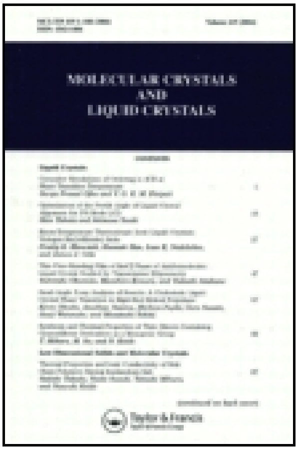

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Synthesis and Characterization of Some Terminally Cyano-Substituted Side-Chain Liquid Crystalline Polyacrylates

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To cite this article: Nelly Lacoudre , Alain Le Borgne , Nicolas Spassky , Jean-Pierre Vairon , Pierre Le Barny , Jean-Claude Dubois , Sophie Esselin , Claude Friedrich & Claudine Noël (1988): Synthesis and Characterization of Some Terminally Cyano-Substituted Side-Chain Liquid Crystalline Polyacrylates, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 155:1, 113-127

To link to this article: http://dx.doi.org/10.1080/00268948808070357

Mol. Cryst. Liq. Cryst., 1988, Vol. 155, pp. 113-127
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Printed in the United States of America

SYNTHESIS AND CHARACTERIZATION OF SOME TERMINALLY CYANO-SUBSTITUTED SIDE-CHAIN LIQUID CRYSTALLINE POLYACRYLATES

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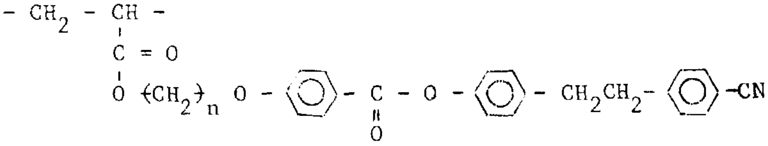
Abstract The synthesis of a series of liquid crystalline side-chain polyacrylates in which the mesogenic group is 1-(4-benzoyloxyphenyl)-2-(4'-cyanophenyl) ethane is reported. Methylenic spacer groups of different lengths have been used. Polymers were prepared by radical polymerization (AIBN as initiator) of the corresponding acrylates. The liquid crystalline nature of these polymers was established by calorimetric measurements, optical texture observations and X-ray investigations. For the polymer where $n = 6$, the unusual I-N-S_{Ad}-N_{re} sequence was observed.

INTRODUCTION

It is known that the properties (nature of mesophases) of side-chain liquid crystalline polymers depend upon the nature of the polymer backbone, the nature of mesogenic group and the nature and the length of the spacer unit[1].

Thus it is, in principle, possible to adjust the properties of a liquid crystalline polymer to that required for a given application by structural modifications of polymer components.

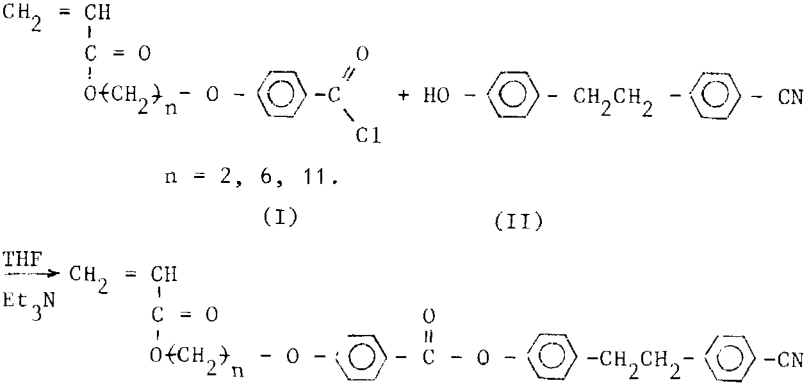
We report, in the present paper, the synthesis of a new series of polyacrylates of general structure :



These polyacrylates are prepared by radical polymerization of the corresponding monomers. The mesogenic group is linked to the polyacrylate backbone through methylenic units of different lengths (n = 2, 6, 11). The polymer without a spacer group has been also prepared.

SYNTHESIS OF MONOMERS

The acrylates are synthesized by coupling the two following building units[2].



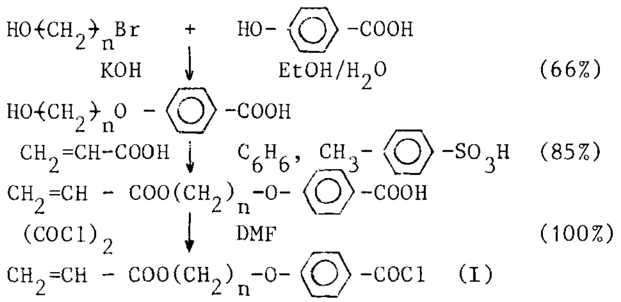
n = 2, 6, 11.

(I) (II)

The yields of reaction for different monomers are respectively : n = 2 and n = 6 yield = 55 %, n = 11 yield = 47 %.

The preparations of precursor compounds (I) and (II) are reported below.

Preparation of (I) (n = 2, 6, 11) Yield

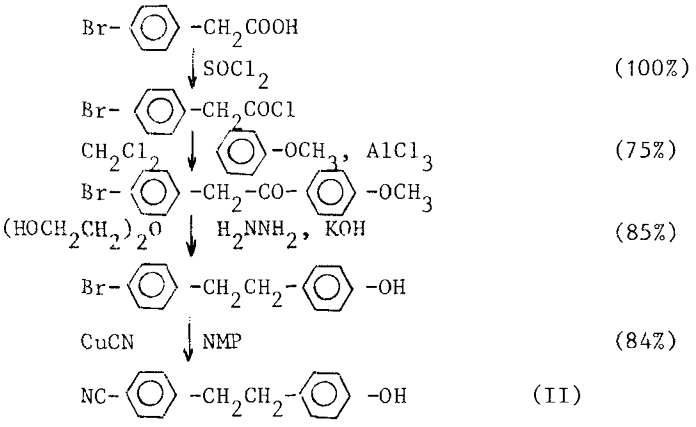


4-(ω - propenoyloxyalkoxy) benzoic acids were synthesized according to[3]. The given yields correspond to the synthesis of the derivative with n = 6.

For the preparation of the acyl halide,oxalyl chloride is used instead of thionyl chloride in order to preserve the acrylate function.

p-Acryloyloxybenzoic acid (no methylenic spacer group) is prepared by reacting acryloyl chloride with p-hydroxybenzoic acid in dry DMF and in the presence of Et_3N ; (yield 43 %).

Preparation of (II) Yield



NMP : N -methylpyrrolidone

It must be noticed that the reduction of the carbonyl function according to the HUANG-MINLON method (step 3) is accompanied by cleavage of the methoxy group.

The prepared monomers are purified by column chromatography (silica gel, CH_2Cl_2/cyclohexane/ethyl acetate).

Their structures are substantiated by IR spectroscopy and ^1H NMR. As an example, the ^1H NMR spectrum (250MHz) of the monomer with a $(CH_2)_6$ spacer group is shown in Figure 1.

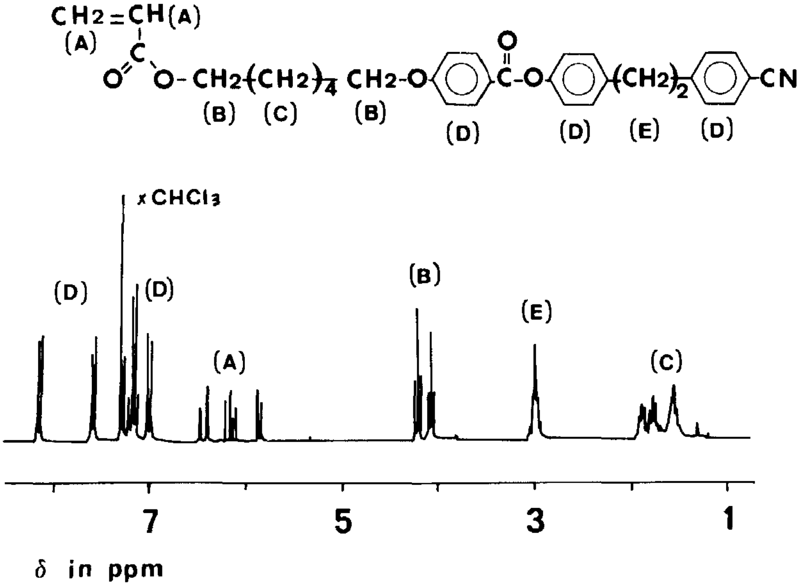
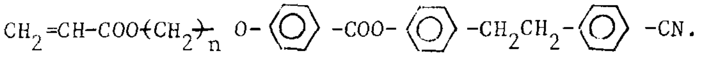


FIGURE 1. 250 MHz ^1H NMR spectrum.

Satisfactory elemental analyses have been obtained for all prepared monomers (Table 1).

TABLE I Elemental analyses for monomers



Monomer n	C %	H %	N %
no spacer	74.90 (75.56)	4.99 (4.78)	3.51 (3.52)
2	73.04 (73.47)	5.22 (5.22)	3.19 (3.17)
6	74.93 (74.85)	6.33 (6.24)	2.81 (2.81)
11	76.42 (76.19)	7.30 (7.23)	2.49 (2.47)

( ) calculated values.

POLYMERIZATION

Polymers were obtained by radical polymerization of the above monomers using azobisisobutyronitrile (AIBN) as initiator in chlorobenzene or DMF solution at 70°C during 4 days. Polymerization data are given in Table II.

TABLE II Polymerization of various acrylate monomers. $\left(\frac{(\mathrm{AIBN})}{(\mathrm{Monomer})} = 0.5\ \%\ \text{molar ratio}\right)$.

Monomer n	Conversion (%)	$\overline{M}_n$ (GPC)*	$\overline{M}_w$ / $\overline{M}_n$
no spacer	80	5900	1.55
2	77	5700	1.4
6	45	5100	1.4
11	43	7200	1.4

* Polystyrene standards.

All polymers were purified by two precipitations using methanol and dried in vacuo at 60°C.

RESULTS AND DISCUSSION

The transition temperatures for the monomers are listed in Table III :

TABLE III Thermal properties of monomers

n	Transition Temperatures (°C)						
	K		S_A		N		I
-	.	168*					
2	.	114	-		.	134	.
6	.	114	-		.	142	.
11	.	111	.	115	.	126	.

* Optical microscopy of this monomer does not reveal any specific texture at the melting point. Thermal polymerization occurs above 180°C, which makes it impossible to identify the mesophase.

Initial classification of the phase type was based on microscopic observations of the textures exhibited by these materials. Typically, for the n = 2 and n = 6 homologues the nematic phase separates from the isotropic liquid on cooling in droplets (Fig. 2) ; these coalesce and form a typical threaded texture (Fig. 3). The monomer where n = 11 exhibits both nematic and smectic A phases. Figures 4 and 5 show the schlieren texture of the nematic phase and the focal conic fan texture of the smectic A phase, respectively.

Confirmation of the classification of the N and S_A phases was obtained by X-ray diffraction (Fig. 6). The layer thickness of the S_A structure is 48.2 Å which is considerably in excess of the extended model length. Thus, the mole-

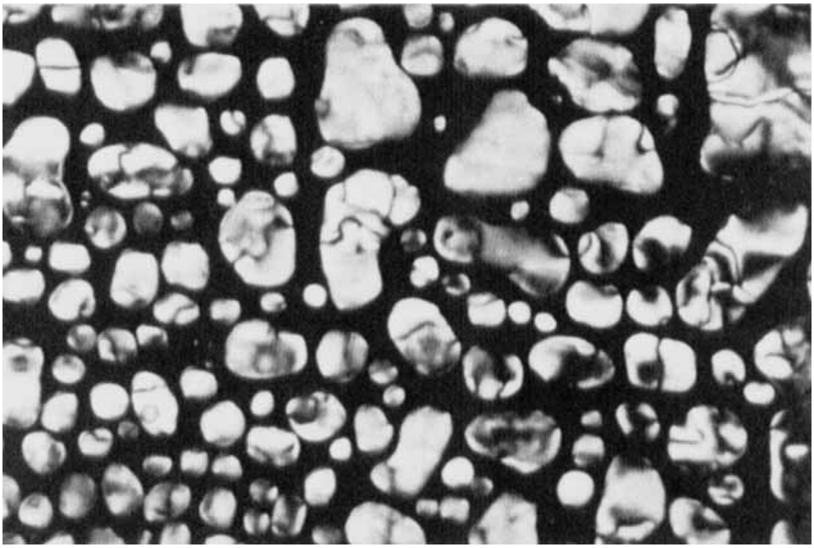


Fig.2 : Nematic droplets at the clearing point.
Monomer where n = 6

See Color Plate II.

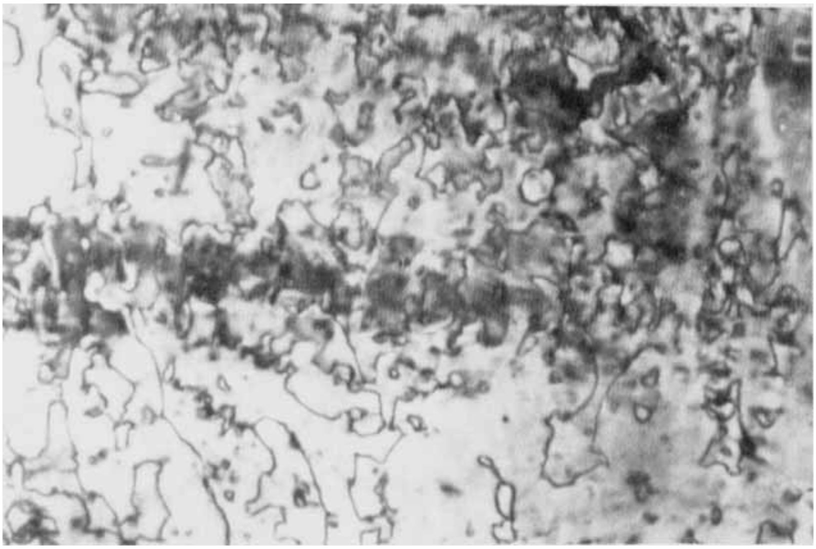


Fig.3 : Nematic threaded texture. Monomer where n = 6

See Color Plate III.

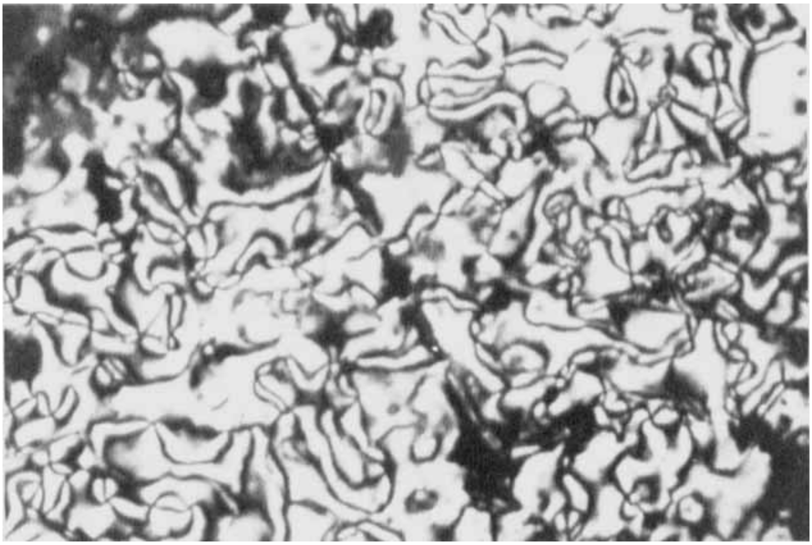


Fig.4 : Nematic schlieren texture. Monomer where n = 11
See Color Plate IV.

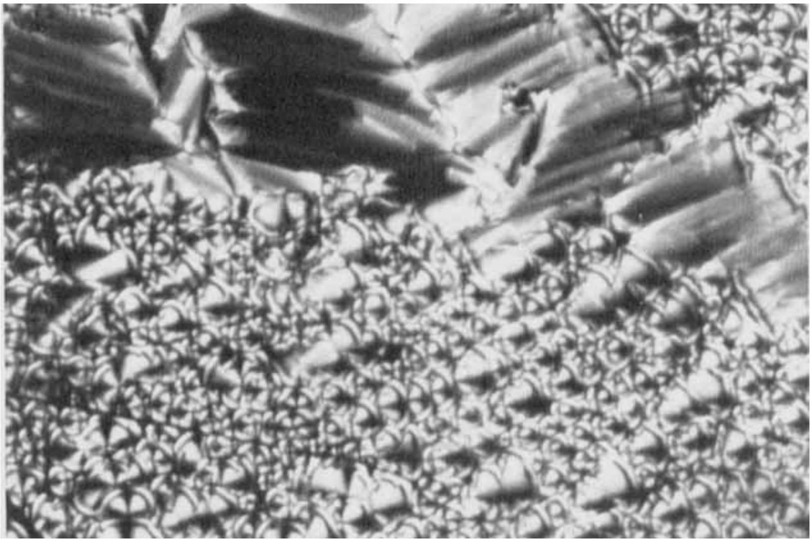


Fig.5 : S_A texture . Monomer where n = 11
See Color Plate V.

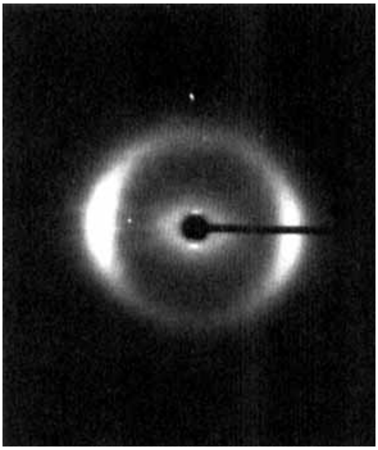


Fig.6 : X-ray diffraction photograph from the monomer where n = 11. Oriented fiber (the X-ray beam is perpendicular to the fiber axis)

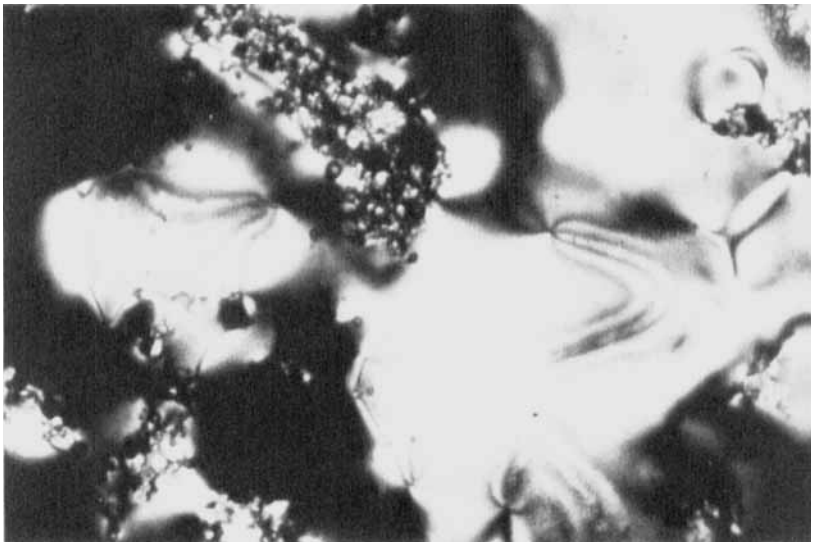


Fig.7 : Photomicrograph of high temperature nematic phase from polymer where n = 6

See Color Plate VI.

cules are arranged in an antiparallel overlapping interdigitated structure and the S_A structure is of S_{Ad} type.

The liquid crystal behavior of the polymers listed in Table IV shows a strong dependence on the length of the spacer, n. The polymer in which the mesogenic group is directly linked to the ester group shows a strong stiropalescence between T_m (217°C) and T_I (322°C). However, optical observations do not reveal any particular morphological features useful in defining the type of mesophase. In contrast, the

TABLE IV Thermal properties of polymers

n	Transition Temperatures (°C)
-	$G\ 38\ ,\ K \xleftrightarrow{217} LC \xleftrightarrow{322} I$
2	$G \xleftrightarrow{68} N \xleftrightarrow{208} I$
6	$G \xleftrightarrow{37} N_{re} \xleftrightarrow{100} S_{Ad} \xleftrightarrow{170} N \xleftrightarrow{190} I$
11	$K \xleftrightarrow{66} S_1 \xleftrightarrow{75} S_2 \xleftrightarrow{125} S_3 \xleftrightarrow{192} S_4 \xleftrightarrow{204} I$

polymer where n = 2 forms a nematic phase. Upon cooling the isotropic melt, the nematic phase begins to separate at the clearing point in the form of typical droplets which, after further cooling, join together to form a threaded texture.

The polymer with medium value of n (n = 6) exhibits the unusual N S_A N_{re} sequence. On cooling from the isotropic state, the high temperature nematic phase appears at 190°C as a schlieren texture (Fig. 7). Thin layers of this mesophase exhibit other nematic characteristics such as scintillation effects and a marked tendency to be homeotropic. Further reduction in temperature to about 170°C, produces a focal-conic fan texture (Fig. 8) which is consistent with a

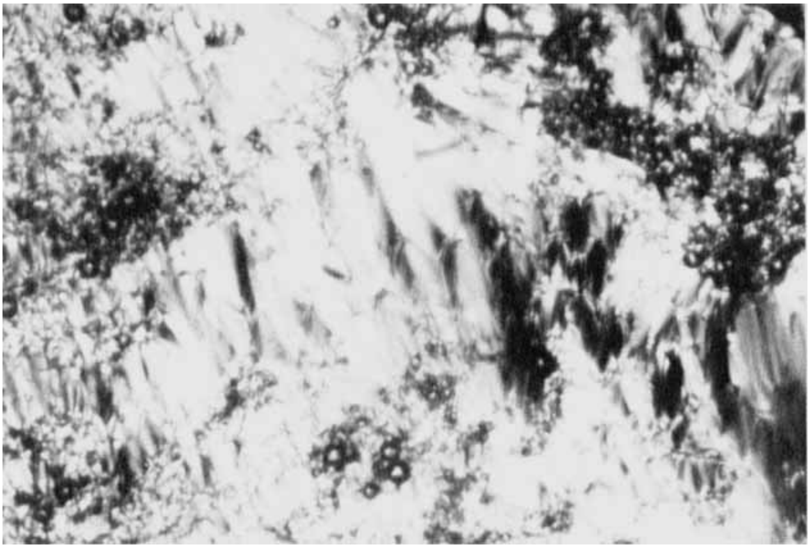


Fig.8 : Photomicrograph of smectic A phase from polymer where n = 6
See Color Plate VII.

Fig.9 : Photomicrograph of re-entrant nematic phase from polymer where n = 6
See Color Plate VIII.

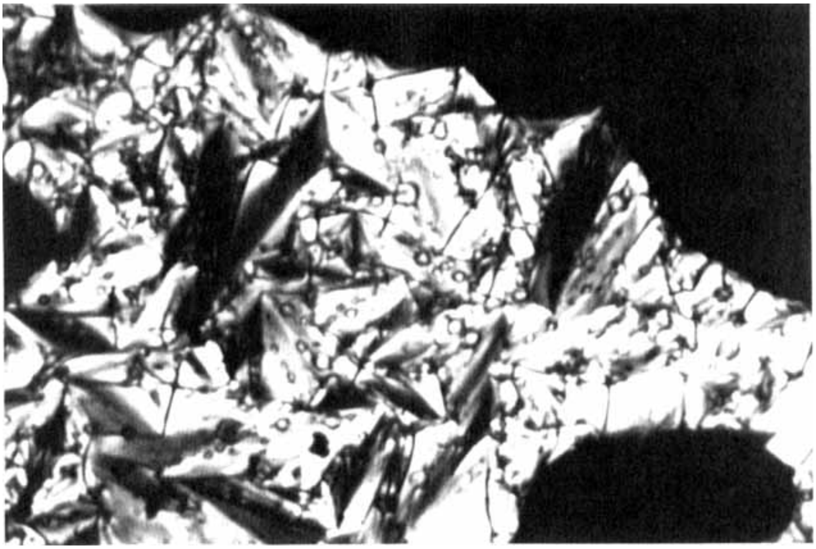


Fig.10 : The focal-conic fan texture of the S_4 phase of polymer where n = 11. T = 203°C

See Color Plate IX

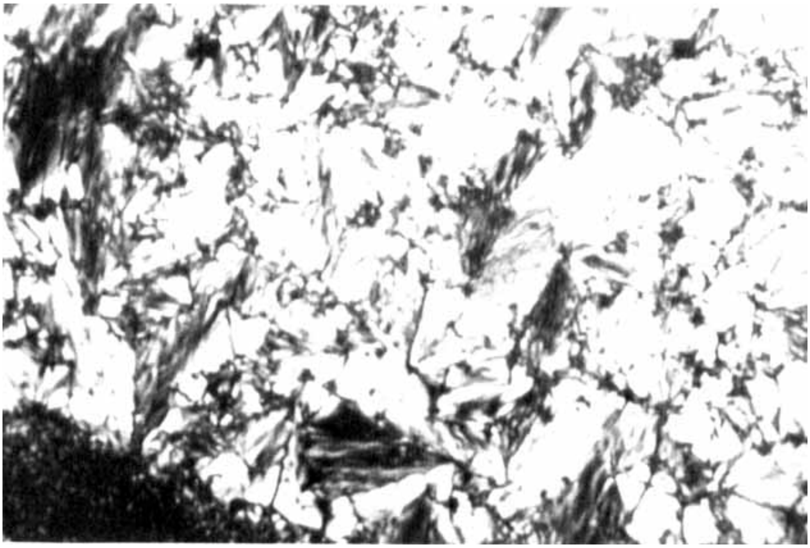


Fig.11 : The focal-conic fan texture of the S_3 phase of polymer where n = 11. T = 180°C

See Color Plate X.

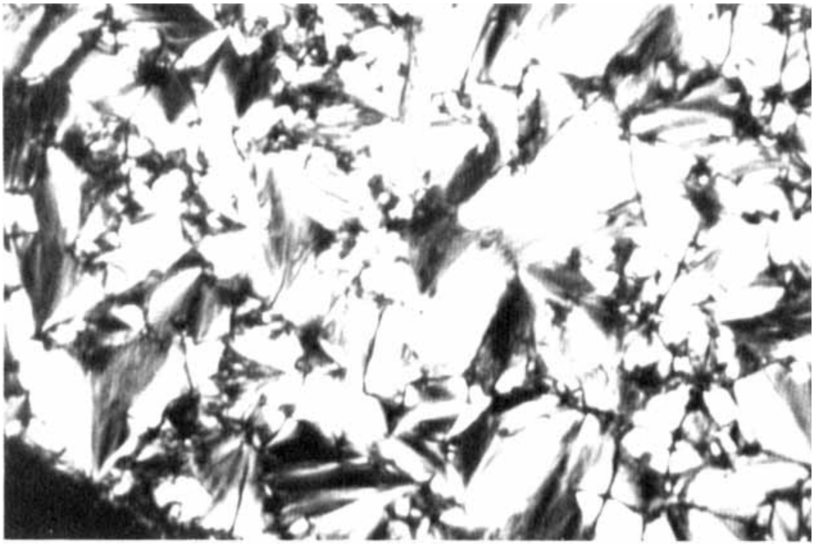


Fig.12 : The focal-conic fan texture of the S_2 phase of polymer where n = 11. T = 92°C
See Color Plate XI.

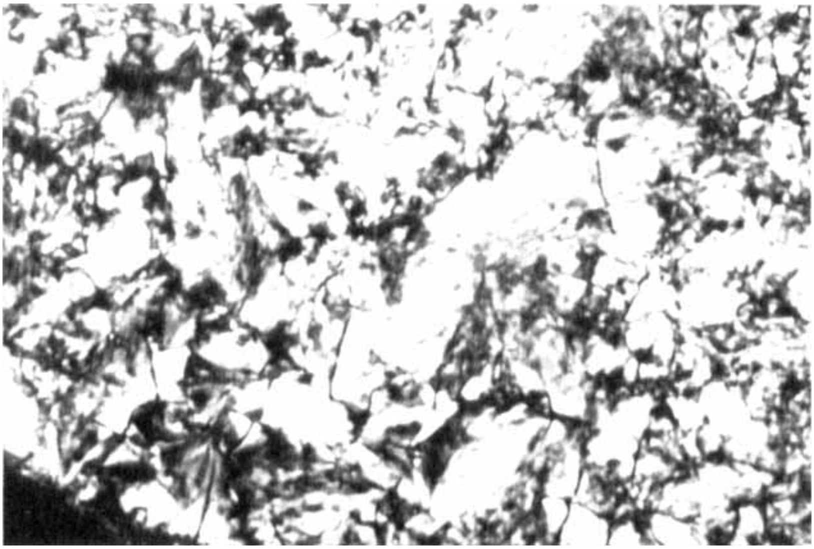


Fig.13 : The texture of the S_1 phase of polymer where n = 11. T = 72°C
See Color Plate XII.

S_A phase. Below 100°C, either a schlieren texture is progressively restored or a paramorphic fan shaped texture is formed (Fig. 9). Recently, the same N S_A N_{re} sequence has been observed for two other polymers containing spacers of six methylene units[4] and a di(ethylene oxide) spacer[5], respectively. Interestingly, all the polymers presently known to exhibit such an unusual sequence have spacers of comparable lengths.

The polymer with the longest spacer (n = 11) forms only smectic phases, the textures of which are reminiscent of those of low molar mass smectics A and C (Figs. 10-13). The X-ray diffraction patterns obtained for powder samples are also consistent with fluid lamellar structures ("fluid" meaning without three-dimensional long range periodicities but with a liquid short range order). It should be noted that several distinct S_A and S_C phases have been recently identified for low molar mass liquid crystals with a terminal polar group[6]. A more detailed X-ray diffraction study using oriented samples is in progress to establish more precisely the structure of the S_1, S_2, S_3 and S_4 phases and to determine their positions with respect to the (S_{A1},S_{A2},S_{Ad}, $S_{\tilde{A}}$,S_C,S_{C2},$S_{\tilde{C}}$) phases of low molar mass cyano compounds[6].

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