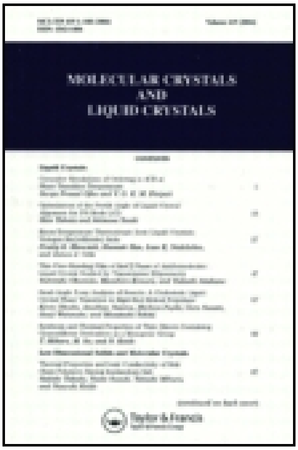

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Some NMR Results on a Linear Nematic Polyester in the Bulk and in Mixtures with a Low Molecular Mass Nematic

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SOME NMR RESULTS ON A LINEAR NEMATIC POLYESTER IN THE BULK AND IN MIXTURES WITH A LOW MOLECULAR MASS NEMATIC

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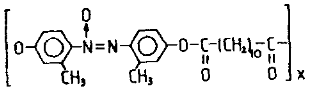
Abstract Proton and deuterium NMR results from a study of a nematic polyester (poly (4,4' -dioxy- 2,2' dimethylazoxybenzene dodecanedioyl)) in bulk and in mixtures with perdeuterated para-azoxy-anisole (PAAd14) are presented. Two compounds are considered : polymer DDA9-L with an average degree of polymerisation ∿ 9 and the partially deuterated model compound 9DDA9-S d20. Both compounds exhibit a nematic plus isotropic (N + I) biphase. In the nematic phase, the molecules are aligned along the director with the spacers in an extended conformation. Relative fractions of N and I components and order parameter S are estimated. For DDA9-L, undulations of S with temperature suggest that in the N + I biphase, the nematic component is enriched with the longest molecular species. In the mixtures, S of DDA9-L and of PAA are estimated. The values and temperature dependence of S and of the relative order of the spacers and mesogens in the polymers are studied as a function of composition.

INTRODUCTION

Thermotropic liquid crystalline polymers (PLCs) have been extensively studied in recent years due to possible applications and theoretical aspects associated with these systems[1] Linear PLCs can be prepared by alternation of prolate and rather rigid mesogenic units, similar to the aromatic core of low molecular mass (LMM) liquid crystals, and flexible spacers, generally alkyl chains.

The phase situation in these systems can be characterized by various methods such as differential scanning calorimetry, optical methods, X-ray diffraction and nuclear magnetic resonance (NMR). When the sample can be macroscopically aligned, NMR turns out to be a very powerful method to obtain information concerning molecular structure, conformation and orientational order.

Polymers of general chemical formula



formed by condensation between 4-4' -hydroxy- 2,2' dimethylazoxybenzene and the acid chloride of dodecanedioic acid have been recently synthesized and show broad nematic ranges at moderate temperatures[1 2 3 4 5].

From the chemical point of view, the samples are characterized by the average number of repeating units $\bar{x}$, by the distribution of lengths (or of molecular mass) around $\bar{x}$, and by the ratio R of aromatic to aliphatic end groups[5]. The values of $\bar{x}$ for actual samples range typically from a few units (oligomers) to ∿ 40.

From the physical point of view, the microstructure of the various phases at a given temperature often depends on thermal history. These systems generally exhibit a nematic plus isotropic (N + I) biphase between the pure isotropic and pure nematic phases, and a (soft) crystalline plus nematic (K + N) biphase in the solid state[5]. The pure nematic phase can be locked in the solid phase, in some instances[5].

In this paper, we shall present some NMR results obtained by our groups with these systems. Some of them have already been published[5 6 7 8 9] and some other are new. In the first part, the NMR spectra (proton and deuterium) of some typical samples, and their temperature and thermal history dependences, will be presented and discussed in terms of the structure of the various phases. In the second part, line shapes in the nematic phase and in the N + I biphase will be discussed in detail in terms of molecular order and conformation. In the third part, results on mixtures of one of these samples (DDA9-L) with perdeuterated para-azoxy anisole (PAAd14) will be discussed in terms of the conformation and orientational order of both the solvent and solute molecules, as a function of relative concentration and temperature.

NMR RESULTS : MICROSCOPIC ASPECTS

Polymer DDA9-L

Fig. 1A-F shows six typical proton spectra of polydisperse sample DDA9-L ($\bar{x} \approx 9$, $R \sim 1.5$) obtained by cooling from 150° C in the isotropic phase, namely A) isotropic phase ; B) N + I biphase ; C) pure homogeneously aligned nematic phase ; D) transition spectrum ; E,F) solid phase.

The following quantities can be measured on these spectra : (i) the fraction f_N of nematic phase in the N + I biphase, which can be deduced either directly from the spectra or from the F.I.D. signals ; (ii) the splittings $2\delta_N$ (as defined on spectrum (C)) which are proportional to the nematic order parameter S (see the next section) ; (iii) the full widths $2\Delta_{1/2}$ and $2\Delta_{1/4}$ at half and at a quarter of maximum on the solid spectra, as defined on spectrum (F). Fig. 2 shows the variation of $2\delta_N$, $2\Delta_{1/2}$ and $2\Delta_{1/4}$ versus temperature for DDA9-L and DDA9-L II, obtained by cooling after the samples have been equilibrated at 150° C in the isotropic phase. Sample DDA9-L II was separated from DDA9-L after removal of the longest and shortest chains initially present in L ($\bar{x} \approx 11$, $R \sim 1.5$).

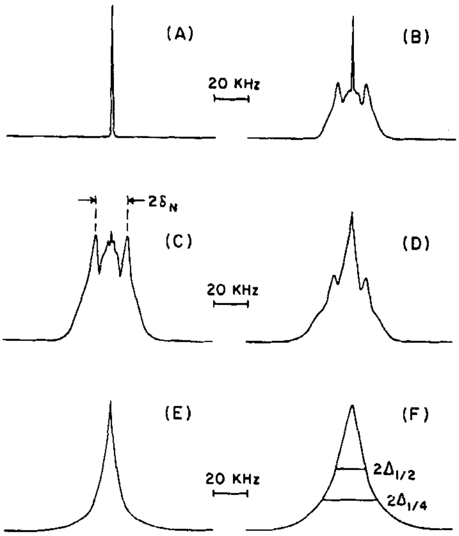


FIGURE 1. Some representative line shapes of DDA9-L obtained on cooling A) isotropic phase at 147°C, B)N+I biphase at 129°C, C) macroscopically aligned nematic phase at 110°C, D) transition spectrum at 85°C, E,F) solid phase at 78°C and 40°C (from [5]).

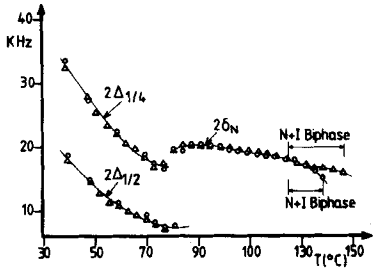


FIGURE 2. Spacings $2\delta_N$ and line widths at a quarter and half height $2\Delta_{1/4}$ and $2\Delta_{1/2}$, as a function of temperature on cooling : Δ : DDA9-L ; O : DDA9-L II (from [5]).

The corresponding nematic fraction f_N and order parameter S are plotted in fig. 3. These results show that : (i) the samples are macroscopically aligned in the nematic phase ; (ii) this macroscopic alignement is destroyed in the solid phase although no drastic changes in the time scale of the molecular motion seem to occur at the transition ; (iii) the width of the N + I range is larger for DDA9-L than for DDA9-L II ; (iv) the order parameter is larger for DDA9-L than for DDA9-L II in the N + I biphase, but is smaller in the pure nematic phase, and exhibits undulations. Points (iii) and (iv) seem to indicate that in the N + I biphase, the nematic phase is enriched with the longest species and the isotropic phase with the shortest ones [9].

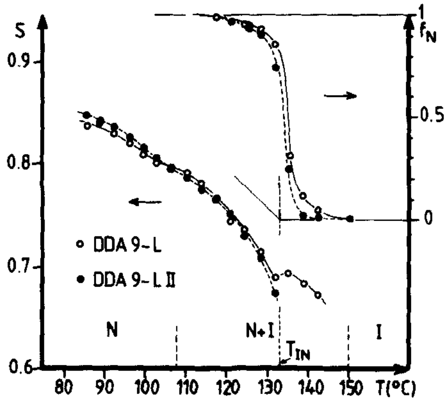
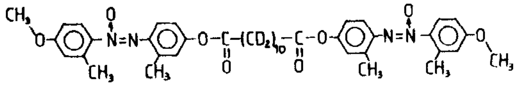


FIGURE 3. Nematic order parameter S and nematic fraction f_N obtained on cooling for DDA9-L and DDA9-L II. T_{IN} is the isotropic-nematic transition measured by DSC (from [9]).

Let's discuss in more detail these past points. Landau-de Gennes' theory predicts that for nematic systems composed of semi-flexible polymers, both the isotropic-nematic transition temperature T_c and the order parameter at the transition S_c increase with molecular mass before levelling off [10]. This trend is indeed observed for our compounds, as $\bar{x}$ is varied [5]. If we assume that, as the temperature is lowered from the isotropic phase into the N + I biphase, the molecules are transferred into the nematic phase sequentially in order of decreasing chain length, one can consider that the average molecular weight of the nematic component decreases. This may explain the undulation observed for DDA9-L around T_{IN}[9]. Indeed, around this temperature the nematic 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, which is not compensated by the natural increase produced by 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 transferred into the nematic phase. The larger $\bar{x}$ value of DDA9-L II explains that in the pure nematic phase, S is slightly higher than for DDA9-L. The experiment has been repeated with a different thermal history. The values of T_{IN} and S are slightly changed, but the main phenomenon (undulation of S around T_{IN} is preserved.

Model compound 9DDA9-S d20

The compound studied has the following chemical formula



It can be considered as the shortest oligomer of the DDA9 series, inasmuch as the spacer group is doubly linked (constrained at both ends), which allows intramolecular correlation between mesogens. We know from investigation of odd-even effects in this series of polymers[4] [19] that the orientational order of the mesogen is imposed via the spacer. Indeed, entropy of isotropisation and nematic order parameter of model 9DDA9, though lower than in polymer DDA9, are significantly higher than in LMM nematics [5].

Model 9DDA9 is a monotropic nematic : K 110 I (I 99 N 85 K) [11] which although pure, displays a narrow but definite N + I biphase on cooling from the isotropic phase. This might indicate that the system is very sensitive to trace impurities, as it is the case of plastic crystals, for example [12].

Figs 4a and 4b show typical proton and deuterium spectra of model compound 9DDA9-S d20.

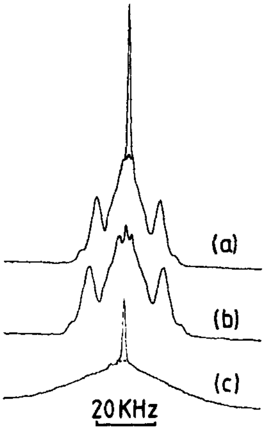


FIGURE 4a. PMR spectra of 9DDA9-S d20 obtained on cooling a) N + I biphase at 95°C, b) macroscopically aligned nematic phase at 78.5°C, c) crystalline + amorphous (K + A) biphase at 71.5°C. The separation between sharp and broad components is indicated in spectra a) and c).

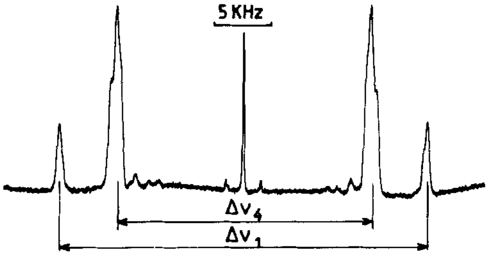


FIGURE 4b. DMR spectrum of 9DDA9-S d20 in the N + I biphase. The central sharp line corresponds to the isotropic phase.

Figs 5a and 5b represent the fraction f of broad component (to be identified in the N + I biphase with the nematic fraction f_N) versus temperature. For proton NMR, (fig. 5a) the experiment was performed first by heating the sample. It is observed that the transition to the isotropic phase occurs by continuous transformation of the crystalline component into the amorphous (isotropic) component (K + A biphase). The nematic to solid transition is characterized by the reappearance of the sharp (amorphous) component. The system seems to be reversible in the solid phase since the same spectra are obtained on cooling and on heating.

A similar behaviour is obtained with the deuterium spectra (fig. 5b). The reappearance of the sharp component at the nematic-solid transition is more spectacular in this case than for PMR. The fact that f is found to be the same in the PMR and DMR experiments is a proof that the sharp and broad components of the solid spectra do correspond to molecules in different phases and not to different parts of the molecules with different mobilities in an homogeneous phase.

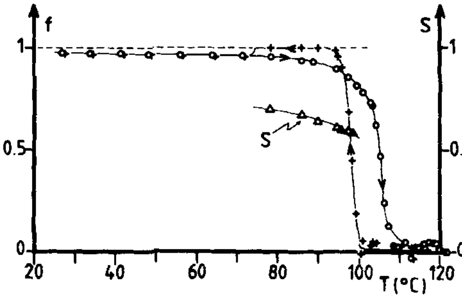


FIGURE 5a. Left hand scale : fraction f of the total intensity contained in the broad component of the PMR spectra of 9DDA9-S d20 : O, obtained on heating ; +, obtained on cooling ; right hand scale : nematic order parameter S.

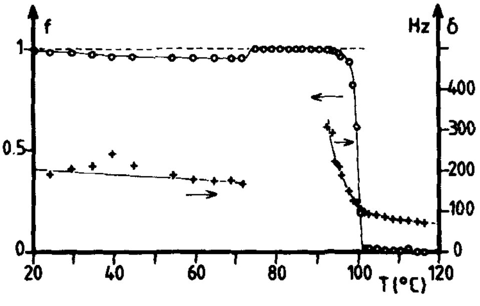


FIGURE 5b. Left hand scale : idem as in fig. 5a for the DMR spectra on cooling ; right hand scale : full width at half maximum δ of the sharp (isotropic and amorphous) component.

Other quantities could be measured (i) the order parameter S was deduced from the PMR spectra as for DDA9-L (cf sect. 2a) and the result is shown in fig. 5a. (ii) the width δ of the sharp component in the I, N + I and K + A phases was measured in the DMR experiment, and is plotted in fig. 5b. It is seen that in the isotropic (I) and amorphous (A) phases, this width varies very little with temperature. This is to be contrasted with what is observed in the N + I biphase where this width seems to diverge. This last phenomenon is presumably caused by order parameter fluctuations which are also responsible for the divergence of the induced magnetic birefringence (Cotton-Mouton effect)[13] [14] as the isotropic-nematic transition is approached. The originality of 9DDA9 compared to LMM nematics is that the effect is amplified and can be followed in the N + I biphase.

Conclusion

As a conclusion of this section, it thus appears that these nematic polymers as well as the model compound exhibit phase situations which are significantly different from LMM nematics : existence of biphases, importance of thermal history, relatively high order parameter... However, in some other respects they are similar to LMM nematics : order parameter fluctuations in the isotropic phase ; very similar line shapes in the nematic phase. In the next section, we discuss in more detail the line shape problem in terms of molecular properties.

NMR : LINE SHAPE ANALYSIS AND TEMPERATURE DEPENDENCE

Proton NMR

The proton NMR spectrum of polymer DDA9-L in the macroscopically aligned nematic phase is shown in fig. 1c (see also fig. 7a). This spectrum is similar to those of LMM nematics and has been simulated in [7] using an approximate method. Contributions of the mesogenic units and of the spacers are pictured in fig. 6.

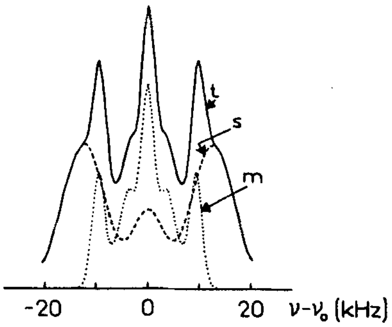


FIGURE 6. Simulation of the PMR spectrum of DDA9-L and decomposition into its mesogenic unit (m) and spacer (s) components (from [7]).

The two peaks at ∿ ± 10 KHz mainly correspond to dipole-dipole interaction between ortho-protons of the rings while the ring methyl groups are mainly responsible for the two shoulders at ± 5 KHz. The two broad shoulders on the external parts of the spectrum should be, on the other hand, mainly attributed to the spacers in a rather extended conformation. The best fits are obtained assuming a mean dihedral angle between the two rings of ∿ 36° . A simple relation between order parameter S of the mesogenic units and the main splitting $2\delta_N$ could be obtained from the study, namely

$$2\delta_N/\mathrm{KHz} \approx 24.08\ S \qquad (1)$$

This relation was used to calculate all the order parameter values of section 1. This analysis of the PMR spectra of DDA9-L is supported by recent measurements on compounds selectively deuterated in the spacers. Fig. 7a and 7b show the spectra of DDA9-L and of a similar compound deuterated on the spacer (DDA9-E d20). It is seen that the two external shoulders have disappeared in spectrum 7b. This is a direct proof that they are due to the spacers in spectrum 7a. In the same manner, the PMR spectrum of model compound 8DDA8 (similar to 9DDA9 but without the ring methyl groups) show that the shoulders at ± 5 KHz in fig. 6 are indeed mainly due to these methyl groups [15].

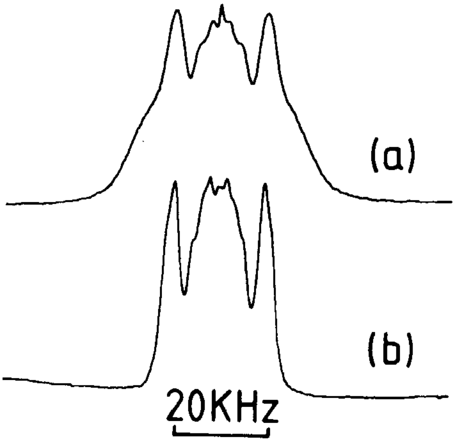


FIGURE 7. PMR spectra of DDA9-L (a) and DDA9-E d20 (b) corresponding to the same degree of order. Note the absence of external wings due to the spacer in spectrum (b).

Deuterium NMR

The deuterium NMR study of DDA9-E d20 is published in [16]. Here we shall present results obtained with 9DD9-S d20. The molecular information is contained in the values and temperature dependence of the various splittings $\Delta\nu_i$ associated with the CD_i bonds of the spacer. As seen in fig. 4b one observes practically only two doublets $\Delta\nu_1$ and $\Delta\nu_4$ with relative intensities 1 to 4. Doublet $\Delta\nu_1$ clearly corresponds to the methylene groups adjacent to the mesogens and $\Delta\nu_4$ to all the other methylene groups of the spacer, which necessarily have nearly the same "orientational order". This is possible only if the long molecular axis is a symmetry axis for the mean conformation of the spacer. Let's discuss these data in more detail. Assuming uniform rotation around the long axis Oz_o, the splitting $\Delta\nu_i$ associated with bond CD_i is given by

$$\Delta\nu_i = \frac{3}{2}\,\frac{e^2q_iQ}{h}\,S\,|\langle P_2(\cos\beta_i)\rangle| = \frac{3}{2}\,c_i S\,|s_i| \qquad (2)$$

where β_i is the angle (CD_i, Oz_o) and the brackets stand for an average over the internal rotations. With c_i = 172 KHz and using the values of S measured by PMR (fig. 5a), one can deduce $|s_1|$ and $|s_4|$. The result is shown in fig. 8 and calls for the following comments :

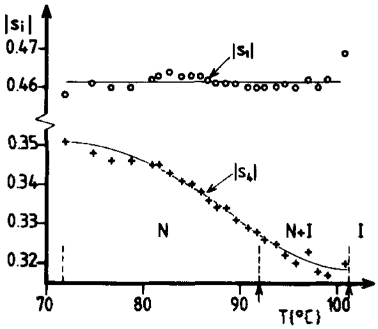


FIGURE 8. Internal order parameter $|s_i| = |\langle P_2(\cos\beta_i)\rangle|$ as defined in Eq. (2) versus temperature for 9DDA9-S d20. $|s_1|$ corresponds to the methylene groups attached to the rings, and $|s_4|$ to the other methylene groups of the spacer.

(i) $|s_i|$ is found to be independent of temperature. This means that the first methylene groups have always the same mean orientation with respect to the mesogenic units, and in this respect, they should be considered as part of them. From $|s_1| \approx 0.46$, we deduce that the CD_1 bonds are in average nearly perpendicular to the long axis since $|s_1| = 0.5$ for $\beta_i = 90°$.

(ii) $|s_4|$ is found to decrease with increasing temperature. This means that the amplitude of the rotational fluctuations around the various CC bonds in the spacer increase, with some tendency to level off in the N + I biphase. In other words, the spacer disorders "faster" than the aromatic core. More detailed analysis of these DMR data requires modelisation of the internal motions in the spacer. A model is proposed in [16] where similar results have been found. Other descriptions are possible, but will not be discussed here.

In conclusion to this section, PMR and DMR lineshape analysis show that, in the nematic phase, the degree of order of the mesogenic groups of DDA9 compounds is rather high and the spacers are in a rather extended conformation. This is consistent with a picture where the polymers are stretched with no or a very small number of defects [2]. However, the molecular motions are fast, in agreement with the fluid and/or soft character of these mesophases.

DDA9-L/PAAd14 MIXTURES

In addition to the pure systems, mixtures of polymer DDA9-L with perdeuterated para-azoxyanisole (PAAd14) where studied by PMR and DMR. The two compounds are miscible in all proportions in the nematic, N + I and isotropic phases. The order parameter S and nematic fraction f_N were measured by PMR by looking at the polymer, and by DMR by looking at PAAd14.

The PMR lineshapes of DDA9-L have the same general shape shown in fig. 1 for all concentrations studied (down to 5 % weight polymer). The order parameter $S^{DDA9-L}_{Solution}$ and the nematic fraction $f^{DDA9-L}_{N_{Solution}}$ were measured in the same manner as for the pure compound. Fig. 9 shows typical DMR spectra of PAAd14 for two concentrations and in the pure nematic phase.

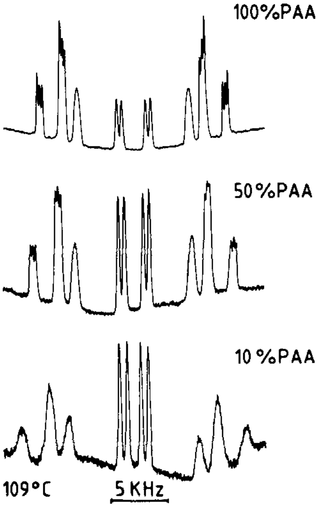


FIGURE 9. DMR spectra of PAAd14 in the nematic phase for the pure compound and dissolved in DDA9-L. Percentages are by weight. Experimental conditions are the same.

The spectra in solution resemble those of pure PAAd14. The main difference is that the fine structure is less resolved for small PAA concentrations, although the overall spectra are wider. The order parameter $S^{PAA}_{Solution}$ was deduced from these spectra according to a method developped by us [17] which turns out to yield the generally accepted values[18] for pure compound. The nematic fraction $f^{PAA}_{N_{Solution}}$ was also measured in the usual way. If the measurements are made by cooling after equilibrating at the same temperature ($\sim$150°C) in the PMR and DMR experiments, we find that $f^{PAA}_{N_{Solution}} = f^{DDA9-L}_{N_{Solution}}$ at least at low concentration of PAAd14. This means that PAA has the same solubility in the nematic and in the isotropic phases of DDA9-L. This is illustrated in fig.10 for 10% by weight PAA. Concerning order parameters, fig. 11 shows the results for the same 10% concentration, as well as the values for the pure compounds for comparison. It is observed that in the homogeneous nematic phase, $S^{PAA}_{bulk} < S^{PAA}_{Solution} \approx S^{DDA9-L}_{Solution} < S^{DDA9-L}_{Bulk}$. In the N + I biphase however, $S^{PAA}_{solution}$ is smaller than $S^{DAA9-L}_{Solution}$, but tends to $S^{DDA9-L}_{Solution}$ as $f_N \rightarrow 0$. The observed re-increase of $S^{PAA}_{Solution}$ around 135°C is to be related with the undulations of S observed for pure DDA9-L (fig. 3) and might indicate that the longest molecules, which are selectively transferred to the anisotropic phase at the I → I + N transition, favor nematic ordering of PAA. At low polymer concentration, the biphasic range becomes very small and the order parameter of DDA9-L has the same temperature dependence as that of pure PAA.

Information concerning the molecular properties of the polymer and of PAA can also be extracted from the spectra. Fig. 12 represents the variation of the ratio ρ of the width at 2/5 of maximum as defined in the inset to the main splitting $2\delta_N$, for DDA9-L and for 50% and 5% DDA9-L in PAA. As explained in section 3a, $2\delta_N$ pictures the order of the mesogenic units while $2\delta_{2/5}$ is rather linked to the order of the spacers. It is seen that ρ decreases with increasing temperature, showing that the spacer disorders faster as the nematic-isotropic transition is approached (the same

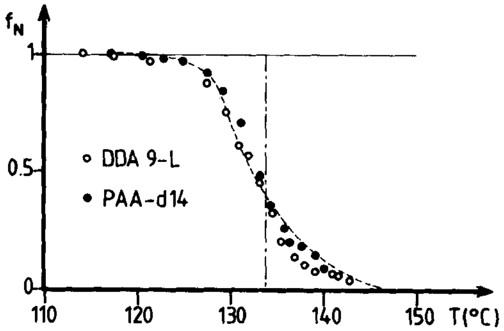


FIGURE 10. Nematic fraction f_N in the N + I biphase for the 90 % DDA9-L/10 % PAAd14 mixture, obtained by cooling from the isotropic phase : 0 : measured by PMR using DDA9-L spectra ; ● : measured by DMR using PAAd14 spectra. The dashed line is the curve for pure DDA9-L and the vertical line pictures the isotropic-nematic transition of PAAd14.

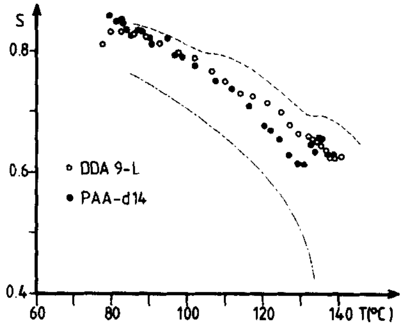


FIGURE 11. Nematic order parameter S for the 90 % DDA9-L/ 10 % PAAd14 mixture, obtained by cooling from the isotropic phase : 0 : deduced from the PMR spectra of DDA9-L ; ● : deduced from the DMR spectra of PAAd14. The dashed line is the curve for pure DDA9-L and the dashed-dotted line for pure PAAd14.

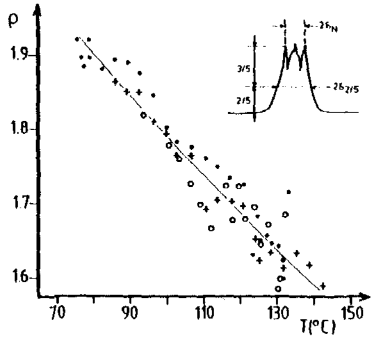


FIGURE 12. Ratio $\rho = 2\delta_{2/5}/2\delta_N$ as defined in the inset on the PMR spectra of DDA9-L : + : pure compound ; : 50 % DDA9-L in PAAd14 ; 0 : 5 % DDA9-L in PAAd14.

trend was found for model compound 9DDA9-Sd20), but this effect is independent of PAA concentration within experimental accuracy. This shows that the temperature dependence of the relative order of the two moities depends little on the nature of the nematic medium in which they are inbedded. This effect should show up more neatly in DMR using polymers with deuterated spacers. In this case, we expect that for all compositions, $|s_4|$ (cf. fig. 4) behaves similarly versus temperature.

Concerning PAA, using the model developped in [17] for bulk PAA, it can be shown that the mean conformation and/or degree of uniformity of the internal rotations in the mixtures are different compared to the bulk. The results of this analysis will be presented elsewhere[20].

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REFERENCES

1. a) "Liquid Crystalline Order in Polymers" Ed. A. Blumstein, Academic Press (1978)
   b) "Mesomorphic Order in Polymers". Ed. A. Blumstein, ACS Symposium Series 74 (1978).
   c) "Polymer Liquid Crystals" Ed. A. Ciferri, W.R. Krigbaum and R.B. Meyer, Academic Press (1982)
   d) "Developments in Oriented Polymers", 1, Ed. I.M. Ward, Applied Science Publishers (1982)
   e) Proceedings of Symposium on Polymeric Liquid Crystals, Washington (1983), Ed. A. Blumstein, Plenum Press (in press).
   f) Proceedings of the ESF Sixth Polymer Workshop, Lyngby (1983), Ed. L.L. Chapoy, Elsevier Science Publisher (in press).
2. A. Blumstein and S. Vilasagar, Mol. Cryst. Liq. Cryst. (Letters) 72, 1 (1981).
3. A. Blumstein, S. Vilasager, S. Ponrathman, S.B. Clough, G. Maret and R.B. Blumstein, J. Polym. Sci., Polym. Physics Ed. 20, 877 (1982).
4. A. Blumstein and O. Thomas, Macromolecules 15, 1264 (1982).
5. R.B. Blumstein, E.M. Stickles, M.M. Gauthier, A. Blumstein and F. Volino, Macromolecules, 17, 2, 177 (1984).
6. F. Volino, A.F. Martins, R.B. Blumstein and A. Blumstein, J. Physique (Lettres) 42, L-305 (1981)
7. A.F. Martins, J.B. Ferreira, F. Volino, A. Blumstein and R.B. Blumstein, Macromolecules, 16, 279 (1983)
8. R.B. Blumstein, A. Blumstein, E.M. Stickles, M.D. Poliks, A.M. Giroud and F. Volino, Polymer Preprints, 24, 2, 275 (1983).
9. F. Volino, J.M. Allonneau, A.M. Giroud-Godquin, R.B. Blumstein, E.M. Stickles and A. Blumstein, Mol. Cryst. Liq. Cryst.(Letters) 102, 21 (1984).
10. A. Ten Bosch, P. Maissa and P. Sixou, J. Physique (Lettres) 44, L-105 (1983) ; J. Chem. Phys., 79, 3462 (1983)

11. M.D. Poliks, Masters'Thesis, University of Lowell, Lowell (Mass.) (1983)
12. See eg. P. Bladon, N.C. Lockhart and J.M. Sherwood, Mol. Cryst. Liq. Cryst., 19, 315 (1973).
13. G. Maret, F. Volino, R.B. Blumstein, A.F. Martins, A. Blumstein, Proc. 27th Int. Symp. Macromolecules Strasbourg (1981).
14. G. Maret, Polymer Preprints, 24, 2, 249 (1983)
15. R.B. Blumstein, M.D. Poliks, E.M. Stickles, A. Blumstein and F. Volino, A.C.S. Meeting, St-Louis (1984).
16. E.T. Samulski, M.M. Gauthier, R.B. Blumstein and A. Blumstein, Macromolecules, 17, 479 (1984).
17. A.J. Dianoux, J.B. Ferreira, A.F. Martins, A.M.Giroud and F. Volino, Mol. Cryst. Liq. Cryst. (to be published)
18. E.G. Hanson and Y.R. Shen, Mol. Cryst. Liq. Cryst., 36, 193 (1976).
19. A. Blumstein, R.B. Blumstein, M.M. Gauthier, O. Thomas and J. Asrar, Mol. Cryst. Liq. Cryst. (Letters) 92, 87 (1983).
20. F. Volino, A.M. Giroud, A.J. Dianoux, R.B. Blumstein and A. Blumstein, Proceedings of the 10th Liquid Crystal Conference, York (1984).