Thermal transitions of liquid crystal polyesters: Poly(decamethylene-4,4'-diphenoxy terephthalate)

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Summary

The thermal transitions of liquid crystalline poly (decamethylene-4,4'-diphenoxy terephthalate) have been studied by differential scanning calorimetry, X ray diffraction and thermoptical microscopy.
At room temperature a three dimensional order and a smectic mesophase coexist. The crystal–smectic mesophase transition occurs at 240°C and at higher temperature , 250-260°C, a transition from smectic C to nematic has been observed, before the isotropic transition at 290°C. The no previously known smectic C–nematic transition has been detected by microscopy, observing bars and striated textures, and by X ray diffraction patterns obtained in the whole range of temperatures.

Introduction

Thermotropic polyesters are one of the more developed types of main chain liquid crystalline polymers. Different polyesters with several mesogenic units and methylene spacers have been reported in the literature (1,2).The properties of these systems, particularly the mesogenic transition temperatures have been investigated and the influence of the spacer size and the mesogenic units on the transitions and on the mesophase formation has been considered (3,4).

Polyesters prepared from a series of 4,4'-dihidroxy-α,ω-diphenoxy alkanes and terephthalic acid with the general structure:

$$\left[O-\left\langle\bigcirc\right\rangle-O-(CH_2)_n-O-\left\langle\bigcirc\right\rangle-OOC-\left\langle\bigcirc\right\rangle-CO\right]$$

(1)
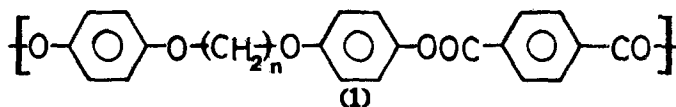
have been previously described by Lenz et al (1,5), where n ranges from 5 to 10. The effect of the length of the flexible spacer on the thermotropic characteristics was investigated (6).

Microscopic and SALS examination was considered as evidence of a nematic texture for most of these polymers. However, information about the kinetics of mesophase or crystalline formation in polymer liquid crystals is very scarce. Only in few cases kinetics studies have been carried out on thermotropic polyesters (7-10). In our laboratory, we have initiated a

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general project on the properties and mechanism of mesophase formation in liquid crystals based on different mesogenic units and linear and branched substituted polyglycols, including the one with the structure given in (1).

In this work we report the analysis of the polymer with n=10 , poly (decamethylen -4,4'- diphenoxy terephthalate) and the differences with previous reports (5,6). Prior to the study of the kinetics, that will be reported elsewhere , special emphasis has been placed on the influence of the thermal history on the transitions and on the nature of the mesophase.

Experimental

Synthesis and characterization

The monomer, 4,4'-dihidroxy-α,ω-diphenoxy decamethylene, DHDFD, was synthetized as described by Griffin and Havens (12) from hydroquinone andα ,ω-dibromodecamethylene.

Poly (decamethylene- 4,4'-diphenoxy terephthalate),PTDFD, was prepared by a method described by Lenz et al (5). Characterization of DHDFD and PTDFD was carried out by elemental analysis , IR, H^1 NMR and C^{13} NMR methods.The results from elemental analysis were:

DHDFD. Found, %C 72.97; %H 8.68. Calculated, %C 73.74, %H 8.38.

PTDFD. Found, %C 73.35; %H 6.79. Calculated, %C 73.77, %H 6.55.

IR spectrum of DHDFD exhibited the characteristic bands of the aromatic rings, ether, hydroxylic and methylene groups. The spectrum of PTDFD presents the same bands and the corresponding of the ester group.

^{1}H NMR and ^{13}C NMR spectre were recorded on a 200 MHz Bruker spectrometer, in solution, at 50°C .Dimethylsulfoxide and 50/50 pentafluorophenol –chloroform mixture were used as solvent for DHDFD and PTDFD respectively. The ^{1}H NMR spectre show the following chemical shifts:

DHDFD:^{1}H NMR (DMSO): δ =8.71(2H hidroxylic group), δ =6.69(8H hidroxyphenyl), δ =3.83 (4H methylene), δ =1.6(4H methylene), δ =1.28(12H methylene).

PTDFD:^{1}H NMR (pentafluorphenol/CDCl$_3$), δ =8.32 (4H terephthalate), δ =7.15(4H, ester phenyl), δ =6.94 (4H ether phenyl), δ =4(4H methylene), δ =1.8 (4H methylene),δ =1.38 (12H methylene).

The chemical shifts of the ^{13}C NMR spectra are:

DHDFD: ^{13}C NMR (DMSO): δ =151.4, 150.9, 115.3 (hidroxy phenyl group), δ =67.89 (methylene), δ =28.65 (methylene), 25.29 (methylene).

PTDFD: ^{13}C NMR (pentafluorphenol/CDCl$_2$): δ =166.64 (carbonyl group), δ =157.19, 144.31, 122.21, 115.81 (ether phenyl), δ =135.4, 131 (ester phenyl) , δ =69.6, 29.4, 25.9 (methylene group).

Physical properties

The thermal transitions were measured in a DSC Mettler TA 3000 with a DSC-30 furnace, coupled to a computer with TA72 software. The heating rate was 10°C/min and the maximum of the peaks were taken as the transitions temperatures. Thermogravimetric analysis was carried out on a Perkin Elmer TGA 7 , using nitrogen as the purge gas with a heating rate of 10°C min^{-1}. In another experiment, the isothermal curve at 300°C was recorded for more than one hour.

Wide angle X-ray diffractograms were obtained using a Philips Geiger counter X- ray diffractometer with an Anton Paar 300 temperature camera. Samples for analysis were prepared from the original polymer powder or from

samples thermally treated as recorded in each case.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. Pinhole collimation and a flat plate camera were also used with a Siemens K710 generator to obtain photographic diffraction patterns throught Polaroid plates.

Microscopy studies and thermoptical analysis were carried out using a Reichert polarizing microscope, Zetopan Pol, equipped with a Mettler FP80 hot stage and Nikon FX 35A camera.

Small angle light scattering studies were carried out with an instrument similar to that described by Stein (32) using a He-Ne , λ =6328 nm laser. The scattering patterns were recorded on Polaroid plates.

Results and Disscussion.

PTDFD has been obtained and perfectly characterized as a linear polymer.The elemental analysis, IR, ^{1}H and ^{13}C NMR data reported in the experimental part, show that the structure of the resulting polymer corresponds to the predicted theoretical structure. From the intensity ratios of the ^{13}C and ^{1}H NMR results, it is also possible to discard the existence of the monofunctional premonomer.

The inherent viscosity of the polymer in p-chlorophenol at 45°C was 0.45 dl.g^{-1}. This value is very close to the one obtained by Lenz et al (5). In any case, it seems to be in a region in which molecular weight should not affect the crystalline and liquid crystalline properties of the polymer.

The thermal behaviour of PTDFD was studied by DSC using samples with several heating and cooling cycles. Previously, in order to determine the thermal stability of this polymer, thermogravimetric analysis was carried out under dynamic and isothermal conditions in a nitrogen atmosphere. The polymer is shown to be stable up to 300°C during sixty minutes at least. A 10% loss is obtained at 425°C in the dynamic experiment.

The transition from liquid crystal to the isotropic liquid occurs, as it will be show below, at 289-290°C, slightly lower than the starting degradation temperature. It is well known that many liquid crystal polymers have the isotropization and degradation temperatures very close.

Figure 1 shows the DSC scans. The sample directly obtained with no thermal treatment shows a curve with two endothermic transitions, (Fig.1a). The first one has a maximum at 241°C with two different shoulders at 229°C and 250°C, and it corresponds to the crystal-liquid crystal transition as it will be demostrated by microscopy and X-ray studies. The second, endothermic peak is located at 289°C and it is related with the mesophase -isotropic transition as confirmed by thermoptical observation of the clearing temperature. No glass transition was observed in this scan indicating probably a high fraction of three and two dimensional order. When the sample is cooled down from 330°C to room temperature (Fig.1b) a crystallization peak was observed at 217.5°C with an enthalpy of 54.6 J.g^{-1} (13.1 cal.g^{-1}). During a subsequent heating cycle of this sample two very well differentiated peaks were observed in the region of the crystal-mesophase transition, one at 227°C and another at 238.8°C, with a shoulder at 198°C. Similar results were obtained when the sample was quenched in liquid nitrogen and subsequently heated. However, the main difference is that a glass transition at 67.1°C is clearly detected. The total enthalpy for the crystal-liquid crystal transitions was 60.2 J.g^{-1}
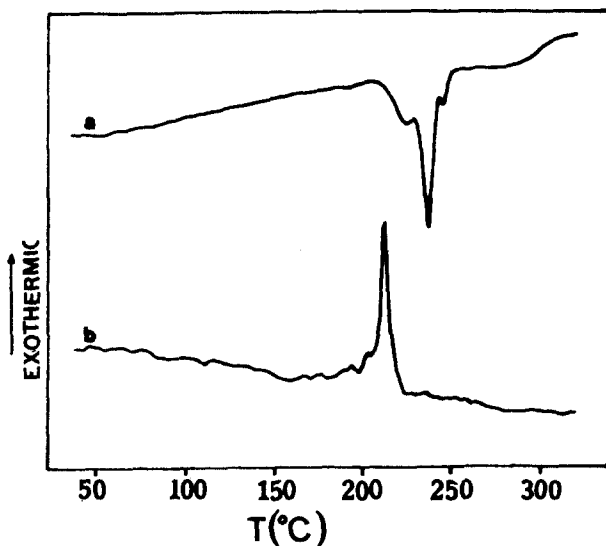
FIGURE 1: DSC curves of PTDFD: a) Original sample heated up to 330°C. b)Sample "a" cooled down to room temperature. The DSC curves were obtained at a heating rate of 10°C.min^{-1}.

(14.4 cal.g^{-1}).Multiple melting peaks have been found in semicrystalline polymers (13-18) and in thermotropic polyesters (11,19-24).

Wide angle X-ray diffraction patterns of PTDFD were obtained from the original and from thermally treated samples (Fig.3). The original one presented a sharp reflection at $2\theta=3°$ with a weak reflection at $2\theta=6.1°$ and several reflections at $2\theta=19.9°,21.6°,23.6°,28.4°$ and $30.4°$ as shown in Fig.3a. These reflections, except the ones at 3° and 6°, are associated with inter and intramolecular order in the three dimensional crystalline structure. The reflections at $2\theta=3°$ and 6.1° may correspond to the intermolecular order related to a smectic mesophase , as it will be discussed later. When the polymer is cooled down or quenched from the mesophase , the indicated reflections are maintained.

These results, together with the calorimetric analysis, indicate that PTDFD is a semicrystalline polymer which exhibits thermotropic behaviour. Contrary to the results found for polyphosphazenes (25-27) and other thermotropic polyesters (11,22), the different thermal treatments do not substantially affect the transition temperatures or the X-ray diffraction patterns at room temperature . In table 1 the temperatures and the enthalpies of the transitions are listed. The H_1 is aproximately two times the values reported previously by Lenz et al (5,6). This means , in principle, a higher value of three dimensional order in the sample. The value found for T_i is smaller than some of those reported for a relatively wide range of molecular weights (5). This fact can be attributed to the high rate of heating reported in the calorimetric experiments (20°C/min) and consequently to possible effects of overheating, compared with the one used in this work.

In order to study the transitions with different techniques, thermoptical analysis of films was carried out. When the film is cooled down at room temperature and heated, differences in intensity are shown at 240°C with a light gain at 265°C and a complete loss of intensity at 310°C due to the isotropic transition (Fig.2). In a cooling cycle, the same transition appears and, in both cases , the transitions are in the range detected by calorimetry. When the sample is quenched from the mesophase, the film at room temperature does not show threaded-Schlieren textures.

Table 1–Thermal transitions and thermodynamical parameters of PTDFD

Sample	$T_c{}^a$(°C)	ΔH_c(J.g^{-1})	$T_l{}^a$(°C)	ΔH_l(J.g^{-1})	$T_i{}^a$(°C)	ΔH_i(J.g^{-1})	ΔT^b(°C)
2a	–	–	241	56.6	290	8.2	49
2b	217.5	54.6	–	–	–	–	–
2c	–	–	227–239	57.2	290	5.6	c
2d	–	–	228–239	55.7	293	5.6	c
2e	–	–	223–239	51.8	290	5.8	c

(a) Maximun of the transitions
(b) $\Delta T = T_i - T_l$
(c) It could not be evaluated.

Schlieren textures are found as it is known in a great number of nematic and smectic B and C liquid crystals (28-30) . In PTDFD, only marbled structure can be observed. However, when the temperature increases up to 260°C, it is possible to distinguish the typical transition bars and striated texture corresponding to the transition smectic C-nematic (31). At temperatures higher than 260°C a blurred schlieren texture is observed.

Small angle light scattering experiments have been carried out in order to disclose the morphology of this system in the crystalline and in the mesophase region. To this purpose, a film from the mesophase was cooled down to room temperature, presenting only circular spots. When this film was heated at 10°C/min from 40°C up to the isotropic temperature the same spots were obtained without any significant change until reaching T_i, where no scattering pattern was observed. In any case, the four-leaf cross pattern claimed for the nematic melt of this polymer (6) has not been obtained. It is very important to remark that the diameter of the spots are not the same at the different temperatures which have been used and a
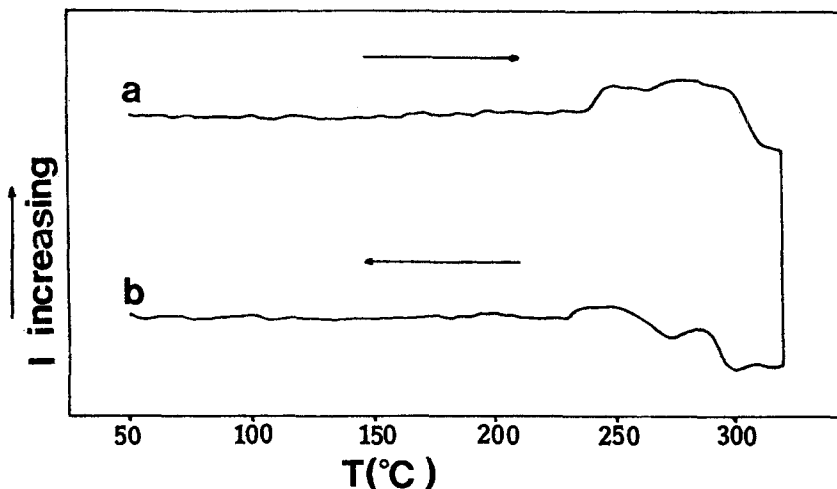

FIGURE 2: Thermoptical analysis of PTDFD: a) Heating cycle. b) Cooling cycle. The heating rate was 10°C.min^{-1}.

substancial change at 265°C has been observed. This temperature is higher than the one related with the crystal -liquid crystal transition (240°C) and it can be associated to the step in the mesophase region observed in the TOA experiments.

The light scattering arise from regions, having correlated orientation and dimensions which are comparable with the light wave length. Thus, the characteristics of the mesophases can be predicted theoretically and experimentally studied (32-35). The smectic A and B states present a four-leaf clover Hv pattern, and smectic C mesophase have been reported to give circularly symmetric and azimuthally independent patterns. The same patterns have been found in the nematic mesophase (33). Therefore, the spot can be associated to the smectic C phase, commented above.

As it was previously described, the X-ray pattern at room temperature, shows several reflections. Only a sharp reflection in the low angle region appears at 2θ =3°, which in principle, can be assigned to a smectic mesophase. These reflections in PTDFD have been investigated for three different thermal histories , that is to say, the original powder without any thermal treatment, after cooling from the mesophase to the room temperature and after quenching from the mesophase. Although the same spacing are found for the three cases, there are some interesting changes in the relative intensities of the peaks at 19.9° and 3°. In the original sample, this ratio is 2.9 meanwhile the samples cooled from the mesophase and quenched present ratios of 2.6 and 1.7 respectively. In principle, these results mean that the reflection at 3° can not be related with the crystalline order in the system and must be atributted to a smectic mesophase which is more intense in the poorly crystallized sample when it is quenched.

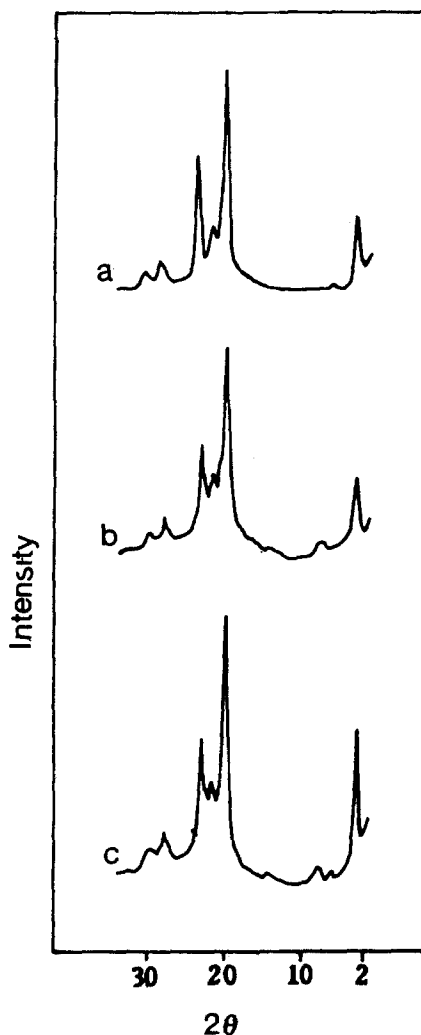We have also undertaken the analysis of the X-ray diagrams at

FIGURE 3:X-ray diffractograms of PTDFD at room temperature of: a) Original sample.b) Sample cooled down from 260°C to room temperature. c)Sample quenched into liquid nitrogen from 260°C.

different temperatures, between room temperature and 250°C (Fig.4). All these reflections are persistent up to 239°C with a slight increase in the ratio of the intensities of the peaks at 19.9° and 3° corresponding, in principle , to any increase of the total order of the system. However , at 220°C a decrease of the ratio is apparent, indicating a decrease of the crystalline order or an increase of the mesophase.At temperatures T>239°C, corresponding to the transition from the three dimensional order to the mesophase, the reflection in the low angle region disappears and only an amorphous diagram persists up to the isotropization temperature.

After the precedent discussion of the X-ray diagrams, we can conclude that the reflection at low angle observed between room temperature and T_1 does not correspond to a reflection characteristic of the three dimensional order in the system. Although the existence of a low angle reflection corresponding to the three dimensional order has been described in some systems (36,37), we have attributed this reflection to the smectic mesophase. The Bragg spacing corresponding to the reflection at $2\theta=3°$ is 29.4 Å .The length of the repeating unit for this polyester corresponds to 30.5 Å in its fully extended all trans conformation. The disapparance of this reflection at T=239°C seems to indicate the existence of a smectic mesophase that experiments transition to a nematic mesophase at a temperature close to T_1. This conclusion agrees with the microscopic observation of the smectic C-nematic transition which occurs in a rather limited range of temperatures.

FIGURE 4: X-ray diffractograms of PTDFD original sample as a function of temperature.

References

1. Jin J I , Antoun S, Ober C, Lenz R W (1980) Brit Polym J 12:132
2. Economy J (1984) J Macromol Sci Chem 121: 1705
3. Lenz R W (1985) J Polym Sci Symp 72: 1
4. Meurisse P, Noel C, Monnerie L, Fayolle B (1981) Brit Polym J 13: 55
5. Chen G, Lenz R W (1984) J Polym Sci Polym Chem 22: 3189
6. Antoun S, Lenz R W, Jin J I (1981) J Polym Sci Polym Chem 19: 1901
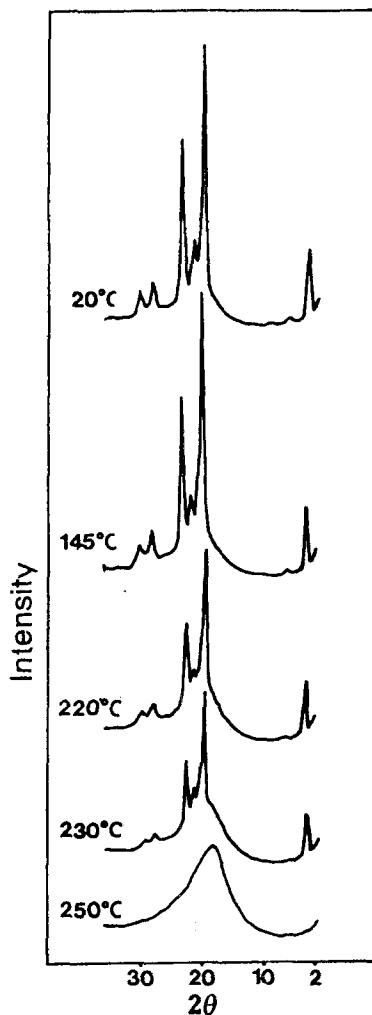7. Grebowicz J, Wunderlich B (1983) J Polym Sci Polym Phys 21: 141

8. Warner S B, Jaffe M (1980) J Cryst Growth 48: 184
9. Pracella M, Frosini V, Galli G, Chiellini E (1984) Mol Cryst Liq Cryst 113: 201
10. Yoo Y D, Kim S C (1988) Polym J 20: 1117
11. Marco C, Lorente J, Gómez M A, Fatou J G, Polymer (to be published).
12. Griffin A C, Havens S J (1981) J Polym Sci Polym Phys 19: 951
13. Lovering E G, Wooden D C (1969) J Polym Sci Polym Phys 7: 1639
14. Fernandez S, Fatou J G (1972) Eur Polym J 8: 575
15. Mandelkern L, Stack G M, Mathieu P J M (1984) Analytical Calorimetry. In: Plenum, New York
16. Alamo R, Mandelkern L (1986) J Polym Sci Polym Phys 24: 2087
17. Snyder R G, Scherer J R, Reneker D H, Colson J P (1982) Polymer, 23 1286
18. Marco C, Lazcano S, Fatou J G (1990) Makromol Chem 191: 1151
19. Krigbaum W R, Watanabe J, Ishikawa T (1983) Macromolecules 16: 1271 .
20. Kalika D S, Shen M R, Yu X M, Denn M M, Iannelli P, Masciocchi N, Yoon D Y, Parrish W, Friedrich C, Noël C (1990) Macromolecules 23: 5192
21. Kricheldorf H R, Pakull R (1989) New Polym. Mat. 1: 165
22. Frosini V, Petris S, Chiellini E, Galli G, Lenz R W (1983) Mol Cryst Liq Cryst 98: 223
23. Roberts R C (1970) Polym. Lett. B8: 381
24. Frosini V, Magagnini P L, Newman B A (1977) J Polym Sci Polym Phys 15: 2239 (1977)
25. Tanaka H, Gómez M A, Tonelli A E, Chichester-Hicks S V, Haddon R C (1988) Macromolecules 21: 2301
26. Tanaka H, Gómez M A, Tonelli A E, Chichester-Hicks S V, Haddon R. C. (1989) Macromolecules 22: 1031
27. Gómez M A, Marco C, Fatou J G, Chichester-Hicks S V, Haddon R C (1990) Polym Commun 31: 308
28. Sackman H, Demus D (1973) Mol Cryst Liq Cryst 21: 239
29. Krigbaum W R (1985) J Appl Polym Sci Appl Polym Symp 41: 105
30. Asrar J, Toriumi H, Watanabe J, Krigbaum W R, Ciferri A (1983) J Polym Sci Polym Phys 21: 1119
31. Scheffer T J, Gruler H, Meier G (1972) Solid State Commun 11: 253
32. Stein R S, Rhodes M B, Porter R S (1968) J Colloid Interface Sci 27(3) 336
33. Takase A, Sakagami S, Nakazima M (1973) Mol Cryst Liq Cryst 22:67
34. Stein R S (1969) Mol Cryst Liq Cryst 6: 125
35. Rhodes M B, Porter R S, Chu W, Stein R S (1970) Mol Cryst Liq Cryst 10: 295
36. Kricheldorf H R, Döring V (1988) Makromol Chem 189: 425
37. Ober C K, Delvin A (1990) J Polym Sci Polym Phys 28: 1047