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A novel thermotropic polyester with a flexible side group: synthesis and characterization, as well as rheology of its poly(ethylene terephthalate) blends

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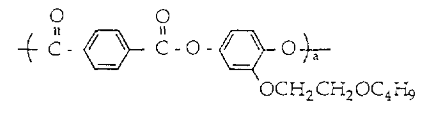
A thermotropic liquid crystalline (LC) polyester containing the 2-butoxyethyleneoxy-1,4-phenylene terephthalate unit (PBEPT) was synthesized and characterized by viscosity measurements, thermogravimetry (t.g.a.), d.s.c. and polarizing microscopy. The polymer exhibited liquid crystallinity in the processing temperature range of poly(ethylene terephthalate) (PET). Blends of PBEPT and PET were prepared. Rheological measurements of the blends were conducted, and compared with data for pure PET, in order to evaluate the effect of the LC polyester on the viscoelasticity of the matrix polymer. Dynamic oscillatory shear, as well as steady shear measurements, indicated a depression of the melt viscosity of PET by 80% caused by the addition of 2–5% of PBEPT.

(Keywords: LC polyester; PBEPT; rheology)

INTRODUCTION

The thermotropic behaviour of various aromatic polyesters based on substituted hydroquinones has been studied in detail by different groups[1–5]. The structure–property relationships of a series of thermotropic poly(2-n-alkyl-1,4-phenylene terephthalate) and poly(2-n-alkoxy-1,4-phenylene terephthalate) were studied by Lenz and co-workers[6,7]. These thermotropic liquid crystalline polymers (LCPs) containing the oxyethylene substituted hydroquinones were considered to be good candidates for use as components in molecular composites in blends with poly(ethylene terephthalate) (PET). The flexible pendent group lowers the transition temperatures of the LCP into the processing temperature range of PET. In addition, electrostatic and dipolar interactions between the ether oxygen of the pendent group and the carbonyl group of PET were expected to result in dipolar attractions to enhance the molecular level mixing of the two components in a blend. In fact, poly(ethylene oxide) is known to be miscible with many polyester systems.

In another earlier study in our laboratory, a series of random copolyesters based on the ethoxydiethyleneoxyhydroquinone monomer, ethylene glycol and terephthaloyl chloride was synthesized and characterized[8]. From the properties of the blends of the 60:40 copolyester with poly(butylene terephthalate) (PBT), it was concluded that there was a good dispersion of LCP within the isotropic matrix. In addition, there was observed some increase in strength and modulus of the blends over pure PBT. However, additional work with the ethoxydiethyleneoxyhydroquinone system showed that the polymers exhibited thermal instability which was attributed to the large number of ether groups in the pendent moiety. It was desirable to choose a system with a minimum number of ether groups but a sufficiently long alkyl chain to obtain the transition temperatures in the PET range. The polymer based on 2-butoxyethyleneoxyhydroquinone was chosen for study:



PBEPT

The objective of this paper is to describe the synthesis and characterization of poly(2-butoxyethyleneoxy-1,4-phenylene terephthalate) (PBEPT). The rheological characterization of the PBEPT blends with PET is also discussed.

EXPERIMENTAL

All the chemicals were obtained from Aldrich Chemical Co. Terephthaloyl chloride was purified by sublimation. The solvent used for polymerization, methylene chloride, was distilled over phosphorus pentoxide. Triethylamine was distilled over sodium hydroxide.

Viscometry was carried out to obtain a relative idea of the molecular weight of the polymer. G.p.c. analysis could not be done because of the insolubility of the

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polymer in common organic solvents. The polymer was dissolved in *p*-chlorophenol at high temperatures and the inherent viscosity was measured at 50°C for a polymer concentration of 0.5 g dl^{-1} using a Cannon Ubbelohde viscometer.

The phase transition temperatures of the LCP were measured on a differential scanning calorimeter (DSC, Perkin–Elmer IV), under a nitrogen flow with a heating and cooling rate of 20 K min^{-1}. The temperature axis of the d.s.c. thermogram was calibrated prior to use with high purity indium. The peak maxima were chosen as the phase transition temperatures. A second heating cycle, after slow cooling, as well as a cooling cycle for a sample heated to 300°C were recorded. For the study of the mesophases formed by the polyester, optical micrographs were taken with a 35 mm camera mounted on a Carl-Zeiss polarizing light microscope equipped with a hot stage (Mettler FP model). The polymer sample, placed between two microscope cover glasses, was heated well above its melting transition on a hot plate melting point apparatus and rapidly quenched. The mesophase behaviour was then observed as a function of temperature on the hot stage.

Monomer synthesis

2-Butoxyethyleneoxyhydroquinone is a new monomer synthesized using a procedure described by Lenz and co-workers for ethoxydiethyleneoxyhydroquinone[7]. The purity of the monomer was confirmed by elemental analysis. Calculated for $C_{12}H_{18}O_4$: C, 63.70%; H, 8.02%. Found: C, 63.99%; H, 7.96%.

Polymer synthesis

The LC polyester was synthesized by solution condensation polymerization. The detailed procedure is described below.

To a 500 ml three-neck flask, were added 2-butoxyethoxyhydroquinone (0.03932 mol, 8.897 g), and triethylamine (0.08 mol, 11 ml) as the acid-acceptor. Then methylene chloride (200 ml) was cannulated into the flask followed by vigorous agitation to form a solution. Thereafter, a solution of terephthaloyl chloride (0.0394 mol, 8.00 g) in methylene chloride (200 ml) was added slowly to the reaction mixture, and the contents of the flask were stirred for 24 h with a magnetic stirrer at room temperature, and then refluxed for 24 h. At the conclusion of the refluxing period, the mixture was cooled to room temperature and it was added to a three-fold excess of methanol. The polymer was filtered to obtain the product (3.5 g) which was dried and then extracted with acetone/methanol in a Soxhlet extractor to obtain a purer polymer (yield 89%).

Rheological measurements

The PET and LCP components of the blends were tumble-mixed for 24 h at room temperature and then compression-moulded into a disc at 280°C for 30 s. The disc was then ground and sifted. Since it was difficult to blend LCP powders with PET pellets, it was found more effective to compression mould the mixture to make a more densified and homogeneous sample. After redrying the blends, the powders were compression-moulded under vacuum into discs of 25 mm diameter. This was done in order to ensure a 100% contact with the fixtures of the rheometers, especially at the edges.

The dynamic mechanical measurements were carried out on a Rheometrics dynamics spectrometer (RDS-7700). The sample geometry featured a gap width of 1 mm in a concentric plate arrangement, with a plate radius of 12.5 mm. During the cooling experiments, a frequency of 10 rad s^{-1} was applied. All measurements started at 290°C. The average cooling rate was 1.5 K min^{-1}.

Steady-step shear rate experiments were conducted with the Rheometrics mechanical spectrometer (RMS-800). Here too, parallel plate geometry with the same dimensions as with the dynamic experiments, was used. Three rates of 0.1, 1 and 10 s^{-1} were successively applied at five different temperatures, and each step shear rate test lasted, at most, 200 s. Due to low torque values, the data for 0.1 s^{-1} were not as consistent as those for the higher rates. Since all tests proceeded in the viscoelastic terminal zone, the differences in the viscosities at different rates were sufficiently small ($\ngtr 5\%$). This justified an averaging of isothermally measured data. In order to avoid destruction by oxidation, the samples were held under a dry nitrogen atmosphere during all tests.

RESULTS AND DISCUSSION

The inherent viscosity measured for PBEPT in *p*-chlorophenol gave a value of 0.4 dl g^{-1}. In contrast, the intrinsic viscosity of the PET was 2.04 dl g^{-1} (ref. 9). Thermogravimetric analysis of PBEPT in nitrogen and air showed that the polymer was stable to 350°C. The d.s.c. thermograms of PBEPT for the second heating cycle and for the subsequent cooling cycle are given in *Figure 1*. Visual observations by optical microscopy revealed that the polymer softened over a broad range from 190 to 228°C, ultimately melting at about 240°C. A fairly well defined endotherm, corresponding to a nematic–nematic transition, was observed at about 245°C in the heating thermogram in *Figure 1*, and this assignment was also confirmed by optical microscopy. The cooling cycle thermogram shows an exotherm peaking around 220°C, which probably corresponds to a mesophase–crystal transition consistent with the large supercooling. The transition temperatures were fairly reproducible in subsequent heating and cooling cycles.

Polarized optical microscopy examination of the polyester, PBEPT, at various temperatures, clearly showed the formation of a threaded texture indicative of a nematic phase even at room temperature. There was a

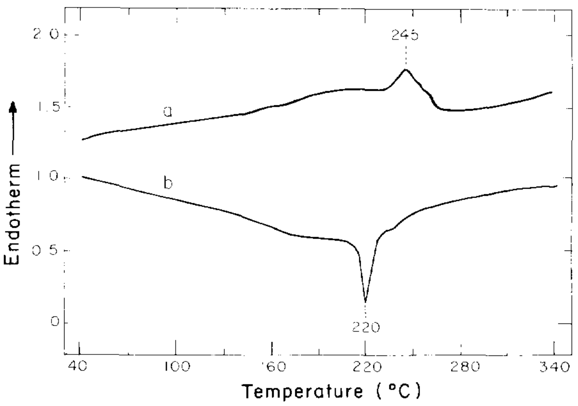

Figure 1 D.s.c. thermograms for PBEPT recorded on the second heating (a) and subsequent cooling (b) cycle at a rate of 20 K min^{-1}

reorganization of the LC state morphology as the temperature was raised. When the temperature was increased, the number of threads diminished and simultaneously, the threads became loose and decreased in length. Formation of closed loops followed by their disappearance to give a homogeneous colour pattern was observed around 245°C, which is the temperature corresponding to the second endotherm in the d.s.c. An intense movement within the melt and scintillation effects due to Brownian motion is a characteristic of a nematic mesophase which was observed in the sample up to 320°C. The sample was not heated above that temperature as degradation may set in and hence the isotropization temperature could not be determined. *Figure 2* shows the LC texture at 220°C and the residual nematic threads still present at 300°C.

A homeotropic texture caused by the spontaneous orientation of the sample was also observed at high temperatures. In the homeotropic regions, the field of view remained uniformly dark as the slide or stage was rotated. However, when the cover-glass was touched, the original dark field of view brightened instantly.

Rheological studies

Melt blending studies with PET showed that PBEPT was not a good reinforcing agent[10]. Specifically, Joslin *et al.* reported a drop in Young's modulus from 17 to 13 GPa, when PET was blended with 20% PBEPT (which was named PBEM in ref. 10, e.g. see Table 2 in ref. 10). Also, the ultimate strength dropped from 1100 MPa (pure PET) to 600 MPa (PET and 20% PBEPT). Nevertheless the thermal shrinkage of the fibres formed from the blend was smaller (9%) compared to pure PET (15%). Furthermore it was observed that it was easier to spin fibres from the blends, which indicates the potential of using the LCP in a small concentration as a processing aid for PET. In order to quantify these observations, rheological measurements were carried out, both in the dynamic and steady shear mode.

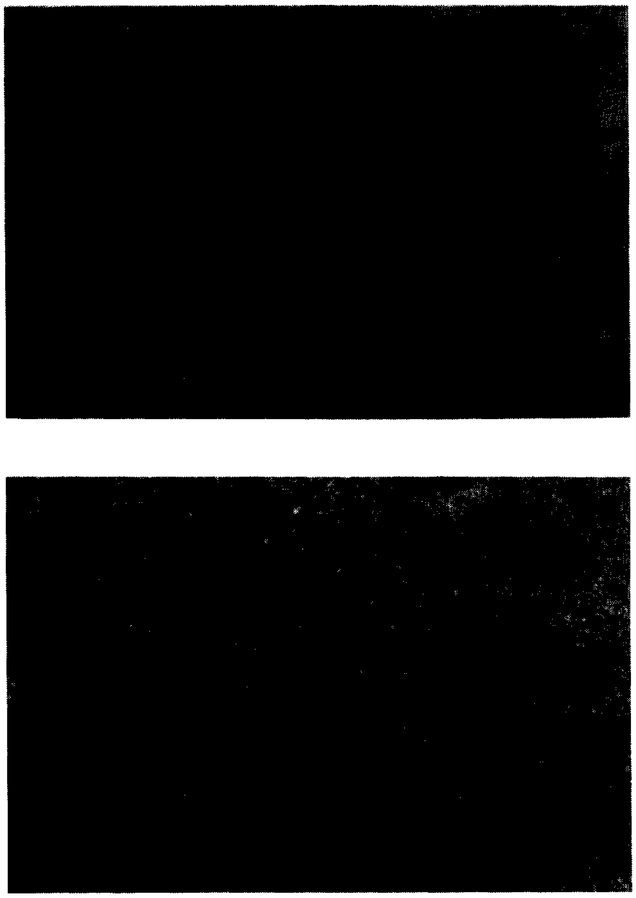

Figure 2 Optical micrographs for PBEPT (magnification 220 ×): (a) 300°C; (b) 220°C (after cooling from 320°C at a rate of 10 K min^{-1})

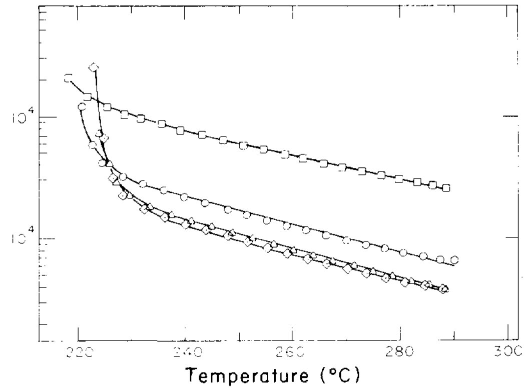

Figure 3 Complex viscosity measured in the dynamic mode *versus* temperature for the PBEPT and blends with PET. Frequency 10 rad s^{-1}

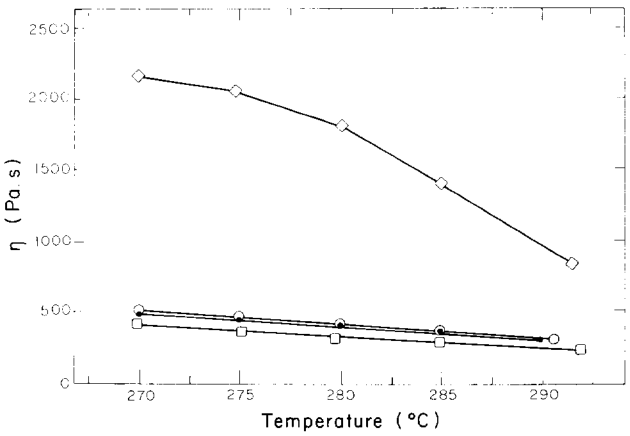

Figure 4 Arrhenius plot of data from *Figure 3*

In *Figure 3*, the evolution of the complex viscosity, measured in the dynamic mode, with temperature is shown for all materials. The viscosity increases steadily with falling temperature. The cooling rate was small enough to allow the materials to crystallize, and this process was recognizable by the steep increase of the viscosities in the temperature range between 230°C and 220°C. The figure combines the data for three blend samples with the data set for pure high molecular weight, fibre grade PET, which was scanned as a reference material. Clearly, PBEPT does influence the flow behaviour of PET. The data showed a marked depression of viscosity of almost an order of magnitude lower than PET, even at the low PBEPT concentrations of 2.5 and 5 wt%. The energy of activation for the flow process, however, does show only a slight increase in the blends, as indicated by the data in *Figure 4*. The data from *Figures 3* and *4* are summarized in *Table 1*.

The flow behaviour of conventional engineering thermoplastics (TPs) changes when blended with LCPs.

Table 1 Effect of PBEPT on the flow behaviour of PET blends

PBEPT (wt%)	η^* (270°C, 10 rad s^{-1}) (Pa s)	E_A (kJ mol^{-1})
0	3802	56.7
2.5	617	65.3
5	562	67.6
10	1000	62.2

This topic has been reviewed by several authors[11–13]. In most cases, blends with small concentrations of LCP form phase-separated systems which show a drop in viscosity, dependent on flow rate or frequency[14]. On the other hand, increasing viscosity effects, or negligible effects of the LCP have been reported for a few cases by Lee[15], Sukhadia and co-workers[16] and Isayev and Subramanian[17] for dynamic and steady shear experiments.

Blends of LCPs with PET have shown results consistent with the above-mentioned reduction in viscosity in the PET-rich part of the phase diagram, using dynamic and steady shear methods. Specifically, this was reported for blends with the stiff LCP Vectra A-900[18–20], as well as for blends with several semi-rigid mesogenic polymers[20–22]. It was found that the presence of flexible segments in the polymeric chain of the LCP enhances solubility in PET[21], at least for low concentrations up to 10 wt% LCP. The precise mechanism for this enhancement of fluidity is not clear. For biphasic blends, interfacial slipping, as well as flow orientation of the dispersed LCP phase have been proposed[14c]. For non-phase-separated blends, Lin and co-workers[22] found a 50–70% decrease of melt viscosity in a PET/LCP blend containing 2 wt% LCP. They attributed this lowering effect to a disentangling influence of the hard mesogenic segments of the LCP. A comparison of G′(ω) and G″(ω) between pure high-molecular-weight PET and the blends implied fundamental changes in the relaxation time spectrum of PET. Specifically, the longest relaxation time was shifted to lower values.

In the system which is under discussion here, a similar mechanism may be responsible for the effects observed. However, our data contrast with those of Lin and co-workers[22] since the lowering effect did not persist by further increasing the concentration in PBEPT. The blend with 10 wt% PBEPT has a higher viscosity than the other two blends with lower percentages. Similar effects were reported earlier, and reviewed by LaMantia and Valenza[12]. They have shown that the viscosity of the LCP must be higher, or at least equal to that of the TP, in order to yield a viscosity minimum at intermediate concentrations. We have not investigated the pure LCP, since blending studies were our main focus. Whether this behaviour can be attributed to macrophase separation, is a question which will be studied in the future.

The supercooling effect observed here, is similar to that seen in previously investigated systems[22]. The shift of the rheological crystallization temperature of the blends to higher values is indicated in *Figure 3* and was previously reported[23]. The LCP has a nucleating influence on PET, which was explained by activated-site initiation on interfaces in phase-separated blends[24]. In homogeneous systems, a higher molecular mobility due to disentanglement, as proposed by Lin and co-workers[22], provides an explanation for this effect.

For comparison, steady-shear scans were conducted with the same materials in the higher temperature region[10]. They showed the same tendency with LCP concentration, as indicated by the data in *Figure 3*. However, the material did not entirely fill the gap between the fixtures, which led to lower measured viscosity data.

CONCLUSIONS

A three-step monomer synthesis was employed to prepare a new monomer, 2-butoxyethyleneoxyhydroquinone. Solution polymerization of the monomer with terephthaloyl chloride in methylene chloride led to the formation of a thermotropic LC polyester, with an inherent viscosity of 0.4 dl g^{-1}. The polymer was stable to 350°C and melted around 240°C. It exhibited a nematic texture under crossed polars and there was observed a distinct LC–LC transition at 245°C shown by d.s.c. and confirmed by optical microscopy. Conveniently, it exhibited liquid crystallinity in the processing temperature range of PET. Melt blending studies showed no significant mechanical reinforcement of PET by the LCP, but there was a reduction in thermal shrinkage for the blends as compared to PET. Also, a decrease in melt viscosity of the blends was observed which facilitated processing. Quantification of this observation was done by rheological measurements. As expected, a quantitative decrease in the viscosity of the PBEPT blends was observed when compared to PET, even for a concentration as low as 2.5%. These results indicate that the polymer may function as a processing aid for PET.

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