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Thermal transitions in poly(alkyl-4,4′-diphenoxy terephthalate)s

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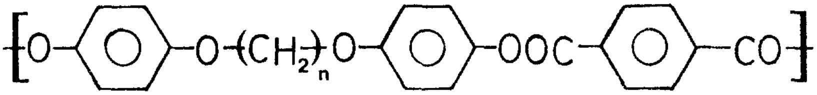
Summary

The thermal transitions of poly(alkyl-4,4'-diphenoxy terephthalate)s, in which the flexible spacer contains 5,6 and 7 methylene groups, have been studied by thermogravimetry, differential scanning calorimetry, X ray diffraction, thermoptical microscopy and small angle light scattering. The series shows a marked influence of the even and odd number of methylene groups on the crystal-liquid crystal transition temperatures and on the isotropization transition temperature. Nematic mesophases have been observed for the odd terms, and a transition from a smectic to a nematic mesophase has been observed for the even term.

Introduction

Polyesters prepared from a series of 4,4'-dihydroxy -α,ω-diphenoxy alkanes and terephthalic acid have been described by Lenz et al (1-3), with the general structure:



These polyesters are semicrystalline and, although the transition temperatures have been reported for some terms of the series, with n from 5 to 10 (1-6), there are some important differences in these temperatures due to either the influence of different thermal histories or the texture of some of the polymers. Thus, we have recently reported the transitions in the polymer with n=10 (7). A crystal-smectic mesophase transition occurs at 240°C and at a higher temperature of between 250°-260°C, a transition from smectic C to nematic occurs before the isotropic transition.

In our laboratory , studies of the kinetics of crystallization from the isotropic state or from the mesophase have been initiated (8,9). Prior to these studies, the analysis of the thermal transitions, the correlated thermodynamic parameters and the effect of the length of the flexible spacer on these transitions and on the nature of the mesophase must be investigated.

Therefore, the aim of this work is the analysis of these factors for the members of the series with n=5,6 and 7, and the comparison of the results with those previously reported by others (1-6).

Experimental

Materials

The polymers, poly (pentamethylene-4,4'-diphenoxy terephthalate), PPDPT, poly

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(hexamethylene-4,4'-diphenoxy terephthalate), PHXDPT, and poly (heptamethylene-4,4'-diphenoxy terephthalate), PHDPT, were synthetized by a method described by Lenz et al (2).

The monomers, 4,4'-dihidroxy-α,ω-diphenoxy alkanes were prepared as described by Griffin and Havens (10) from hydroquinone and α,ω-dibromoalkanes.

The polymers were obtained by melt polycondensation of the corresponding monomer with the stoichiometric amount of terephthaloyl chloride, under nitrogen. The polymers were dissolved in boiling p-chlorophenol, filtered, and the solvent eliminated in a rotary evaporator. The final products were washed thoroughly with ethanol, and then dried at room temperature under vacuum.

The characterization of the polymers was carried out by elemental analysis, IR, ^{1}H-NMR and ^{13}C-NMR methods. ^{1}H-NMR spectra were recorded on a 200MHz-Brucker spectrometer, in solution, at 50°C, using 50/50 pentafluorophenol-chloroform mixture as solvent. The ^{1}H-NMR spectra show the following chemical shifts:

PHDPT: δ=8.21 (4H terephthalate), δ=6.99 (4H ester phenyl), δ=6.76 (4H ether phenyl), δ= 3.92 (4H methylene), δ=1.69 (4H methylene), δ=1.36 (6H methylene).

PHXDPT:δ=8.34 (4H terephthalate), δ=7.13 (4H ester phenyl), δ=7.03 (4H ether phenyl), δ=4.06 (4H methylene), δ=1.88 (4H methylene), δ=1.59 (4H methylene).

PPDPT: δ=8.34 (4H terephthalate), δ=7.13 (4H ester phenyl), δ=6.89 (4H ether phenyl), δ=4.08 (4H methylene), δ=1.9 (4H methylene), δ=1.7 (2H methylene).

The inherent viscosities of the polymer solutions were measured in an Ubbelhole viscosimeter, at a concentration of 0.45 dl.g^{-1} in p-chlorophenol at 45°C and are shown in Table 1.

Procedures

Thermogravimetric analysis was carried out on a Mettler TA-4000 TG-50 thermobalance, using nitrogen as the purge gas, with a heating rate of 10°C.min^{-1}. The thermal transitions were measured in a Mettler DSC TA 3000 with a DSC-30 furnace coupled to a computer with TA72 thermal analysis software. The heating rate was 10°C.min^{-1} and the peak maxima were taken as the transition temperatures. The transition temperatures are given in Table 1.

X-ray diffractograms of the samples with different thermal treatments were obtained using a Philips Geiger counter X-ray diffractometer with an Anton Paar 300 temperature camera. The diffractograms were recorded in a 2θ range between 3° and 32° at a rate of 2° .min^{-1}, using Ni filtered CuK$_\alpha$ radiation.

Microscopic and thermoptical analysis were carried out using a Reichert Zetopan Pol polarizing microscope , equipped with a Mettler FP80 hot stage and a Nikon FX35A camera.

Small angle light scattering studies were carried out with an instrument similar to that described by Stein (11), using a He-Ne laser (λ=632.8 nm) , and scattering patterns were recorded on Polaroid plates. In some cases, morphological analysis was carried out at a range of temperatures using a Mettler FP80 hot stage.

Results and discussion

The three polymers, poly (pentamethylene-4.4'-diphenoxy terephthalate), PPDPT, poly (hexamethylene-4,4'-diphenoxy terephthalate), PHXDPT and poly (heptamethylene-4,4'-diphenoxy terephthalate), PHDPT, have been characterized by elemental analysis, IR, ^{1}H and ^{13}C NMR. These techniques show that the structures of the resulting materials in these three cases correspond to a linear polymer with the predicted theoretical structure. The inherent viscosities of the polymers in p-chlorophenol at 45°C are shown in Table I.

n	η_{inh} (dl.g^{-1})	T_g (°C)	T_l (°C)	T_i (°C)	ΔH_l (J.g^{-1})	ΔH_i (J.g^{-1})	Ref
5	0.26	112	168	251	13.6	7.5	This work
	0.328	-	242	355	22	-	3
6	0.366	51	255	360	36	-	This work
	-	-	267	330	21.3	-	3
	0.23	-	267	351	20.3	11.6	4
7	0.11	67.3	162	203	37.4	3.7	This work
	0.339	-	239	326	19.7	2.06	3
10	0.45	67.1	241	290	56.6	8.2	7
	0.174	-	237	265	23.12	5.7	3
	0.41	-	240	297	-	-	2
	0.54	-	238	267	-	5.1	5
	0.21	-	240	267	-	-	4
	0.79	183	272	327	-	-	6

Table I- Inherent viscosities and thermal transitions of Poly (alkyl-4,4'-diphenoxy terephthalate)s.

In order to determine the thermal stability, thermogravimetric analysis was carried out under dynamic conditions in a nitrogen atmosphere. PHDPT is shown to be stable up to 350°C, and only a 10% weight loss is observed at 400°C. Under isothermal conditions at 320°C, this polyester was shown to be stable for at least sixty minutes . PHXDPT is stable up to 350°C with a 10% weight loss at 390°C, and PPDPT is stable at 300°C with a 10% weight loss at 355°C.

The thermal transitions were studied by DSC using several heating and cooling cycles for the same sample. For PHDPT, when the original sample is heated at a rate of 10°C.min^{-1}, a change in the specific heat is found at 67°C, followed by a multiple endotherm at 162°C and finally a broad endotherm at 203°C (Fig. 1a).The first transition is related to a glass transition, and the first endothermic peak corresponds to the crystal-liquid crystal transition, as it will be shown by microscopy and X-ray analysis. The second endothermic peak is related with the liquid crystal-isotropic transition. When the sample is cooled down to room temperature at 10°C.min^{-1}, a crystallization peak is observed at 170°C with an enthalpy of 16 J.g^{-1} (Fig.1b). A subsequent heating cycle shows two peaks in the region of the crystal-mesophase transition, and the isotropization temperature at 203°C. It is important to note that the different thermal treatments do not affect the transition temperatures, contrary to the results obtained for other polymer liquid crystals (12-16).

The same thermal cycles have been studied in the case of PHXDPT and PPDPT and the values obtained for the thermal parameters are compiled in Table 1.

A general observation is the existence of multiple melting peaks. This fact occurs very

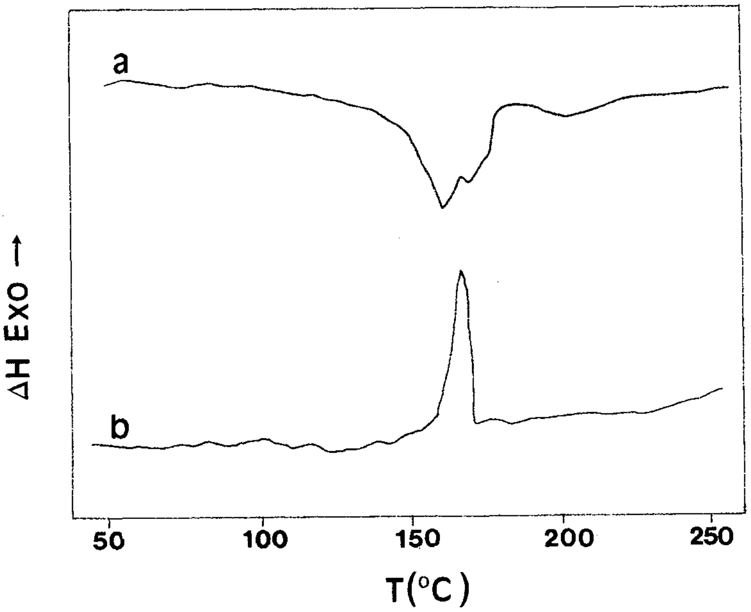

Figure 1: DSC curves of PHDPT: a) Original sample heated up to 250˚C. b) Sample "a" cooled down to room temperature.

often in many semicrystalline polymers (17-22) and in thermotropic polyesters (15,23-27). The origin of this effect has been widely discussed and in some cases, it has been attributed to different crystalline forms (17,18), differences in the crystallite size or the crystallite size distributions (19,21), and to melting -recrystallization processes (20,22). It is evident from the X-ray analysis, which will be commented below, that in any case v e have found polymorphism and only the two other reasons may be operative in this series.

In order to study the transitions and its characteristics, we have completed the analysis by wide angle X-ray diffraction, optical microscopy and small angle light scattering.

Wide angle X-ray diffraction patterns were obtained from the original sample and from the thermally treated samples. In the case of PHDPT, the reflections appear at $2\theta=19.5^\circ, 23^\circ, 28^\circ$ and 29°, with a small reflexion at $2\theta=7^\circ$. PHXDPT shows reflections at 3.5°, 7.3°, 19.8°, 23.5°, 28.3° and 30° and PPDPT at 3.8°, 19.2°, 23° and 27° (Fig.2).

In the three cases, the reflection at high 2θ is associated with order in the crystalline structure and the reflections at low 2θ in PHXDPT may correspond to intermolecular order related with smectic mesophases. In PPDPT and PHDPT, the reflections at low 2θ are very diffuse, as can be observed for nematic mesophases.

These reflections are maintaned after the different thermal cycles. However, at the temperatures corresponding to the crystal-liquid crystal transitions, the high 2θ reflections disappear and only an amorphous halo persists up to the isotropization temperature, (Fig.2). Only in the case of PHXDFT, a transition from the smectic to the nematic mesophase has been observed. A similar transition, only few degrees above T_1, was reported for the polymer of the same series with n=10 (7).

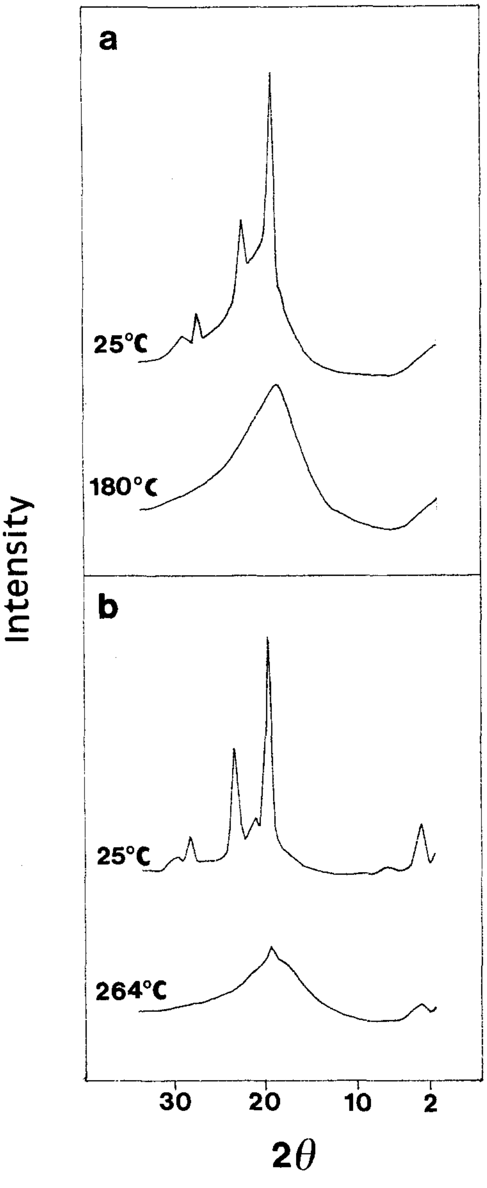

Figure 2.-X-ray diffractograms as a function of temperature for: a)PHDPT, b) PHXDPT.

The values of the transition temperatures T_l and T_i are related with the number of the methylene groups in the spacer and show an odd-even effect, with higher temperatures for the even terms of the series. The dependence of T_l and T_i with n corresponds to the usual behaviour of other polyesters with flexible methylene spacers (10,28,29).

The values of T_l are lower than those reported by others (1-3). Higher values are probably due to overheating during the determination resulting from inadequate heating rates. The enthalpies for this transition range from 1.36 to 6.6 Kcal.mol^{-1} and these values are higher than those previously published (1-3), indicating a higher content of three dimensional order. The corresponding values of ΔH_l and ΔS_l increase with the number of methylene groups, contrary to previous results (3), in which these two parameters are practically constant.

The endotherm associated to the liquid crystal-isotropic transition is very wide and takes place in a range of about 50°C. The values of T_i follow an odd-even zig-zag pattern (Fig.3) in contrary to previous data, an observation, which could not be explained (3).

The odd-even effect in T_l and T_i has been observed in monomeric compounds and it has been explained as due to changes of the molecular polarizability (30) or conformational effects (31,32).

The glass transition temperature found above room temperature decreases with the number of methylene groups, due to differences in molecular mobility. The analysis of the origin of this transition in this series and its correlation with other glassy transitions will be discussed elsewhere (33). It is, however, very important to remark the existence of two glass transition temperatures below T_l , determined by DSC and by dynamomechanical analysis, both transitions related with the amorphous phase and the glassy mesophase, respectively.

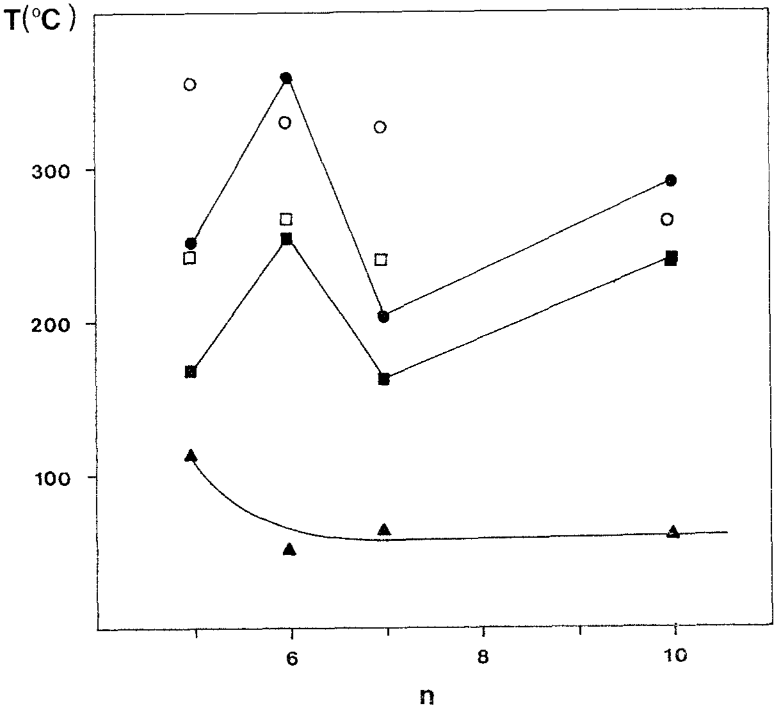

Figure 3.- Dependence of thermal transition temperatures on the length of the flexible spacer:(○) T_i ref.3 , (●) T_i this work, (□) T_l ref.3, (■) T_l this work, (▲) T_g this work.

On the other hand, to disclose the morphology of these polyesters in the crystalline and in the mesophase region, we have used optical microscopy and SALS. When thermoptical analysis is used for PHDPT, at about 180°C an increase in birrefrigence is observed which corresponds to the crystal-liquid crystal transition and a complete loss of intensity at 230°C, when the isotropization temperature is reached. When the polymer is quenched in liquid nitrogen from the isotropic state, a sharp loss of birrefrigence at 180°C is observed. In principle, this indicates the existence only of crystalline order without the coexistence of a mesophase at room temperature. With other thermal treatments, both crystalline and liquid crystal phases coexist and at the melting temperature of the crystalline phase,T_l, the birrefringence of the mesophase is still observed.

Although Schlieren textures have been reported for these polymers (3), only marbled textures have been found for PHDPT and also for PHXDPT and PPDPT. However, in these two last cases, also blurred Schlieren textures, typical for nematic mesophases, have been observed.

Small angle light scattering experiments show only circular spots in the three polymers. It is known that the characteristic of the mesophase can be predicted from this type of experiments (11,34-36) and the smectic A and B states present a four-leaf clover H_v pattern, and smectic C and the nematic mesophases have been reported to give circularly symmetric patterns (34).

If the X-ray analysis is combined with the microscopy studies, we can conclude that PHXDPT presents a transition from an smectic mesophase to a nematic mesophase slightly above T_i. This conclusion is similar to that found for PDDPT (7). Thus, polyesters with an even number of methylene groups present a sharp refflexion at low 2θ in the WAXS patterns, associated with smectic mesophase, which undergoes a transition to a nematic mesophase at temperatures close to T_i. The polyesters with an odd number of methylene groups only show the nematic mesophase.

These conclusions agree with previous results on the influence of the odd-even nature of the methylene groups in polyesters (10,37,38), through changes in the conformation of the mesogenic units and/or the methylene groups. Preliminary analysis by ^{13}C solid state NMR seems to confirm the existence of different conformations between the even and odd series with different orientation of the rings in the mesogenic unit for the odd terms (39). Moreover, theoretical conclusions (40) have shown that the type of bond between the mesogenic group and the spacer is a determining factor for the conformations of the chains and, consequently , for the formation of a given mesophase.

Acknowledgment
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