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R. B. Blumstein [a] & A. Blumstein [a]

[a] Polymer Science Program, Department of Chemistry, University of Lowell, Lowell, MA, 01854

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Inherently Flexible Thermotropic Main Chain Polymeric Liquid Crystals

R. B. BLUMSTEIN and A. BLUMSTEIN

Polymer Science Program, Department of Chemistry, University of Lowell, Lowell, MA 01854

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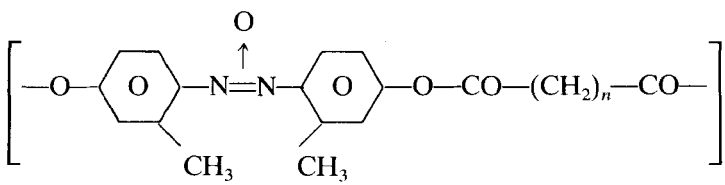
Phase behavior (isotropic—nematic transition, disorder in the crystal) and order of chains in the mesophase (orientational and conformational) are investigated in the homologous series of polymers



and corresponding siamese twin models. Results from the following experiments are presented: DSC (normal and high pressure), polarizing microscopy, broad line NMR (PMR and DMR), small angle X-ray and neutron scattering, induced magnetic birefringence and melt rheology. Influence of chain length, spacer length and parity, temperature and concentration in nematic solutions on nature and level of order is discussed. Molecular segregation by chain length in the nematic—isotropic biphase is considered in relation to its impact on morphology of the isotropic, nematic and solid phases. This series provides a model system for characterization of inherently flexible main chain PLCs formed by alternating mesogens and spacers. Such PLCs are easily processable materials with potentially high levels of micro and macroorder.

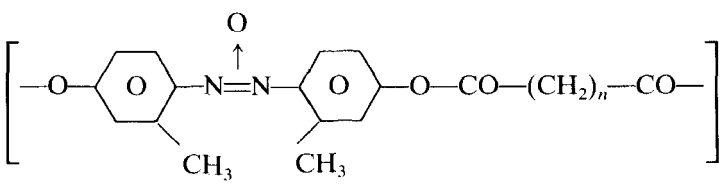
I. INTRODUCTION

Investigations in the field of polymeric liquid crystals (PLCs) are actively sustained by applications and potential applications in the areas of electro-optics, biomimetic and high performance materials, as well as by the numerous fundamental questions associated with the behavior of such chains.[1–10]

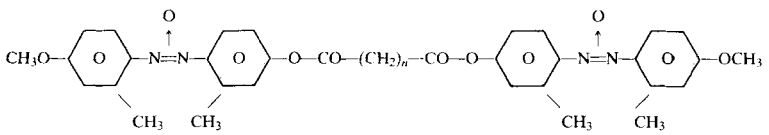
Thermotropic PLCs are traditionally subdivided into main chain and side chain structures, with mesogenic units in the main or side chain respectively. However, hybrid structures with mesogens in the main and side chain have also been synthesized.[11] In side chain polymers the rigid mesogenic groups are usually attached to conventional flexible backbones via flexible spacer groups. On the level of first approximation, the mesogens can be considered as decoupled from the backbone and can reorient in an external field independently of the latter. As a result, side chain polymers may combine the viscoelastic properties of polymers (backbone) with the electro-optic properties of low molecular mass liquid crystals (LMLC).[12,13] In main chain PLCs, the desirable properties associated with such structures (high strength-high modulus, for example) derive from a combination of long range order and extension of backbone. Fully aromatic main chain homopolymers such as poly (imino-phenyl-imino-terephtaloyl) [Kevlar] decompose before melting but phase transition temperatures can be brought down to tractable levels by introducing flexible spacers or chemical disorder into the backbone (via copolymerization, random lateral substitution or kinks in the mesogen).[14,15]

In this paper discussion will be restricted to thermotropic main chain polymers formed by regularly alternating mesogen moieties and flexible spacer groups. Such polymers are referred to as rigid-flexible (RF) PLCs. Molecules formed by a mesogen-spacer-mesogen (RFR) sequence provide the model compounds ("siamese twin models")[16] for RF PLCs, where a flexible spacer moiety is constrained between two mesogens.

Twin RFR structures were first reported by Vorlander[17] and RF PLCs first described by Roviello and Sirigu.[18] Numerous nematic, smectic and cholesteric RF PLCs were subsequently synthesized in rapid succession. Theoretical modeling of RF systems has been described by a number of authors (see for example 19–24). Literature on RF PLCs through 1984 is reviewed in References 14 and 15. A number of more recent studies are described in References 7–10, but comprehensive review of literature is beyond the scope of this paper which focuses solely on an experimental approach to investigation of structure-property correlations in a single homologous series of polyesters with spacer length $n = 3 - 20$



(referred to as the ME9-Sn series). This series and the corresponding twin model compounds



are among the most thoroughly characterized RF and RFR systems and will serve to illustrate their general properties. Phase behavior, orientational and conformational order and rheological properties are described.

II. INVESTIGATION OF THE ME9-Sn SERIES

II.1. General structural considerations

Selected structures synthesized in our laboratory are shown in Table I in order to illustrate the versatility of RF sequencing and to underscore the influence of details of chemical structure (especially the interplay between mesogens, linking groups and spacers) on the mesophase. The reader is referred to (14, 15, 25) for a more comprehensive discussion of structure-property correlations in RF PLCs.

Structures based on the 2,2′-dimethyl-azoxybenzene (mesogen ME9) display the following trends. Lateral substitution on the mesogen drastically lowers the phase transition temperatures of the polymer without significant narrowing of the mesophase range (compare polymers i) and k) Table I). Inversion of the carbonyl at the linking group tends to destroy the mesophase (compare structures i) and k) with j) and m)). The destabilizing influence of the CO—O linking group is rationalized in (24) using a statistical-mechanical approach. The mesophase has limited tolerance toward branching in the spacer (structures o), p) and q)).

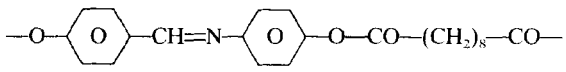
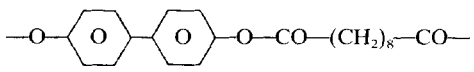
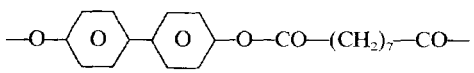
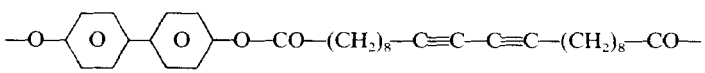
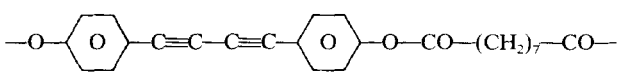
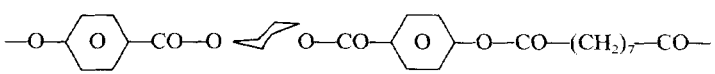
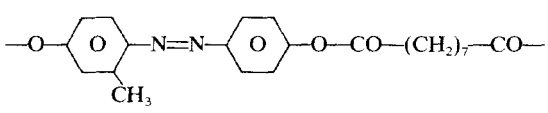
II.2. Inherent flexibility of chains. Pretransitional behavior.

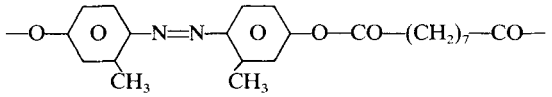
The chains are inherently flexible and randomly coiled in the isotropic (I) phase. This conclusion is based on a combination of induced magnetic birefringence experiments in the isotropic melt and in the I solution,[33,34] dilute solution studies[35] and radius of gyration measurements by neutron scattering in the I phase.[36]

The values of the Cotton-Mouton constant (CM) obtained from magnetic birefringence experiments in the isotropic melt, well above

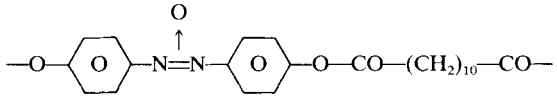
TABLE I

Selected RF PLCs

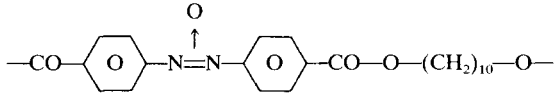
	Repeating Unit	Transitions °C	Ref.
a)		K201S235I	(26)
b)		K202S262I	(26)
c)		K186N208I	(27)
d)		K122S161I	(28)
e)		$K_1$93$K_2$108$K_3$156N250I	(29)
f)		K215N251I	(30)
g)		K146N191I	(25)

h) 

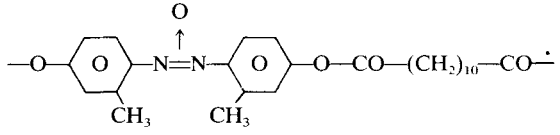
K140I (25)

i) 

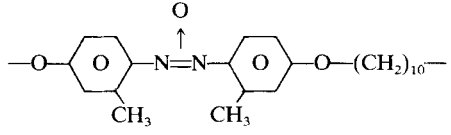
K216N265I (25)

j) 

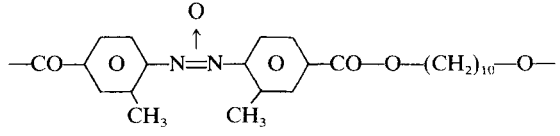
K198; 210I (25)

k) 

K118.2N 163.5I (25)

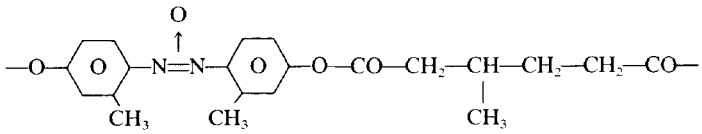
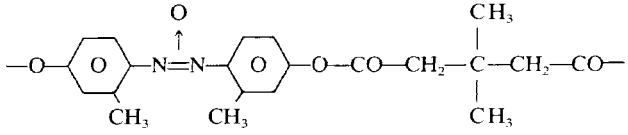
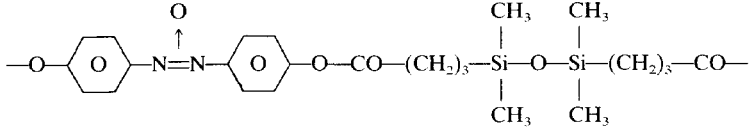
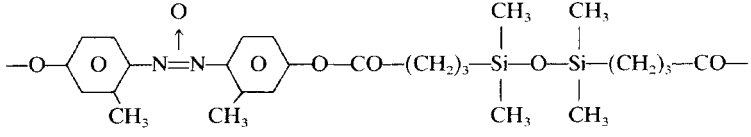
l) 

K134.5N 157.3I (31)

m) 

K95; 101I (25)

TABLE I (continued)

	Repeating Unit	Transitions °C	Ref.
n)		K151N210I	(25)
o)		g68I	(25)
p)		I84N32K*	(32)
q)		K62I	(32)

*monotropic N

TABLE II

Characteristics of the I → N transition from magnetic birefringence data (33, 34)

Compound	T_c (°C)[a]	$T_c - T_*$ (°C)[b]
PAA	134	5
n=10 twin model compound	99	14.5
DDA-9 (n=10) polymer ($\overline{DP} \sim 9$)	135	27
AZA-9 (n=7) polymer ($\overline{DP} \sim 7$)	131	14.5

[a]Clearing temperature T_c measured as the temperature at which strong scattering of light due to appearance of large nematic domains sets in.

[b]T_*, virtual second order transition temperature, obtained by extrapolation of $\Delta n^{-1}(T)$ to 0.

the clearing temperature T_c, imply a persistence length of the order of the monomeric unit. The isotropic—nematic (I/N) transition is cooperative and strongly first order, compared to a standard LMLC such as *p*-azoxyanisole (PAA). This is reflected in the unusually high values of $T_c - T_*$ extracted from the temperature dependence of pretransitional magnetic birefringence Δn (see Table II). Comparison of PAA with the $n = 10$ twin model and polymer shows that the model behaves qualitatively as the polymer. This is a general characteristic of RFR model behavior (see below). Similarly, the pretransitional temperature dependence of the deuterium NMR linewidth of twin models[37] and polymers[38] selectively deuterated on the spacer is indicative of strong pretransitional order parameter fluctuations. The exponent α for the molecular mass dependence of complex viscosity

$$|\eta|^*_{\omega \to 0} \propto \overline{M}_n^a \tag{1}$$

was measured for polymers $n = 10$ and 7 (subsequently designated as polymers DDA9 and AZA9, respectively) in the range of molecular weights 5000–15000.[39] In the isotropic melt, in the vicinity of T_c, $a \sim 4$, a value rather close to $a = 3.5$ observed in standard flexible chains.

II.3 Orientational and conformational order

The level and nature of order in the Me9-Sn series are determined by spacer length n, spacer parity (odd-even alternation of properties), chain length and (in the case of oligomers) the nature of end groups. Recent results on orientational and conformational order are summarized for the polymers in the bulk mesophase and in nematic solution in PAA.

II.3.a. Influence of molecular mass on the level and nature of LC order. Phase transition temperatures of ME9-Sn polymers are shown in Table III. Mesogen ME9 by itself is not mesomorphic and the mesophase must be stabilized by intramolecular orientational correlations that are propagated via the spacer.[40,41] The virtual clearing temperature of 2-2'-dimethyl-4,4'-diacetoxy azoxybenzene (compound 1, Table VI) is 200 K.[42] The siamese twin models are monotropic LCs, except for spacer n = 6 which promotes an enantiotropic *N* phase.[43] Otherwise 4–5 repeating units/chain are required for development of enantiotropic transitions.[40]

A systematic investigation of influence of chain length and chain ends on the level of order was carried out for DDA-9 ($n = 10$).[44] In the oligomeric range (degree of polymerization $\overline{DP}$ < ca. 10 repeating units/chain), aliphatic chain ends destabilize LC order. Isotropization entropies, enthalpies and mesogen order parameter S_{zz} increase strongly with increasing chain length and "plateau" at $\overline{DP} \sim 10$, displaying values significantly larger than standard LMLCs such as PAA. For a DDA-9 of mass 4000, for example, S_{zz} ranges from ~0.65 to 0.8 between T_{NI} and T_{KN} (Figure 1),[45] with analysis of the PMR lineshape suggesting that spacer and mesogen both have the same high level of order (i.e. the chain is extended). This is similar to the values found by other authors for n = even spacers in RF polymers where the aromatic moiety is a good mesogen.[46,47,48] In view of the poorly mesomorphic character of the ME9 moiety these data clearly point toward the role of the spacer as an integral part of LC order in RF polymers. Siamese twins have an order intermediate between standard MLLCs and polymers.[41,49]

Although the level of order in the bulk mesophase appears to plateau at $\overline{DP}$ ca. 10, influence of chain length is actually more subtle. Mesogen and spacer order in dilute solutions of DDA-9 in nematic PAA (5% weight polymer) both were found to increase continuously with polymer molecular weight, in the range investigated ($\overline{DP}$ 4–40).[50]

TABLE III

Thermodynamic data for the ME9-Sn series

n	$\overline{M}_n$	Transitions (°C)	$-\Delta S_{IN}$ J/mru · K*	Reference	ΔV_{KN}[b] ($\times 10^3 cm^3/g$)	ΔV_{NI}[b] ($\times 10^3 cm^3/g$)	T*[b] (K)
5	13,300	K135.8N173.8I	4.14	[a]			
6	27,000	K160.3N230.3I	12.67	[a]			
7	36,000	K98.3N164.6I	5.35	[a]	4.92	3.82	305
8	36,400	K136.8N188.3I	14.55	[a]	4.73[c]	2.28[c]	–
9	17,800	K121N144I	6.44	[a]	12.88	4.70	391
10	18,000	K118.2N163.5I	16.22	[a]	13.15[c]	8.90[c]	–
11	34,000	K100.8N132.8I	7.73	[a]	14.63	5.97	329
12	17,500	K110.8N143.8I	18.10	[a]	11.65	10.23	–
13	37,200	K106.8N122.8I	9.03	[d]	12.97	6.00	–
14	25,000	K121.0N134I	19.56	[a]	11.72	10.65	–
15	7,000	K108.5N116.7I	8.84	[d]			
16	17,000	K116.0N156I	20.24	[d]			
17		no mesophase		[d]			
18	16,000	I105S_c85.0K**	27.75	[d]			

[a](57).

[b](58).

[c]Note discontinuity observed at n = 8 in crystalline packing mode of related n = even RF polymers (59). Although no crystallographic data are available for the ME9-Sn series discontinuity in $\Delta V_{KN}(n)$ and $\Delta V_{NI}(n)$ may have the same origin.

[d](51).

*mru = mole of repeating unit.

**monotropic mesophase.

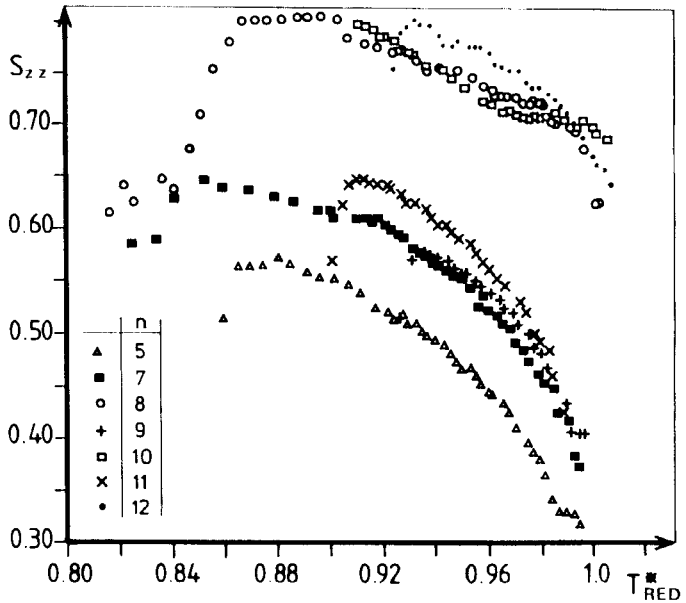


FIGURE 1 Nematic order parameter S_{zz} versus arbitrary reduced temperature T^*_{RED} for representative samples in the ME9-Sn series (data from References 52, 62, 38). The samples are polydisperse, at or slightly below "plateau" region of order. Reduced temperature is arbitrarily defined by taking T_c in the middle of the nematic—isotropic biphase (note that S_{zz} is strongly dependent on temperature within the biphasic region). The scatter of S_{zz} values observed for n odd is most likely due to fluctuations in chain length and arbitrary definition of T^*_{RED}. Note the collapse of macroscopic alignment on crystallization (see II.5.b.).

Experimental evidence also suggests a continuous transition in the nature of order, from cybotactic nematic (Nc) to smectic C upon increasing molecular mass in polymer ME9-S18.[51] This conclusion was reached on the basis of miscibility, X-ray and rheological data. In the case of DDA-9 ($n = 10$), only a nematic phase was observed but the progressive development of a broad SAX halo with increasing molecular mass suggests the possibility of a continuous shift to a smectic phase,[25,52] that is, a continuous spectrum of axial registry.[53]

II.3.b. Influence of spacer parity: odd-even alternation in the level of order. In conventional LMLCs such as *p-p'-n*-alkoxybenzenes the flexible tails are constrained by the nematic potential. This is reflected in an odd-even alternation of isotropization temperatures and enthalpies,[54] order parameters[55] and other properties. In general, i. the odd-even effect dampens out rapidly, at $n \geq 4$; ii. nematic and smectic phases coexist at $n \sim 7-8$ and only smectic phases remain at

high values of n; ii. there is no odd-even alternation in the level of order (both n = odd and n = even display the same mesophase over the same range of n).

When the aliphatic moiety is enclosed between two mesogens,[17] or between a mesogen and an aromatic ring,[56] the odd-even alternation at the LC/I transition becomes amplified. Numerous investigations have recently been devoted to this phenomenon which the ME9-Sn series illustrates in a striking fashion.

Table III shows that odd-even alternation of isotropization temperatures, enthalpies and entropies, as well as alternation in the specific volume change ΔV_{NI} at T_{NI}. The chain lengths of the samples are well into the "plateau" region discussed in section II.3.a. and the transition temperatures, measured as the DSC peak maxima are sharp.[57]

On the basis of an X-ray investigation of quenched aligned samples a "normal" nematic level of order was proposed for the n = odd series[25,60] while for the n = even structures through n = 16 the organization is "a micellar cybotactic nematic" (Nc)[35] in which the polymer chains are extended and confined to layers skewed by 41–45° with respect to the nematic director (angle between the director and normal to the plane of the layer). The mesophase collapses at n = 17 for n = odd and n = 20 for n = even. At n = 18 the polymer displays a monotropic phase (Nc or Sc) (see II.3.a.).

Between n = 3 and n = 16 values of ΔH_{NI} and ΔS_{NI} fit on two straight lines, the lower values corresponding to n = odd and the higher to n = even. If one considers the intercepts and the slopes of these lines as the respective contributions of mesogen order and spacer conformational changes at the I/N transition, it is clear from these simple calorimetric experiments that: i. the spacers become extended for both n = odd and n = even; ii. The mesogen order is much larger for n = even than n = odd (and regularly alternating between n = odd and even). The data are illustrated in Table IV. These conclusions are indeed confirmed by NMR studies[37,45,49,52] (see Figures 1 and 3), and are in qualitative agreement with recent statistical mechanical theoretical treatments of such molecules.[23,24]

The values of the characteristic temperature T* shown in Table III for n = odd provide a measure of orientation dependent interactions.[63] They were computed from high pressure thermodynamic data and values of S_{zz} as described in Reference 58. These values of T* which are in the vicinity of 300 K are consistent with the "normal" N level of order. For n = even the orientation dependent energy is much higher, in keeping with the strong orientational correlations observed, but could not be reliably computed from available data.

TABLE IV

Characteristics of the N → I transition from calorimetric data (n = 3 through 16)

	ΔH_{even} kJ	ΔH_{odd}	ΔS_{even} kJ	ΔS_{odd}
Orientational Order Contribution/ Mole of Mesogen	4.7[a]	0.94	7.55	1.41
Conformational Order Contribution/ Mole of Methylene	0.16[ab]	0.19[b]	0.87	0.57

[a]Compare with 3.1 kJ/mesogen and 0.41 kJ/methylene calculated for another n=10 polymer (48).

[b]Corresponding to 6–10% increase in trans conformer population at the I/N transition based on 2-3KJ/mole CH_2 for the gauche → trans isomerization energy (61).

II.3.c. Temperature and concentration dependence of spacer order. Spacer extension in RF PLCs was first mentioned to our knowledge in Reference 64 and subsequently investigated by a number of authors. Results of thermodynamic, X-ray, broad line NMR and neutron scattering experiments performed on the ME9-Sn series are summarized here.

The enthalpy increase/methylene unit shown in Table IV corresponds to a modest (ca. 6–10%) increase in trans conformer population at the I/N transition, suggesting considerable chain flexibility within the N phase in the vicinity of T_{NI}. Indeed, the exponent in Equation 1 is the same on both sides of the I/N transition (within experimental error), for a series of fractions of DDA-9 and AZA-9 polymers studied at reduced temperatures 1.05 and 0.95.[39] This is in agreement with the values of trans conformer population n_t reported by Kothe et al. for spacer $n = 10$ in another RF polymer, with $n_t = 0.46$ in the N phase in the vicinity of T_{NI}.[46]

Temperature dependence of spacer order was followed by broad line DMR. Spacer reorientational mobility of a DDA-9 oligomer was found to decrease by approximately 40% as the temperature is lowered through the nematic phase.[65] The corresponding RFR twin shows qualitatively the same behaviour although temperature dependence of spacer flexibility is less pronounced.[37] Figure 2 shows representative DMR spectra of polymers selectively labelled on the spacer. The spacer order at location CD_xi is computed from quadrupolar splittings $\Delta\nu$i as outlined in References 37 and 65. Splittings $\Delta\nu_1$ and $\Delta\nu_4$

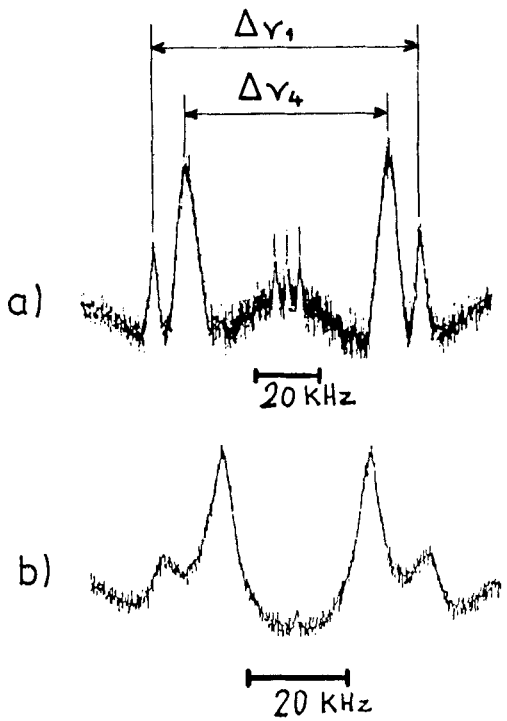


FIGURE 2 DMR spectra of samples deuterium labelled on the spacer. a) $n = 10$; $\overline{M}_n = 2{,}500$; temperature = 107°C; $f_N \approx 1$; b) $n = 7$; $\overline{M}_n = 4{,}300$; temperature = 128°C; $f_N \approx 1$. Data from Reference 88.

f_N: fraction of nematic component deduced by integration of the sharp line of the isotropic component as described in 37

$\Delta\nu_1$: quadrupolar splitting corresponding to the deuterons in α to the ester linkage

$\Delta\nu_4$: remaining deuterons

correspond to the deuterons in α to the ester linkage (which are orientationally coupled with the mesogen) and the remaining deuterons (internal part of the spacer), respectively. Orientional order appears to be uniform along the internal portion of the spacer. Figure 3 illustrates the temperature dependence of the ratio $\Delta\nu_4/\Delta\nu_1$ which was used to follow the relative order of spacer to mesogen. In addition to the bulk mesophase, nematic solutions of polymers and model compounds in perdeuterated PAA-d14 were investigated by a combination of PMR and DMR, so that solute and solvent order could be independently followed.

The NMR results can be summarized as follows:

i) at a given reduced temperature both the mesogen and spacer order are smaller for n = odd.

ii) the spacer disorders faster than the mesogen as the N/I transition is approached; it extends significantly on cooling.

iii) at a given reduced temperature, relative order of spacer is an inherent property of the chain and is independent of concentration in nematic solutions in PAA. It increases with increasing chain length in dilute solutions (see II.3.a.).[50]

iv) in the vicinity of Tc, relative spacer order displays the same limiting values, irrespective of chain length and concentration. This appears to be the minimum level of relative order still compatible with nematicity.

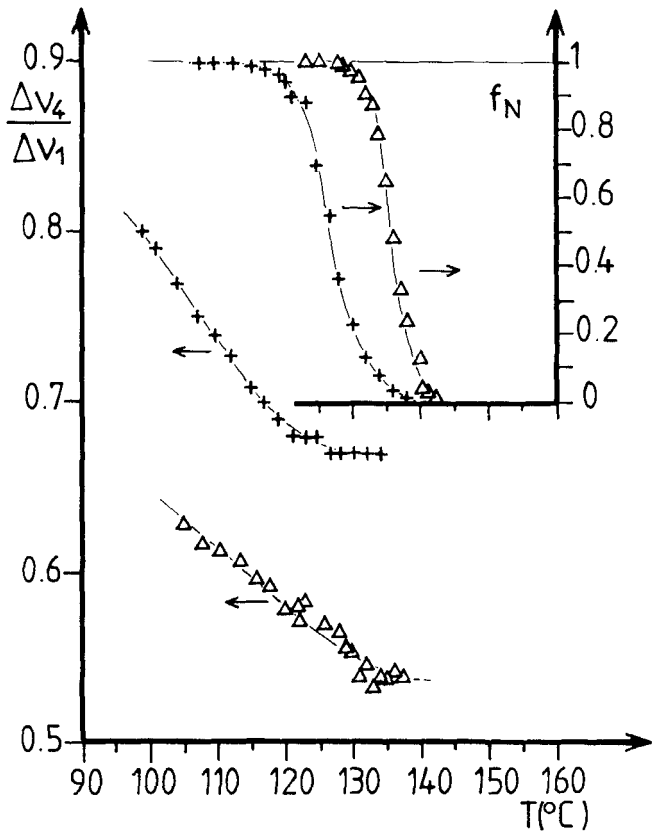


FIGURE 3 Temperature dependence of the ratio $\Delta\nu_4/\Delta\nu_1$ and nematic fraction f_N for (+) $n = 10$ and (Δ) $n = 7$. This ratio gives the order of spacer relative to mesogen as explained in Reference 37. Data from Reference 88.

v) systems that are fairly dilute in PAA appear to form ideal solutions for all chain lengths, in the pure nematic phase (i.e. $S_{solute} \sim S_{solvent}$).[37] Systems that are dilute in polymer (5% polymer by weight) form ideal solutions only with the longest chains investigated (DP ~ 40), and only in the vicinity of the clearing temperature. Otherwise, $S_{polymer} < S_{PAA}$.[50]

NMR studies underscore the coupling between orientational fluctuations of mesogen and conformational order of spacer (e.g. n = odd chains fluctuate more from the extended conformation than do n = even, as confirmed by theoretical modeling).[24] This result is also illustrated by small angle neutron scattering (SANS) experiments performed on DDA-9 and AZA-9 samples in the pure melt and in dilute solutions in PAA-d14.[36] The experimental radius of gyration R_G in the I phase is equal to the value calculated for a gaussian chain, illustrating the inherent flexibility of RF sequencing (II.2.). In the N phase, however, a large and spacer dependent anisotropy in chain shape is observed, as measured by the ratio $R_{/\!/}/R_{\perp}$ of the average chain extension parallel and perpendicular to the nematic director. Molecular mass and temperature dependence of $R_{/\!/}/R_{\perp}$ parallels the NMR results discussed above.

Chain extension is also illustrated on Figure 4 where SAX data for polymers that display the N_c layered pattern in aligned samples (section II.3.b.) are summarized. Length of the repeating unit is calculated as in Reference 35. Except for n = 11, the data fit a fully extended repeat unit, but the large experimental error (~.0.8 Å) inherent in the diffuseness of these SAX patterns is compatible with a relatively small fraction of gauche conformers (see section II.5.b). On Figure 4 the samples were aligned by a magnetic field, except ME9-S11 where the chains were oriented by fiber drawing, as orientation by a magnetic field did not produce a layered N_c SAX pattern. These data suggest that layered superstructures may be induced with spacers of odd parity upon application of mechanical forces.

The severe restriction of alkyl chain flexibility at lower reduced temperatures, a feature that is unique to the RF systems, opens a way for design of highly ordered and oriented specimens, starting with easily processable materials (see II.5.b.). Orientational and conformational order of individual chains (microorder) is determined by an interplay of spacer length, spacer parity, chain length and temperature. Extent of macroscopic alignment (macroorder) is discussed in Section II.5.b.

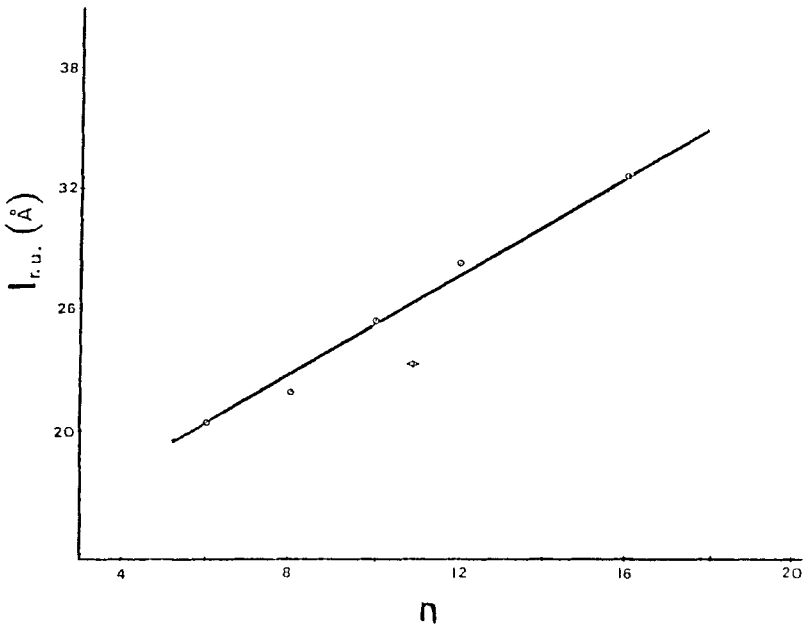


FIGURE 4 Length of the repeating unit $l_{r.u.}$ from SAX data. Samples aligned in a magnetic field as described in References 35, 25 [n = 6, 8, 10, 12, 16] or by spinning a fiber from the melt[51] [n = 11]. Solid line corresponds to the length of the repeating unit in all trans conformation.

II.4 The nematic—isotropic biphase

Main chain PLCs are characterized by the presence of a broad nematic—isotropic (N + I) biphase and polyesters of the ME9-Sn series provide excellent model systems for investigation of phase equilibria in this region. Due to their easy solubility in standard solvents samples are readily characterized in dilute solution. Molecular mass dependence of isotropization temperatures has been carefully established for DDA-9 and AZA-9 for unfractionated samples[44] and for fractions.[62,66]

In these homopolymers, polydispersity in chain length brings about polydispersity in isotropization temperatures without the need to consider heterogeneity in composition, as would be the case in copolymers. Phase transition temperatures are sufficiently low to permit lengthy thermal treatment without chain degradation and/or reorganization (such as the frequently observed transesterification of mesogens with a central ester group).

II.4.a. Molecular segregation in the biphase. Homogeneity of the pure N and I Phases. Kinetic and thermodynamic aspects of phase separation have been investigated by a combination of polarizing microscopy, DSC and broad line NMR.[66,67,68,88] Selective partitioning of chain lengths was observed, the longer chains being preferentially transferred into the N component of the biphase. This was first inferred from undulations observed in the temperature dependence of S_{zz} through the biphase of DDA-9[69] and subsequently confirmed by direct fractionation.[70]

Isothermal evolution of the system at a given temperature within the biphase is decomposed into two stages:

i. Actual phase separation between the I and N components.

This process is governed by the usual nucleation and growth phenomena. Conformational and orientational ordering of chains and selective partitioning of chain lengths between the I and N components take place at this stage. Recent DMR and PMR experiments suggest that compositional equilibration (i.e. equilibration of chain length distributions across phase boundaries) occurs rapidly: no measurable net migration of chains across I and N phase boundaries was detected following equilibration of instrumental response.[68]

ii. Coalescence—homogenization stage.

This stage is observed upon isothermal annealing within the biphase as the coalescence of the I and N domains until equilibrium (macroscopic) domain demixing is achieved. It is governed by factors such as diffusional and interfacial properties of the system and strikingly illustrates the molecular segregation by chain length imposed during phase separation. Complete demixing affords a macrodomain morphology with sharply defined boundaries and uniform distribution of chain lengths within boundaries. Upon partial demixing the shortest and longest chain lengths are found at the respective cores of the I and N domains while intermediate chains accumulate at their boundaries. Coalescence of these domains takes place concurrently with homogenization of their respective chain length distributions without measurable net migration of chains across phase boundaries.

Thermal history of the system in the N + I biphase is reflected in the morphology of the resulting isotropic, nematic and solid phases. Morphology of the biphase at various stages of coalescence is preserved by cooling to the solid phase and the formerly nematic and formerly isotropic components of the biphase can be clearly distinguished upon subsequent reheating.[66–68] For example two cold crystallization, two melting and two isotropization peaks can be observed

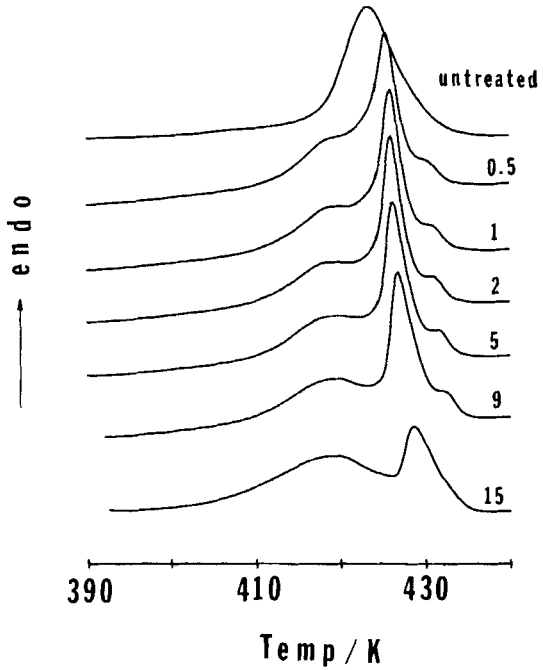


FIGURE 5 Isothermal evolution of the N/I transition peak recorded by DSC as a function of annealing time within the biphase. Sample: DDA-9 $\bar{M}_n$ = 4,600; annealing temperature = 419K; annealing time in hours; heating runs following cooling from 419K. Upon incomplete demixing three gaussian peaks are observed, the central peak corresponding to a broad boundary region of intermediate chain lengths. Complete demixing shows two peak morphology from which values of nematic fraction f_N can be extracted by peak deconvolution. See Reference 67 for details.

in macroscopically demixed samples, one for each component of the biphase.[67] Figure 5 illustrates various stages of incomplete demixing as reflected in the N/I transition.

Molecular morphology of the nematic phase, its dependence on thermal history and kinetics of isothermal evolution were investigated by a combination of PMR and DMR using the deuterium spectrum of PAA-d-14 as a probe in a model system of small molecules and in AZA-9 and DDA-9 polymers.[68] On cooling from a well isotropized I phase nematic droplets are first nucleated from the longest chains and continue to grow by adding roughly concentric shells of smaller and smaller average chain length.

As a result of this molecular segregation the nematic phase is inevitably formed of metastable "domains" (defined as regions segregated by chain length and, hence, level of order). Initial morphology de-

pends on sample thermal history and spacer parity with dimensional scale of heterogeneity varying from ca. 20μ to macroscopic.[68] Investigation of the kinetics of "domain" evolution is expected to shed light on fundamental problems of textures, morphology and rheological behavior in PLCs. Kinetics of macroscopic homogenization of the I or N phase can be followed by DSC as described in Reference 67 and related to the thermal history in the precursor biphase. Homogenization on the molecular level was followed by NMR and is extremely slow in these viscous media.[68] Extent of molecular segregation and initial heterogeneity is invariably stronger for n = even. Biphasic gap and extent of segregation in n = odd chains is roughly intermediate between n = even and standard LM nematics.

II.4.b. Supercooling at the I/N Transition. One consequence of molecular segregation in the N + I biphase is the difference between the temperature dependence of the nematic fraction f_n on heating and cooling as illustrated on Figure 6 where f_n (T) is shown for several thermal histories of a DDA-9 sample. The biphase on heating extends until temperature T_{sc}, while a well homogenized I phase persists on

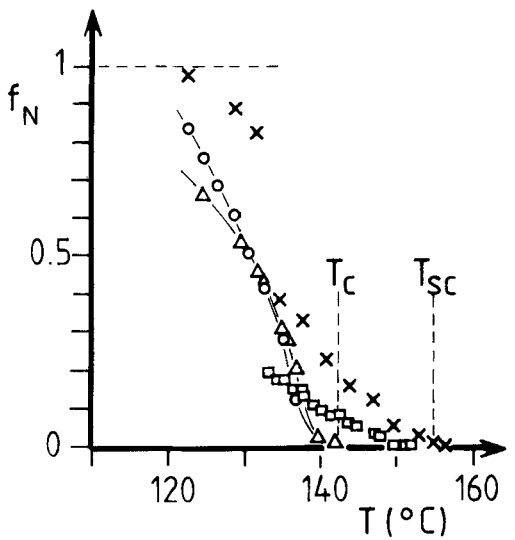


FIGURE 6 Nematic fraction measured by DSC[67] [○ cooling; × heating] and PMR[68] [△ cooling; □ heating]. Sample DDA-9 $\bar{M}_n$ = 5,200. Note: points × recorded on heating from a completely demixed sample (see legend of Figure 5); points □ on heating an untreated sample brutally placed in the biphase at 133°C. Cooling runs are from well isotropized samples. See Reference 68 for details.

cooling until T_c (the system was followed isothermally for over 24 hours at several temperatures between T_c and T_{sc} but no nematic component was detected). On heating, the longest chains are concentrated by molecular segregation and isotropize in the vicinity of their thermodynamic transition temperature; on cooling from a homogenized I phase, these same chains are more nearly molecularly diluted within a "multicomponent" system. The interval $T_c - T_{sc}$ appears to be a pretransitional zone where fluctuations of chain length distribution in a homogenized medium alone are unable to nucleate a mesophase.

Supercooling of the N phase in main chain PLCs is generally assumed to be slight, in comparison to LMLCs.[71] In our experience, however, the I/N transition in RF PLCs under normal scanning conditions is supercooled by a few K to some 30K. Although chain length (viscosity) plays a part, extent of supercooling is primarily driven by spacer parity and is much larger for n = even than n = odd.[72] Nucleation of the N phase may be more difficult in the case of n = even because of the strongly first order nature of its I/N transition.[73] (See Table II). This characteristic may also explain the existence of amorphous glasses in RF polymers. Partial quenching of the isotropic phase to an amorphous glass has been reported in smectic RF polymers.[74,75] In the case of nematics the only report to our knowledge concerns quenching DDA-9 in liquid nitrogen: an isotropic glass —$(T_g)_I$— and a nematic glass —$(T_g)_N$— were observed; n = odd chains could not be quenched to an amorphous glass (Table V).

TABLE V

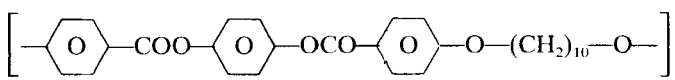
Partial quenching of the isotropic phase (76)

Sample	Treatment	Isotropic Glass	Nematic Glass
n=10		$(Tg)_I$(°C)*	$(Tg)_N$(°C)*
$\overline{M}_n$ = 14,500	A	−7	+15
	B		+13
n=10	A	−8	+13
$\overline{M}_n$ = 3,000[a]	B		+13
n = 7	A		+19
$\overline{M}_n$ = 8,000	B		+19

a: aromatic end groups (44).
A: quenching in liquid nitrogen.
B: cooling at >80°C/min.
*measured by DSC on heating (20°K/min).

II.5.a. Consequences of RF sequencing. Disordered nature of the crystals. Volume change on melting to the mesophase does not appear to depend on spacer parity and ranges within 0.5–1.5% (for spacers n = 7–14, Table III),[58] compared to ~8% for PAA. This suggests a high degree of imperfection in the crystalline phase, in agreement with the collapse of the crystalline WAX pattern upon application of pressures >4Kbar observed in a recent study of DDA-9.[77] Thermodynamic investigation of the same polymer[49,78] also suggests a high degree of imperfection of the crystalline phase. The heat of melting (extrapolated to 100% crystallinity) is about 5 times lower than in normal polyesters.

Solid state NMR studies also point to the same conclusion, based on an analysis of PMR lineshapes of DDA-9 and related structures.[45] Kothe et al[46] have investigated conformation and dynamics in nematic polymer



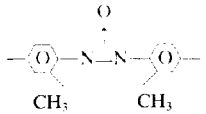
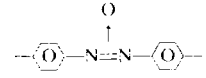
using multipulse DMR spectroscopy. In the solid phase the crystalline (immobile) and LC (mobile) components are distinguished by their lineshape and relaxation behavior. Upon solidification from the melt the trans conformer population of the spacer abruptly jumps from n_t = .69 to n_t = .80 for the immobile component, and retains this value throughout the solid phase indicating a high level of conformational disorder in the crystal. For the LC component the value of n_t increases slowly to .76 upon cooling. Both components display trans-gauche isomerization, with correlation times $1.5 - 5.10^{-6}$s for the former and $5.10^{-9} - 8.10^{-8}$s for the latter (between T_m and T_g).

Disorder in the crystalline phase of RF structures most likely results from the mismatch between crossections of the mesogens and spacers, which encourages conformational disorder in the latter, and, thus, should be observed in RF chains in general, whether mesomorphic or not. This is illustrated in Table VI where the total entropy of melting (all transitions combined) is listed for some representative low mass molecules and polymers. Well ordered crystals (compounds 1 and 11, for example) display a value of 10–11 J/K mole of rigid groups.[61] Values for RF and RFR models, mesomorphic or not, are intermediate between well ordered crystals and RF polymers (the latter being very low).

Molecules based on rigid-flexible sequences (low mass mesogens or RF polymers) might form condis (conformationally disordered)

TABLE VI

Phase transitions in model compounds

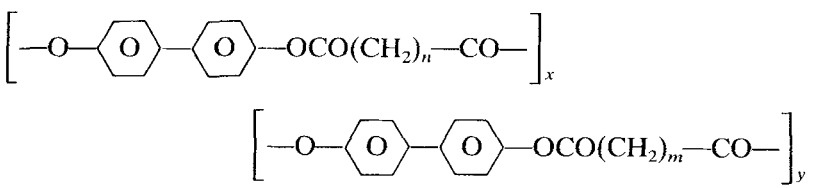
	R	Compound	Transitions (°C)	ΔS*	Ref.
					
1)		CH_3—CO—O—R—O—CO—CH_3	K151I	10.67	(49)
2)		CH_3—$(CH_2)_{10}$—CO—O—R—OCH_3(M)	K41.4;59.4I	5.87	(49)
3)		$CH_3(CH_2)_7$—CO—O—R—OCH_3(M)	K32.3;39.9I	6.23	(49)
4)		$CH_3(CH_2)_{10}$—CO—O—R—O—CO—$(CH_2)_{10}$—CO—O—R—O—CO—$(CH_2)CH_3$	K41;58.6;70.2I	6.28	(49)
5)		CH_3O—R—O—CO—$(CH_2)_{10}$—CO—O—R—OCH_3(M)	K92;112;122I (I100N832K)	7.12	(49)
6)		CH_3O—R—O—CO—$(CH_2)_{10}$—CO—O—R—OCH_3(ONN)	K112I (I99N85K)	7.94	(49)
7)		CH_3O—R—O—CO—$(CH_2)_8$—C≡C—C≡C—$(CH_2)_8$—$(CH_2)_8$—CO—O—R—OCH_3(M)	K61;75;90I (I41N)	7.41	(79)
8)		n=10 polymer (DDA-9)	K118N163I	3.6**	(49)
					
9)		$CH_3(CH_2)_6$—CO—O—R—OCH_3(M)	K72N114I	5.70	(80)
10)		CH_3O—R—O—CO—$(CH_2)_8$—C≡C—C≡C—$(CH_2)_8$—CO—O—R—OCH_3(M)	K131N148I	6.76	(79)
11)		CH_3O—R—OCH_3 (PAA)	K114.5N136I	10.67	(49)

M = mixture of structural isomers.
ONN = ONN isomer.
*total entropy of melting computed in J/K · mole of rigid chain groups defined as in (61).
**extrapolated to 100% crystallinity.

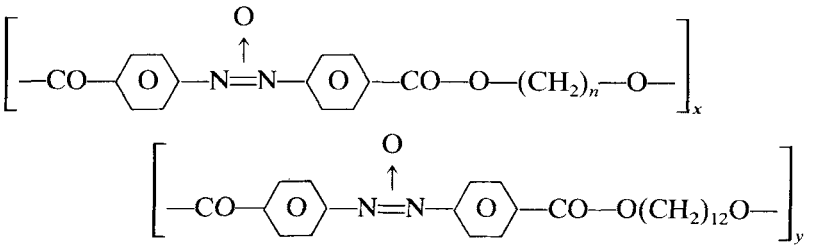
crystals. According to Wunderlich et al.[71,81] such crystals constitute a mesophase class combining long range orientational and positional order with dynamic conformational disorder. Condis crystals might form if one of two types of disorder are present: ring-flips or jumps in the aromatic moieties and conformational disorder in the flexible moieties.[81] Both types of disorder are likely to be found in RF structures.

A third source of disorder is additionally found in structures based on the ME9 moiety: structural isomerism at the azoxy group along with the distorted nature of the mesogen (the torsional angle between aromatic groups is ca. 36°).[45,82] This is most readily apparent in the low mass derivatives of ME9. Melting temperatures of several structures are listed in Table VI. Unsymmetrically substituted molecules are characterized by multiple melting peaks, three for the twins and two for the other structures. Each melting peak corresponds to another structural isomer, with three possible combinations in the case of twins: ONN—ONN, NNO—NNO and the hybrid ONN—NNO.[49]

A corollary of disordered crystalline packing is the frequently cited occurrence of cocrystallization between RF PLCs and LMLCs as well as crystallinity in random copolymers, mesomorphic or not. Watanabe and Krigbaum[83] have investigated copolymers



and observed cocrystallization to lamellar crystals as long as spacer lengths n and m are not very different. The non mesomorphic series based on p,p'-azoxybenzoate (homologues of structure j Table I) is even more striking.



($x = y$ and $n = 4$, 6, 8, 10 and 12).[84] Crystallinity was observed in all cases. A model was introduced to account for packing of chains into a lattice with small angle spacing roughly intermediate between the spacings of the corresponding homopolymers.[59] Note that at $n = 4$ only the lateral d spacings corresponding to paracrystalline packing of the mesogens into an orthorombic cell remain.

II.5.b. Relation with molecular organization in the precursor mesophase. The solid phase is always preceded by a biphase and a pure N phase, whether produced by cooling from the melt or by solvent removal (solvent-non solvent precipitation, film casting from solution). A lyotropic mesophase is crossed in the latter case. In solutions of DDA-9 in nitrobenzene, for example, a nematic phase is retained until solvent concentrations ~15% (w/w), with drastic depression of both I/N and N/K transitions, as expected.[62] Preliminary results suggest domain segregation by chain length upon solvent evaporation (Reference 67 and work in progress), similar to segregation discussed in Section II.4.a.

As previously mentioned, both spacer and mesogen reach a high level of microorder upon cooling through the mesophase. Macroscopic alignment may be achieved under suitable conditions. Alignment in magnetic fields is limited by the high values of rotational viscosity coefficients in polymers of relatively high mass. The order developed by the magnetic field can be preserved by quenching the oriented mesophase.[85] On the other hand, crystallization developed upon slow cooling is a catastrophic event which may or may not destroy macroorder. Thus, crystallization disrupts macroscopic alignment in the ME9-Sn series (see collapse of S_{zz} on Figure 1) but not in polymer i) (Table I), for example.[35,85] Studies of crystallography and crystallization kinetics of such systems would probably explain such selective preservation of order but have not yet been carried out.

Elongational flow provides an approach to development of highly extended chains in highly aligned fibers. Such fibers are obtained by spinning from the nematic melt of RF PLCs followed by quenching. X-ray diffraction[35,85] and pulsed dynamic DMR[86] studies show high chain extension and high values of macroorder in these fibers which also display excellent mechanical properties.[86] This sets the stage for potential applications of such systems as ultrahigh modulus fibers in spite of the fact that the numerous textural defects introduced by the spacer have opposed efforts in this direction. Improvements in methods of extrusion and introduction of reinforcing functional groups

into the main chain[87] provide a potentially fruitful field of investigation.

Acknowledgments

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