Routine ^{2}H NMR in Ternary Mixtures of Poly(γ-benzyl-L-glutamate) – a Useful Tool for Studying Molecular Shape, Symmetry, and Conformational Motions

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^{2}H NMR measurements of deuterated solute molecules in a poly(γ-benzyl-L-glutamate) (PBLG)/dichloromethane or chloroform liquid-crystalline solvent are presented. The quadrupolar splittings of solutes were determined in order to make good use of them in stereochemical and conformational analyses. The results obtained for achiral model compounds of different size, symmetry, shape, and flexibility are interpreted qualitatively. Emphasis is put on the routine application of this technique. Advantages of working in such lyotropic liquid-crystalline solvents, namely the enhanced signal dispersion or the rich information content of the ^{2}H spectra compared with those recorded in isotropic media, are emphasised.

Introduction

Partially or completely deuterated molecules are often prepared or are alternatively formed as products during chemical research. Isotropic liquid-phase ^{2}H NMR spectroscopy is widely used to characterise these molecules. The ^{2}H nucleus, however, being weakly quadrupolar, suffers from certain disadvantages. While its chemical shift dispersion is small, for example, the usual line widths, though dependent on the size of the molecules, are often relatively large. To overcome this problem there are two options: (a) one can try to get rid (at least partly) of the quadrupolar effect e.g. by raising the sample temperature or (b) one can make good use of it. The latter approach is the subject of this paper.

It has long been known that anisotropic interactions, such as the quadrupole coupling, in anisotropic media do not average to zero, i.e. they can be observed in the spectra.[1] NMR spectroscopy of partially ordered systems or of solute molecules dissolved in them soon became a theoretically challenging and even practically interesting field of its own right,[2] but has never really been used by the greater community of organic and inorganic chemists.

Perhaps, or hopefully, the interesting papers published more recently by Courtieu and co-workers[3] could bring a breakthrough in this respect. They have elegantly demonstrated the outstanding capacity of this technique in a very important practical application, namely enantiomeric analysis. In contrast to many early works Courtieu and coworkers used a liquid-crystalline ternary mixture consisting of a chiral polyamino acid, in this case poly(γ-benzyl-L-glutamate) (PBLG), a co-solvent, and the solute.

We would like to point out that besides the enlarged signal dispersion described recently,[4] there can be further reasons for recording the ^{2}H spectra in such chiral lyotropic media. The purpose of this paper is to draw attention to the general utility and relative simplicity of such routine applications in exploring stereochemistry, conformational aspects, and anisotropic motions of organic or inorganic molecules.

Theory:[1,2] In uni-axially oriented phases the ^{2}H spectrum consists of doublets. The appearance of doublets centred on the isotropic chemical shifts is due to the quadrupolar perturbation of the Zeeman levels. The phenomenon and the underlying theory that weakly quadrupolar, and therefore relatively slowly relaxing nuclei, exhibit residual quadrupolar splitting in partially oriented materials such as liquid-crystalline phases has been known for a long time.[2] The reason for this phenomenon is the restricted molecular motion of molecules dissolved in such ordered media that does not allow the system to achieve the isotropic extreme narrowing situation, a precondition for eliminating quadrupolar interactions. The magnitude and sign of the residual quadrupolar coupling, $\Delta\nu_Q$ depend on the magnitude and sign of the quadrupole coupling and those of a geometrical factor called order parameter,[2e] which describes the time-averaged orientation of the quadrupolar tensor relative to the external magnetic field, B_o. The time-averaged orientation of the liquid crystals (called director) in a magnetic field depends on the sign of the diamagnetic susceptibility anisotropy ($\Delta\chi$) of the crystals. If $\Delta\chi$ is positive, as in our case, the director aligns parallel to the external field. The correlation between the residual coupling and the order parameter can be given by the simple formula of Equation (1), where Q is the quadrupole moment/10^{-28} m^2, q_{zz} = electric field gradient (it is generally assumed that for C–D bonds it is parallel with the bond), and θ is the angle between B_o and q_{zz}. The term (e^2Qq_{zz}/h) is called the quadrupole coupling constant, C_{QF}. The angle brackets denote an ensemble average.

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$$\Delta\nu_Q = \frac{3e^2Qq_{zz}}{2h}\left(\frac{1}{2}\left\langle 3\cos^2\theta - 1\right\rangle\right) \quad (1)$$

Very fortunately, the ranges of the deuterium quadrupole coupling are rather narrow (e.g. 170 ± 5, 185 ± 5, and 200 ± 5 kHz for deuterons attached to sp^3, sp^2, and sp carbon atoms, respectively) and the influence of the chemical environment on them is often negligible.[2b] Therefore, the observed splittings depend primarily on the ordering of the C−D bonds, which is modulated by molecular reorientation motions. These act as a scaling factor for the observed splittings. For anisotropic motions this scaling is not uniform. The residual quadrupolar couplings (normally somewhere between 20−3000 Hz at room temperature when using this particular polypeptide) are different for deuterons (C−D bonds) that possess an even slightly different ordering parameter [$S = (3\cos^2\theta - 1)/2$]. Molecular ordering can also be described by a 3 × 3 matrix; this ordering matrix is symmetric and traceless, and has a maximum of five independent elements. However, depending on the symmetry of the solute molecule, the number of independent elements needed to describe the molecular orientation varies from zero (molecules with tetrahedral or cubic symmetries do not orient) to five (molecules without a plane of symmetry).[2e]

Since the sign determination of the residual couplings cannot be considered routine we prefer the use the term "splitting" by which we mean the absolute values of the residual couplings. For our purposes this is normally sufficient except in some cases of fast exchange processes. In these cases we sometimes have to assume a different sign for the coupling or order parameters of exchanging deuterons in order to be able to interpret the change we see.

Concerning the other possible anisotropic interactions in the particular ternary mixture of PBLG we are working with, the motions are usually fast enough to average out or scale down to a few Hz the homo- or heteronuclear dipolar interactions. Anisotropies of deuterium chemical shielding are considered negligible.

$T_{1/2}$ relaxation: Even in case of weakly quadrupolar nuclei such as ^2H, the dominating relaxation mechanism is the quadrupole one, $T_{1/2(Q)}$ i.e. by the interaction between the nuclear quadrupole and the surrounding electric field gradient; see Equation (2), where η is the asymmetry parameter of the electric field gradient (its value is close zero for a C−D bond that normally has axial symmetry), τ_c is the molecular reorientational correlation time, I = nuclear spin-quantum number ($I = 1$ for ^2H).

$$\left(\frac{1}{T_1}\right)_Q = \left(\frac{1}{T_2}\right)_Q = \frac{3}{10}\pi^2\frac{2I+3}{I^2(2I-1)}C_{QF}^2\left(1+\frac{\eta^2}{3}\right)\tau_c \quad (2)$$

By simple rearrangement of Equations (1) and (2) one can see that the relaxation rates are proportional to the square of the residual quadrupole couplings.

Results and Discussions

Study of Stereochemistry and Conformational Motions: Rigid versus Flexible Molecules

Stereochemistry, conformational motions, anisotropic shape and consequent motions of molecules are reflected in the residual coupling values in a rather complex way, in most of the cases we have no means by which to separate them. Nevertheless, we discuss them under separate subtitles. Old textbook-example molecules are used here as model compounds to demonstrate the capacity of the method in distinguishing stereoisomers and to follow conformational changes as a function of the temperature.

cis,trans-[D_{18}]Decahydronaphthalene (cis,trans-Decalines)

Both molecules have already been thoroughly studied in thermotropic liquid crystals by Boeffel et al.[5] and by Samulski et al.[6] (in ZLI2452). More recently we have reported on the ^2H spectrum of *trans*-[D_{18}]decalin in PBLG/$CHCl_3$ at room temperature.[4] It has also long been known that while the *trans* form (C_{2h} symmetry) is relatively rigid the *cis* isomer (C_2 symmetry) easily undergoes ring inversion with a barrier of about 13.6 kcal/mol[7] to 14.9 kcal/mol,[5] therefore it seemed instructive to compare the temperature dependence of the two.

In case of the *trans* isomer, we have recorded the spectra in the temperature range between 333 and 268 K and in case of the *cis* isomer between 353 and 223 K using $CHCl_3$ as co-solvent for both samples. In the room-temperature spectrum of the *trans* isomer (see Figure 1, a), the five doublets that correspond to the five chemically different deuterium atoms (three equatorial and two axial)[4] of the dominant *chair*−*chair* form do not change upon cooling the sample, except that a gradual increase of all splitting values is observed (see Figure 1, b). We have earlier given a tentative assignment[4] based on chemical shift and symmetry considerations and also on ^2H T_1 relaxation data. Unambiguous assignment of all spectral lines is not straightforward, however.

Spectra of the *cis* isomer, however, show drastic changes as the temperature is lowered (see Figure 2, a, b). Above room temperature we observe nine doublets, although with a certain degree of overlap, at room temperature all doublets, but two are already rather broad, whereas at 223 K we most probably have 18 doublets, though some of them heavily overlap.

The two doublets that remain relatively sharp throughout the whole temperature range can be assigned to deuterons attached to the annealing carbon atoms. We know from very early variable-temperature ^{13}C NMR studies[7] that these carbon atoms exhibit no kinetic averaging due to identical chemical environments in both conformational forms. It is noteworthy that the coalescence temperature of all other deuterium signals is about 273 K, which is rather close to that observed in the isotropic ^{13}C spectra (about 285 K). A complete assignment of the deuterium spectrum was given more recently by Boeffel et al. using *cis*-decalin specifically deuterated in the β-position and 2D exchange

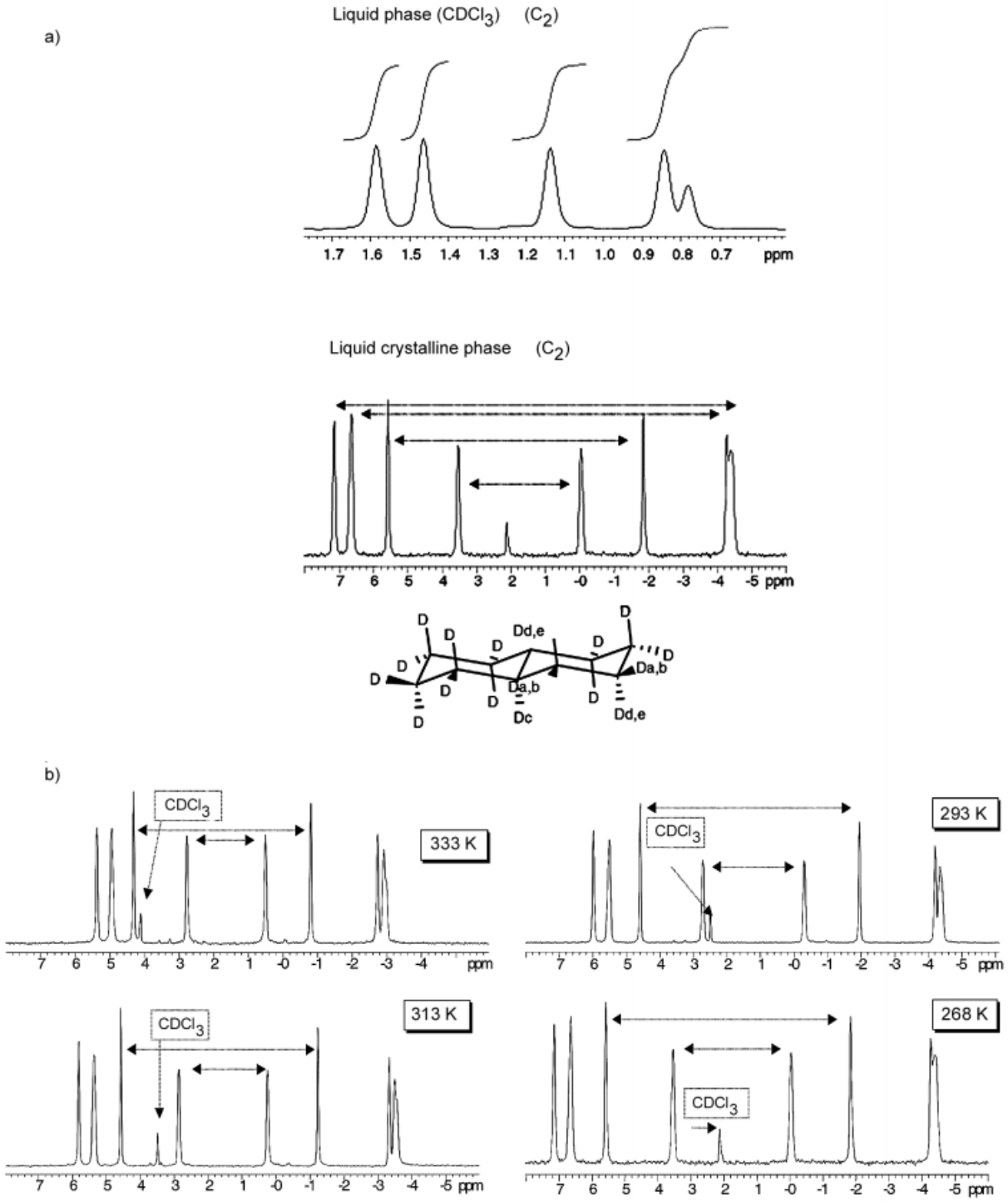

Figure 1. a): *trans*-[D_{18}]Decahydronaphthalene room-temperature ^{2}H NMR spectra recorded at 46.051 MHz, liquid phase spectrum in $CDCl_3$ at 293 K (top), liquid-crystalline phase spectrum (bottom), 15 μL of solute, 120.6 mg of PBLG (MW 296000), 0.6 mL of $CHCl_3$ in 5-mm sample tube at 293 K; b): *trans*-[D_{18}]decahydronaphthalene variable-temperature liquid-crystalline phase ^{2}H NMR spectra recorded at 46.051 MHz, 15 μL of solute, 120.6 mg of PBLG (MW 296000), 0.6 mL of $CHCl_3$ in 5-mm sample tube; for clarity only the equatorial deuteron doublets are indicated by arrows; for tentative assignments see ref.[4]

spectroscopy.[5] Note, however, that in the thermotropic liquid-crystalline solutions they used (ZLI2452 and S1131BCH) the molecule kept its C_2 symmetry even at 268 K.

[D_{12}]Cyclohexane

This has also been studied in thermotropic liquid-crystalline solvents by Poupko and Luz[8] and by Panar and coworkers.[9] The latter authors reported a quadrupole coup-

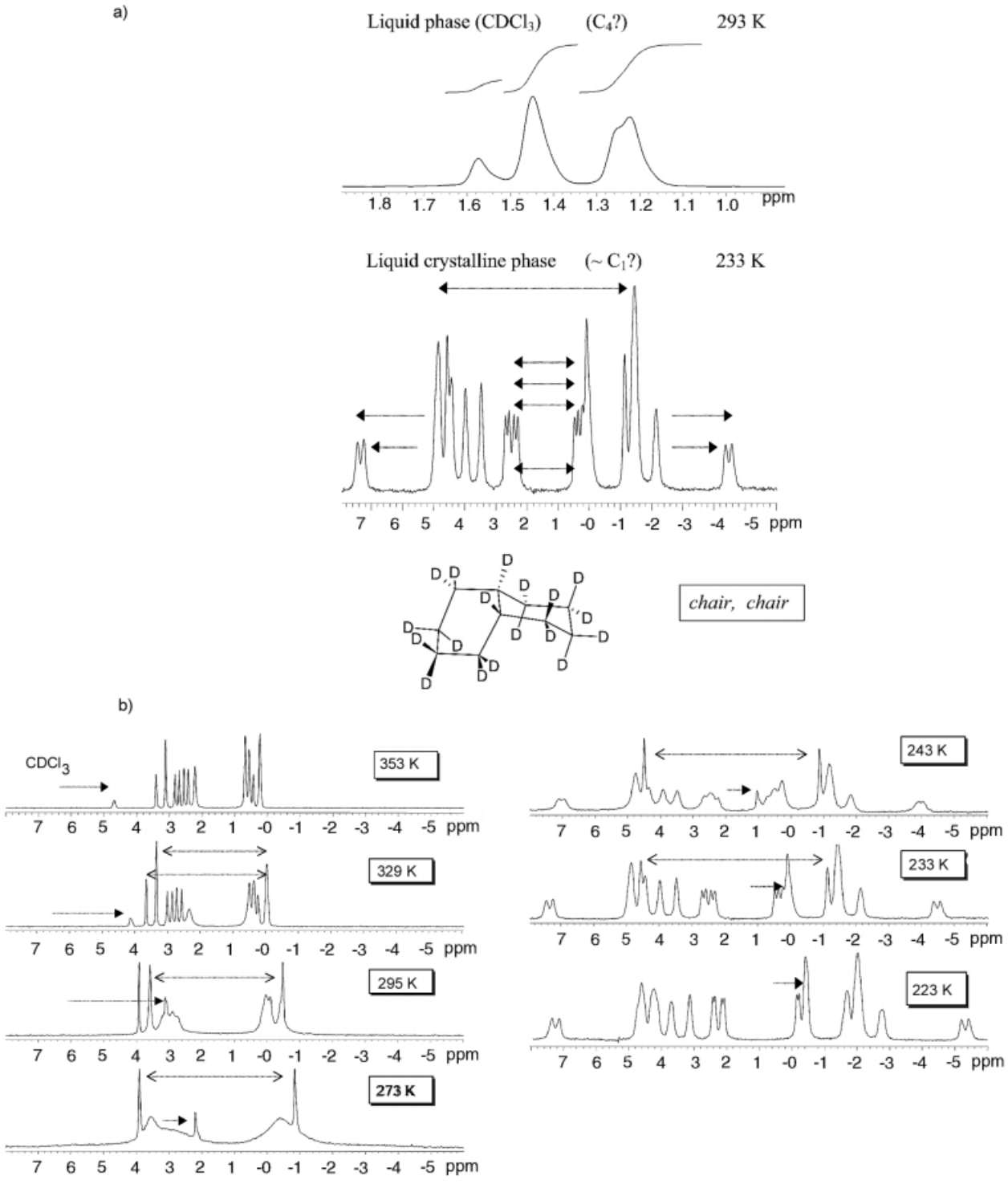

Figure 2. a): *cis*-[D_{18}]Decahydronaphthalene ^2H NMR spectra recorded at 46.051 MHz, liquid phase spectrum in $CDCl_3$ at 293 K (top), liquid-crystalline phase spectrum (bottom), 14 μL of solute, 123 mg of PBLG (MW 296000), 0.6 mL of $CHCl_3$ in 5-mm sample tube at 233 K; b): *cis*-[D_{18}]decahydronaphthalene variable-temperature liquid-crystalline phase ^2H NMR spectra recorded at 46.051 MHz, 14 μL of solute, 123 mg of PBLG (MW 296000), 0.6 mL of $CHCl_3$ in 5-mm sample tube; deuterons attached to the annealing carbon atoms are indicated by arrows

ling (e^2Qq_{zz}/h) value of 174 kHz. We observed the following splittings in PBLG/CH_2Cl_2: one sharp doublet ($H_{eq,ax}$) of 43.2 Hz ($\Delta\nu_{1/2}$ = 2.2 Hz) at 273 K, and this values practically does not change until 233 K (Figure 3). (The equatorial and axial deuterons have residual quadrupolar couplings of different sign as proved experimentally by Samulski et al.[6])

Below this temperature we observe broad lines (coalescence) that upon further cooling convert into two relatively

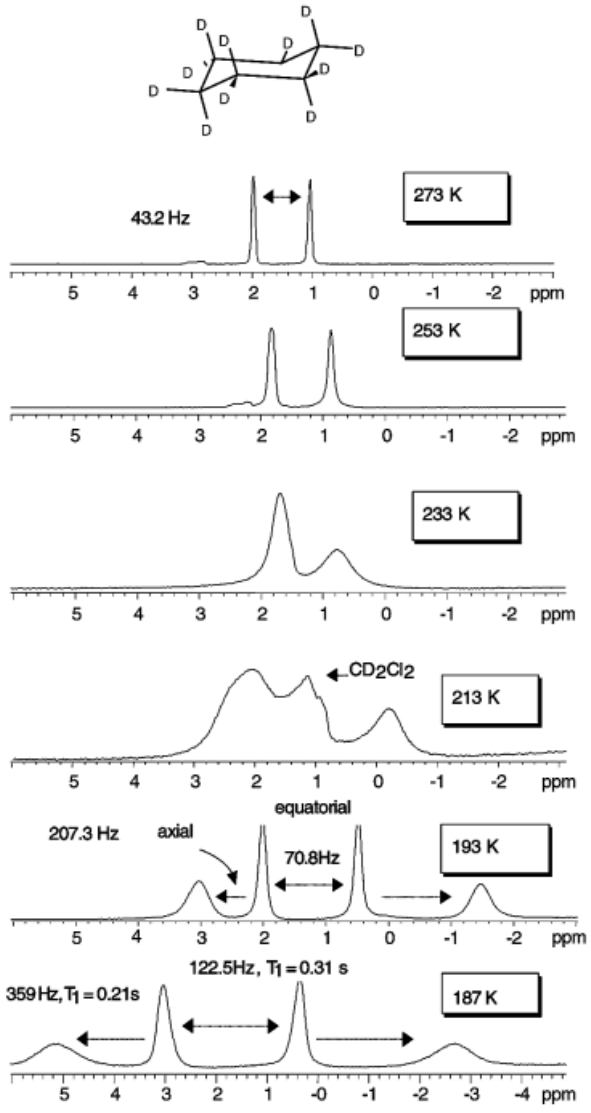

Figure 3. [D_{12}]Cyclohexane variable-temperature ^{2}H NMR spectra recorded at 46.051 MHz, 10 μL of solute in 119 mg of PBLG (MW 296000), 0.6 mL of CH_2Cl_2 in 5-mm sample tube; number of scans = 2

sharp doublets of 122.5 Hz (H_{eq}: δ = 1.7, T_1 = 0.31 s) and 359 Hz (H_{ax}: δ = 1.27, T_1 = 0.21 s) ($\Delta\nu_{1/2}$ = 12 and 31 Hz, respectively) at 190 K. The coalescence temperature is about 206−212 K, i.e. it is rather close to that observed by Jensen et al.[10] in isotropic phase (−67 °C).

[D_8]1,4-Dioxane

In PBLG/$CHCl_3$ at 293 K the splitting is 78 Hz ($\Delta\nu_{1/2}$ = 2.2 Hz), but is 241 Hz ($\Delta\nu_{1/2}$ = 16 Hz) at 213 K. Unlike cyclohexane its value decreases slowly as the temperature goes down, it is 122.5 Hz at 233 K, but there is a drastic increase below that temperature. Using the less viscous CH_2Cl_2 as co-solvent, however, in the fast-exchange regime the splitting is much smaller and does not increase very much, e.g. ca. 35 Hz at 293 K, 55 Hz at 213 K, and only 62 Hz at 183 K (but already at this temperature very broad lines are evident!). Presumably in the latter case $\Delta\nu_{Q,eq}$ and $\Delta\nu_{Q,ax}$ are of different signs. The coalescence temperature is about 180 K or even slightly less. We know from quite early studies that at the energy minimum the ring has a *chair* conformation and the barrier to *chair*−*twisted-chair* conversion is about 9.7 kcal/mol (calcd.10.1 kcal·mol).[11]

Studies of Anisotropic Internal and Molecular Motions

[D_7]DMF

Values of ^{2}H quadrupole coupling constant and asymmetry parameter obtained in low molecular weight nematic poly(L-glutamic acid) crystals have been reported previously.[12] In PBLG/$CHCl_3$ at 295 K we observe three doublets (Figure 4), the largest one (128 Hz, $e^2q_{zz}Q/h$ = 197

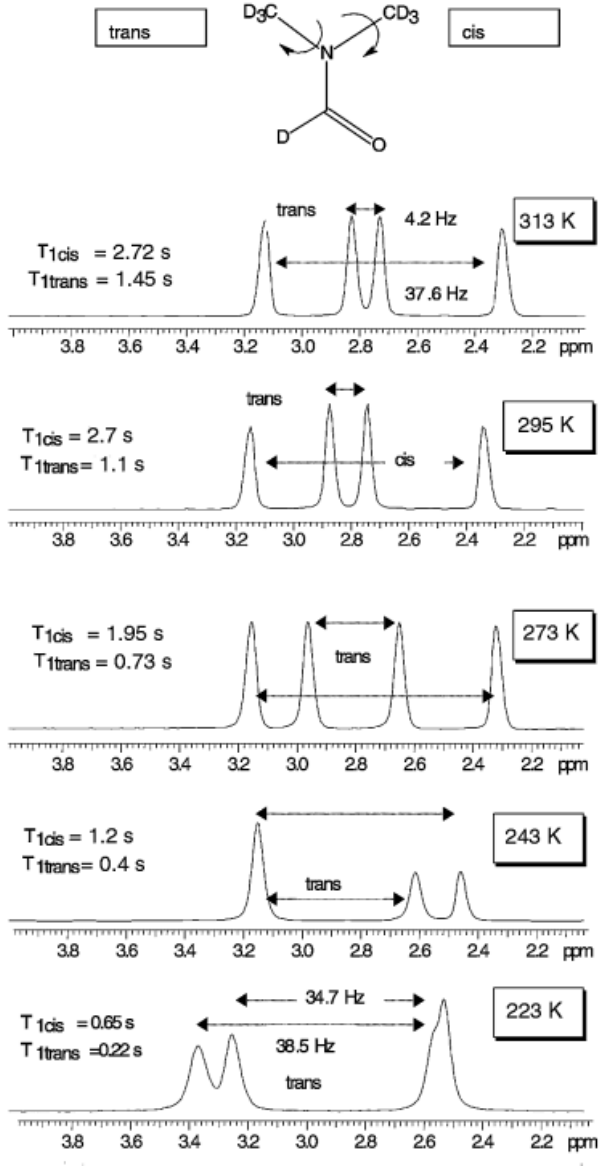

Figure 4. [D_7]-*N*,*N*-Dimethylformamide variable-temperature ^{2}H NMR spectra recorded at 46.051 MHz, 10 μL of solute in 119 mg of PBLG (MW 296000), 0.6 mL of $CHCl_3$ in 5-mm sample tube; the T_1 values were measured by the inversion-recovery technique; only the methyl region is shown

kHz[12]) at δ = 8.02 (this was used as an internal chemical shift reference), a small one (splitting = 6.1 Hz) at δ = 2.88 and a much larger one (splitting: 37.3 Hz) at δ = 2.80.

No doubt, the large doublet at the highest frequency belongs to the amide deuteron. Assignment of the methyl deuterium signals is not as straightforward. Provided we can adopt results from liquid-phase studies,[13] the small doublet is due to the CD_3 group *trans* to the C=O group and then the larger one should be assigned to the CD_3 group *cis* to the C=O group. These assignments agree with those reported by Smith et al.[14] on the basis of ^2H spin-lattice relaxation times. The T_1 values measured in liquid-crystalline phase are also in good quantitative agreement with those of obtained in solution phase. We obtained 1.1 and 2.7 s for the *trans*- and *cis*-CD_3 groups, respectively, whereas Smith et al. reported 1.6 s for the *trans* group and 3.0 s for the *cis* one, and explained the difference in terms of anisotropic rotation of the molecule.[14] We looked at the temperature dependence of splitting and T_1 values (Figure 4) to confirm this explanation.

Interestingly enough, the amide and *cis*-methyl deuterons [these C−D bonds are roughly perpendicular to the assumed main rotational axis of the molecule that goes through the O=(C)−N-*trans*-methyl atoms][14] do not change their splittings significantly upon cooling the sample to 223 K. At the same time, splittings of the *trans*-methyl deuterons show a ninefold increase (4.2 Hz at 313 K but 38.5 Hz at 223 K) upon cooling. All T_1 values show a monotonic decrease, but the ratio between the relaxation rates of *trans* and *cis* groups does not change much.

The fact that only one splitting shows significant change upon cooling the sample indicates that the overall molecular ordering basically does not change. We interpret the increased splitting of the *trans* group deuterons as a result of the slowing of the rotation, either along the main molecular axis or of the methyl group along the C_{trans}−N bond, i.e. even the *trans* methyl group rotation becomes hindered at this temperature.

[D_1]Phenylacetylene

In this molecule the acetylenic deuteron has a rather short ^2H T_1 relaxation time (we measured 0.3 s in PBLG/CH_2Cl_2, while 0.25 s was reported in CCl_4).[14] At the same time, however, the absolute value of the room-temperature residual coupling is surprisingly small (69 Hz). This is noteworthy since earlier results[3b] and also our own experiences with phenyl derivatives of similar size (see below) have shown that *para*-deuterons of phenyl rings lying on the preferred axis of rotation, while relaxing fast, posses by far the largest splitting values.

A possible explanation can be a strongly anisotropic "in-plane" rotation, the fact that under similar conditions for benzene we obtained a doublet of about 41 Hz (however, T_1 is about 0.9 s) is in support of this assumption. On cooling the sample we observe a tremendous increase in the splitting (Figure 5.), e.g. at 193 K its value (ca. 500 Hz) exceeds even that of the CD_2Cl_2 deuterons (445 Hz).

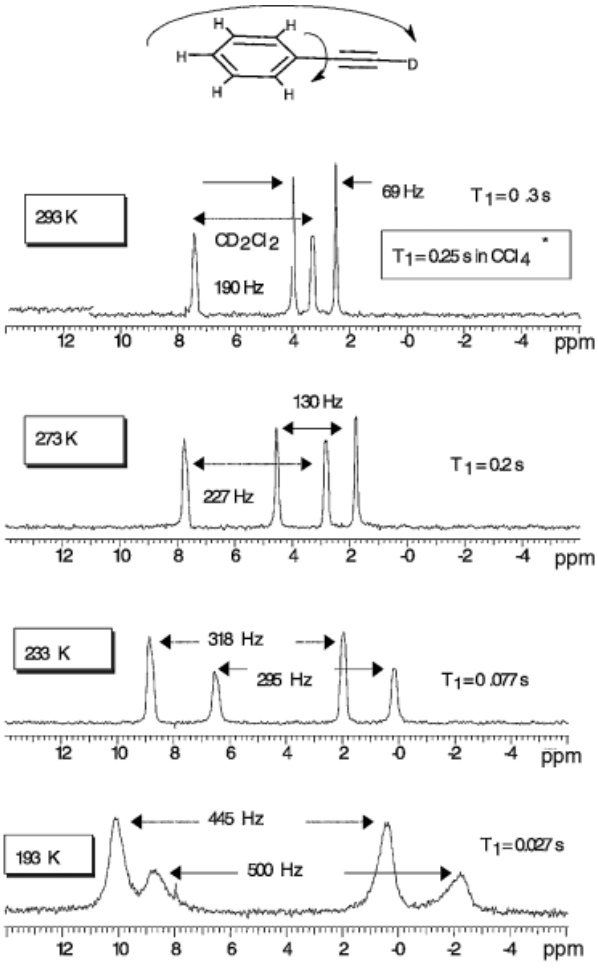

Figure 5. [D_1]Phenylacetylene variable-temperature ^2H NMR spectra recorded at 46.051 MHz, 10 μL of solute and 4 μL of CD_2Cl_2, 124.5 mg of PBLG (MW 296000), 0.6 mL of CH_2Cl_2 in 5-mm sample tube; *reported by Smith at al. in ref.[14]

The fast T_1, T_2 relaxation of this deuteron remains to be explained since it assumes nonefficient averaging of the quadrupole effect, which contradicts, however, the observed magnitude of the splitting value. At the same time, presence of any other competitive relaxation mechanism is unlikely.

Molecular Shape versus Residual Couplings (Order Parameters)

It is known that there is a correlation between molecular shape and molecular ordering. It has been shown by Burnell and de Lange that based on molecular size and shape it is possible to predict ordering parameters with an accuracy of about ±10%,[15] however, this possibility was said to be limited to systems where the long-range electrostatic interactions are close to zero. Others[6] argue that solute ordering can be accurately described in terms of purely hard-body (short range repulsive) interactions with the solvent molecules.

Concerning the ternary mixture of PBLG we used, it's probably not a "magic" (zero electric-field gradient) solvent.[15] Furthermore, the solutes we want to study can be of

Table 1. ^{2}H splitting (absolute values of residual quadrupolar couplings) [Hz] and T_1 values [s] measured in PBLG/$CHCl_3$ mixtures, T_1^{PBLG} (PBLG ≈ 120 mg, WT ≈ 296000, solutes ≈ 6−15 mg, $CHCl_3$ ≈ 0.6 mL) and in pure liquid phase ($CHCl_3$) at 295 K, T_1^{liquid}

	$\Delta\nu_Q$(*ortho*)/T_1^{PBLG}/T_1^{liquid}	$\Delta\nu_Q$(*meta*)/T_1^{PBLG}/T_1^{liquid}	$\Delta\nu_Q$(*para*)/T_1^{PBLG}/T_1^{liquid}	$\Delta\nu_Q$(methyl)/T_1^{PBLG}/T_1^{liquid}
[D_6]Benzene[a]	41[a]/1.5/1.0	41/1.5/1.0	41/1.5/1.0	
[D_5]Pyridine	48.5/0.63/0.38	73/0.48/0.58	216/0.37/0.37	
[D_8]Toluene	46.8[b]/0.48/ca. 0.5	50.5[b]/0.38/ca. 0.5	249.2/0.53/ca. 0.6	71[c]/2.9/3.6 (4.3[14])
[D_{10}]Biphenyl	167[b]/0.26/[d]	149[b]/0.27/[d]	593/0.14/[d]	
[D_{14}]Terphenyl	294[b]/0.1/[d]	282[b]/0.1/[d]	1739/0.05/[d]	
	ortho: 312[b]/0.1/[d]			

[a] Reported quadrupole coupling value 193 kHz.[9] − [b] Tentative assignments. − [c] Reported quadrupole coupling value 165 kHz.[9] − [d] Could not be measured due to lack of resolution.

any kind i.e. we cannot assume that they are "magic" either in the sense that their electronic structure precludes the presence of anisotropic electrostatic interactions.[15]

Benzene, Pyridine, Toluene, Biphenyl, Terphenyl

The molecular size and the shape anisotropy increases in this order, and we looked at the residual couplings to find out how, if at all, these parameters are reflected in their values. For the sake of comparison, data reported earlier for biphenyl and terphenyl[4] are also included in Table 1 together with those of benzene (used also as an internal reference).

Apart from obvious trends such as the decrease in relaxation times as the molecular mass increases, or the reducing effect of the independent rotation of methyl groups, the impact of molecular shape seems to dominate in benzene, toluene, biphenyl, and terphenyl. The large values observed in pyridine compared to benzene, however, suggest the presence of electrostatic long-range orientation forces too.

After all, to explain the different temperature dependencies of the different solutes is rather difficult. We have to assume the presence of both long-range (electrostatic) and short-range (repulsive) orientation mechanisms. In order to obtain a simplified qualitative view of the possible interplay of long- and short-range effects we prepared a sample containing five solute molecules of different sizes, dipole moments, and shapes ($CDCl_3$, CD_2Cl_2, [D_{12}]cyclohexane, [D_{10}]biphenyl, and C_6D_6) in PBLG/CH_2Cl_2 mixture with an averaged PBLG molecular weight of about 176000. We looked at the temperature dependencies of residual couplings of all solutes (Figure 6). This way we could get rid of certain effects such as the temperature, the viscosity of the solvent, the molecular weight of the PBLG used, or the ratio of the co-solvent. Ideally all these should be kept constant to avoid further ambiguities.

An important conclusion of this experiment is that under such conditions the solute molecules do not influence each other. While the splittings of benzene and biphenyl deuterons show a more or less linear increase in the temperature range between 303 and 213 K, the cyclohexane spectrum does not change above the coalescence temperature (as we have already discussed). Nonlinear temperature dependence is definitely observed for CD_2Cl_2 and especially

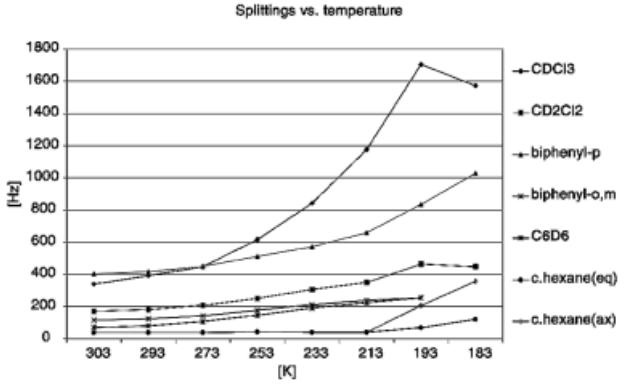

Figure 6. Temperature dependence of the residual splitting values of $CDCl_3$ (3 μL), CD_2Cl_2 (3 μL), [D_{10}]biphenyl (6 μL), C_6D_6 (4 μL), and [D_{12}]cyclohexane (5 μL) with 0.5 mL of CH_2Cl_2 as co-solvent and 121 mg of PBLG (MW 296000)

for $CDCl_3$. In chloroform at room temperature the $CDCl_3$ doublet is 429 Hz, but it goes up to 1705 Hz at 193 K. We take this as evidence of effective long-range orientation mechanisms. At temperatures near or below the assumed freezing point of the co-solvent $CHCl_3$ (< 200 K), changes of splittings are less rational.

Conclusions

Advantages and characteristics of using PBLG/co-solvent/solute ternary mixtures for recording ^{2}H spectra of solute (guest) molecules can be summarised as follows:

− Due to the presence of residual quadrupolar couplings the spectra show enhanced signal dispersion relative to those recorded in isotropic liquids.

− Shape-dominated ordering: In many but not all cases short-range repulsive (hard-body) orientation mechanisms prevail, i.e. molecular shapes correlate with residual coupling values through the anisotropic molecular tumbling actions.

− Qualitative stereochemical analyses of solute molecules are often possible by simple symmetry considerations.

− In these mixtures we observe liquid-like molecular motions and T_1, T_2 values. Consequently, residual couplings are smaller at least by one or two orders of magnitude relat-

ive to those observed in thermotropic liquid crystalline molecules. Practically all interactions except the quadrupolar one vanish, making the spectra deceptively simple.

– Concerning the dynamic range of the variable-temperature experiments, no real gain in the highest exchange rates ($1/\tau$) relative to isotropic liquids was achievable. The mixtures can usually be overcooled by about 10–20 K, relative to the freezing point of the co-solvents.

– Chemical shielding effects are present that can assist the signal assignments in many cases.

– Last but not least, in this chiral medium we often witness the total loss of symmetry due to the slightly different ordering of C–D bonds, found e.g. in chiral or prochiral groups, which otherwise cannot be distinguished.

Experimental Section

The spectra shown were recorded with a Varian Unity 300 spectrometer without field/frequency lock mostly with temperature regulation using a standard 5-mm broad-band Varian probe. – The important experimental details of the sample preparation and testing have already been published elsewhere.[3,4] To mention just a few, although we have used mostly perdeuterated samples for demonstration, the degree and selectivity of deuteration is not crucial. The solute quantity one needs is ca. 1–3 mg in case of medium field strengths and medium level of deuterium incorporations. Under such conditions 2–4 scans give sufficient signal to noise ratio. Relaxation delays of ca. 1 s or less were applied. Repeated centrifugation of the sealed samples at about 1000 rpm almost always resulted in better resolution. Line widths of 2–6 Hz can be achieved routinely. We have added a few μL of CD_2Cl_2 or $CDCl_3$ to the samples, and its signal was used as chemical shift reference and also for checking the quality of the liquid-crystalline phase.

However, limitations such as the solubility of solute in the co-solvent, do exist. Effects of PBLG molecular weight and concentration must be taken into account. We have purchased the deuterated solutes and PBLG from Sigma/Aldrich, unfortunately the degree of polymerisation changes from product to product. It is advisable to use higher molecular weight, except when working at very low temperatures. In fact, by changing the solvent/co-solvent ratio one can influence to some extent the magnitude of the observed splittings. From a practical point of view it is noteworthy that in these ternary mixtures of PBLG with $CHCl_3$ or CH_2Cl_2 as co-solvents the technically available temperature range is at least as large as in isotropic liquids, sometimes even larger. At some temperatures, transition to an ordered gel phase can occur, but no direct evidence of this was noticed.

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