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Cross relaxation of polymer dispersed liquid crystal droplets

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A study of proton relaxation for polymer dispersed liquid crystal samples was performed using the techniques of magic-angle spinning and magnetization transfer. By the use of these procedures it is possible to determine the cross relaxation rate between the polymer and the liquid crystal directly. The cross relaxation rate is dependent on the curing temperature, which affects the size of the liquid crystal droplets. It is also dependent on the curing time, which affects the droplet size as well. The cross relaxation rates for the aromatic and aliphatic protons of the liquid crystal are very similar, indicating that the liquid crystal molecules probably orient themselves lengthwise on the polymer surface. Differential scanning calorimetry analysis was also performed in order to study the effect of curing time upon the thermal properties of the polymer.

I. INTRODUCTION

Liquid crystals have wide applications in electro-optic displays due to their unique physical and optical properties. Various problems inherent with currently used display devices have lead to the research and development of alternate types of liquid crystal displays. One of these new materials is called nematic curvilinear aligned phase^{1,2} (NCAP) or polymer dispersed liquid crystal (PDLC).^{3,4} They are a composite material consisting of small nematic liquid crystal droplets confined in a polymer matrix, and can be fabricated into large or even flexible sheets. The diameter of the droplets is ordinarily in microns or submicrons, and the polymer is transparent for use in display applications. Various properties of these materials have been described in some detail.⁴⁻⁸

At the interface the liquid crystal molecules are attached to the polymer surface with a certain anchoring energy. The total anchoring energy and other surface phenomena are highly dependent upon the size of the nematic droplets. As the average droplet size decreases, the surface to volume ratio and consequently the percentage of liquid crystal molecules in direct contact with the polymer increases. Furthermore, when the droplets are smaller, the effect of the surface induced order extends farther into the interior. Many physical properties of the liquid crystal droplets are influenced by these surface effects. NMR is a powerful tool for the study of liquid crystals as well as molecular interactions at the interface. An extensive investigation of the proton and deuterium NMR of PDLC's have been performed by Doane and co-workers.⁹⁻¹⁹ Our study is concerned with the proton relaxation of liquid crystals in PDLC's. Here we show that the cross relaxation rate between the polymer and the liquid crystal can be directly obtained with the use of magic-angle spinning (MAS) and polarization transfer.

The technique of MAS is well known in the field of solid state nuclear magnetic resonance (NMR). The application of MAS and VAS (variable-angle spinning) to the study of liquid crystals was first introduced independently by Cour-

tieu *et al.*,^{20,21} and by Teeäär *et al.*²² They studied the macroscopic alignment of nematic liquid crystals being spun rapidly about an axis forming an angle θ with respect to the magnetic field. They found that nematic liquid crystals with a positive anisotropy of the magnetic susceptibility would align along the spinning axis for $\theta < 54^\circ 44'$ (the magic angle) and perpendicular to the spinning axis for $\theta > 54^\circ 44'$ while those with negative anisotropies would behave in an opposite way.

Since rapid spinning at or near the magic angle causes a considerable line narrowing liquid crystals,²⁰⁻⁴⁶ it allows measurement of the proton relaxation for both the aromatic and aliphatic portions of the liquid crystal molecules.⁴⁶ The technique of magnetization transfer was introduced by Bryant of co-workers to study the cross relaxation between water and bovine serum albumin,⁴⁷ and has been applied to other biological systems. We have shown that by the use of a combination of these two methods, it is possible to directly determine the cross relaxation rate at the polymer/liquid crystal interface in PDLC samples.⁴⁶ We now report further studies of the dependence of the cross relaxation rate on the curing temperature and curing time of these samples. Differential scanning calorimetry (DSC) analyses were used to corroborate the NMR results.

II. EXPERIMENT

The PDLC samples were prepared by mixing the commercially available liquid crystal E7 (EM chemicals) with the two components of an epoxy resin, Epon 828 and Capcure 3-800 (Miller-Stephenson), in a 1:1:1 weight ratio. One sample was cured at room temperature while the other was baked in an oven at 75 °C. Both samples were allowed to cure for 24 h before beginning the NMR experiments, which were carried out over a period of 2 weeks. The NMR experiments were performed on a Varian XL-300 spectrometer operating at 300 MHz, using a Doty Scientific MAS probe. The experiments consisted of inversion-recovery measurements for a

pure E7 sample and each PDLC sample from 15 °C to 75 °C in one degree intervals. The spin lattice relaxation time (T_1) for the PDLC samples were first measured with no off-resonance irradiation and then with off-resonance irradiation. The data was then processed using a Varian VXR-4000 data station by fitting it to a single exponential function with three parameters. The error for the data decreased with increasing temperature. This effect was caused by the dramatic increase of the signal-to-noise ratio with temperature. At low temperatures the aromatic peak was very broad and scarcely discernible from the base line noise, leading to extremely large errors in the T_1 values from this region. Because of this problem, all data with errors in excess of 8% (mainly the aromatic region below 30 °C) were discarded. The rest of the data were then used to calculate the cross relaxation as explained in the next section.

DSC analysis was also performed using a Perkin Elmer DSC-2 instrument. Samples made concurrently with the ones used for NMR were studied. The measurements were taken at much shorter time intervals in order to study the rate of curing, changes occurring in the glass transition temperature, and the nematic to isotropic phase transition.

III. RESULTS AND DISCUSSION

The proton NMR spectra of the liquid crystal E7 in a PDLC sample are shown in Fig. 1. Because the spectra were obtained with MAS, the aromatic and aliphatic regions are well resolved, making it possible to measure T_1 for each por-

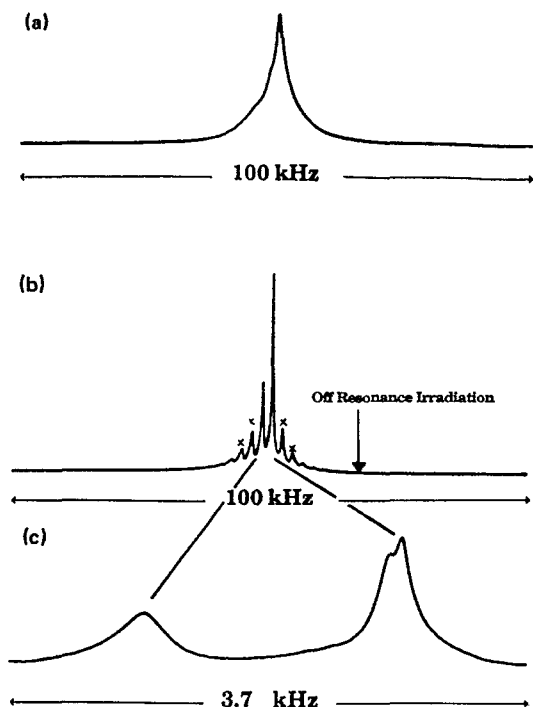


FIG. 1. Proton NMR spectra (300 MHz and 25 °C) of a PDLC sample with liquid crystal E7 dispersed in an epoxy polymer matrix. (A) Nonspinning. (B) MAS with a spinning rate of 1.7 kHz. The peaks marked with \times are spinning sidebands; the polymer peak appears as a broad background only. (C) Expansion of (B).

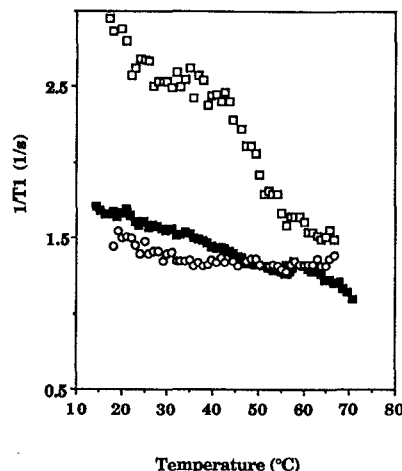


FIG. 2. Aliphatic proton relaxation rates of the liquid crystal E7 at 300 MHz with MAS. ■, Bulk E7 aliphatic protons; ○, PDLC sample with no off-resonance irradiation; □, PDLC sample with off-resonance irradiation.

tion separately (Figs. 2 and 3). At low temperatures, as explained above, the peaks are very broad and the intensity measurements did not yield very accurate results; therefore, the data are more scattered than those at higher temperatures.

In general, proton T_1 is determined by both intramolecular and intermolecular dipole-dipole interactions. For systems with large interface areas, such as the liquid crystal droplets in the PDLC samples, cross relaxation between the two phases may have a substantial contribution to the rate of proton relaxation. In order to study the effect of cross relaxation in PDLC, we used the method of magnetization transfer. This consisted of applying an off-resonance irradiation approximately 15 kHz from the center of the spectral window. The application of the off-resonance irradiation does not affect T_1 of bulk E7 within experimental error. However, it shortens the apparent T_1 of E7 in the PDLC samples (Figs. 2 and 3). The reason for this decrease is the following.

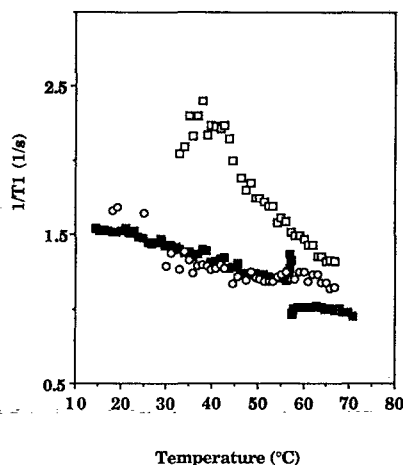


FIG. 3. Aromatic proton relaxation rates of the liquid crystal E7 at 300 MHz with MAS. ■, Bulk E7 aliphatic protons; ○, PDLC sample with no off-resonance irradiation; □, PDLC sample with off-resonance irradiation.

When a weak off-resonance irradiation is applied, the polymer protons with Larmor precessions at the corresponding frequency are caused to rapidly undergo transitions between their spin energy levels. Because the polymer protons are tightly coupled, spin diffusion serves to excite all the possible transitions of the polymer protons. To verify this point, the experiment was repeated with an off-resonance frequency of -15 kHz, and no discernible difference was observed. Although the liquid crystal protons are not directly affected by the off-resonance irradiation, the effect of magnetization changes is transmitted by cross relaxation with the polymer protons.

The mathematical formulation for the effect of cross relaxation with and without off-resonance irradiation is given in the following. It is assumed that there is a single relaxation time for the polymer (P) and each resolvable component of the liquid crystal (L). For simplicity this assumption is made and the spin density matrix is not considered. The general time dependent equations for the decay of the magnetizations are

$$dM_L/dt = (-M_L + M_L^0)/T_{1L} - R_{LP} \cdot M_L + R_{PL} \cdot M_P, \quad (1)$$

$$dM_P/dt = (-M_P + M_P^0)/T_{1P} + R_{LP} \cdot M_L - R_{PL} \cdot M_P, \quad (2)$$

where T_{1L} is the longitudinal relaxation time of the liquid crystal protons; T_{1P} is the longitudinal relaxation time of the polymer protons; R_{LP} and R_{PL} are the rates of magnetization transfer between the two systems, respectively; R_{LP}/R_{PL} is equal to the ratio between the parts of spin systems P and L that are coupled to each other; the superscript 0 refers to equilibrium values. These are a set of simultaneous linear nonhomogeneous first order differential equations with the well-known solutions

$$M_L = M_L^0 + C_1 \cdot e^{-\lambda_1 t} + C_2 \cdot e^{-\lambda_2 t} \quad (3)$$

and

$$M_P = M_P^0 + C'_1 \cdot e^{-\lambda_1 t} + C'_2 \cdot e^{-\lambda_2 t}, \quad (4)$$

where

$$\lambda_{1,2} = (A + B)/2 \pm [(A + B)^2 + 4(A \cdot B - R_{LP} \cdot R_{PL})]^{1/2}/2,$$

with

$$A = 1/T_{1L} + R_{LP},$$

and

$$B = 1/T_{1P} + R_{PL}.$$

According to Eq. (3), the decay of the magnetization of the liquid crystal protons should be a biexponential function of time. Because the two exponents are not very different from each other, the data can be fit to a single exponential function with an error no more than those which show a true single-exponential decay, such as the case described below. When a five-parameter biexponential fit was attempted, the uncertainties were large and no reproducibility of the parameters was possible. The cross relaxation, therefore, cannot be obtained with any accuracy by using the biexponential fit. However, by saturating the polymer spin system with

off-resonance irradiation, the cross relaxation rate can be obtained because this causes $M_P = 0$ and $dM_P/dt = 0$ so that the solution of Eq. (1) becomes

$$M_L = [M_{L_0} - M_L^0/(A \cdot T_{1L})] e^{-At} + M_L^0/(A \cdot T_{1L}), \quad (5)$$

where M_{L_0} = magnetization of M_L at $t = 0$; $M_{L_0} = -M_L^0$ for a perfect π pulse. This is a single exponential with time constant $1/A$, which can be easily obtained with a normal three-parameter fitting procedure. Since T_{1L} is the longitudinal relaxation time for bulk E7, the cross relaxation can be obtained by

$$R_{LP} = A - 1/T_{1L}. \quad (6)$$

The effect of resonance offset in magnetization transfer experiments has been considered recently.^{48,49} Because we used a weak irradiation with an offset of ± 15 kHz, the problem of "RF bleed"⁴⁸ can be neglected. The effect of gradually changing the offset frequency⁴⁹ needs to be considered in future experiments.

By using Eq. (6), and drawing the best fit line through the experimental data ($1/T_1$), the cross relaxation rate was calculated. The results are presented in Fig. 4. The data indicate that the rate of cross relaxation (R_{LP}) for the sample cured at 75°C is greater than that for the sample cured at 25°C . This is reasonable because electron micrographs show that the droplets of the sample cured at 75°C are much smaller and more homogeneous than those for the sample cured at 25°C , having average radii ca. $1\ \mu\text{m}$ and $3\ \mu\text{m}$, respectively. Because the smaller droplets have a larger surface to volume ratio, a greater percentage of the liquid crystals would participate in the cross relaxation process at the interface. Values of R_{LP} for the aromatic and aliphatic protons are quite similar for both samples. This indicates that the liquid crystal molecules probably orient themselves lengthwise on the polymer surface (parallel anchoring) so that both parts of the molecule have similar spin interactions with the polymer protons. The R_{LP} values for the aliphatic chain are somewhat smaller due to its flexibility.

There have been several computer stimulations of equilibrium nematic director configurations for PDLC drop-

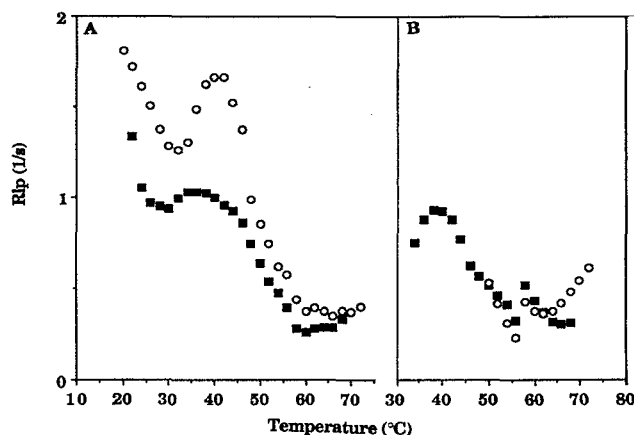


FIG. 4. Proton cross relaxation rates (300 MHz) of the liquid crystal E7 in a PDLC sample. (A) Aliphatic protons; (B) aromatic protons. O, Sample cured at 75°C ; ■, sample cured at 25°C .

lets.^{12,14,50} These stimulations have shown that there are several configurations possible, namely bipolar, concentric, axial, and radial configurations. The bipolar and the concentric configurations are both characterized by parallel anchoring at the interface while the axial and radial structures are characterized by perpendicular anchoring. Except for special cases, the liquid crystal molecules adopt parallel anchoring on the polymer surface in PDLC materials. A number of recent investigations by the use of scanning tunneling microscope (STM) also show that liquid crystal molecules orient lengthwise on the surfaces studied.⁵¹⁻⁵⁶ Although the polymer in our PDLC samples is not the same as the solid substrates in the STM work, it is interesting to note that liquid crystal molecules have parallel anchoring on many different types of surfaces but perpendicular anchoring only occurs in special cases.⁵⁰

Another way to determine the cross relaxation rate is to consider the ratio of the magnetization for the normal experiment and that for the off-resonance experiment. At $t = \infty$, Eqs. (3) and (5) become

$$M_{LN}(\infty) = M_L^0, \quad (7)$$

$$M_{LY}(\infty) = M_L^0/A \cdot T_{1L}, \quad (8)$$

where $M_{LN}(\infty)$ and $M_{LY}(\infty)$ are the magnetizations of the liquid crystal protons with no off-resonance irradiation and with off-resonance irradiation, respectively. The ratio of these two terms is thus $A \cdot T_{1L}$. By substituting this ratio into Eq. (6) we obtain

$$R_{LP} = [M_{LN}(\infty)/M_{LY}(\infty) - 1]/T_{1L}. \quad (9)$$

Therefore, the cross relaxation rate can be evaluated from the value of the magnetizations at equilibrium. Since the peaks are quite broad and partially overlap with each other [Fig. 1(C)], the peak height at $t = \infty$, obtained from fitting the relaxation data into a single exponential function, was used in place of the magnetization. The results are given in Fig. 5. Because the values of the peak height do not represent the total intensity, the rate of cross relaxation calculated in this way would not be very accurate. Nevertheless, the re-

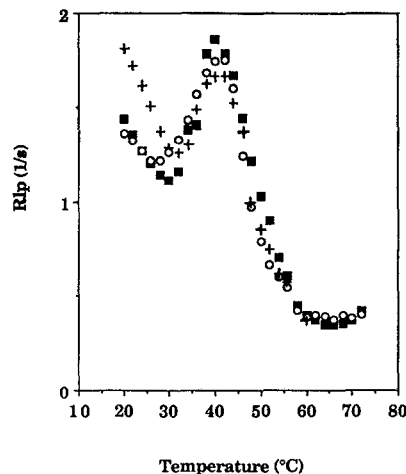


FIG. 6. Aliphatic proton cross relaxation rates (300 MHz) of the liquid crystal E7 in a PDLC sample cured at 75 °C. +, after 24 h; ■, after 1 week; O, after 2 weeks.

sults are of the correct order of magnitude and the temperature dependence is the same as that in the corresponding plot obtained by the first method. Obtaining the same shape from two different sets of data gives further credence to the validity of the methods used.

The relaxation rate for the bulk liquid crystal E7, $1/T_1$, decreases monotonically from 15 °C to 75 °C (Figs. 2 and 3); the discontinuity at 57 °C is due to first order nematic-to-isotropic phase transition. On the other hand, the plots in Figs. 4 and 5 for R_{LP} show a prominent maximum at ca. 40 °C. Moreover, this maximum depends on the curing condition and curing time of the PDLC samples. For the sample cured at 75 °C for 24 h and left at room temperature, the maximum does not change appreciably with time (Fig. 6); for the sample cured at 25 °C, the maximum was fairly noticeable after 24 h, but becomes more prominent as time progresses (Fig. 7). Because the PDLC samples were made

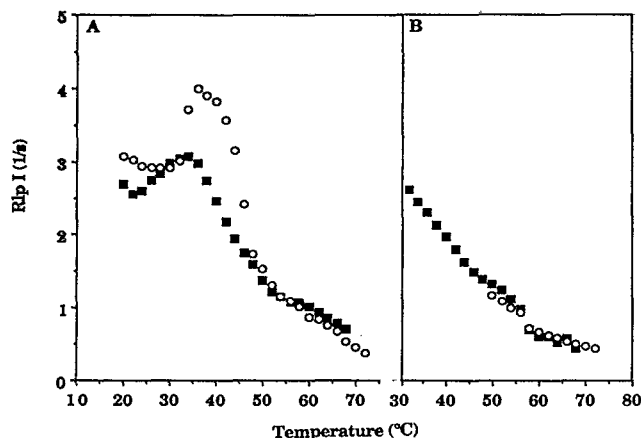


FIG. 5. Proton cross relaxation rates (300 MHz) of the liquid crystal E7 in a PDLC sample. Obtained from intensity ratios. (A) Aliphatic protons; (B) aromatic protons. O, Sample cured at 75 °C; ■, sample cured at 25 °C.

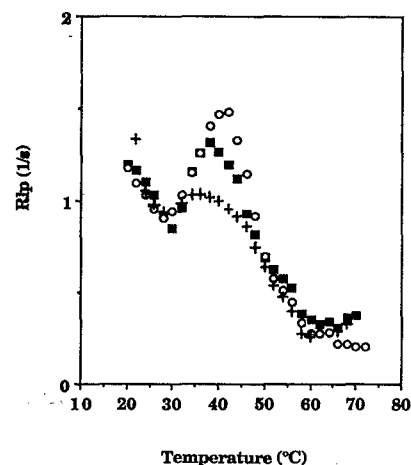


FIG. 7. Aliphatic proton cross relaxation rates (300 MHz) of the liquid crystal E7 in a PDLC sample cured at 25 °C. +, after 24 h; ■, after 1 week; O, after 2 weeks.

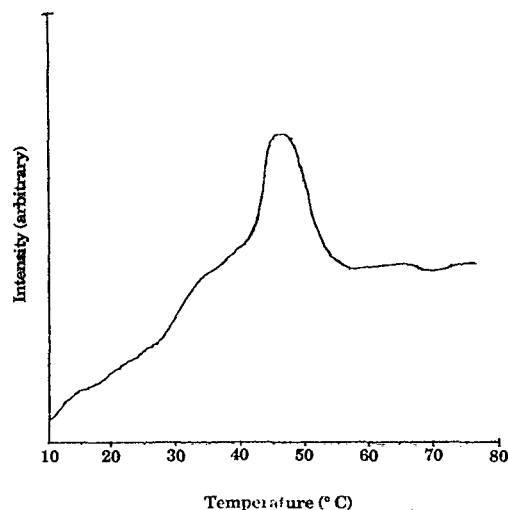


FIG. 8. DSC profile for a liquid crystal E7 in an epoxy polymer matrix (PDLC). Obtained after curing at 25 °C for 8 d.

by mixing the liquid crystal E7 with the epoxy resin Epon 828 and the curing agent Capcure 3-800 in a 1:1:1 ratio, the time required for stabilization is much longer than the curing time of the pure resin, which is about 24 h at room temperature. This is due to incomplete phase separation; the stabilization time for a sample cured at room temperature is approximately 3 weeks, and that for the sample cured at 75 °C for 24 h is less than 2 d. This is shown by the R_{LP} data and the DSC data to be discussed below.

Because the physical properties of the polymer influence the shape of the R_{LP} curve, the DSC profile of the PDLC were studied over time. Figure 8 shows a DSC curve for a PDLC sample. The shoulder at approximately 35 °C is due to the glass transition of the polymer. It can be seen that this transition corresponds to the same temperature at which the maximum in the R_{LP} curve occurs. The prominent peak occurring at ca. 47 °C is the nematic to isotropic phase transition of the liquid crystal. For the sample cured at 25 °C the peak initially occurs at 43 °C. It steadily moves upward to a limiting value of 55 °C after a period of 3 weeks. The sample cured at 75 °C has an initial peak occurring at 55 °C, and does not change significantly with time. Because the only noticeable change over time for the DSC curves is the migration of the peak due to the nematic to isotropic phase transition, the physical change giving rise to this change must also be responsible for the change of the cross relaxation rate shown in Fig. 7. A possible explanation of the mechanism for the change in R_{LP} is the following. Although the initial phase separation is established rather quickly (24 h), some monomer would dissolve in the liquid crystal droplets and cause a depression of the clearing point. As time elapses these monomers migrate to the polymer wall and polymerize, thus slightly decreasing the droplet size and increasing the clearing temperature. Because the cross relaxation rate is dependent upon the droplet size, this would cause a slight increase in R_{LP} , explaining the time dependence of these curves. For this discussion, it is evident that the glass transi-

tion of the polymer at ca. 35 °C causes the maximum in the cross relaxation rate R_{LP} . On the other hand, the origin of the minimum in R_{LP} at ca. 30 °C (Figs. 6 and 7) is not clear, and further investigation is needed to elucidate this phenomenon.

IV. CONCLUSION

We have demonstrated that the method of MAS with off-resonance irradiation is very valuable for extracting information on proton cross relaxation between the liquid crystal molecules and the polymer matrix in PDLC samples. The results show that the polymer has a pronounced effect on the cross relaxation of these systems as demonstrated by the dependence of the cross relaxation rate on the curing temperature and curing time. It is interesting to note that the cross relaxation rate increases as the glass transition is approached, reaching a maximum at the glass transition, and decreases rapidly with the increase of temperature after the glass transition is passed. Because the cross relaxation rate gives insight into interactions occurring at the liquid crystal/polymer interface, studies such as these can be used to establish how the anchoring properties of the liquid crystal molecules are dependent upon the particular composition of the PDLC, and complement results of deuterium NMR and optical studies.⁹⁻¹⁹

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- ¹J. L. Fergason, US Patents 4,435,047 (1984), and 4,616,903 (1986).
- ²J. L. Fergason, SID Dig. Tech. Pap. **16**, 68 (1985).
- ³J. W. Doane, N. A. Vaz, B. G. Wu, and S. Zumer, Appl. Phys. Lett. **48**, 269 (1986).
- ⁴J. W. Doane, A. Golemme, J. L. West, J. B. Whitehead, Jr., and B. G. Wu, Mol. Cryst. Liq. Cryst. **165**, 511 (1988).
- ⁵N. A. Vaz, SPIE Proc. **1080**, 2 (1989).
- ⁶N. A. Vaz, G. P. Montgomery, Jr., J. Appl. Phys. **62**, 8 (1987).
- ⁷P. S. Drzaic, SPIE Proc. **1080**, 11 (1989).
- ⁸G. P. Montgomery, Jr., SPIE Proc. **1080**, 242 (1989).
- ⁹A. Golemme, S. Zumer, D. W. Allender, and J. W. Doane, Phys. Rev. Lett. **61**, 2937 (1988).
- ¹⁰A. Golemme, S. Zumer, and J. W. Doane, Phys. Rev. A **37**, 559 (1988).
- ¹¹M. Vilfan, V. Rutar, S. Zumer, G. Lahajnar, R. Blinc, J. W. Doane, and A. Golemme, J. Chem. Phys. **89**, 597 (1988).
- ¹²S. Zumer, M. Vilfan, and I. Vilfan, Liq. Cryst. **3**, 947 (1988).
- ¹³S. Zumer, E. Kardelj, J. W. Doane, M. Vilfan, and R. Blinc, SPIE Proc. **1080**, 258 (1989).
- ¹⁴S. Kralj, M. Vilfan, and L. Zumer, Liq. Cryst. **5**, 1489 (1989).
- ¹⁵S. Zumer, S. Kralj, and M. Vilfan, J. Chem. Phys. **91**, 6411 (1989).
- ¹⁶G. Crawford, R. O. Crawford, and W. Doane, SPIE Proc. **1455**, 2 (1991).
- ¹⁷G. Crawford, D. Yang, S. Zumer, D. Finotello, and W. Doane, Phys. Rev. Lett. **66**, 723 (1991).
- ¹⁸G. Stannarius, G. Crawford, L. Chien, and W. Doane, J. Appl. Phys. **1** (1991).
- ¹⁹G. Crawford, R. Stannarius, and J. Doane, Phys. Rev. A **44**, 4 (1991).
- ²⁰J. Courtieu, D. W. Alderman, and D. M. Grant, J. Am. Chem. Soc. **103**, 6783 (1981).
- ²¹J. Courtieu, D. W. Alderman, and D. M. Grant, J. Chem. Phys. **77**, 723 (1982).
- ²²R. Töcäar, M. Alla, and E. Lippmaa, Org. Magn. Reson. **19**, 134 (1982).
- ²³B. M. Fung and M. Gangoda, J. Chem. Phys. **83**, 3285 (1985).
- ²⁴B. M. Fung and J. Afzal, J. Am. Chem. Soc. **108**, 1107 (1986).

- ²⁵B. M. Fung, J. Afzal, T. L. Foss, and M.-H. Chau, *J. Chem. Phys.* **85**, 4808 (1986).
- ²⁶B. M. Fung, C.-D. Poon, M. Gangoda, E. L. Enwall, T. A. Diep, and C. D. Bui, *Mol. Cryst. Liq. Cryst.* **141**, 267 (1986).
- ²⁷C.-D. Poon, C. M. Wooldridge, and B. M. Fung, *Mol. Cryst. Liq. Cryst.* **157**, 303 (1988).
- ²⁸C. B. Frech, B. M. Fung, and M. Schadt, *Liq. Cryst.* **3**, 713 (1988).
- ²⁹P. Forster and B. M. Fung, *J. Chem. Soc. Faraday Trans. 2*, **84**, 1083 (1988).
- ³⁰C.-D. Poon and B. M. Fung, *Liq. Cryst.* **4**, 1159 (1989).
- ³¹C. B. Frech, B. M. Fung, and M. Schadt, *SPIE Proc.* **1080**, 215 (1989).
- ³²C.-D. Poon and B. M. Fung, *J. Chem. Phys.* **91**, 7392 (1989).
- ³³W. Richter, B. M. Fung, and M. Schadt, *Liq. Cryst.* **8**, 63 (1990).
- ³⁴W. Richter, D. Reimer, B. M. Fung, R. J. Twieg, and K. Betterton, *Liq. Cryst.* **8**, 687 (1990).
- ³⁵W. Guo and B. M. Fung, *Liq. Cryst.* **9**, 1, 117 (1991).
- ³⁶J. P. Bayle, A. Khandar-Shahabad, and J. Courtieu, *Liq. Cryst.* **1**, 189 (1986).
- ³⁷J. P. Bayle, A. Brossi, A. Guillois, and J. Courtieu, *Liq. Cryst.* **2**, 665 (1987).
- ³⁸N. T. Lai, J. P. Bayle, J. M. Ouvrard, and J. Courtieu, *Liq. Cryst.* **3**, 745 (1988).
- ³⁹J. P. Bayle, F. Perez, and J. Courtieu, *Liq. Cryst.* **3**, 753 (1988).
- ⁴⁰J. P. Bayle, E. Lafontaine, and J. Courtieu, *J. Chim. Phys.* **85**, 10 (1988).
- ⁴¹J. P. Bayle, E. Lafontaine, and J. Courtieu, *Liq. Cryst.* **6**, 231 (1989).
- ⁴²W. A. Heeschen, D. W. Alderman, and D. M. Grant, *J. Magn. Reson.* **59**, 318 (1984).
- ⁴³T. Väänänen, J. Jokisaari, and M. Seläntaus, *Chem. Phys. Lett.* **129**, 399 (1986).
- ⁴⁴T. Väänänen, J. Jokisaari, and M. Seläntaus, *J. Magn. Reson.* **72**, 414 (1987).
- ⁴⁵J. Forbea, C. Husted, and E. Oldfield, *J. Am. Chem. Soc.* **110**, 1059 (1988).
- ⁴⁶B. M. Fung and C. W. Cross, *Magn. Reson. Imaging* **9**, 717 (1991).
- ⁴⁷J. Grad, D. Mendelson, F. Hyder, and R. G. Bryant, *J. Magn. Reson.* **86**, 416 (1990).
- ⁴⁸X. Wu, *J. Magn. Reson.* **93**, 186 (1991).
- ⁴⁹H. N. Yeung and S. D. Swanson, *J. Magn. Reson.* (in press).
- ⁵⁰R. Ondris-Crawford, E. Boyko, B. Wagner, J. Erdmann, S. Zumer, and W. Doane, *J. Appl. Phys.* **69**, 9 (1991).
- ⁵¹J. S. Foster and J. E. Frommer, *Nature* **333**, 542 (1988).
- ⁵²D. P. E. Smith, H. Horber, Ch. Gerber, and G. Binnig, *Science* **245**, 43 (1989).
- ⁵³J. K. Spong, H. A. Mizes, L. J. LaComb, Jr., M. M. Dovek, J. E. Frommer, and J. S. Foster, *Nature* **338**, 137 (1989).
- ⁵⁴J. S. Foster, J. E. Frommer, and J. K. Spong, *SPIE Proc.* **1080**, 200 (1989).
- ⁵⁵T. J. McMaster, H. Carr, M. J. Miles, P. Cairns, and V. J. Morris, *J. Vac. Sci. Technol. A* **8**, 1 (1990).
- ⁵⁶T. J. McMaster, H. Carr, M. J. Miles, P. Cairns, and V. J. Morris, *Liq. Cryst.* **9**, 1, 11 (1991).