Polymer Vol. 36 No. 12, pp. 2463-2466, 1995

0032-3861/95/$10.00+0.00

Thermotropic random copolyesters containing ethoxydiethyleneoxy-1,4-phenylene and ethylene terephthalate units

A. Tendolkar, S. Narayan-Sarathy, S. W. Kantor* and R. W. Lenz*
Polymer Science and Engineering Department, University of Massachusetts, Amherst, MA 01003, USA
(Received 26 May 1994; revised 8 January 1995)

A series of thermotropic random copolyesters was prepared by the reaction of ethoxydiethyleneoxyhydroquinone and ethylene glycol with terephthaloyl chloride. The purpose of this study was to investigate the effect of the flexible pendent oxyethylene group on the thermal and liquid crystalline (LC) properties of the copolyesters which were designed to form composites at the molecular level with flexible coil polyesters such as poly(ethylene terephthalate). The LC copolymers were characterized by viscosity measurements, elemental analysis, thermogravimetry (t.g.a.), d.s.c. and polarizing microscopy. The inherent viscosity as well as the temperature corresponding to the crystalline–nematic transition of the copolyesters decreased with increasing ethylene glycol content up to 60 mol% content. Beyond this composition, the viscosity values levelled off and there was an increase in the temperatures corresponding to the melting transitions. Polarizing microscopy studies revealed that the polymer melts were anisotropic and developed a nematic LC texture. At compositions beyond 60 mol% of the flexible ethylene glycol unit, a biphasic melt consisting of a predominant isotropic phase was observed.

(Keywords: LC copolyesters; EDEH; ethylene terephthalate)

INTRODUCTION

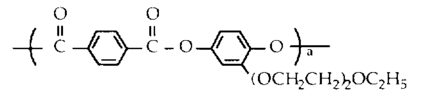
In the past, many aromatic polyesters with rigid backbones have been examined for their thermotropic liquid crystalline (LC) properties. Poly(*p*-phenylene terephthalate), which is a representative polyester, has a melting transition above its decomposition temperature which does not allow the proper characterization of the mesophase. In order to lower these transition temperatures without destroying thermotropic behaviour, one of the approaches that has been adopted is the use of asymmetrically substituted hydroquinones. One of the earliest reports in this area was described in a patent assigned to ICI in 1965[1]. Somewhat later, a series of patents assigned to DuPont and Eastman Kodak focused on the thermotropic behaviour of various aromatic polyesters based on substituted hydroquinones and many different aromatic or cycloaliphatic diacids[2–6]. The synthesis and characterization of chloro- and methyl-substituted hydroquinone containing polymers was later reported by Jin and co-workers[7]. The structure–property relationships in a series of thermotropic poly(2-n-alkyl-1,4-phenylene terephthalate) were studied by the same group[8]. In this series, the transition temperatures were almost independent of the pendant size but were molecular weight dependent. Krigbaum and co-workers also concluded that halogen, alkyl or phenyl substituents on one or both of the aromatic rings result in the lowering of transition temperatures as well as the degree of crystallinity[9]. Subsequently, the effect of alkoxy substituents on the hydroquinone ring was studied[10] and an exponential decrease in the melting temperature with increase in the length of the substituent was observed.

The present paper is concerned with the design, synthesis and properties of LC polyesters which could serve as components in molecular composites with flexible coil poly(ethylene terephthalate) (PET) as the matrix. For this purpose, thermotropic liquid crystalline polymers (LCPs) were prepared containing the substituted hydroquinones in which the substituent was a flexible pendent group which could reduce the transition temperatures of the LCP to the processing temperature range of PET and also impart dipolar interactions between the ether oxygen of the pendent group and the carbonyl group of PET. These polymers were expected to mix with PET at the molecular level to form a molecularly dispersed blend. Compatibilization could be further enhanced by the introduction of PET segments in the LC copolyester, to promote the interaction of the isotropic segments in the melt state. The objective of this paper is to describe the synthesis and characterization of a series of random copolyesters based on ethoxydiethyleneoxyhydroquinone (EDEH), ethylene glycol

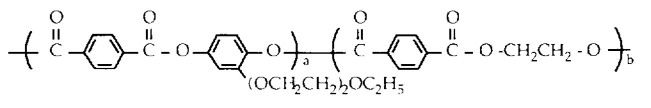
---

* To whom correspondence should be addressed

and terephthaloyl chloride moieties. The chemical structure of the polyesters described in this paper is:



P(EDEPT)



P(EDEPT - co - ET)

EXPERIMENT

All the chemicals were purchased from Aldrich Chemical Company. Terephthaloyl chloride was purified by sublimation. The solvent used for polymerization, methylene chloride, was distilled over phosphorus pentoxide and stored under argon. Triethylamine was distilled over sodium hydroxide. Inherent viscosities of the copolyesters was measured in 4-chlorophenol at 50°C at a polymer concentration of $0.5\,\mathrm{g\,dl^{-1}}$ with a Cannon–Ubbelohde viscometer. The d.s.c. measurements were done on a Perkin–Elmer DSC-2 instrument calibrated with indium and at a heating and cooling rate of $20^\circ\mathrm{C\,min^{-1}}$. The LC textures of the polymers were observed on an optical polarizing microscope (Carl Zeiss) equipped with crossed polarizers and a hot stage (Mettler). T.g.a. measurements were done on a DuPont 2100 instrument at a heating rate of $20^\circ\mathrm{C\,min^{-1}}$ in air and nitrogen atmospheres.

Monomer synthesis

EDEH was synthesized as described by Bhowmik and co-workers[10]. The purity of the monomer was confirmed by proton n.m.r. and elemental analysis.

Polymer synthesis

All the copolyesters were synthesized by a solution condensation polymerization process. A detailed procedure illustrating the preparation of a random copolymer with a 60:40 ratio of substituted hydroquinone:ethylene glycol is described below. To a three-neck flask were added EDEH (0.018 mol), ethylene glycol (0.012 mol) and triethylamine (0.06 mol) as an acid-acceptor. Methylene chloride (350 ml) was added to the flask and the reactants were stirred vigorously with a mechanical stirrer until dissolution. Terephthaloyl chloride (0.03 mol) was added slowly to the reaction mixture and the contents of the flask were stirred for 24 h at room temperature and for another day under reflux conditions. At the end of the period, the reaction was terminated by adding the contents of the flask to a three-fold excess of methanol, and the polymer was filtered from the solution to give a 90% yield of the crude material. The polymer was dried and purified by Soxhlet extraction with acetone to obtain the pure copolyester (yield 88%).

RESULTS AND DISCUSSION

Six polyesters containing the 2-ethoxydiethyleneoxy-1,4-phenylene terephthalate (EDEPT) unit were synthesized and characterized. The characterization results of the polyesters by viscometry and elemental analysis are listed in *Table 1*. The d.s.c. thermograms and optical micrographs of representative polymers are given in *Figures 1–3* and a summary of the thermal and optical properties are listed in *Table 2*.

The inherent viscosities of the polymers decreased with an increase in the molar composition of the ethylene terephthalate (ET) units but the values levelled off at ~60 mol% content of the flexible ET units. The decrease in viscosity may be attributed to the incorporation of flexible units into the polymer backbone interrupting the rigidity of the structure imparted by the mesogenic units. In addition, it is known that solution polymerization to form PET by the acid chloride method leads to lower molecular weights due to formation of cyclic oligomers[11] or to other side reactions including ether formation[12]. Since several side reactions have been reported previously for copolymers containing ET segments, it is probable that an increasing extent of side reactions is the dominant cause for the decrease in inherent viscosity with increasing ethylene glycol content. The elemental analyses were satisfactory, but they were not very sensitive to the compositional variations. All the polymers formed strong fibres when drawn from the melt, which was an indication of a molecular weight adequate for mechanical properties[13].

As can be seen from *Table 2*, the incorporation of a sequence of the flexible ET units into the backbone of the polymer resulted in decreasing the melting transitions of the copolymers from that of the LC homopolymer.

Table 1 Polyesters containing EDEPT and ET units

Polymer no.	Polymer composition x:y[a]	Yield (%)	Inherent viscosity ($\mathrm{dl\,g^{-1}}$)	Elemental analysis: Calculated C	Calculated H	Found C	Found H
1	100:0	91	2.1	64.52	5.38	63.95	5.39
2	80:20	90	0.9	64.09	5.13	63.86	5.34
3	60:40	89	0.7	63.73	4.89	63.83	5.30
4	40:60	90	0.5	63.33	4.65	62.45	4.39
5	20:80	92	0.5	62.92	4.41	63.06	4.77
6	0:100	95	0.5	62.52	4.16	62.43	4.12

[a] x = mol% EDEPT; y = mol% ET

Table 2 Thermal and optical properties of the copolyesters containing EDEPT and ET units

Polymer no.	Thermal transitions from d.s.c. (°C)		Thermal transitions from melting point apparatus (°C)		Thermal transitions from optical microscopy (°C)		Texture
	T_m[a]	$T_{LC/LC}$	T_m	$T_{LC/LC}$[b]	T_m	$T_{LC/LC}$[c]	
1	–[d]	257	210	257	212	257	Nematic
2	–[d]	232	187	242	192	242	Nematic
3	225	254	157	254	162	254	Nematic
4	225	–	157	–	162	227	Nematic
5	212	–	185	–	212	–	Biphasic
6	256	–	256	–	256	–	Spherulitic

[a] Melting of polymer

[b] Decrease in the melt viscosity of the polymer

[c] LC texture changes from dense nematic threads to highly birefringent Schlieren pattern

[d] Melting characterized by a broad maximum

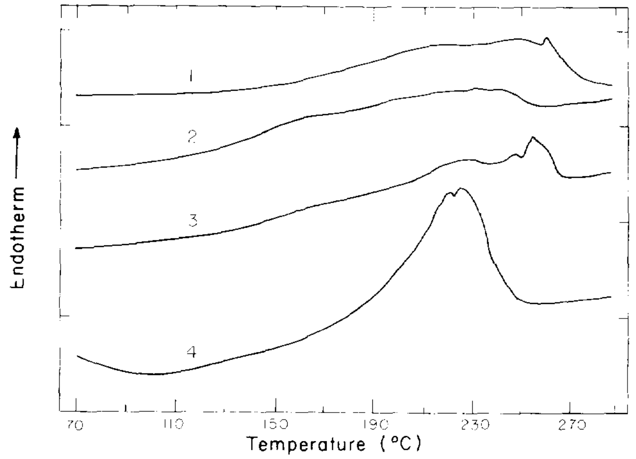
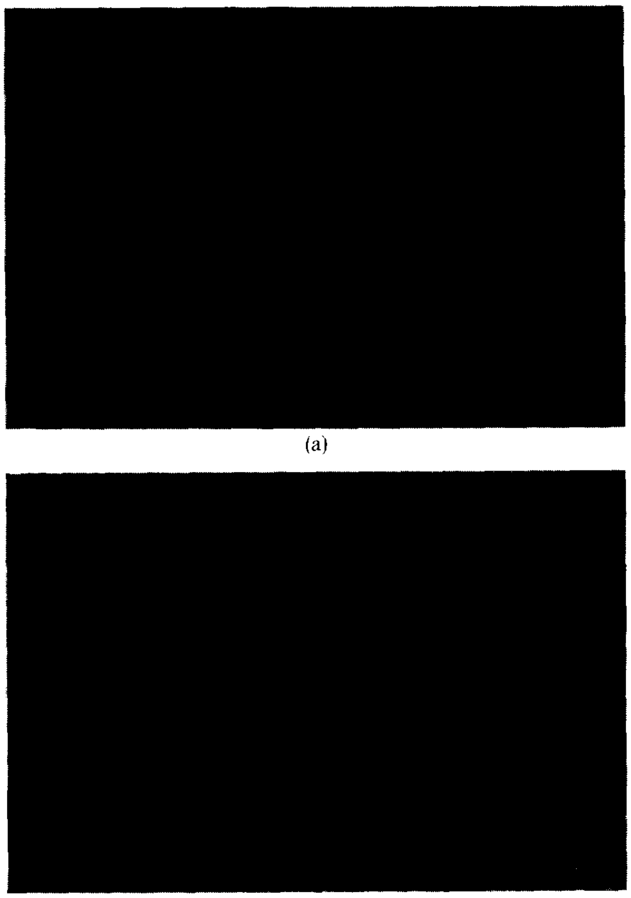


Figure 1 D.s.c. thermograms for polymers **1**–**4** recorded in the second heating cycle at a rate of 20°C min^{-1}

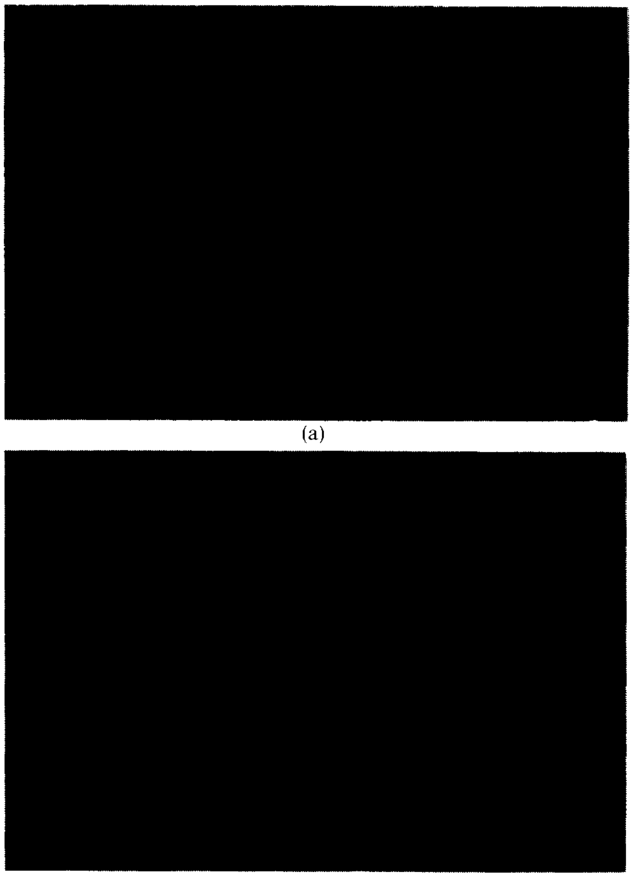
P(EDEPT). This trend is reversed above a 50 mol% content of the ET units. The minimum in melting point with increasing ET content is consistent with the behaviour of random copolymers. In contrast, LC copolymers show melting points of the separate segments that are not significantly affected by each other[14]. *Figure 1* shows the d.s.c. thermograms of the homopolymer and the copolyesters recorded in the second heating cycle. Polymers **1** and **2** show a very broad endothermic transition, which is comprised of two thermal transitions that were identified by optical microscopy observation. Both occurred more clearly in polymer **3**. The first transition is fairly broad and corresponds to a crystal–nematic transition of the LC polyesters. The second endotherm is a transition from one LC phase to another LC phase which is characterized by a change from a dense threaded nematic texture to a highly birefringent Schlieren texture. This transition is accompanied by a decrease in the melt viscosity and easier fluid flow of the polymer. This second transition is absent in the d.s.c. thermograms of polymers **4** and **5**. An endotherm corresponding to isotropization was not observed for any of the polymers up to the decomposition temperature of 320°C. The drop in viscosity observed for polymers **1**, **2**, **3** and **4** is characteristic of the nematic transition and was also reported in a similar polymer, poly(2-butoxyethyleneoxy-1,4-phenylene terephthalate)[15].


(a)

(b)

Figure 2 Optical micrographs for polymer **1** (magnification 720×): (a) room temperature; (b) 275°C

Polarizing light microscopy revealed two transitions in the copolyesters containing up to 60 mol% of ET units (polymers **1**–**4**). The samples for the microscopy studies were made by heating the polymers above their melting points in a melting point apparatus and quench cooling them rapidly from that high temperature. A dense threaded worm-like texture corresponding to a nematic phase was observed at room temperature for these samples. When they were heated at a rate of 10°C min^{-1}


(a)

(b)

Figure 3 Optical micrographs for polymer **5** (magnification 720 ×): (a) room temperature; (b) 215°C

on a hot stage to a point beyond the melting transition, a nematic texture, with a very low thread density and high birefringence, was observed close to the second transition temperature. These texture changes are illustrated in *Figures 2a* and *b*. Polymers containing up to 60 mol% of ET units showed this type of behaviour, but for a content of ~ 80 mol% of the flexible unit and above, formation of a biphasic texture in the melt, containing a LC phase and an anisotropic phase, was observed under crossed polars as shown in *Figure 3*. Evidence for a biphasic morphology is not apparent from the d.s.c. results and is only observed by polarizing microscopy. Complete isotropization was not observed for any of the polymers up to 320°C. This biphasic type of phase separation was not previously observed for copolyesters containing both mesogenic and non-mesogenic units[16]. However, in the earlier work, the chemical structures of the mesogenic and non-mesogenic units were closely related.

CONCLUSIONS

A series of copolyesters based on EDEPT units in the rigid segment and flexible ET units was synthesized by solution condensation polymerization. The inherent viscosities of the copolyesters were much lower than that of the LC homopolymer. All the copolyesters showed a nematic texture under crossed polars and a transition from a dense threaded nematic texture to a highly birefringent Schlieren pattern at high temperatures which was independent of the copolymer composition. A biphasic texture was observed for the copolyesters with 80 mol% or higher ET content.

ACKNOWLEDGEMENT

Financial support of this work by AKZO Nobel Inc. is gratefully acknowledged.

REFERENCES

1 Goodman, I., McIntyre, J. E. and Alfred, D. H. *Br. Pat. 993 272*, 1965

2 Kleinschuster, J. J., Pletcher, T. C., Shaefgen, J. R. and Luise, R. R. *Ger. Offen. 2520819* and *2520820*, 1975

3 Pletcher, T. C. *US Pat. 399 101 3*, 1976; Kleinschuster, J. J. *US Pat. 399 101 4*, 1976

4 Elliott, S. P. *Ger. Offen. 275 158 5*, 1978

5 Payet, C. R. *Ger. Offen. 275 165 3*, 1978

6 Jackson Jr, W. J., Gebeau, G. G. and Kuhfuss, H. F. *US Pat. 415 377 9*, 1978

7 Jin, J. I., Antoun, S., Ober, C. and Lenz, R. W. *Br. Polym. J.* 1980, 132

8 Majnusz, J., Catala, J. M. and Lenz, R. W. *Eur. Polym. J.* 1983, **19**, 1043

9 Krigbaum W. R., Hakemi, H. and Kotek, R. *Macromolecules* 1985, **18**, 965

10 Bhowmik, P. K., Garay, P. O. and Lenz, R. W. *Makromol. Chem.* 1991, **192**, 415

11 Foti, S., Giuffrida, M., Maravigna, P. and Montaudo, G. *J. Polym. Sci., Polym. Chem. Edn.* 1984, **22**, 1201

12 Ignatious, F., Lu, C., Kim, J. H., Kantor, S. W. and Lenz, R. W. *J. Polym. Sci., Polym. Chem. Edn* in press

13 Joslin, S. L., Giesa, R. and Farris, R. J. *Polymer* 1994, **35**, 4303

14 Ignatious, F., Lenz, R. W. and Kantor, S. W. *Macromolecules* 1994, **27**, 5248

15 Narayan-Sarathy, S., Wedler, W., Lenz, R. W. and Kantor, S. W. *Polymer* 1995, **36**, 2467

16 Reddy, C. R., Rao, K. K., Jin, J. I. and Lenz, R. W. *J. Polym. Sci., Polym. Chem. Edn* 1990, **28**, 2269