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SYNTHESIS AND PROPERTIES OF SOME SEMIFLEXIBLE POLYESTERS

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Abstract The synthesis and the thermotropic behavior of polyesters based on a flexible spacer of eight methylene units and two aromatic ester triads built up with terephthalic acid and hydroquinone or 2-methylhydroquinone have been studied. Polymer synthesys took place through the preliminary preparation of the rigid monomers, which display liquid crystal properties in spite of their diphenolic character. A low molecular weight model of appropriate chemical structure was also prepared. The structural influence of the rigid segment on the thermotropic behavior of low and high molecular weight compounds is discussed in terms of onset, nature and thermal stability of the mesophases.

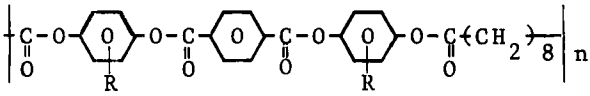
INTRODUCTION

During the last few years a great number of liquid crystalline polymers were synthesized due to the increasing interest on their potential application as new materials with unique properties[1-4]. The chemical natures of polymers suitable to develop thermotropic behavior are various; anyhow

most of them are polyesters, where the mesogenic moieties are connected together through flexible spacers forming the polymer backbone.

Many attempts have been made to delineate relationships between chemical structure and liquid crystal behavior of this class of polyesters[5-7], but so far a complete rationalization has not been achieved.

Our approach to this problem is based on the study of two polyesters



with R = H or CH_3, which we prepared starting from the synthesis of the rigid diphenolic aromatic triads.

Both the rigid monomers and the semiflexible polyesters exhibit thermotropic behavior. The results obtained, in terms of phase transition temperatures and ranges of stability of the mesophases are discussed, by comparison with literature data, to underline two main effects: the role of lateral substituents on the mesogenic unit and the influence of the direction of internal and external ester bridging groups.

EXPERIMENTAL

PREPARATION OF THE MONOMERIC AROMATIC TRIADS

A solution of terephthaloyl dichloride (0.1 mol) in dry

dichloromethane was added dropwise under vigorous stirring to a solution of hydroquinone or 2-methylhydroquinone (0.3 mol) in dry ethyl ether containing 0.2 mol of freshly distilled triethylamine. The reaction mixtures were allowed to stay for 20 hrs at room temperature under dry nitrogen and then filtered to separate the white precipitates from the solutions. The unsubstituted triad was isolated from the precipitate, washed several times with water to remove the ethylamine hydrochloride and recrystallized from ethylacetate. The methyl substituted diphenol, soluble in the reaction medium, was separated by removal of the solvent under flowing nitrogen and washed several times with water to remove the unreacted 2-methylhydroquinone; finally it was purified by liquid chromatography on a silica gel column using as eluent a mixture of toluene : dichloromethane : ethylacetate = 5:4:1 or by fractional crystallization from toluene. Hydroquinone, 2-methylhydroquinone and terephthaloyl dichloride were commercial products recrystallized before use from ethanol, toluene and n-exane respectively.

SYNTHESYS OF POLYESTERS

Polyesters were prepared under nitrogen atmosphere by adding dropwise a solution of sebacoyl chloride (0.1 mol) in tetrachloroethane to a stirred solution of the unsubstituted diphenol (0.1 mol) in dry pyridine/tetrachloroethane or to a solution of the ring-methylated diphenol (0.1 mol)

in tetrachloroethane containing 0.4 mol of triethylamine. The reaction mixtures were maintained at temperatures ranging from 25 to 50°C for 0.75-24 hrs. In the first case the insoluble polymer was filtered, washed several times with water and acetone and dried in vacuum at 50°C. In the second case the polymer was isolated by pouring the reaction mixture into ethanol; the precipitate was filtered, washed with water and ethanol and dried i.v.

PREPARATION OF THE MODEL COMPOUND

1,4-phenylene bis (4'-n-valeroyloxy) terephthalate was obtained by adding slowly a solution of freshly distilled valeroyl chloride (0.3 mol) in tetrachloroethane to a solution of the unsubstituted diphenol (0.1 mol) in dry pyridine/tetrachloroethane. The reaction was performed under nitrogen at 60°C for 45 hrs and the product was isolated by precipitation in methanol and purified by successive crystallizations from 1,4 dioxane and chloroform. The yield was 82 ÷ 84% by weight.

IDENTIFICATION OF THE PRODUCTS AND DETERMINATION OF THE TRANSITION TEMPERATURES

Classical tests of purity were carried out on the monomeric diphenols and on the model compound: thin layer chromatography, gas chromatography, elemental analysis, IR (Perkin Elmer 983) and NMR (Bruker AM-270) spectroscopy, thermal analysis (DSC-2 Perkin Elmer). Polyesters were characterized

by intrinsic viscosity measurements and thermal analysis. For each compound the phase transition temperatures were investigated both by differential scanning calorimetry and by optical microscopy (Reichert Zetopan) using a Mettler FP-52 hot-stage.

RESULTS AND DISCUSSION

RIGID MONOMERS

We will first consider the unsubstituted diphenol (monomer 1). The tests performed reveal that we are dealing with a pure compound with high melting temperature and enthalpy (T_m = 317°C, ΔH_m = 39 cal/g; scan speed 10°C/min). It exhibits proper elemental analysis (see Table I) and consistent spectral properties. Intense vibrational absorptions appear in the infrared region at 3360 cm^{-1} (O-H stretching, H bonded), at 1728 cm^{-1} (C=O stretching) and at 1410-1610 cm^{-1} (phenyl ring C-C vibrations); moreover six vibrational bands occur between 1000 and 1300 cm^{-1} (C-O stretching region).

TABLE I Elemental analysis of monomers.

Sample	% C		% H	
	ealcd.	found	calcd.	found
MONOMER 1	68.57	68.60	4.00	3.95
MONOMER 2 (1BT)	69.84	69.82	4.76	4.69
MONOMER 2 (2BT)	69.84	69.78	4.76	4.78

In the NMR spectrum made in deuterioacetone with the addition of CD_3OD a sharp singlet, due to the absorption of the hydrogens of the central aromatic ring, appears at 8.18 ppm downfield from TMS, while the absorption due to the hydrogens of the two lateral rings is revealed by two symmetrical doublets around 6.95-6.74 ppm (Figure 1).

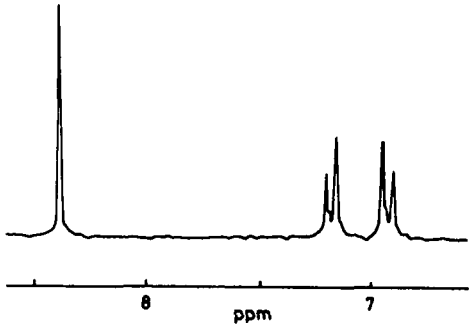


FIGURE 1. NMR spectrum of monomer 1

Gaschromatography of the silylate monomer 1, obtained by reaction with hexamethyldisilazane and trimethylchlorosilane in pyridine, is shown in Figure 2 (retention time 22 min).

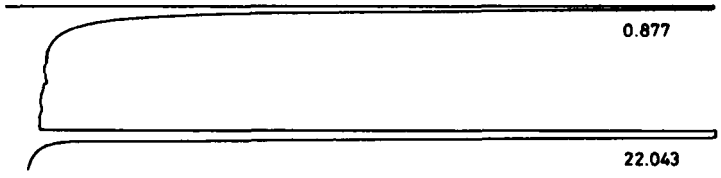
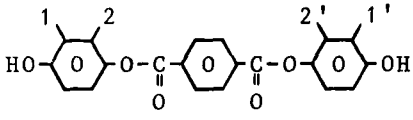


FIGURE 2. Gaschromatography of silylate monomer 1 (SE 30 sterols, Flux 150, heating rate 10°C/min)

The thermal behavior of monomer 1 seems to suggest that it melts to a nematic phase at 317°C; at higher temperatures degradation occurs. By cooling at 10°C/min from 320°C four exotherms appear at 310°, 280°, 250° and 145°C with enthalpies of 4, 0.6, 2.5 and 0.9 cal/g respectively. We are unable to attribute these effects to mesophase-mesophase or solid-solid transitions,due to the limited reliability of our hot-stage at temperatures higher than 300°C.

The ring-methylated diphenol (monomer 2) is actually a mixture of 3 isomers, depending on the relative position of the CH_3 groups. Several attempts have been made to separate them; up to now, either by liquid chromatography or by fractional crystallization, we have obtained only mixtures of the three isomers with different compositions. An example of the results achieved on two different fractions (1BT, 2BT) is here reported. For both specimens elemental analysis values are consistent with the calculated ones (Table 1). IR spectra show characteristic vibrations as for monomer 1; in addition three bands corresponding to CH_3 stretching appear between 2850 and 2985 cm^{-1} and O-H stretching is shifted to 3450 cm^{-1}. The most interesting result arises from the comparison of NMR spectra of the two fractions (Figure 3), registered in the same conditions as for monomer 1. If we consider the three structural isomers corresponding to monomer 2,



as far as protons of the terephthalic ring are concerned, one can expect a multiplet for the asymmetric isomer A (1,2' or 2,1'). For the symmetric ones S and S' (1,1' and 2,2') two singlets are foreseen; indeed in this case the 4 hydrogen atoms are equivalent.

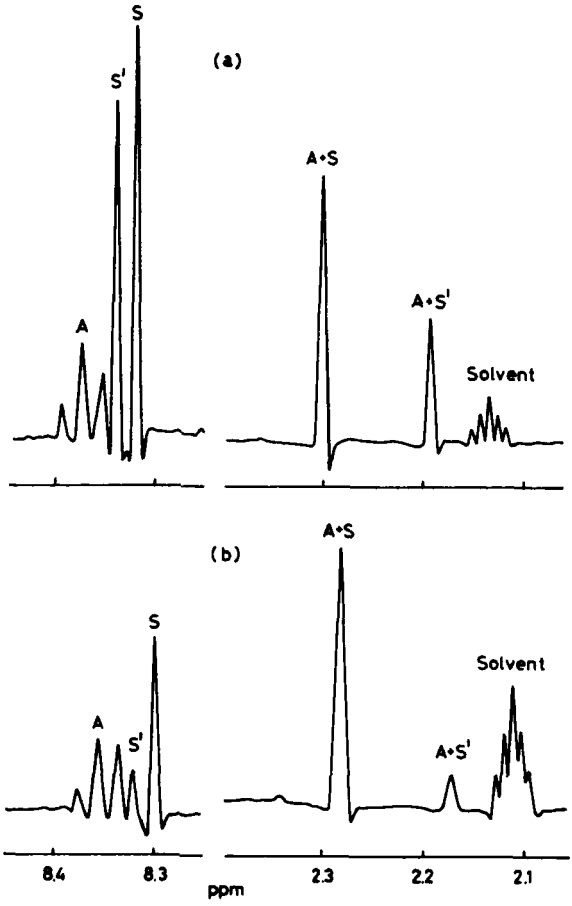


FIGURE 3. NMR spectra of monomer 2.

In Figure 3a two sharp singlets and a multiplet are present in the region between 8.3-8.4 ppm, tentatively attributed to S, S' and A forms. In the CH_3 region between 2.15 and 2.35 ppm the two singlets are related to the different absorption of methyl-protons in 1,1' or 2,2' positions. Figure 3b deals with the spectral behavior of fraction 2BT; in this case the signal indicated as S' is considerably reduced and this fact appears to be in good agreement with the situation registered in the CH_3 region, where the singlet labelled A+S' is less intense. We deduce that samples 1BT and 2BT are both mixtures of the three isomers S,S' and A, but in fraction 2BT the relative amount of the S' form is remarkably lowered. From the integral curves of the methyl absorptions we can try to classify monomer 2 fractions in terms of relative amount of A+S and A+S' forms. Full reports on this aspect will appear in a forthcoming paper. Monomer 2 thermal behavior is complicated by its variable composition; the low melting isomer gives rise to a nematic phase at about 170°C. However, due to the relative solubility of the three isomers in the melted state, transition temperatures must be related to the mixture composition. Typically, by cooling down from the isotropic state a monomer 2 fraction, a nematic phase appears, which transforms into a smectic A phase at lower temperature. Crystallization does not occur under fast cooling (10°C/min) and the smectic texture is maintained up to room temperature (Figure 4).

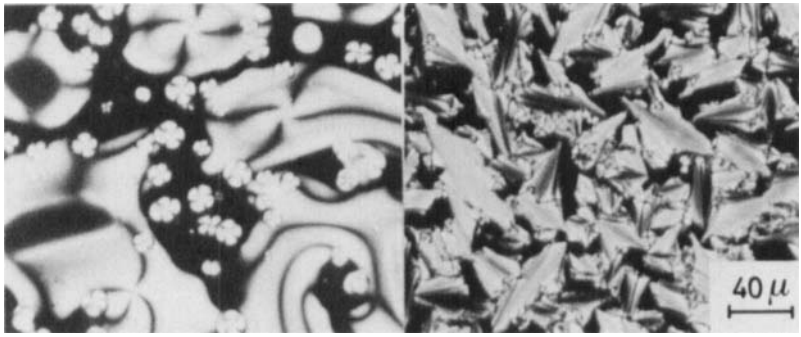


FIGURE 4. Fraction 1BT on cooling (T = 184°C and 165°C).

POLYMERS AND MODEL COMPOUND

The thermal properties of the polymers containing either monomer 1 or 2 as mesogenic unit, are given in Table II.

TABLE II Comparison of the transition temperatures of the two polymers

Polymer	Mesogenic unit	$T^{a)}_{K\rightarrow N}$ °C	$T^{a)}_{N\rightarrow I}$ °C	$T^{a)}_{N\rightarrow K}$ °C	$[\eta]_{25°C}$, dl/g
1	monomer 1	257	$>T_D$	242	0.39*
2	"	261	$>T_D$	247	0.46*
3	monomer 1BT	177	319	128	0.6**
4	"	177	320	139	1.74**

a) As determined by DSC; T_D = decomposition temperature

*) In o-chlorophenol; **) in tetrachloroethane.

As expected polymers 1 and 2 exhibit a fairly high melting temperature and DSC curves show that decomposition occurs before the isotropization takes place. If the heating is stopped at 310°C the sample crystallizes. Samples 3 and 4, whose mesogenic moiety bears two CH_3 groups (they are actually copolymers), have much lower melting temperature and exhibit a clearing point. It must be pointed out that, on cooling, crystallization appears only when the heating cycle is stopped below the isotropization, which means that polymers 3 and 4 decompose just above T_I. The transition temperature decrease can be related to the different geometry of the mesogenic moiety, since the presence of the lateral substituents cause a broadening of the molecule. As a consequence the long axes of the molecules are forced apart and their interactions are reduced[8]. Optical observations show the existence of a nematic phase in all the samples (Figure 5).

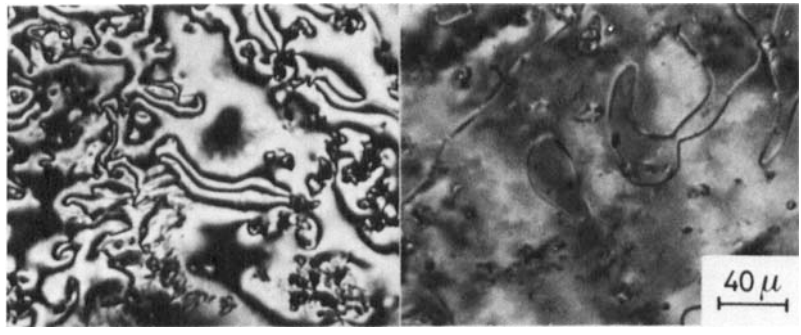


FIGURE 5. Nematic textures of polyesters 2 and 3 (at 280°C and 230°C respectively)

Model compound obtained from monomer 1 (elemental analysis calcd. C% 69.50, H% 5.79; found C% 69.23, H% 5.77) displays two thermally reversible transitions at 216° and 254°C (Figure 6). Melting and isotropization entalpies of 22.6 and 0.4 cal/g are registered. Supercooling of 8 and 6 degrees are associated to the overmentioned transitions. A typical photomicrograph taken at the clearing point is given in Figure 6.

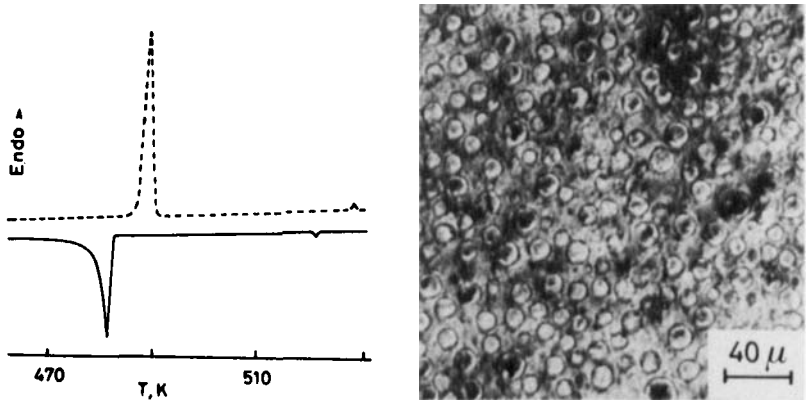


FIGURE 6. DSC profile (scan rate 10°C/min) and texture at 253°C of the model compound.

STRUCTURAL CONSIDERATIONS

Monomers 1 and 2 exhibit mesomorphic properties, which is a very peculiar behavior for diphenols[9]; indeed very few examples of diphenolic liquid crystals are reported[10-11].

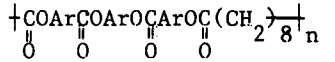
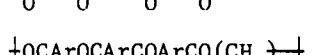
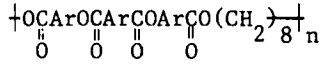
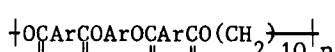
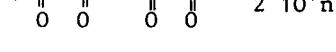
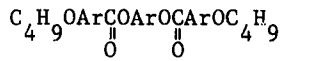
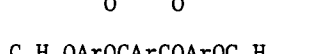
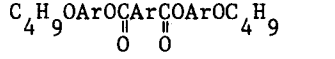
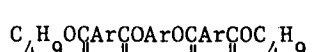
According to literature data, which show phase transition temperatures depending on the polymerization degree[12],

we have found that T_m and T_I of polyesters 1 and 2 increase by increasing the molecular mass of the polymer and that they are both higher than those of the corresponding model compound[13]. The high melting temperatures are due to the regular structure and simmetry of the mesogenic unit. The high values of T_I, in spite of the non-linearity of the mesogenic moiety[14], must be ascribed to the presence of terminal -Ar-O-C(=O)- groups, which affect the polarizability and the rigidity of the molecules.

By comparing the thermal behavior of polymers 1 and 2 with that of polymers 3 and 4 one can say that methyl groups reduce the molecular symmetry and depress T_m, while the effect on T_I is probably lower. In order to estimate the influence of different orientation of the ester linkages in the mesogenic unit, we compare our results with literature data on similar high and low molar mass liquid crystals. An accurate evaluation of the data quoted in Table III points out that the thermal behavior of polyesters and model compounds is strongly affected by the orientation of the external ester bridges. Indeed, by comparing polymers A and C, we observe a considerable decrease of T_I, while the substitution of the central terephthalic moiety with a hydroquinone residue (see A and B, C and D, F and E) produces a slight effect on the clearing point. This behavior is also evidenced by model A which, despite the direction of the central carboxyls, has T_I about 100°C higher than that of model G. The thermal stability of the mesophase ap-

pears to be controlled by the presence of the terminal Ar-O-C(=O)- bridges also in the case of methyl substitution on the aromatic rings (see I and L).

TABLE III Thermal behavior of polyesters and model compounds.

	Compound	T_m, °C	T_I, °C	η_{inh} dl/g	Ref.
A		261	> T_D	0.46	
B		245	> T_D	-	15
C		165	220	0.20	16
D		231	267	0.68	17
E		156	253		18
F		183	229		19
G		139	155		18
H		216	254		
I		177	319	0.6	
L		188	>300	0.36	20

(Ar = C_6H_4, Ar' = $CH_3C_6H_3$)

In polymer C a contribution to the stability of the mesophase could arise from the mutual conjugation between the internal oxygens and the external carbonyl groups; such mutual conjugation is lacking in A and I, nevertheless they show higher nematic-isotropic transitions.

We must conclude, according to Dewar and Riddle[14], that the predominant factors in determining mesophase stability are geometric, whereas polarity seems to play a minor role. Reversal of the external ester linkages alters the electronic distributions of the resulting compounds, but essentially affects the axial ratio of the mesogenic unit, which is lengthened by the terminal Ar-O-C(=O)- group, because of the oxygen carbonyl conjugation. In addition this effect results in shortening the size of the flexible spacer ($\leftarrow CH_2 \rightarrow_8$ instead of $-O(CH_2)_8O-$), whereas the terminal O-C bonds are in both cases parallel. The addition of methyl groups should increase the intermolecular separation and reduce the coplanarity of the molecule, because of the twisting effect around C-O bonds due to steric hindrance. Unfortunately we are unable to evaluate the real variation of T_I due to the methyl substitution. Finally, the nematic character of the mesophase observed with polymers 3 and 4 is not surprising, if we consider that smectic mesomorphism in monomer 2 can arise from intermolecular H-bonding between adjacent molecules[11].

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