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Thermotropic polyesters with alkylene spacers in the main chain prepared in diphenyl ether

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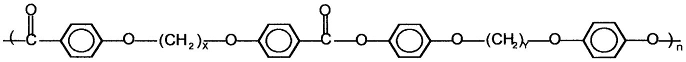
ABSTRACT

A series of linear thermotropic polyesters derived from 4,4'-dihydroxy-α, ω-diphenoxy alkanes and 4,4'-dichloroformyl-α ω-diphenoxy alkanes, was prepared by polycondensation in diphenyl ether. This method yielded polyesters that were characterized by a wider persistence range of the nematic phase with respect to the corresponding polyesters prepared by a conventional technique. The linear polyester series was characterized by calorimetric, optical microscopy, and thermogravimetric measurements. The linear thermotropic polyester series formed a stable nematic liquid crystalline phase in the melt and presented high thermal stabilities in the range of 410-449ºC.

INTRODUCTION

In thermotropic liquid crystalline polymers, the transition temperature from the solid to the liquid crystalline state is usually high. It is possible to lower the transition temperature of the main chain polymer by introducing a flexible moiety between the rigid mesogenic groups (1-4). The structure of the mesogenic core as well as of the flexible segments, together with the intermolecular and intramolecular cooperative forces imposed by their macromolecular nature, constitute the fundamental elements responsible for the ultimate characteristics of the polymers.

Thermotropic polyesters prepared from 4,4'-dihydroxy-α,ω-diphenoxy alkanes and 4,4'-dichloroformyl-α,ω-diphenoxy alkanes were primarily prepared by the conventional polycondensation method according to the interfacial technique described by reference (1). The present work concerns the mesomorphic properties and the thermal stability of a series of polyesters prepared in diphenyl ether, as described in previous report (4). The structures of thermotropic polyesters with alkylene spacers in the main chain, P66, P610, P106 and P1010 are closely related as schematically represented:



Polyester series, x or y = 6, 10

x	y	Sample
6	6	P66
6	10	P610
10	6	P106
10	10	P1010

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EXPERIMENTAL

The synthesis procedure of the polyesters employed in this study was described (4). The characterization of the polyesters was carried out by optical microscopy, DSC, TGA and viscometry.

Polarized optical microscopy was used to observe the texture of the mesomorphic. phase and the phase transition of the polyesters. A Reichert hot-stage microscope, under cross polarized light, with a programmable temperature controller was used. Inherent viscosities were measured with an Ubbelohde viscosimeter in phenol/1, 1,2,2,tetra-chloroethane mixture, volume ratio:6/4, at a concentration of 0,35g/dL at 30°C. Calorimetric measurements were performed with a Perkin Elmer DSC-7 differential scanning calorimeter under a nitrogen flow with both heating and cooling with 20°C/min. The maximum or the minimum of the endotherm or exotherm was taken as the transition temperature. Enthalpy changes were calculated from the endotherm or exotherm peak areas in the thermogram. The thermal stability of the polyesters was studied by thermogravimetric analysis under dynamic conditions, using a Perkin-Elmer TGA-7 instrument. The analyses were carried out in a nitrogen atmosphere with heating with 20°C/min, recording the percentage weight loss as a function of temperature.

RESULTS AND DISCUSSION

The polyesters prepared by polycondensation in diphenyl ether exhibited nematic schlieren texture in the melt between the melting and isotropization temperatures by polarized optical microscopy. The polymers were studied by polarizing microscopy and DSC. The polyesters showed a similar texture in the solid state. The nature of the stable mesophase was identified as nematic by textural observations and by the isotropizations enthalpy values in the range of 3.5 and 9.4 KJ/mol, consistent with the low degree of order of nematic molecular packing (1). Table 1 summarizes the combination of diols and diacid chlorides used in the preparation of the polyesters and lists the main thermal transitions of the polyesters. The transition temperature on melting (Tm) and the transition temperature on isotropization (Ti) decrease with increasing the length of the flexible chain (alkylene), as show in Table 1. The explanation for a reduction of isotropization temperature with increased spacer length is generally based on the effect of increasing the number of possible conformations of the long spacers with the resulting distortions of the cylindrical shape of the molecule. Most models assume that the entire molecule behaves as a rigid cylinder, and any change in geometry caused by bond rotation in the flexible unit that leads to a violation of the cylindrical shape results in formation of the isotropic phase (2).

TABLE 1 Thermal Transitions of Polyester serie

Sample	Tm^a (°C)	Ti^a (°C)	Tc^b (°C)	Td^b (°C)	ΔT (°C)
P66	209	274	173	272	65
P610	203	241	179	231	38
P106	189	217	160	207.5	28
P1010	175.5	210	156	200	34.5

Tm - melting, Ti - isotropization, Tc - crystallization, Td - deisotropization, ΔT= Ti-Tm
a- from DSC, 20°C/min heating rate, second heating run. b- from DSC, 20°C/min cooling rate, first cooling run.

The melting and isotropization transitions were reproducible, while slight deviations were observed in the successive heating-cooling cycles. The thermal behavior of P1010 is shown in Figure 1. Some solid samples exhibit DSC curves different from the samples from which thermal data were obtained. DSC curves show peaks at temperatures well bellow the transition to the nematic phase. These peaks were also observed by Griffin and Havens (1,5).

Two phase transitions occur in the polyesters as shown by DSC measurements. Two endothermic peaks, the transition temperature on melting (Tm) and of that on forming the isotropic liquid (Ti), were observed on heating and two exothermic peaks were also detected on cooling. The polymers exhibit a mesomorphic phase both on heating and on cooling. The enantiotropic phase transition is clearly observed. The highest temperature by DSC shows the transition temperature from the mesomorphic phase to the isotropic liquid observed by polarized microscopy. The thermal properties of polyesters are summarized in Table 2. The enthalpy change for the transition from the mesomorphic state to the isotropic liquid is larger than the melting enthalpy. The enthalpy changes for the melting transition for small molecule liquid crystals are normally an order of magnitude larger than the enthalpy changes for the isotropization transition (1). From the enthalpy change for the melting transition of polyesters listed in Table 2, it is observed that these values are smaller than the enthalpy change for the isotropization transition. Although the transition temperatures observed on heating of the polyesters prepared in diphenyl ether are lower than those prepared by Griffin and Havens (1), the magnitudes of the enthalpy change are close to those determined by them. This result is probably due to the relatively lower molecular weights. The polyesters prepared in diphenyl ether show the mesophase in the 28-65°C range while the same polyesters obtained by interfacial polymerization, as reported by Griffin and Havens, is in the 24-30°C range.

TABLE 2 Thermal Properties of Polyester serie

Sample	ΔHm^a (J/g)	ΔHi^a (J/g)	ΔHc^b (J/g)	ΔHd ^{b}(J/g)
P66	7.5	22.9	9.3	12.8
P610	11.1	24.4	14.0	29.5
P106	4.8	10.4	8.4	21.9
P1010	8.9	25.6	8.9	27.8

a- from DSC, 20°C/min heating rate, second heating run. b- from DSC, 20°C/min cooling rate, first cooling run.

The polyesters crystallizes easily on cooling, with a relatively low degree of supercooling (6-8). Supercooling was always very low in the case of isotropic phase as compared to the solid phase (Table 3). This property is apparently due to increased order in a solid polymer.

The influence of the spacer length on the thermal decomposition of polyesters was also verified. The polyesters were investigated by thermogravimetric analysis between room temperature and 700°C, and found to be thermally stable. The thermal stability of the polymers did not change. The degradation temperatures did not show a significant change. The thermal stability limit, which is taken as the temperature at which 5% weight loss ocurred, varied from 410-449°C indicating that the polyesters had good thermal stabilities for melt processing at elevated temperatures. These polyesters appear to have appropriate intrinsic character for blending with commmercially available polyolefins (PP). An investigation is in progress on these thermotropic polyester blends. All polyesters are insoluble in common organic solvents. The solubility was obtained with hot phenol/1, 1,2,2,-tetrachloroethane mixtures (volume ratio:6/4). The polyesters have similar molecular weights as indicated by solution viscosities. The inherent viscosity is in the range of 0,29-0,33 dL/g.

TABLE 3 Supercooling of Solid Phase and Isotropic Phase of Polyester serie

Sample	(Tm-Tc) (°C)	(Ti-Td) (°C)
P66	36	2
P610	24	10
P106	29	9.5
P1010	19.5	10

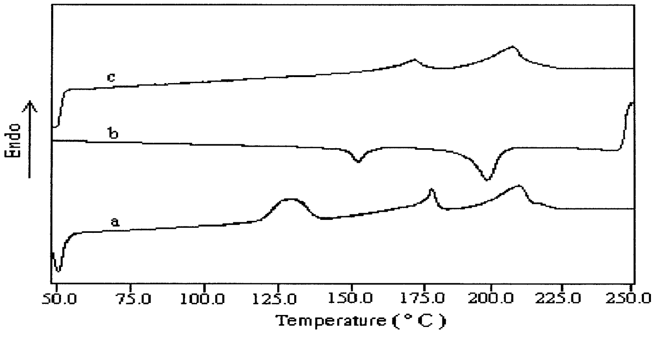

Fig. 1. DSC behavior of P1010. First heating run (curve a), first cooling run (curve b), second heating run (curve c). Temperature scanning rate: 20°C/min

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