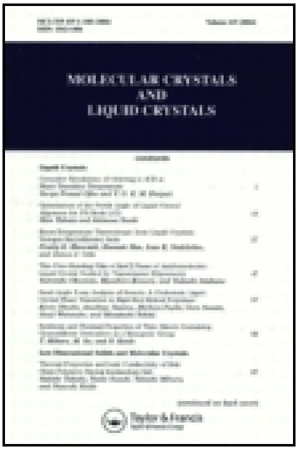

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Molecular Mass and Structure Dependence of Liquid Crystalline Properties for a Homologous Series of Polyesters

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MOLECULAR MASS AND STRUCTURE DEPENDENCE OF LIQUID CRYSTALLINE PROPERTIES FOR A HOMOLOGOUS SERIES OF POLYESTERS

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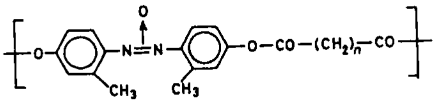
Abstract Mesomorphic properties of higher homologues of flexible main chain thermotropic polyesters based on regularly alternating p-dioxy,2,2'dimethylazoxybenzene mesogen and (α,ω)-alkanedicarboxylic acid were investigated. Attention was given to changes from cybotactic nematic to smectic C ($N_c \longrightarrow S_c$) mesophases. On the basis of SAX data, rheology and miscibility diagrams with low M compounds displaying both a S_c and N_c mesophase it was shown that the polyester with n=18 and M > 3,000 displays a S_c monotropic mesophase. The data suggest that while polyesters of odd spacer parity in the nematic quiescent state do not display any tendency toward formation of layered order, polyesters with n even exhibit a pronounced tendency toward the formation of layered order. This tendency increasing with n and M is favored by a decrease of temperature. It may be argued that the observed passage $N_c \rightarrow S_c$ is continuous. The formation of layered (N_c) order was also observed for large n and M for a spacer of odd parity but only as a result of fiber drawing.

INTRODUCTION

In a previous work performed with flexible thermotropic main chain liquid crystal polymers based on regularly alternating p-dioxy-2,2'dimethylazoxybenzene mesogen and (α,ω)-alkanedicarboxylic acids:



Polyester I

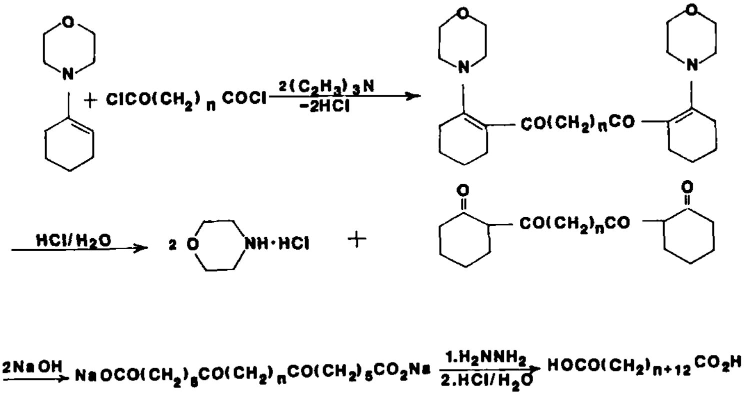
we have explored the properties of this homologous series for $3<n<14$. It was shown that in addition to the oscillation of the clearing temperature $T_{L.C./I}$, $\Delta H_{I/L.C.}$, $\Delta S_{I/L.C.}$ and of the order parameter, S[1-2], a substantial difference in the organization of the nematic phase takes place for n even and n odd. The even homologues when oriented in a magnetic field and subsequently quenched below the glass transition temperature T_g, display an x-ray pattern characteristic of cybotactic nematic mesophases[3], while the homologues of odd parity are characterized by the absence of such pattern[4-5]. It was also shown that unoriented polyesters I of even parity, when quenched from the nematic phase below T_g display a rather broad peak or halo at low angles. This difference in mesophasic behavior is rooted in the difference of the strength of orientation dependent attractive forces acting on the mesogen in homologues of even and odd parity. These can be expressed by the Flory-Ronca characteristic temperature T*. From high pressure studies performed on homologues of polyester I, T* was found to be ~320°K[13] for odd parity homologues. This is in good agreement with the values of T* found for ordinary low molecular mass nematics such as PAA (280°K). No reliable value of T* was obtained for homologues of even parity.

We have also noted some time ago,[5,14] for the n=10 homologue, a progressive development of a broad SAX diffraction peak with molecular mass M in samples quenched below T_g from the unoriented nematic mesophase. This result suggested the possibility of a continuous shift from a nematic to a smectic mesophase in flexible main chain polyesters of the type described here. There are only a few passing references in the literature concerning this question. Besides our own references to this problem[6], Krigbaum, et.al. made an allusion to the influence of molecular mass on mesophase stability for a polyester based on 4,4'-dioxybiphenyl mesogen and nonanedioic acid[7], Thomas and Wood[8] emphasized a continuous spectrum composed of axially disordered nematics and axially ordered smectics.

In this work attention has been centered around the influence of molecular mass M and of the spacer length n on the possible mesophasic change $N_c \rightarrow S_c$. It appeared to us from previous observation that longer spacers favor formation of layered order. The study was consequently extended to n=20 spacer lengths, beyond which no mesophasic behavior was observed.

EXPERIMENTAL

The (α, ω)-alkanedicarboxylic acids were synthesized in accordance with the procedure reported by Hunig et. al[9] for docosanedioic acid (n=20). The synthetic scheme is depicted below and the details are given in [10].



The following modifications were introduced in the separation -purification procedure to maximize the yields of the diacids: in the case n=16 diacid, the crude moist product was dissolved in 95% warm ethanol, stirred with activated charcoal for 3-4 hours and filtered. The filtrate was concentrated and added to boiling water cautiously. This mixture was cooled to 10°C overnight. The precipitated diacid was recrystallized from ethanol-water mixture. In the case of n=18 diacid, the crude product was dissolved in absolute ethanol, stirred with activated charcoal and filtered in the hot condition. The precipitated diacid can be recrystallized from hot ethanol on cooling. For n=20 diacid the purification procedure was outlined in ref 9.

The polyesters were prepared by a Schotten-Baumann reaction, using an interfacial technique reported already[1]. The polymers thus produced had M in the range 12,000-20,000. The polyesters were fractionated at 27°C using non-solvent addition method, with CH_2Cl_2 as the solvent and methanol as the precipitant. Mechanical mixtures of the polymer and LMLC's were obtained by a combination of solution and melt mixing. Known amounts of both components were dissolved in $CHCl_3$ (1%). The solvent was evaporated off overnight and the residue heated in vacuum to slightly above the clearing temperature for about 6 hours to obtain homogeneous mixture. The molecular masses were estimated from the equation, $[\eta] = 4.65x10^{-4} M_n^{0.76}$ where $[\eta]$ is the limiting viscosity number. The dilute solution viscosity measurements were made at 30±0.1°C using a Cannon-Ubbelhode viscometer (no. 76L-315) with sym-tetrachlorothane as the solvent. Transition temperatures and enthalpies were determined from DSC measurements with a scanning rate of 20°/min., with peak temperature being taken as the transition temperature. The x-ray scattering scans were recorded using a Rigaku Diffractometer with operating parameters of 45 kV and 20 mA. Scanning rates of 1,2 and 4 deg./min were used. The supercooled (quenched) samples used in this study were obtained as follows: the polymer, packed densely into a 2 mm. Lindemann x-ray capillary, was heated to the desired temperature by enclosing it with a test tube, surrounded by heating tape, controlled by a rheostat. The temperature was monitored by means of a thermocouple. This assembly at a constant temperature was immersed in liquid nitrogen to get a supercooled specimen of the polyester. Rheological measurements were performed on a Rheometrics viscoelastic tester under oscillatory shearing mode with a parallel plate geometry. Further detail can be found in[11].

RESULTS AND DISCUSSION

Fig. 1 gives DSC traces on heating and cooling for a fractionated and unfractionated polyester with n=18. While the fractionated specimen gives on cooling two distinct peaks separable by peak deconvolution, the unfractionated sample gives a single broad peak. A single broad peak is also observed on heating. The transition takes place over 10-15° in unfractionated samples due to a large biphase. It may possibly encompass the C/L.C. and L.C./I transitions. In fractionated samples, on the other hand, a distinct I/L.C. transition can be observed.

Table I gives the values of enthalpy and entropy of transition for unfractionated samples of polyester I with n=10, 16 and 18. One can see that $\Delta H_{I/L.C.}$ for n=18 is substantially higher than the corresponding values for the other two homologues. This value falls out of the

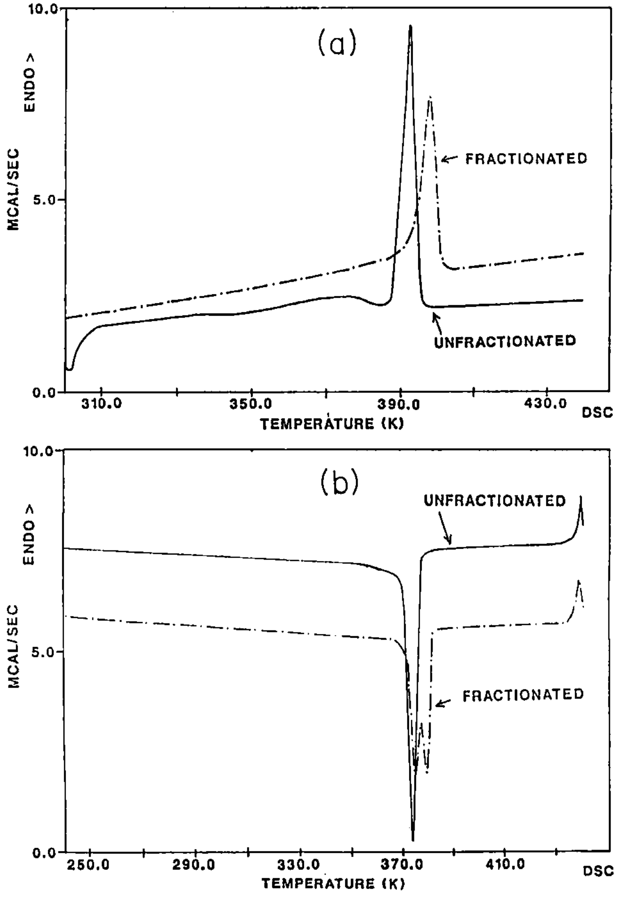


FIGURE 1. Comparison of DSC thermograms of fractionated and unfractionated samples of polyester with n=18. Fractionated sample [η]=1.15 dl/g; unfractionated sample [η]=0.85 dl/g: (a) on heating (b) on cooling.

TABLE I Transition enthalpies and entropied for higher homologues of unfractionated polyester I.

n	Enthalpy (kJ/mru)				Entropy (J/mru.°K)			
	$\Delta H_{C/L.C.}$	$\Delta H_{L.C./I}$	$\Delta H_{I/L.C.}$	$\Delta H_{L.C./I}$	$\Delta S_{C/L.C.}$	$\Delta S_{L.C./I}$	$\Delta S_{I/L.C.}$	$\Delta S_{L.C./I}$
10	8.8	6.3	7.0	8.9	22.4	14.4	16.2	24.6
16	10.9	7.3	8.4	9.4	28.5	17.2	20.2	26.8
18*	(25.1)		10.4	11.6	(65.6)		27.8	32.1

* monotropic mesophase; values on cooling obtained by peak deconvolution.

linear trend for the ΔH_{IN} and ΔS_{IN} which can be well described by equations

$\Delta H_{IN}=4.7+0.16n$ (kJ/mru); and $\Delta S_{IN}=7.55+0.87n$ (J/mru.°K) for the even numbers of the homologous series[6]. This can also be seen in Fig. 2 giving $\Delta S_{I/L.C.}$ as a function of n for the homologous series of the polyester I. For n = 20 and n = 17 no mesomorphism was observed.

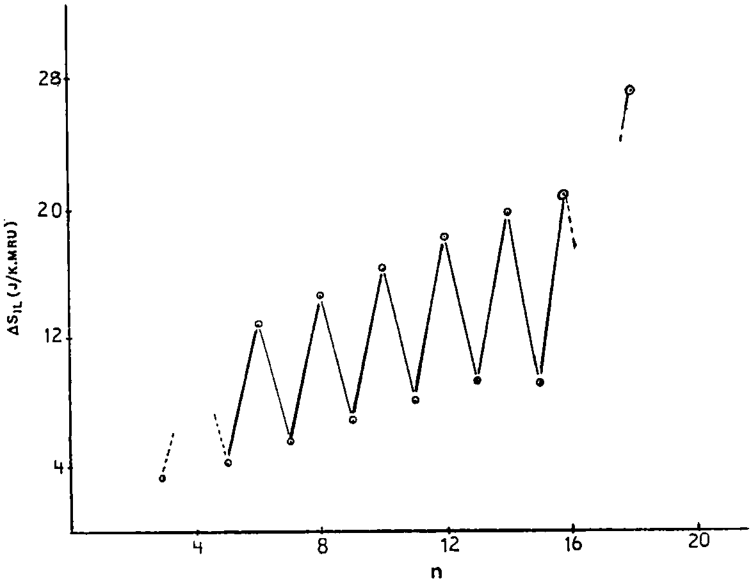


FIGURE 2. Entropy of I/L.C. transition as a function of the spacer length, n.

TABLE II Effect of molecular mass on thermodynamic properties of polyester I with n = 16 and n = 18.

Sample	Fraction	[η] dl/g	Transitions (°C) Heating	Transitions (°C) Cooling	$\Delta H_{I/L.C.}$ (kJ/mru)	$\Delta S_{I/L.C.}$ (J/mru°K)
n=18 *	1	1.15	C125I	I106L.C.101C	11.6	30.6
	2	0.73	$C_1$92$C_2$113I	I105L.C.85C	10.4	27.3
	3	0.5	C113.3I	I102.2L.C.83C	10.1	26.6
	4	0.26	$C_1$100.2$C_2$109	I100L.C.85C	8.2	22.0
n=16	1	0.76	C116N156I	I143.8N82C	8.9	20.7
	2	0.47	C116.5N154I	I144.6N65.5C	8.0	18.7
	3	0.26	C113N145I	I135.5N70C	8.0	19.1

* The values of $\Delta H_{I/L.C.}$ for n=18 were determined by peak deconvolution.

Table II gives the thermodynamic data on phase transition for different molecular masses of fractionated samples of homologues n=16 and n=18. It is apparent that here again the polyester with n=18 differs from other homologues in giving a monotropic mesophase characterized by $\Delta H_{I/L.C.}$ significantly higher than expected from the linear trend reflected by the equation above. The values of $\Delta H_{I/L.C.}$ increase substantially with M and reflect enhanced ordering in the mesophase for high molecular mass fractions of n=18 polyester.

The thermodynamic data prompted us to examine the x-ray behavior of the higher homologues of polyester I. In Fig. 3 a comparison has been made of the scattering scans of samples of polyester I with n=7, 10, 16 and 18 of approximately similar M, supercooled from the mesophase to below T_g. It is apparent from Fig. 4 that the low angle halo transforms, for n=18, to a peak characteristic of a lamellar mesophase. This peak corresponds to d=21.9Å, 13.3Å short of the fully extended length of the repeat unit (Table III). Assuming strata composed of extended repeating units one calculates an angle of tilt α =39.5°, where α is the angle between the normal to the plane of the stratum and the direction of the chain. This tilt is close to the values found for other homologues of even parity from SAX photographs obtained from samples oriented in a strong magnetic field of 10-15 Tesla[5]. Fibers drawn from a nematic melt and rapidly quenched to T below T_g (in taking care to avoid crystallization) may also display a similar pattern. Such photographs are characterized by a "four-spot" centro-symmetrical SAX pattern[3,5] from which d and α can independently be obtained.

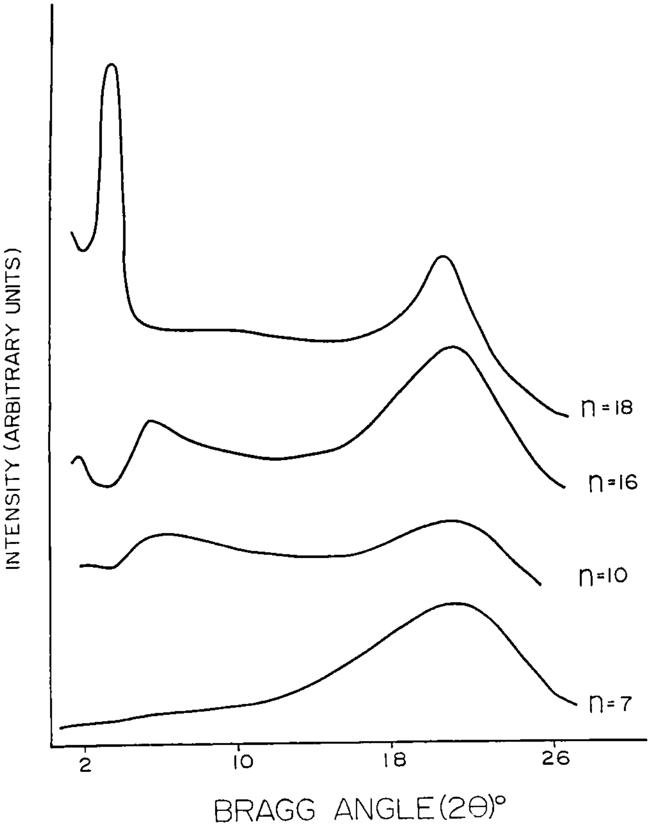


FIGURE 3. X-ray scattering scans of supercooled specimens of polyesters n=7, [η]=1.3 dl/g; n=10, [η]=0.74 dl/g; n=16, [η]=0.76 dl/g; n=18, [η]=0.73 dl/g quenched at T_{red}=0.95.

A good agreement was found between the observed values and values calculated from the model assuming extended repeat units (see Table III and Fig. 8). Attempts to quench oriented specimens of the polyester with n=18 were unsuccessful due to the narrow smectic interval and rapid crystallization. The sharp peak at 21.9Å for the unoriented specimen observed on cooling from the isotropic phase (prior to the onset of crystallization and also present after crystallization) indicates a smectic C structure for the mesophase with a tilt angle α of approximately 39°. These results suggest a tendency of polyester I for extended chain crystallization when cooled from the isotropic melt.

TABLE III X-ray data for higher homologues of polyester I.

n	$[\eta]$ dl/g	d Å	α deg	α deg[b]	Type	l^a_{ru} Å
8	0.18	14.2	40.1	40.0	N_c	22.7
10	0.33	17.4	43.2	44.0	N_c	25.7
12	0.24	19.4	43.2	44.4	N_c	27.7
16	0.35	22.9	44.5	45.0	N_c	32.7
18	0.39	21.9	38.5	d	S_c	35.2

a: length of fully extended repeat unit.

b: measured from the diffraction pattern obtained for sample oriented in the mesophase in a magnetic field of 15T and subsequently kept quenched below T_g.

d: no x-ray pattern of oriented sample due to crystallization during exposure; reported values were obtained from diffraction patterns for an unoriented sample exposed at 112°C.

To verify that the quenching of n=18 does not change the nature of the mesophase, x-ray scattering scans were performed at the temperature of the corresponding mesophase on unoriented samples of n=16 and n=18 of similar M. The temperature of the nematic mesophase was reached on cooling from a temperature approximately 10-15°C above the clearing point.

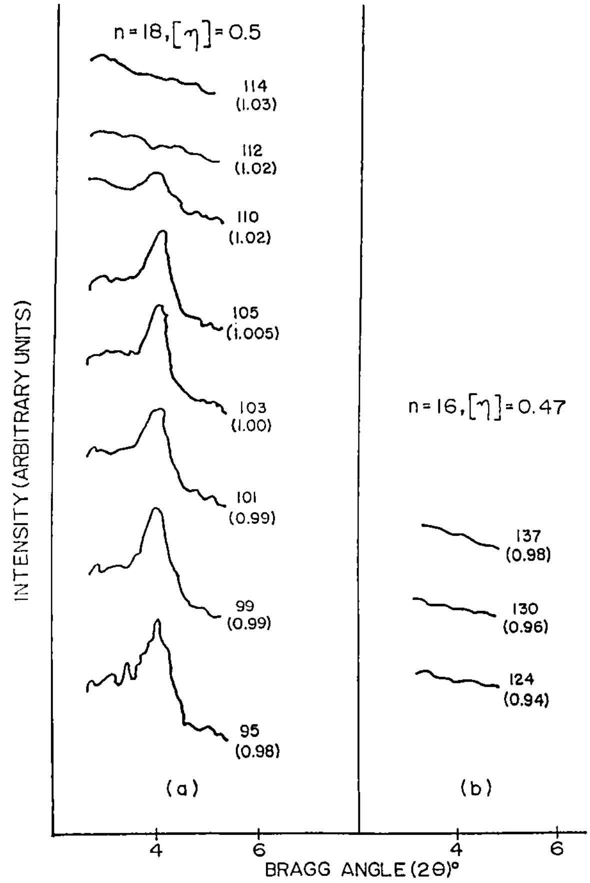


FIGURE 4. X-ray scattering scans at different temperatures for the polyesters with n=16 and n=18 (values in parentheses are in reduced temperatures).

Fig. 4 gives traces of x-ray scattering scans for unoriented n=16 and n=18 polyesters in the region of the expected SAX peak. It can be seen that a pattern characteristic of a smectic phase with a peak corresponding to d=21.9-22Å appears in the temperature range 95-110°C (crystallization sets in at 90°C). There is no corresponding peak for n=16 homologue. X-ray scattering data indicate that a smectic C mesophase replaces the cybotactic nematic phase for sufficiently long methylene sequences in homologues of even parity of n.

The smectic nature of the n=18 polyester is also confirmed by rheological studies of complex melt viscosity $|\eta^*|$. Such studies have been performed previously on polyesters n=7 and n=10 showing the drop of melt viscosity on cooling across the isotropic/nematic phase boundary typical for nematic compounds[11]. In Fig. 5 $|\eta^*|$ is plotted as a function of reduced temperature $T_{red}=T/T_c$ for the polyesters n=7, 10, 16 and 18. While all polyesters with the exception of n=18 display a drop of $|\eta^*|$ on passing from the isotropic to liquid-crystalline phase, the polymer with n=18 displays a reverse trend, characteristic of fully developed smectic mesophases.

The transition from N mesophases to a smectic S_c mesophase on increasing the spacer length from n=16 to n=18 is however blurred by two factors. One is the continuous increase in the development of a stratified order in glasses obtained from quenching below T_g of unoriented nematic melts on increase in n. The evolution of SAX halos for such systems with n for n=7, 10, 16 of comparable M is given in Fig. 3. The other factor is the increase of such order for a given n with molecular mass M[5].

In order to explore the influence of M on the mesophasic behavior of polyester n=18 we have examined the

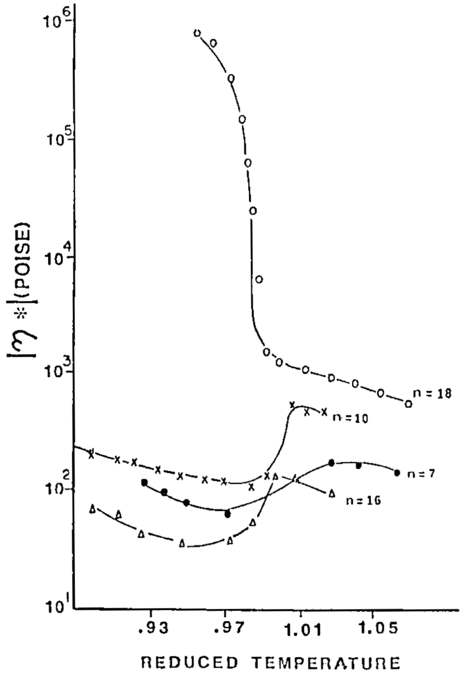


FIGURE 5. Complex viscosity as a function of reduced temperature: for the polyesters with n=7 ([η] = 0.38 dl/g); n=10; ([η] = 0.41 dl/g; n=16, ([η] = 0.25 dl/g and n=18, ([η] = .39 dl/g).

rheology of various fractions of this polyester. The variation of $|\eta^*|(T_{red})$ for three different M for polyester n=18 is given in Fig. 6. While the highest M displays an almost vertical raise of $|\eta^*|$ at the transition this surge of $|\eta^*|$ is more attenuated for the lower M and reversed for the lowest molecular mass. This last behavior is more typical of a nematic than of a smectic melt (see Fig. 5). A question may be asked: is this reversal of mesophasic behavior a continuous function of M? To answer this question phase diagrams were made of two

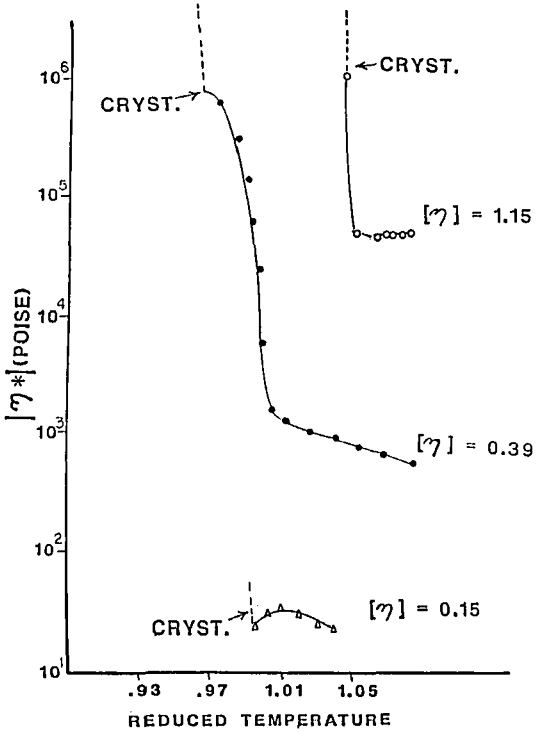


FIGURE 6. Complex viscosity as a function of reduced temperature for the polyester with n=18 at different molecular weights.

fractions of different M of polyesters n=18 with a LMMLC displaying both a cybotactic nematic and smectic mesophase. Fig. 7a and b show the phase diagrams obtained for the mixture of p-heptyloxyazoxybenzene (PHAB) and polyester n=18 for two molecular masses M = 4,000 ([η] = 0.26 dl/g) and M=30,000 ([η] = 1.15 dl/g). It is apparent from Fig. 7 that the realm of smectic and nematic

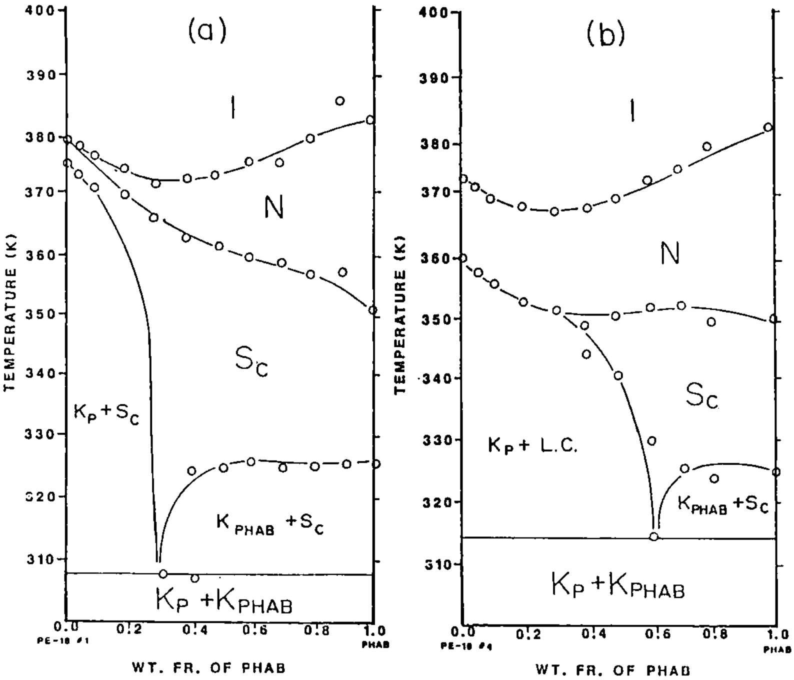


FIGURE 7. Phase diagrams of binary mixtures of the polyester with n=18 and PHAB: (a) for a fraction with [η] = 1.15 dl/g; (b) for a fraction with [η]= 0.26 dl/g.

mesophases is molecular mass dependent: while the large M sample displays a smectic behavior in mixtures with PHAB throughout the whole range of compositions, the smectic mesophase shrinks considerably at lower M. A nematic mesophase is prevalent throughout the whole range of compositions for such low M. Thus, within the range of molecular masses studied, our data strongly suggest that the stability and realm of smectic phase decreases for low M in a continuous fashion acquiring characteristics of a nematic phase for M<3,000. The formation of a smectic C mesophase from a cybotactic nematic mesophase may thus be a continuous function of M. The similarity between both phases is far-reaching.

On comparison of Figs. 3 and 4 it becomes apparent that the SAX halo characteristic of nematic mesophases of the polyesters of even parity develops on quenching the nematic phase of the n=16 polyester as well. Quenching of the nematic mesophase from decreasing temperatures has produced in all cases an enhancement of the intensity of the SAX halo. This suggests an increase in the tendency toward a layered axial order with the decrease of temperature within nematic (cybotactic) mesophases displayed by polyester I. This is in agreement with previous studies showing an increase of the order parameter with decreasing T for both the mesogen and the spacer for polyester I[15-16]. Thus at least 3 factors contribute to the tendency in polyesters I to promote the formation of layered order: the length of the spacer n, the molecular mass M and the quenching temperature. Another factor could well be related to the extended conformation of the repeating unit in the nematic state. In Fig. 8 is plotted the length of the repeating unit obtained from the corresponding samples of polyester I oriented in a strong magnetic field (10-15T) and quenched below T_g (avoid crystallization). The data can be placed on a straight line representing the completely extended repeating unit[5]. We are therefore inclined to think that the extension of the chain is an additional factor favoring packing of chains into cybotactic layered arrays. As mentioned previously[5] such arrays are more easily formed with spacers of even parity in which the long axes of the mesogens tend to assume parallel conformations as the chain extends, in contrast to homologues of odd parity in which long axes of mesogens intersect at an acute angle for a trans extended methylene sequence[5].

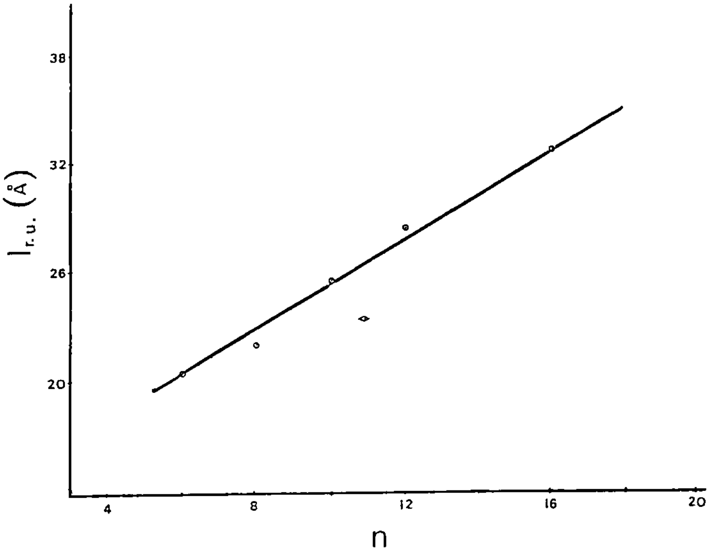


FIGURE 8. Length of the repeating unit l_{ru} as a function of n obtained from SAX data. The continuous line corresponds to the length of a fully extended repeating unit.

An interesting observation[14] was made on drawing fibers from the nematic melt of high molecular mass polyesters and quenching below T_g. While polyesters of even parity displayed in their glassy state the characteristic four-point SAX pattern, the fibers from polyesters of odd parity for $n < 9$ did not display such patterns. For n=11 however a quenched four-point centrosymmetric pattern was observed. The length of the repeating unit obtained from this pattern was plotted on Fig. 8 and placed slightly below the line corresponding to the fully extended spacer. (For n=9 and n=13 crystallinity developed with concommitant changes in crystallographic parameters). This observation indicates that simple nematic mesophases of homologues of odd parity of appropriate M can develop layered (cybotactic) nematic order provided the spacers exceed a certain length and the chains are oriented by drawing. The length of the spacer appears here as an important parameter facilitating a microphase separation and a parallel packing of chains. As it was pointed out[14] a parallel packing of mesogen moieties in homologues of odd parity requires an increased population of ±g conformers of methylene linkages of the spacer when compared to the overwhelmingly t-conformer population of the spacers of even parity. The relative population of g-conformers compatible with a parallel orientation of mesogen axes is smaller for longer spacers. This may explain why longer spacers are necessary to induce layered (cybotactic) nematic order in polyesters of odd parity.

In conclusion,our data suggest for the homologous series of polyesters investigated above that while polyesters of odd spacer parity in the quiescent state do not display any tendency toward formation of smectic mesophases, and behave as classical nematics, polyesters with even n exhibit a pronounced tendency for the formation of smectic mesophases. This tendency increases with n and M. It may be argued on the basis of SAX scattering and phase diagrams of mixture with LMMLC that the passage from cybotactic nematic to smectic C with increasing molecular mass is continuous. It is probable that n and M act synergistically to increase the tendency toward the formation of layered nematic and smectic C mesophase by increasing the stability and the size of macrmolecular clusters with axial registry through increased tendency for microphase separation and decreased level of segmental motion (increase in viscosity).

The formation of cybotactic nematic phase from polyesters of odd spacer parity has not been observed in their unperturbed state. This can well be due to the nonparallel conformation of mesogens for extended chains and hence unfavorable packing conditions for lateral registry. Nonetheless for long spacers of high M and oriented by elongational forces x-ray pattern characteristic of oriented N_c phases have been observed. Here again the increased length of the spacer appears to be important as a promoter of microphase separation facilitating the necessary energetically unfavorable conformational inversions in order to promote parallel packing of mesogen moieties.

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