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Phase Transitions in Alkylene Glycol Terephthalate Copolyesters Containing Mesogenic p-Oxybenzoate Units*

Giancarlo Galli[1], Enzo Benedetti[1], Emo Chiellini[1], Christopher Ober[2] and Robert W. Lenz[2]

[1] Instituto di Chimica Organica Industriale, Universita di Pisa, Via Risorgimento 35, 56100 Pisa, Italy

[2] Materials Research Laboratory, Chemical Engineering Department, Goessmann Laboratory, University of Massachusetts, Amherst, MA 01003, USA

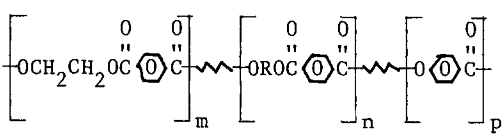
SUMMARY

Terephthalate copolyesters containing ethylene glycol and either tetramethylene, TMG, or hexamethylene, HMG, glycol and p-oxybenzoate, OB, units were investigated by DSC and IR spectroscopy for the relationship between composition and thermal transitions. Copolymers containing more than 30 mole% OB units showed melt birefringence indicative of thermotropic liquid crystalline behaviour. The IR results were applied quantitatively by plotting optical densities as a function of temperature over the melting range of the copolyesters.

INTRODUCTION

A great deal of attention has recently been attracted to the preparation and characterization of polymers with thermotropic liquid crystal properties associated with the presence of mesogenic units in the main chain[1]. Many of these polymers have been obtained by the insertion of stiff aromatic units into poly(ethylene terephthalate), such as those derived from p-acetoxybenzoic acid or diacetoxy hydroquinone[1-4].

As a part of our studies on the preparation of functional hemocompatible polymeric materials to be used for fabrication of artificial kidney devices,[5,6] we have recently carried out the synthesis of some terephthalate copolymers based on two different glycols having different hydrophilic characters and containing the p-oxybenzoate unit as a potential mesogenic group in the main chain[7], as follows:



in which R is either $-(CH_2)_3-$, $-(CH_2)_4-$, $-(CH_2)_6-$ or $-CH_2CH_2-O-CH_2-CH_2-$; m = n and p is approximately 0.2 - 0.4 (m + n + p = 1).

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* ***Dedicated with fondness and best wishes to Prof. Dragutin Fleš on his 60th birthday***

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In this report are described the results of IR (infrared) spectroscopy and DSC (differential scanning calorimetry) investigations carried out on copolymers containing equimolar amounts of two different glycols: ethylene glycol and either tetramethylene, TMG, or hexamethylene, HMG, glycol and varying amounts of oxybenzoate, OB, units in an attempt to correlate some absorption characteristics with the solid and melt state properties of the samples in the vicinity of their thermal transitions. In fact, although IR spectroscopy has been widely applied for a long time to polymer analysis[8,9], and in particular to poly(terephthalate)s[8,10], very few reports have appeared on the study of liquid crystal polymers by IR spectroscopy as a function of temperature. Recently a report has been published using this technique on a comb-like polymer displaying thermotropic liquid crystalline behaviour[11], but most references are available only on low molecular weight liquid crystals[12].

EXPERIMENTAL

Homopolymer and copolymer samples were prepared by a catalytic melt-phase polycondensation[7,13], and the insertion of p-acetoxybenzoate units into the preformed polyesters was carried out under catalyst-free conditions at 275°C, as previously reported[2,7]. Some data relevant to the synthesis and the chemical characterization of the copolyesters under investigation are summarized in Table 1.

TABLE 1

Copolymer structure and properties before and after insertion of oxybenzoate, OB, units

	Initial Copolymer[a]			OB-Containing Copolymer[b]	
Polymer Designation	Glycol Comonomer	$[\eta]^c$ dl/g	T_m °C	OB Content mole%	$[\eta]^c$ dl/g
E_0	TMG	0.29	165-187	0	-
E_1				42	0.16
E_2				22	0.30
F_0	HMG	0.76	110-127	0	-
F_1				31	0.27
F_2				20	0.35

a. Contains 50 mole% ethylene glycol residues and 50 mole% of either tetramethylene glycol, TMG, or hexamethylene glycol, HMG residues in a terephthalate copolyester.

b. Fraction of insertion reaction product which is soluble in boiling trifluoroacetic acid.

c. In tetrachloroethane-phenol mixed solvents (40-60 by weight) at 25°C.

DSC thermograms were recorded on a Perkin-Elmer DSC-2 apparatus. A constant flow of nitrogen was maintained throughout the experiments, and the heating rate was 10-20°C/min. Indium standards were used for temperature calibration and for calculation of heats of fusion. IR spectra were recorded by a Perkin-Elmer 180 Spectrophotometer on either thin films, cast by slow evaporation of the solvent from polymer solution, or on KBr discs. Wide angle X-ray measurements were performed with a Philips PW 1010/25 diffractometer on powdered samples.

RESULTS AND DISCUSSION

As previously pointed out[7] the oxybenzoylation of terephthalate copolymers leads in all cases to marked changes in the profiles and the positions of the DSC melting endotherm peaks of the original polymer. Even more pronounced differences were seen in the comparsion with the parent terephthalate polymers. In particular, the melting transitions were found to occur over a noticeably broader range of temperatures and to be slightly dependent on the rate of cooling from the isotropic melt[14]. In some cases the samples developed more or less structured endotherms, after the first heating and cooling cycle, as shown in Figure 1, probably due to non-isothermal crystallization during the scan[7]. The melting transitions observed in these copolymers were presumably those of the poly(ethylene terephthalate) crystalline regions, although these constituted less than half of the units of the final copolymers. For the samples containing more than 30 mole% oxybenzoate, OB, units strong indications of liquid crystal behaviour were observed. Sample F_1 with 31 mole% OB units (see Table 2) inserted into the HMG copolymer when examined under the polarizing microscope showed a moderate degree of melt birefringence and remained so up to approximately 280-300°C. The DSC thermogram of this sample exhibited several phase transitions (see Figure 1), including a relatively intense endotherm corresponding to the melting transition from 94-143°C (Table 2) and a very broad and shallow endotherm occurring over the temperature range of approximately 160-300°C corresponding to the clearing temperature (the transition from the liquid crystalline to the isotropic state) in agreement with the observations of the birefringent melt. This last transition vanished in successive heating-cooling cycles, but a reproducible structuring of the melting endotherm took place as shown in Figure 1.

Sample E_1 with 42 mole% OB units inserted in the TMG copolymer showed a similar melting endotherm on DSC analysis with a peak extending from 137-189°C (Table 2), and it also had a very broad and shallow endotherm extending over the temperature range of approximately 200-280°C, which can be assigned to the clearing transition.

In both cases, it is likely that the liquid crystallinity was formed by the association in the melt of sequences of one to three OB units adjacent to a terephthalate unit[3]. The broad temperature range and small heat of transition for the clearing transitions observed by DSC analysis suggest that the amount of liquid crystal regions were small for both Samples E_1 and F_1 and were probably quite poorly defined because the copolymers contained mixtures of sequences of different lengths and compositions[15].

The inclusion of OB units in the copolymers, in spite of their rigidity, was found to decrease markedly the crystallinity of the starting copolyesters, analogous to what has already been observed for related copolymers[2,4]. In fact, the X-ray spectra showed a low degree of crystallinity, even after long annealing times. However, as expected, such a treatment yielded a larger

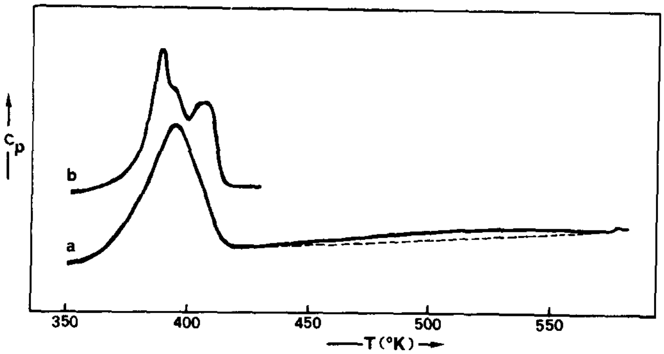


Figure 1. DSC thermograms of poly[(ethylene-*co*-hexamethylene) terephthalate-*co*-p-acetoxybenzoate], Polymer F_1:

a. First heating cycle, b. Second heating cycle.

TABLE 2
Thermal properties of copolyterephthalates containing p-oxybenzoate, OB, units

Polymer	OB Content, mole %	Melting Range, °C by DSC	Melting Range, °C by IR[a)]	ΔH cal/g[b]
E_0	0	165-187	160-190	8.6
E_2	22	127-187	137-177	7.5
E_1	42	137-189	-	4.8
F_0	0	100-127	96-122	5.6
F_2	20	93-139	67-134	8.0
F_1	31	94-143	81-142	6.0

a. Based on the ratio $D_{1335\ cm^{-1}}/D_{1020\ cm^{-1}}$

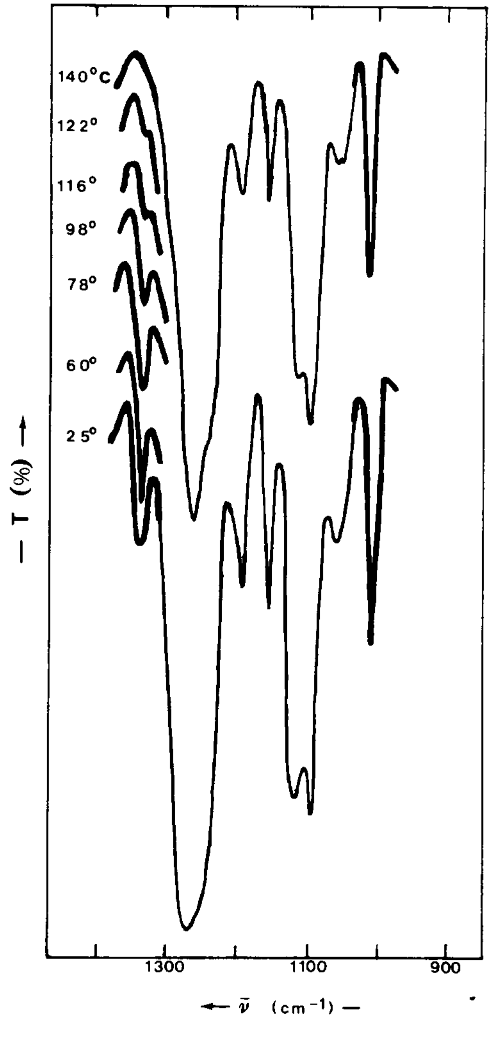
b. Calculated from DSC thermograms.

amount and/or more perfection of the crystallites in the copolymers, as clearly evidenced by the high temperature shift of the melting transitions.

After insertion of the OB units and analysis by infrared spectroscopy at different temperatures from room temperature up to the melting point, the copolymers showed noticeable differences throughout almost the entire spectral region investigated for both the positions and intensities of the bands observed. Most marked changes occurred in the absorptions at 1335 cm^{-1} (Figure 2), in the methylene wagging and twisting region, and at 415 and 395 cm^{-1} (Figure 3) in the skeleton vibration spectral region. The optical densities of such bands, after comparison with a suitable reference band, were plotted as a function of the temperature as shown in Figures 4 and 5.

A substantial decrease in the optical densities occurred over a temperature range closely related to that of the melting transition as detected by the DSC analysis (Table 2), indicating that

Figure 2. Variation of the 1335 cm^{-1} IR band with temperature in poly[(ethylene-*co*-hexamethylene)terephthalate-*co*-p-oxybenzoate], Polymer F_2 .



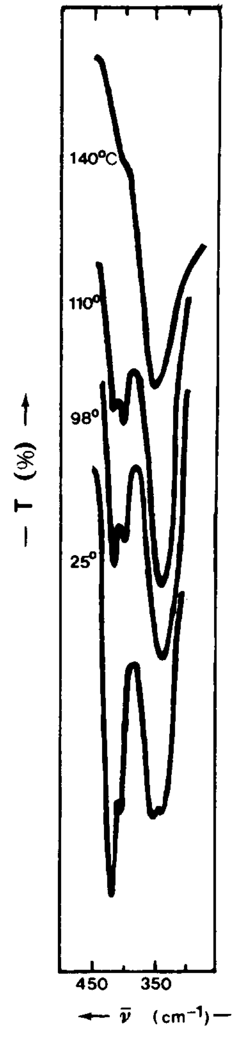


Figure 3. Variation of the 415 and 395 cm^{-1} IR bands with the temperature in poly[(ethylene-*co*-hexamethylene)tereph-thalate-*co*-p-oxybenzoate], Polymer F_2.

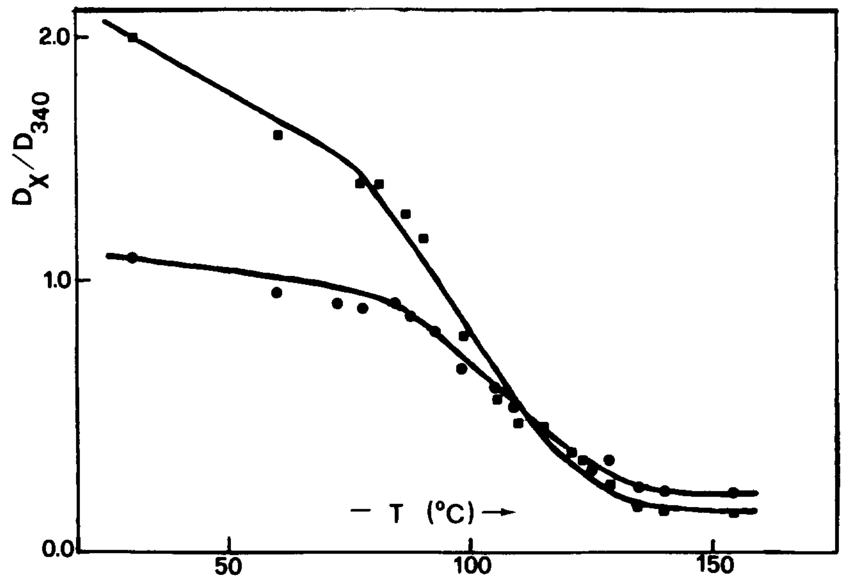


Figure 4. Variation of IR optical density ratio ($D_{1335cm^{-1}}/D_{1020cm^{-1}}$) with the temperature for following copolymers:

—0— poly[(ethylene-*co*-hexamethylene)terephthalate-*co*-p-oxybenzoate], Polymer F_0.

-■- poly[(ethylene-*co*-hexamethylene)terephthalate-*co*-p-oxybenzoate], Polymer F_1.

—●— poly[(ethylene-*co*-hexamethylene)terephthalate-*co*-p-oxybenzoate], Polymer F_2 .

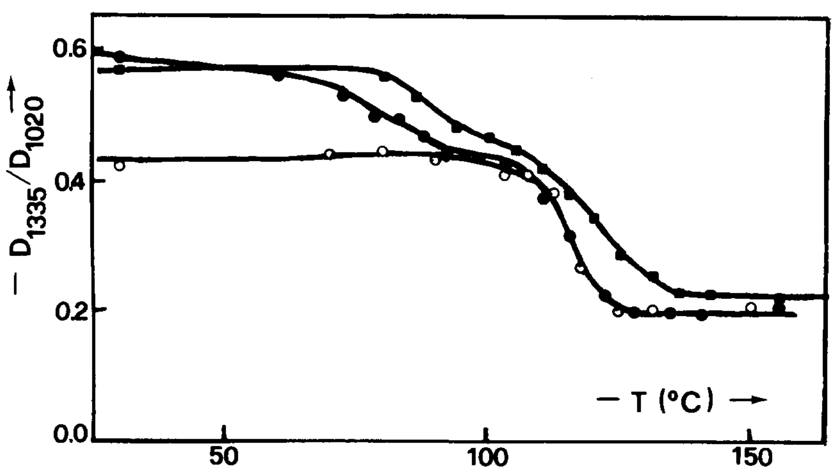


Figure 5. Variation of IR optical density ratios —■— $D_{415cm^{-1}}/D_{340cm^{-1}}$ and —●— $D_{395cm^{-1}}/D_{340cm^{-1}}$ with temperature for poly[(ethylene-*co*-hexamethylene) terephthalate-*co*-p-oxybenzoate]. Polymer F_2.

this method was very sensitive to the measurement of phase changes in the copolymers under investigation. After being cooled to room temperature, the once-melted samples displayed the original set of bands with practically the same relative intensities,which indicated that the absorption changes were not associated with any degradation phenomena but most likely with some conformational changes in the polymer at its phase transition.
For some particular cases (Samples F_1 and F_2), the infrared analysis seemed to be even more sensitive than the DSC analysis, and it allowed the detection of the occurrence of some additional solid-solid transitions, which apparently were not revealed by the conventional DSC thermal analysis as seen in Figure 1a. Moreover in the F copolymer series containing HMG units, the optical density ratio D_{1335}/D_{1020} of the copolymer with the higher OB content, F_1 with 31 mole%, was unaffected over a fairly broad temperature range below the melting point (25-80°C), while the same ratio for the F_2 copolymer containing 20 mole% OB units decreased continuously from room temperature to the melting point, indicating the existence of a very broad phase transition in this copolymer; see Table 2. This result suggests that the copolyester containing the lower amount of glycol terephthalate units may have actually had a more regular structure, possibly a more blocky structure, which may have been formed by a crystallization-induced reorganization during insertion of the OB units in the copolymer[3]. This much broader melting range for copolymer F_2 was not noticed in the DSC analysis.
The investigations now in progress have been expanded to an unequivocal assignment of the IR absorption bands and to a better understanding ot the structural changes involved in the preparation of the copolymers.

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