Aromatic and heteroatomic polyesters:
2. The effect of a range of disrupting units on 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

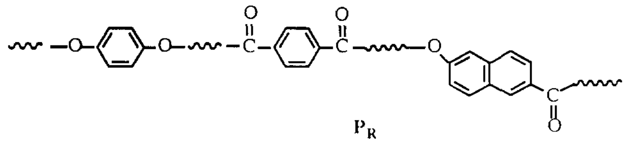
and John Emans, David M. Smith*, Trevor Bowen and Ian W. Harvey
Department of Chemistry, University of St. Andrews, Purdie Building, St. Andrews, Fife, KY16 9ST, UK
(Received 21 May 1992; revised 12 March 1993)

The liquid-crystalline polyester (designated P_R), synthesized from hydroquinone diacetate, terephthalic acid and 6-acetoxy-2-naphthoic acid (1:1:2) by melt-phase transesterification, may be considerably modified in properties by the replacement of one or more of the monomers by a 'disrupting' unit. The disruption may be angular, as for example when isophthalic acid replaces terephthalic acid, or 2,7-diacetoxynaphthalene replaces hydroquinone diacetate, or it may be lateral, as when 1,5-diacetoxynaphthalene is used. The effects of these disrupting units on the thermal behaviour of the polymers, especially liquid crystallinity, and on their propensity to form fibres, are discussed. Although liquid crystallinity may be observed when the polymers are formed from up to 50% of angular units, the fibre formation is significantly diminished whenever the acetoxynaphthoic acid is replaced by *p*-acetoxybenzoic acid.

(Keywords: liquid-crystalline polyesters; 1,3,4-oxadiazole; 1,3,4-thiadiazole; 6-acetoxy-2-naphthoic acid; diacetoxynaphthalenes; fibres)

INTRODUCTION

In part 1[1] we have described how the properties of a conventional liquid-crystalline polyester, P_R, composed of *p*-phenylenedioxy, terephthaloyl and 6-oxy-2-naphthoyl units in the proportion 1:1:2, may be modified by the introduction of a 2,5-diaryl-1,3,4-oxadiazole unit as a total or partial replacement for one or other (or both) of the standard monocyclic components. The 1,3,4-oxadiazole unit acts as an 'angular disruptor' in the polymer chain, and serves in some cases to lower the temperature at which the onset of liquid crystallinity is observed (and hence the temperature at which the processing of the polymer, e.g. into fibres, becomes feasible). In the present paper, we examine the effect of several other disrupting groups, both angular and lateral, on the same reference polymer P_R, and attempt a qualitative comparison of these polymers with the oxadiazole-containing polymers described in part 1. For the purposes of this comparison, the new monomers and polymers described in this paper are numbered sequentially with those in part 1.



P_R

The monomers used for the preparation of P_R are hydroquinone diacetate (M1), terephthalic acid (M2) and 6-acetoxy-2-naphthoic acid (M3). The monomers (M4–M19) containing the disrupting groups, as in part 1, are also diacetates, dicarboxylic acids, or acetoxy-acids, and are listed in *Scheme 1*.

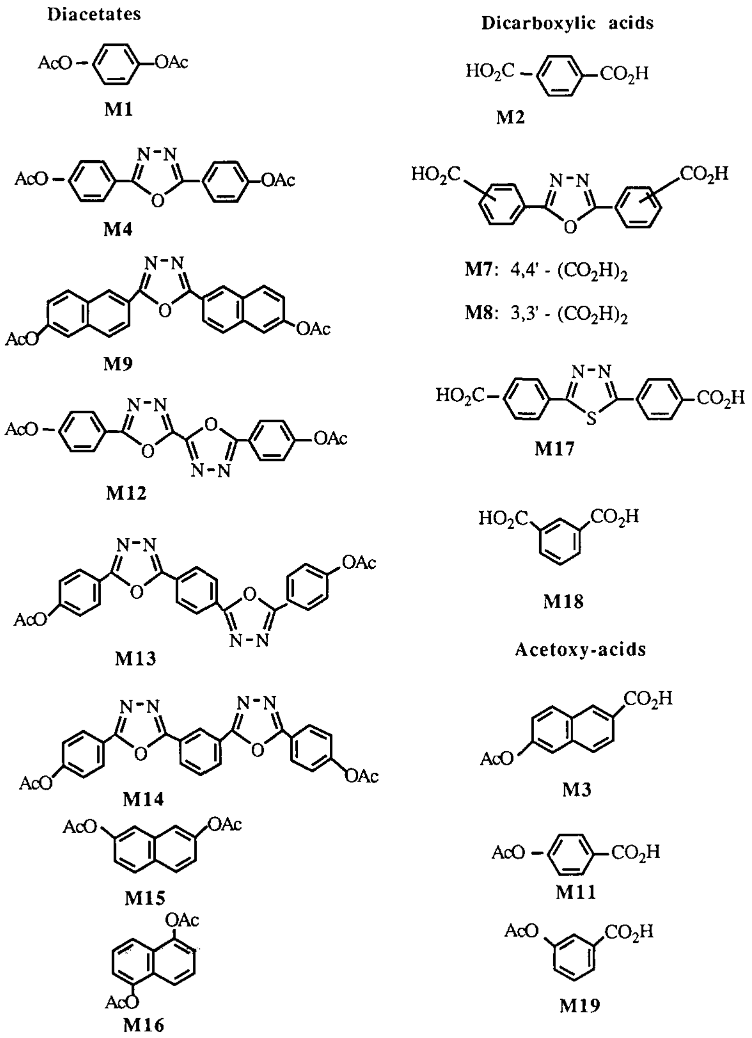
The fact that the incorporation of an angular disruptor, e.g. M4, into the polymer chain of P_R does not, *per se*, suppress its liquid crystallinity[1] has encouraged us to use *meta*-phenylene monomers such as isophthalic acid (M18) and *m*-acetoxybenzoic acid (M19), although these are non-mesogenic[2]. 2,7-Diacetoxynaphthalene (M15) provides the means of investigating the effect of an arylenedioxy unit which is shorter but more sharply angled than M4 ($\sim 60°$, compared with 47°)[3]. 1,5-Diacetoxynaphthalene (M16), on the other hand, introduces a substantial lateral disruption.

The most novel monomers used are those that contain a 1,3,4-thiadiazole unit, and those in which two oxadiazole units are incorporated. The angle introduced by the thiadiazole unit (*Figure 1*)[4–6] is only about 20°, i.e. less than half of that caused by the oxadiazole, and a thiadiazole-containing polymer ought therefore to be less disrupted than its oxadiazole-containing counterpart. Unfortunately, however, we have been unable to obtain sufficient quantities of the thiadiazole analogue of M4 by either of the published methods[7,8] to use this in polymerization procedures, and the dicarboxylic acid M17 is therefore the only thiadiazole used in this study.

---

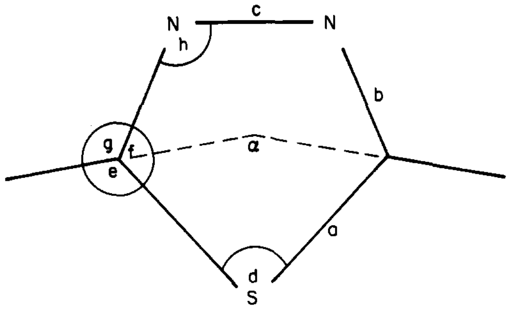
* To whom correspondence should be addressed

0032-3861/93/214481-07



Scheme 1 Monomers used

Figure 1 Dimensions of the 1,3,4-thiadiazole-2,5-diyl unit



A, X-ray crystallographic data (parent compound at $-53°C$)[4]
B, Data based on microwave spectra[5]
C, Data derived from electron diffraction (gas phase)[6]

	A	B	C
Bond lengths (Å)			
a	1.74	1.721	1.722
b	1.31	1.302	1.304
c	1.38	1.371	1.381
Interbond angles (deg)			
d	87.0	86.4	86.4
e	123.0	122.5	124.1
f	114.0	114.6	114.8
g	123.0	122.9	121.1
h	113.0	112.2	112.0
α (deg)	159.0	158.6	161.8

The two bis-oxadiazole monomers M12 and M13 are of interest since in theory each may act as an angular or a lateral disruptor: each may adopt a conformation (shown in the list) in which the angle introduced by one oxadiazole group is cancelled out by the second. M14, on the other hand, offers a number of possibilities for angular disruption, depending on the preferred conformation of the unit within the polymer chain.

As in part 1, the primary objective of this survey is to identify those polymers that show fibre-forming potential, and the selection of polymers for full characterization is based on this alone. Particular attention is directed towards those polymers which are obviously fibrous as synthesized (i.e. without further processing).

EXPERIMENTAL

Infra-red spectra are those of Nujol mulls, and ^1H n.m.r. spectra are those of solutions in d_6-dimethyl sulfoxide.

Preparation of monomers

The monomers M1–M4, M9, M11 and M19 are described in part 1[1], and M7, M8 and M17 in an earlier paper[9]. Isophthalic acid (M18) was standard (Aldrich) reagent grade.

The bis-oxadiazolyl M12 (*see* Scheme 1). Oxalyl bis-[2-(*p*-acetoxybenzoyl)hydrazide]. A solution of *p*-

acetoxybenzoyl chloride[1] (34 g, 0.17 mol) in dioxan (90 ml) was added dropwise, with stirring, to a suspension of oxalyl dihydrazide (10.0 g, 0.085 mol) and sodium carbonate (9.0 g, 0.085 mol) in dioxan (210 ml). Stirring was then continued for 2 h, and the mixture was set aside overnight. The product was filtered off, washed well with water and recrystallized from dimethylformamide. Yield 23.0 g (61%), m.p. 261°C. (Found: C, 53.8; H, 4.3; N, 12.6. $C_{20}H_{18}N_4O_8$ requires C, 54.3; H, 4.1; N, 12.7%.) ν_{max} (cm^{-1}) 3200 (NH), 1750 and 1700 (CO); δ_H 2.33 (6H, s, 2 × Me), 7.32 and 7.95 (8H, AA′BB′ pattern, Ar–H), 10.55 (4H, 4 × NH). The mass spectrum showed no molecular ion.

2,2′-Bis-[5-(*p*-acetoxyphenyl)-1,3,4-oxadiazolyl] (M12). The foregoing bis-hydrazide (19 g) was heated under reflux with thionyl chloride (475 ml) for 4 h. The excess of thionyl chloride was removed by distillation at reduced pressure, and the residue washed with water and recrystallized from dimethylformamide; yield 11.5 g (66%). Compound M12 had m.p. 285–286°C. (Found: C, 59.1; H, 3.5; N, 13.8. $C_{20}H_{14}N_4O_6$ requires C, 59.1; H, 3.4; N, 13.8%.) ν_{max} 1740 cm^{-1} (CO); δ_H 2.35 (6H, s, 2 × Me), 7.42 and 8.25 (8H, AA′BB′, Ar–H); *m/z* 406 ($M^{+\bullet}$).

The bis-oxadiazoles M13 and M14 (*see* Scheme 1). Terephthaloyl dihydrazide. Hydrazine hydrate (27.7 g, 0.55 mol) was added to a solution of diethyl terephthalate (61.2 g, 0.27 mol) in hot ethanol (~40 ml), and the resulting solution heated under reflux for 4 h. (Precipitation of the product began after about 40 min.) The mixture was cooled, and the product was filtered off, washed with boiling ethanol and dried in air at 100°C. It was used without further purification. Yield 49.2 g (94%); m.p. >340°C (lit.[10] >300°C).

Isophthaloyl dihydrazide was generously provided by ICI.

Terephthaloyl bis-[2-(*p*-acetoxybenzoyl)hydrazide][7]. A solution of *p*-acetoxybenzoyl chloride[1] (7.80 g) in dioxan (30 ml) was added with stirring to a mixture of terephthaloyl dihydrazide (3.54 g), sodium carbonate (1.91 g) and dioxan (50 ml). The stirred mixture was heated to 100°C for 5 h, then set aside overnight. Aqueous sodium hydroxide (5M, 25 ml) was added, with stirring, and the product filtered off; it had m.p. 308–309°C, and weighed 6.56 g (62%); ν_{max} (cm^{-1}) 3180 (NH), 1750 (CO), 1590, 1540.

Isophthaloyl bis-[(*p*-acetoxybenzoyl)hydrazide] was similarly obtained (yield, 66%) from isophthaloyl dihydrazide (10.0 g), *p*-acetoxybenzoyl chloride (20.4 g) and sodium carbonate (5.4 g). The product had m.p. 303–303°C; ν_{max} (cm^{-1}) 3190 (NH), 1740 (ester CO), 1675 and 1635.

Neither of the above bis-hydrazides was sufficiently soluble in any of the common solvents to be readily purified for analysis; each was cyclized directly, without further purification, as described below.

1,4-Bis-[5-(*p*-acetoxyphenyl)-1,3,4-oxadiazol-2-yl]-benzene (M13). Terephthaloyl bis-[2-(*p*-acetoxybenzoyl)-hydrazide] (12.0 g) was mixed with sufficient dimethylformamide (~100 ml) to make a slurry; thionyl chloride (120 ml) was then added and the mixture heated under reflux for 9 h and set aside overnight. The solid product was filtered off and washed with water; recrystallized from dimethylformamide, it had m.p. 318–320°C. (Found: C, 64.3; H, 3.6; N, 11.3. $C_{26}H_{18}N_4O_6$ requires C, 64.7; H, 3.8; N, 11.6%.) Yield 6.25 g (56%). ν_{max} 1740 cm^{-1} (CO); $M^{+\bullet}$ absent. No n.m.r. spectrum was obtained for this compound owing to its low solubility in the usual solvents.

1,3-Bis-[5-(*p*-acetoxyphenyl)-1,3,4-oxadiazol-2-yl]-benzene (M14), m.p. 294–296°C (from acetic acid), was obtained (7.8 g, 48%) by heating isophthaloyl bis-[2-(*p*-acetoxybenzoyl)hydrazide] (17.4 g) and thionyl chloride (435 ml) together, under reflux, for 4 h. (Found: C, 64.3; H, 3.8; N, 11.3. $C_{26}H_{18}N_4O_6$ requires C, 64.7; H, 3.8; N, 11.6%.) ν_{max} 1750 cm^{-1} (CO); *m/z* 482 ($M^{+\bullet}$). No n.m.r. spectrum was obtained because of low solubility.

2,7-Diacetoxynaphthalene (*M15*) *and 1,5-diacetoxynaphthalene* (*M16*). These were prepared by standard acetylations of the appropriate naphthalenediols. The 2,7-isomer (M15), m.p. 127–129°C (from ethanol; lit.[11], 129°C), was obtained in 97% yield, and the 1,5-isomer (M16), m.p. 157–159°C (from tolune; lit.[12], 159–160°C), in 79% yield.

Preparation and characterization of polymers

In all cases the polymerization procedure was that described in part 1[1]. The monomer mixture was heated, with vigorous stirring and in an atmosphere of nitrogen, at a rate of 10°C min^{-1} up to an end-temperature of 320°C. Unless otherwise indicated, this end-temperature was maintained for 2 h, or until the viscosity of the polymer made stirring impossible.

Details of the characterization by differential scanning calorimetry (d.s.c.), thermal gravimetric analysis (t.g.a.) and optical hot-stage microscopy (h.s.m.) were also described in part 1. H.s.m. for the compounds described below was carried out using an Olympus BHS-P microscope equipped with a Stanton Redcroft TH600 hot stage.

RESULTS AND DISCUSSION

Thirty-one new polymers are described in this paper. As in part 1, they are conveniently grouped together according to their compositional relationship to the reference polymer P_R. Comparisons with oxadiazole-containing polymers already described in part 1 are also made where appropriate.

It was noted in part 1 that the d.s.c. thermograms for liquid-crystalline polymers of this type are frequently difficult to interpret, and that the glass transition temperature, T_g, is usually ill-defined. The same holds true for the polymers described here. It was also noted in part 1 that the determination of molecular weight, molecular-weight distribution and end-groups in these polymers was not possible because of their very restricted solubility in a wide range of solvents investigated; the same is true again here. All we have been able to do, in respect of molecular weight, is to try to obtain products of comparable viscosity — the maximum attainable by this method — by conducting the polymerizations under standard conditions and continuing the reactions where possible until the stirrer seized.

Eight series of polymers are discussed. Tabulated data in parentheses relate to polymers described in part 1.

Series A. Variation in the proportion of angular units in the monomer mixture

[P_R:	$(M1)_1$	$(M2)_1$	$(M3)_2$	No angular units, $T_f = T_{cn} = 300$]
[P7:	$(M4)_1$	$(M2)_1$	$(M3)_2$	25% angular units, $T_f = 270$, $T_{cn} = 290$]
[P19:	$(M4)_1$	$(M2)_1$	$(M11)_2$	25% angular units, $T_f = 280$, $T_{cn} = 300$]
P24:	$(M4)_1$	$(M18)_1$	$(M3)_2$	$T_f = T_{cn} = 240$
P25:	$(M4)_1$	$(M2)_1$	$(M19)_2$	Not liquid crystalline (T_g not observed, $T_m = 395$)

(where T_f = temperature (°C) at which fluidity is first observed (by h.s.m.). T_{cn} = temperature (°C) corresponding to the lower d.s.c. endotherm (cf. part 1[1]). (This notation, indicating a crystalline-to-nematic transition, is used for consistency even though the degree of crystallinity in some cases is very low.) T_m = melting temperature).

We showed in part 1 that replacement of the (linear) hydroquinone-derived unit in P_R by the (angular) diphenyloxadiazole unit, as in P7 and P19, had no significant effect on the liquid-crystalline characteristics of the polymer. However, there was only a small drop in T_f, and no obvious advantage over P_R in terms of melt-processability.

In the new polymer P24, the terephthaloyl unit of P7 is replaced by isophthaloyl, so that 50% of the monomer units are now angular in nature. This polymer is still liquid crystalline, and was an obvious candidate for further evaluation (see below), being hard, fibrous and light in colour. Polymer P25, on the other hand, in which the 6-oxy-2-naphthoyl unit of P7 is replaced by *m*-oxybenzoyl (i.e. 75% of the monomer units are angular), is darker, tough and no longer liquid crystalline.

Series B. Polymers containing the 2,7-naphthylenedioxy-unit

This series is based on a monomer mixture in which 2,7-diacetoxynaphthalene (M15) replaces the bis-acetoxyphenyl-oxadiazole (M4) of the previous series.

P26:		$(M15)_1$	$(M2)_1$	$(M3)_2$	$T_f = 300$, $T_{cn} = 310$ (broad)	(cf. P7)
P27:		$(M15)_1$	$(M2)_1$	$(M11)_2$	$T_f = 285$, $T_{cn} = 305$ (broad) ($T_g = 156$)	(cf. P19)
P28:		$(M15)_1$	$(M2)_1$	$(M19)_2$	Not liquid crystalline ($T_g = 170$, $T_m = 245$)	(cf. p25)
P29*:		$(M15)_1$	$(M18)_1$	$(M3)_2$	$T_f = 280$, $T_{cn} = 295$ ($T_g = 150$)	(cf. P24)
P30*:		$(M15)_1$	$(M18)_1$	$(M11)_2$	$T_f = 325$, $T_{cn} = 300$ ($T_g = 231$)	
P31:	$(M4)_{0.5}$	$(M15)_{0.5}$	$(M2)_1$	$(M3)_2$	$T_f = 235$, $T_{cn} = 280$	(cf. P7 and P26)
P32:	$(M4)_{0.5}$	$(M15)_{0.5}$	$(M18)_1$	$(M3)_2$	$T_f = 230$, $T_{cn} = 280$ (v. broad)	(cf. P24 and P29)

Of the first three, each containing a terephthaloyl unit, only P26 is sufficiently hard and fibrous to warrant further characterization. P27, although liquid crystalline, forms much weaker fibres, and P28, containing 75% of angular units, is a dark, brittle resin. In general, these polymers are similar in nature to their *p*-oxadiazole-containing counterparts, but their fibrous character is apparently diminished. The same is true of the two isophthaloyl-containing polymers P29 and P30*: the former is obtained as much weaker fibres than P24, and the introduction (in P30) of the *p*-oxybenzoyl unit results in a non-fibrous, brittle resin (which is, however, still liquid crystalline).

P31 is a compositional 'hybrid' of P7 and P26, and visually resembles both; P32 is similarly a 'hybrid' of P24 and P29, and is intermediate between these both in appearance and in the strength of fibre produced. The additional degree of randomness introduced by the additional monomer does indeed lower T_f, as expected, but apparently at the expense of fibre strength.

Series C. Polymers containing the 1,5-naphthylenedioxy-unit

The series contains a lateral disruptor, in contrast to the angular disruptors of the previous series.

P33:	$(M16)_1$	$(M2)_1$	$(M3)_2$	$T_f = 185$, T_{cn} not observed	(cf. P7 and P26)
P34:	$(M16)_1$	$(M2)_1$	$(M11)_2$	$T_f = 240$, $T_{cn} = 275$ (v. broad)	(cf. P19 and P27)
P35:	$(M16)_1$	$(M2)_1$	$(M19)_2$	Not liquid crystalline ($T_g = 154$, $T_m = 255$)	(cf. P25 and P28)
P36:	$(M16)_1$	$(M18)_1$	$(M3)_2$	$T_f = 225$, $T_{cn} = 270$ (v. broad)	(cf. P24 and P29)
P37*:	$(M16)_1$	$(M18)_1$	$(M11)_2$	$T_f \sim 350$ (dec.), T_{cn} not observed	(cf. P30)

There is an obvious similarity between these and their analogues in the last series, namely P26–P30. P33, like P26, was selected for further characterization. P34 and P37, containing the *p*-oxybenzoyl unit, and P36, containing the isophthaloyl unit, form structurally weaker materials, and P37 is too high-melting, in any case, to be melt-processable. P35, containing the *m*-oxybenzoyl unit, is dark and resinous and, like its counterparts P25 and P28, is not liquid crystalline.

Series D. Polymers containing the dinaphthyloxadiazole unit

Some members of this series have been described in part 1. P21, in particular, was attractive as a candidate for further examination on account of its low T_f. The series is completed below.

[P21:	$(M9)_1$	$(M2)_1$	$(M3)_2$	$T_f = 195$, $T_{cn} = 235$]
[P23:	$(M9)_1$	$(M2)_1$	$(M11)_2$	$T_f = 240$, $T_{cn} = 270$ (broad)]
P38:	$(M9)_1$	$(M2)_1$	$(M19)_2$	$T_f \sim 310$, not liquid crystalline, $T_g = 200$
P39†:	$(M9)_1$	$(M18)_1$	$(M3)_2$	$T_f \sim 360$ (dec.), T_{cn} (?) $= 280$
P40†:	$(M9)_1$	$(M18)_1$	$(M11)_2$	$T_f \sim 350$ (dec.), $T_m \sim 370$
P41:	$(M9)_1$	$(M18)_1$	$(M3)_3$	$T_f = 260$, $T_{cn} = 300$ (broad)

Several comparisons are valid here. P21, P23 and P38 show the familiar pattern: replacement of M3 by M11 gives a harder, powdery, less fibrous polymer, with a higher T_f, and the replacement by M19 gives a black, non-liquid-crystalline resin. P39 and P40, containing isophthaloyl units, are both hard, non-fibrous and have a high T_f; however, P41 is fibrous and has a lower T_f, suggesting that it may be possible, in this series at least, to compensate for the angular isophthaloyl unit by increasing the proportion of M3.

Series E. Variation in the proportion of the 6-oxy-2-naphthoyl unit

The surprisingly fibrous character of P24, containing 50% of angular units, and the difference between P39 and P41 (series D), invited investigation of the series

---

* In the preparation of these polymers (for details, see part 1), the reaction mixture gradually solidifies when the vacuum is applied (to remove residual acetic acid), and so stirring cannot be maintained for the normal period of time. It must therefore be recognized that the molecular weight range in these polymers may be very different from the others

† In the preparation of these polymers (cf. part 1), the reaction mixture solidifies immediately when the vacuum is applied. The final period of stirring is therefore omitted, and the *caveat* in the previous footnote applies here also

below, in which the proportion of M3 is varied.

[P14: $(M4)_1$ $(M2)_1$ $(M3)_1$ $T_f = 280$, $T_{cn} = 300$]

[P7: $(M4)_1$ $(M2)_1$ $(M3)_2$ $T_f = 270$, $T_{cn} = 290$]

[P15: $(M4)_1$ $(M2)_1$ $(M3)_3$ $T_f = 270$, $T_{cn} = 270$]

P42*: $(M4)_1$ $(M18)_1$ $(M3)_1$ $T_m = 350$

[P24: $(M4)_1$ $(M18)_1$ $(M3)_2$ $T_f = 240$, $T_{cn} = 250$]

P43: $(M4)_1$ $(M18)_1$ $(M3)_3$ $T_f = 315$, $T_{cn} = 305$

In the first three members of the series, which contain terephthaloyl units, variation in the proportion of M3 has only a marginal effect on the appearance and melting characteristics of the polymers. Of the remaining three polymers, however, which are derived from isophthalic acid, only P24 and P43 are fibrous, and similar to P14, P7 and P15. P42 is brittle, crumbly, and gives a melt which, although containing some liquid-crystalline domains, is largely isotropic.

Series F. Polymers derived from the oxadiazolediyl-dibenzoic acids M7 and M8

The fibrous character of P24 also suggested that there might be fibre-forming potential in members of the following series, containing another angular dicarboxylic acid. Although P16–P18 (part 1) had shown no obvious propensity towards fibre formation, it was hoped that a different combination of disrupting units, angular and lateral, might prove more effective.

[P16: $(M4)_1$ $(M7)_1$ $(M3)_2$ $T_f \sim 230$, not liquid crystalline]

[P17: $(M1)_1$ $(M2)_{0.5}$ $(M7)_{0.5}$ $(M3)_2$ $T_f = 290$, T_{cn} not observed]

[P18: $(M1)_1$ $(M8)_1$ $(M3)_2$ $T_f = 175$, $T_{cn} = 190$]

P44: $(M1)_1$ $(M7)_{0.5}$ $(M18)_{0.5}$ $(M3)_2$ $T_f = T_{cn} = 270$

P45: $(M15)_1$ $(M7)_1$ $(M3)_2$ $T_f = T_{cn} = 200$

P46: $(M16)_1$ $(M7)_1$ $(M3)_2$ $T_f = T_{cn} = 220$, $T_m = 420$

P47‡: $(M15)_1$ $(M8)_1$ $(M3)_2$ $T_f = 180$, $T_{cn} = 210$

P48§: $(M16)_1$ $(M8)_1$ $(M3)_2$ $T_f = 185$, $T_{cn} = 205$

However, like P16–P18, none of the new polymers in the series shows obviously fibrous character. P44 has an almost ceramic-like appearance, and P45–P48 are all hard, dark and glassy. Interestingly, however, these last four have relatively low solid-to-liquid-crystalline transition temperatures, and flow readily at these temperatures to produce threaded nematic melts. Whether these unusual characteristics genuinely represent the structural consequences of the oxadiazole-containing unit, or whether they merely reflect a lower degree of polymerization, is not yet clear.

Series G. Polymers derived from the thiadiazolediyl-dibenzoic acid M17

It was hoped that the less angular nature of this monomer (cf. *Figure 1*) would result in polymers with more fibrous character than those of the preceding series.

P49†: $(M1)_1$ $(M17)_1$ $(M3)_2$ $T_f = 215$, $T_{cn} = 230$

P50¶: $(M15)_1$ $(M17)_1$ $(M3)_2$ $T_f = 185$, $T_{cn} = 210$ (v. broad)

P51: $(M16)_1$ $(M17)_1$ $(M3)_2$ $T_f = 235$, $T_{cn} = 245$

All three of the above, however, are very similar in physical appearance to their oxadiazole-containing counterparts. They are considerably less stable thermally: all three undergo extensive decomposition, with gas evolution, at temperatures between 350 and 400°C.

Series H. Polymers derived from the bis-oxadiazole monomers M12–M14

These tetracyclic monomers were of interest not only on account of their length, but because of the various disruptive effects possible.

P52: $(M12)_1$ $(M2)_1$ $(M3)_2$ $T_f = 170$, $T_{cn} = 190$

P53*: $(M13)_1$ $(M2)_1$ $(M3)_2$ $T_f = 320$, $T_{cn} = 345$

P54†: $(M14)_1$ $(M2)_1$ $(M3)_2$ T_f not observed

P52 is a smooth, but brittle, light brown polymer, whereas P53 and P54 are both rough textured. Both P52 and P53 are liquid crystalline. P52 forms a highly mobile liquid-crystalline phase at temperatures above 200°C, and P53, although more intractable, flows readily at 370°C, and is still liquid crystalline (although extensively decomposed) at temperatures as high as 450°C. However, P54 is still essentially solid at 500°C, well above the temperature at which decomposition sets in.

Selection of polymers for further evaluation

Since the ultimate objective of this study was the production of polymer fibres, the following nine polymers were selected for further evaluation:

(i) P24, P26, P31 and P33, all of which, as originally made, are obviously fibrous in character;

(ii) P46, P48, P50 and P52, which, although not obviously fibrous, are liquid crystalline and possess a sufficiently low T_f to be melt-processable at relatively low temperatures;

(iii) for comparison purposes, P25, which is not liquid crystalline.

The thermal stability of all these polymers, determined by t.g.a. (*Table 1*), is adequate for the fibre-forming study. It is interesting to note that the thiadiazole-containing polymer P50 is the least stable, by a considerable margin;

Table 1 Thermal stability of the selected polymers

	Temperature (°C) corresponding to weight loss of		
Polymer no.	2%	5%	10%
[P_R	493	496	499]
P24	415	429	439
P25	356	400	405
P26	396	428	444
P31	420	435	448
P33	448	453	462
P46	391	400	420
P48	351	381	400
P50	336	349	356
P52	381	391	410

---

* In the preparation of these polymers (for details, see part 1), the reaction mixture gradually solidifies when the vacuum is applied (to remove residual acetic acid), and so stirring cannot be maintained for the normal period of time. It must therefore be recognized that the molecular weight range in these polymers may be very different from the others

† In the preparation of these polymers (cf. part 1), the reaction mixture solidifies immediately when the vacuum is applied. The final period of stirring is therefore omitted, and the *caveat* in the previous footnote applies here also

‡ In the preparation of this polymer, the end-temperature was 280°C, since the melt appeared to be isotropic at 230°C

§ In the preparation of this polymer, the end-temperature was 220°C

¶ In the preparation of this polymer, the end-temperature was 280°C, since decomposition set in at 320°C this confirms the visual observation (by h.s.m.) of decomposition at temperatures above 350°C, and this degradation is also evident from the d.s.c. thermogram (*Figure 4*). Whether or not this degradation is the result of thermolysis of the heterocyclic ring, akin to that previously reported for poly(*p*-phenylene-1,3,4-thiadiazole)[13], remains an open question.

CONCLUSIONS

From the information collected here and in part 1[1], some general trends have become apparent, both within and across the various series.

Fibrous character

Replacement of the linear *p*-phenylenedioxy-unit (from M1) in P_R by any of the angular arylenedioxy units derived from M4, M9 or M15, or by the laterally disrupting 1,5-naphthylenedioxy unit (from M16), makes very little difference, visually at least, to the fibrous character of the polymer. The additional replacement of the terephthaloyl unit by isophthaloyl, as in P24, still produces a fibrous polymer, although now the proportion of the 6-oxy-2-naphthoyl unit (from M3) becomes more critical. Use of the other angular dicarboxylic acids (M7, M8 and M17) in place of terephthalic acid, however, produces non-fibrous polymers. Fibre formation during the polymerization is also less pronounced when the laterally-disrupting 6-oxy-2-isophthaloyl unit is replaced by *p*-oxybenzoyl, and incorporation of *m*-oxybenzoyl units produces polymers which are both non-fibrous and non-liquid-crystalline.

Thermal behaviour

The d.s.c. thermograms for the nine selected polymers are reproduced in *Figures 2–4*, along with those of P7, P19 and P21 (cf. part 1)[1] for comparison purposes.

Figure 2 relates to four polymers based on the oxadiazole-containing diacetate M4, and shows the effect of varying the dicarboxylic acid or acetoxy-acid component. Replacement of the terephthalic acid, as in P7, by isophthalic acid, as in P24, brings about a lowering of T_{cn} by about 50°C; this presumably reflects the increased proportion of angular disruptors in the latter. Replacement of the acetoxynaphthoic acid, as in P7, by *p*-acetoxybenzoic acid, as in P19, causes a slight increase in T_{cn}. P25, as already noted, is not liquid crystalline, with the higher d.s.c. endotherm corresponding to the visually observed melting point.

The five thermograms in *Figure 3* relate to polymers formed from terephthalic acid, 6-acetoxy-2-naphthoic acid and a variety of diacetates. Replacement of the bis-acetoxyphenyl-oxadiazole M4, as in P7, by the (presumably more rigid) 2,7-diacetoxynaphthalene (M15), as in P26, causes a small increase in T_{cn}. Replacement of only half of M4 by M15, however, as in P31, depresses the value of T_{cn}, presumably because of increased randomization within the polymer chains. Replacement of M4 by 1,5-diacetoxynaphthalene (M16), which is mesogenic, ought to result in an increase in T_{cn} and, although the endotherm is not in fact observed for P33, the observed increase in T_f points in the correct direction. Replacement of M4 by the bis-acetoxynaphthyl-oxadiazole M9, as in P21, causes a significant lowering of T_{cn}; this diacetate, of course, may be expected to exert both angular and lateral disruptive effects.

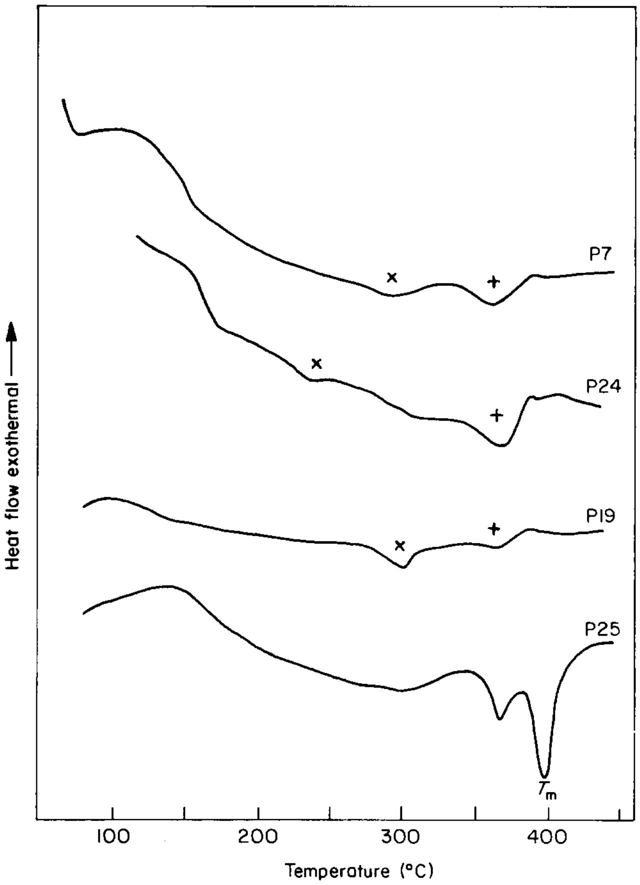


Figure 2 D.s.c. thermograms of P7, P19, P24 and P25 (heating rate 50°C min^{-1}): ×, 1st endotherm; +, 2nd endotherm

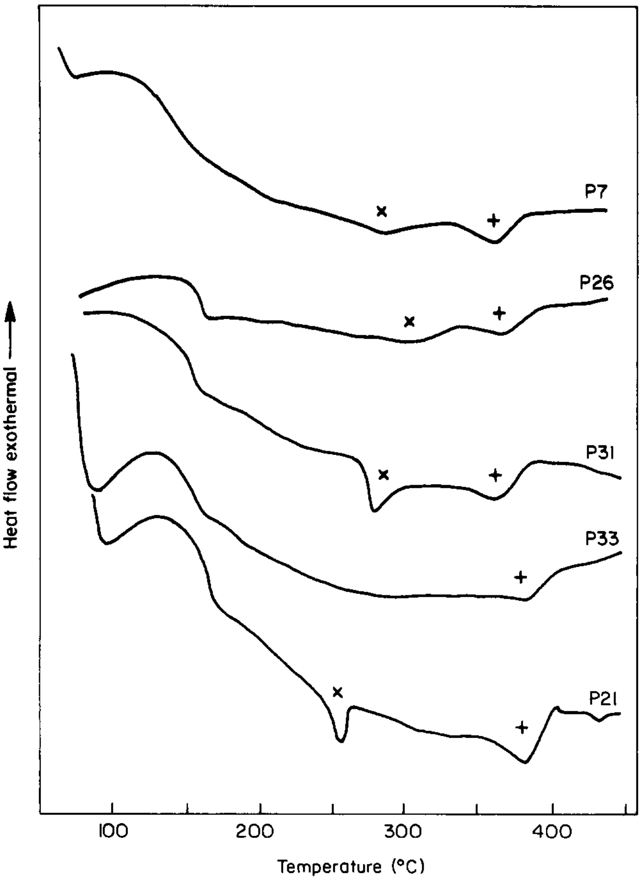


Figure 3 D.s.c. thermograms of P7, P21, P26, P31 and P33 (heating rate 50°C min^{-1}): ×, 1st endotherm; +, 2nd endotherm

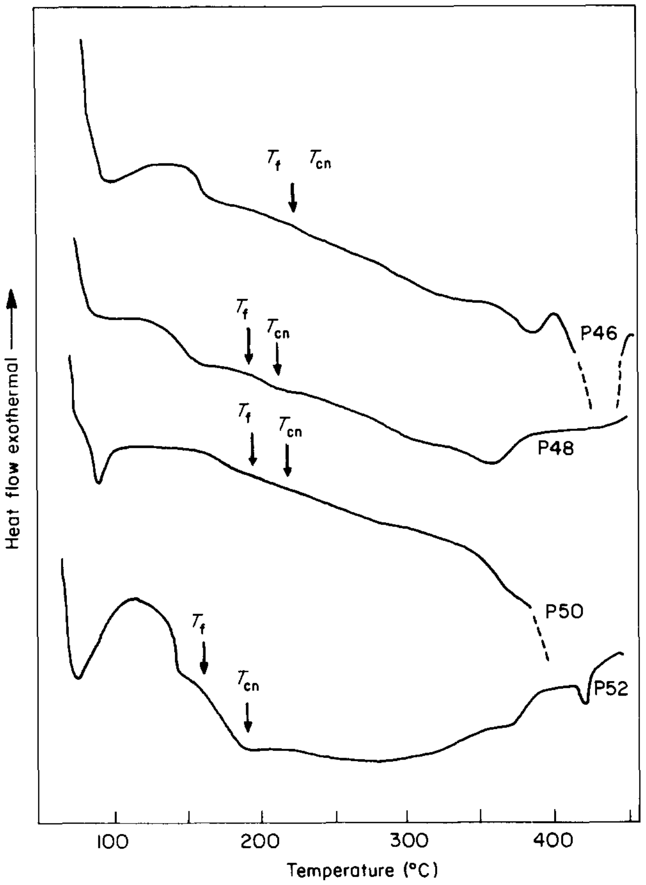


Figure 4 D.s.c. thermograms of P46, P48, P50 and P52 (heating rate 50°C min^{-1}): ×, 1st endotherm; +, 2nd endotherm

The final group of thermograms (*Figure 4*) are those obtained from P46, P48, P50 and P52, which were selected for further evaluation (see above) on the basis of their observed liquid crystallinity and on their relatively low T_f values. Of these four, only P52 shows an endotherm corresponding to T_{cn} at the normal recorder amplification. For the other three, which are derived from oxadiazoledicarboxylic acids, the heat changes associated with this transition are very small, and a much higher amplification is required before they are readily discernible on the thermogram. In such cases, where the thermogram is relatively featureless, h.s.m. provides the only reliable method for determining the temperature at which the transition occurs.

The formation and characteristics of fibres from these selected polymers, and a similar selection from part 1[1], will be described in part 3[14].

ACKNOWLEDGEMENTS

The authors thank Dr W. A. MacDonald and Mr I. D. Luscombe (ICI Materials Research Centre, Wilton), respectively, for valuable discussions and assistance with hot-stage microscopy and are indebted to ICI for the gift of some monomers and glassware. Mrs S. Smith, Mrs M. H. Smith and Mr C. Millar (St Andrews) are thanked for microanalysis, n.m.r. spectra and mass spectra, respectively; Mr I. B. McGann (Galashiels) for the illustrations; and the SERC for the award of a Research Studentship to J. E.

REFERENCES

1 Brydon, D. L., Fisher, I. S., Emans, J., Smith, D. M. and MacDonald, W. A. *Polymer* 1989, **30**, 619
2 Lenz, R. W. and Jin, J. I. *Macromolecules* 1981, **14**, 1405
3 Saalfrank, R. W., Weiss, B., Peters, K. and von Schnering, H. G. *Chem. Ber.* 1985, **118**, 4026
4 La Cour, T. *Acta Cryst.* (*B*) 1974, **30**, 1642
5 Bak, B., Nygaard, L., Pedersen, E. J. and Rastrup-Andersen, J. *J. Mol. Spectr.* 1966, **19**, 283
6 Markov, P. and Stoelevik, R. *Acta Chem. Scand.* 1970, **24**, 2525
7 Jensen, K. A. and Pedersen, C. *Acta Chem. Scand.* 1965, **15**, 1087, 1097 and 1124
8 Mazzone, G., Puglisi, G. and Bonina, F. *J. Heterocycl. Chem.* 1983, **20**, 1399
9 Javaid, K. and Smith, D. M. *J. Chem. Res.* 1984, (S) 118, (M) 985
10 Davidis, E. *J. Prakt. Chem.* 1896, **54**, 81
11 Weber, A. *Ber. Dtsch Chem. Ges.* 1881, **14**, 2206
12 Bernthsen, A. and Semper, A. *Ber. Dtsch Chem. Ges.* 1887, **20**, 934
13 Rode, V. V., Bondarenko, Ye. M., D'yachenko, A. V., Krongauz, Ye. S. and Korshak, V. V. *Polym. Sci.* (*USSR*) 1969, **11**, 935
14 Brydon, D. L., Fisher, I. S., Emans, J. and Smith, D. M. in preparation