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R. L. Silvestri [a] & J. L. Koenig [a]
[a] Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio, 44106
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Solid-State 2-D NMR Correlation of Structure and Motion in Polymer Dispersed Liquid Crystals

R. L. SILVESTRI and J. L. KOENIG*
Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106

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Two-dimensional Nuclear Magnetic Resonance (NMR) spectroscopy is used to characterize polymer dispersed liquid crystals (PDLCs) in the solid-state. The wideline separation (WISE) pulse sequence is used to correlate structure and mobility in a PDLC. The PDLC is 40% E7 as 0.4 μ droplets in an Epon 828 matrix. The WISE pulse sequence generates ^{1}H wideline spectra in one dimension for each high resolution solid state ^{13}C resonance in the other dimension. For each ^{13}C resonance, the width of the ^{1}H line shape reflects the mobility of the protons in the vicinity of the respective ^{13}C. Spin diffusion is incorporated into the WISE pulse sequence to determine the relative spatial positions of components with different mobilities. The aliphatic portions of E7 exhibit extremely narrow ^{1}H line widths of a few hundred hertz. Therefore, the aliphatic pendant groups of E7 undergo pseudo-random isotropic motions with rates above 1 MHz. The aromatic portions of E7 exhibit pronounced spinning sidebands in the ^{1}H dimension. Therefore, the aromatic core of E7 undergoes anisotropic motions; specifically, ring flipping of the phenyl rings about their para axes. This ring flipping also occurs with rates exceeding 1 MHz.

Keywords: NMR spectroscopy, 2-D NMR, solid-state NMR, polymer dispersed liquid crystals

I. INTRODUCTION

Polymer dispersed liquid crystals (PDLCs) are low molecular weight liquid crystals dispersed as sub-micron sized droplets in an epoxy matrix.[1,2] Although heterogeneous on the molecular level, the bulk material successfully combines the unique properties of the liquid crystal and the polymer.

Solid-state Nuclear Magnetic Resonance (NMR) spectroscopy can be used to characterize the structure and motion of PDLCs. In particular, the wideline separation (WISE) pulse sequence (Figure 1a) generates a two-dimensional heteronuclear correlation of structure and mobility.[3,4] The WISE pulse sequence yields a ^{1}H wideline spectrum in one dimension for each high resolution solid-state ^{13}C resonance in the other dimension. Each ^{13}C resonance has a separate proton wideline spectra reflecting the $^{1}H—^{13}C$ dipolar coupling in the proximity of the respective ^{13}C moiety.[3]

Because the dipolar line width is reduced by motion, segmental mobility is reflected in the ^{1}H line shape. That is, motional averaging narrows the ^{1}H line shape. In particular, large-amplitude motions with rates exceeding the dipolar coupling, typically 50 kHz, average the proton line shape. Thus for a given ^{13}C resonance, a narrow ^{1}H lineshape indicates high segmental mobility of the chemical structure assigned to

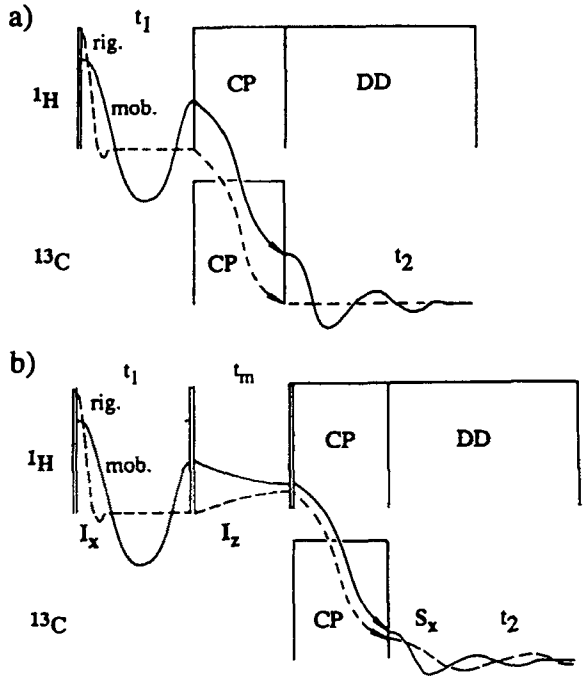


FIGURE 1 (A) Wideline separation (WISE) pulse sequence and (B) WISE pulse sequence with exploitation of ^1H spin diffusion (Adapted from reference [3]).

the ^{13}C resonance. Therefore, the chemical structure is reflected in the ^{13}C resonance position and molecular mobility is reflected in the ^1H line width. In this respect, the WISE pulse sequence establishes a heteronuclear correlation of chemical structure and segmental mobility.[3]

As shown in Figure 1a, the WISE pulse sequence is simply a cross polarization (CP) pulse sequence with a ^1H evolution period t_1 inserted between the initial ^1H 90° pulse and the CP contact pulse.

To expand on the WISE technique, ^1H spin diffusion may be incorporated into the pulse sequence. Figure 1b shows the WISE pulse sequence with a mixing time t_m inserted for ^1H spin diffusion. ^1H spin diffusion can be exploited to determine the relative spatial positions of components with different mobilities. Exchange of ^1H magnetization by spin diffusion transfers the ^1H lineshapes among diffusing moieties.[3]

If regions of a heterogeneous sample are sufficiently close in space, they exchange ^1H magnetization during t_m by spin diffusion. Therefore, the ^1H line shapes are exchanged. A mobile region with a narrow line shape transfers this narrow line shape to neighboring rigid segments via spin diffusion. Therefore, the rigid segment will display its characteristic wide line, but now with a narrow line superimposed.[3]

For a relatively short mixing time, line shapes can be exchanged only between segments that are in close proximity. By increasing the length of time that spin diffusion is allowed to progress, spin diffusion may occur over larger distances. If spin diffusion is

allowed to progress for a length of time t_m, the distance the magnetization diffuses or mean absolute displacement $\langle|x|\rangle$ can be calculated from

$$\langle|x|\rangle = (D\,\pi/4\,t_m)^{1/2} \tag{1}$$

where D is the spin diffusion coefficient.[3,5]

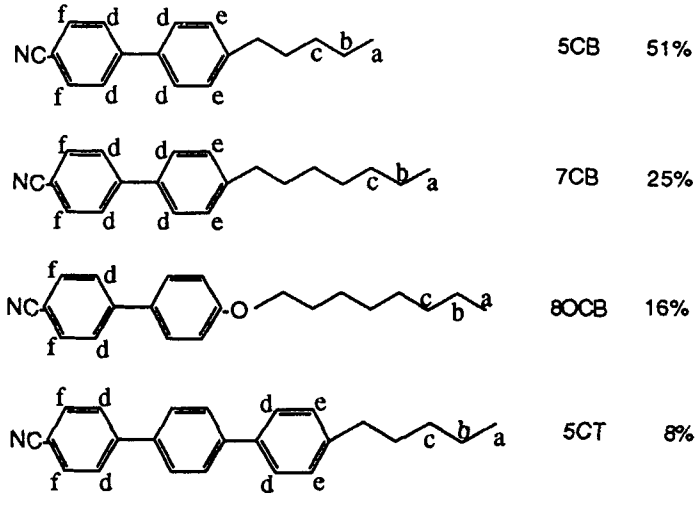
The WISE technique is particularly suited for the study of polymer systems that are heterogeneous on a scale of a few tens of nanometers. For example, the WISE technique has been used to study block copolymers and polymer blends.[3] In these heterogeneous polymer materials, spin diffusion exchanged ^{1}H line shapes between the rigid and mobile segments.[3] It was this that prompted us to use the WISE technique to study PDLCs, which are also heterogeneous on a sub-micron scale. Furthermore, the WISE technique is an experimentally simple pulse sequence for two-dimensional heteronuclear correlation in the solid-state as it avoids the use of sophisticated CRAMPS techniques.

II. EXPERIMENTAL

Polymer dispersed liquid crystals were made using the liquid crystalline mixture E7 and a three part epoxy. The PDLC consisted of 40% E7 and 60% epoxy.

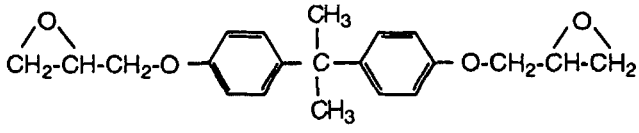
E7 is a mixture of four liquid crystals as shown in scheme 1. The E7 was manufactured by BDH Limited, Poole, England and distributed by EM Industries, Inc., Hawthorne, NY. The epoxy consisted of 9.1% Epon 828, 17.1% Heloxy WC97 and 33.8% Capcure 3-800 curing agent as shown in scheme 2.

E7

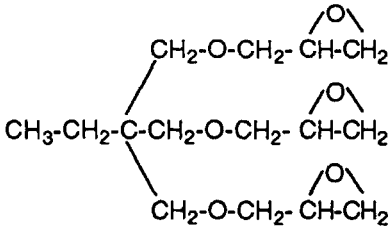


SCHEME 1

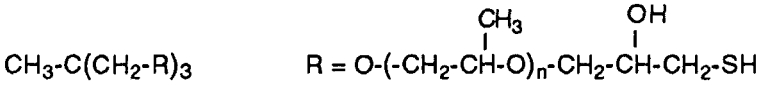
Epon 828



Heloxy WC97



Capcure 3-800



SCHEME 2

The raw materials were mixed by hand, centrifuged and cured at 90°C for 1.5 hours. Based on previous electron microscopy studies, the average droplet diameter of a PDLC made using this recipe is 0.4 μ.[6,7]

Solid-state NMR spectra were collected on a Bruker MSL 300 spectrometer at a ^{13}C measuring frequency of 75.47 MHz using a Bruker double resonance probehead. All experiments were carried out with cross polarization (CP), gated high powered dipolar decoupling (GHPD) and magic angle spinning (MAS). Rates of 2930 to 2970 Hz were used for magic angle sample spinning. Samples were spun in 7 mm outer diameter Zirconia rotors with Kel-F caps and the magic angle was set by maximizing the ^{79}Br

peak intensities of KBr.[8] The radio frequency (rf) field was 29 kHz as calculated from the length of the 90° pulse. The 90° pulse length was determined from the null intensity of adamantane at 180°. The Hartmann-Hahn match was set by maximizing the peak intensities of adamantane in a cross-polarization experiment with a 3 ms contact pulse. The chemical shift scale was set from the known peak positions of adamantane. All spectra were collected at ambient temperature, approximately 25°C.

Two-dimensional WISE NMR spectra were collected without and with exploitation of proton spin diffusion using the pulse sequences shown in Figures 1a and 1b, respectively. Mixing times (t_m) of 0.5 ms, 20 ms and 200 ms were used for proton spin diffusion. The recycle delay between pulse sequence repetitions (T_R) was 2 sec. A 1 ms contact time was used for the spin-locking pulse for cross polarization.

Typically 256 to 336 scans were signal averaged for each ^{13}C free induction decay (FID). FIDs with 800 data points were collected and zero filled to 2 k data points before Fourier transformation. A ^{13}C spectral width of 12,820 Hz or 170 ppm was used. To establish the second dimension 256 ^{13}C FIDs were collected. The proton evolution time t_1 was initially set to a negligibly small value of 1 μs then incremented by 20 us. The t_1 increment of 20 μs results in a ^1H spectral width of 50,000 Hz. The 256 t_1 increments were zero filled to 1 k prior to Fourier transformation.

All spectra were collected with quadrature phase detection in the ^{13}C dimension. However, the pulse sequence does not provide quadrature phase detection in the ^1H dimension. As a result, the spectra are symmetrized in the ^1H dimension. This is not a concern as the ^1H line shapes are expected to be approximately symmetric. Furthermore, the center of the one-dimensional ^1H line shape was set on resonance.

No window functions were used in either dimension, and a non-phase sensitive magnitude type two-dimensional Fourier transform was applied. All 1-D proton line shapes were transferred via ethernet to a MicroVax III+ for subsequent spectral manipulation using "in house" programs written in Fortran 77.

III. RESULTS

Figure 2 shows the 2D WISE NMR spectrum of a PDLC with 40% E7. The WISE spectrum shown in Figure 2 was collected using the pulse sequence without ^1H spin diffusion. ^{13}C resonances are observed for (A) C_a at 15 ppm, (B) C_b at 23 ppm, (C) C_c at 33 ppm, (D) C_d at 127 ppm, (E) C_e at 130 ppm and (F) C_f at 133 ppm, where the carbon subscripts correspond to those labeled in the molecular structure for E7.

Peak assignments were made by combining information from (A) known chemical shifts of similar compounds,[6,9-12] (B) chemical shift calculations including a knowledge of the resonances of similar atoms that will be overlapping,[9] and (C) quantitative NMR peak areas accounting for the ratios of the various components of the E7 mixture. The chemical shifts of C_a are overlapping for all four components of the E7 mixture because the molecular structures are identical up to the ε position. Similar arguments hold true for the other overlapping resonances of the mixture. Complete descriptions of the peak assignments have been previously published for E7[6] and for 5CB (the main component of the E7 mixture).[10,11] Furthermore, the chemical shifts of the aromatic portion of 8OCB are similar to those previously published for 5OCB.[12]

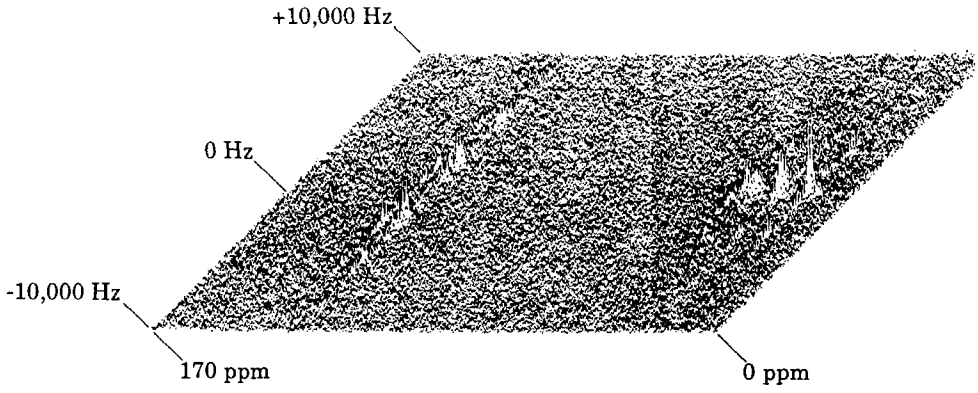


FIGURE 2 Two-dimensional WISE NMR spectrum of a PDLC (40% E7).

The most striking feature of the WISE spectrum is the exceptionally narrow ^{1}H line shapes. This is evidence that the E7 is highly mobile. A quantitative discussion will be presented briefly.

Mixing times (t_m) of 0.5 ms, 20 ms and 200 ms were used for proton spin diffusion. The minimum effective mixing time t_m is one half of the CP contact time.[3] Therefore, due to the CP contact time of 1 ms the minimum effective t_m is 0.5 ms. Using Equation 1, the distance the magnetization diffuses or mean absolute displacement $\langle|x|\rangle$ can be calculated for each t_m. Assuming a spin diffusion coefficient of $D = 0.62\,\text{nm}^2/\text{ms}$,[13,14] the mixing times of 0.5 ms, 20 ms and 200 ms correspond to displacements of 4.9 Å, 31 Å and 99 Å, respectively. These values of $\langle|x|\rangle$ are approximations based on the assumed value of D. The value of $D = 0.62\,\text{nm}^2/\text{ms}$ is for hydrocarbons that are dense in protons, and this value should change little from one hydrocarbon to another provided that the proton density does not change.[13,14] Figures 3a–f show traces of the ^{1}H line shapes for the various lengths of spin diffusion.

The ^{1}H line shapes in Figures 3a–f have a relatively poor S/N ratio. Signal averaging 336 scans with a 2 sec recycle delay (T_R) and collecting 256 ^{13}C FIDs (t_1 increments) results in a total experiment time of 48 hours. Improving the S/N by signal averaging more scans would result in an excessive experiment time. Also, 256 t_1 increments were needed for sufficient resolution in the ^{1}H dimension to curve fit the ^{1}H line shapes. Furthermore. apodization was not used to improve the S/N of the spectra because apodization causes an increase in line-width. This would affect the quantitative discussion of line-widths to be presented briefly.

Molecular Motions of the Allphatic Portions of the E7 Mixture

Typical rigid methylene groups can have broad proton spectra with a full width at half maximum (FWHM) of up to 70 kHz. Indeed, for motionally narrowed adamantane we measured broad proton lineshapes of 24 kHz for carbon resonance at 29.5 ppm. and

27 kHz for the carbon resonance at 38.6 ppm. Furthermore, Schmidt-Rohr *et al.*[3] measured a proton line width of 20 kHz for the methyl in polycarbonate.

Without spin diffusion the FWHM for the methyl carbon C_a at 15 ppm shown in Figure 3a is 288 Hz, two orders of magnitude smaller than typical aliphatic line shapes.

TABLE I

Full width at half maximum (FWHM) of the ^{1}H wideline spectra for the methyl carbon C_a at 15 ppm for various lengths of spin diffusion, t_m.

t_m	FWHM
–	288 Hz
0.5 ms	407 Hz
20 ms	425 Hz
200 ms	418 Hz

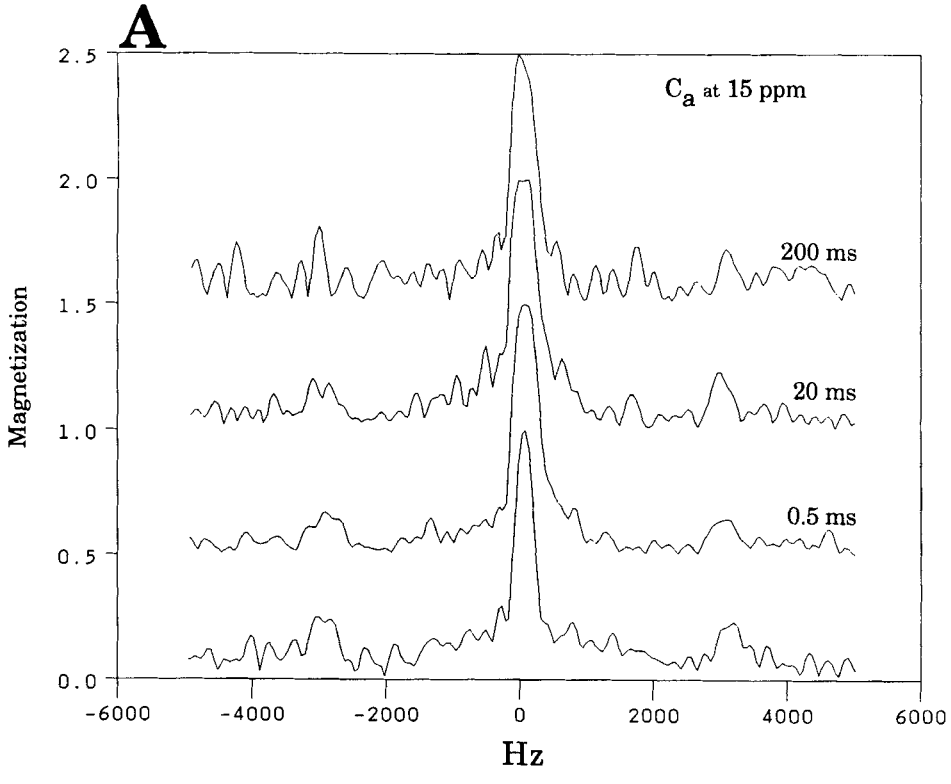


FIGURE 3 ^{1}H wideline spectra of a PDLC without exploitation of ^{1}H spin diffusion, and with 0.5 ms, 20 ms and 200 ms of ^{1}H spin diffusion for (A) C_a at 15 ppm, (B) C_b at 23 ppm (C) C_c at 33 ppm, (D) C_d at 127 ppm, (E) C_e at 130 ppm and (F) C_f at 133 ppm.

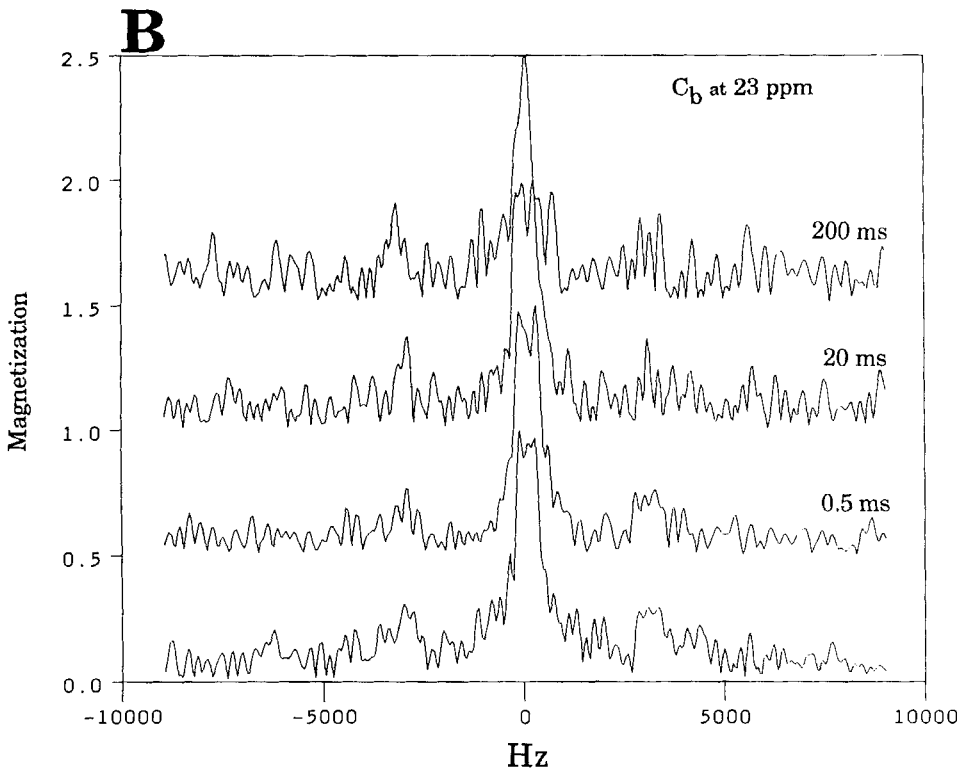


FIGURE 3 *(Continued)*

The line widths were determined by baseline correcting and fitting the peaks to a curve with an arbitrary fraction of Lorntzian/Gaussian character. Table I lists the FWHM for this peak for the various mixing times. For all three mixing times the linewidths are approximately equal with an average value of 417 Hz. Spin diffusion transfers this larger linewidth to the peak from a more rigid portion of the PDLC. It is not surprising that the methyl carbon C_a is the most mobile portion of the PDLC as the methyl group is at the end of an aliphatic pendant group; furthermore, the methyl group is free to spin about its C_3 axis adding another degree of motion. However, it is interesting that the line width reaches its maximum value for even the shortest mixing time. Spin diffusion has reached an equilibrium in 0.5 ms, demonstrating that the portion of the molecule transfering its line shape to the methyl group is within 4.9Å.

The other aliphatic peaks, C_b at 23 ppm and C_c at 33 ppm, are not precisely on resonance in the ^1H dimension. Because the pulse sequence does not provide quadrature phase detection in the proton dimension, Figures 3b and 3c show folding around the center frequency that gives the appearance of horns. These peaks are not precisely on resonance due to their ^1H chemical shifts. That is, it is not possible to set all of the ^1H chemical shifts on resonance simultaneously.

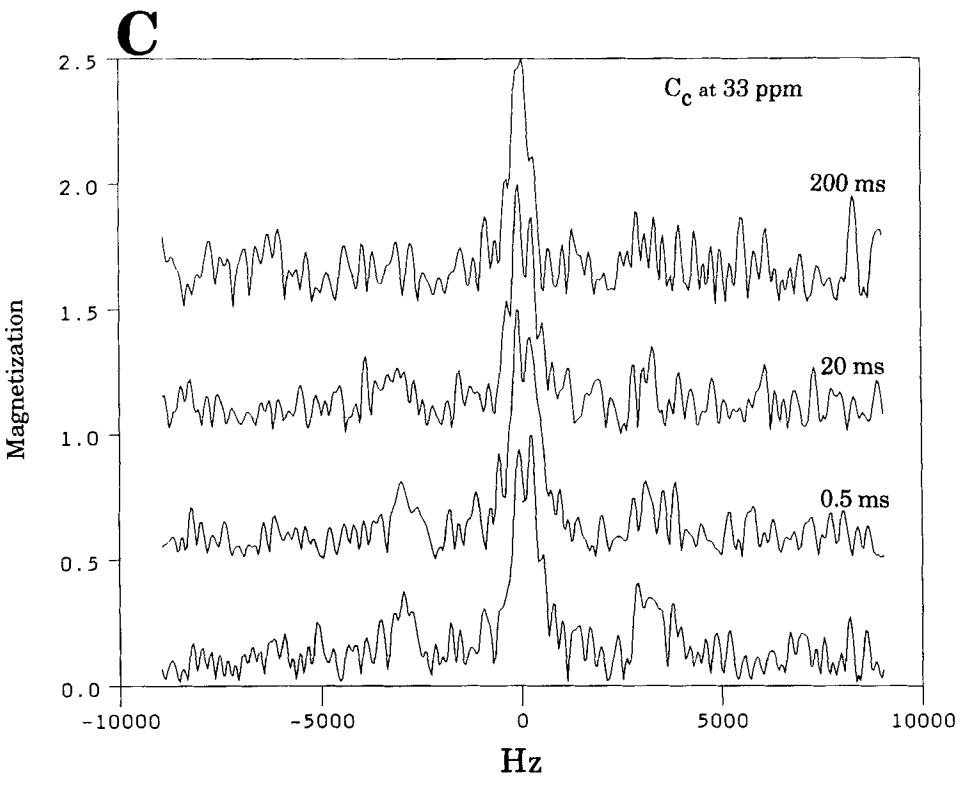


FIGURE 3 *(Continued)*

Molecular Motions of the Aromatic Portions of the E7 Mixture

Due to conjugation, the aromatic portion of a molecule is expectedly more rigid than the aliphatic portion of a molecule. Therefore, proton line widths for aromatic groups should be relatively large. Indeed, Schmidt-Rohr *et al.*[3] measured proton line widths of 50–75 kHz for the aromatic peaks in polystyrene. However, the aromatic line widths shown in Figures 3d–3f are orders of magnitude narrower.

Also, note that the phenyl signals exhibit pronounced spinning sidebands in the proton dimension at approximately 3000 Hz. Simple proton wideline spectra are not always observed in the proton dimension. In the case of restricted molecular motions there is an anisotropic averaging of the chemical shift tensor. In particular, if there is rotation about a single axis, then spinning sidebands appear in the ^{1}H dimension. This indicates that the aromatic rings are flipping about their para axis. Schmidt-Rohr *et al.*[3] have also observed characteristic spinning sidebands for flipping phenyl rings. Flipping of the phenyl rings weakens the intermolecular dipolar interactions, while the dipolar interactions of the phenyl protons parallel to the flip axes are unchanged.[3] As a result, these relatively isolated proton pairs yield spectra with spinning sidebands.[3]

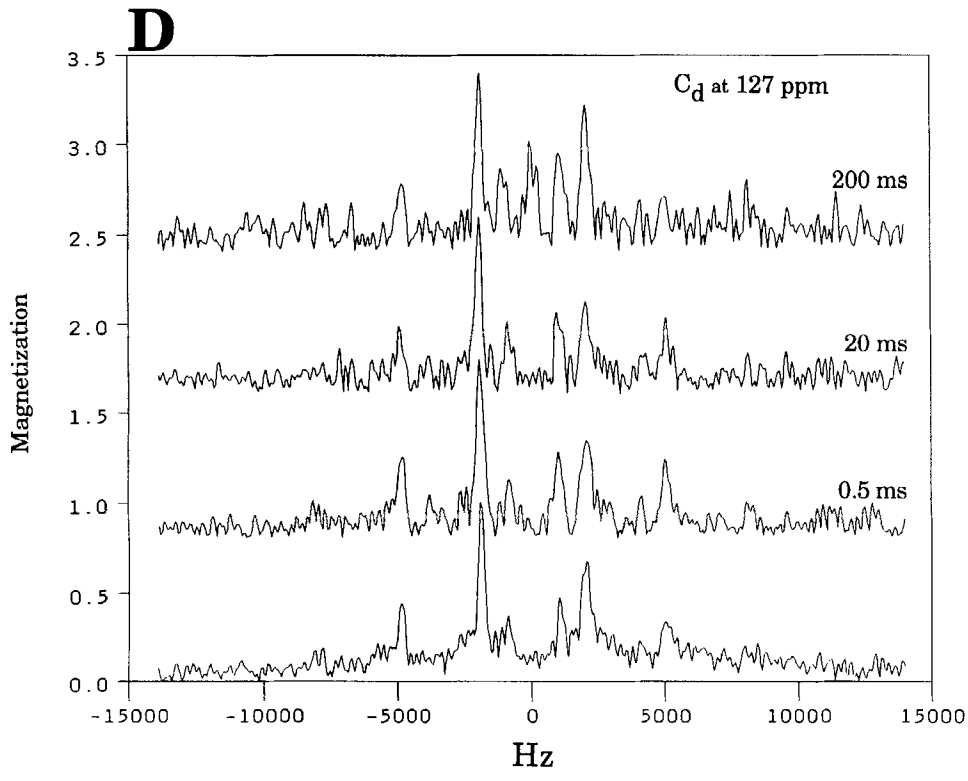


FIGURE 3 *(Continued)*

These characteristic proton spinning sidebands are proof that the aromatic rings are flipping about their para axis. Moreover, ring flipping is the obvious motion to suggest in keeping with the thought that the only internal motions allowed in solids and liquids are symmetry operations.[15,16] Use of the term "flipping" is not to imply discrete 180° jumps of the phenyl rings, but only to signify rotation about the para axis.

After 200 ms of spin diffusion a peak appears at 0 Hz for C_e at 130 ppm as shown in Figure 3e. Then after 200 ms of spin diffusion this peak grows in intensity as spin diffusion progresses further towards equilibrium. On the other hand, only after 200 ms of spin diffusion a peak appears at 0Hz for C_d at 127 ppm and C_f at 133 ppm, as shown in Figures 3d and 3f, respectively. Recall that after a mixing time of 20 ms spin diffusion reaches a displacement of 31Å, and after 200 ms spin diffusion reaches a displacement of 99Å. Spin diffusion reaches C_e in only 20 ms, but takes 200 ms to reach C_d and C_f. Therefore, that portion of the PDLC transfering its lineshape to the aromatic resonances is closer to C_e than to C_d and C_f. Note that C_e is adjacent to the aliphatic pendent group, whereas C_d and C_f are to the opposite end of the molecule.

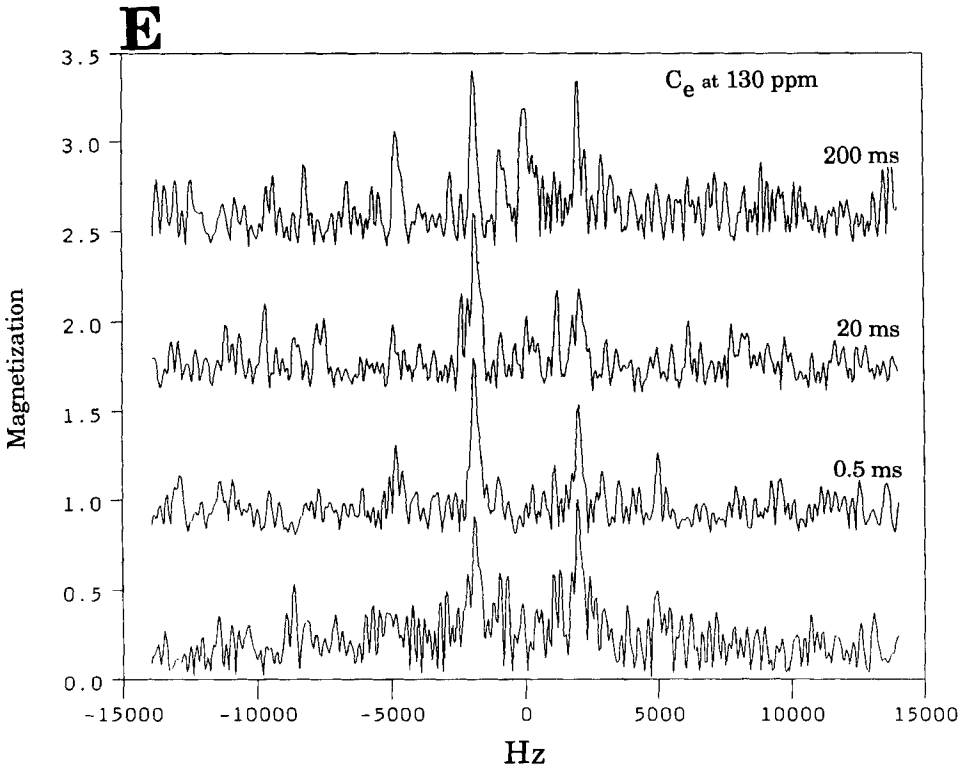


FIGURE 3 *(Continued)*

IV. DISCUSSION

Both the aliphatic and the aromatic portions of the various component molecules of the E7 mixture undergo fast molecular motions. This is seen by the exceptionally narrow proton line shapes. Ordinarily, motions with rates exceeding a few tens of kilohertz reduce the dipolar line width.[3] However, line widths as narrow as those observed herein are certainly reduced by motions with rates above 1 MHz.[3] This fast motion causes the carbon-protons to be only weakly dipolar coupled.

A ^1H line narrowed to a width below 1 kHz must be due to motions resulting in nearly isotropic averaging with rates exceeding 1 MHz.[3] Therefore, the aliphatic portions of E7 undergo nearly random isotropic reorientation. Furthermore, the motions of the aliphatic pendant groups occur with rates above 1 MHz.

In addition, ^1H spinning sidebands indicate anisotropic motions with rate also exceeding 1 MHz.[3] Therefore, the phenyl rings undergo ring flipping with rates above 1 MHz.

Upon closer inspection note that spinning sidebands also appear for the aliphatic peaks. However, the spinning sidebands are less pronounced for the aliphatic

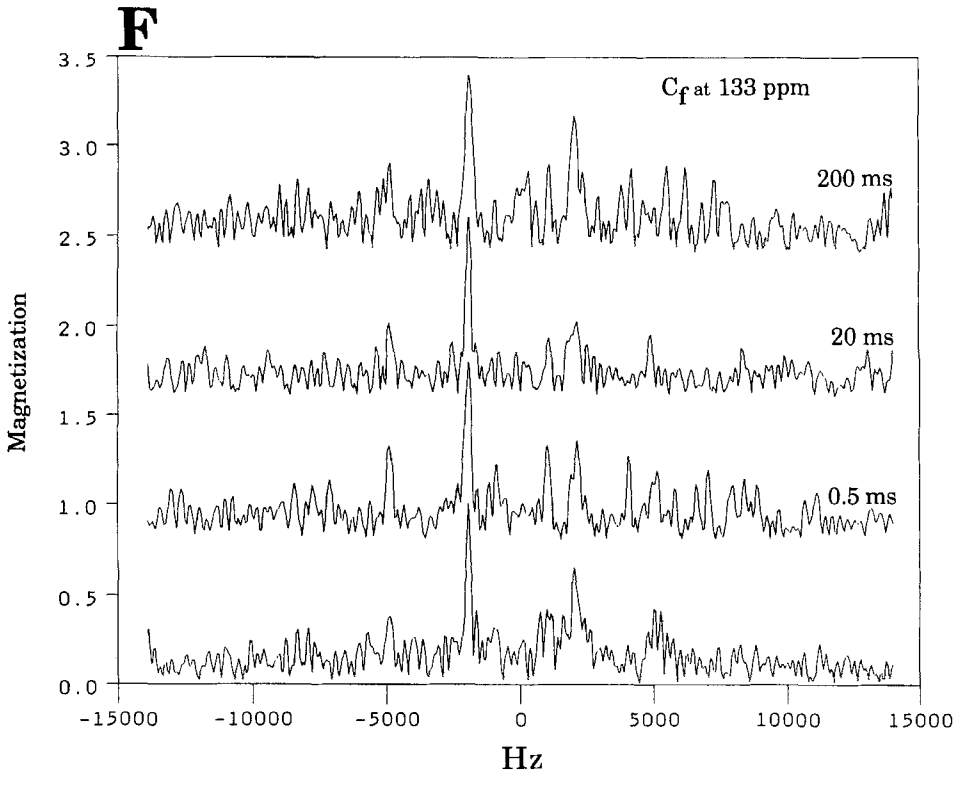


FIGURE 3 *(Continued)*

peaks as compared to the aromatic peaks. Therefore, the motion of the aliphatic pendant groups is not completely random and isotropic. There is some small fraction of anisotropy in the motion of the aliphatic pendant groups. This can be expected because the pendant group is not a sphere but a chain; and furthermore, the chain is attached to an aligned nematic core. None the less, the "wagging" of the pendant chain off of the nematic core can be considered nearly a random isotropic reorientation.

In summary, fast motions occur in both the aliphatic and aromatic portions of E7. However, nematic alignment is maintained even with such fast rates of motion. In fact, the "wagging" of the aliphatic pendant group may be considered the cause of liquid crystallinity because without the fast motion of the pendant group the rigid core would surely crystallize.

V. CONCLUSIONS

In summary, fast motions occur in both the aliphatic and aromatic portions of the various component molecules of the E7 mixture.

The aliphatic portions of E7 exhibit extremely narrow ^1H line widths of a few hundred Hertz. Therefore, the aliphatic pendant groups of E7 undergo pseudo-random isotropic motions with rates above 1 MHz.

The aromatic portions of E7 exhibit pronounced spinning sidebands in the ^1H dimension. Therefore, the aromatic core of E7 undergoes anisotropic motions; specifically, ring flipping of the phenyl rings about their para axes. This ring flipping also occurs with rates exceeding 1 MHz.

Acknowledgements

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