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Liquid Crystals

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Liquid-crystalline main chain polyesters derived from *p*-phenylenediacyrylic acid

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4,4'-(*p*-phenylenediacyroyloxy)-dibenzoyl chloride was polycondensed at 220°C with several diols in order to obtain liquid-crystalline polymers. The mesomorphic properties were studied by optical microscopy and differential scanning calorimetry. Gelation due to thermal crosslinking occurred at higher temperatures. With the exception of 2,2'-biphenyldiol derivative, all the polymers derived from aliphatic diols, dihydroxy ethers and aromatic diphenols exhibit mesogenic behaviour.

1. Introduction

The use of the polymers with cinnamate or *p*-phenylenediacyrylate units in their structure is of interest because of their applications, mainly due to on their light sensitivity and photoreactivity [1-3].

Recently we have reported [4] some main chain liquid crystalline polyesters obtained by polymerization of several complex diacids or their dichlorides with some biphenols and aliphatic diols. One of the dichlorides used as a monomer was a *p*-phenylenediacyrylic acid derivative: 4,4'-(*p*-phenylene-diacyroyloxy)-dibenzoyl chloride (**I**; see scheme). The aim of the work reported here was to study the potential mesomorphic properties of 12 main chain polymers obtained by high temperature solution polymerization of the dichloride (**I**) with a series of dihydroxylic monomers, including linear aliphatic α,ω -diols (**D**₁, **D**₂, **D**₃, **D**₄ and **D**₅), α,ω -dihydroxy-ethers (**D**₆ and **D**₇), cycloaliphatic diols (**D**₈ and **D**₉) and aromatic diphenols (**D**₁₀, **D**₁₁ and **D**₁₂).

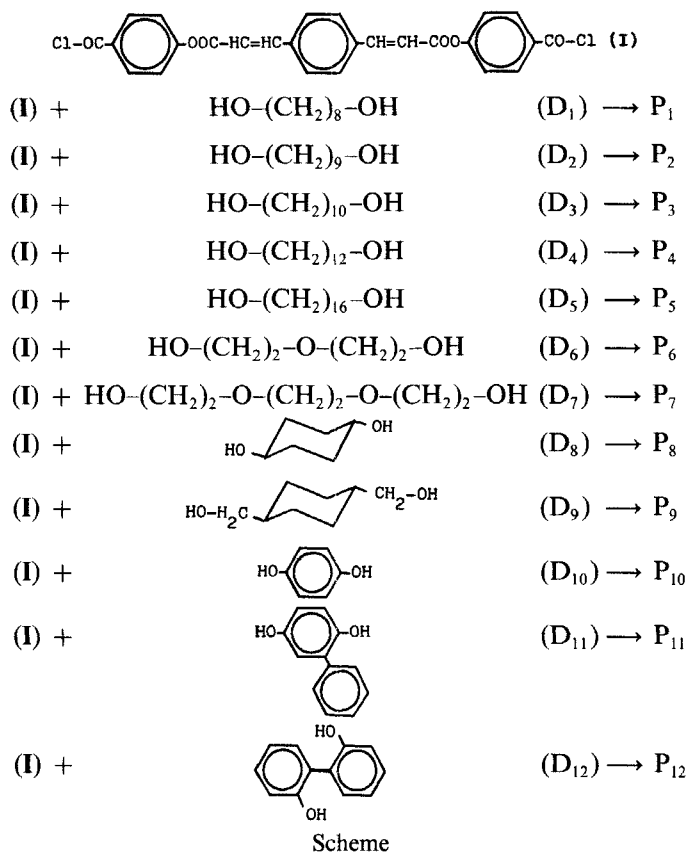
Polymer **P**₃ has been described previously [4]. The rest have not been reported before. The phase behaviour of these polymers were investigated by optical microscopy and differential scanning scanning calorimetry (D.S.C.).

The aim of this paper is to serve as a general approach to the thermal behaviour of the polymers mentioned above. Therefore, the study has been carried out only on pure polymers. Obviously, for application purposes copolymers and mixtures should be used in order to improve the thermal and mechanical properties.

2. Results and discussion

2.1. Synthesis of the polymers

The use of **I** as a monomer for building up polyesters introduces reactive conjugated double bonds into the polymeric chains, which could lead to undesirable thermal crosslinking [5, 6]. For this reason high temperature melt transesterification would be an unadvisable method for the synthesis of polymers containing such units. The low temperature solution method of polymerization would avoid thermal



crosslinking, but frequency the molecular weight of the polymers prepared by this method is limited. For these reasons we chose the high temperature solution polymerization method and used a suitable solvent which allowed the diols to react with monomer I as a means of obtaining high molecular weight polyesters [7], and thus avoiding undesirable side reactions.

Dichloride I was polycondensed with the appropriate diol in diphenyl ether at 200–220°C for 2 h to obtain, after precipitation from toluene, white powdered polymers.

3. Mesomorphic properties

The transition temperatures and thermogravimetric data of the 12 polymers are collected in table 1. The elemental analysis results, infrared (I.R.) data and inherent viscosity values are listed in Table 2.

Polymers P₁–P₁₁ are mesogenic, only polymer P₁₂ (derived from 2,2'-dihydroxybiphenyl) melts to isotropic liquid at 256°C. Direct microscopic examination of polymers P₂–P₇ and P₉ under polarized light above the melting points afforded threaded Schlieren optical textures typical of N and S_C mesophases. However, some observations at higher temperatures (when viscosity decreases) confirm the N mesophase (see the figure):

- (a) textures with surface disclinations and free threads;
- (b) marbled textures with predominant inversion walls and
- (c) the texture does not flash when it is subjected to mechanical stress, but on the other hand homeotropic areas were obtained in this process.

Table 1. Transition types and temperatures, and thermogravimetry data of the polymers

Polymer	Transition	$T/^\circ\text{C}$ (a)	TG (b)	(DTG) (c)
P ₁	C-C' (d)	205	371	(415)
	C'-N	343		
	N-I	(e)		
P ₂	C-N	258	377	(422)
	N-I	334		
P ₃	C-N	196	376	(420)
	N-I	330		
P ₄	C-N	152	375	(420)
	N-I	259		
P ₅	C-N	159	380	(425)
	N-I	271		
P ₆	C-C' (d)	142	382	(436)
	C'-N	246		
	N-I	333		
P ₇	C-N	142	374	(429)
	N-I	305		
P ₈	C-N	310	339	(363)
	N-I	325		
P ₉	C-N	228	394	(438)
	N-I	322		
P ₁₀	C-C' (d)	271	439	(463)
	C'-N	322		
	N-I	(e)		
P ₁₁	C-N	355	426	(446)
	N-I	(e)		
P ₁₂	C-I	256	374	(423)

(a) Maximum peak positions of D.S.C. diagrams.

(b) Thermogravimetry, onset of curves.

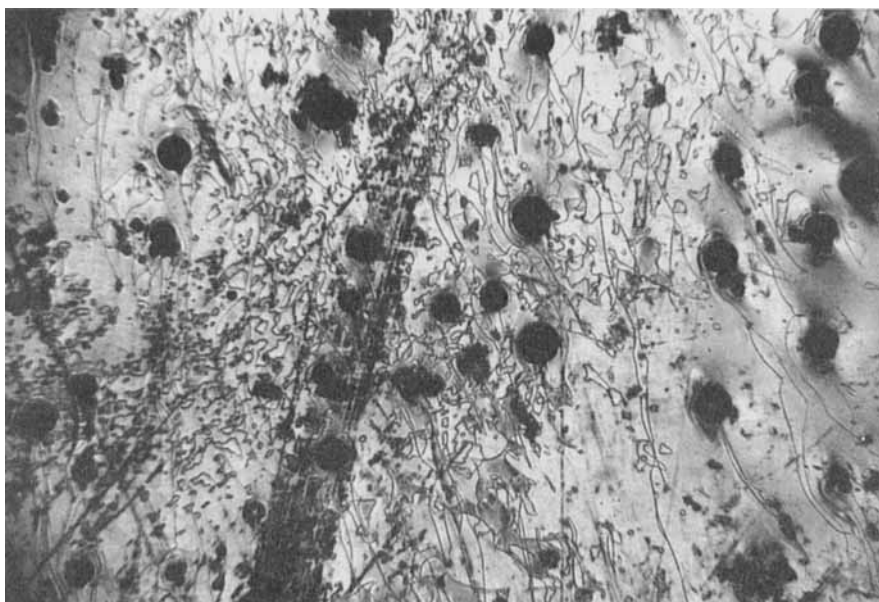
(c) Differential thermogravimetry, maximum peak positions of curves.

(d) These transitions remained after the previous thermic treatment.

(e) Transition not detected.

The polymers with high melting points could not be studied by direct observation in the optical microscope, because the gelation process masked the T_m transition. Polymers P₁, P₈, P₁₀ and P₁₁ had to be studied by a different method [8]. A small amount of the sample was placed between two glass plates on a hot stage preheated to 350°C. When the polymer melted it was promptly quenched in an ice-water bath. The quenched specimens were analysed optically and were found to have structures similar to those of other polymers (in P₁₁ polymer, phenylhydroquinone derivative, only a portion appeared to have melted and the rest remained unchanged) because of the similarity to previous observations we attribute nematic behaviour to these polymers, but we were unable to confirm it by direct examination of the quenched samples.

In polymers with lower melting points the gelation process can be studied by direct observation under the microscope. At first the mesophases are very viscous and the



Photomicrograph of polymer P₄ taken at 220°C during the heating cycle (crossed polarizers, × 100).

Table 2. Elemental analysis and I.R. spectroscopy data, and inherent viscosities of the polymers.

Polymer	Elemental analysis				I.R. peaks (in KBr)/cm ⁻¹		Inherent viscosity/dl g ⁻¹
	C/per cent		H/per cent		C=O	C=C	
	Found	(calc.)	Found	(calc.)			
P ₁	70.74	(71.83)	5.53	(5.63)	1725	1635,970	0.72
P ₂	72.02	(72.16)	5.95	(5.84)	1725	1635,975	0.60
P ₃	71.37	(72.46)	6.21	(6.09)	1740,1715	1625,960	0.76
P ₄	72.07	(73.06)	7.02	(6.45)	1720,1700	1625,968	0.47
P ₅	73.52	(74.10)	7.44	(7.11)	1720	1625,970	1.23
P ₆	67.54	(68.18)	5.02	(4.54)	1720	1630,975	0.40
P ₇	64.24	(64.56)	5.30	(5.06)	1720	1630,970	0.33
P ₈	69.85	(71.37)	5.01	(4.83)	1720,1710	1655,970	0.51
P ₉	70.89	(72.08)	5.62	(5.30)	1720,1710	1655,970	0.39
P ₁₀	71.53	(72.18)	4.05	(3.76)	1730	1630,970	—
P ₁₁	74.26	(75.00)	4.16	(3.95)	1740	1635,970	1.48
P ₁₂	73.77	(75.00)	4.37	(3.95)	1730	1630,980	0.31

viscosity decreases as the temperature increases. However, at about 300°C the mesophases become more viscous, until a gel is finally obtained due to the formation of crosslinked structures [4]. As the gelation process progresses the textures characteristic of nematic mesophase disappear but the gel remains highly birefringent.

In the D.S.C. study most of the polymers gave rise to several peaks corresponding to the melting process. This multiple melting behaviour may be due to the existence of different crystalline structures formed when the polymers were precipitated from

the reaction solution. In general it is very useful to study the transitions in the second heating cycle, because the previous thermal history of the sample is removed by the first heating cycle. In the polymers synthesized this treatment was possible only for polymers P_4 and P_5 . With the other polymers the gelation process prevented this. Polymers P_2 - P_7 , P_9 and P_{12} were heated to their melting points and quickly cooled to eliminate the C-C' transitions. All the other polymers were annealed at 200°C for 6 h to favour the reorganization process of the chains in order to sharpen the melting peaks. In spite of this, wider melting peaks were obtained for some of the polymers studied.

The N-I transition temperatures correspond to the maximum of the peak detected by D.S.C. before the onset of the crosslinking process, which can be seen by the drastic change in the slope of the curve. Under the D.S.C. work conditions (heating rate 40°C min⁻¹ and nitrogen atmosphere) the crosslinking process begins between 330 and 400°C, depending on the polymers. In the case of the polymers P_1 , P_{10} and P_{11} the N-I transition could not be detected.

All the polymers derived from linear aliphatic diols are mesogens. In polymers P_1 - P_4 the presence of additional methylene groups cause a decrease in the melting points; however polymer P_5 has similar properties to P_4 . This behaviour is similar to that observed in low molecular weight compounds.

The comparatively low melting points of polymers P_6 and P_7 , derived from dihydroxyethers is noteworthy. Polymer P_7 , which differs from polymer P_1 in that two methylene groups have been replaced by oxygen atoms in the flexible spacer, has a melting point of 142°C, which is 200°C lower than that of polymer P_1 . This is probably due to the greater flexibility of the spacer containing oxygen atoms, smaller and less hindered than the methylene groups.

In polymers P_8 and P_9 , derived from cycloaliphatic diols, there is a restricted flexibility in the polymers chains. Polymer P_8 has a very high melting point (310°C) and decomposes very quickly. This process of decomposition was observed by D.S.C. and thermogravimetric techniques and was attributed to the breaking of the ester linkage between the aromatic and the cycloaliphatic groups. On the other hand, in polymer P_9 , derived from cyclohexane dicarbinol, with two additional methylene groups in the repeating unit, there must be more flexibility, and as a result there is a considerable decrease in the melting point.

Polymers P_{10} and P_{11} show very high T_m transitions. This is due to the rigidity of the highly conjugated polymeric chains. These polymers are the most stable of all the polymers studied and remain practically unchanged after 24 h at 270°C in a nitrogen atmosphere. In polymer P_{12} , derived from 2,2'-biphenyldiol, the distorted geometry decreases the melting point but prevents the appearance of mesomorphism.

4. Experimental

4.1. Diacid chloride (I) Preparation

To a solution of 14 g (0.1 mol) of *p*-hydroxybenzoic acid in 100 ml of 2 M NaOH, vigorously stirred, a solution of 12.7 g (0.05 mol) of *p*-phenylenediacyryloyl chloride in 30 ml of chloroform was added at once. After 30 min of stirring the white precipitate was collected, washed with water, 1 M HCl, acetone, and dried, to yield 18.5 g (81 per cent) of 4,4'-(*p*-phenylenediacyryloyl)-dibenzoic acid, which was refluxed with thionyl chloride to yield dichloride (I), which was recrystallized from toluene: yield 12.5 g (62 per cent).

4.2. Polymer preparation

One gram (2 mmol) of diacid chloride (**I**), 2 mmol of the appropriate diol and 10 ml of diphenyl ether were introduced into a polycondensation tube and dry nitrogen was bubbled at room temperature for 30 min. The tube was then placed into a salt bath heated at 220°C for 2 h and the hot viscous solution was poured into 75 ml of toluene. The precipitated polymer was collected, washed with water, extracted with acetone in a Soxhlet apparatus and vacuum dried: yield 80–90 per cent.

4.3. Techniques

The mesophases were identified by optical microscopy using a Meiji polarizing microscope fitted with a Mettler FP-82 heating stage and an FP-80 control unit.

D.S.C. measurements were performed with a Perkin–Elmer DSC-2 at a heating rate of 40°C min⁻¹. The apparatus was calibrated with indium (m.p. 156.6°C) and tin (m.p. 231.9°C). All samples were run under nitrogen atmosphere and the transition temperatures were read at the maximum peak positions.

Thermogravimetric analysis was carried out with a Perkin–Elmer TGS-2 equipped with a System 4 microprocessor controller, at a heating rate of 10°C min⁻¹ under nitrogen. In table 1, thermogravimetric data are reported as the onset of the curves. Differential thermogravimetric data are reported as the maximum peak position of the curves.

The viscosities of the polymers were determined at 50°C in a solution of a mixture of *p*-chlorophenol and 1,1,2,2-tetrachloroethane (weight ratio 3 : 2) at a concentration of 0.5 g dl⁻¹ using a Cannon–Fenske viscosimeter. The viscosity of polymer P₁₀ could not be determined because of its insolubility.

The identification of the polymers was carried out by I.R. spectroscopy in KBr mulls using a Perkin–Elmer 783 spectrophotometer and by elemental analysis using a Perkin–Elmer 240 C microanalyser. Monomer (**I**) was characterized by I.R. and ¹H-N.M.R. spectroscopy and elemental analysis. Proton N.M.R. spectra were obtained with a Varian XL-200 instrument in CDCl₃ solutions.

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