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Thermotropic polyesters: effect of heat treatment on thermal transitions of highly disordered copolymers

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The effect of thermally annealing five non-crystalline liquid-crystalline copolyesters, each derived from five or more different ester-forming monomers, has been examined. Four of the compositions developed low crystallinity, which was sufficient to suppress flow at temperatures below the melting temperature of crystallites. The fifth developed no crystallinity and flowed at a temperature below 190 °C.

1. Introduction

The constitution of main-chain thermotropic liquid-crystalline (TLC) copolymers used as high-performance engineering materials is such as to ensure that their crystal–nematic mesophase transition occurs at temperatures which are at least 30 °C below the onset of their thermal decomposition [1, 2]. For these materials it is desirable to maintain crystallizability. Indeed, the higher the crystallinity in the manufactured "shaped article", the less pronounced will be the undesirable decrease in the stiffness above the glass transition (usually 120–140 °C) [1–3].

However, there is now a growing interest in utilization of TLC materials as processing aids for conventional linear flexible-chain polymers [4, 5]. For some of these applications it is desirable to design TLC polymers with low flow temperatures. Materials where crystallization is completely suppressed, i.e. where nematic glass is transformed directly into nematic melt, would be particularly advantageous for this purpose.

Our previous work [6] explored the possibility of suppressing the crystallization in fully aromatic nematogenic copolyesters. The approach selected for achieving this objective was to use between four and seven different reactants selected from those shown in Fig. 1. The constitutent units in the resulting copolymers contained rod-like 1,4-phenylene and 4,4′-biphenylene groups, the crankshaft 2,6-naphthylene group, and the rigid angular 1,3-phenylene group (Fig. 1).

Sixteen copolymers were synthesized (Table I) and characterized by wide-angle X-ray scattering (WAXS) and by a range of thermo-analytical techniques. The absence of discrete reflections in WAXS patterns and the absence of a melting endotherm in differential scanning calorimeter (DSC) curves were used as the main evidence for the absence of crystallites in the "as-made" materials. Some of the materials were semicrystalline according to both WAXS and DSC criteria (category (i), Table I). Several materials which did not show any sharp reflections in their WAXS patterns displayed a melting endotherm in their DSC curves (category (ii), Table I). Whilst the crystallites in such materials are too small and/or imperfect to be detected by WAXS, the endotherm indicates that the crystallization has not been suppressed completely [7]. The remaining six materials appeared to be non-crystalline according to both WAXS and DSC criteria category (iii), Table I). However, hot-stage optical microscopy (HSOM) showed that the flow temperature of polymer XV belonging to category (iii) was about 250 °C; this has been ascribed to the presence of a small number of highly imperfect crystallites preventing the flow above the glass transition temperature revealed by DSC at 115 °C. This material cannot, therefore, be classified as completely non-crystalline.

From the results of the previous exploratory work [6] it is concluded that by using a large number of different units of three different types (i.e. rod-like, crankshaft, and rigid angular) it is possible to suppress crystallization (Table II). The absence of crystallinity in the "as-made" materials does not mean that they are non-crystallizable. The objective of this work was to establish whether extensive heat treatment induces crystallization in these materials.

Because it is known that elongational flow resulting in increased chain alignment encourages crystallization [8, 9], these materials were also melt-spun into oriented fibres, which were then subjected to heat treatment. As in the previous work, WAXS, DSC and HSOM were used to detect the development of crystallinity.

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TABLE I Composition of highly disordered copolyesters (for abbreviations see Fig. 1)

Polymer	Unit (mol %)								Type[a]
	OPCO	OPO	COPCO	OMCO	OMO	COMCO	ONCO	OPPO	
I	25	0	0	0	0	25	25	25	(i)
II	30	10	10	0	0	25	0	25	(i)
III	40	0	10	10	0	15	0	25	(ii)
IV	15	0	10	10	0	15	25	25	(iii)
V	20	0	10	0	0	30	0	40	(i)
VI	30	0	10	10	0	20	0	30	(i)
VII	0	0	20	10	0	20	10	40	(i)
VIII	10	0	0	10	0	20	40	20	(iii)
IX	50	10	10	10	10	10	0	0	(i)
X	50	0	10	10	10	10	0	10	(ii)
XI	30	10	10	10	0	20	0	20	(ii)
XII	10	0	10	10	0	20	20	30	(i)
XIII	0	10	10	10	0	20	30	20	(iii)
XIV	0	10	10	10	10	10	50	0	(iii)
XV	25	10	10	10	10	10	25	0	(iii)[b]
XVI	10	10	10	10	10	10	40	0	(iii)

[a] (i) Semicrystalline according to both WAXS and DSC evidence; (ii) semicrystalline according to DSC evidence only; (iii) non-crystalline.
[b] Flow temperature, $T_f = 250\,^{\circ}C$ (HSOM).

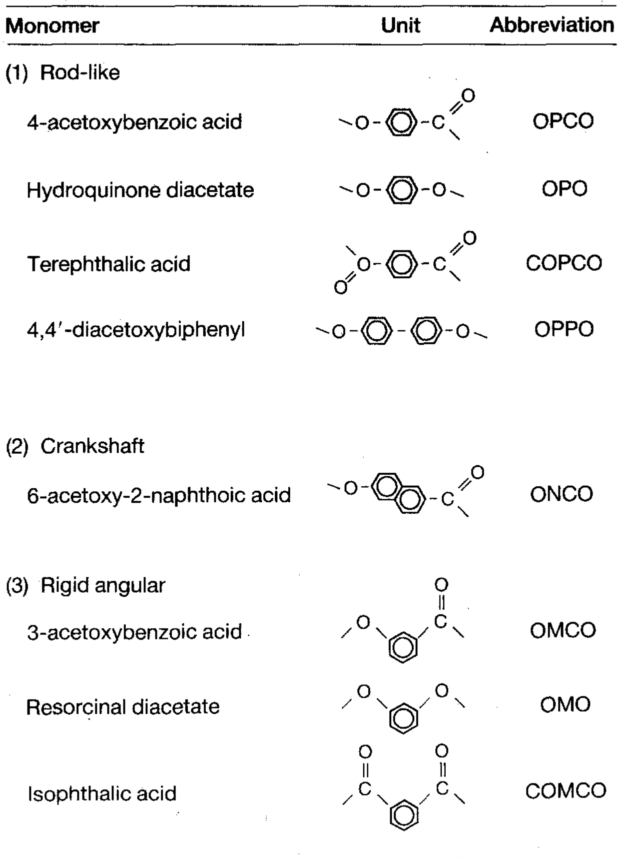

Figure 1 Monomers and resulting constituent units.

2. Experimental procedure

2.1. Polymers

The polymers investigated were the same as those previously described [6]; their solution viscosities were measured at 25 °C in a 60/40 wt/wt mixture of phenol and tetrachloroethane at a concentration of 0.25 $g\,dl^{-1}$. The heat treatments were carried out in a DSC (see below).

2.2. Fibre formation

Dried polymers (3.5 h at 100 °C under vacuum) were melt-spun from the nematic mesophase using a laboratory microspinner, which consisted of an electrically heated barrel (inner diameter 10 mm, maximum polymer capacity approximately 5 g) with a motor-driven piston. Fibres were produced at 235 °C using a single-hole spinneret (diameter 0.5 mm) and a winding speed of 120 $m\,min^{-1}$. The drawdown ratio, calculated from the cross-sectional area attenuation, was approximately 40.

Bundles of "as-spun" fibres, mounted taut in an X-ray sample holder, were heat treated in a circulating air oven. Chopped fibres were heat treated in a DSC.

2.3. Characterization of polymers and fibres

Wide-angle X-ray patterns were recorded on film in a flat-plate camera using nickel-filtered CuK_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 Analyser with software developed by Dobb and Park [10].

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

Microscopic observations of flow temperatures, T_f, 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 cover slips 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.

TABLE II Thermal transition of non-crystalline highly disordered copolyesters after heat treatment (18 h at 190 °C); n, number of different units; $[R]$, concentration of rod-like aromatic units containing 1,4-phenylene groups; $[N]$, concentration of crankshaft units containing 2,6-naphthylene groups; $[M]$, concentration of units containing rigid angular 1,3-phenylene groups

	Polymer				
	IV	VIII	XIII	XIV	XVI
n	6	5	6	6	7
$[R]$ (mol %)	50	30	40	20	30
$[N]$ (mol %)	25	40	30	50	40
$[M]$ (mol %)	25	30	30	30	30
η_{inh} (dl g^{-1})	0.63	0.74	0.62	0.54	0.58
Flow temperature (°C)	214	217	225	230	182
Glass transition					
Range (°C)	107–118	118–129	117–129	115–127	114–122
T_g (°C)	112	122	123	123	119
ΔC_p (J g^{-1} K^{-1})	0.25	0.28	0.26	0.22	0.25
Melting endotherm					
Range (°C)	199–270	200–270	196–264	200–263	[a]
Peak (°C)	221	225	221	225	[a]
ΔH (J g^{-1})	2.7	3.3	3.4	3.0	[a]

[a] Not detected.

TABLE III Features of "as-spun" (AS) and heat-treated (1 h at 145 °C) fibres (HT): B, integral breadth obtained from azimuthal scan of the equatorial scatter (WAXS); T_f, flow temperature (HSOM)

Fibre	B (deg)		T_f(°C)	
	AS	HT	AS	HT
IV	29	53	260[a]	255[a]
VIII	45	54	175	175
XIV	42	48	160	178
XVI	35	47	150	172

[a] Fibres soften at 165 °C.

3. Results

3.1. Heat treatment of polymers

The temperature for the heat treatment of the copolymers which were classified as non-crystalline (Table II) was selected as follows: according to Callundan and Jaffe [3], the minimum melting temperature of TLC copolyesters containing 1,4-phenylene, 2,6-napthylene, and 1,3-phenylene groups is around 255 °C. Because the copolymers investigated contain the same groups, we have assumed that if they crystallize, their melting temperatures should be close to this value. As the maximum rate of crystallization usually occurs at a temperature around the mid-point between the glass transition temperature (in this case about 120 °C) and the melting temperature, the heat treatment was carried out at 190 °C. The duration of the heat treatment was 18 h.

The WAXS patterns of heat treated copolymers IV, VIII, XIII and XIV revealed two or more weak but discrete reflections superimposed on the strong halo ($d \simeq 0.44$ nm) present in the "as-made" materials [6]. The most prominent reflection has a d-spacing between 0.455 and 0.465 nm; it corresponds to the strong (1 1 0) reflection in the type I structure of poly(4-oxybenzoate) [11]. The second reflection detected in these four copolymers has a d-spacing of 0.370–0.375 nm, corresponding to the (2 0 0) reflection in poly(4-oxybenzozate) [11]. Additional reflections ($d \simeq 0.33$ and 0.31 nm) were extremely weak.

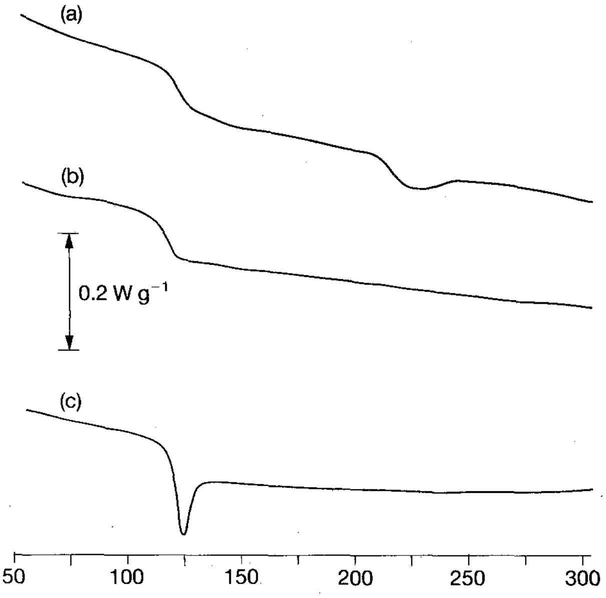

Figure 2 DSC curves of (a) polymer VIII heat treated for 18 h at 190 °C; (b) polymer XVI heat treated for 18 h at 190 °C; (c) polymer XVI heat treated for 18 h at 100 °C.

The DSC curves of these four heat-treated copolymers IV, VIII, XIII and XIV showed a broad small endotherm ($\Delta H \simeq 3$ J g^{-1}; Table II) together with a distinct endothermic step assigned to the glass transition, which was the only feature observed for the "as-made" materials (Fig. 2). The peak temperatures of the melting endotherms were about 30–35 °C above the heat-treatment (Table II). The flow temperatures observed by HSOM were close to the endotherm peak temperatures. Thus, WAXS, DSC and HSOM evidence are in agreement, showing that copolymers IV, VIII, XIII and XIV are crystallizable, although the crystallinity is obviously very low.

In contrast, the polymer XVI subjected to the same heat treatment (18 h at 190 °C) did not show any signs of crystallization as judged by WAXS or DSC and HSOM (Table II). The same results were obtained after 18 h heat treatment at 210 and 160 °C. A heat treatment below T_g (18 h at 100 °C) resulted in the appearance of an endotherm with a peak temperature of 125 °C (Fig. 2). This phenomenon, which is common in linear flexible-chain polymers [12], is ascribed to enthalpy relaxation ("physical ageing") in the glassy state.

3.2. "As-spun" fibres

The prominent feature of the WAXS patterns of the "as-spun" fibre is a broad asymmetrical equatorial scatter in the 2Θ range between 12° and 30°, as illustrated in Fig. 3. The values of integral breadths of the azimuthal intensity scans are listed in Table III.

Previous work [6] showed that the WAXS patterns of fibrillar portions of "as-made" polymers revealed one or two meridional reflections. These became more prominent in the "as-spun" fibres, particularly after increasing the X-ray film exposure time. The number of observed meridional reflections varied between one (fibre IV) and four (fibres XIV and XVI); their *d*-spacings are given in Table IV and an example of a meridional intensity trace is shown in Fig. 4. The data for fibres XIV and XVI show that the meridional reflections are aperiodic, a feature well documented for random copolymers consisting of OPCO and ONCO units [13]. It should be emphasized that the presence of such meridional reflections is not evidence of crystalline order; they arise from intramolecular interactions in extended rigid chains [14, 15].

The broad equatorial scatter and the meridional reflections were the only WAXS features of fibres produced from polymers VIII, XIV and XVI. However, the fibre produced from polymer IV showed in addition a very weak but sharp reflection with a *d*-spacing of about 0.45 nm, indicating the presence of an ordered structure.

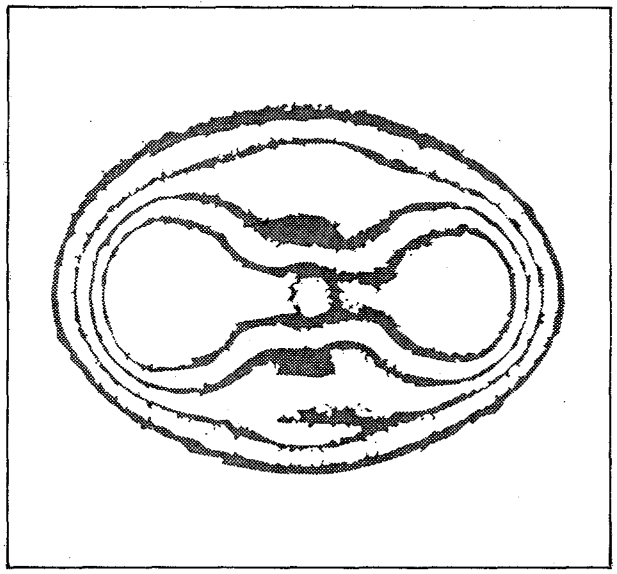

Figure 3 WAXS contour map of "as spun" fibre from polymer XIV. Fibre axis is vertical.

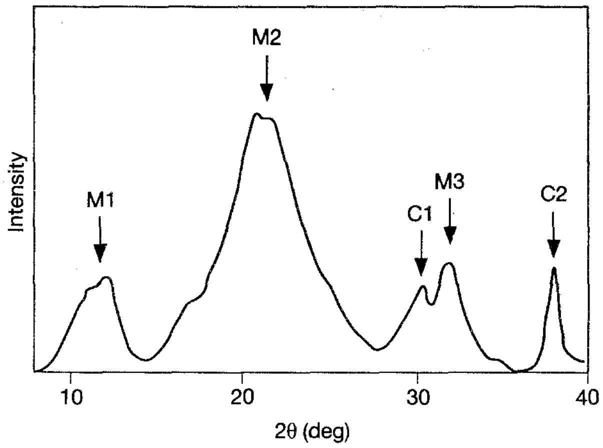

Figure 4 WAXS of "as-spun" fibre from polymer XIV: meridional intensity trace. Peaks C1 and C2 are due to silver foil used for calibration.

TABLE IV Meridional reflections in "as-spun" fibres

Reflection	*d*-spacing (nm)			
	IV	VIII	XIV	XVI
M1	0.69	0.69	0.70	0.69
M2	–	0.39	0.40	0.40
M3	–	–	0.28[a]	0.29[a]
M4	–	–	0.20[a]	0.20[a]

[a] Very weak.

DSC curves of all the "as-spun" fibres displayed only the glass transition. The HSOM flow temperatures of fibres VIII, XIV and XVI were similar to those of the "as-made" polymers. However, fibre IV only softened at the flow temperature of the polymer, but the onset of flow was observed at a much higher temperature (Table III). Thus, although this "as-spun" fibre did not show a melting endotherm, it can not be regarded as non-crystalline due to the WAXS and HSOM evidence.

3.3. Heat treatment of fibres

A temperature of 145 °C, which is below the flow temperature determined by HSOM for the "as-spun" fibres (or, in case of fibre IV, below the softening temperature) was selected for the heat treatment of bundles of fibres held at a constant length. After 1 h there was a noticeable fibre-to-fibre fusion. The WAXS patterns did not show any additional features compared with the "as-spun" fibres; the only change was an increase in the azimuthal integral breadth values (Table III), indicating that the heat treatment, even at this low temperature, results in a loss of chain alignment. The DSC curves and HSOM flow temperatures (Table III) were essentially the same as those of the "as-spun" fibres.

Extended heat treatments (18 h) of chopped fibres produced from polymer IV were carried out in DSC pans at temperatures between 170 and 230 °C. As in the case of the "as-made" polymer, this resulted in the appearance of a small broad melting endotherm ($\Delta H \simeq 2\,\mathrm{J\,g^{-1}}$). Unexpectedly, the difference between the endotherm peak temperature, T_m, and the heat-treatment temperature, T_t, increased with increasing T_t; thus, at $T_t = 170$ °C the difference ($T_m - T_t$) was 32 °C, increasing to 63 °C for $T_t = 230$ °C (Table V).

In agreement with the result obtained with the "as-made" polymer XVI, the heat treatment (18 h at 190 °C) of the chopped fibres produced from this polymer did not result in the appearance of a melting endotherm.

4. Discussion

The absence of crystallinity in "as-made" polymers listed in Table II has been deduced from WAXS patterns, DSC evidence and from behaviour observed by HSOM. It has been ascribed [6] to a large number of constituent units ($n \geq 5$) of three different types (rod-like, crankshaft and rigid angular). Melt spinning resulted in alignment of chains along fibre axis but did not induce crystallization.

WAXS patterns of "as-spun" fibres showed, in addition to broad equatorial scatter, between one and four meridional reflections (Table IV). The aperiodic nature of these reflections for polymers XIV and XVI indicates that the sequence of units of different lengths is essentially random [13, 16]. This is undoubtedly an important factor in the suppression of crystallization.

At ambient temperature the state of both "as-made" polymers and "as-spun" fibres is a nematic glass. Upon heating they are transformed directly into nematic melts. The devitrification takes place over a narrow temperature interval of approximately 12 °C (Table II) which is typical for non-crystalline materials. In contrast, partially crystalline TLC copolymers display a very broad devitrification temperature interval, ΔT_g; thus, Cao and Wunderlich [17] found a ΔT_g of approximately 200 °C for copolymers consisting of OPCO and ONCO units.

TABLE V Effect of an 18 h heat-treatment at temperature T_t on the melting endotherm of fibre IV; T_m is the endotherm peak temperature

T_t (°C)	Endotherm			$T_m - T_t$ (°C)
	Range (°C)	T_m (°C)	ΔH ($\mathrm{J\,g^{-1}}$)	
170	182–239	202	1.8	32
190	200–259	225	2.3	35
210	221–281	255	2.0	45
230	263–318	293	1.8	63

The increase of heat capacity associated with the glass transition is between 30 and 35 $\mathrm{J\,K^{-1}\,mol^{-1}}$ (Table VI) which is in agreement with the values measured for other TLC copolymers [17, 18] and with that obtained by Wunderlich's [19] empirical rules based on the "bead" contributions concept.

The endotherm found for polymer XIV heat treated below the glass transition results from enthalpy relaxation in the nematic glassy state. Thus a nematic glass obtained by rapid cooling of a nematic melt is not in an equilibrium state, but behaves like glasses obtained by rapid cooling of linear flexible-chain polymers.

Extensive heat treatment of polymers IV, VIII, XIII and XIV consisting of five or six different units resulted in crystallization detected by WAXS, DSC and HSOM. Heat-treatment experiments with "as-spun" fibres showed that increased chain alignment did not enhance the rate of crystallization, in contrast to some other TLC materials [8, 9].

The ΔH values of the crystal–nematic melt transition were very low, about 3 $\mathrm{J\,g^{-1}}$. To put this value into proper context, the value of heat of fusion of completely crystalline poly(ethylene terephthalate), obtained by various extrapolation procedures, is $140 \pm 20\,\mathrm{J\,g^{-1}}$ [20] and the heat of fusion estimated for the crystalline phase in TLC poly(4-oxybenzoate-co-1,4-phenylene isophthalate) is 115 $\mathrm{J\,g^{-1}}$ [21]. Thus, the fractional degree of crystallinity of the heat-treated copolymers investigated is estimated to be less than 0.03. Even this very low level of crystallinity was sufficient to prevent the flow of these materials up to the melting of the crystallites (Table II).

The low level of crystallinity is also manifested in the low intensity of the discrete X-ray reflections. The structure of the resulting ordered regions is most likely of the non-periodic layer type identified first in copolymers consisting of OPCO and ONCO units by Windle *et al.* [22] and later investigated in detail by a variety of techniques [23–25]. Extensive annealing of a fibre

TABLE VI Glass transition in highly disordered copolyesters: [ONCO], concentration of 6-oxy-2-naphthoyl units; $\bar{M}_u$, average molecular weight of the constituent units; N, number of tests; ΔC_p, increase in heat capacity

	Polymer				
	IV	VIII	XIII	XIV	XVI
[ONCO] (mol %)	25	40	30	50	40
$\bar{M}_u$ ($\mathrm{g\,mol^{-1}}$)	132.6	140.1	135.1	145.1	140.1
N	10	8	4	8	10
T_g (°C)	114 ± 2	122 ± 1	122 ± 1	119 ± 2	118 ± 1
ΔC_p ($\mathrm{J\,g^{-1}\,K^{-1}}$)	0.23 ± 0.04	0.23 ± 0.05	0.24 ± 0.05	0.24 ± 0.05	0.24 ± 0.04
ΔC_p ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	30.5 ± 5.3	32.3 ± 7.0	32.4 ± 6.8	34.8 ± 7.2	33.6 ± 5.7

produced from the copolymer with OPCO = 0.25 showed that the resulting lateral chain packing is similar to that present in type I structure of poly(4-oxybenzote) [26]. Accordingly, the prominent X-ray reflections found in our heat-treated copolymers can be assigned to this type of structure.

Polymer XVI, consisting of seven different units with almost equimolar quantities of the three different types (Table II), was the only one where the heat treatment conditions employed did not result in crystallization. It is, of course, impossible to state categorically that this material is non-crystallizable but there is no doubt that crystallization will not take place during its processing. Our further work aimed at development of TLC processing aids will therefore concentrate on more detailed investigation of this composition and those closely related to it.

5. Conclusion

The overall aim of this work is to produce TLC polymers which do not crystallize. It has been found that certain random copolyesters consisting of five or more different units of different types form non-crystalline nematic glasses, even where the material is highly oriented.

Extensive heat treatment of copolymers containing five or six different units resulted in the formation of non-periodic layer crystallites; although the fractional degree of crystallinity was very low (< 0.03), it suppressed the flow below the melting temperature of these crystallites.

A copolymer consisting of seven different units of different types, where the molar fractions of rod-like units, crankshaft units and rigid angular units were 0.30, 0.40, and 0.30, respectively, did not crystallize after extensive heat treatments and is, therefore, suitable for evaluation as a low-temperature processing aid.

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