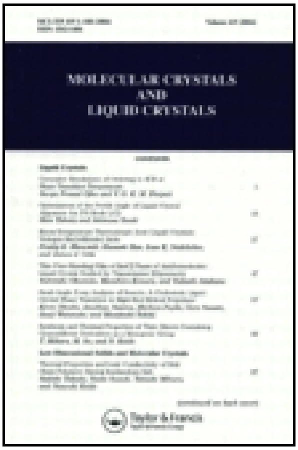

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Orientation of Thermotropic Liquid-Crystalline Polyesters in High Magnetic Fields

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Orientation of Thermotropic Liquid-Crystalline Polyesters in High Magnetic Fields

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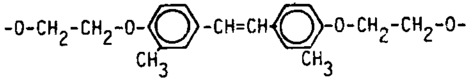
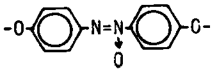
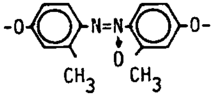
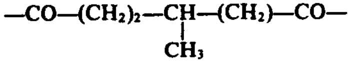
Strongly oriented poly-crystalline samples of polyesters containing mesogenic moieties and flexible spacers in the main chain have been produced by slowly cooling the molten samples in magnetic fields of up to 16 Tesla. This simple method appears to be successful for those polymers forming a "true" nematic phase over an extended range of temperatures. Cholesteric polymers are not oriented. Mesogenic polymers (such as SEB-5, SUC-5, and SEB-7) which pass only through a state of partial parallel ordering of chain segments before cystallizing cannot be oriented macroscopically. In these samples crystallization may interfere with the chain alignment in the magnetic field. In contrast to low molecular weight liquid crystals, the isotropic-liquid crystalline transition of the polyesters investigated has a strong thermal hysteresis.

INTRODUCTION

We have described recently[1-5] the synthesis and some properties of polyesters with mesogenic moieties (i.e. moieties promoting liquid-crystalline behavior) and flexible spacers in the main chain (see also Table I). Such polyesters are characterized by a random coil conformation and a very high flexibility in dilute solution, as well as in the melt well above the liquid crystal to isotropic transition temperature.[5] On cooling from the melt, these polymers may transit through nematic, smectic or cholesteric mesophases before crystallizing. They are expected to combine properties specific to low molecular weight liquid-crystals and poly-

TABLE I

The liquid crystalline polyesters are sequential copolymers of one of the mesogenic groups 5, 7, 8 or 9 and one of the flexible spacer groups SEB, MAA, DDA or SUC, respectively.

	Mesogenic Group Number
	5
	7
	8
	9
	Spacer
$-CO-(CH_2)_8-CO-$	SEB
 $-CO-(CH_2)_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-(CH_2)-CO-$	MAA
$-CO-(CH_2)_{10}-CO-$	DDA
$-CO-(CH_2)_4-CO-$	SUC

mers, with potential applications as materials with highly anisotropic thermal, mechanical and optical properties.

Because of the flexibility of the spacer such polymers differ substantially from worm-like mesogenic polymers which have found recently similar applications. The effect of the spacer is to increase the solubility, to decrease the melting temperature and to extend the liquid crystalline temperature range.

On a molecular level the flexible polyesters differ substantially also from low molecular weight liquid crystals: there is a strong coupling between translational and orientational motions of mesogenic groups in the polymers; the isotropic to liquid crystal transition of the polymers is probably associated with a large loss of configurational entropy and with conformational energy barriers both due to the local extension of individual chains. This may render the transition of these polymers more strongly first order and may result in a pronounced dependence of the liquid crystalline properties on factors such as the length and structure of the flexible spacer as well as the distribution of molecular weights in the sample.

The existence of mesophases in such polymers is usually established through a combination of microscopic observations and differential scanning calorimetry. X-ray patterns are often too diffuse to be of help especially for unoriented nematics or cholesterics. The above methods can be misleading because of the difficulty with which polymeric liquid crystals give specific textures due to the multiphase nature and high melt viscosity of polymers. The birefringent pattern, for example, of a dispersion of small crystallites in an amorphous matrix can be easily confused with that of a dispersion of liquid-crystalline domains.

It is well known that a homogeneous nematic phase can be fully oriented even by modest magnetic fields (≤ 1 Tesla) because of very extended correlations of molecular orientations. In the isotropic melt small correlations in orientation and their characteristic pretransitional variation can be detected by high resolution birefringence measurements in strong magnetic fields.[6,7] We have, therefore, submitted a number of polyesters to the test or orientation in strong magnetic fields. Table I summarizes the building blocks used in the preparation of the mesogenic systems investigated. A first simple experiment was to slowly cool the samples from the isotropic melt or the liquid crystalline phase below the crystallization temperature under a constant strong magnetic field and to check the resulting orientation by X-rays at room temperature. One sample was also rapidly quenched. For a few samples the magnetically induced birefringence and optical transmission (being a measure of turbidity) was determined in the isotropic phase down to the vicinity of the liquid crystalline transition temperature.

EXPERIMENTAL

For the X-ray studies the polymers in powder form were carefully pressed into thin capillaries (Lindemann-type glass tubes of 1 mm or 2 mm in diameter) and heated briefly above the temperature of melting. The capillaries were placed at room temperature in a standard Bitter-solenoid producing in a 5 cm bore a homogeneous vertical field of up to 20 Tesla along the axis of the capillary, quickly heated to the maximum experimental temperature t_e (Table II) and then cooled at various rates $\dot{t}$ and at different field strengths through the isotropic-liquid crystalline and/or liquid crystalline-crystalline transitions (Table II).

The magnetic birefringence $\Delta n = n_{\parallel} - n_{\perp}$, ($n_{\parallel}$, $n_{\perp}$ being the refractive index for light propagating perpendicular to the magnetic field H with polarization parallel and perpendicular to H, respectively) was continuously measured using a slightly modified version[8] of a combined photoelastic modulation and compensation technique described earlier.[9] For low viscosity melts of polymer chains (i.e. well above the liquid crystalline transition temperature) the orientation was in thermal equilibrium with the magnetic field at any instant during the field sweep and $\Delta n = CM\,\lambda H^2$; CM is the Cotton-Mouton-constant and λ the wavelength of light used ($\lambda = 632.8$ nm).

Optical transmission was measured simultaneously with Δn by d.c.-converting the second harmonic of the photo-elastically modulated laser light intensity.

RESULTS AND DISCUSSION

In Table II are summarized the orientation in the poly-crystalline state at room temperature of several polyesters cooled under various experimental conditions in a strong magnetic field, as revealed from X-ray fiber patterns. Because of rather large supercooling effects (see below) the thermal transitions have been recorded on heating only. The −8 series give on heating rather large endotherms and the transition temperature data for this series are based on thermal microscopy rather than on D.S.C. Intrinsic viscosities are also given in Table II. The number average molecular weights are only given for polymers sufficiently soluble in chlorinated solvents.

TABLE II

Orientation of polyesters placed in constant magnetic field H of high intensity and cooled from the isotropic and/or liquid crystalline melt.

Polymer	$[\eta]\frac{dl}{g}$	$\bar{M}_n$	Transition t(°C) (on heating)	$t_e/\dot{t}/H$(**)	Orientation
SUC-5	0.28	—	K191?196I	235/1/11	none
SEB-5	0.48	—	K156?163I	194/1/11	none
SEB-7	0.28	4,500	K114?129I	135/4/11	none (Figure 2)
MAA-8 (racemic)	0.39	—	K221N294I(*)	235/1/11	v. strong (Figure 1d)
MAA*-8	0.38	—	K221C294I(*)	235/1/11	none (Figure 1c)
DDA-8	0.76	—	K216N265I(*)	235/1/11	v. strong (Figure 1f)
MAA*-DDA-8(10/90)	—	—	K185C263I(*)	235/1/11	none (Figure 1e)
MAA*-DDA-8(50/50)	0.50	10,800	K162C278I(*)	212/2.4/16	none
MAA-DDA-8(45/55)	0.29	4,380	K162N278I	207/2.4/16	strong
MAA-9 (racemic)	0.74	16,000	K173N233I	194/1/11	strong (Figure 1b)
MAA*-9 (chiral)	0.42	7,800	K151C210I	194/1/11	none (Figure 1a)
DDA-9	1.00	20,000	K119N169I	138/1/11	weak
DDA-9L	0.2	3,500	K99N135I	160/.5/12	medium (Figure 1g)
DDA-9L	0.2	3,500	K99N135I	160/~100/12	strongly oriented glass (Figure 1h)

(*) Observed by microscopy

(**) t_e: maximum experimental temperature (°C)

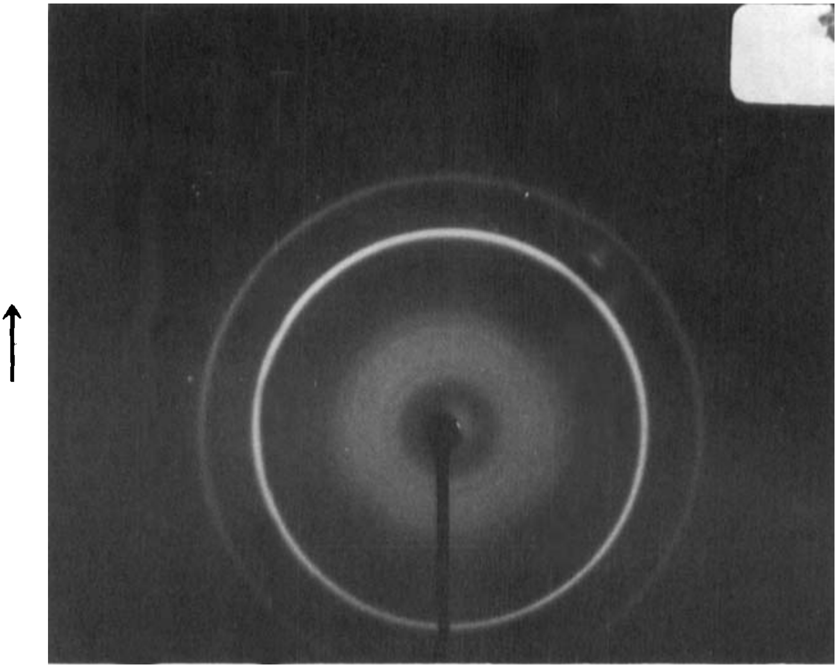
$\dot{t}$: cooling rate (°/min)

H: magnetic field strength (tesla)

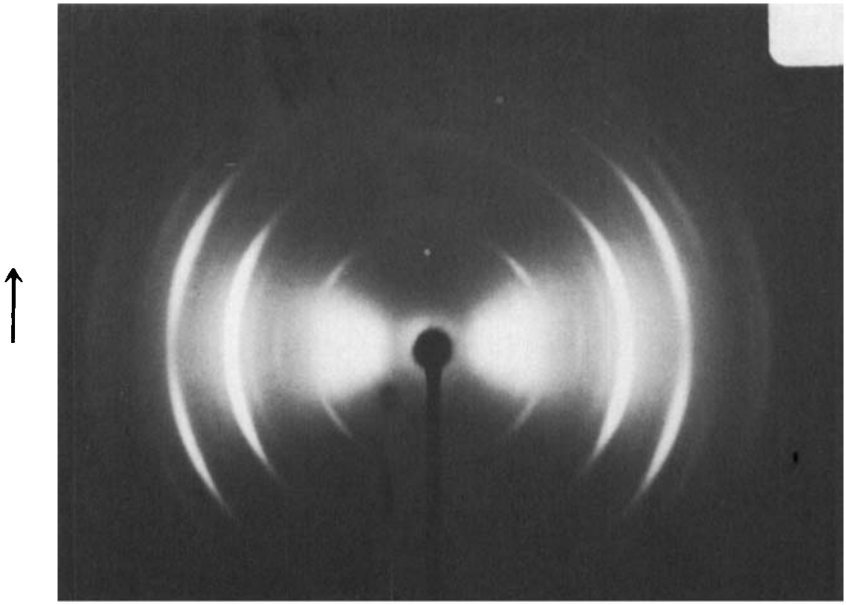
The $[\eta]$ viscosities were taken at 30°C in the following solvents: 1,1,2,2 tetrachloroethane for the 9 series; (1/1)m-cresol-chloroform mixture for the 8 series; (1/1)m-cresol-1,1,2 trichloroethane for the SEB and SUC series.

Typical X-ray patterns are shown in Figure 1. DDA-8, DDA-9 and the racemic mixtures MAA-8, MAA-9 and MAA-DDA-8 are strongly oriented, whereas all others are not. We conclude that this first group of the investigated polymers has a "true" homogeneous nematic phase. This agrees with microscopic observations and D.S.C.[3,4] The orientation induced by the magnetic field in DDA-9 in its nematic state has been "locked in" by thermal quenching and a strongly oriented glass was obtained.[10] The X-ray pattern (Figure 1g) is very similar to the pattern for oriented nematic mesophases of p. Azoxyanisole.[11,12] The poly-crystalline fiber of DDA-9 (Figure 1g) obtained by much slower cooling in the magnetic field is less oriented. This indicates that the crystallization process can diminish the macroscopic magnetic orientation.

The chiral polyesters (MAA*-8, MAA*-9, MAA*-DDA-8 and MAA*-DDA-9) very probably display cholesteric mesophases as indicated by the temperature dependent irridescence which is also dependent on the chiral content (partially reported in Ref. (3)). The chiral polymers do not orient appreciably in a magnetic field up to 16 Tesla. This



(a)



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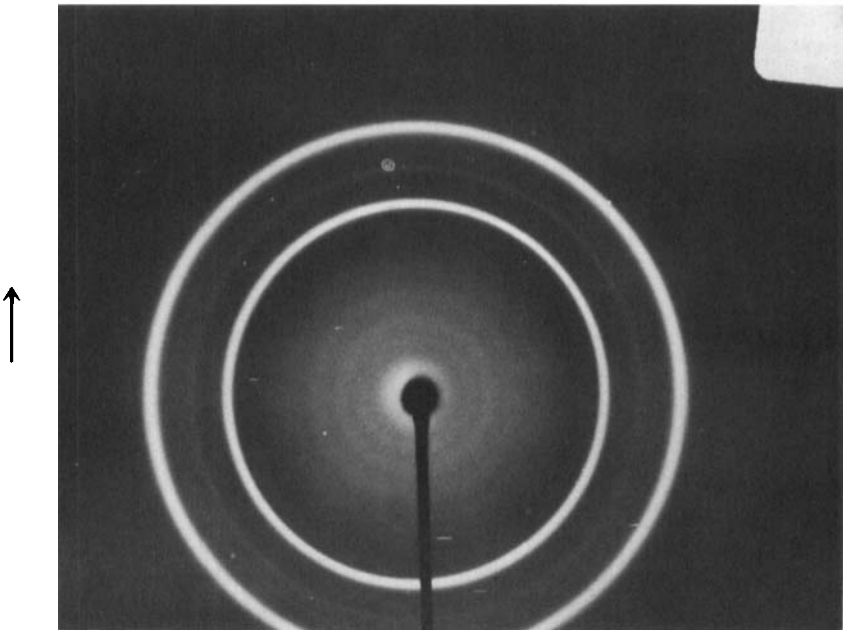
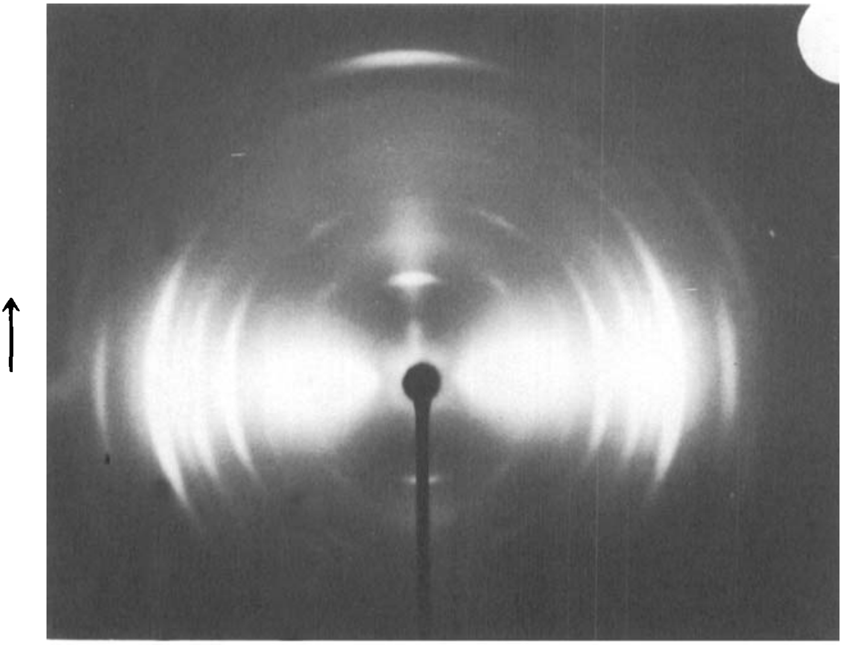
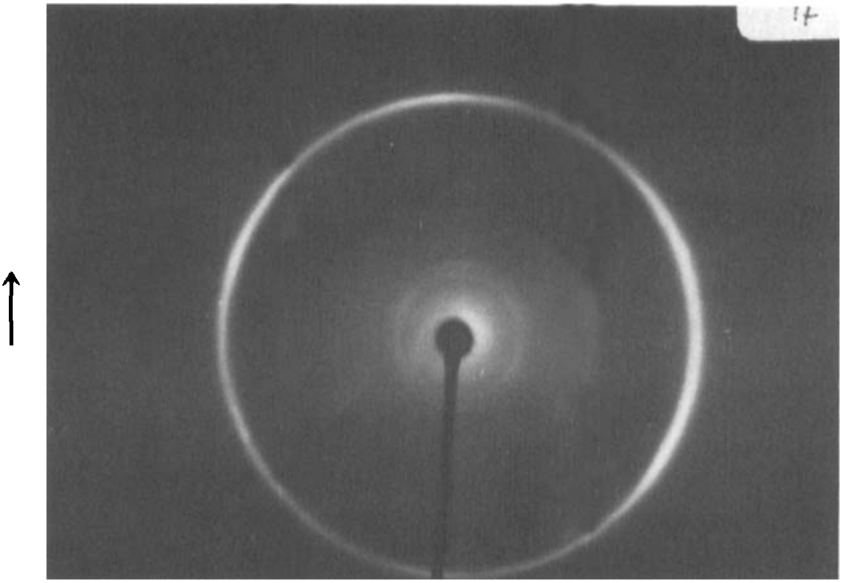


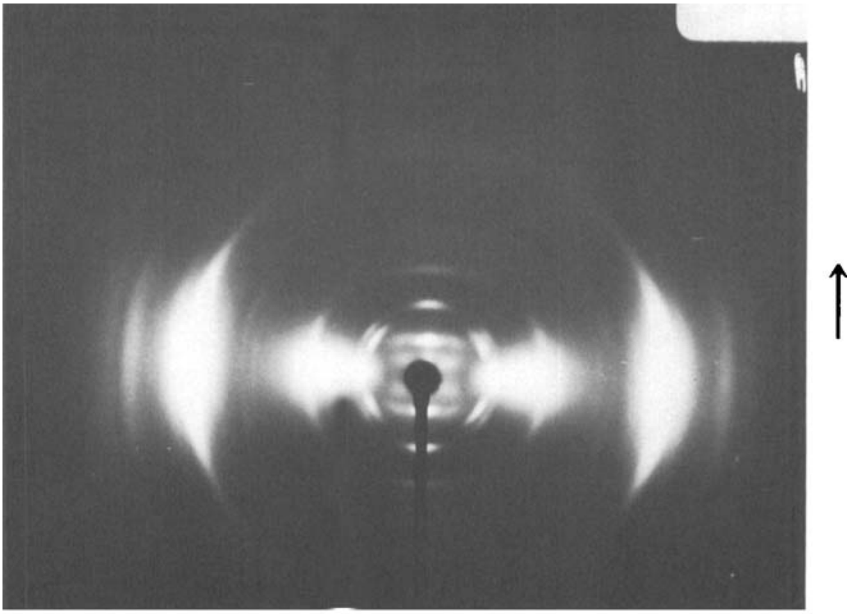
(c)



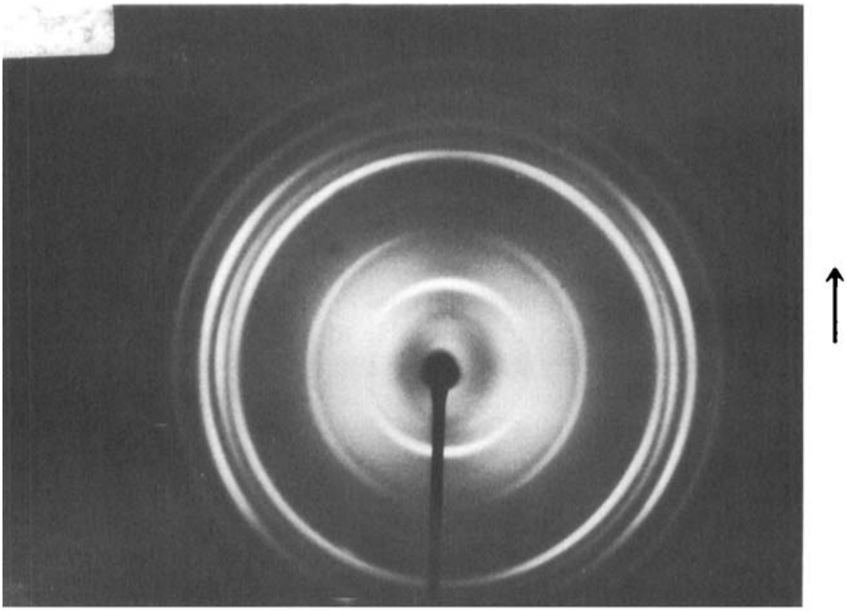
(d)



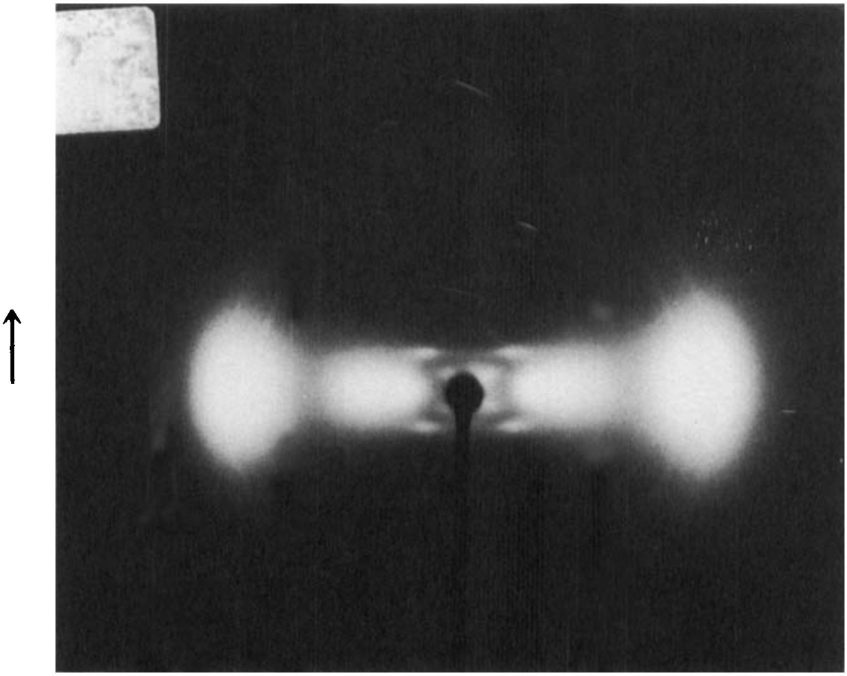
(e)



(f)



(g)



(h)

FIGURE 1 Flat chamber transmission X-ray pattern from various polyesters cooled from the liquid crystalline state through the crystallization point in a strong vertical magnetic field. Ni-filtered Cu-radiation and 0.5 mm collimator were used, the sample—fiber distance was 8 cm, the arrow corresponds to 1 cm on the film. Additional experimental details are given in Table II. (a) MAA*-9, (b) MAA-9, (a) and (b) cooled from 194°C at 1°/min in 11 Tesla, (c) MAA*-8, (d) MAA-8, (e) MAA*-DDA-8(10/90), (f) DDA-8, (c)–(f) cooled from 235°C at 1°/min in 11 Tesla, (g) DDA-9L cooled from 160°C at 5°/min in 12 Tesla, (h) DDA-9L quenched from 160°C at ~100°/min in 12 Tesla.

seems understandable because typical low molecular weight cholesterics when having a pitch comparable to optical wavelengths are expected to untwist only at fields above 30 Tesla;[11] this will hold also for our high molecular weight cholesterics if one assumes that the twist elastic constant is similar in magnitude to that of a typical low molecular weight cholesteric compound. In addition the high viscosity of macromolecular mesophases makes the untwisting even more difficult than in the case of low molecular weight mesophases: All mesogenic segments of a chain, in the process of unwinding would have to rotate into orientations parallel to the segments in the neighboring planes; this rotation is hindered by entanglements and conformational barriers. Note (Figure 1.e, 1.f) that even the presence of 10% of chiral groups within the mesogenic moieties prevents almost completely the orientation in the magnetic field (MAA*-DDA-8 (10/90) vs DDA-8). A similar situation exists for MAA*-DDA-9 (10/90) when compared to DDA-9 (data not shown).

From a comparison of various X-ray patterns (data partially shown in Figure 1), we can draw some general conclusions which could be of help for future applications of this new and simple method to produce strongly oriented para-crystalline polymer samples of any volume (smaller than about 4 cm in diameter in our case) and any shape. Within the investigated range of experimental parameters (excepting the quenched DDA-9L sample), there is no effect of the cooling rate or of the magnetic field strength on the overall orientation nor on crystallinity. To obtain a good orientation, there is no need to heat the sample to the isotropic transition temperature, but well above the crystal to nematic transition. If the maximum experimental temperature exceeds the crystallization point only by a few degrees, crystallinity and orientation are substantially decreased. The remarkable magnetic orientation of the nematic polyesters can be used to elucidate in detail the structure of the crystalline and of the nematic phase of these polymers. Our X-ray patterns demonstrate, that in the nematic phase the polymer chains orient parallel to the magnetic field and are substantially extended. This agrees with observations made by others.[10,13,14]

The lack of orientation of SUC-5, SEB-5 and SEB-7 (see Table II) none of which contains chiral groups is striking, because from microscopy and D.S.C. data one could suspect the existence of a mesophase[1,2] though only within a narrow temperature range. To elucidate this point, we have carried out simultaneously magnetic birefringence and optical transmission measurements above the "clearing" temperature. Typical data on SEB-7 are given in Figure 2. Data on SUC-5 and SEB-5 are similar.

In the isotropic melt for temperatures more than some 10°C above the transition temperature (on cooling) the measurements of the magnetic birefringence give low values of the Cotton-Mouton constant. We find $CM = 1.35 \times 10^{-4} T^{-2} \mathrm{cm}^{-1}$ at 135°C for SEB-7 (Figure 2) and similar values for SEB-5, SUC-5 and DDA-9L.[5,10] These values are very close to those of similar polyesters in dilute solution,[5] of monomeric model compounds in dilute solution,[5] of low molecular weight liquid crystals in the isotropic phase[6,10,11] and of flexible polymers such as polystyrene[15-17] and polycarbonate[16,18] in the melt. This clearly indicates that these mesogenic polyesters in the isotropic melt are very flexible with a statistical segment length approaching the length of the repeat unit.[5]

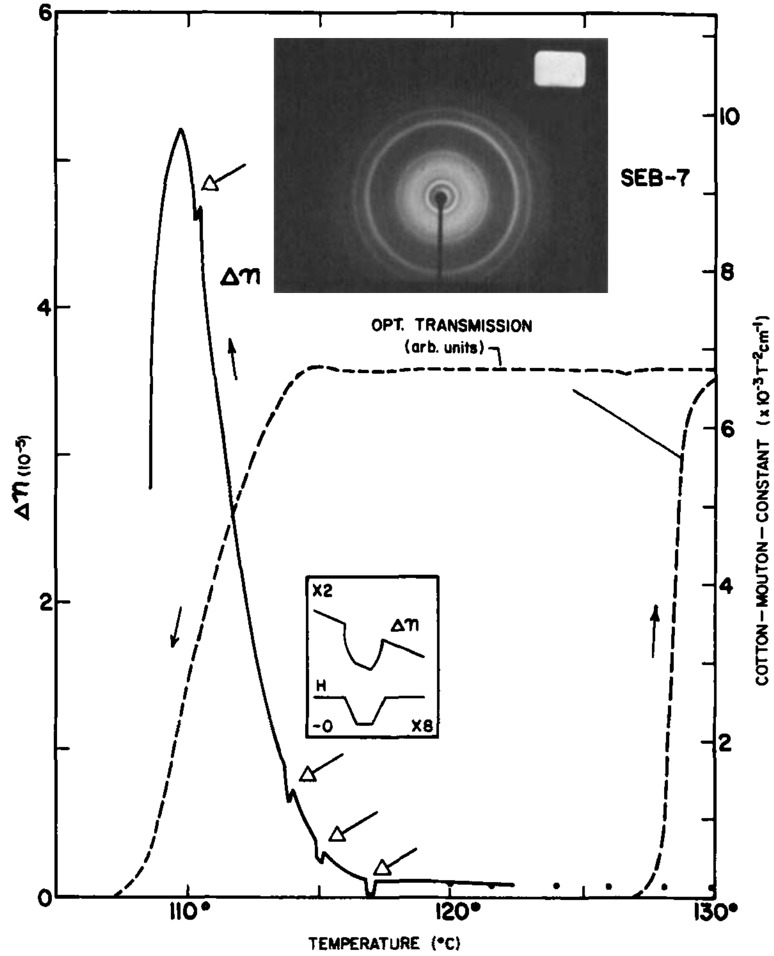


FIGURE 2 Temperature dependence of birefringence Δn (-) and optical transmission (---) in a constant magnetic field of 9.13 Tesla, and Cotton-Mouton-constant *CM* (·) for SEB-7. The temperature was changed in the direction indicated by black arrows at a rate of 0.12°/min on cooling and 0.5°/min on heating. The sample was confined in a rectangular optical quartz cell of 1 cm width and 2 mm optical path; it was tempered before the experimental run for 30 min at 135°C. During cooling the magnetic field H was transiently switched off four times (white arrows) as indicated in the insert.

In Figure 2 is also given the optical transmission of SEB-7 for a temperature cycle between the crystalline and the isotropic phase. A large and time-independent hysteresis of the clearing temperature is observed. Similar observations were made on the other polyesters tested, SUC-5, SEB-5 and MAA*-DDA-9 (10/90). This hysteresis is much larger than the hysteresis of the isotropic-nematic transition of low molecular weight compounds (which rarely exceeds a few hundredth of a degree). A significant supercooling of an isotropic melt with respect to the nematic phase has been observed (to our knowledge) only on highly viscous compounds forming branched chains.[19] We believe that the hysteresis of the polyesters can be explained in terms of conformational energy barriers which have to be surmounted when chains go from a random conformation with entanglements to a state of local parallel order.

The transitional behavior of SEB-7 differs also with respect to other features from that known for classical liquid crystals:

In the isotropic phase near the clearing temperature T_c classical nematics generally show[6,7] a pretransitional increase of both magnetic orientability and turbidity on cooling; the Cotton-Mouton-constant is proportional $(T - T_*)^{-1}$, indicating pretransitional long range orientational correlations typical for a second order transition at T_*; T_* as obtained by extrapolation is usually about 1° below the thermodynamic first order transition temperature T_c (clearing point); the isotropic to nematic transition of low molecular weight compounds is called "weakly" of first order. Even in the intimate vicinity of the clearing point the orientational relaxation is sufficiently fast to make possible standard Cotton-Mouton measurements.[6,7] Qualitatively similar pretransitional effects have been observed[10] on DDA-9L, a polyester which shows a "true" nematic phase (as was outlined above).

For SEB-7, however, in the vicinity of the transition temperature, Δn only slightly decreases (does not decay to zero) when the magnetic field is switched off; it even further increases in zero field on cooling (magnified insert of Figure 2, see also other white arrows in Figure 2). This observation combined with the onset of strong turbidity is consistent with the progressive formation of nematic or crystalline "domains" in this temperature range. These domains grow on cooling in an orientation which appears to be locked in space. In addition, one can see from Figure 2 that Δn does not increase proportionally to $(T - T_*)^{-1}$. Instead Δn passes through a maximum value ($\sim 5.10^{-5}$) which is more than 3 orders of magnitude smaller than $\sim 10^{-1}$ the value for completely oriented SEB-7, expected from anisotropies of optical bond polarizabilities[20] and from experimental birefringence values of simple nematics.[21] The small value of the maximum birefringence combined with the very strong increase in turbidity throughout the transitional range again indicates the formation of large domains (size comparable to optical wave lengths) which are on average only very slightly oriented.

The sharp decrease on cooling is probably related to the progressive appearance of crystallites: it seems possible that small nematic domains serve as nuclei for crystalization and that crystallization occurs in the growing nematic domains before a homogeneous "true" nematic phase is reached. The growing nematic domains and crystallites would produce increasing stress in the disordered regions because some chains would belong to different crystallites; this could result in the destruction of macroscopic orientation even in a magnetic field, in agreement with the observed maximum in Δn (Figure 2) and the unoriented X-ray pattern (Table II). As mentioned above for DDA-9L, crystallization interferes with magnetic orientation also in SEB-7.

In conclusion, those mesogenic polyesters that form a "true" nematic phase (MAA-8, DDA-8, MAA-DDA-8 (45/55), MAA-9, DDA-9) can be oriented in a magnetic field. The variation of the orientational order parameter on both sides of the isotropic to nematic transition is qualitatively similar[10] to that known for low molecular weight liquid crystals; quantitative differences are discussed in a separate publication.[10] For SEB-7, SEB-5 and SUC-5 the isotropic to nematic transition is confused with crystallization; on cooling from the isotropic melt an increase of the orientational correlation is observed, but crystallization sets in prior to the development of a stable homogeneous nematic phase. A similar phenomenon has been observed recently on alcanes of various molecular weights and on polyethylene.[22,16]

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