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F. Volino [a] , A. M. Giroud [a] , A. J. Dianoux [b] , R. B. Blumstein [c] & A. Blumstein [c]

[a] Centre d'Etudes Nucléaires de Grenoble, Département de Recherche Fondamentale, 85 X, 38041, Grenoble, France

[b] Institut Laue Langevin, 156 X, 38042, Grenoble, Cédex, France

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

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Deuterium Magnetic Resonance Study of Perdeuterated Para-Azoxy-Anisole in Solution in a Linear Nematic Polymer†

F. VOLINO‡ and A. M. GIROUD§

Centre d'Etudes Nucléaires de Grenoble, Département de Recherche Fondamentale, 85 X, 38041 Grenoble, France

A. J. DIANOUX

Institut Laue Langevin, 156 X, 38042 Grenoble Cédex, France

R. B. BLUMSTEIN and A. BLUMSTEIN

Department of Chemistry, Polymer Science Program, University of Lowell, MA 01854 (USA)

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A deuterium magnetic resonance (DMR) study of perdeuterated para-azoxy-anisole (PAAd14) in solution in the linear nematic thermotropic polymer DDA9-L is presented. Three concentrations are considered: 5%, 10%, 50% by weight. Information on the nature of the various phases formed with the PAA/DDA9-L mixtures is deduced from the shape of the DMR spectra. Information concerning the molecular structure, conformation and orientational order of PAA is deduced from the temperature and concentration dependence of the six quadrupolar splittings, by means of a model previously used for bulk nematic PAAd14. It is found that in the mixtures, the nematic order parameter of PAA is higher, and the molecular conformation slightly different, than in bulk. It appears that PAAd14 dissolved at low concentration (≤10% w/w) is a good DMR spin probe for the study of the DDA9 systems.

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‡Member of CNRS, Equipe de Physico-Chimie Moléculaire, Service de Physique.
§Member of CNRS, LA321.

1 INTRODUCTION

Mixtures of liquid crystals, either monomeric or polymeric, are of great theoretical and practical interest. A few years ago, a spin one-half, spin-one lattice gas model was introduced to represent liquid crystal mixtures, and a large variety of temperature-concentration phase diagrams were predicted.[1] More recently, a different approach combining the Maier-Saupe theory of the nematic-isotropic transition and the Flory-Huggins theory of mixtures has been developed in three different situations, namely $(M_A + M_B)$, $(M_A + P_A)$ and $(P_A + P_B)$, where M and P stand for low molecular mass and polymeric nematics, respectively.[2] The morphology of the phase diagrams is found to be very similar as in Reference 1, but in addition, predictions concerning the order parameters S_A and S_B of the two species have been made. Thus, measurement of these quantities in relevant situations should be helpful. On the other hand, information on the molecular structure, conformation and nature of the internal motions is also of interest.

Recently, we have undertaken an NMR study of mixtures of the thermotropic polyester[3,4] poly(4-4′-dioxy-2,2′ dimethylazoxybenzene dodecanedioyl), DDA9-L, with the low molecular mass nematic para-azoxy-anisole, PAA. In order to study separately the molecular properties of DDA9-L and of PAA, fully deuterated PAA (PAAd14) is used. In this way information concerning DDA9-L and PAA can be obtained by proton magnetic resonance (PMR) and deuterium magnetic resonance (DMR), respectively. In this paper, we present DMR data concerning three mixtures, namely 5%, 10% and 50% w/w PAAd14 in DDA9-L, and their analysis in terms of orientational order, structure and conformation of the PAA molecule. Similar results concerning DDA9-L obtained by PMR and their comparison will be presented in a forthcoming paper.

In section 2, we summarize the current knowledge about pure DDA9-L and pure PAAd14. In section 3, we present the phase diagram for the mixtures. We show DMR spectra of PAAd14 corresponding to typical points of this phase diagram and give the temperature and concentration dependences of the various splittings. These data are analysed in section 4 in terms of a model developed by us[5] for the pure sample. The values of the order parameter and of some conformational averages are deduced. It is shown that this model can explain self-consistently all the data if one assumes very slight changes of the molecular structure with concentration. Besides the information concerning molecular properties of PAA of the mix-

tures, it is shown that these results also provide a further support for the model used to analyse the corresponding DMR data.

2 PRESENT KNOWLEDGE ABOUT DDA9-L AND PAAd14

2a DDA9-L

The chemical formula of polyester DDA9 is shown in Figure 1a. It is a linear polymer prepared by alternation of prolate and rather rigid mesogenic units similar to the aromatic core of low molecular mass liquid crystals, and flexible alkyl chains with ten methylene groups. These compounds exhibit broad nematic range at moderate temperatures. The various 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. In the particular case of DDA9-L, $\bar{x} \approx 10$ with a rather broad distribution, and $R \sim 1.5$. This system exhibits a nematic plus isotropic ($N + I$) biphase between the pure isotropic and pure nematic phase and a (soft) crystalline plus nematic ($K + N$) biphase in the solid state. The existence of such biphases, which is general for the DDA9 systems, is presumably linked to a large extent to the distribution of molecular lengths and on the existence of several structural isomers. These systems have been characterized and studied by a number of

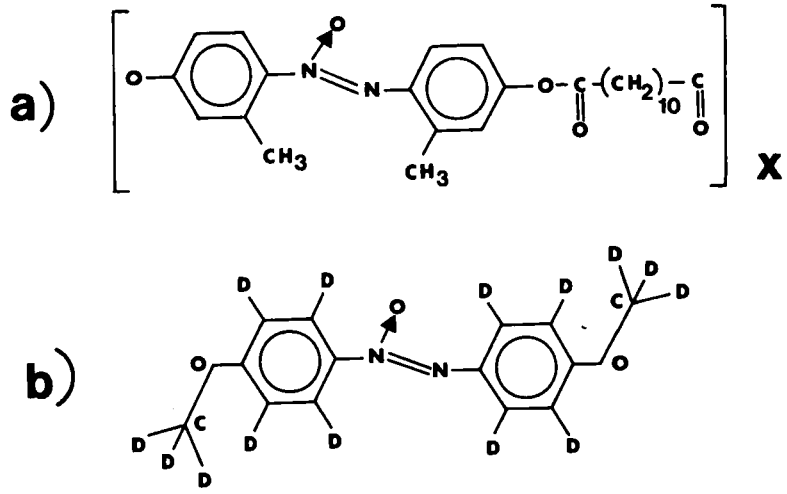

FIGURE 1 Chemical formulae of DDA9 polymer (a) and PAAd14 (b). The compound DDA9-L corresponds to $\bar{x} = 10$. Note the similarity between the aromatic cores of DDA9 and of PAA.

methods, including NMR[6-13] to which the reader is referred for details.

2b PAA

PAA is a well known low molecular mass nematic (*I* 136°*N* 89°*K*) which has been the subject of a considerable number of studies, in particular DMR studies (for a bibliographic review, see Reference 14). Recently, the interpretations of DMR data on liquid crystals have given rise to some controversy.[15-17] Very recently, we have developed a simple model which can explain self-consistently a large amount of the NMR data[5] on nematic PAA with results which are in complete agreement with results obtained by other methods. The physical quantities which have been extracted with this approach are the nematic order parameter, some conformational averages and structural angles, as well as their temperature dependence where relevant. We shall use this model to analyse the DMR data of PAAd14 in the mixtures with DDA9-L.

3 EXPERIMENTAL

3a Phase diagram

The phase diagram of DDA9-L/PAA system is presented in Figure 2. It has been established by differential scanning calorimetry (DSC) using a cooling rate of 10°C/min. Both compounds appear to be soluble in all proportions in the isotropic and nematic phases. It is observed that the (N + I) and (K + N) biphases of pure DDA9-L are also found in the mixtures. This phase diagram cannot be directly compared with the theory[1,2] since DDA9-L is not, strictly speaking, a one component system due to the distribution of molecular lengths and existence of structural isomers. For this reason and because our purpose is rather to describe the molecular properties of PAA in the mixtures, this aspect will not be discussed in this paper.

3b DMR data

DMR spectra were obtained using a pulsed Brücker NMR spectrometer WM 250 working at 38.4 MHz. Temperature homogeneity in the samples was estimated to be ~0.5°C. Spectra were taken after the samples had been equilibrated at 150°C in the isotropic phase during ~20 min and slowly cooled down to the required temperature in steps of 1 to 3°C. The experimental conditions were similar as those used in the experiment with pure PAAd14 described in Reference 5. Three concentrations were studied, namely 5%, 10% and 50% w/w

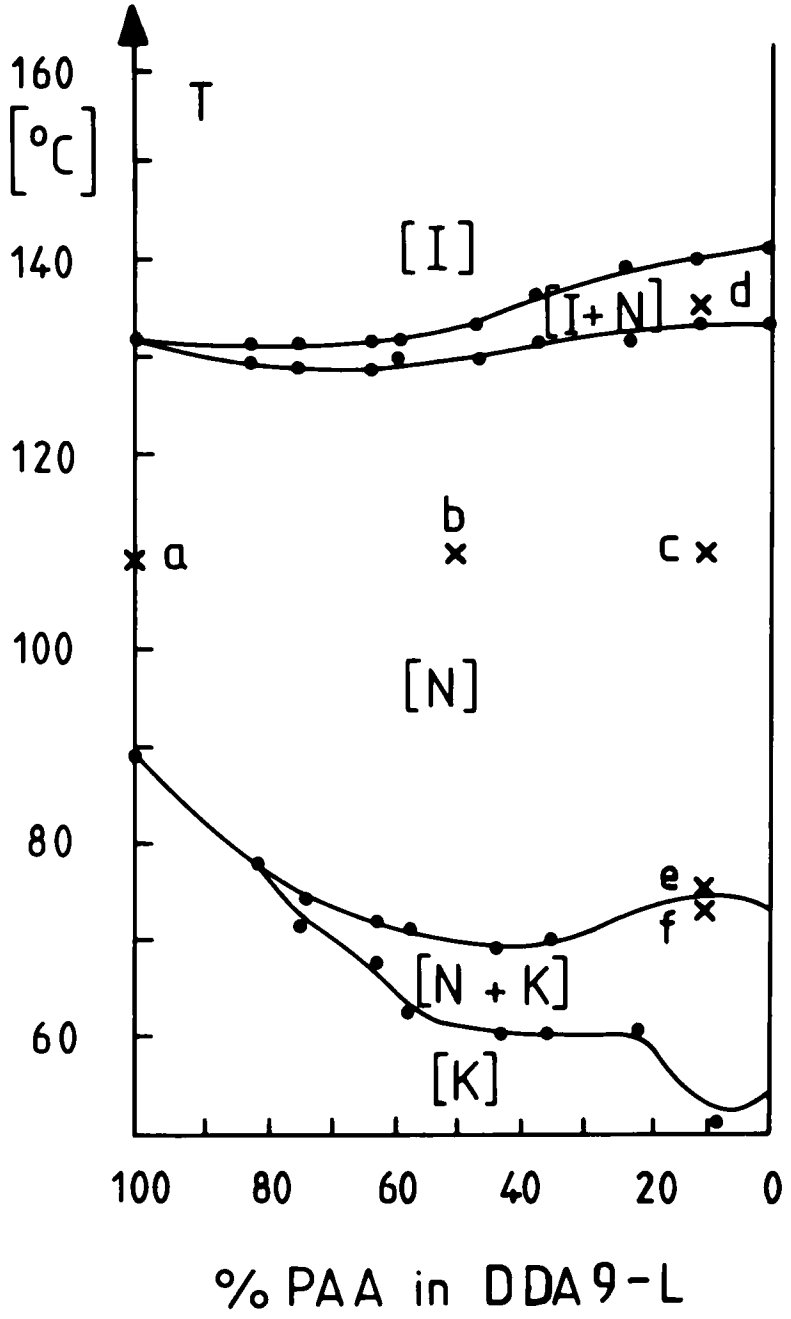

FIGURE 2 Phase diagram of the DDA9-L/PAA system established by DSC using a cooling rate of 10°/min. Concentrations are by weight/weight.

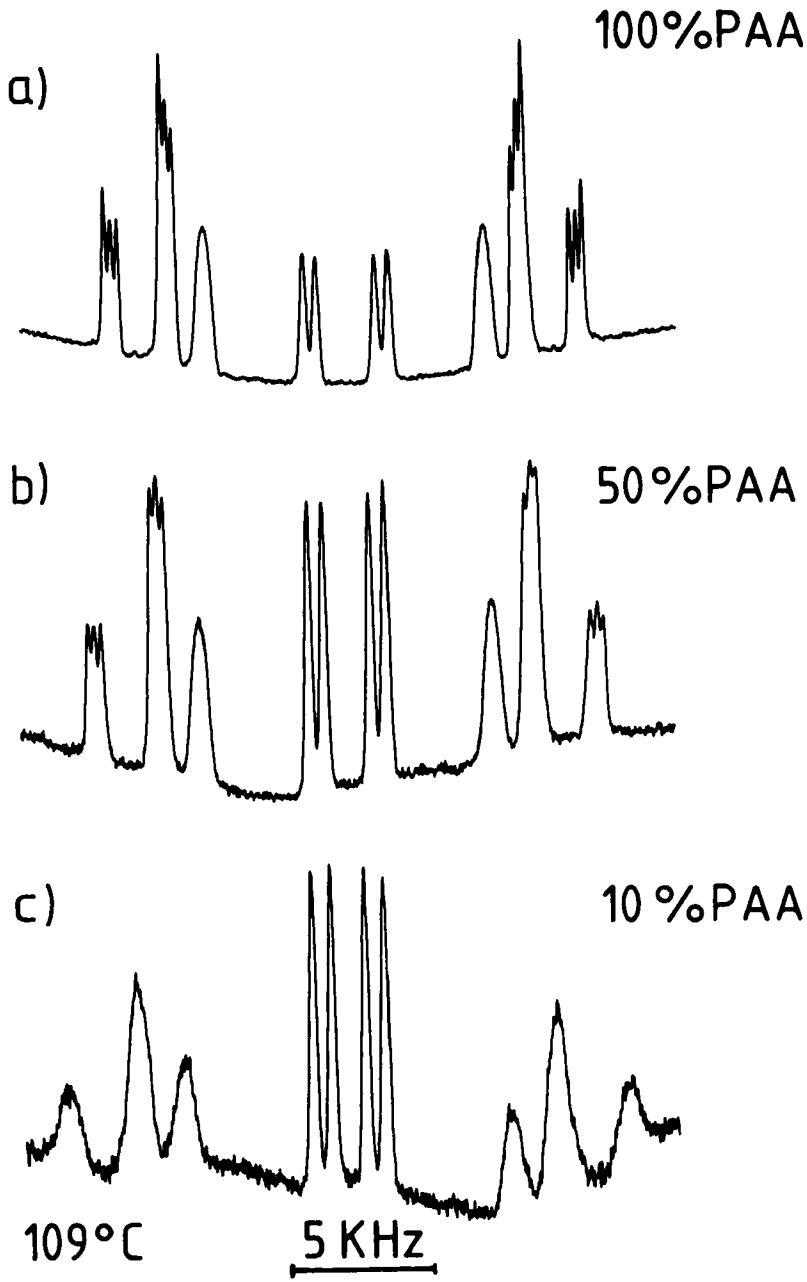

FIGURE 3a–f Typical 38.4 MHz DMR spectra of PAAd14 corresponding to various points of the phase diagram in Figure 2 as indicated by the label a to f. The repetition rate for recording spectra is 0.2 sec.

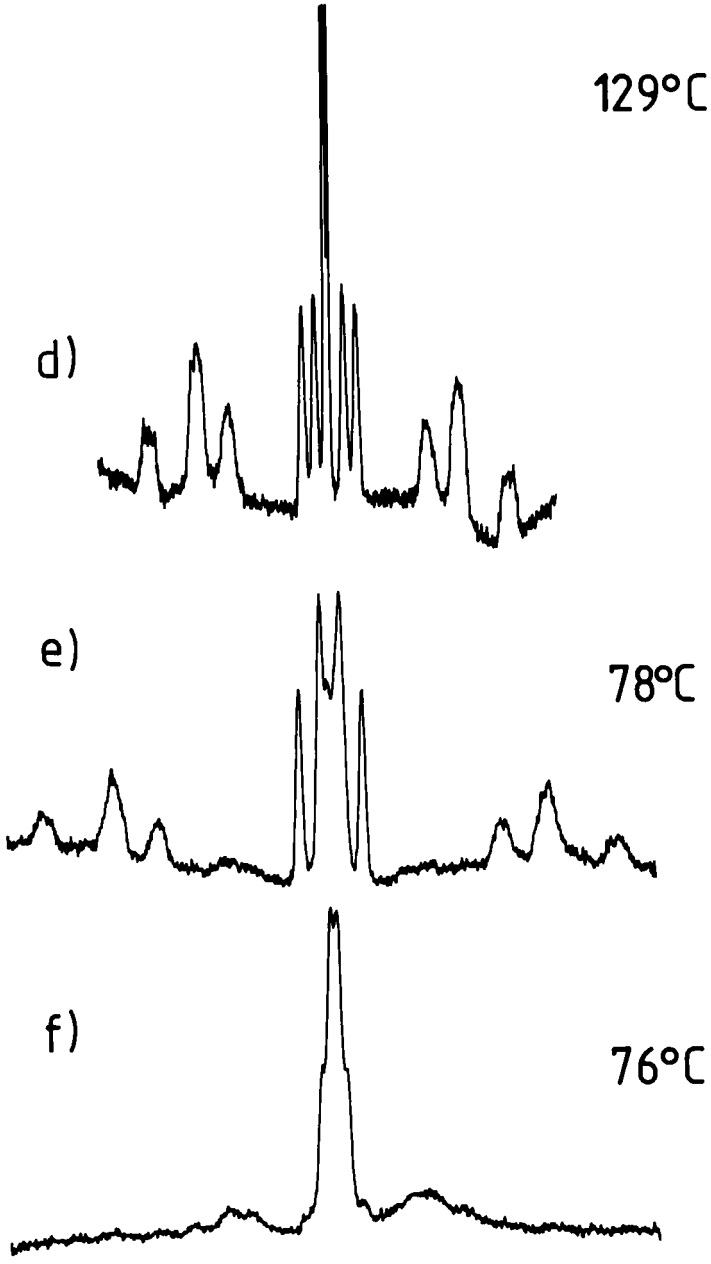

FIGURE 3a–f Continued

of PAAd14 in DDA9-L. Typical spectra corresponding to points a to f of the phase diagram (Figure 2) are shown in Figures 3a–f. Figure 3a, b, c shows how the spectra change with concentration at a fixed temperature in the pure N phase. As the PAA concentration decreases it is observed that (i) the overall breadth of the spectra increases suggesting an increase of the orientational order (ii) the spin-lattice relaxation time of the methyl deuterons decrease, suggesting a slowing down of the motion of these groups (cf. the intensity of the four central lines) and (iii) the spectra are less and less resolved. In Reference 11 it was suggested that the latter phenomenon may be related to segregation by molecular mass of the polymer into nematic regions with slightly different order parameters. Figure 3d shows a typical spectrum in the $N + I$ biphase. The central sharp line, which does not exist in the other spectra, corresponds to the PAAd14 molecules in the isotropic component of the biphase. The better resolution of the nematic part of this spectrum compared to spectrum 3c, which corresponds to the same concentration, is explained in the same way as above.[11] Figure 3e shows a spectrum just before the $N \rightarrow K + N$ transition, and Figure 3e just after this transition, where the fraction of K component is very small. It can easily be shown that if spectrum 3e corresponds to a nematic phase macroscopically aligned along the magnetic field, spectrum 3f corresponds to the same spectrum averaged over all orientations of the director with respect to the field. In other words, transition to the $N + K$ biphase destroys the macroscopic alignment of the nematic component. This result should be compared with a similar result[7,9] found by PMR with pure DDA9-L. This proves that PAAd14 dissolved at low concentrations can be considered as a good spin probe for studying this phenomenon in DDA9 polymers.

From intensity measurements, one can deduce the relative fraction of nematic and isotropic components in the $N + I$ biphase. Figure 4 shows the variation of the nematic fraction f_N^{PAA} with temperature for the three concentrations considered. It is seen that the sigmoidal shape of these curves does not allow a clear cut definition of the $I \rightarrow I + N$ and $I + N \rightarrow N$ transition temperatures. The observation that the width of the biphasic range increases with decreasing concentration is in agreement with the phase diagram in Figure 2. Moreover, the variations of f_N^{PAA} for 10% and 5% w/w are very similar to the same quantity f_N measured by PMR on the pure polymer.[7,11] This proves that, at least at low concentration, PAA has the same solubility in the nematic and isotropic components of the $N + I$ biphase of the polymer. Again this shows that PAAd14 is a good spin probe for this system.

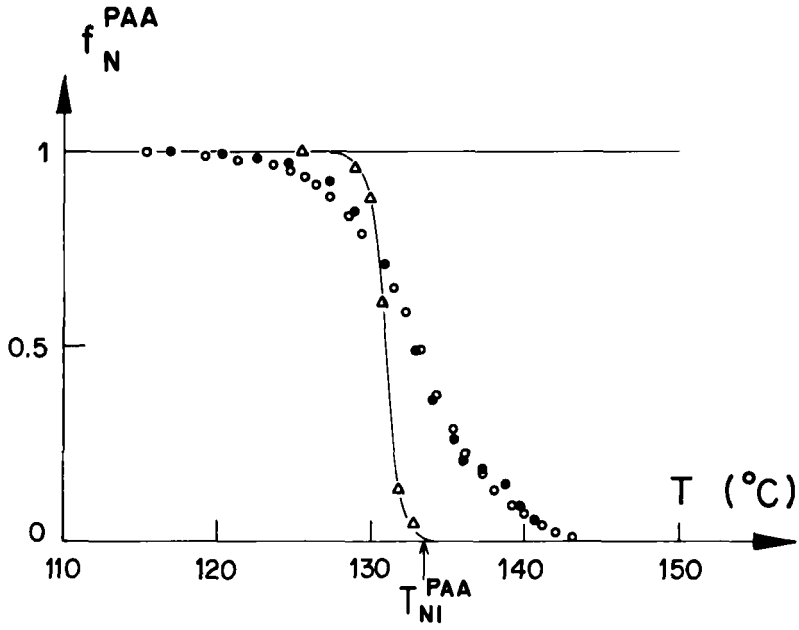

FIGURE 4 Fraction of PAAd14 molecules in the nematic component of the $N + I$ biphase of the mixtures, obtained by cooling from the isotropic phase: •: 5% w/w mixture, ○: 10% w/w mixture, △: 50% w/w mixture, T_{NI}^{PAA} is the clearing temperature of pure nematic PAA.

The information concerning the molecular properties of PAAd14 is contained in the values of the various quadrupolar splittings. Figure 5 extracted from Reference 5 shows the definition of the various splittings and their assignment to the different deuterons of the PAAd14 molecule. Figure 6a–e shows their variation with temperature for the three concentrations studied, and for pure PAAd14 for comparison. It is seen that the values and temperature dependences change significantly with concentration, in particular for the methyl deuterons. Analysis of these data in terms of molecular structure, conformation and orientational order of PAAd14 is the aim of the remainder of this paper.

4 ANALYSIS OF THE DMR DATA

4a The model

The model which will be used to analyse the various DMR splittings is described in Reference 5 to which the reader is referred for details.

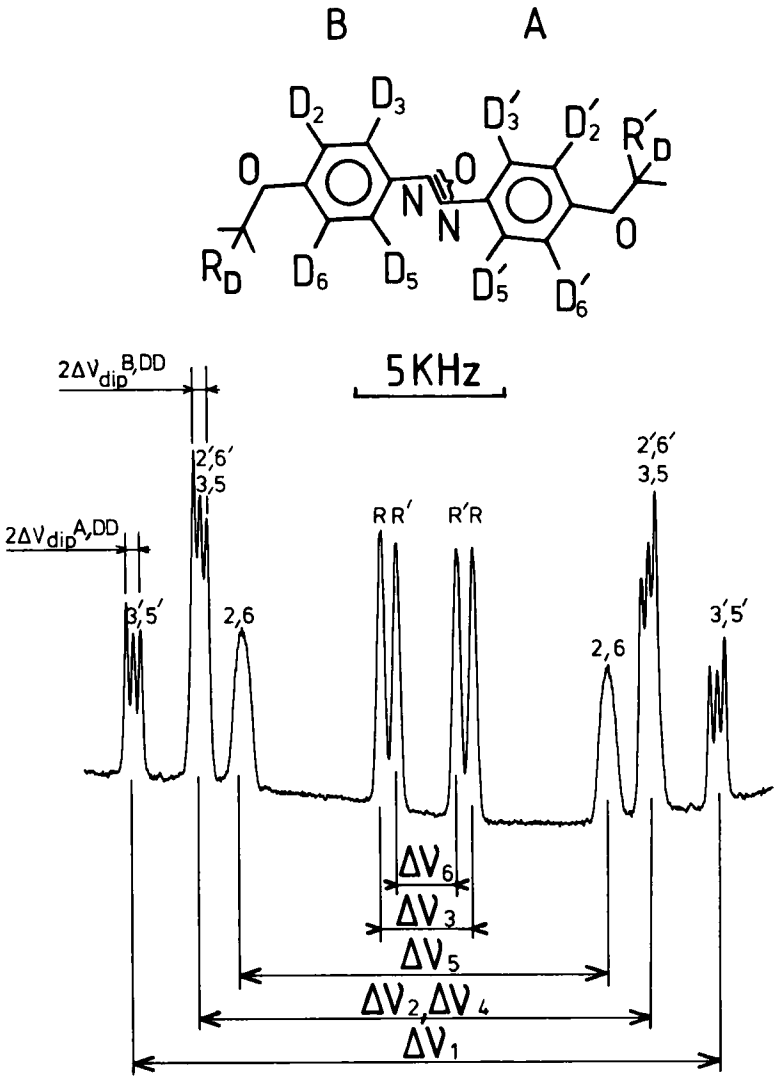

FIGURE 5 38.4 MHz DMR spectrum of PAAd14 in the supercooled nematic phase showing the assignment of the various lines to *A* and *B* anisole fragments and the definition of the various splittings (cf. Reference 5 for details).

Here we shall only summarize its main features and define the relevant parameters. In short, the molecular motions are split into external and internal components. We define the most probable molecular conformation as the conformation such as all the dihedral angles between the various molecular fragments correspond to min-

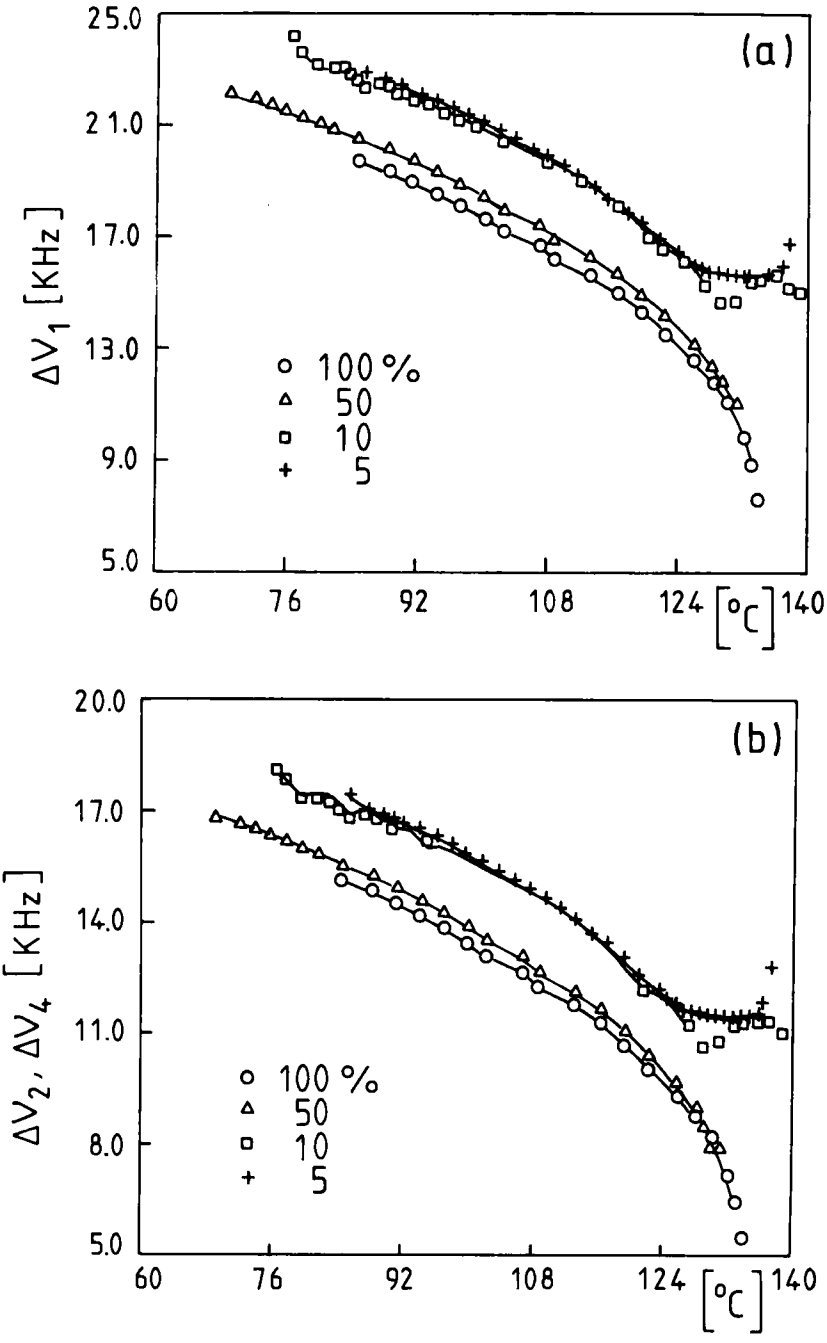

FIGURE 6

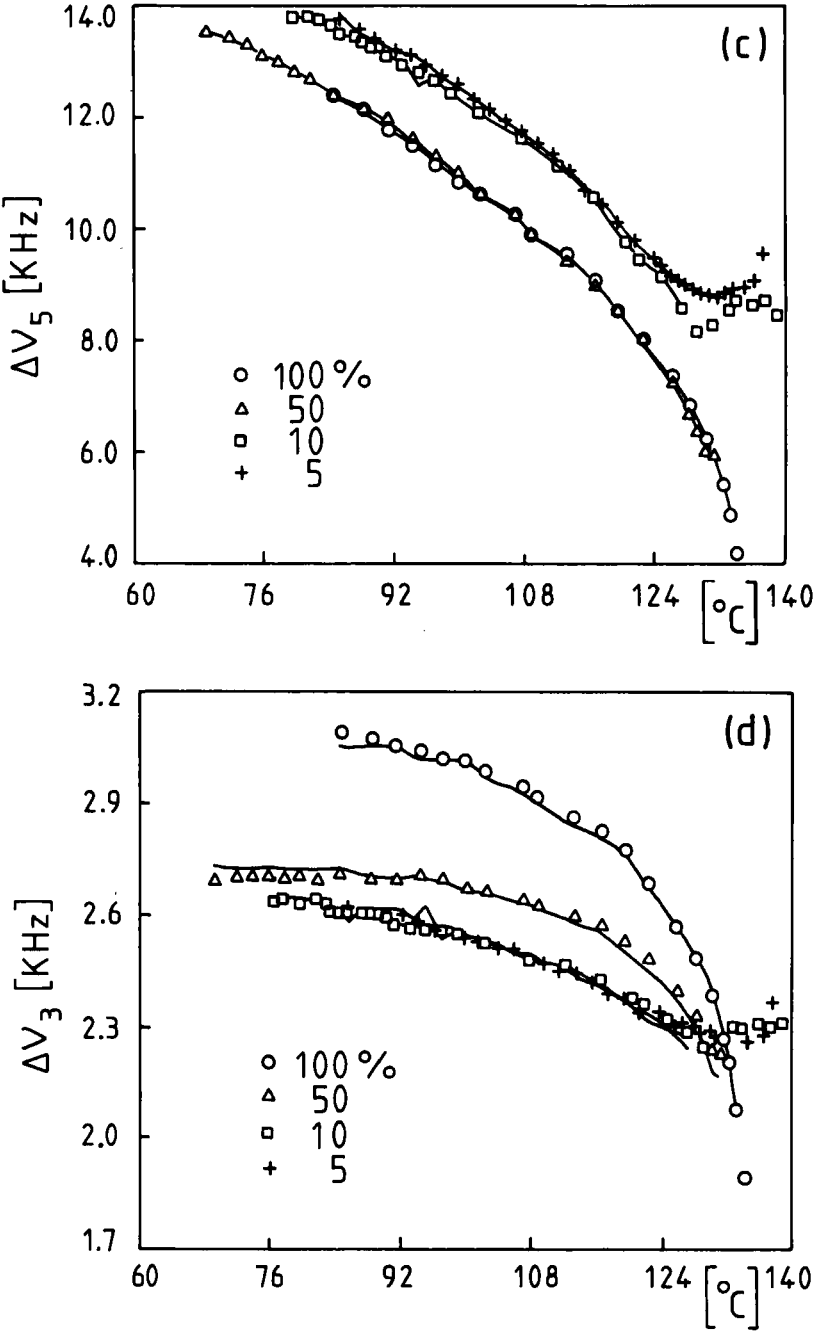

FIGURE 6 Continued

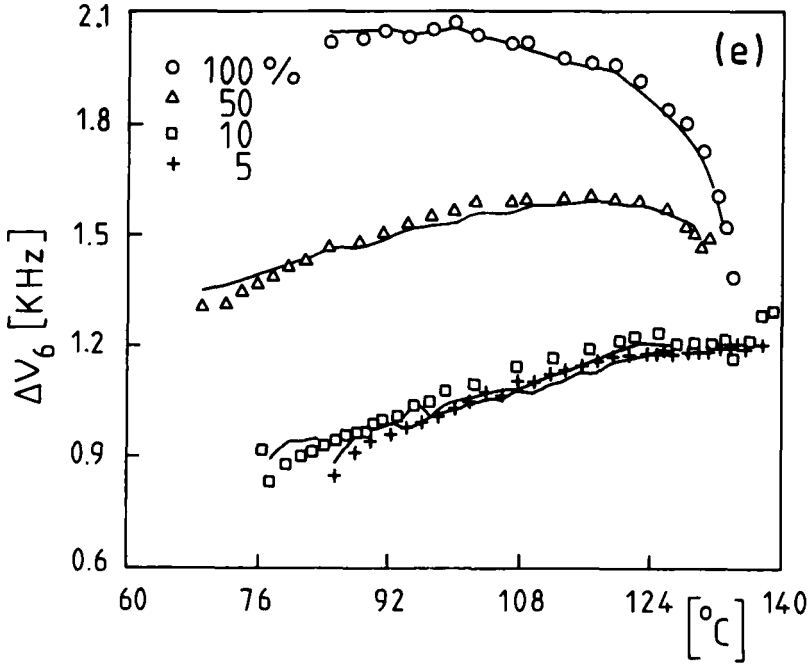

FIGURE 6 Temperature dependence of the various splittings as defined in Figure 5 for four concentrations as indicated. The data corresponding to 100% (bulk PAAd14) are those of Reference 5. The continuous (broken) lines correspond to calculated splittings using the values of the various parameters found in the fit.

ima of the potentials hindering the rotations around the single covalent bonds. We introduce a long molecular axis Oz_0 which can be identified with the local nematic director of the continuum theories of nematics. The external motions are described as uniform rotations of this most probable conformation around Oz_0 and fluctuations of Oz_0 about the macroscopic director (the static magnetic field of the NMR spectrometer). The internal motions are fast rotation of the methyl groups around their C_{3v} axis and rotation of the anisole moieties A and B (cf. Figure 5) as a whole around the N–ϕ bonds in potentials of C_{2v} symmetry. In addition, the phenyl rings also perform individual π flips. The time scale of thse various motions is discussed in Reference 5, but all are fast on the DMR time scale ($\sim 10^{-6}$ s).

The structural and conformational angles which are useful are shown in Figure 7a,b which sketches the lateral view of one anisole moiety in a planar conformation (a) and a view along the para-axes of the rings assumed to be parallel, of the most probable conformation (b). The long axis Oz_0 is defined by its polar and azimuthal angles (ϵ_A,

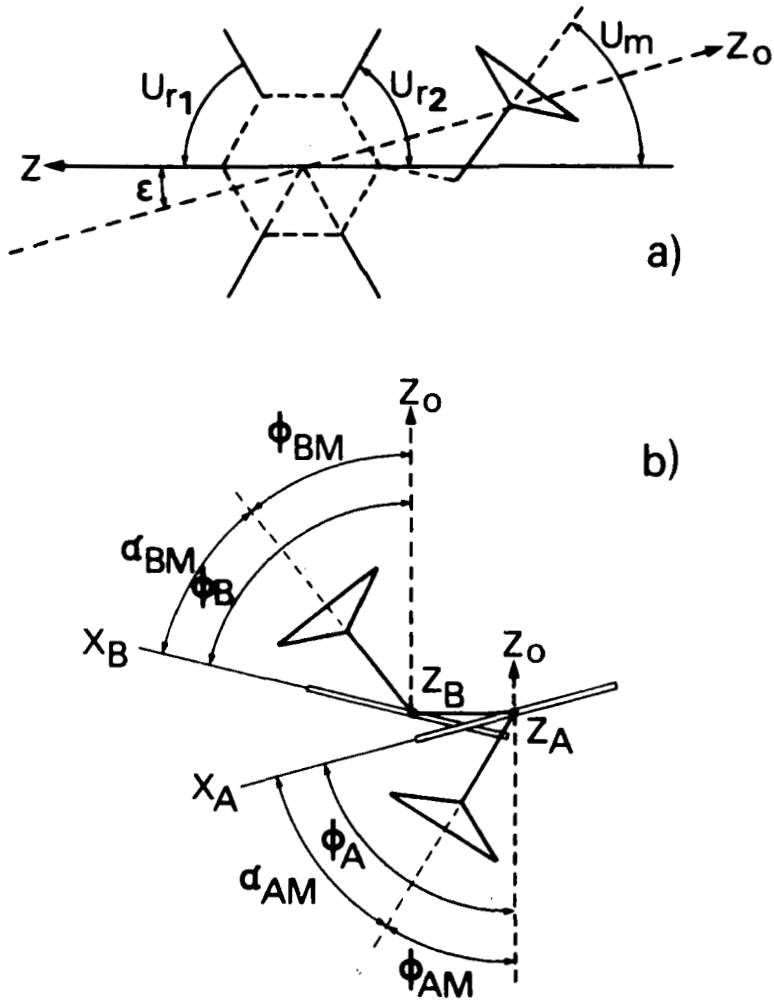

FIGURE 7 Sketch showing the definition of the various axes and angles which are useful in the calculation of the DMR splittings of PAAd14: (a) lateral view of one anisole moiety in a planar conformation; (b) view, along the para-axes of the rings assumed to be parallel, of the most probable conformation.

ϕ_A) and (ϵ_B, ϕ_B) in frames attached to the most probable rings, with the z axis along the internal rotation axes Oz_A and Oz_B, and Ox in the plane of the rings. In these frames, the polar angles of the various CD bonds are $u_{r1}^{A,B}$, $u_{r2}^{A,B}$ and $u_m^{A,B}$ as defined in Figure 7a. In a similar way, Oz_0 can be defined with respect to frames attached to the most probable methoxy groups by the angles (ϵ_A, ϕ_{AM}) and (ϵ_B, ϕ_{BM}). The dihedral angles between rigid fragments are simply related to the

azimuthal angles ϕ (cf. Figure 7b). The dihedral angles α_{AM} between phenyl ring A and associated methoxy group is given by (idem for B):

$$\alpha_{AM} \approx \phi_A - \phi_{AM} \tag{1}$$

The dihedral angle α between the two phenyl rings is given by

$$\alpha \approx \pi - \phi_A - \phi_B \tag{2}$$

Note that these equations are exact only if the internal rotation axes $Oz_{A,B}$ are strictly parallel.

The dynamic averages which are involved in the model are the usual nematic order parameter S and the two internal averages $\langle \cos 2\psi'_A \rangle$ and $\langle \cos 2\psi'_B \rangle$. These latter quantities describe the degree of uniformity of rotation of the two anisole moieties as a whole around the internal rotation axes. Their extreme values are 1 (pure π flips) and 0 (uniform rotation).

The structural quantities which are directly obtained from the fit are the two angles ϵ, the six angles u, the two conformational parameters λ_A and λ_B defined as (idem for B):

$$\lambda_A = \frac{\cos 2\phi_{AM}}{\cos 2\phi_A} \tag{3}$$

The corresponding dynamical quantities are the order parameter S and the two conformational averages T_A and T_B given by (idem for B):

$$T_A = \langle \cos 2\psi'_A \rangle \cos 2\phi_A \tag{4}$$

4b *Fitting procedure*[5,17]

Before any fit can be attempted it is important to check if the model which was established for pure PAAd14 is *a priori* also valid for PAAd14 dissolved in DDA9-L. For pure PAA an important feature of the model was that, on the time scale of the internal rotations described by the current angles ψ'_A and ψ'_B, the anisole moieties are rigid. This implies that the two ratio plots formed by the three quadrupolar splittings associated with each anisole moiety are linear.[5] Figures 8a and b show such plots for the 50% and 10%w/w PAA

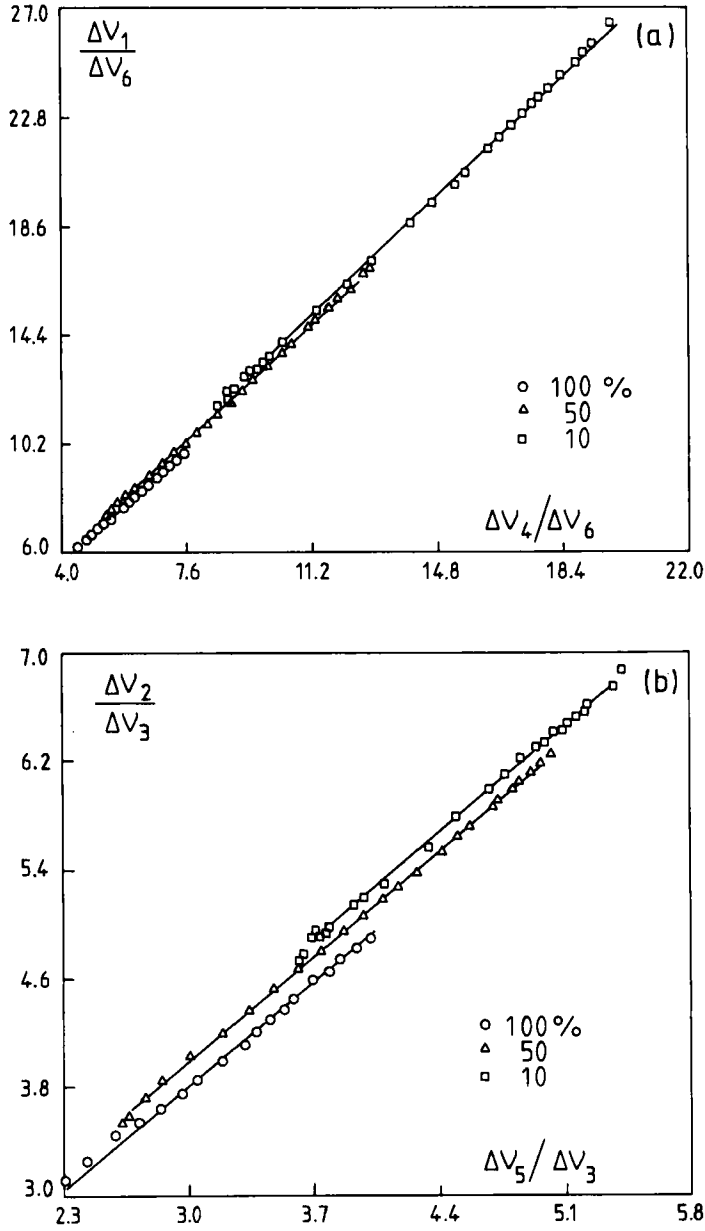

FIGURE 8a–b Ratio plots associated with anisole moiety *A* (a) and with anisole moiety *B* (b). The continuous line is the theoretical straight line calculated using the values of the parameters found in the fit. The data corresponding to the 5% w/w mixture are essentially the same as for the 10% w/w mixture and are not shown. See text and Reference 5 for details.

concentration, as well as those for pure PAA for comparison, and it is seen that in all cases the plots are linear, showing that the above condition is also fulfilled in the mixtures. However, the points do not lie on the same straight lines and this means that the structural and/or conformational parameters ϵ, u and λ are (slightly) different in the three cases (the 10% and 5% w/w mixtures yield practically the same results). This means that in fitting the data for the mixtures, we cannot fix these parameters to exactly the same values as for pure PAAd14.

The other difference with the case of pure PAAd14 is that in the mixtures the order parameter S is not known and should be considered as a parameter to be determined by the fit. This is not an important drawback since we have a sufficient amount of data. Indeed, for each temperature we have six DMR splittings $\Delta\nu_1$ to $\Delta\nu_6$. For ~20 temperatures, this corresponds to ~120 independent data sets. The temperature dependent parameters are S, T_A, T_B, (i.e. $3 \times 20 = 60$). The constant parameters are the two ϵ, the six u and two λ values i.e. 10. In summary, 70 parameters have to be determined with 120 data sets (for pure PAAd14, the number of parameters was only 50).

The fit was performed in a similar manner as before,[5] using only the data corresponding to the pure N phase of the mixtures. It turns out that if the quality of the fit is very sensitive to the actual values of the constant parameters and on the temperature dependences of S and $T_{A,B}$, there is some indeterminacy concerning the scaling factors of S and $T_{A,B}$. However, these two factors are linked together. More specifically, if one increases the value of one factor, e.g. that of S, one should decrease the scaling factors of T_A and T_B in order to obtain a fit of the same quality. Considering that $T_{A,B}$ should be negative, that S of PAA cannot be larger than S of the pure polymer,[7,11] and that the various parameters should be continuous functions of the concentration, one is left with practically one single solution for each concentration, which will be presented below. The fit is characterized as in Reference 5 by the mean square difference between calculated and experimental splittings δ_{fit}. The result is δ_{fit} = 28.4, 46.8, 30.2 Hz for 50%, 10% and 5% w/w concentrations respectively, to be compared with δ_{fit} = 27.6 Hz found[5] with pure PAAd14. All these values are of the order of the experimental uncertainty. The quality of the fit is shown in Figures 6a–e and Figure 8a,b where the continuous (broken) lines join the theoretical points calculated using the values of the various parameters which give the best fits.

5 RESULTS AND DISCUSSION

5a Structural parameters

The values of ϵ_A and ϵ_B could be taken as invariant with concentration and were systematically fixed to the values found for pure PAA, namely $\epsilon_A = 15.10°$ and $\epsilon_B = 15.61°$. Figure 9 summarises the results for the other constant parameters. It is seen that, contrary to ϵ_A and

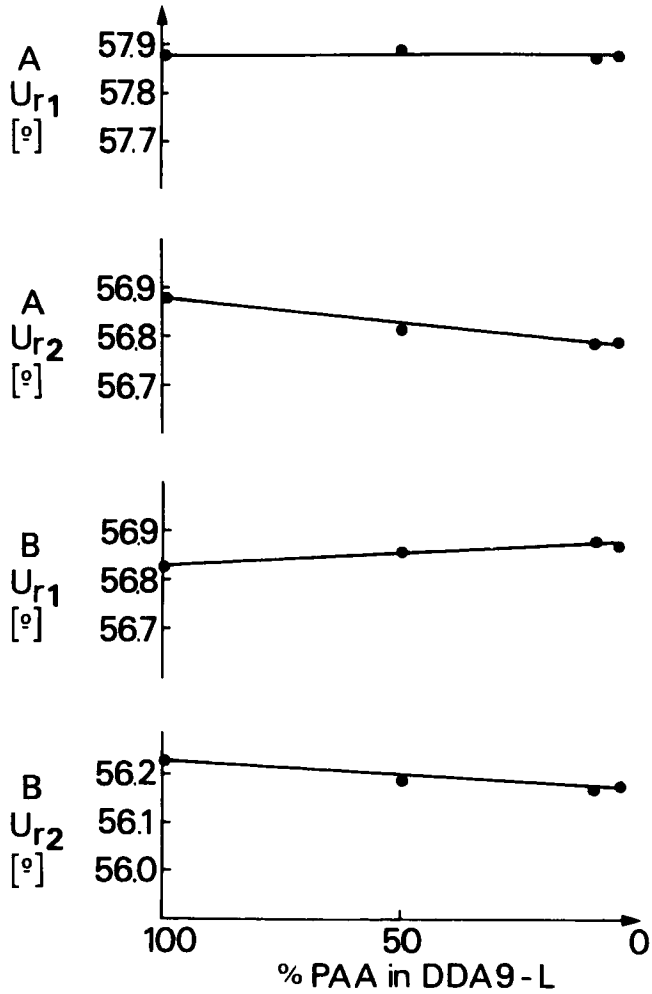

FIGURE 9 Concentration dependence of the structural angles u_i^A and u_i^B as defined in Figure 7 and of the conformational parameters λ_A and λ_B.

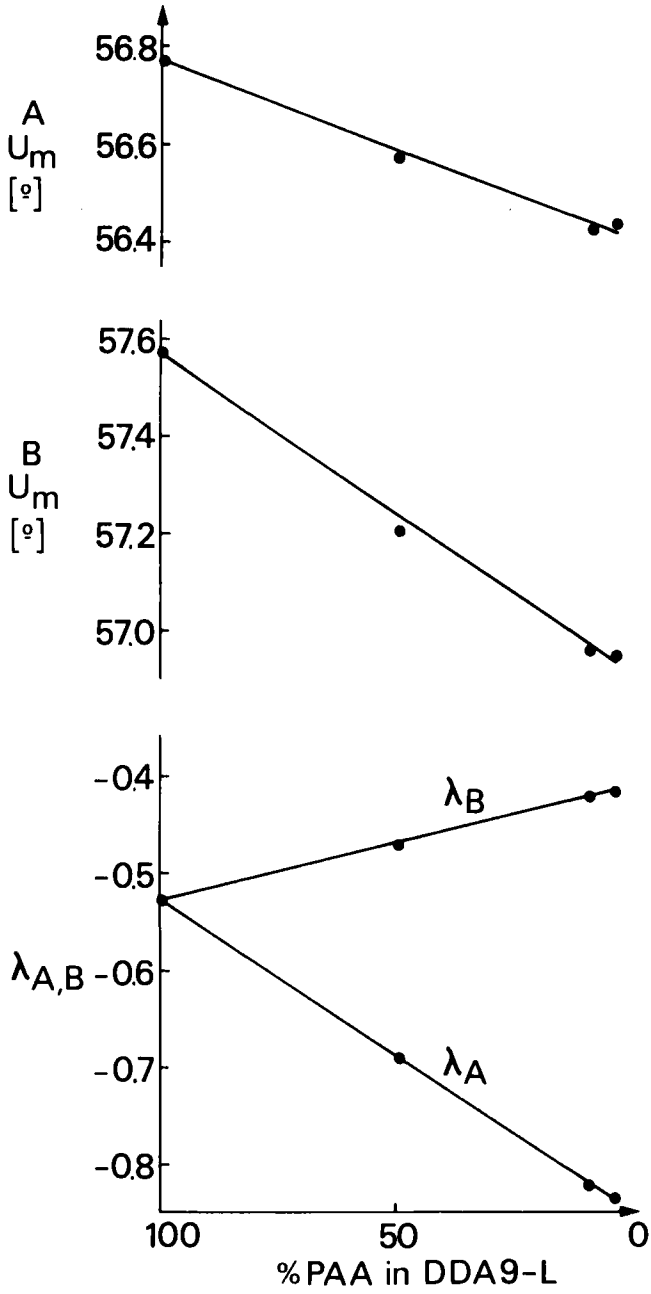

FIGURE 9 Continued

ϵ_B, the angles u need to be slightly changed, by ~0.1° for the u_r and ~0.5° for the u_m. The observation that $u_{r1}^{A,B}$ should be increased while $u_{r2}^{A,B}$ and $u_m^{A,B}$ should be decreased as concentration decreases, suggests that the anisole moieties are more aligned with the long axis in the presence of polymer than in bulk nematic PAA (cf. Figure 7a). The conformational parameters λ_A and λ_B, on the other hand, which are equal for pure PAA,[5] are found to vary in opposite manners as concentration decreases. This means that the two anisole moieties which are almost equivalent in pure PAA[5] tend to become progressively different. This result is discussed in more detail below.

5b Dynamic averages

The temperature dependence of the nematic order parameter in the pure N phase of the mixtures and in bulk for comparison is shown in Figure 10. It is seen that S is higher in the mixtures at least for concentrations lower than 50% w/w. The values of S for concentra-

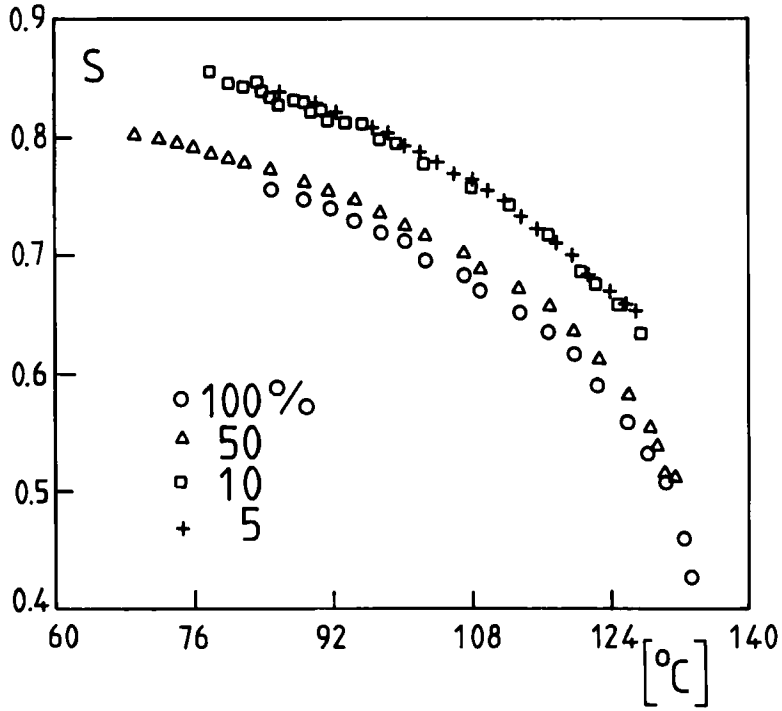

FIGURE 10 Temperature dependence of the nematic order parameter in the pure N phase of the mixtures for four concentrations. The values corresponding to 100% (bulk PAA) are those of Reference 5.

tions 5% and 10% w/w should be compared with the corresponding values of S measured by PMR on the pure polymer[7,11] where one finds that, although the latter are slightly higher, they are comparable. This shows that measurement of S of pure PAAd14 dissolved at low concentration in DDA9-L (probably in all DDA9 polymers) yields reliable information concerning the degree of order in the pure polymer, and in this respect, this result confirms the fact that PAAd14 is a good spin probe for studies on these systems. On the other hand, the finding that S increases with decreasing concentration is consistent with the above observation that the anisole moieties are more aligned with the long axis or equivalently that the PAA molecules are more stretched in the mixtures than in bulk. Concerning the $N + I$ biphase, although the data were not considered for the fit, the observation that for the lowest concentrations the splittings stop decreasing or even reincrease as temperature increases (cf. Figure 6a–e) can only be explained by a similar variation of S.

This phenomenon is to be related with the undulations of S observed for the pure DDA9-L and might indicate that the longest DAA9-L molecules, which are selectively transferred to the anisotropic phase at the $I \rightarrow I + N$ transition, favour nematic ordering of PAA.[13]

The variation of the conformational averages T_A and T_B is shown in Figures 11a,b. For all concentrations they behave similarly, i.e. $|T_A|$ and $|T_B|$ decrease as temperature increases. In terms of the model of Reference 5, this essentially means that the internal rotations become more and more "easy," mainly due to an increase of the molecular free volume (thermal expansion). Concerning absolute values, $|T_A|$ and $|T_B|$ are found to increase with decreasing concentration. According to Eq. 4 this means that $\langle \cos 2\psi'_{A,B} \rangle$ and/or $\cos 2\phi_{A,B}$ increase with concentration. Increase of $\langle \cos 2\psi'_{A,B} \rangle$ means that, at a fixed temperature, the internal rotations are more difficult in the mixtures than in bulk and this result would be consistent with the above findings that S is larger and the molecules are more elongated. In addition, it is observed that while T_A and T_B are equal in the bulk, they become more and more different with decreasing concentration. This is to be compared with the result concerning λ_A and λ_B and confirm that the two anisole moieties become different in the mixtures. This is considered in detail in the next section.

5c *Conformation of PAA in the mixtures*

From the above results, it is possible to deduce some rather specific information concerning the actual conformation of PAA in the mix-

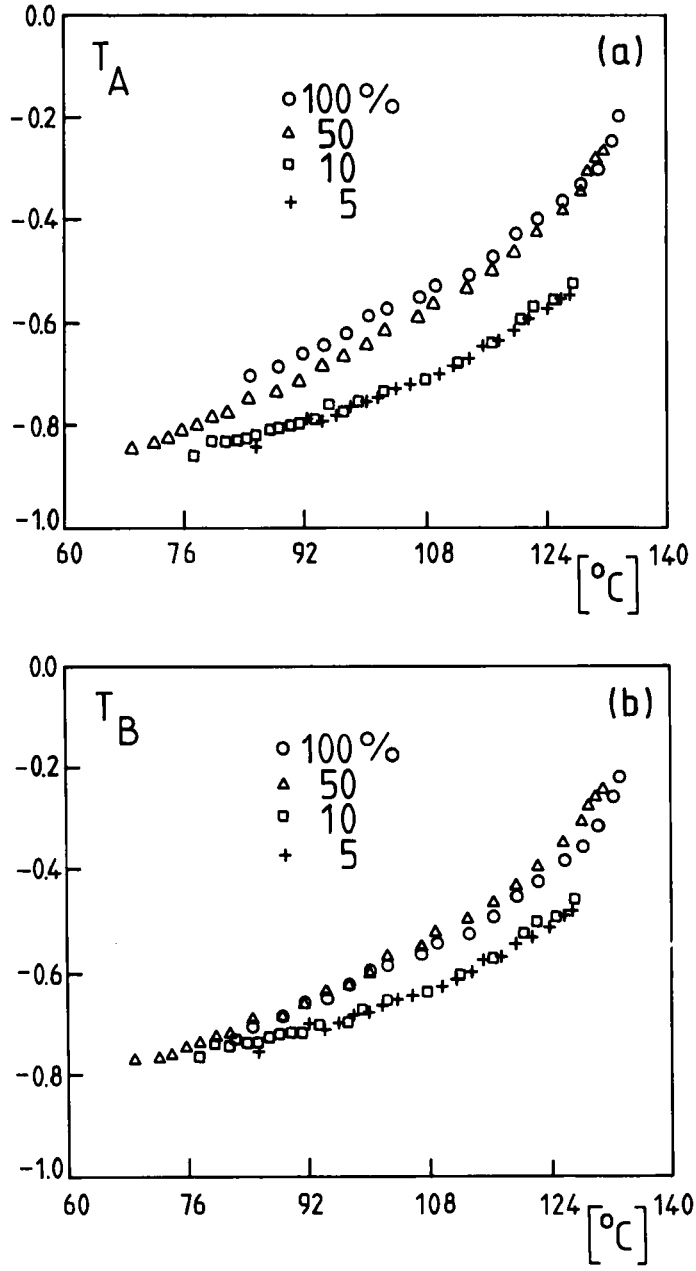

FIGURE 11a–b Conformational averages T_A (a) and T_B (b) in the pure N phase of the mixtures, for four concentrations. The values corresponding to 100% (bulk PAA) are those of Reference 5.

tures, provided some (weak) assumptions are made. For bulk PAAd14, we found[5] $\phi_A \approx \phi_B \approx 69°$, $\phi_{AM} \approx \phi_{BM} \approx 33.5°$, $\alpha_{AM} \approx \alpha_{BM} \approx 35.5°$ and $\alpha \sim 42°$. From this result, it was possible to deduce that the value of $\langle \cos 2\psi'_A \rangle$ and $\langle \cos 2\psi'_B \rangle$, at the lowest temperature in the supercooled nematic phase, was ~ 0.95. At the lowest temperature in the mixtures where S is larger, we expect that the internal rotations are even more difficult. Thus we can suggest, with some confidence, that at this temperature we have $\langle \cos 2\psi'_A \rangle \approx \langle \cos 2\psi'_B \rangle \approx 1$ (pure π flips). Consider the 10% w/w PAAd14 mixture. At the lowest temperature, we have $T_A \approx -0.86 \approx \cos 2\phi_A$ and $T_B \approx -0.76 \approx \cos 2\phi_B$ (cf. Figure 10a,b). From this, we deduce $\phi_A \approx 77.4°$ and $\phi_B \approx 71.6°$. From Eq. 3 and the values found in the fit for λ_A and λ_B, namely $\lambda_A = -0.82$ and $\lambda_B = -0.42$ (cf. Figure 9), we deduce $\phi_{AM} = 21.0°$ and $\phi_{BM} = 35.2°$. From Eqs. (1A, B and 2) we obtain $\alpha_{AM} \approx 52.1°$, $\alpha_{BM} \approx 34.0°$ and $\alpha \approx 35.6°$.

These results show that in the 10% w/w mixture, (i) at variance with what is found in the bulk, the two anisole moieties do not have the same conformation, as in the solid phase of pure PAA[5,18] and (ii) the dihedral angle between the two phenyl rings is smaller than in bulk PAA, but still relatively larger than in the solid phase ($\sim 22.6°$).[5,18] A similar calculation shows that the situation in the 50% w/w mixture is intermediate between the bulk, and the 10% w/w mixture. It is not possible to make a more accurate comparison between absolute values of dihedral angles because Eqs. (1) and (2) are only approximate and also probably because of limitations of the model. However, the finding that α_{AM} and α_{BM} become relatively very different between themselves and different to the bulk values can possibly be tested by using partial deuteration on the rings: PAAd8.[5] Indeed, in this case, it should be possible to estimate the dipolar splittings between ring deuterons and methyl protons in each anisole fragment, which are strong functions[5] of α_{AM} and α_{BM}. Such an experiment is foreseen and a positive result would constitute further strong support for the model used. Finally, it is interesting to note that, although in the mixtures $T_A \neq T_B$, the ratio T_A/T_B is nearly constant. At the lowest temperature this ratio is equal to $\cos 2\phi_A / \cos 2\phi_B$. Assuming that, as in the bulk,[5] these angles do not vary with temperature, this result implies that $\langle \cos 2\psi'_A \rangle \simeq \langle \cos 2\psi'_B \rangle$, and probably means that also in the mixtures, rotation of the two anisole moieties around the $N - \phi$ bonds occurs on the same time scale. The relatively higher values of $\langle \cos 2\psi'_{A,B} \rangle$ in the mixtures in comparison to the bulk is consistent with the slower motion of the methyl deuterons (cf. sect. 3b).

6 CONCLUSION

In conclusion, the present DMR study of mixtures of the (nondeuterated) nematic polymer DDA9-L with perdeuterated PAAd14 has a given number of rather specific results concerning the nature of the various phases and the molecular properties of PAA in a nematic medium other than its bulk nematic phase. The quantitative analysis has been possible only because a method based on the model developed in Reference 5 was available. The self-consistency of all the present results is, in our opinion, further support for the validity of this model. The results found with the lowest concentrations show that PAAd14 is a good DMR spin probe to study the properties of DDA9-L, and more generally the DDA9 systems. The reason for this is presumably linked to the similar nature of the aromatic cores of the two molecules (cf. Figure 1). In the mixtures, the molecular arrangement is probably similar to that in bulk PAA[18] with phenyl rings of both molecules on average close to one another. This means that PAA reflect the local properties of the medium near the aromatic core of the polymer rather than near the spacer.[13] A more detailed study of this problem will be presented elsewhere.

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