Effect of branched alkyl spacers in liquid crystalline poly[2,2-dimethyl(trimethylene)terephthaloyl-bis-4-oxybenzoate]

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The effect of introducing lateral substituents in liquid crystalline poly[(trimethylene)terephthaloyl-bis-4-oxybenzoate] has been analysed. The 2,2-dimethyl derivative has been synthesized and has shown liquid crystalline behaviour. The temperature for the crystal–liquid crystal transition and the mesophase–isotropic transition have been considerably lowered with respect to the unsubstituted polymer. Such transitions have been characterized by X-ray, differential scanning calorimetry and optical microscopy and analysed as a function of the thermal treatment.

(Keywords: liquid crystalline polymers; smectic mesophases; branched alkyl spacers; poly[2,2-dimethyl(trimethylene) terephthaloyl-bis-4-oxybenzoate])

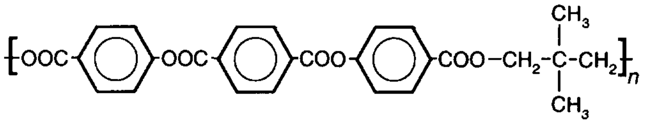
Introduction

Recently a lot of attention has been paid to the study of polymeric liquid crystals. There are two main structural possibilities which can produce thermotropic behaviour in these materials: the introduction of rigid groups into the main chain or the introduction of rigid side chains.

One of the more developed types of main chain liquid crystalline polymers are the thermotropic polyesters; the 4,4′-terephthaloyldioxy dibenzoic acid mesogen being one of the most commonly used. Previous work involving the synthesis and characterization of this type of polyester with linear flexible alkyl spacers has been reported in the literature[1–5]. However, even with flexible spacers some of these polyesters have very high transition temperatures[4,5]. Consequently, there is considerable interest in attempting to reduce these temperatures in order to favour the industrial application of these materials. The main possibility for this is the introduction of branched alkyl spacers to increase intermolecular separation, producing less thermally stable mesophases and reducing the melting point. However, if the incorporation of these lateral substituents produces too great an inhibition in the efficient packing of the molecules, the liquid crystalline character may be lost.

Several attempts to reduce the transition temperatures by incorporating lateral substituents in the flexible spacers have already been reported[6–9]. The introduction of dimethyl and diethyl substituents in the spacer ($-CH_2-CX_2-CH_2-$) of poly[trimethylene (*p,p*′-tribenzoate)] produced a reduction in the transition temperatures with respect to the unsubstituted polymer, and the effect was more pronounced as the substituent size was increased[6]. In the case of polymers with the 4,4′-terephthaloyldioxy dibenzoic acid mesogen, only the introduction of asymmetrical substituents has been attempted[7–9]. In these cases, isomers of dipropylene glycol were mainly used giving chiral liquid crystalline polymers with very different mesophases and thermal responses[8,9].

In this communication, we report for the first time the synthesis and characterization of the dimethyl substituent of poly[(trimethylene)terephthaloyl-bis-4-oxybenzoate] with the structural formula:



The transitions of the unsubstituted polymer have already been reported[10,11]. The main objective of this work, as part of a research programme aimed at correlating the effect of symmetrical and asymmetrical substitution on the structure–properties relationship in thermotropic polyesters, is the study of the effect of the lateral methyl groups on the liquid crystalline behaviour and on the temperature transitions of this polymer.

Experimental

Poly[2,2-dimethyl(trimethylene)terephthaloyl-bis-4-oxybenzoate], PDTTBO, was synthesized by the method described by Bilibin and co-workers[4,12,13]. The synthesis was carried out in two stages with isolation of terephthaloyl-bis(4-oxybenzoylchloride), TOBC, which reacted with 2,2-dimethyl(trimethylene) glycol, in a polycondensation process over an 8-h period. Diphenyl oxide was used as the solvent, and the reaction was carried out under nitrogen gas at 200°C. The polymer was precipitated in toluene, washed several times with ethanol and dried under vacuum.

Infra-red (i.r.) spectra of PDTTBO exhibited the characteristic bands of the aromatic ring and the ester group and the doublet at 1375 and 1490 cm^{-1} corresponding to $C(CH_3)_2$.

^1H nuclear magnetic resonance (n.m.r.) spectra were recorded in CF_3COOH solution at room temperature, on a 200 MHz Bruker spectrometer. The following chemical shifts were shown for PDTTBO: δ (ppm from TMS) 8.27 (4H, terephthalate); 8.10–8.06 (4H, 2,6-carbonylphenyl); 7.28–7.23 (4H, 3,5-carbonylphenyl); 4.32 (4H, methylene); 1.15 (6H, methyl).

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The inherent viscosity of the polymer solution was measured in an Ubbelohde viscometer at a concentration of 0.5 g dl^{-1} in *p*-chlorophenol at 45°C.

The differential scanning calorimetry (d.s.c.) apparatus used to measure the thermal properties of the sample was a Mettler TA3000 with a DSC-30 furnace, coupled to a computer with TA72 software. The maximum temperatures of the peaks were taken as the transition temperatures.

Thermogravimetric analysis was performed on a Perkin Elmer TGA4, using nitrogen as the purge gas, with a heating rate of 10°C min^{-1}.

Microscopy studies and thermo-optical analysis were carried out using a Reichert polarizing microscope, Zetopan Pol, equipped with a Mettler FP80 hot stage and a Nikon FX35A camera.

Wide angle X-ray diffractograms were obtained using a Philips Geiger counter X-ray diffractometer with an Anton Paar 300 temperature camera. The diffractograms were recorded at 2°C min^{-1} in the 2θ range between 3° and 32° using Ni-filtered CuKα radiation.

Results and discussion

The polymer PDTTBO was prepared by the method described by Bilibin *et al.* for the same family of polyesters with linear methylenic spacers[12]. This synthesis takes place through the synthesis and isolation of the mesogenic monomer TOBC. Using this process complete characterization of the monomer and polymer is possible, in contrast to alternative synthetic methods[5]. It is important to note that the results obtained from our i.r. and ^{1}H n.m.r. results confirm the structures of TOBC and the polymer used in this work.

The inherent viscosity of the polymer in *p*-chlorophenol at 45°C is 0.1 dl g^{-1}. Although this value is low, it is similar to the viscosity values obtained for other branched polyesters[9], and should not affect any of the liquid crystalline properties of the sample to any significant extent.

The thermal stability of PDTTBO was studied by thermogravimetry under dynamic conditions, using a heating rate of 10°C min^{-1}, and nitrogen as the purge gas. As demonstrated in *Figure 1a*, the polymer is stable up to 300°C and shows a loss of ~ 10% at 380°C.

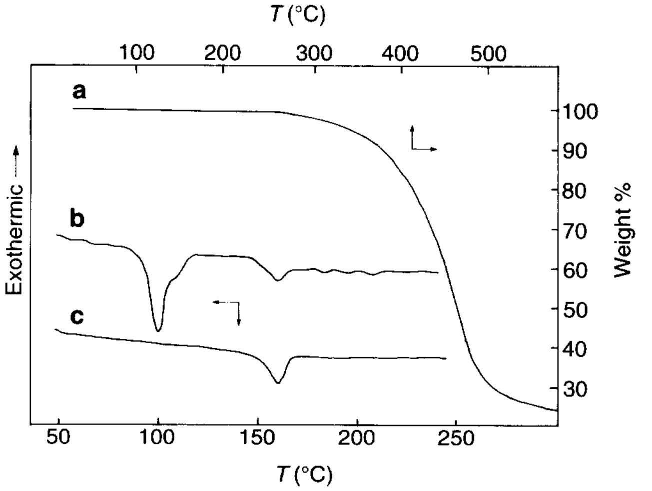

Figure 1 (a) Thermal stability of PDTTBO at a heating rate of 10°C min^{-1}. (b) D.s.c. curve of an original sample of PDTTBO (heating rate 10°C min^{-1}). (c) D.s.c. curve of a sample quenched from 130°C to room temperature (heating rate 10°C min^{-1})

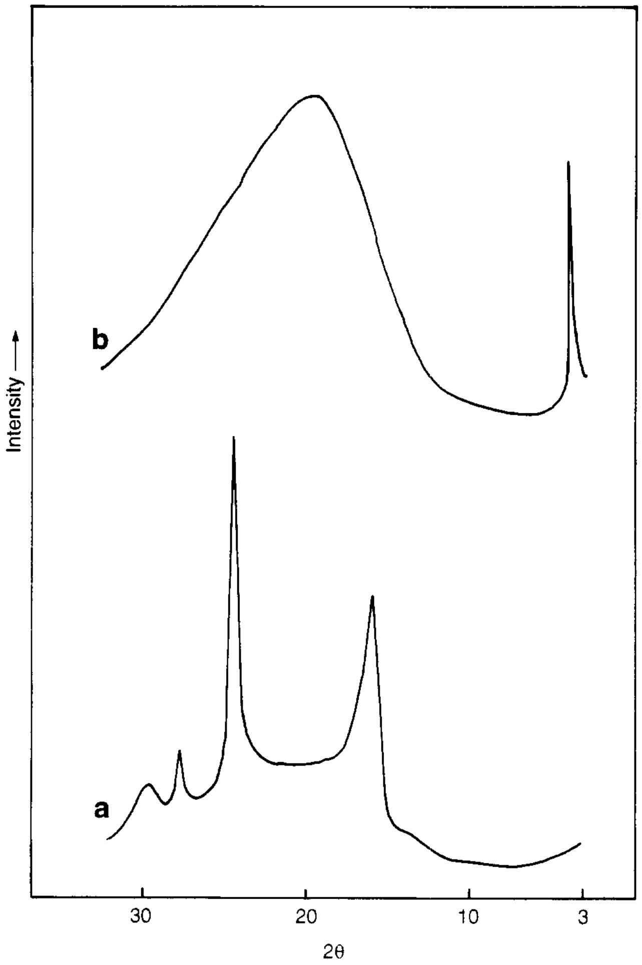

Figure 2 X-ray diffractograms of PDTTBO at room temperature: (a) original sample; (b) sample quenched from 130°C to room temperature

The thermal behaviour of PDTTBO was studied by d.s.c. using several heating and cooling cycles. The curve obtained by heating an original sample, with no thermal treatment, up to 250°C at a heating rate of 10°C min^{-1} is shown in *Figure 1b*. Three endothermic transitions can be observed: the first has a maximum at 100°C with an enthalpy of 20.6 J g^{-1}; a second weaker and broader endotherm is located at 160°C with an enthalpy of 5.1 J g^{-1}; and a final transition is observed between 180°C and 210°C with a low enthalpy of 1.6 J g^{-1}. However, if PDTTBO was cooled down from 130°C to room temperature and subsequently heated to 250°C, only the endotherm at 160°C was observed, as shown in *Figure 1c*. The transition at 100°C was not observed in this run. Similar d.s.c. heating curves were observed when the samples were cooled down from 180 and 230°C, with the absence of the first endotherm at 100°C.

X-ray diffraction experiments were performed on the PDTTBO samples. The X-ray diffractogram of an original sample presented two main reflections at $2\theta = 16.0$ and 24.4° and two weaker features at 27.8 and 29.6°, as shown in *Figure 2a*. *Figure 2b* shows the diffractogram of a sample of PDTTBO quenched from 130°C to room temperature. A sharp reflection at $2\theta = 3.9°$ and an amorphous halo centred at 20° was observed. Similar diffraction patterns were observed when the sample was quenched from 180 and 230°C to room temperature.

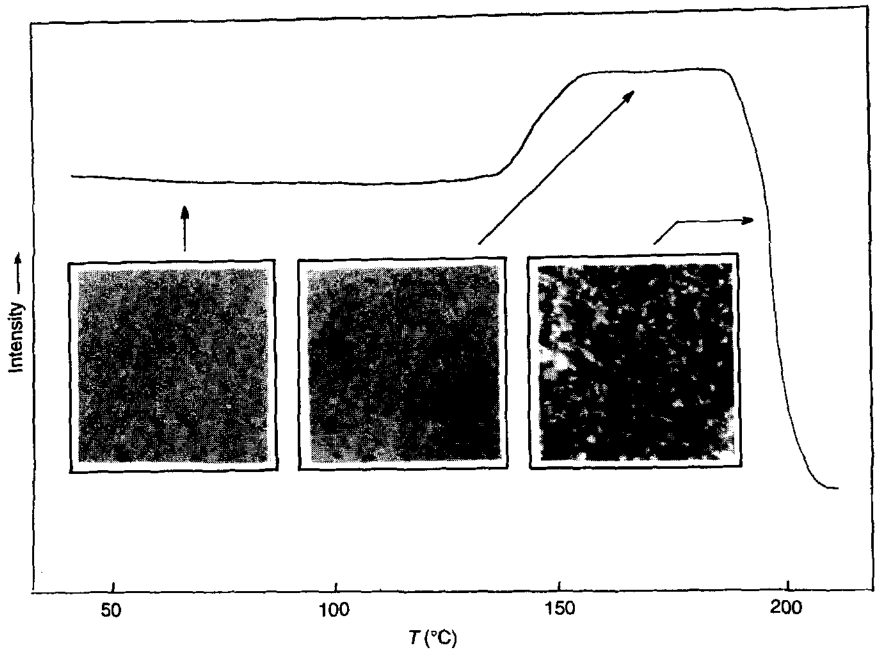

Figure 3 Thermo-optical analysis of PDTTBO sample prepared from the isotropic state, and the corresponding microphotographs (heating rate 10°C min^{-1})

The d.s.c. and X-ray results indicate that PDTTBO is a semicrystalline polymer which exhibits thermotropic behaviour under different thermal treatments. Therefore, the original sample, as obtained from the synthesis, has a crystalline content of ~40% calculated from wide angle X-ray scattering, and upon heating shows a crystal–liquid crystal transition located at 100°C. A second transition located at 160°C could be attributed to a mesophase–mesophase transition. However, we cannot eliminate the possibility of a reorganization process after the first transition. A detailed study of the transition as a function of the temperature will be the subject of further work[14]. The last endotherm observed by d.s.c. corresponds to the mesophase–isotropic transition as confirmed by thermo-optical observation of the clearing temperature (*Figure 3*).

When the polymer is heated up above any of these transitions and then cooled to room temperature, the crystalline phase does not appear and the same mesophase structure is manifested. The X-ray pattern of this mesophase structure is typical of a disordered smectic phase with a sharp reflection at 3.9°, corresponding to a Bragg spacing of 2.26 nm, and an amorphous halo at 20°, corresponding to an average intermolecular distance of 0.44 nm. This diffractogram can be assigned either to an orthogonal smectic phase (Sa) or a tilted phase (Sc) following de Vries' classification[15]. The distance obtained from the low angle peak (2.26 nm) can be related to the length of the repeating unit in its most extended all *trans* conformation (2.33 nm) calculated from known distances and bond angles[11,16]. Therefore, either there are some *gauche* bonds in the flexible spacer and the chains are placed orthogonal to the smectic layers (Sa) or the polymer chains are tilted by an angle of 14° to the normal of the layers, maintaining all bonds of the spacer in the *trans* conformation (Sc). At the present time, we cannot rule out either of these possibilities. X-ray diffraction studies on drawn fibres and solid state n.m.r. studies are in progress to help us to define the type of smectic phase[14].

The phase transitions observed in PDTTBO can be compared with those already reported for poly(trimethylene-terephthaloyl-bis-4-oxybenzoate), PTTBO[10,11]. PTTBO shows a crystal–mesophase transition at 240°C and a second endotherm at 265°C associated with a mesophase–mesophase transition[10]. The X-ray spectra of the liquid crystal phase recorded at 272°C, i.e. above the second d.s.c. endotherm, shows only two broad halos centred at $2\theta = 21$ and 4.6° which are consistent with the occurrence of a nematic mesophase[10]. Finally, PTTBO shows a broad endothermic transition at 312°C that corresponds to the isotropization of the liquid crystal phase. At lower temperatures, in addition to the transitions already mentioned, this polymer shows further transitions characterized by endothermic peaks that may be due to different phenomena such as solid–solid phase changes, the melting of various polymorphic forms, or the reorganization of performed crystalline entities on heating. The inherent viscosity reported[10] for PTTBO is 0.27 $\mathrm{dl\,g}^{-1}$.

The dimethyl derivative of PTTBO reported in this paper shows a crystal–mesophase transition which appears 140°C lower than that of the unsubstituted polymer, and a mesophase–mesophase transition some 105°C lower. The clearing temperature is also reduced by 100°C in the dimethyl derivative. In spite of the differences in viscosity, which may to some extent affect the transition temperatures, we can conclude that the addition of the methyl groups to the flexible spacer of this thermotropic polyester considerably lowers the transition temperatures. Moreover, a smectic mesophase is obtained by quenching the dimethyl derivative from a temperature higher than any of the endothermic transitions, in contrast with the nematic mesophase observed in the case of linear polymer. Therefore, we have observed a very important effect of the substituents in the spacer, not only in the transition temperatures but also in the properties of the mesophases formed.

The presence of methyl and ethyl pendant groups has been found to lower transition temperatures in other thermotropic polymers. The introduction of dimethyl and diethyl in the spacer ($-CH_2-CX_2-CH_2-$) of poly(trimethylene-*p*,*p*'-tribenzoate) reduced the crystal–liquid crystal transition to 256 and 117°C, respectively [compared to 322°C for ($-CH_2-$)$_2$ and 340°C for ($-CH_2-$)$_4$][6]. The mesophase–isotropic liquid transitions were also reduced, to 348°C in the dimethyl derivative, and to 187°C in the diethyl derivative.

In summary, we have presented for the first time the synthesis and characterization of PDTTBO. This polymer exhibits a crystal–liquid crystal transition and a possible mesophase–mesophase transition before it reaches the isotropic melt. All of these transitions present temperatures which are considerably lower with respect to those of the unsubstituted polymer. By quenching from any of the mesophases, or the isotropic melt, the crystalline phase is not regenerated and only a smectic mesophase is observed.

A detailed study of the transitions, mesophase characterization and kinetics of crystal and mesophase formation in PDTTBO, as well as a comparison with longer symmetrical substituents, will be presented in a forthcoming paper[14].

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