the bis-*meta*-substituted acid (**M8**) was used, as in

P18: $(\mathbf{M1})_1$ $(\mathbf{M8})_1$ $(\mathbf{M3})_2$

the solid was once again brittle.

*Replacement of **M1** by **M4** and **M3** by* p*-acetoxybenzoic acid (**M11**)*

P19: $(\mathbf{M4})_1$ $(\mathbf{M2})_1$ $(\mathbf{M11})_2$
P20: $(\mathbf{M4})_1$ $(\mathbf{M7})_1$ $(\mathbf{M11})_2$

The first of these was hard and coherent, although not obviously fibrous. Again, however, replacement of **M2** by **M7** gave a brittle material.

*Replacement of **M1** by the dinaphthyloxadiazole monomer **M9***

P21: $(\mathbf{M9})_1$ $(\mathbf{M2})_1$ $(\mathbf{M3})_2$
P22: $(\mathbf{M9})_1$ $(\mathbf{M2})_1$ $(\mathbf{M3})_3$
P23: $(\mathbf{M9})_1$ $(\mathbf{M2})_1$ $(\mathbf{M11})_2$

The first of these was tough and fibrous, the second also fibrous but more brittle, and the third hard and brittle. Only **P21** was studied in more detail.

The eight polyesters **P7**, **P10**, **P11**, **P12**, **P14**, **P15**, **P19** and **P21** , along with $\mathbf{P_R}$, were then subjected to more detailed investigation.

Solubility

None of the polymers was appreciably soluble in any of the solvents tried (e.g. *o*-chlorophenol). The best solvent system found was trifluoroacetic acid/dichloromethane (30:70), but even this system dissolved only those polymers which contained a significant proportion of oxadiazole rings. $\mathbf{P_R}$ and **P12** were insoluble, and **P11** dissolved only very slowly.

Thermal stability

The results of thermal gravimetric analysis of the polymers are listed in *Table 2*. All eight polymers showed excellent thermal stability in air up to temperatures >400°C, although none exhibited such remarkable stability as $\mathbf{P_R}$.

Hot-stage microscopy (h.s.m.) and differential scanning calorimetry (d.s.c.)

Thermally induced transitions in the polymers were investigated by a combination of these two techniques. The h.s.m. observations are collected in *Table 3*. The temperatures recorded (solid → liquid-crystal phase) correspond to the onset of liquid-like mobility of the polymer, found by pressing the sample between the two microscope slides. The isotropization temperature was

Table 2 Thermal stability of the selected polymers

Polymer no.	Temperature (°C) corresponding to weight loss of		
	2%	5%	10%
$\mathbf{P_R}$	493	496	499
P7	410	420	437
P10	389	426	444
P11	392	421	437
P12	434	439	448
P14	425	429	450
P15	420	425	439
P19	416	421	426
P21	410	429	444

Table 3 Onset of fluidity in the selected polymers

Polymer no.	Temp. (°C) at which fluidity first observed by h.s.m.	T_{cn} (°C) (by d.s.c.)
$\mathbf{P_R}$	300	300
P7	270	290 (broad: range 275–320)
P10	220	320 (very broad: range 220–340)
P11	220	330 (broad: range 270–340)
P12	260	265
P14	280	300
P15	270	270
P19	280	300 (broad: range 265–310)
P21	190	255

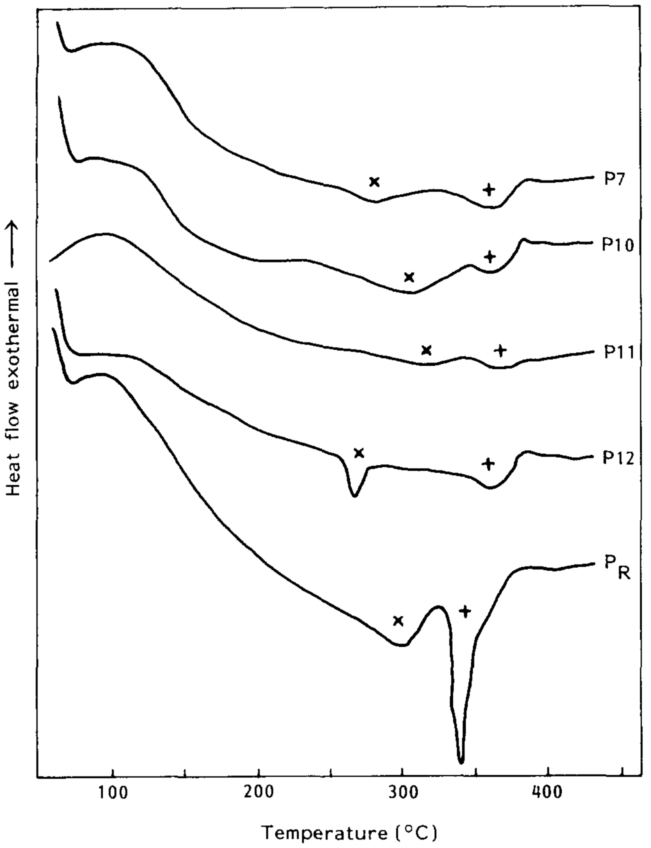


Figure 4 D.s.c. thermograms of $\mathbf{P_R}$, **P7**, **P10**, **P11** and **P12**: (×) first endotherm; (+) second endotherm

rarely recorded, since this was generally greater than 350°C and was thus outside the range of observation.

Figure 4 illustrates the d.s.c. thermograms obtained for $\mathbf{P_R}$, **P7**, **P10**, **P11** and **P12**. In all cases T_g is ill-defined, and the oxadiazole unit does not appear to alter T_g significantly. All the polymers apparently show double melting points, a phenomenon that has been observed by several other groups[27–29]. The highest endotherm on a thermogram is generally broad and corresponds to a transition from a liquid-crystalline phase to an isotropic phase. Transitions from the solid to a liquid-crystalline phase may be accompanied by one or more first-order transitions. Where multiple transitions occur, it is presumed that, of the lower-temperature d.s.c. peaks, the solid-to-liquid-crystal transition corresponds to the peak of the highest transition temperature. One possible explanation of the multiple melting phenomenon is that it arises from a crystallization of the polymer chains, a view supported by the relative changes in size of the two endotherms as the d.s.c. heating rate is altered. With increasing heating rate, the higher-temperature endotherm becomes smaller, and the lower-temperature endotherm becomes proportionally larger. The higher-temperature endotherm thus may result from the melting of polymer crystals formed from the amorphous polymer by simultaneous melting and recrystallization at lower temperatures. The melting endotherm and the recrystallization exotherm are thought to cancel each other, thereby explaining the absence of a recrystallization exotherm[30]. Since higher heating rates allow for less recrystallization, the relative magnitude of the higher-temperature transition is diminished. This is shown in *Figure 5*, which illustrates thermograms of $\mathbf{P_R}$ at heating rates of 10, 30, 50, 70 and 90°C min^{-1}. It should be noted that the two endotherms are separated by a large temperature difference (~60°C).

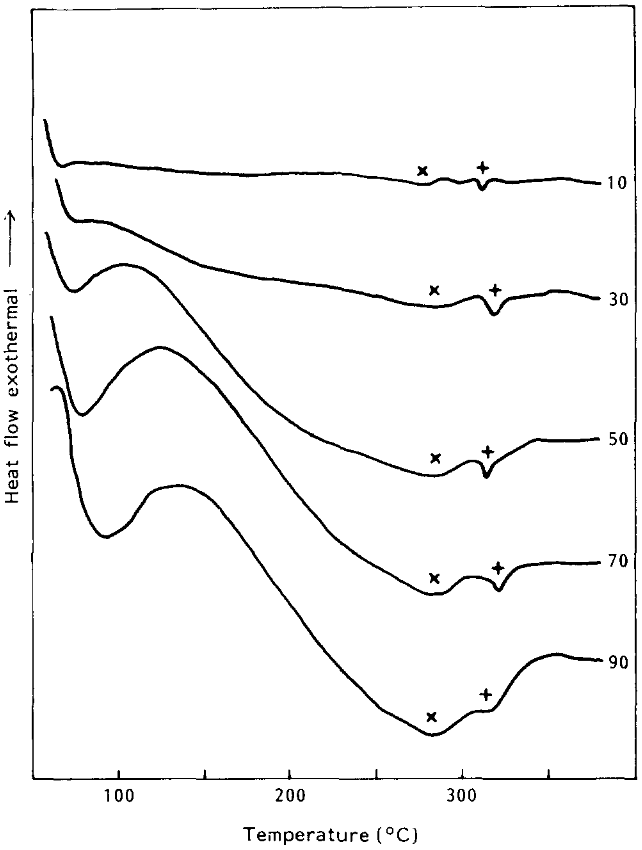


Figure 5 D.s.c. thermograms of $\mathbf{P_R}$ at various heating rates (°C min^{-1}): (×) first endotherm; (+) second endotherm

The use of more sophisticated h.s.m.*, using temperatures of up to 600°C, showed that $\mathbf{P_R}$, **P7**, **P10**, **P11** and **P12** were all liquid-crystalline up to temperatures of ~450°C, when they then started to degrade. Thus the second endotherm in these cases is believed to correspond not to a liquid-crystalline-to-isotropic transition, but to the melting of a more stable crystalline form, and the lower endotherm is believed to represent the melting temperature of a less stable crystalline form. If the polymer did not crystallize at all, then only a gradual endothermic process would be observed as the amorphous material gradually softened, and this would result in only a sloping baseline on the thermogram.

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* Stanton Redcroft model TH600 (University of Leeds)

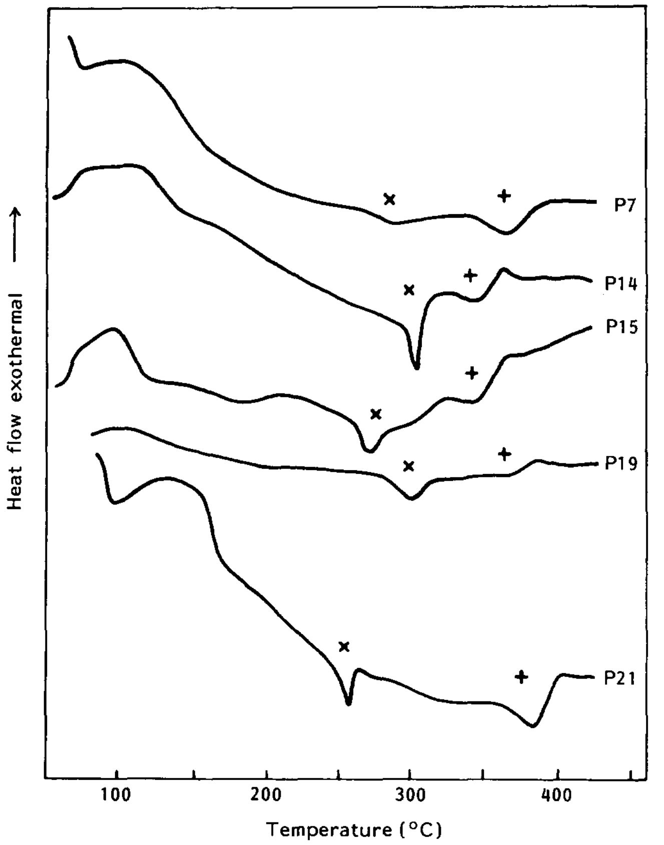

Figure 6 D.s.c. thermograms of **P7**, **P14**, **P15**, **P19** and **P21**: (×) first endotherm (heating rate 50°C min^{-1}); (+) second endotherm

Previous investigations of several polymers with well-defined double endotherms under a polarizing microscope at temperatures between their endotherms showed no fluidity due to a transition from the less perfect crystal form to the nematic phase$^{27-29}$. However, the partial melting of the sample still leaves the crystal structure of the more stable form intact, and it would not be expected that the sample as a whole would become fluid until both crystal forms had melted.

In the present work, the results obtained by d.s.c. and h.s.m. are sometimes in disagreement. In these cases, fluidity was observed by h.s.m. at temperatures well below those expected from the d.s.c. thermograms (see *Table 3*). It is suggested that these polymers, **P7**, **P10**, **P11**, **P12**, **P19** and **P21**, are completely amorphous, because of the angular segments, and that, even at very slow heating rates, the degree of crystallization is quite small. Thus these polymers remain mostly amorphous, and on further heating behave like any other amorphous polymer; above T_g, a 'rubbery state' is obtained, and with further heating a 'rubbery flow' is obtained. It could thus be this 'rubbery flow' that is being observed by h.s.m. at temperatures below the first endotherm. This would also explain why at this stage the polymers are viscous, uniform, olive-green in colour, and display birefringence only at the edges (where they are thinnest), and why they gradually brighten to a silver-coloured, very bright, thin 'melt', with a threaded texture, as the temperature approaches that of the first endotherm.

In the case of $\mathbf{P_R}$, since it contains no angular disrupting groups, it may undergo a recrystallization at slower heating rates, and thus its d.s.c. thermograms should be affected by heating rates to a greater extent than those of the other polymers which contain angular segments. We have verified this for **P11**; the second endotherm is of much less significance than in the case of $\mathbf{P_R}$.

The effect of varying the proportion of the **M3**-derived units in the polymer is shown in *Figure 6*, which compares the thermograms of **P7**, **P14** and **P15**. Increase in the proportion of **M3** leads to a drop in the temperature at which the lower endotherm is observed. Comparison of **P7** with **P19** and **P21** (*Figure 6*) also demonstrates the influence of the mesogenic, laterally disrupting 2,6-naphthylene component on the position of the lower endotherm: in **P19**, where **M3** is replaced by the (non-disrupting) **M11**, the endotherm appears at a higher temperature, whereas in **P21**, where two components (**M3** and **M9**) both contain the 2,6-naphthylene unit, the endotherm appears at a considerably lower temperature.

In summary, the 1,3,4-oxadiazole-2,5-diyl unit is an effective angular disruptor in these aromatic polyesters. Incorporation of the disruptive unit permits melt processing at lower temperatures, without obvious effect on liquid crystallinity or T_g; the only disadvantages are a slight loss in thermal stability and in crystallinity.

As with other main-chain liquid-crystal polymers such as $\mathbf{P_R}$, it has not been possible to obtain information on molecular weight, molecular-weight distribution, or end-groups, because of restricted solubility.

Various other disruptors will be considered in part 2, and fibre formation from all these polymers will be discussed in part 3.

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