Thermotropic polyesters: synthesis and properties of highly disordered copolymers

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Sixteen nematogenic copolyesters were synthesized from four to seven different aromatic reactants, with the objective of suppressing crystallization. The constituent units contained rod-like 1,4-phenylene and 4,4'-biphenylene groups, crankshaft 2,6-naphthylene group and rigid angular 1,3-phenylene group. Wide-angle X-ray diffraction, differential scanning calorimetry and hot-stage optical microscopy showed that five of the copolyesters could be classified as lacking three-dimensional order. Within the range of compositions studied, a large number of different units of different types is conducive to suppressing crystallization.

INTRODUCTION

Rigid-chain homopolyesters, such as poly(4-oxybenzoate) and poly(1,4-phenylene terephthalate), are not melt processable owing to their high melting temperatures. Methods of modification of the constitution of these parent homopolymers, resulting in melt-processable nematogenic copolymers, are well documented[1,2]. For polymers intended to be used as high-performance materials, the objective of these modifications is to reduce the crystal–nematic transition temperature at least about 30°C below the thermal stability limit. For practical exploitation of these materials it is desirable that their ability to crystallize is maintained.

However, there is another potentially important range of applications of nematogenic copolymers, as minor components in blends with linear flexible-chain polymer[3,4]. Significant reduction of melt viscosity resulting from even small proportions of a liquid-crystalline polymer has been reported[5,6] and detailed investigations of morphology and flow properties of blends containing liquid-crystalline copolyesters have been carried out[7,8]. Liquid-crystalline polymers also have a significant effect in reducing the orientation of fibres produced by melt spinning of conventional fibre-forming polymers[9].

Hitherto, liquid-crystalline polymers designed primarily as high-performance materials have been used as processing aids in blends. These materials generally have a melting temperature that is too high to satisfy the requirements of lower-melting matrices. Development of liquid-crystalline polymers with lower flow temperature is therefore highly desirable. Heitz and Schmidt[10] argued

that materials in which crystallization is completely suppressed would be particularly suitable.

Krigbaum et al.[11] indicated that poly(phenyl-1,4-phenylene phenyl terephthalate) did not crystallize, and Heitz and Schmidt[10] synthesized several other non-crystalline disubstituted poly(1,4-phenylene terephthalate)s. Sinta et al.[12] made a range of liquid-crystalline copolyesters where crystallinity has been eliminated using substituted 1,4-phenylene groups and 2,2'-disubstituted 4,4'-biphenylene groups.

The purpose of the work reported here was to explore the possibility of suppressing the crystallization in unsubstituted fully aromatic nematogenic copolyesters using up to seven readily available monomers selected from those listed in *Table 1*.

EXPERIMENTAL

Monomers

4-Acetoxybenzoic acid (m.p. 194°C) was prepared from 4-hydroxybenzoic acid (BDH) and acetic anhydride[13]. The product was recrystallized twice from chloroform and dried under vacuum. Hydroquinone diacetate (m.p. 125°C), obtained by acetylation of hydroquinone

Table 1 Monomers employed and the resulting constituent units

Monomer	Unit	Abbreviation
4-Acetoxybenzoic acid	4-Oxybenzoyl	OPCO
Hydroquinone diacetate	1,4-Phenylenedioxy	OPO
Terephthalic acid	Terephthaloyl	COPCO
3-Acetoxybenzoic acid	3-Oxybenzoyl	OMCO
Resorcinol diacetate	1,3-Phenylenedioxy	OMO
Isophthalic acid	Isophthaloyl	COMCO
6-Acetoxy-2-naphthoic acid	6-Oxy-2-naphthoyl	ONCO
4,4'-Diacetoxybiphenyl	4,4'-Biphenylenedioxy	OPPO

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(Aldrich, 99%), was recrystallized from 50% aqueous ethanol and dried under vacuum. Terephthalic acid of fibre-grade purity (supplied by ICI plc) was used without further purification. 3-Acetoxybenzoic acid (m.p. 133°C), obtained by acetylation of 3-hydroxybenzoic acid (Aldrich, 95%), was recrystallized from 50% aqueous ethanol. Preparation of resorcinol diacetate has been described previously[14]. Isophthalic acid (Aldrich, 99%) was used without further purification. 6-Acetoxy-2-naphthoic acid (m.p. 227–230°C), kindly donated by Celanese Inc., was recrystallized from dioxane. 4,4'-Diacetoxybiphenyl (m.p. 164–166°C), obtained by acetylation of 4,4'-biphenol (Aldrich, 97%), was recrystallized twice from ethanol/toluene (80/20) mixture.

Polymer preparation

Polymers were prepared on a 0.03 mol scale without added catalyst, following the procedure described previously[15]. Unless otherwise stated, the mixture of monomers (*Table 2*) was maintained at 282°C for 1 h under dry nitrogen and then for a further 1 h under vacuum (10 Pa). During the first stage the stillhead was kept cold in order to diminish the evaporation or sublimation of the monomers. Only in the trials where terephthalic acid was absent was the mixture of melted monomers clear. Terephthalic acid at first remained undissolved in the melt in the form of white particles but later swelled and formed flakes suspended in the clear melt phase. With the exceptions indicated in *Table 2*, polymers were liquid after the completion of the reaction. They were pulled from the polymerization tube using a fitting glass tube. In some cases this resulted in the development of a distinct fibrillar texture.

Polymer characterization

Solution viscosities were measured at 25°C in a 60/40 wt/wt mixture of phenol and tetrachloroethane at a concentration of 0.25 g dl^{-1}.

Microscopic observations of flow (T_f) and decomposition (T_d) temperatures were carried out using an Olympus polarizing microscope (model BH-2) equipped with a Stanton–Redcroft hot stage (type TH600) fitted with nitrogen purge. Samples were placed between glass coverslips under a load of 0.27 N. The heating rate was 20°C min^{-1}. The difference between repeated measurements did not exceed 6°C for flow temperatures and 8°C for decomposition temperatures.

Transition temperatures and enthalpies were determined using a DuPont 910 Differential Scanning Calorimeter controlled by a Thermal Analyst 2000 system. The sample weight was approximately 8 mg; the heating rate was 20°C min^{-1}.

A DuPont 951 Thermogravimetric Analyzer controlled by a Thermal Analyst 2000 system was used for studying the content of low-molecular-weight species in the polymers and for the assessment of thermal stabilities. The sample weight was 8–10 mg. Evaluation was carried out under nitrogen (50 ml min^{-1}) at a heating rate of 20°C min^{-1}.

Wide-angle X-ray patterns were recorded on film in a flat-plate camera using nickel-filtered Cu K_α radiation and reproduced using a video camera coupled to a Mitsubishi Video Printer. The integral breadths of azimuthal intensity distributions were obtained from X-ray films using a Quantimet 570 Image Analyzer with software developed by Dobb and Park[16].

The diffractometer traces were obtained with a Spectrolab Series 3000 diffractometer with Inel XRG-3000 X-ray generator and Inel CPS-120 curved position-sensitive detector, using a procedure described elsewhere[17].

RESULTS AND DISCUSSION

The concentrations of the reactants used for the synthesis of the polymers investigated are shown in *Table 2*. The polymerization conditions have not been optimized, and

Table 2 Composition of highly disordered copolyesters (abbreviations as in *Table 1*)

Polymer	η_{inh} (dl g^{-1})	Amount of unit (mol%)							
		OPCO	OPO	COPCO	OMCO	OMO	COMCO	ONCO	OPPO
I	0.58[d]	25	0	0	0	0	25	25	25
II	0.47[d]	30	10	10	0	0	25	0	25
III	0.80	40	0	10	10	0	15	0	25
IV	0.63	15	0	10	10	0	15	25	25
V[a]	_[c]	20	0	10	0	0	30	0	40
VI[b]	0.55[d]	30	0	10	10	0	20	0	30
VII[a]	_[c]	0	0	20	10	0	20	10	40
VIII	0.74	10	0	0	10	0	20	40	20
IX	0.41[d]	50	10	10	10	10	10	0	0
X	0.66	50	0	10	10	10	10	0	10
XI	0.75	30	10	10	10	0	20	0	20
XII	0.59	10	0	10	10	0	20	20	30
XIII	0.62	0	10	10	10	0	20	30	20
XIV	0.54	0	10	10	10	10	10	50	0
XV	0.58	25	10	10	10	10	10	25	0
XVI	0.58	10	10	10	10	10	10	40	0

[a] Polymers solidified at polymerization temperature of 310°C
[b] Polymer solidified
[c] Insoluble in phenol/tetrachloroethane (60/40) mixture
[d] Partially soluble; fraction of undissolved material was less than 5%

no attempt has been made at this stage to compensate for the loss of volatile monomers[14,18], which in this case would be the two phenylene diacetates. Nevertheless, the solution viscosities (*Table 2*) were sufficiently high for a meaningful evaluation of the properties of these materials. Some polymers were either insoluble or partly insoluble in the solvent employed.

All the polymers showed good thermal stability (*Table 3*), as expected for fully aromatic polyesters. The onset of decomposition observed by hot-stage microscopy ranged from 473 to 490°C, and the temperatures $T(5\%)$ corresponding to 5% weight loss (obtained from t.g.a. curves, see *Figure 1*) were between 461 and 519°C. Typically, the temperatures corresponding to 2% weight loss, $T(2\%)$, were between 30 and 50°C below $T(5\%)$. However, three polymers (II, VII and IX) showed larger

Figure 1 T.g.a. curves of the following polymers: (a) V, (b) VII, (c) IX

Table 3 Thermal stabilities of highly disordered copolyesters determined by hot-stage microscopy, T_d, and by t.g.a., $T(2\%)$ and $T(5\%)$

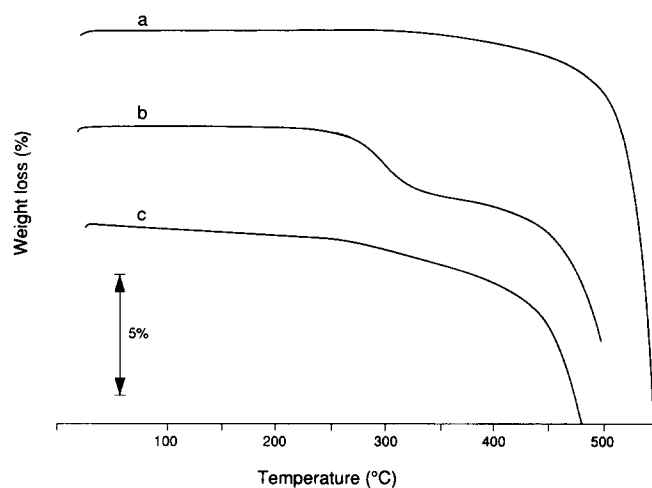| Polymer	T_d (°C)	$T(2\%)$ (°C)	$T(5\%)$ (°C)
I	488	451	489
II	476	364ᵃ	469
III	490	457	490
IV	489	435	484
V	490	489	519
VI	490	455	493
VII	482	327ᵃ	463
VIII	490	445	484
IX	480	385	461
X	488	450	484
XI	484	443	490
XII	478	442	488
XIII	490	458	490
XIV	473	444	478
XV	474	438	470
XVI	482	444	474

ᵃ Two-step t.g.a. curve

Table 4 Features of highly disordered copolyesters: n = number of different units; [R] = concentration of rod-like aromatic units containing 1,4-phenylene or 4,4'-biphenylene groups; [N] = concentration of crankshaft units containing 2,6-naphthylene groups; [M] = concentration of units containing rigid angular 1,3-phenylene groups

Polymer	n	Amount of units (mol%)			WAXSᵃ	D.s.c.ᵇ
		[R]	[N]	[M]		
I	4	50	25	25	C	c
II	5	75	0	25	C	c
III	5	75	0	25	H	c
IV	6	50	25	25	H	nd
V	4	70	0	30	C	c
VI	5	70	0	30	C	c
VII	5	60	10	30	C	c
VIII	5	30	40	30	H/M	nd
IX	6	70	0	30	Cᶜ	c
X	6	70	0	30	H	c
XI	6	70	0	30	H	c
XII	6	50	20	30	C	c
XIII	6	40	30	30	H	nd
XIV	6	20	50	30	H/M	nd
XV	7	45	25	30	H	nd
XVI	7	30	40	30	H/M	nd

ᵃ C = sharp reflections present; H = broad halo only; H/M = broad halo together with at least one meridional reflection
ᵇ c = d.s.c. curve shows melting endotherm; nd = melting endotherm not detected
ᶜ One sharp reflection only

differences between $T(2\%)$ and $T(5\%)$; this is ascribed to loss of low-molecular-weight species, taking place before the onset of decomposition. Two of these materials, II and VII, displayed a step in their t.g.a. curves, corresponding to a weight loss of about 1% and 3%, respectively.

From the t.g.a. evidence, in conjunction with the acceptable values of solution viscosities, it is concluded that the compositions of copolymers do not differ substantially from those calculated from the concentrations of monomers.

Table 4 expresses the features of the constitution of the copolymers in more general terms, giving the number of different units, n, the total concentration of rod-like aromatic units containing 1,4-phenylene or 4,4'-biphenylene groups, [R], the concentration of crankshaft units containing 2,6-naphthylene groups, [N], and the concentration of units containing rigid angular 1,3-phenylene groups, [M].

In polymers I–IV the concentration of angular units [M] was 25 mol%, but in polymers V–XVI it was increased to 30 mol%. Previous work[14,18] showed that this level of angular disruptor units is not enough to destroy the nematogenic character of otherwise rigid-rod aromatic copolyesters. This has been confirmed for the present series of copolymers; in all cases the nematic mesophase was formed above the flow temperature and persisted until the onset of decomposition.

The appearance of the polymer at the polymerization temperature (282 or 310°C, see *Table 2*) gave the first indication whether the attempt to suppress the crystallization had been successful. The formation of smectic mesophases in the copolymers investigated can be ruled out, because of the absence of periodicity along the chain required for their occurrence. Hence, the polymers that solidified during the polymerization (V, VI, VII) had obviously crystallized.

WAXS patterns yield the most direct evidence of the presence of crystalline order. Six of the polymers (I, II, V–VII and XII), including those which solidified during the polymerization, showed diffractometer traces with at least two distinct peaks (*Table 4*). An example of such a trace is shown in *Figure 2a*. The d-spacings of the prominent peaks are about 0.375 to 0.46 nm, respectively (*Table 5*). These correspond to strong reflections in poly(4-oxybenzoate)[19], where $d_{110} = 0.454$ nm
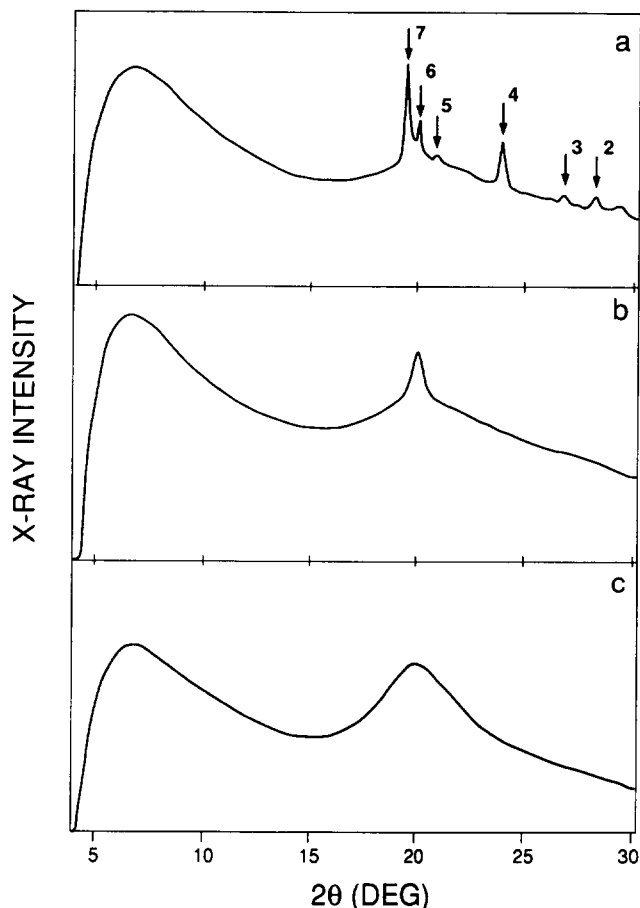
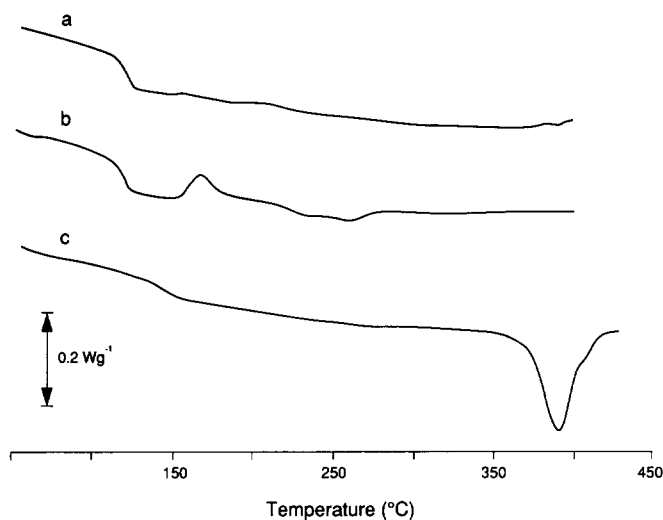**Figure 2** X-ray diffractometer traces of the following polymers: (a) V, (b) IX, (c) III

Figure 3 D.s.c. curves of the following polymers: (a) VIII, (b) XI, (c) V

and $d_{200} = 0.376$ nm; the second rigid-chain homopolyester, poly(1,4-phenylene terephthalate), shows prominent reflections with the following d-spacings (nm): 0.486 (w), 0.437 (vs), 0.390 (m) and 0.316 (m) (see ref. 17).

With the exception of polymer XII, the semicrystalline polymers were either insoluble (V, VII) or only partially soluble (I, II, VI). This is in agreement with previous experience that the presence of crystalline structure results in reduced solubility.

In agreement with the WAXS evidence, the d.s.c. curves (*Figure 3c*) of the semicrystalline polymers revealed broad but identifiable endotherms, corresponding to the onset of flow (*Table 6*). However, the enthalpy changes of crystal–nematic transitions were small, ranging from 6 to 18 J g^{-1}. This indicates a low level of crystallinity, as would be expected for copolymers with at least four constituent units (*Table 4*).

This low level of crystallinity did not result in the disappearance of the stepwise change of heat capacity (*Figure 3*) ascribed to the glass transition, which occurred at temperatures ranging from 107 to 141°C for the whole series (*Table 7*). Significant reductions in ΔC_p were noted only for polymers V and VII, which gave the highest ΔH values of about 18 J g^{-1}.

The WAXS patterns of polymer IX, containing 50 mol% of OPCO units, showed only one sharp peak with a d-spacing of 0.44 nm (*Figure 2b*). However, partial insolubility, a small but distinct endotherm and a high flow temperature of 312°C indicate that this material cannot be classified as non-crystalline.

The WAXS patterns of the remaining nine polymers (*Table 4*) did not reveal any sharp reflections. A typical

Table 5 X-ray reflections in semicrystalline polymers[a]

	d-spacing (nm)					
Peak	I	II	V	VI	VII	XII
1				0.305 vw	0.304 m	
2	0.318 w	0.318 s	0.317 m	0.319 w	0.317 m	0.318 w
3	0.336 w	0.350 m	0.334 m			
4	0.377 vs	0.374 s	0.373 vs	0.377 vs	0.375 vs	0.378 s
5			0.428 w		0.428 w	0.435 m
6	0.450 s	0.447 w	0.446 s	0.449 s	0.446 s	
7	0.461 vs	0.458 vs	0.457 vs	0.462 vs	0.458 vs	0.462 s
8		0.472 m				
9		0.502 vs				

[a] Key: vw = very weak; w = weak; m = medium; s = strong; vs = very strong

Table 6 Melting behaviour of highly disordered copolyesters: flow temperature T_f determined by hot-stage microscopy; melting endotherm determined by d.s.c.

Polymer	T_f (°C)	Endotherm		
		Range (°C)	Peak (°C)	ΔH (J g^{-1})
I	270	230–300	275	10
II	276	238–340	275	6
III[b]	260	200–290	260	3
IV	150	–[a]	–[a]	–[a]
V	422	340–420	387	17
VI	295	230–325	276	12
VII	350	250–386	351	18
VIII	165	–[a]	–[a]	–[a]
IX	312	229–356	270	3
X	240	190–280	238	2
XI[c]	260	210–296	257	4
XII	290	225–325	280	6
XIII	185	–[a]	–[a]	–[a]
XIV	200	–[a]	–[a]	–[a]
XV	250	–[a]	–[a]	–[a]
XVI	200	–[a]	–[a]	–[a]

[a] No clear endotherm detected
[b] D.s.c. heating curve showed a small crystallization exotherm between 136 and 192°C, peak at 150°C, $\Delta H \simeq 2$ J g^{-1}
[c] D.s.c. heating curve showed a small crystallization exotherm between 146 and 220°C, peak at 167°C, $\Delta H \simeq 3$ J g^{-1}

Table 7 Glass transitions of highly disordered copolyesters

Polymer	Range (°C)	T_g (°C)	ΔC_p (J g^{-1} K^{-1})
I	109–122	116	0.25
II	100–117	107	0.24
III	107–120	114	0.28
IV	107–119	114	0.24
V	136–151	141	0.12
VI	109–125	119	0.21
VII	116–133	124	0.17
VIII	117–126	122	0.23
IX	101–120	109	0.19
X	103–117	110	0.25
XI	112–125	120	0.25
XII	113–124	119	0.27
XIII	115–126	122	0.23
XIV	111–125	117	0.25
XV	107–121	115	0.21
XVI	110–125	118	0.22
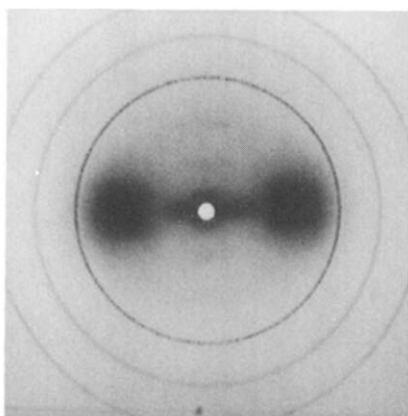
Figure 4 Wide-angle X-ray pattern of the fibrillar portion of polymer XIV; sharp rings are due to silver foil used for calibration

diffractometer trace (*Figure 2c*) displays only a broad halo with an average d-spacing of about 0.44 nm. Interestingly, the X-ray patterns revealed that these as-made polymers were oriented (*Figure 4*), particularly the regions with pronounced fibrillar texture originating from extension during removal from the polymerization tubes. The integral breadths of the azimuthal scans of the halo were between 45 and 80°. In addition to the halo centred around the equator, polymers VIII and XVI (40 mol% of ONCO units) showed a weak meridional reflection with a d-spacing of about 0.675 nm. Polymer XIV, containing 50 mol% of ONCO units, showed in addition a second very weak meridional reflection with a d-spacing of about 0.42 nm. These meridional reflections were more pronounced in the fibrillar portions. Such aperiodic meridional reflections have been described in other thermotropic copolymers containing 2,6-naphthylene groups[20] or 1,3-phenylene groups[21]. The presence of these meridional reflections is not evidence of crystalline order. They are attributed to intramolecular correlations[22]; in the case of poly(4-oxybenzoate-*co*-1,4-phenylene isophthalate)s, this interpretation has been confirmed using Fourier transforms of model chains[23].

The occurrence of sharp reflections in WAXS patterns represents the most direct evidence for the presence of crystallinity, but their absence does not completely rule

out the possibility that the material contains small imperfect crystallites[24]. In order to establish the absence of crystallinity it is essential to consider also the thermal transitions detected by d.s.c. and the flow behaviour revealed by direct observations by hot-stage microscopy. The d.s.c. curve of polymer X revealed a very small endotherm coinciding with the onset of flow and formation of a nematic mesophase. Polymers III and XI showed small exotherms above the glass transition region (*Figure 3b*), which are assigned to crystallization, and endotherms, arising from the subsequent melting of the crystallites, that coincided with the onset of flow (*Table 6*). Hence, these three materials cannot be classified as truly non-crystalline.

The remaining six polymers (IV, VIII, XIII–XVI) did not display any discernible endotherms. Their flow temperatures (*Table 6*) ranged from 150 to 250°C, i.e. between 30°C (polymer IV) and 130°C (polymer XV) above the glass transition region. In all cases the resulting nematic mesophase remained stable until the onset of decomposition. In spite of the lack of WAXS and d.s.c. confirmation, the high flow temperature of polymer XV may indicate the presence of some ordered structures.

SUMMARY AND CONCLUSIONS

The main purpose of this exploratory investigation was to identify the features of chain constitution required for suppressing crystallization in wholly aromatic unsubstituted nematogenic copolyesters. In order to maintain the nematogenic character, the total concentration of rigid angular units (OMCO, OMO and COMCO) did not exceed 30 mol%. Since the reactivities of the monomers are unlikely to be identical, the copolymers may not be entirely random. However, at this stage no attempt has been made to establish the unit sequence.

The copolymers investigated can be divided into three categories: (i) semicrystalline, based on both WAXS and d.s.c. evidence; (ii) semicrystalline, based on d.s.c. evidence only; (iii) non-crystalline, based on both WAXS and d.s.c. evidence.

As far as the last category is concerned, the absence of WAXS and d.s.c. features ascribed to crystalline structures does not prove that crystallization has been suppressed completely. Here, quantitative evaluation of rheological behaviour as a function of temperature and time would be valuable[25]. Furthermore, although these polymers are classified as non-crystalline, there is no evidence that they are not crystallizable. Investigation of the effects of increased orientation and heat treatments, which should encourage crystallization, is in progress.

Inspection of *Table 4* reveals that the tendency to crystallize decreases with increasing number of constituent units, n. However, it is essential that these units are of different types. This can be illustrated by considering polymers IX–XIV where $n=6$ and concentration of angular units, [M], is 30 mol%. In polymers IX–XI, where the crankshaft units were absent ([N]=0), the crystallization has not been suppressed. Increasing [N] to 20 mol% (polymer XII) was still insufficient for suppressing crystallization. However, polymers XIII and XIV, with [N]=30 and 50 mol% respectively, were non-crystalline. Note that polymer VIII with $n=5$ but with almost equal shares of different unit types ([R]=[M]=30 mol%, [N]=40 mol%) did not crystallize.

It is concluded that it is possible to suppress crystallization in fully aromatic unsubstituted nematogenic copolyesters. At present it is not possible to give a general formula for such copolymers. This work shows that one viable strategy is to use a large number of different units of different types.

ACKNOWLEDGEMENTS

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