CHARACTERIZATION OF SOME THERMOTROPIC POLYESTERS BY DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

The thermal properties of semiflexible thermotropic polyesters and low molecular mass model compounds were investigated by differential scanning calorimetry. An account is given of some peculiar aspects strictly related to the polymeric nature of the specimens. In particular, the influence of molecular mass and thermal treatments on the transition temperatures of the polymers is evidenced. The occurrence of polymesomorphism was revealed by the appearance of multiple DSC peaks.

INTRODUCTION

Liquid crystal compounds are useful materials for application because of their ability to show spontaneous anisotropy and readily induced orientation in the liquid crystal state. Low molecular mass mesogens are generally formed of a rigid core and two flexible tails [1]. Mesophase-forming polymers may possess different basic structures; however, most of them are thermotropic main chain polyesters with regularly alternating rigid mesogenic moieties and flexible spacers [2,3].
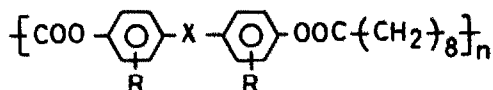
Differential scanning calorimetry (DSC) can be successfully used to determine phase transitions in thermotropic liquid-crystalline systems; it is also complementary to optical microscopy and X-ray diffraction for the identification of the nature of the mesophases.

Some examples of the thermal behaviour of semiflexible thermotropic polyesters and of low-molecular-mass models are considered here.
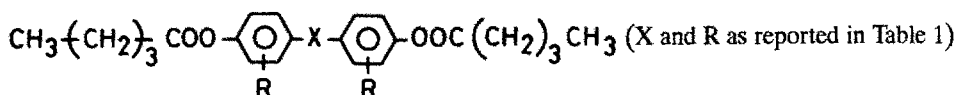
EXPERIMENTAL

Materials

Polymers 1, 2 and 3:

$$\left[COO - \bigotimes_{R} - X - \bigotimes_{R} - OOC + CH_2 \right]_{8} \Big]_n$$

and models 1 and 2

$$CH_3 + CH_2 \big]_3 COO - \bigotimes_{R} - X - \bigotimes_{R} - OOC (CH_2)_3 CH_3 \quad \text{(X and R as reported in Table 1)}$$

were obtained by low temperature solution polycondensation and esterification reactions, as described elsewhere [4,5]. Tests of purity and sample characterization (elemental analysis, IR and NMR spectroscopy, optical microscopy) have also been reported in the same references.

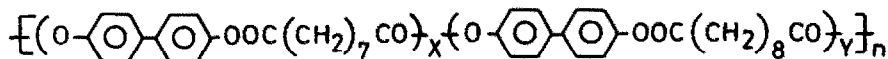Polyesters C7 with different inherent viscosities

$$\left[O - \bigotimes - \bigotimes - OOC (CH_2)_7 CO \right]_n$$
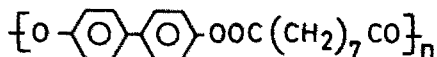
were synthetized from 4,4'-diacetoxybiphenyl and azelaic acid by a three steps melt polycondensation with a progressive temperature increase (up to 553 K) and pressure reduction (down to 0.2÷0.3 mmHg), using CH_3COONa as catalyst [6,7].

Polyester C8

$$\left[O - \bigotimes - \bigotimes - OOC (CH_2)_8 CO \right]_n$$
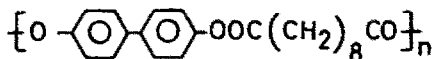
as well as copolymers C7-C8

$$\left[(O - \bigotimes - \bigotimes - OOC (CH_2)_7 CO)_x (O - \bigotimes - \bigotimes - OOC (CH_2)_8 CO)_y \right]_n$$

were prepared by interfacial polycondensation under stirring, using a 50% (w/w) mixture of tetrachloroethane-chlorobenzene as organic phase and trimethylbenzylammonium chloride as accelerator [7,8].
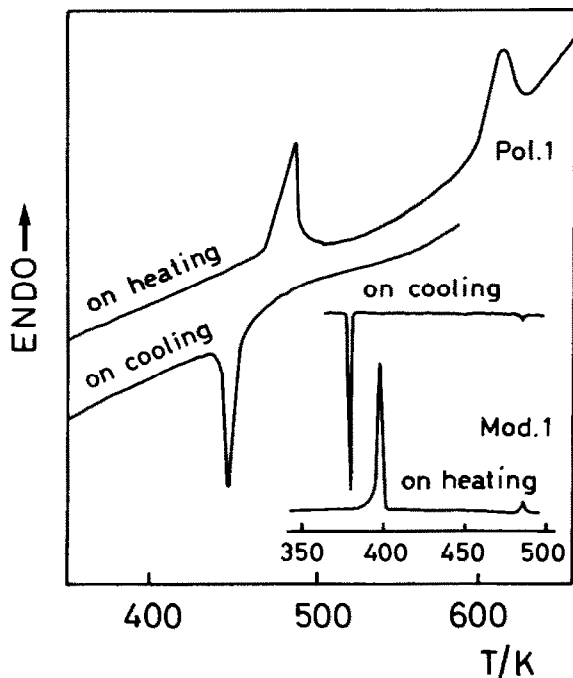
Fig. 1. Thermal behaviour of polyester 1 and model 1. Scanning rate 10 K min⁻¹.
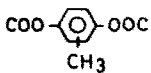
<u>Differential scanning calorimetry</u>
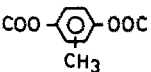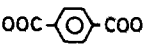
Heating and cooling runs were performed at different rates (from 2.5 to 20.0 K min⁻¹) upon 5÷10 mg samples, using a Perkin Elmer DSC 2 calorimeter, equipped with a 3500 Data Station apparatus to evaluate enthalpies and transition temperatures. Indium was used as a reference for calibration. Uncertainities in the temperatures and enthalpies obtained were estimated to ±2K and ±10% respectively. Transition temperatures were defined by both DSC and hot stage optical microscopy; the two series of values show considerable agreement.

RESULTS AND DISCUSSION

DSC investigations can be applied to liquid crystal polymers just as to low-molecular-mass models; however, the polymeric nature broadens the transition peaks and complicates the thermal profiles. An example is given in Fig. 1, where the melting and crystallization curves of Pol. 1 (intrinsic viscosity [η]=1.04 dl g⁻¹ measured in tetrachloroethane sym. at 298 K) are compared

TABLE 1

Transition temperatures and enthalpies of polyesters 1, 2 and 3 and models 1 and 2.

Samples	X	R	Melting		Isotropization		Crystallization	
			T/K	ΔH/cal g^{-1}	T/K	ΔH/cal g^{-1}	T/K	ΔH/cal g^{-1}
Pol.1[a]	coo-⟨O⟩-ooc CH$_3$	H	484	2.2	611	2.5	447	1.6
Pol.2[b]	ooc-⟨O⟩-coo	H	530	9	>T$_D$[d]	-	515	7
Pol.3[c]	ooc-⟨O⟩-coo	CH$_3$	450	2	593	3.0	412	2
	coo-⟨O⟩-ooc CH$_3$	H	399	19	487	0.8	378	18
Mod.2	ooc-⟨O⟩-coo	H	489	23	527	0.4	481	18

[a] $[\eta]$ = 1.04 dl g^{-1} in tetrachloroethane sym. at 298 K
[b] $[\eta]$ = 0.39 dl g^{-1} in o-chlorophenol at 298 K
[c] $[\eta]$ = 1.74 dl g^{-1} in tetrachloroethane sym. at 298 K
[d] T_D = decomposition temperature

with those of the corresponding model compound.

The very broad nematic-isotropic transition for the polymer indicates the presence of a biphasic region, where the anisotropic and isotropic phases coexist. This behaviour, very common in the case of polymeric mesogens, generally fits the polarizing microscope observations. It was suggested that the extent of the biphasic region broadening is mainly determined by the low end of the molecular weight distribution [9].

Transition temperatures and the relative enthalpies obtained for five of our samples at a scanning rate of 10 K min^{-1}, are set out in Table 1. The reported T values correspond to endotherm maxima and exotherm minima of DSC curves.

Optical microscope investigations indicate that all the samples listed in Table 1 present nematic mesophases with similar morphologies. Characteristic threaded and schlieren textures [10] appear spontaneously after the melting point or form on cooling from the isotropic state.

Melting enthalpies increase from polyesters to model compounds, while an opposite trend is shown by heats of isotropization. This means that the model

compounds exhibit a considerably higher order in the crystalline state. On the contrary, the degree of order in the liquid crystalline state is higher for polymers than for mesogenic mods. 1 and 2, even when a substituent on the aromatic ring is introduced. The simplest explanation of the latter result is that the increased molecular mass reduces the entropy of the nematic phase by limiting the mobility of the molecules. Motions parallel to the long molecular axes are hindered in the nematic state, while this effect is less pronounced in the randomly-oriented isotropic liquid. The overall results agree with recent reports by Griffin *et al.* [11] on similar compounds.

It is well known that the crystal melting in crystalline polymers is strongly affected by both the molecular mass and the thermal history of the samples; this effect can also be found for the isotropization temperature T_i of thermotropic materials. The dependence upon the inherent viscosity of the DSC transition temperatures for polyesters C7, Pols.1 and 3 is illustrated in Table 2. In the case of C7 samples, as η_{inh} is lowered both T_m and T_i decrease, but the temperature range between melting and isotropization appears to be virtually unaffected in the examined interval of viscosity. The behaviour is different for very low values of η_{inh}, as reported in the literature [7]. This lower limit of η_{inh} can vary

TABLE 2

Transition temperatures as a function of inherent viscosity.

Sample	η_{inh}/dl g^{-1}	T_m/K	T_i/K
C7[a]	0.28	491	500
	0.40	503	511
	0.57	504	513
	1.02	512	520
Pol.1[b]	0.24	414	>573[c]
	0.35	462	>573[c]
	0.81	483	611
	1.02	484	611
Pol.3[b]	0.27	403	>553[c]
	0.60	450	592
	1.72	450	593

[a] In phenol/tetrachloroethane sym. 60/40 (w/w) at 298 K
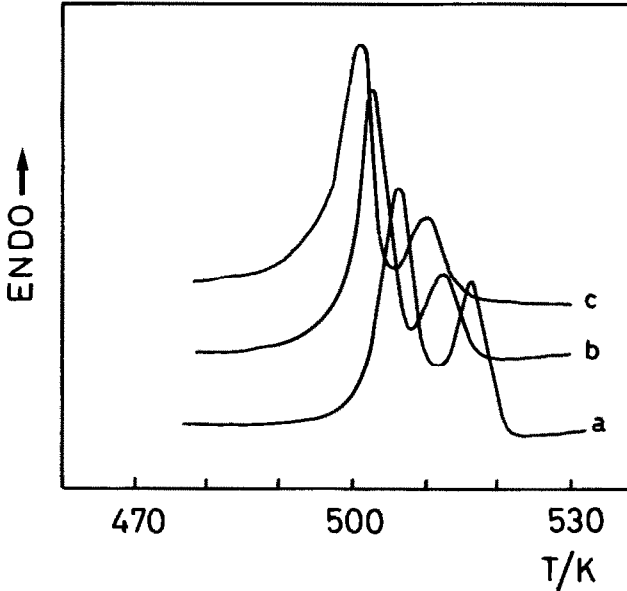[b] In tetrachloroethane sym. at 298 K
[c] Large biphasic regions

Fig. 2. Melting profiles at 2.5 K min^{-1} of samples subjected to different crystallization rates in the preceding cycle: (a) 2.5 K min^{-1}; (b) 10 K min^{-1}; (c) 20 K min^{-1}.

with the chemical structure of the system, as shown by Pols.1 and 3.

Both of the transitions first increase with the molecular mass and then level off when it reaches a critical value, as observed by many authors in experiments on different polymeric samples [7,12] and by ourselves on Pol.1 and Pol.3 (see Table 2).

Fig. 2 shows that both T_m and T_i of polyester C7 with η_{inh}=0.57 dl g^{-1} (peak at lower and higher temperature respectively), depend on the preceding thermal treatment and are shifted toward higher values for samples crystallized at slower rates. All the specimens were maintained at 550 K for 12 min and then cooled down at the selected rates.

The dependence of the isotropization temperature on the thermal history has been recently discussed by Feijoo et $al.$ [12] for a nematic polyether. These authors suggest that, simply as measured, T_i may not correspond to the equilibrium value below a certain molecular weight and also that in this case the samples must be annealed to approach equilibrium conditions.

All the samples so far considered exhibit nematic phases, as evidenced by optical observations; however, by using DSC, it is also possible to detect the presence of multiple transitions in liquid crystalline systems. This situation is shown in Fig. 3, where the melting curves of two mesogenic homopolymers C7
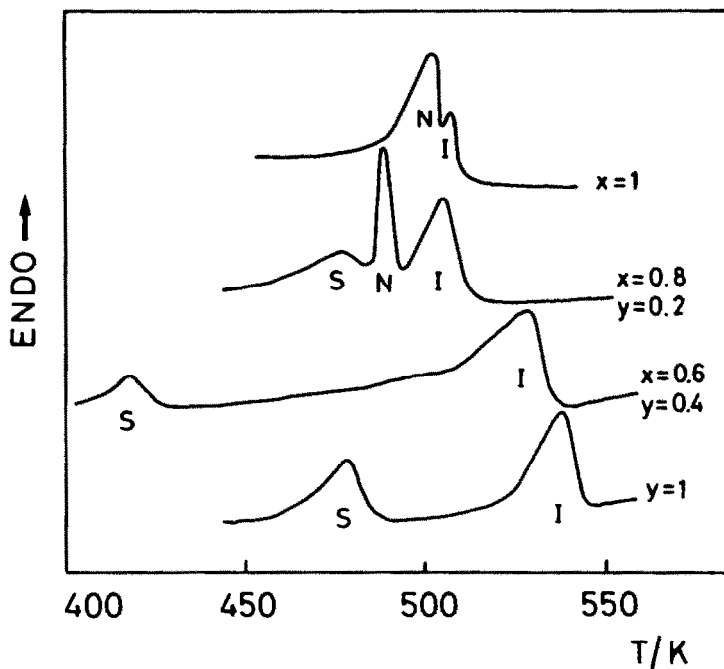
Fig. 3. DSC profiles at 20 Kmin⁻¹ of polyesters C7 (x=1) and C8 (y=1) and of two copolyesters C7-C8 (80:20 and 60:40). η_{inh} in the range 0.35-0.45 dl g⁻¹. N,S,I indicate nematic smectic and isotropic phases, respectively.

and C8 (which give, before reaching the isotropic state I, a nematic N and a smectic S mesophase respectively) are reported, together with the curves of two copolymers C7-C8 of different compositions.

Various observations are consistent with a smectic mesophase for polymer C8: the appearance of a batonnet texture [13] from the isotropic phase, a larger supercooling at the I-S transition and a higher viscosity of the mesophase [7,8] as compared with the nematic phase. Both a smectic and a nematic phase were found for copolyesters containing up to 70 mol% of "C7 units", while only a smectic phase appeared below this percentage. These findings are in good agreement with the results of Watanabe and Krigbaum [14], who determined phase diagrams of several random copolymers based on the 4,4'-dihydroxybiphenyl rigid unit. The introduction of "C7 units" in homopolymer C8 reduces the degree of crystallinity but does not disrupt the mesophase structure, meaning that copolymerization affects the structure of the crystalline phase much more than that of the liquid crystal.

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