Polymers with mesogenic elements in the main chain: A nematic aromatic copolyester*

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Properties of a copolyester based on methylhydroquinone, pyrocatechol and terephthalic acid have been described. Light scattering data for the copolyester in chloroform and dichloroacetic acid are well represented by $\bar{M}_w = 220\,000$ while the intrinsic viscosity is 0.22 dl g^{-1}, which implies a compact arrangement of the molecule in dilute solution. Differential scanning calorimetry (d.s.c.) traces show that the copolyester is essentially non-crystalline in character. Polarizing microscopy (texture observations, miscibility tests) provides definite proof as to the nematic structure of the melt. Well aligned samples can be produced either by subjecting nematic melt to a magnetic field ($H_c = 0.6$ T) or by suitable treatments of the slides between which the melt is observed. The conoscopic interference pattern corresponds to that of a uniaxial system showing an optically positive character. A structural model is proposed to account for the X-ray patterns obtained from oriented samples.

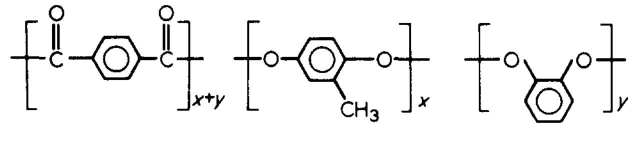
Keywords

INTRODUCTION

Nematic liquid crystallinity is exhibited by certain compounds with relatively rigid, polar, rod-shaped molecules that tend to be oriented with their long axes parallel because of the anisotropy of the interactions[1]. When such a compound is heated, the crystalline solid melts to a birefringent, anisotropic liquid (nematic mesophase) in which adjoining molecules lie parallel to one another. At a higher temperature, the mesophase undergoes transition to an isotropy liquid.

For practical purposes, there is a need for nematic mesophases at relatively low temperature. Unfortunately, the molecular characteristics that are necessary for nematic mesomorphism also produce stable crystalline lattices. Accordingly nematic compounds generally have high melting points. One way to lower crystal–mesophase transitions is to use substances having a relatively high degree of molecular dissymmetry. In most cases, the linkage of benzene rings through the *o*- or *m*-positions and/or the introduction of *o*- or *m*-substituents into already *p*-substituted systems depress the solid–mesophase melting point while the mesophase–isotropic transition temperature varies only slightly. However, if the inability to pack molecules regularly is too much enhanced, the resultant compound does not form liquid crystals.

We became interested in this problem in connection with physicochemical studies of thermotropic polymeric liquid crystals. We therefore decided to synthesize the copolyester containing the recurring units:



In the first part of this paper, the method of preparation and the characterization of copolyester will be given. The second part will be devoted to the identification of the nematic mesophase and its alignment.

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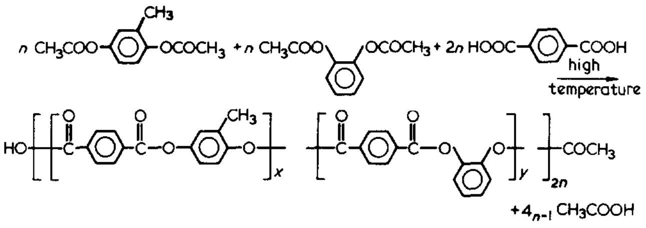
EXPERIMENTAL

Materials

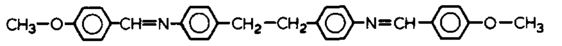
The copolyester was prepared in the Centre de Recherches des Carrières de Rhône-Poulenc, by acidolysis reaction from the 2-methylhydroquinone and pyrocatechol bis-acetates and terephthalic acid:



Elemental analysis: Calc. C, 70.44%; H, 3.64%; O, 25.91%. Found C, 69.5–69.8%; H, 3.5–3.6%; O, 26.06–26.55%.

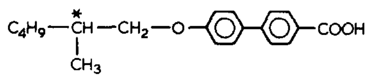
Bis-acetates were synthesized by acetylation of 2-methylhydroquinone and pyrocatechol with acetic anhydride containing a trace of sulphuric acid catalyst followed by recrystallization from ethanol[2,3].

The reference compound used to identify the polymeric mesophase was *N*,*N*′-bis(*p*-methoxybenzylidene)α,α′-bi-*p*-toluidine (B) (Eastman Organic Chemicals):



$$\text{Solid} \overset{190°C}{\rightleftharpoons} \text{Nematic} \overset{322°C}{\rightleftharpoons} \text{Isotropic}$$

The conversion of polymeric mesophase to the cholesteric form was performed by the addition of the following active solute (C): 4′-(2-methylhexyloxy)-biphenyl-4-carboxylic acid[4]:



Techniques

The high-resolution ^{13}C N.M.R. spectrum was determined on 5% (w/v) deuterochloroform solution at 62.9 MHz with a Brüker WP-250 spectrometer. Chemical shifts were determined by referring to the $CDCl_3$ resonance, assumed to be 76.9 ppm from tetramethylsilane. Assignment of the aromatic resonances is obtained by using empirical parameters for the calculation of chemical shifts in substituted benzenes[5].

The cross-polarization magic angle spinning (CP MAS) ^{13}C n.m.r. spectrum was recorded at 12.07 MHz on a home-built spectrometer constructed around a 12 in Varian electromagnet and employing ^{2}D field-frequency stabilization, solid-state class-A transmitters and double-tuned single-coil probes[6]. Spectra were obtained at room temperature using magic angle spinning in a Henriot–Huguenard design[7] hollow rotor made of Kel-F and spinning speed of 2 kHz. Spectra were obtained by cross-polarization from the spin-locked protons[8] with the Hartmann–Hahn[9] matching condition met, followed by high-power proton decoupling. Amplitudes of the radio-frequency fields expressed in frequency units, for both the carbons and the protons, were 32 kHz. Spin-temperature inversion techniques were systematically employed to minimize baseline noise and roll[10]. Flip-back[11] allowed us to shorten the delay time between two successive pulse sequences.

Light scattering measurements were performed on a Fica 50 photometer; the wavelength of the vertically polarized incident light was 5460 Å. Optical purification of solutions and solvents was carried out by centrifugation at 14 000 rpm for 3 h. Refractive-index increments were determined with a Brice–Phoenix differential refractometer. At 23°C, the refractive increment, d*n*/d*c*, for green light 5460 Å, was 0.150 $cm^3\ g^{-1}$ and 0.130 $cm^3\ g^{-1}$ for copolyester in chloroform and dichloroacetic acid, respectively.

Intrinsic viscosity of copolyester in chloroform was measured at 25°C in an Ubbelohde viscometer.

Melt viscosity data were obtained from a cone–plate rheometer by conventional techniques.

D.s.c. measurements were carried out on a differential thermal analyser Du Pont 990. The copolymer samples ($\sim$10 mg) were examined under dry nitrogen flow. Heating rate was 20K min^{-1} in all experiments.

The texture of the mesophase was observed between cover slips with a polarizing microscope (Olympus BHA-P) equipped with a heating stage (Mettler FP 5 or Reichert). The shape of the isobaric phase diagram was determined using the well known contact method[12]. Well defined compositions were examined for the phase diagram to insure a degree of accuracy for the composition coordinate.

The alignment of the mesophase was achieved by using cells made of two rectangular glass plates, 1 × 2 cm in size, each having been made anisotropic either by surface treatment or by directed oblique evaporation of silicon oxides[13]. The two glass plates were assembled into a sandwich with a steel spacer holding them apart. The cell was formed keeping the treated surfaces inside. The copolyester was introduced into the sandwich by capillary action, taking care to avoid air spaces and bubbles. Here, the introduction was made in the liquid crystalline state at a temperature of about 280°C to reduce the viscosity of copolyester. The weak effect due to the flow action on the copolyester chains can provide a preferential alignment of these molecules so that the sample was first stored for 20 min at 280°C and then rapidly quenched by pouring liquid nitrogen on top of the preparation.

X-ray diffraction patterns were recorded on flat films using Ni-filtered Cu K_α radiation. The samples were contained in 1 mm Lindemann glass tubes which were mounted in a heater, the temperature of which was controlled within 0.2K using a platin resistor as sensing element. For temperature calibration, the melting points of standard compounds were used. As previously observed[14], specimens in the liquid crystalline state can be aligned by means of a magnetic field. Thus, aligned samples have been obtained by inserting in the heater a permanent magnet which gave a field of about 0.8 T perpendicular to the X-ray beam and to the capillary axis. In addition, the polymer was oriented by stretching in the temperature range 135°–150°C and cooling to room temperature.

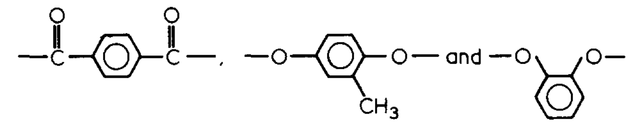
The distribution of intensity on the equatorial layer line was studied using a θ–2θ diffractometer equipped with a bent quartz monochromator and a scintillation detector, operating in the transmission mode.

RESULTS AND DISCUSSION

General properties

The copolyester was almost completely insoluble at room temperature in virtually all common solvents with the exception of chloroform and dichloroacetic acid.

The molecular structure was verified by high-resolution ^{13}C n.m.r. analysis (*Figure 1*). Assignment of aromatic resonances, given in *Table 1*, confirms the presence of segments:



in the copolyester.

Moreover, although such a measurement is not strictly quantitative, the comparison of the relative aromatic CH line intensities suggests that x is slightly higher than the value of 0.5 expected assuming equal reactivity of the bis-acetates of 2-methylhydroquinone and pyrocatechol with terephthalic acid. Besides, the lineshape of the CO (162.9_5–164.0_2 ppm) and $C_{1,4}$ (133.1–133.8 ppm) carbons of the terephthaloyl unit, which is sensitive not only to the nature of the next neighbouring rings but also to that of the more distant ones, is consistent with a random sequence distribution.

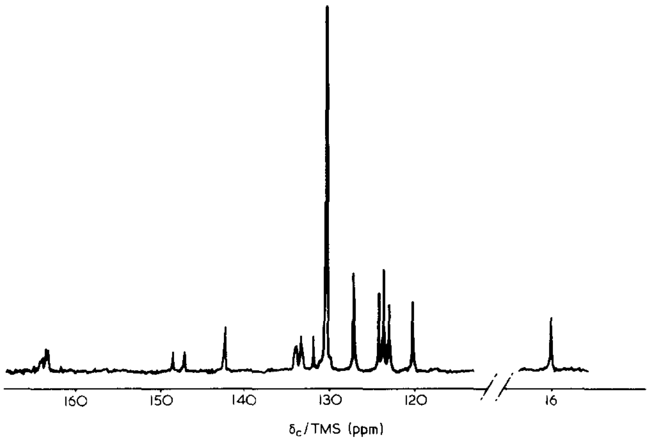
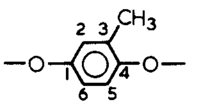
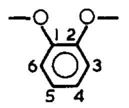
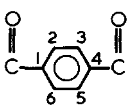


Figure 1 High-resolution ^{13}C n.m.r. spectrum of copolyester in $CDCl_3$ solution

Table 1

Recurring unit	Chemical shift (ppm) Calculated value	Experimental value
		
1	149.5	146.8
2	124.3	123.96
3	132.8	131.70
4	150.3	148.15
5	123.5	122.78
6	120.6	119.91
		
1, 2	145.5	142.14
3, 6	123.5	123.43
4, 5	127.5	126.97
		
1, 4	135.1	133.1–133.8
2, 3, 5, 6	129.7	130.15

In *Figure 2a* is shown the CP MAS solid-state ^{13}C n.m.r. spectrum of the copolyester. Carboxyl, aromatic and methyl peak locations are in perfect agreement with results obtained from $CDCl_3$ solution. The delayed-decoupled spectrum[15,16] shown in *Figure 2b* confirms the protonated nature of all the carbons resonating below 131 ppm. The assignment of $C_{1,4}$ carbons of the terephthaloyl unit is also unambiguous.

Table 2 gives the obtained values of the weight average molecular weight $\bar{M}_w$, the second virial coefficient A_2 and the radius of gyration $\langle S^2\rangle^{1/2}$ for copolyester. The data are well represented by $\bar{M}_w = 220.000 \pm 10.000$ and $\langle S^2\rangle^{1/2} = 170$ Å. It should be noted, however, that negative values were obtained for the second virial coefficients, indicating that both chloroform and dichloroacetic acid are poor solvents. Horizontally and vertically polarized incident light was used for determination of the depolarization factor $\rho_u = I_H/I_V$. For the system copolyester–chloroform, a value of 0.03 was obtained for ρ_u, which corresponds to a low anisotropy of the molecule.

At 25°C, the intrinsic viscosity $[\eta]$ is 22 $cm^3\ g^{-1}$ for copolyester in chloroform, which is relatively low in view of the value of 220 000 determined for $\bar{M}_w$ by light scattering. This implies a compact arrangement of the molecule in chloroform. The negative second virial

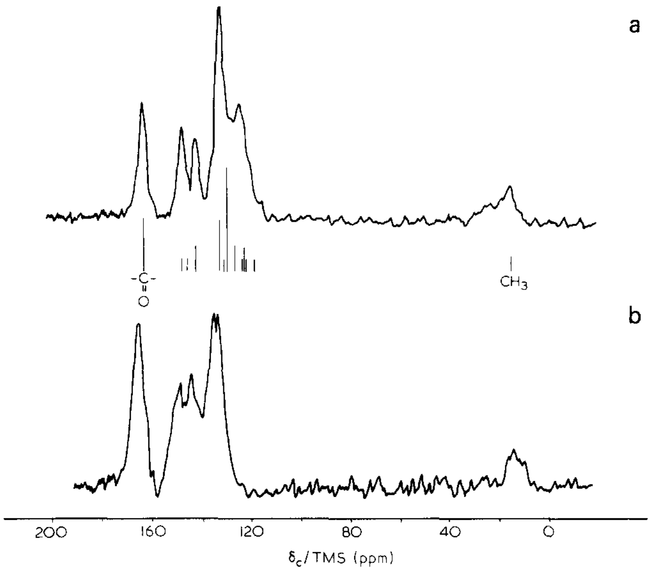


Figure 2 CP MAS ^{13}C n.m.r. spectrum of copolyester at 25°C: (a) spectrum obtained from 5000 accumulations with a CP contact time of 1 ms and experiment repetition time of 0.5 s; (b) delayed decoupled spectrum–delay time 50×10^{-6} s

Table 2 Light scattering data for copolyester at 23°C

Solvent	$\bar{M}_w$ (dalton)	A_2 (ml mol g^{-2})	$\langle S^2\rangle^{1/2}$ (A)
$CHCl_3$	210 000	-1.3×10^{-4}	170
$CHCl_2COOH$	230 000	-0.7×10^{-4}	

coefficient and the low value of the depolarization factor lead additional support to this view.

The synthesized copolyester is essentially non-crystalline in character (*Figure 3*). The d.s.c. trace for thermally untreated sample shows at about 90°C (363K) a heat capacity increase which has the appearance of a glass transition. At higher temperature one observes a small exotherm, which is followed by a marked increase in heat capacity. From microscopic observations it has been shown that in the temperature range 100°–110°C, the sample is becoming birefringent. Such behaviour has been observed by Menczel and Wunderlich[17] for amorphous poly(*p*-acryloyloxybenzoic acid). According to these authors, the probable reason for the exotherm is a conversion of the amorphous phase to mesophase. As shown in *Figure 3*, no upper transition is observed up to 380°C (653K), the temperature at which the mesophase–isotropic liquid transition occurs. Upon cooling the sample, the mesophase is preserved in the glassy state so that, on a second heating, the glass transition shifts to about 109°C (382K). This increase in T_g on change of the amorphous phase to mesophase is similar to the experiments carried out on poly(*p*-acryloyloxybenzoic acid).

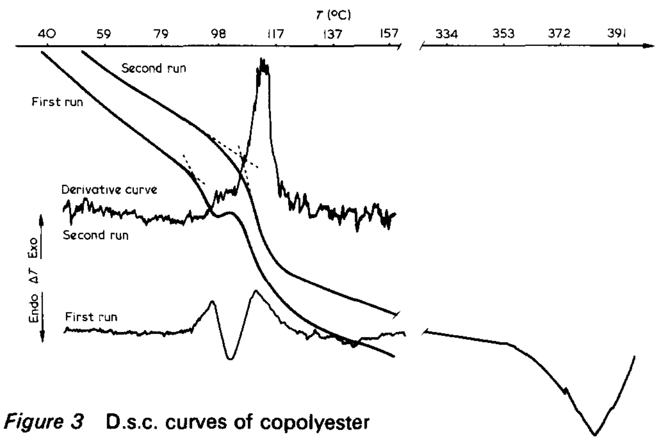


Figure 3 D.s.c. curves of copolyester

Interesting peculiarities are noted in the rheological properties of the copolyester. Even at a temperature of 210°C (483K) the apparent viscosity is low. Above 250°C (523K) the copolyester is uncommonly fluid although light scattering measurements strongly support high molecular weight. Indeed, at a shear rate of $32\ s^{-1}$, the apparent viscosity is 1640 Pa s, 300 Pa s, 109 Pa s and 65 Pa s at 210°, 250°, 280°C (553K) and 300°C (573K), respectively[18]. These low values of viscosity are similar to those obtained for two liquid crystalline copolymers of polyethylene terephthalate and 60 and 80 mol% of *p*-hydroxybenzoic acid[19–21]. As has been proposed by Baird[22,23] for lyotropic nematics and by Wissbrun[24] for thermotropic aromatic polyesters, such low viscosity values may reasonably be interpreted by considering the basic flow unit as an assembly of rod-like molecules which have a common orientation rather than an individual molecule. The rod-like molecules slide smoothly over each other dissipating less energy than randomly oriented and entangled molecules.

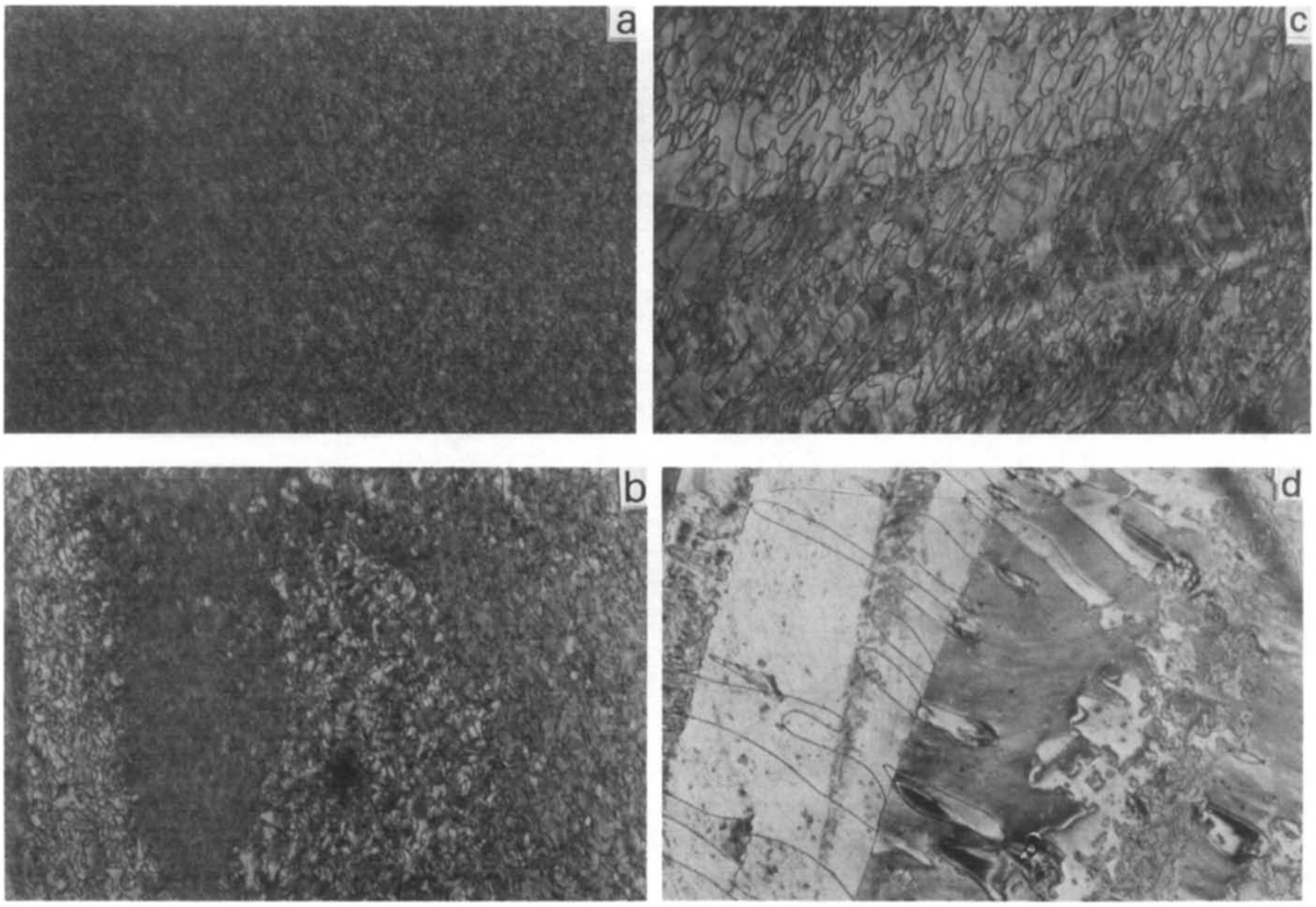


Figure 4 Photomicrographs of nematic phase from copolyester at (a) 200°C, (b) 230°C, (c) 250°C, and (d) 280°C. (Magnification ×300)

Mesophase characterization

Observations with a polarizing microscope indicate a flow temperature of 180°C–186°C (453–459K). At this temperature, evidence of fluidity is found and a small amount of polymer placed between glass slide and cover slip spontaneously gives rise to an anisotropic fluid that exhibits a typical threaded texture (*Figure 4*) which is consistent with a nematic phase. As temperature increases, the number of threads decreases. Simultaneously, the threads have a strong tendency to shrink in length. At about 270°–280°C (543–553K) most of them form closed loops. They are unstable and after some time, or by heating, they become smaller and smaller and to a great extent disappear (*Figures 5* and *6*). As a consequence, near 300°C–320°C (573–593K) samples of copolyester contain no threads and show homogeneous colour across large areas between crossed polarizers. Similar microscopic observations have been reported by Millaud *et al.* for the lyotropic nematic phase of a poly(*p*-phenylene terephthalamide)[25] and the thermotropic nematic phase of poly(azomethines)[26]. As these authors pointed out, such optical behaviour is consistent with disclinations of integer order and, more specifically, of strength +1 following the normal definitions of disclination strength[27–29] (*Figure 7*). Other microscopic observations confirm the existence of integer disclinations within the nematic phase of a copolyester prepared from 40 mol% poly(ethylene terephthalate) and 60 mol% *p*-acetoxy benzoic acid[30]. Although in low molecular weight nematics the existence of singularities with $S = +1/2$, $-1/2$, $+1$ and -1 has been established, it is interesting to note that in polymeric nematic phases, the disclinations of strength $S = +1$ are generally preferred to the other ones. Millaud *et at.*[25] have considered different molecular arrangements. Taking into account the rigidity and the length of the macromolecular chains, these authors argue for a pure radial splay model, which avoids bend energy.

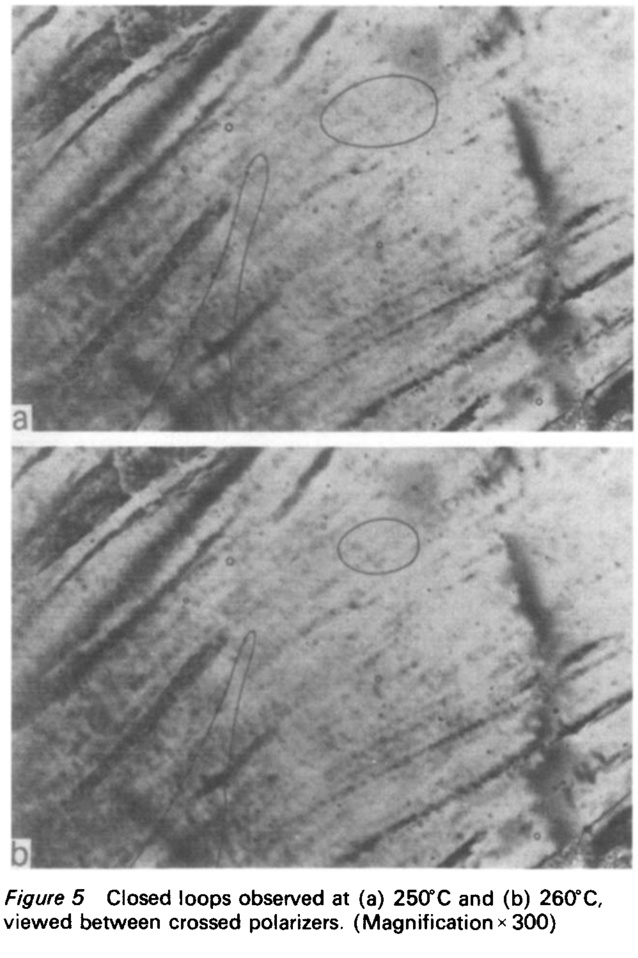
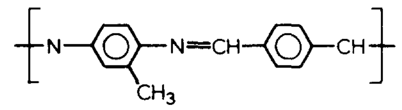


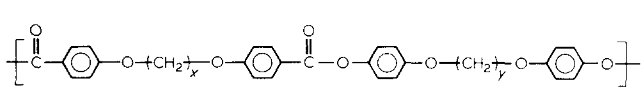
Figure 5 Closed loops observed at (a) 250°C and (b) 260°C, viewed between crossed polarizers. (Magnification × 300)

Another interesting observation is that a homeotropic texture (the director, i.e. the average direction of the molecular long axes, is arranged perpendicular to the glass slides) spontaneously forms above 320°C (593K) (*Figure 8*). At 360°C (633K) perfect layers of this kind can be obtained. When viewed vertically between crossed polarizers, they extinguish the light completely. Such an alignment can easily be disturbed. By slightly touching the cover glass of the preparation, flash-like brightness can be produced, thus distinguishing between homeotropic and isotropic texture. In fact, above 320°C, some degradation occurs: the sample turns brown, the colour deepens with time and gas bubbles are observed. As a consequence, the number of chain ends increases which may be favourable for homeotropic orientation. As has been proposed by Meyer[31], one can describe a perfect, ideal polymer nematic as composed of infinite chains. Each chain end can be considered as a defect in such a perfect nematic. If macromolecular chains are infinite (i.e. no chain ends) they must lie parallel to glass surfaces for energetic reasons. For finite, but long, macromolecular chains, entropy tends to keep chain ends 'dissolved' in the bulk rather than condensed on the surfaces. On the other hand, short chains, i.e. abundant chain ends, may favour a homeotropic texture. Indeed, while entropy tends to distribute chain ends randomly, energy tends to place them so as to relieve strains.

The observation of a threaded texture is not sufficient to warrant identification of the observed mesophase as a nematic one and other evidence has to be produced. According to the rule of selective miscibility 'all liquid crystalline modifications which exhibit an uninterrupted series of mixed liquid crystals in binary systems without any contradiction can be marked with the same symbol'[32]. In this rule 'without contradiction' means that those liquid crystalline modifications that have the same designation in no case exhibit an uninterrupted series of mixed liquid crystals with the liquid crystalline states of another designation. Thus, the nature of a mesophase can be determined by establishing its isomorphy with a known mesophase of a reference compound, that is to say by establishing the isobaric temperature–composition phase diagram of a binary system composed of the polymer and a reference compound. Chronologically, the works that should be mentioned first are those of B. Millaud *et al.*[33] and C. Noël *et al.*[34,35] who have determined the nature of the mesophase of the copolyazomethine



by establishing its isomorphy with nematic reference mesophases. Polyesters of general structure



have also proven to be miscible with *p*-phenylene-bis(4-methoxy benzoate) and terephthal-bis(4n-butylaniline)

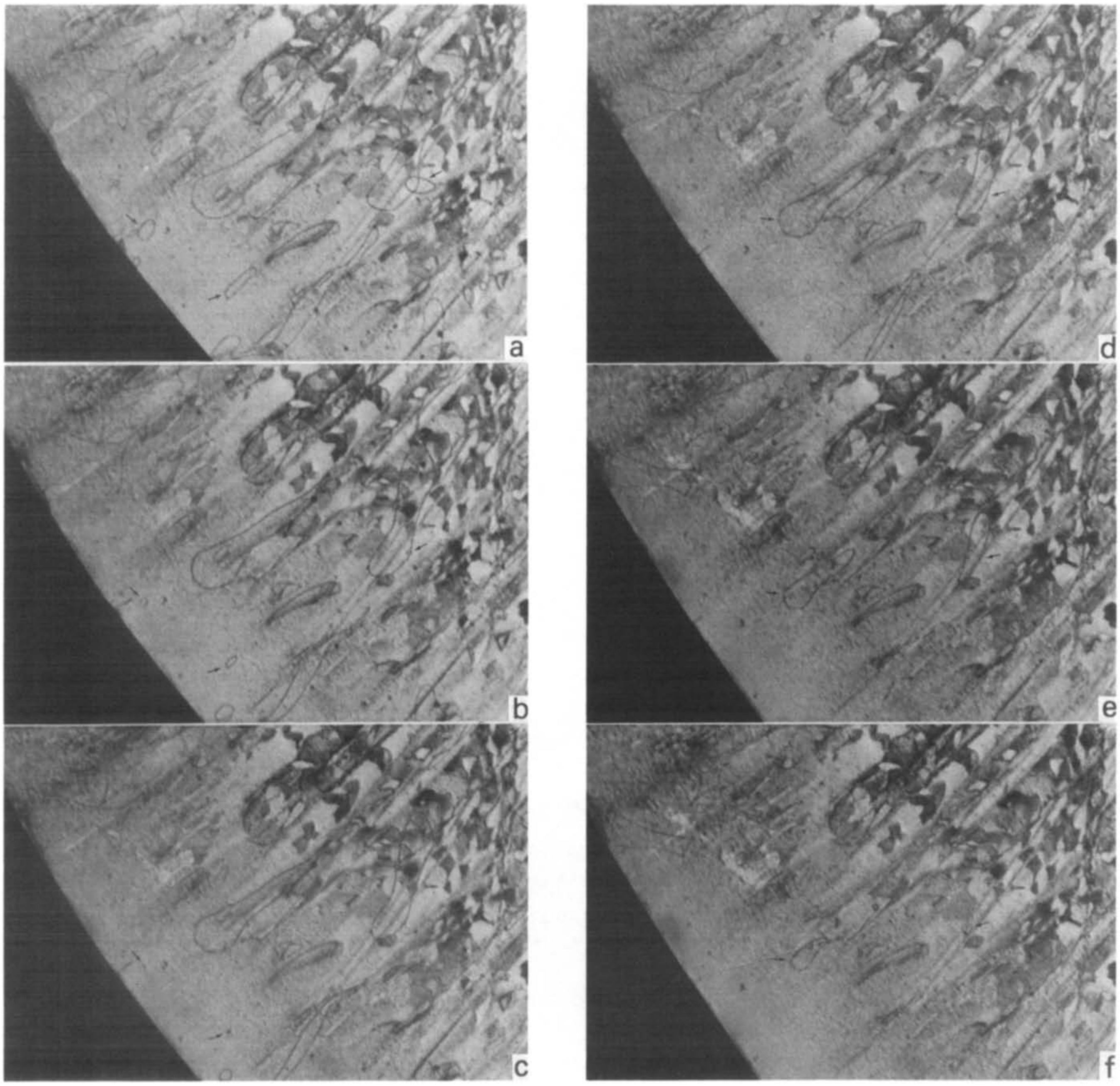


Figure 6 Closed loops viewed between crossed polarizers at 250°C; (a) time $t=0$, (b) $t=2$ min, (c) $t=5$ min, (d) $t=8$ min, (e) $t=15$ min, (f) $t=22$ min. (Magnification ×300)

in the nematic state[36,37]. More recently, Billard *et al.*[38] have identified, by means of the contact method, the nematic and cholesteric mesophases exhibited by polyesters based on 4,4′-azoxybenzene and 4,4′-azoxy 2,2′-methylbenzene.

The diagram of *Figure 9* is typical for mixtures of two nematogens. The mesophase of copolyester is isomorphic with the nematic phase of *N*,*N*′-bis(*p*-methoxybenzylidene)α,α′-bi-*p*-toluidine since there is a continuous pathway from the nematic phase of this reference compound to the mesophase of copolyester.

It is well known that conventional nematic phases can be transformed to cholesteric ones by dissolving an optically active compound in them. *Figure 10* shows that 4′-(2-methylhexyloxy)biphenyl-4-carboxylic acid on addition to the copolyester in the nematic state causes the formation of the typical texture of cholesterics with 'oily streaks'.

Alignment of the nematic phase

Usually, a nematic specimen is split up into domains, the orientation of which varies. However, suitable treatment of the slides or glass surfaces between which the nematic liquid is observed or the application of a magnetic or an electric field will result in a uniform molecular alignment and give a liquid 'single crystal' (single domain) instead of a liquid 'crystalline powder' (poly-domain)[13]. This means that the sample is macroscopically anisotropic with a unique direction of preference for the whole sample volume. In general, for quantitative work it is necessary to study such oriented specimens.

Previously, Noël et al.[14] have shown that practically

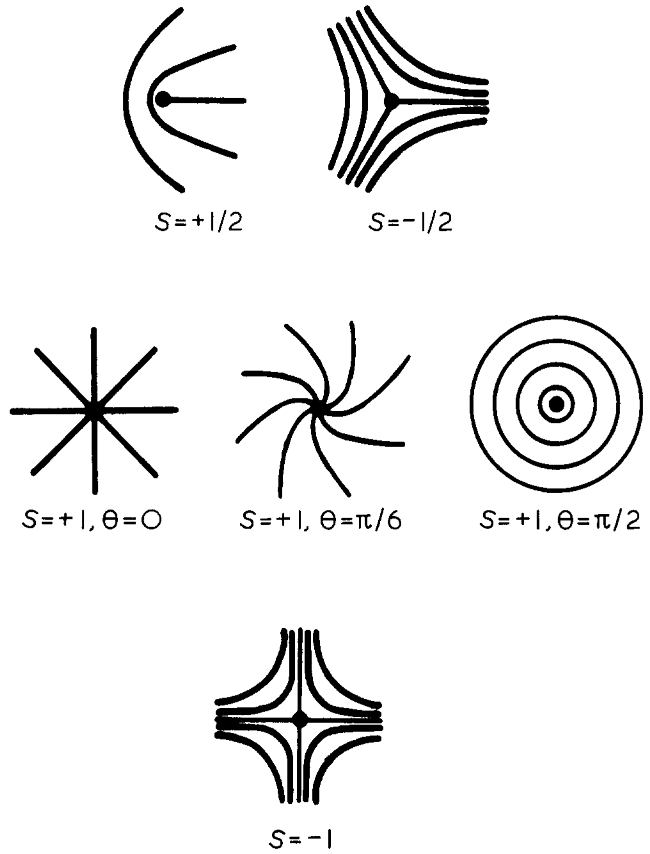


Figure 7 Schematic diagram of molecular trajectories associated with disclinations of strength ±1/2 or ±1

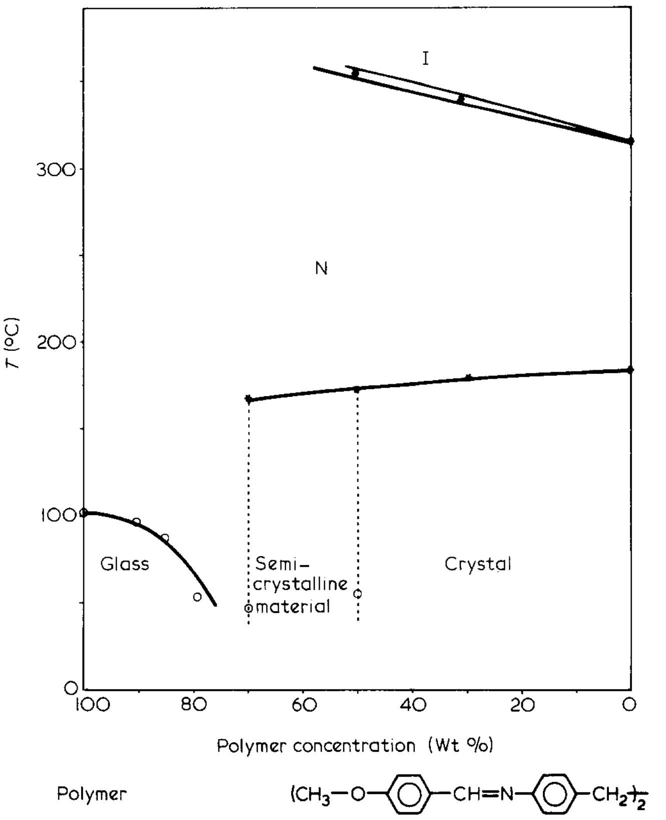


Figure 9 Binary phase diagram of the mixtures of copolyester (on the left) and *N,N'*-bis(*p*-methoxybenzylidene)α,α'-bi-*p*-toluidine (on the right)

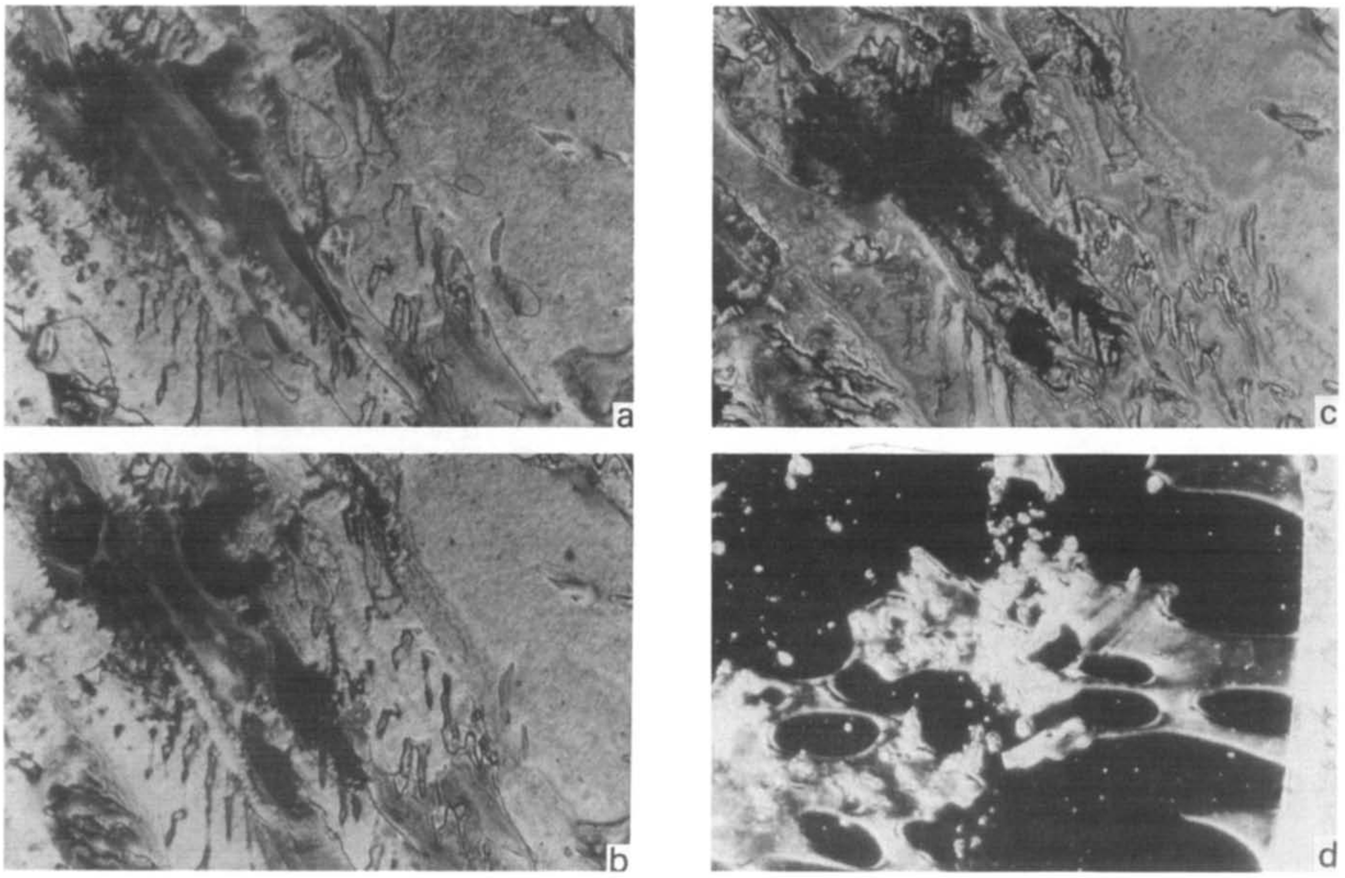


Figure 8 Photomicrographs showing the development of homeotropic texture from copolyester at 330°C (crossed polarizers): (a) time t=0, (b) t=8 min, (c) t=28 min, (d) t=40 min. (Magnification ×300)

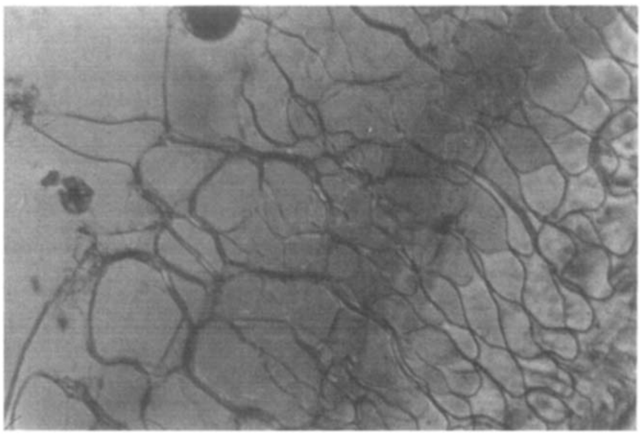


Figure 10 Cholesteric texture obtained by dissolving an optically active compound, 4′-(2-methylhexyloxy)biphenyl-4-carboxylic acid, in the copolyester in the nematic state. (Magnification × 300)

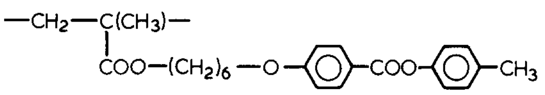
complete orientation for copolyester in the nematic state ($T = 280°C$) is approximated at a magnetic field strength of 0.6 T. Above this threshold field, macromolecules arrange themselves parallel to the magnetic field. It is of interest to note that orientation time is less than 2 min. At high electric field, Finkelmann *et al.*[39] have also determined short orientation times for copolymers with aromatic esters as mesogenic groups, separated by aliphatic spacers of variable length from polymethacrylate chain. The isotropic diamagnetic susceptibility $\bar{\chi}$ was estimated to be -5.26×10^{-7} emu cgs g^{-1} for the powdered copolyester at room temperature and the susceptibility parallel to the magnetic field $\chi_{\parallel H}$ was found to be -4.33×10^{-7} emu cgs g^{-1}. From the equation:

$$\Delta\chi = \frac{3}{2}(\chi_{\parallel H} - \bar{\chi}) = \chi_{\parallel H} - \chi_{\perp H}$$

the anisotropy of the magnetic susceptibility $\Delta\chi$ was calculated as 1.4×10^{-7} emu cgs g^{-1}, a slightly higher $\Delta\chi$ than that of the low molecular weight liquid crystals ($\Delta\chi \simeq 10^{-7}$)[29,40]. Such a discrepancy may be attributed to a greater rigidity of the macromolecular chains as compared to the conventional liquid crystals which contain two free terminal groups, usually alkyl groups.

For the copolymer under investigation, an alignment of macromolecules perpendicular to the substrate, that is to say a homeotropic alignment, can be achieved by simple treatment of glass slides with boiling chromic–sulphuric acid, acetone and methanol (sequentially interspersed with water rinses) and rinsing with hot distilled water. Then glass slides were rinsed in an ultrasonic cleaner with distilled water for 10 min and dried in a desiccator. Films thus prepared appear completely dark when viewed vertically between crossed polarizers. They show no birefringence, which implies that optical axes of the molecules lie in the observation direction, perpendicular to the supporting surfaces. Observations of the conoscopic image formed in a monochromatic beam converging in the sample is needed to check the uniformity of alignment (*Figure 11*). The conoscopic interference pattern corresponds to that of a uniaxial system showing an optically positive character with a half-wave plate being used.

With the aid of conoscopic observations, Finkelmann[41] has also proved the positive uniaxial character of polymers



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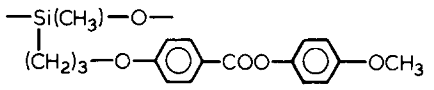
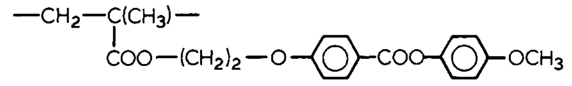


which exhibit textures of conventional nematic phases. It is interesting to note that this author reported contradictory results with polymers



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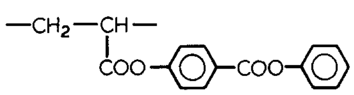


which were found optically negative. It is unclear whether this was due to an erroneous mesophase identification owing to the lack of typical texture or to the chemical structure of polymers. Indeed, a possible explanation for this specific behaviour might be a disturbing effect of the main chain which has to be expected when the polymer backbone and the side chain motions are little or not decoupled by a flexible spacer.

Glass surfaces which have been made anisotropic by directed oblique evaporation of silicon monoxide lead to planar samples in which the director lies parallel to the glass surfaces. Planar alignment was also obtained in experiments using surface deposited hexadecyltrimethyl ammonium bromide (HMAB). In this particular case, prior to the construction of the cell, the substrates were treated by dipping in a 10^{-6} mol l^{-1} chloroform solution of HMAB for 5 min and then withdrawn at a rate of about 1 mm min^{-1}. When such planar samples are viewed from the top between crossed polarizers, birefringence is dependent on the sample orientation with respect to the incoming linear polarized light. Four positions of extinction are found. Using convergent light, a typical

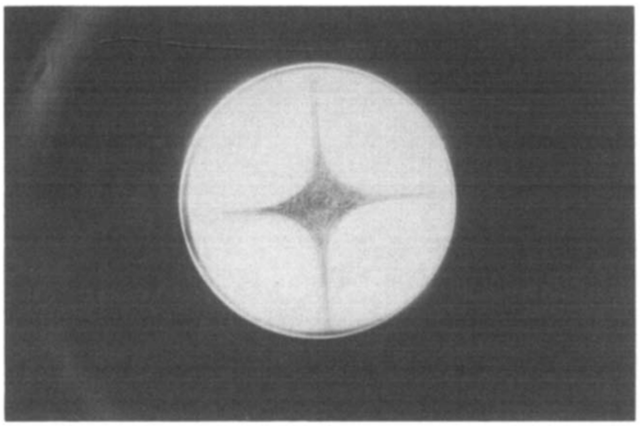


Figure 11 Conoscopic interference pattern given at room temperature by pseudoisotropic (homeotropic) texture of nematic mesophase quenched from 360°C. (Magnification × 300)

interference figure appears which shows families of hyperbolae-like fringes.

The X-ray patterns obtained with unoriented samples in a temperature range 25°–322°C mainly showed two diffuse halos. The outer halo is related to the lateral interactions of neighbouring chains while the inner halo can be ascribed to the short-range positional order existing in a liquid crystalline system[42]. In contrast, the anisotropy shown in the X-ray diffraction patterns of the aligned nematic phase of copolyester (*Figure 12*) clearly demonstrates the liquid crystalline structure of the melt; its nematic nature—previously established by polarizing microscopy–is confirmed by the fact that it orients in a rather low magnetic field with the director perpendicular to the capillary axis (*Figure 12b*). When the copolyester was quenched from the oriented nematic melt the resultant glass retains the liquid crystal alignment. A typical pattern taken at room temperature, is shown in *Figure 13a*. In view of the difficulties in photograph reproduction, schematic representation of this pattern is given in *Figure 13b*. Note that photographs taken with the X-ray beam parallel to the fibre axis showed patterns similar to those obtained for unoriented samples.

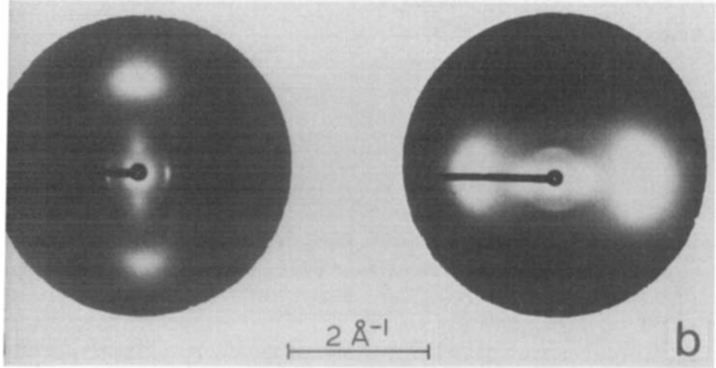
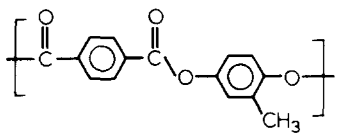


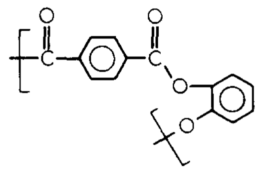
Figure 12 X-ray diffraction patterns of oriented nematic phase taken at 240°C from: (a) a stretching-oriented fibre, the direction of extension of copolyester fibre being horizontal; (b) the same sample, but heated in a magnetic field (~0.8 T), the director now being parallel to the magnetic field direction and perpendicular to the glass capillary axis

The patterns of aligned samples (*Figure 13*) are characterized by the following features: (i) along the equator, in addition to the two pronounced crescents whose intensity maxima are located at $q = 4\pi \sin \theta/\lambda = 1.34$ Å^{-1} (2θ is the scattering angle and λ the radiation wavelength), two diffuse spots are seen at a smaller diffraction angle, i.e. around $q = 0.54$ Å^{-1}; (ii) along the meridian line, which is parallel to the nematic director, two pairs of sharp arcs can be observed—the inner arcs at $q = 0.45$ Å^{-1} are intense, the outer ones at $q = 0.57$ Å^{-1} are visible only when films are overexposed; (iii) there are also some diffuse lines or discs perpendicular to the meridian, around $q = 0.8$, 1.6 and 2 Å^{-1}.

It is now well known[43] that an aligned nematic phase may give rise along the meridian line to a rather complex pattern consisting of several reflections and periodically spaced lines that are straight or slightly fanned[44–47] as observed for the copolyester under investigation. The first well defined Bragg reflection arcs along the meridian correspond to a lattice spacing of 13.9 ± 0.1 Å, which compares reasonably well with the calculated length of the fully extended x moiety, i.e.



On the other hand, the second pair of Bragg reflections, corresponding to a lattice spacing of 11.0 ± 0.1 Å, may be ascribed to the length of the y moiety, i.e.



The diffuse discs perpendicular to the meridian probably arise from periodic repetitions and monomer sequences along the chains that are roughly aligned in a direction parallel to the director[48]. The disc in the region

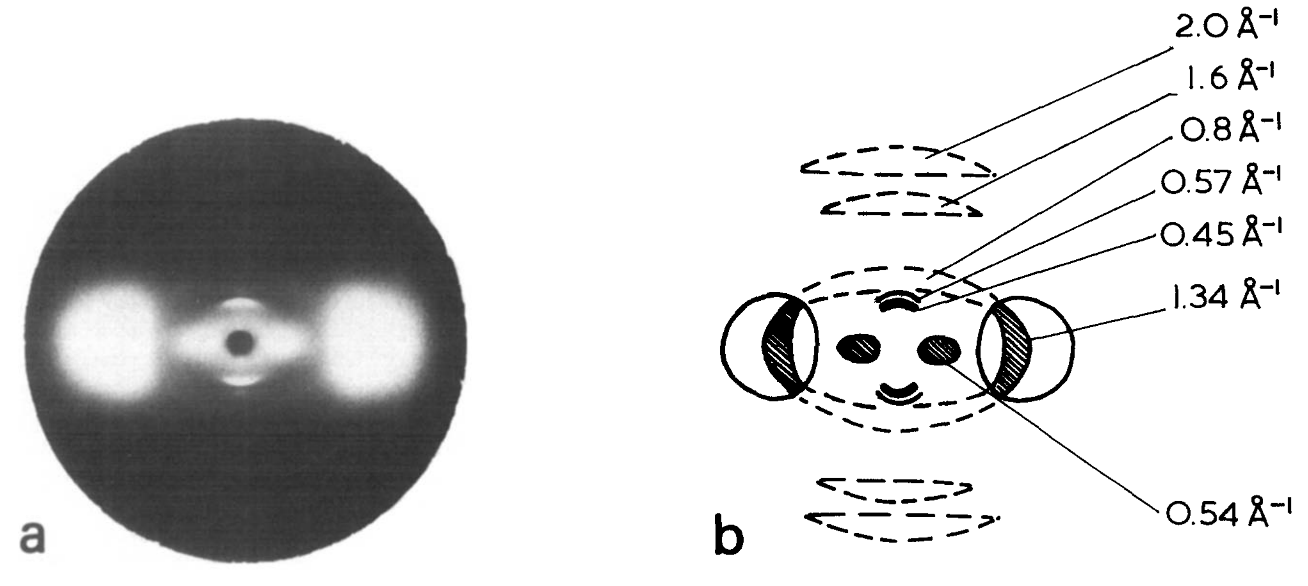


Figure 13 (a) X-ray photograph of a copolyester specimen stretched at 140°C and quenched to room temperature (the X-ray beam is normal to the fibre axis) and (b) its schematic representation

of $d \simeq 7.6$ Å appears to be a small order of the two other discs at 3.9 and 3.2 Å.

Since the molecular arrays in liquid crystals have cylindrical symmetry, the intensity recorded along the equatorial line for aligned mesophases can be used to determine the cylindrical distribution functions[49]. *Figure 14* shows the equatorial diffractometer scan obtained at room temperature from a copolyester specimen oriented by stretching. The shoulder observed around $q = 0.54$ Å^{-1} cannot be ascribed to a spurios effect connected with the 'white noise' of the X-ray spectrum as the radiation for this equatorial diffractometer trace was monochromatic. The molecular distribution function cannot be easily computed from this intensity distribution since the molecular structure factor $F^2(q)$ is unknown barring oversimplifications[50]. However, using an average molecular structure factor

$$F^2(q) = \sum_{1}^{N} f_j^2(q)$$

(f_j is the scattering factor of the N *atoms* j of the monomer unit) to take into account the decrease of the X-ray scattering versus q, the Fourier transform of the equatorial intensity was computed. Such a calculation leads to a first maximum at 5.0 Å. This distance, which is slightly smaller than the one calculated using the De Vries relation[51], i.e. 5.2 Å, gives the average lateral distance between adjacent chains.

As has been observed previously for certain nematic systems[47,52] the other important features of the equatorial data are the two diffuse spots which appear around $q = 0.54$ Å^{-1} for the copolyester under investigation. There is no information at present with regard to their origin. However, it is noteworthy that similar diffraction features have also been observed for helical structures[50,53]. Besides, it has been shown that the structure of aromatic polyesters can remain in the form of a double helix above the melting point[54,55]. Thus, in our analysis of the X-ray patterns we have considered the possibility of such arrangements of the chains, but without long-range order. The two diffuse spots along the equatorial line would be expected for roughly parallel chain bundles (typically 10–12 Å in diameter) in the form of two–four stranded ropes. The polymer chains would be otherwise poorly packed together due to random monomer sequences. They are spaced an average distance $r = 5.0$–5.2 Å apart but are not otherwise correlated. The periodicity along the chains and also the pitches of the helices would give rise to the diffuse discs along the meridian. In many respects, the structural model proposed to account for the diffraction patterns observed for the copolyester under investigation bears a close relationship to the molecular arrays believed to exist in the cybotactic nematic phases[56,57]. In these nematic systems that undergo transition to a smectic C phase, the meridional pair of strong discs in reciprocal space takes on the shape of rings that appear as four separated maxima in a normal beam photograph just above the transition temperature. This strongly suggests that, as such a nematic is cooled in a magnetic field, molecules tend to align themselves to form strings and, close to the nematic–smectic C transition, start grouping into parallel sheets. For the system described here such a transition has not been observed. When copolyester was cooled, a nematic glass was always obtained.

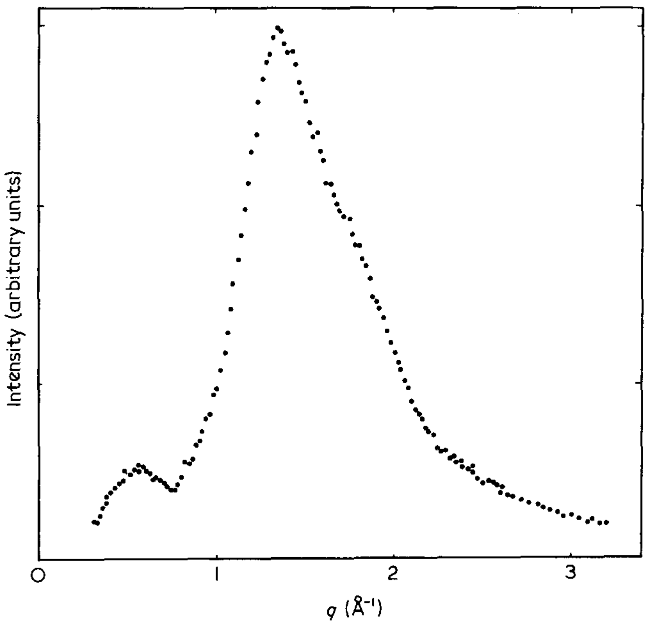


Figure 14 Intensity distribution along the equatorial line. Copolyester specimen oriented by stretching at 140°C and cooling to room temperature

CONCLUSION

Properties of copolyester based on methylhydroquinone, pyrocatechol and terephthalic acid have been described. Light scattering data are well represented by $\bar{M}_w = 220\,000$ and $\langle S^2 \rangle^{1/2} = 170$ Å. The negative second virial coefficients indicate that both chloroform and dichloroacetic acid are poor solvents. This is consistent with the rather low value obtained for the intrinsic viscosity, which implies that copolyester displays compact coiled conformations in dilute solution. As shown by d.s.c. traces the copolyester is essentially amorphous in character. Microscopic observations and miscibility tests unambiguously prove that the copolyester exhibits a nematic phase above T_g ($\simeq 109$°C). The clearing point is at about 380°C. However, some thermal decomposition is observed above 320°–330°C which favours a homeotropic orientation. Suitable treatments of the glass slides between which the nematic phase is observed result in a uniform molecular alignment and conoscopic interference patterns obtained from such aligned samples are consistent with a uniaxial system showing an optically positive character. Complete orientation for copolyester in the nematic state is also approximated at a magnetic field strength of 0.6 T. The anisotropy of the magnetic susceptibility $\Delta\chi$ is determined as 1.4×10^{-7} emu cgs g^{-1}, a slightly higher $\Delta\chi$ than that of the low molecular weight liquid crystals ($\simeq 10^{-7}$). A structural model is proposed to account for the X-ray patterns obtained from oriented samples. It bears a resemblance to the molecular arrays accepted to cybotactic nematic phases.

In conclusion, it appears that, in many respects, the copolyester under investigation behaves in the nematic state as conventional low molecular weight liquid crystals.

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REFERENCES

1 Gray, G. W. 'Molecular Structure and the Properties of Liquid Crystals', Academic Press, New York, 1962
2 Robertson, A and Robinson, R. *J. Chem. Soc. (London)* 1926, 1713
3 Levine, M. and Temin, S. C. *J. Polym. Sci.* 1958, **28**, 179
4 Leclercq, M., Billard, J. and Jacques, J. *C.R. Acad. Sci.* 1968, **266**, 654
5 Wehrli, F. W. and Wirthlin, T. 'Interpretation of Carbon-13 NMR Spectra', Heyden, London, 1976, Chap. 2
6 J. Virlet, to be published
7 Henriot, E. and Huguenard, E. *C.R. Acad. Sci.* 1925, **180**, 1389
8 Pines, A., Gibby, M. G. and Waugh, J. S. *J. Chem. Phys.* 1973, **59**, 569
9 Hartmann, S. R. and Hahn, E. L. *Phys. Rev.* 1962, **128**, 2042
10 Stejskal, E. O. and Schaefer, S. *J. Magn. Reson.* 1975, **18**, 560
11 Tegenfeldt, J. and Haeberlen, U. *J. Magn. Reson.* 1979, **36**, 453
12 Kofler, L. and Kofler, A. 'Thermomikromethoden', Verlag Chemie, Weinheim, 1954
13 Guyon, E. and Urbach, W. 4BBC Symp. Nomen. El. Disp., (Eds. Kmetz and Von Willisen), Plenum Press, New York, 1976, p. 121; J. L. Janning, *Appl. Phys. Lett.* 1972, **21**, 173
14 Noël, C., Monnerie, L., Achard, M. F., Hardouin, F., Sigaud, G. and Gasparoux, H. *Polymer* 1981, **22**, 578
15 Alla, M. and Lippmaa, E. *Chem. Phys. Lett.* 1976, **37**, 260
16 Opella, S. J. and Frey, M. H. *J. Am. Chem. Soc.* 1979, **101**, 5874
17 Menczel, J. and Wunderlich, B. *Polymer* 1981, **22**, 778
18 Achard, M. F., Hardouin, F. and Noël, C. to be published
19 Jerman, R. E. and Baird, D. G. *J. Rheol.* 1981, **25**, 275
20 Baird, D. G. and Wilkes, G. L. *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* 1981, **22** (2), 357
21 McFarlane, F. E., Nicely, V. A. and Davis, T. G. *Contemp. Top. Polym. Sci.* 1977, **2**, 109
22 Baird, D. G. in 'Liquid Crystalline Order in Polymers', (Ed. A. Blumstein), Academic Press, New York, 1978, Chap. 7.
23 Baird, D. G. *J. Appl. Polym. Sci.* 1978, **2**, 2701
24 Wissbrun, K. F. *Br. Polym. J.* 1980, **12**, 163
25 Millaud, B., Thierry, A. and Skoulios, A. *J. Physique* 1978, **39**, 1109
26 Millaud, B., Thierry, A., Strazielle, C. and Skoulios, A. *Mol. Cryst. Liq. Cryst. Lett.* 1979, **49**, 299
27 Demus, D., Richter, L. 'Texture of Liquid Crystals', Verlag Chemie, Weinheim and New York, 1978
28 Frank, F. C. *Discuss. Faraday Soc.* 1958, **25**, 19
29 Kelker, H. and Hatz, R. 'Handbook of Liquid Crystals', Verlag Chemie, Weinheim, 1980, Chap. 3
30 Mackley, M. R., Pinaud, F. and Siekmann, G. *Polymer* 1981, **22**, 437
31 Meyer, B. in 'Symposium on Polymer Liquid Crystals: Science and Technology', Santa Margherita Liqure, 18–22 May 1981; Meyer, B. in 'Seminar on Liquid Crystals', Sunapee, 1–3 July 1981; Meyer, B. in 'Polymer Liquid Crystals', (Eds. A. Ciferri, W. R. Krigbaum and R. B. Meyer), Academic Press, New York
32 Sackmann, H. and Demus, D. *Mol. Cryst. Liq. Cryst.* 1973, **21**, 239
33 Millaud, B., Thierry, A. and Skoulios, A. *Mol. Cryst. Liq. Cryst. Lett.* 1978, **41**, 263
34 Noël, C. and Billard, J. *Mol. Cryst. Liq. Cryst. Lett.* 1978, **41**, 269
35 Fayolle, B. Noël, C. and Billard, J. *J. Phys. (Paris)* 1979, **40**, C3-485
36 Griffin, A. C. and Havens, S. J. *J. Polym. Sci., Polym. Lett. Edn.* 1980, **18**, 259
37 Griffin, A. C. and Havens, S. J. *Mol. Cryst. Liq. Cryst.* 1979, **49**, 239
38 Billard, J., Blumstein, A. and Vilasagar, S. *Mol. Cryst. Liq. Cryst. Lett.* 1982, **72**, 163
39 Finkelmann, H., Naegele, D. and Ringsdorf, H. *Makromol. Chem.* 1979, **180**, 803
40 Hardouin, F., Achard, M. F., Sigaud, G. and Gasparoux, H. *Mol. Cryst. Liq. Cryst.* 1977, **39**, 241
41 Finkelmann, H. in 'Liquid Crystals of One- and Two-dimensional Order', (Eds. W. Helfrich and G. Heppke), Springer-Verlag, Berlin, 1980, p. 238
42 Wendorff, J. H. in 'Liquid Crystalline Order in Polymer', (Ed. A. Blumstein), Academic Press, New York, 1978, p. 13
43 Azaroff, L. V. *Mol. Cryst. Liq. Cryst.* 1980, **60**, 73
44 Chistyarov, G. and Chaikowsky, W. M. *Mol. Cryst. Liq. Cryst.* 1969, **7**, 269
45 Leadbetter, A. J., Richardson, R. M. and Colling, N. C. *J. Phys.* 1975, **36**, C1
46 Adams, W. W., Azaroff, L. V. and Kulshreshtha, A. K. *Z. Kristallogr.* 1979, **150**, 321
47 Usha Deniz, K., Paranjpe, A. S., Amirthalingam, V. and Muralidharan K. V. in 'Liquid Crystals', (Ed. S. Chandrasekhar), Heyden, London, 1980, p. 185
48 Blackwell, J. and Gutierrez, G. *Polymer* 1982, **23**, 671
49 Chistyakov, I. G. and Vainshtein, B. K. *Kristallographia* 1963, **8**, 570 (*Sov. Phys. Cryst.* 1964, **8**, 458)
50 Vainshtein, B. K. in 'Diffraction of X-rays by Chain Molecules', Elsevier, Amsterdam, 1966, Chap. III
51 De Vries, A. *Mol. Cryst. Liq. Cryst.* 1970, **10**, 219
52 Blumstein, A., Vilasagar, S., Ponrathnam, S., Clough, S. B. and Blumstein, R. B. *J. Polym. Sci., Polym. Phys. Edn.* 1982, **20**, 877
53 Bear, R. S. and Hugo, H. F. *Ann. N.Y. Acad. Sci.* 1951, **53**, 627
54 Economy, J., Storm, R. S., Matkovich, V. I., Cottas, S. G. *J. Polym. Sci. Polym. Chem. Ed.* 1976, **14**, 2207
55 Cser, F. in 'Liquid Crystals', (Ed. S. Chandrasekhar), Heyden, London, p. 329
56 Azaroff, L. V. *Proc. Natl. Acad. Sci. USA* 1980, **77**, 1252
57 De Vries, A. *J. Phys. (Paris)* 1975, **36**, C1-1