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Thermotropic polyester: the influence of the spacer on the physical properties

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ABSTRACT

Thermotropic polyesters prepared from series of 4,4'-dihydroxy-α,w-diphenoxy alkanes and 4,4'-dichloroformyl-α,w-diphenoxy alkanes are well known. The substitution of a methylenic spacer by an oxyethylenic spacer in the main chain of these polyesters drastically modifies their physical properties, particularly the mesogenic transition temperatures, as can be observed by DSC and thermooptical analysis. The thermal stability and the polymer solubility in common organic solvents of these polymers did not show a significant change. The physical properties of the two thermotropic polyesters prepared in diphenyl ether were evaluated.

INTRODUCTION

The systematic study of thermotropic main chain polymers started about twenty years ago, so it is not surprising that the understanding of the structure-property relantionships in such polymers is still incomplete (1). Thermotropic liquid crystalline polymers have been a topic of scientific investigation since melt processing, extrusion, and other processing techniques make these systems commercially attractive (2-5). To exploit the advantages of melt processing, low melting transitions are required. The introduction of a spacer in a main chain of a thermotropic polymer can effectively reduce the melting transition temperature while maintaining the liquid crystalline properties. The aim of this study was to verify the influence of replacing a methylenic spacer by an oxyethylenic spacer on the physical properties of the two thermotropic liquid crystalline polyesters prepared by polycondensation in diphenyl ether.

EXPERIMENTAL

Synthesis and Characterization

The monomers were prepared according to procedures reported (6,7). The polyesters were prepared in a flask equipped with a condenser fitted with a drying tube. Diacid chloride (4,3mmol) were mixed with stoichiometric amounts of 1,10-di(4-hydroxyphenoxy) decane in 9.0mL of diphenyl ether. The reaction mixture was heated to 145°C for 24h. The viscous medium was diluted with 20.0mL of diphenyl ether and poured hot into methanol. The precipitated polymer was washed overnight with methanol in a Soxhlet extractor and dried under vacuum at 100°C. The characterization of

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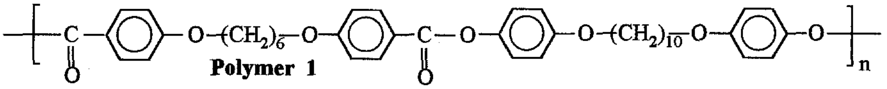
the polymers was carried out using optical microscopy, DSC, TGA and viscometry.

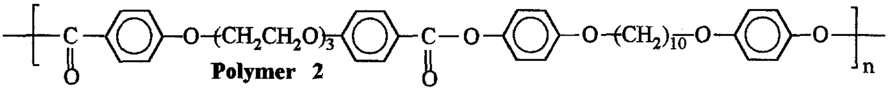
Thermal transitions under polarized light were studied visually by using a Reichert polarizing microscope equipped with a hot stage. Phase transition temperatures were measured on a Perkin-Elmer DSC-7 instrument under a nitrogen flow with both heating and cooling at 20°C/min. The maxima of the peaks were taken as the transition temperatures. Values of ΔH were calculated from the endotherm 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 and the rate of weight loss as a function of the temperature. The solubility of the polymers was measured in several organic solvents at 1% (p/v). Solution viscosities were measured in a phenol/1,1,2,2-tetrachloroethane mixture, volume ratio: 6/4, at 0,35 g polymer per 100mL at 30°C by using a Ubbelohde capillary viscometer.

RESULTS AND DISCUSSION

The structures of the main chain thermotropic polyesters prepared are:



Polymer 1



Polymer 2

The polymers were studied by polarizing microscopic observation and DSC.

The influence of the spacer on the transition temperatures is notable. Figures 1 and 2 show the DSC curves of the synthesized polymers. The two polymers examined by DSC showed at least two endotherms. The highest transition in both cases was broad and corresponded to a transition from a liquid-crystalline phase to an isotropic phase.

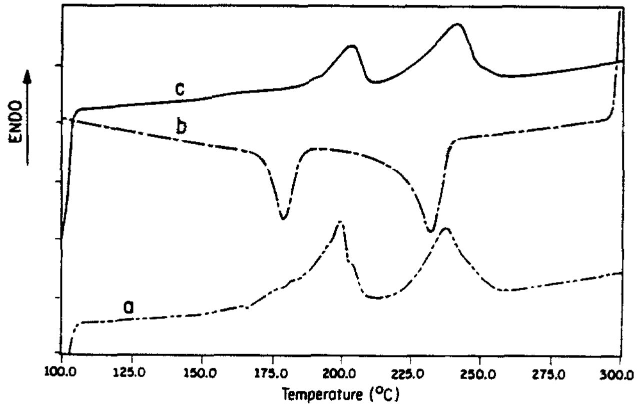


Fig. 1. DSC curves of Polymer 1: (a) first heating run, (b) first cooling run and (c) second heating run.

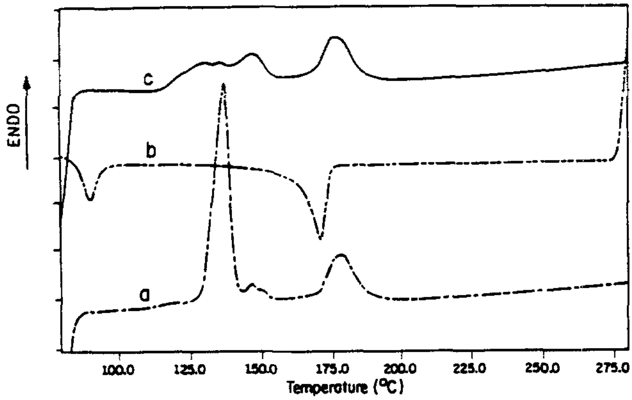


Fig. 2. DSC curves of Polymer 2: (a) first heating run, (b) first cooling run and (c) second heating run.

Polymer 1 showed a melting transition temperature at 203°C while Polymer 2 showed multiple melting endotherms in which the solid-liquid crystal transition corresponded to the peak of the highest transition temperature. Polymer 1 showed a nematic mesophase (6) up to 245°C by polarizing microscope. The DSC curves of Polymer 1 are shown in Figure 1. Two broad endotherms corresponding to the melting and isotropic points appeared in the vicinity of 200-245°C on the first and second heating runs whereas Polymer 2 showed a large and sharp endotherm and other two small endotherms on the first heating run before entering the mesophase, followed by the liquid crystal-isotropic transition endotherm. After cooling, the melting endotherms were widened as can be seen in Figure 2. No fluidity was observed for the sample at temperatures between these transitions. There are obvious exothermal crystallization transitions due to the high degree of crystallization in the polymers. Both polymers showed two crystallization exotherms on cooling from the isotropic melting. The exotherms corresponded to the isotropic-liquid crystal and liquid crystal-solid transitions, respectively. Table 1 shows the transition temperatures and enthalpies of Polymers 1 and 2.

TABLE 1 Thermotropic Properties of the Polymers.

Polymer	*Tm*[a] *(°C)*	*Ti*[a] *(°C)*	*ΔHm*[a] *(J/g)*	*ΔHi*[a] *(J/g)*	*ΔT(°C)*
1	203	241	11,1	24,4	38
2	146,5	175	19,7	14,3	28,5

a-from DSC, 20°C/min heating rate, second heating run.
m-melting, *i*-isotropic

The influence of the spacer on the thermal decomposition of polyesters was also verified. The thermal stability of the two polymers did not change. The degradation temperatures did not show a very significant change between them as can be observed in Table 2. A typical plot of both polymers is shown in Figure 3. The thermal stability limit, which is taken as the temperature at which 5% weight loss ocurred, varied from 403-410°C indicating that the polyesters had good thermal stabilities for melt processing at elevated temperatures .

TABLE 2 Characteristic degradation temperatures[a] and viscosity data

Polymer	*Ti (°C)*	*$T_{5\%}$ (°C)*	*$T_{50\%}$ (°C)*	*T'(°C)*	η_{inh} [b] (dL/g)
1	361	410	474	483	0,32
2	360	403	474	478	0,27

a-from TGA, 20°C/min heating rate, *Ti*-the initial degradation temperature, $T_{5\%}$ and $T_{50\%}$-the temperatures for 5 and 50% weight loss respectively, *T'*-the temperature corresponding to the maximum degradation rate. *b*- inherent viscosity in phenol/1,1,2,2-tetrachloroethane mixture, volume ratio: 6/4, at 30°C and a concentration of 0,35g/dL

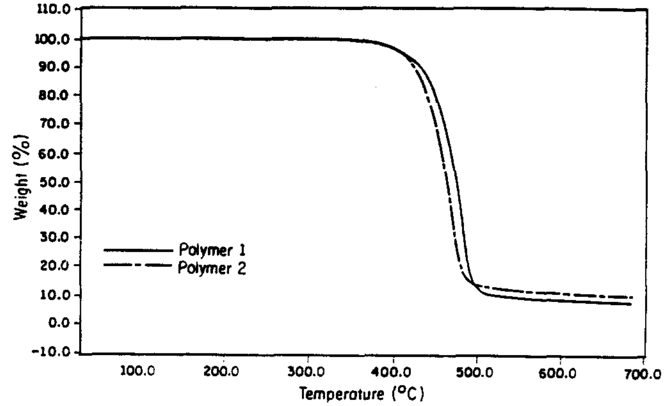
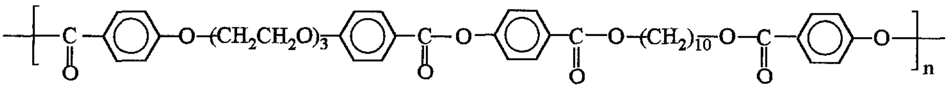


Fig. 3. Thermogravimetric analysis (TGA) of the polymers.

The synthesized polyesters are insoluble in common organic solvents, such as chloroform, dichloromethane, dimethylformamide, 1,1,2,2-tetrachloroethane and dimethylsulphoxide. The introducing of a more flexible spacer containing additional oxygen in the chain of Polymer 2, did not show any significant solubility change at room temperature. Solubility was obtained with phenol/1,1,2,2-tetrachloroethane mixture, volume ratio: 6/4. The polymers have comparable molecular weights as indicated by their solution viscosities (Table 2). The polymer with methylenic spacer (Polymer 1) is soluble in hot cosolvent (phenol/1,1,2,2-tetrachloroethane mixture,volume ratio: 6/4) while the polymer with oxyethylenic spacer (Polymer 2) is soluble in cold cosolvent. This latter result was very different from that obtained for the thermotropic polyesters soluble in chloroform reported by Chiellini et al. (8,9), the structure of which is depicted bellow :



The presence of an additional carbonyl group in the mesogenic core of the polyester improves the chloroform solubility of this polymer. In the absence of this carbonyl group the packing density of the chains increases in the solid state leading to a poor solubility in common organic solvents. It was also observed that the mesomorphic transitions of Polymer 2 were higher than that of the above mentioned polyester.

CONCLUSION

Thermotropic polyesters, in general, have high melting transitions (Tm) and low solubilities in common organic solvents because of their extended rigid structures and high melting enthalpies. The data obtained show the effective role played by the flexible spacer in determining the ultimate physical properties of thermotropic polyesters.

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