Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 20 Apr 2011.

To cite this article: F. Volino , J. M. Allonneau , A. M. Giroud-godquin , R. B. Blumstein , E. M. Stickles & A. Blumstein (1984): NMR Study of Segregation by Molecular Mass in a Polydisperse Nematic Polymer, Molecular Crystals and Liquid Crystals, 102:1, 21-33

To link to this article: http://dx.doi.org/10.1080/01406568408247035

Mol. Cryst. Liq. Cryst. Vol. 102 (Letters), pp. 21-33
0140-6566/84/1021-0021$18.50/0

NMR STUDY OF SEGREGATION BY MOLECULAR MASS IN A POLYDISPERSE NEMATIC POLYMER

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(Received for Publication January 20, 1984)

ABSTRACT

Using proton and deuterium NMR we show that in polydisperse nematic polyesters with mesogenic units in the main chain: (i) in the nematic-isotropic biphase, the nematic phase is enriched with the longest species and (ii) in the nematic phase itself there is additional segregation by molecular mass into nematic domains.

Thermotropic mesomorphic polymers have been the subject of increasing interest in recent years due to possible applications and fundamental problems associated with these systems (1). Through appropriate combination of mesogens and non-mesomorphic moieties, it is possible to synthesize versatile, novel materials. In this respect, polymers formed by regularly alternating mesogenic elements and flexible spacers in the main chain are among the most actively inves-

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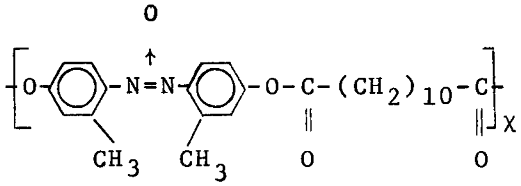
tigated (2).

In this letter, we discuss some results of a NMR investigation of one such polymer, a nematic polyester formed by condensation between 4,4'-hydroxy-2,2'-dimethyl azoxybenzene and the acid chloride of dodecanedioic acid:



(Polymer DDA-9).

The nematic-isotropic transition in polymer DDA-9 is characterized by i) a drastic conformational change and ii) the presence of a nematic-isotropic (N+I) biphase.

Investigation by magnetic birefringence (3) shows that, upon cooling from the isotropic into the nematic phase, the polymer undergoes a transition from a randomly coiled to an extended chain conformation. High degree of chain alignment and extension of spacer in the nematic phase have been confirmed by other methods as well (5), including proton (6) and deuterium (7,8) NMR spectroscopy.

The extent of correlation between repeating units is dependent on molecular mass: entropy of isotropization (9) and nematic order parameter at the I/N transition (8, 10) both increase rapidly with molecular mass, before leveling off. The N/I transition temperature T_{NI} also follows a similar trend, varying from $\sim$75°C for $\overline{M}_n \sim 1,000$ to $\sim$168°C for $\overline{M}_n > \sim 10,000$. As a result of this molecular mass dependence of T_{NI}, a N+I biphase is observed in polydisperse samples. Preliminary NMR investigation of the biphase (10) suggests a preferential transferral of the longest species into the anisotropic phase. Herein, we present additional NMR evidence of segregation according to chain length.

EXPERIMENTAL

Synthesis and characterization of materials have been previously reported (4,9,10). Molecular weight distributions were obtained by gel permeation chromatography in tetrahydrofuran. The instrument was calibrated with model compounds, oligomers and narrow fractions of polymer DDA-9, as will be described elsewhere (11).

Proton NMR experiments were performed on a CXP-100 Brüker spectrometer working at 75 MHz, and deuterium NMR on a WM-250 Brüker spectrometer working at 38.4 MHz. The polymers were degassed and sealed under vacuum in 5mm glass tubes. The samples were equilibrated at 20° above T_{NI} for forty minutes and cooled slowly by steps of 2-3°C. At each temperature, about five minutes were needed to reach thermal equilibrium. The NMR FID signals were then recorded and time Fourier transformed to obtain the absorption spectra. A typical proton spectrum in the N+I biphasic range is shown in the insert of Figure 3. The nematic order parameter S, associated with the mesogenic unit, was deduced from the main dipolar splitting $2\delta_N$ as previously described (6). The nematic fraction f_N was deduced either from the FID signals or from the spectra, taking as reference the intensity in the pure isotropic phase. Both methods give the same result within experimental accuracy. Viscosity measurements were also performed by rotating the aligned sample at 90° to the field and following reorientation as a function of time. To this effect, the splittings $2\delta_N$ were measured on the successive spectra recorded using a single scan.

RESULTS

The two samples which were used in this study are designated as polymer DDA-9L and polymer DDA-9LII. Their average degrees of polymerization are $\bar{x} \approx 9$ and $\bar{x} \approx 10$, respectively. Sample DDA-9LII was separated from DDA-9L as described in reference (10), through removal of the longest and shortest species initially present in DDA-9L. Figure 1 shows the temperature variation of S and f_N upon cooling from the isotropic phase. We can see that the biphasic range is narrower for DDA-9LII and the value of S first observed in the biphase smaller than for DDA-9L, in keeping with the difference in molecular weight distribution of the two samples. The value of f_N varies abruptly around 133°C in both instances, i.e., in the vicinity of the isotropic-nematic transition temperature T_{IN} as detected by DSC on cooling (10). The temperature variation of S is not represented by the standard monotonic curve observed in pure low molecular mass nematics. Sample DDA-9L displays an undulation in the vicinity of T_{IN}; a second, less pronounced undulation is observed around 105°C in both samples.

ANALYSIS AND DISCUSSION

These results can be explained by assuming that as the temperature is lowered from the isotropic phase into the N+I biphase, the longest species are transferred into the nematic phase first, followed by the average length species and, finally, the shortest ones. This means that as temperature decreases, the average molecular mass in the nematic component of the biphase decreases. Landau-de Gennes theory predicts that for nematic systems composed of semiflexible polymers both the isotropic-nematic transi-

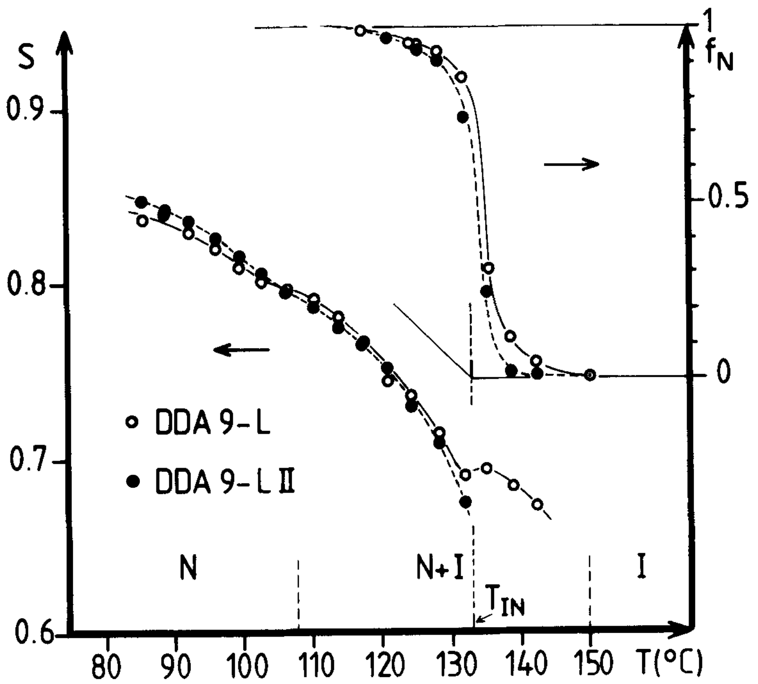


FIGURE 1 Nematic order parameter S and nematic fraction f_N in the N+I biphase: DDA-9L (open circles) and DDA-9LII (filled circles). T_{IN} is the isotropic-nematic transition as measured by DSC on cooling (10). The inset in Figure 3 shows a typical proton NMR spectrum from which S and f_N are deduced (see text for details).

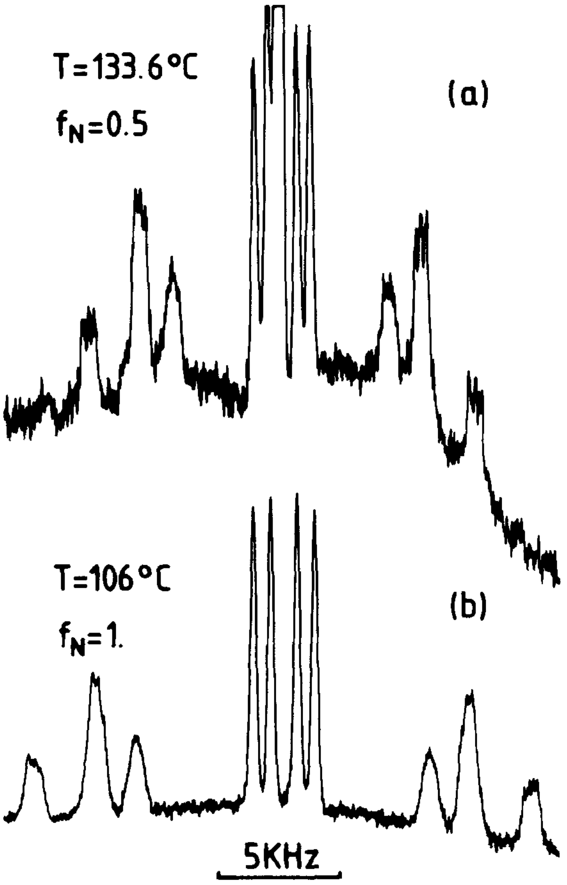


FIGURE 2 DMR spectra of PAAd14 dissolved in DDA-9L at a concentration of 5% by mass, at two temperatures a) 133.6°C in the N+I biphase ($f_N \sim 0.5$), b) at 106°C in the pure nematic phase ($f_N=1$). Note that the dipolar triplets (denoted by an arrow) are much better resolved in case a) than in case b).

tion temperature (T_C) and the order parameter at the transition(S_C) increase with molecular mass, before leveling off (12). This trend is indeed observed in DDA-9, as mentioned previously. Thus, for biphasic systems, where the average molecular mass depends on temperature, one expects that both T_C and S_C depend on temperature. As the nematic phase incorporates more and more short species, the actual values of T_C and S_C, which scale the temperature dependence of S, decrease. This may explain the important undulation observed for DDA-9L around T_{IN}, where the ne-

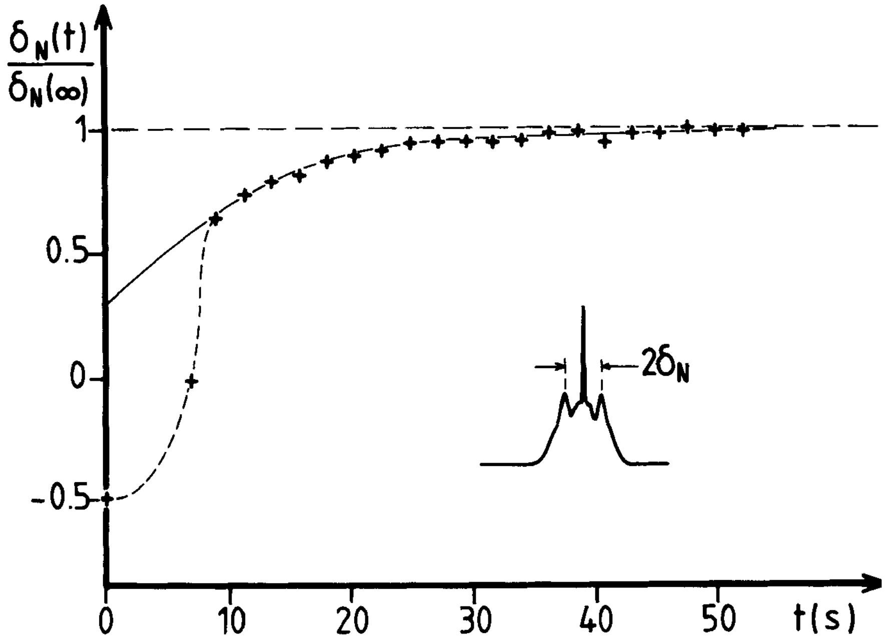


FIGURE 3 Evolution of the dipolar splitting $2\delta_N$ (proportional to S) versus time after sample DDA-9LII had been rotated suddenly by 90° at t=0. The inset shows the proton spectrum at equilibrium ($t \gg 50s$). Temperature: 128.5°C, S=0.72, $f_N \approx 0.9$. The full curve is the best fit to the experimental points taken at t>10s, assuming a single rotational viscosity coefficient γ_1. The dashed line is a guide to the eye through the points (see text for details).

matic phase incorporates a large fraction of shorter species. This causes a large decrease of S_C and T_C (and consequently of S), between 135° and 131°C. This decrease of S is not completely compensated by the natural increase produced on cooling. The second undulation around 105°C is explained in a similar way by the fact that at this temperature S_C and T_C stop decreasing, since all the shortest species have been incorporated into the nematic phase. The larger average molecular mass of sample DDA-9LII explains that, in the pure nematic phase, S is higher than for sample DDA-9L (Figure 1).

These results raise some intriguing questions concerning the homogeneity of the polymeric mesophase. The secondary undulation reported for DDA-9L and DDA-9LII (and observed for other samples as well) would appear to indicate that what is seemingly a homogeneous nematic phase might in fact contain a minor isotropic component. Figure 1 shows that presence of this component deters optimum overall alignment until a temperature ~105°C, that is some 25-30° below the transition to a "homogeneous" nematic phase as observed by polarizing microscopy.

Furthermore, the sequential incorporation of chain lengths into the nematic phase suggests that distribution of molecular mass may not be uniform throughout the sample.

The following two results seem to support the possible existence in the nematic phase of domains segregated by chain length:

a) If the nematic phase is formed by juxtaposition of domains with different molecular mass, each domain will have a different order parameter S_i, smaller for short polymers and higher for long polymers (12). Each domain contributes to the NMR spectrum with an elementary spectrum whose width is, in first approximation, proportional to S_i. Consequently, the overall spectrum of the nematic phase will be the superposition of elementary spectra with different widths. If the distribution of S_i is small, this will simply contribute to the spectra via an additional broadening, whose magnitude will increase with the width of the distribution of the S_i (13). Consequently, we expect the spectra in the pure nematic phase to be less resolved than in the nematic part of the N+I biphase since in this latter case the distribution of S_i is narrower. This effect is difficult to see on the proton spectra because the natural broadening of the various components is already relatively large. However, this effect is clearly seen on the deuterium spectrum of perdeuterated p-azoxyanisole (PAAd14) dissolved in polymer DDA-9L (the two components are miscible in all proportions). At a concentration of 5% by mass the biphasic range is the same as in DDA-9L. Figure 2 shows two typical spectra, in the N+I biphase, and in the pure nematic phase. It is clear that the dipolar splittings between orthodeuterons (the small triplets on the four external lines of the spectra) are significantly better resolved in the N+I biphase, as expected (14). A detailed analysis of these spectra may be used to deduce information on the distribution of S_i.

b) If the domains have different order parameters, we expect them to have different rotational viscosities γ_1. Since γ_1 governs the rotational dynamics of the nematic director and is an increasing function of S ($\gamma \propto S^2$ in usual nematics (15, 16)), the various domains will align along the magnetic field at different rates. The domains with smaller S will reorient faster than those with higher S. Such a model may explain what is observed in practice for the three samples used. Figure 3 shows an example of the evolution of the main dipolar splitting $2\delta_N$ of the proton spectrum, in experiments where the sample has been rotated suddenly at 90° to the field. The full curve represents the best fit to the experimental points taken at $t > 10$ s, of the corresponding law assuming a single γ_1. Namely, calling θ the angle between the director and the field at time t ($\theta = 0$ at equilibrium), we have (15, 17)

$$\delta_N(t) \propto 3\cos^2\theta(t) - 1$$

$$\tan\theta(t) \propto \exp(-t/\tau_{\gamma_1})$$

$$\tau_{\gamma_1} \propto \gamma_1$$

Figure 3 shows that return to equilibrium is relatively fast at short times, and then slows down at larger times, as expected if a distribution of γ_1 exists. Line-shape analysis in the steady state and during return to equilibrium is currently performed.

In conclusion, we have shown evidence that in the N+I biphase the shorter chains gather preferentially in the isotropic phase and the longer chains in the nematic phase. Lattice theory of nematic polymers predicts this type of fractionation in the case of polydisperse systems of rigid rods (18), but not in the case of chains formed by uncorrelated rigid units separated by flexible portions (19). Clearly, in the present case, behavior of individual molecules is dictated by correlations between repeating units, which occur via the spacer moiety.

Undulations observed in the temperature dependence of order parameter S(T) are explained by an interplay between the natural increase of S with decreasing temperature and the sequential incorporation into the nematic phase of chains with decreasing values of S_C.

In addition, the pure nematic phase may be formed of domains segregated by chain length.

ACKNOWLEDGEMENT

This work was supported in part by the National Science Foundation under Grant DMR-8308939.

The authors are grateful to M.M. Gauthier for assistance with molecular weight determination.

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