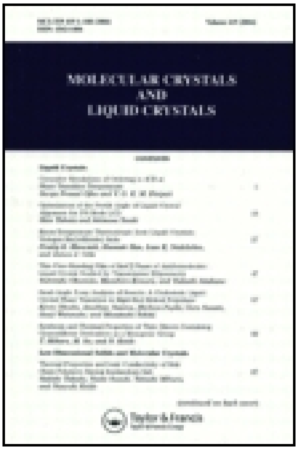

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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SYNTHESIS AND CHARACTERIZATION OF 1,4-BIS(4-VALERYLOXY-BENZOYLOXY)-2-METHYL-BENZENE AND OF THE CORRESPONDING POLYESTER

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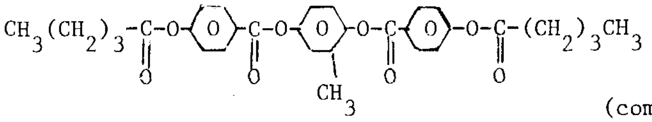
Abstract The synthesis and the thermotropic behavior of 1,4-bis(4-valeryloxy-benzoyloxy)-2-methyl-benzene is described. It exhibits a broad nematic range (about 100°) and high thermal stability. The polyester with the same chemical structure has been also prepared and characterized. It forms a nematic state in the melt and shows a clearing point higher than 300°C. Characterization of the samples has been carried out by IR and NMR spectroscopy, differential scanning calorimetry and polarizing microscopy.

INTRODUCTION

Following our previous results, recently reported[1], devoted to a better understanding of the structure-properties relationship in liquid-crystalline compounds, we have prepared a new thermotropic ester, whose mesogenic group bears one methyl substituent



(comp. I)

The procedure and the conditions related to its synthesis have been accurately studied and are here given. 1,4-Bis(4-valeryloxy-benzoyloxy)-2-methyl-benzene (compound I) has been characterized by using conventional analytical techniques.

Several samples of the corresponding polyester, having different intrinsic viscosities, have been also synthetized and investigated in terms of thermal and mesomorphic behavior.

EXPERIMENTAL

MATERIALS

All the solvents, analytical grade, were dried on molecular sieves; triethylamine (Et_3N), pyridine (Py) and valeryl chloride were distilled under N_2 before use. 2-Methylhydroquinone (MHy) and 4-hydroxybenzoic acid (HA) were crystallized from toluene and water, respectively.

1,4-BIS(4-VALERYLOXY-BENZOYLOXY)-2-METHYL-BENZENE

A quantity of 6,2 g (0.045 moles) of 4-hydroxybenzoic acid was dissolved in 50 ml of tetrahydrofuran (THF) and 9 ml of pyridine at 0°C under vigorous stirring. To this solution 7.1 ml (0.06 moles) of valeryl chloride were added slowly and the solution stirred for 3 hrs. After reducing the solution volume to 15 ml, the product was precipitated with a large amount of water (400 ml), isolated and accurately washed with hot water and twice recrystallized in n-hexane; yield 72% (melting temperature T_m = 159°C; elemental analysis : calcd.C : 64.86% H : 6,31%, found C : 64.25% H : 6.19%).

The obtained 4-valeryloxy benzoic acid was refluxed in a large excess of thionyl chloride for two hours. After removal of the unreacted thionyl chloride by distillation the resultant acid chloride was mixed with 10 ml of tetrachloroethane (TCE) and 1 ml of Et_3N. An appropriate amount of MHy, dissolved in TCE in presence of Et_3N, was added to this solution and the reaction mixture was stirred for 24 hrs under nitrogen atmosphere. The final product was precipitated and recrystallized in ethanol; yield 65%.

POLYESTER

The polymerization runs were performed at room temperature under N_2 for 48 hrs. In a typical example a solution of 0.002 moles of 4,4'-(sebacoyldioxy) dibenzoyl dichloride (obtained following the procedure of Bilibin and coworkers[2], melting point 95.3°C; elemental analysis: calcd.C : 60.13% H : 5.04%, found C : 59.90% H : 5.12%) in 10 ml TCE is added dropwise and under vigorous stirring to a solution of MHy (0.002 moles) in TCE (10 ml) in presence of Et_3N (0.004 - 0.020 moles). The resulting polymers were precipitated in acetone, filtered, washed several times with water and acetone and dried under vacuum.

CHARACTERIZATION

Transition temperatures were determined by thermal analysis (DSC-2 Perkin Elmer) as well as by using a polarizing optical microscope (Reichert Zetopan) equipped with a hot stage (Mettler FP52). Infrared spectra were obtained on KBr disks with a Perkin Elmer 983 spectrometer. Proton NMR spectra were registered with a Perkin Elmer mod. R600 spectrometer (60 MHz); the chemical shifts reported are relative to tetramethylsilane (TMS). Intrinsic viscosity of the polymers were measured in an Ubbelhode viscometer at 25°C in TCE.

RESULTS AND DISCUSSION

We shall first examine the liquid crystal properties of the low molecular weight compound I, which shows proper elemental analysis (calcd. C : 69.91% H : 6.00%; found C : 69.80% H : 6.02%). Transition temperatures were determined both by DSC measurements and optical observations. The corresponding thermograms are shown in Figure 1; the presence of two peaks indicates that the melting and isotropization transitions occur at 125.8 and 214.3°C, respectively. On cooling, at a rate of 10°C/min, two exotherms appear at 211 and 105°C. Melting and isotropization enthalpies of 18.7 and 0.77 cal/g are registered (0.76 and 17.6 cal/g on cooling).

The mesophase is clearly nematic as shown in the micrographs of Figure 2.

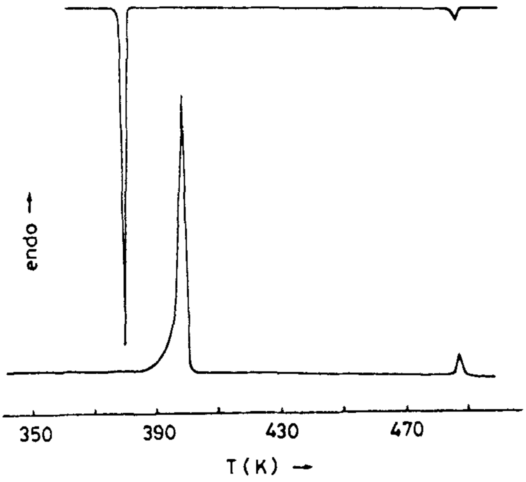


FIGURE 1. DSC traces of compound I (scan rate 10°C/min)

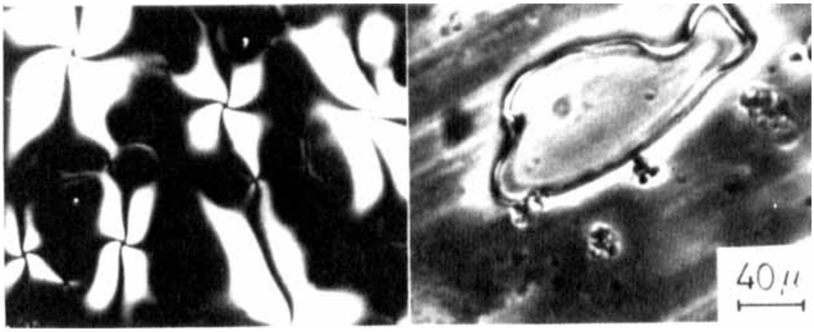


FIGURE 2. Nematic textures of compound I (at 213 and 209°C on cooling)

See Color Plate XVI.

The infrared spectrum of compound I is reported in Figure 3, where vibrational absorptions corresponding to CH_3, C = O, and C - O stretching are present. In the ^1H NMR spectrum (Figure 4) the singlet due to the CH_3 on the aromatic ring appears at 2.25 ppm. The signals between 0.85 and 1.20, 1.18

and 1.95, 2.45 and 2.80 ppm represent the protons of the two aliphatic CH_3, the four $-CH_2-$ and the two $-CH_2-CO-$ groups, respectively. The aromatic protons are evidenced between 7.00 and 8.50 ppm.

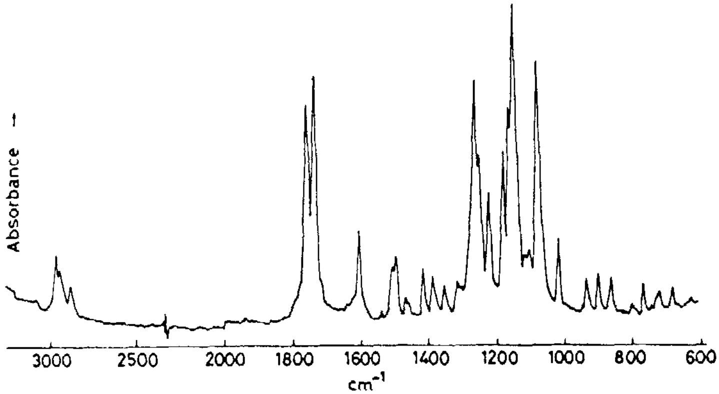


FIGURE 3. IR spectrum of compound I

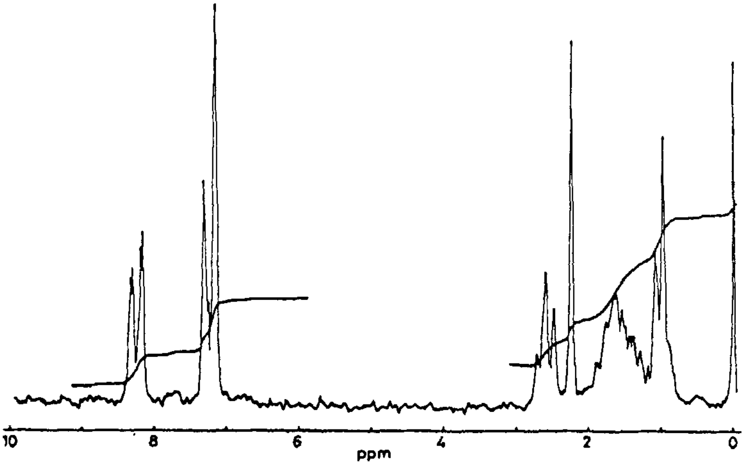
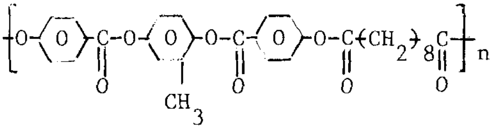


FIGURE 4. NMR spectrum of compound I in $CDCl_3$

As far as the polyester having the same chemical structure of compound I is concerned



several experiments have been performed in order to improve the experimental conditions for the preparation of high molar mass samples with the maximum yield. Indeed, most of the polyesters described in the literature[3-4] rarely exhibit [η]>0.5 dl/g, which can be a strong limitation both to the study of their properties and to their practical applications.

The influence of different amounts of Et_3N, used as acid acceptor in the low-temperature solution polycondensations, is summarized in Table I.

TABLE I Intrinsic viscosities and yields as a function of Et_3N/monomer (M) molar ratio

Sample	$[Et_3N]/[M]$	[η],dl/g	yield, %
Pol.1	2	0.25	75.8
Pol.2	4	0.36	73.5
Pol.3	5	1.04	99.0
Pol.4	10	0.22	73.3

All these samples exhibit liquid crystalline behavior and their melting temperatures, which increase, as expected[5], by increasing the molar mass of the polymer, have been defined both by DSC and hot-stage optical microscopy; the two series of values show a good agreement. On the other hand the liquid crystal to isotropic transition can be evidenced only in the highest molar mass sample.

Transition temperatures and enthalpies are listed in table II; T_2 refers to the appearance of a nematic state and T_3 to the clearing point. T_1, which is displayed only by the lower molar mass samples, is probably due to the presence of a smectic phase.

TABLE II Thermal properties of polyesters

Sample	T_1	ΔH_1	T_2	ΔH_2	T_3	ΔH_3	T_c	ΔH_c
	°C	cal/g	°C	cal/g	°C	cal/g	°C	cal/g
Pol.1	100	3.84	141	1.26	>300	-	-	-
Pol.2	-	-	189	1.41	>300	-	160	1.27
Pol.3	-	-	211	2.20	338	2.50	174	1.60
Pol.4	100	6.20	138	2.40	>300	-	-	-

Threaded and schlieren textures, characteristic of a nematic phase[6], form spontaneously in all the samples when they are heated above T_2 (Figure 5).

Preliminary results from miscibility studies seem to suggest that Pol.2 and 3 are isomorphic with compound I. X-ray diffraction experiments and complete miscibility diagrams are in progress to achieve a conclusive identification of the polyester mesophases. On cooling at a rate of 10°C/min,

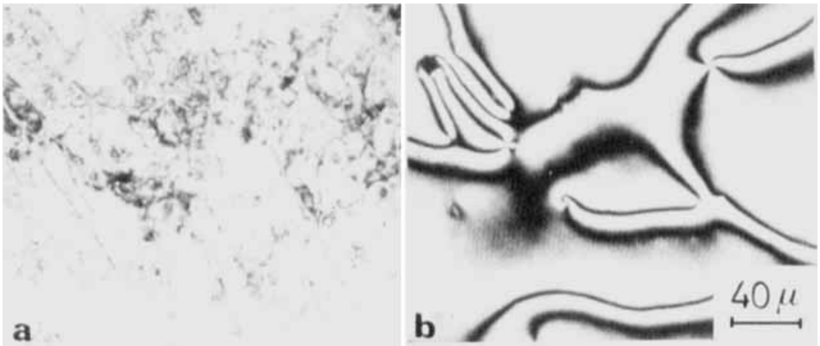


FIGURE 5. Optical textures of the polyester mesophases: a) Pol.3 T = 268°C; b) Pol.4 T = 280°C
See Color Plate XVII.

crystallization occurs only in Pol.2 and 3, if the heating cycle is stopped below 320°C. This means that these samples decompose just above the clearing point. Pol.1 and 4 do not crystallize and a frozen nematic state is maintained up to room temperature.

The infrared spectra of polyesters are similar to that of compound I, except in the region of OH, CH_3 and CH_2 stretching vibrations. Indeed a peak at 3430 cm^{-1} appears, due to the end groups, and the relative intensity of CH_2 bands increases respect to CH_3 and C=O peaks, in agreement with the variation of the ratio CH_3 : CH_2 : C=O . The presence of a longer CH_2 sequence in the polymer is also evident in the region between 700 and 750 cm^{-1}.

In conclusion the low molar mass liquid crystal and the polyester having the same chemical structure exhibit similar mesomorphic properties, but the transition temperatures of the polymer are shifted towards higher values. 1,4-Bis(4-valeryloxy-benzoyloxy)-2-methyl-benzene shows high thermal stability and a nematic phase between 125° and 215°C. The corresponding polyester displays a wider thermotropic range and is thermally stable up to temperatures higher than 300°C. The extended ranges of exhistence of the mesophase and the high clearing points can be qualitatively explained on the basis of the chemical structure of these compounds[1].

Further investigations are in progress to identify the polyester mesophase and to better understand the role played by the conformation of the repeating unit on the mesophase stability.

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