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## Liquid Crystals

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# A note on proton cross-relaxation in polymer dispersed liquid crystals

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Measurements of the proton cross-relaxation rate in the polymer dispersed 4'-pentyl-4-cyanobiphenyl (5CB) droplets were performed by the selective magnetization inversion NMR technique. This method makes possible direct determination of the magnitude of the fast cross-relaxation rate in the MHz regime where the standard spin-lattice relaxation measurements only indicate its presence. In the isotropic phase, the cross-relaxation rate is found to be more than ten times larger in the droplets of pure 5CB than that reported earlier for the liquid crystal mixture E7 in the same polymer. The difference is discussed in terms of dynamic processes in the surface layer.

## 1. Introduction

The term proton cross-relaxation is usually used to describe the coupling between the spin relaxations of two proton systems in a heterogeneous sample [1–3]. The coupling occurs at the boundary where the dipolar magnetic interaction between two protons, each in one system, results in the exchange of the Zeeman spin energy. As a consequence, the spin relaxation rates of both proton systems differ from the respective bulk relaxation rates. The difference is easily observed by a suitable NMR technique if the transfer of magnetization from the boundary layer to the bulk of each phase occurs faster than the spin relaxation. Several processes, like physical exchange of molecules (translational diffusion), proton chemical exchange, and/or spin-diffusion take part in the spread of magnetization. It should be noted, however, that the cross-relaxation effect is considerably reduced by the motion of adjacent spin-bearing molecules at the boundary, whenever it is faster than the inverse dipolar coupling.

Proton cross-relaxation has been most intensively studied for biological systems where it takes place between water and macromolecular protons [2, 4–6]. Information on the degree of rotational freedom of surface-bound water molecules, on their exchange with the free water, and on the macromolecular motion was obtained. The observed presence of cross-relaxation implies in itself the existence of surface-bound molecules which exchange at a rate smaller than the Larmor frequency used in the experiment. The knowledge of cross-relaxation is also essential for a correct

interpretation of spin relaxation data in hydrated biological systems.

Liquid crystals confined into micro-cavities within an organic material represent a two-phase proton system as well. Examples are the well known polymer dispersed liquid crystals (PDLCs) [7–9] noted for their application in electro-optical devices, liquid crystals in organic cylindrical micro-cavities [10–12], and liquid crystals containing embedded polymer networks [13–16]. The proton cross-relaxation has so far been investigated in the dispersion consisting of E7 (Merck Ltd) liquid crystal droplets within a solid, epoxy polymer. From the spin-lattice relaxation data in the rotating frame ( $T_{1\rho}$ ), Vilfan *et al.* [17] obtained the magnitude of the effective cross-relaxation rate as  $k_c \sim 10 \text{ s}^{-1}$ . Using a more sophisticated experimental approach—magic angle spinning and polarization transfer with off-resonance irradiation—Cross and Fung [18, 19] made a detailed study of the cross-relaxation process. In particular, they found that the cross-relaxation rates are similar for aromatic and aliphatic protons and related this fact to the tangential surface-anchoring of molecules. They also showed that  $k_c$  decreases by about one order of magnitude on heating the sample into the isotropic phase and explained this by the glass transition in the polymer that they used.

In this paper we apply a simple, high frequency NMR technique to measure directly the proton cross-relaxation in the PDLC material, which contains spherical droplets of a pure liquid crystal material instead of the commercial mixture E7 used in previous studies. The spin-lattice relaxation measurements in the MHz range give clear evidence of a fast cross-relaxation process, but do not allow an estimate of the magnitude of the cross-relaxation rate. Therefore, the selective magnetization

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inversion NMR technique [2] is used to determine directly the effective proton cross-relaxation rate. We show that  $k_c$  depends strongly on the type of liquid crystal–polymer dispersion, being considerably larger for the pure liquid crystal 4'-pentyl-4-cyanobiphenyl (5CB) than that reported earlier for the mixture E7 in the same epoxy matrix [17]. In the isotropic phase, the difference is larger than one order of magnitude. The measurements obtained by the direct method are in agreement with recent field-cycling NMR studies where the cross-relaxation rate was determined indirectly from the  $T_1$  frequency dispersion [20].

## 2. Theory and method

In a dispersion containing liquid crystal (LC) and polymer (P) protons, the time dependence of the reduced magnetization  $m_i(t)$  after the application of a  $\pi$ -pulse is generally described by the sum of two exponential decays if the condition of fast magnetization transfer within each spin system is fulfilled.

$$m_i(t) = \zeta_i^+ \exp(-(T_1^{-1})^+ t) + \zeta_i^- \exp(-(T_1^{-1})^- t) \quad (1)$$

where  $m_i(t) = -(M_i(t) - M_i(\infty))/2M_i(\infty)$  with  $M_i$  being the time-dependent longitudinal magnetization of the  $i$ -system.  $i$  stands either for LC or P,  $\zeta_i^\pm$  are weight factors, and  $(T_1^{-1})^+$  and  $(T_1^{-1})^-$  are given by [2]

$$2(T_1^{-1})^\pm = (T_1^{-1})_{LC} + (T_1^{-1})_P + k_c \left(1 + \frac{p_{LC}}{p_P}\right) \pm \left\{ \left[ (T_1^{-1})_{LC} - (T_1^{-1})_P + k_c \left(1 - \frac{p_{LC}}{p_P}\right) \right]^2 + 4k_c^2 \frac{p_{LC}}{p_P} \right\}^{1/2} \quad (2)$$

Here  $(T_1^{-1})_{LC}$  and  $(T_1^{-1})_P$  denote the relaxation rates of the liquid crystal and polymer protons as they were in the absence of cross-relaxation.  $k_c$  stands for the rate of magnetization transfer from the whole liquid crystal phase to the bulk of the polymer phase, and  $p_i$  for the fraction of protons in the  $i$ -phase.

When measuring the spin–lattice relaxation time  $T_1$  by the common  $\pi$ - $t$ - $\pi/2$  sequence, intense pulses of a few microseconds are normally used. They induce complete inversion of proton magnetization immediately after the pulse. In such a case  $\zeta_i^-$  tends towards zero and equations (1) and (2) reduce to a simple form in the limit of fast cross-relaxation,  $k_c \gg (T_1^{-1})_{LC}, (T_1^{-1})_P$ :

$$m_i(t) = \exp(-(T_1^{-1})^- t) \quad (3)$$

and

$$(T_1^{-1})^- = p_{LC}(T_1^{-1})_{LC} + p_P(T_1^{-1})_P. \quad (4)$$

## 3. Results

The decay of magnetization of both proton phases is thus mono-exponential with the same decay constant  $(T_1^{-1})^-$ , which is the weighted average of  $(T_1^{-1})_{LC}$  and  $(T_1^{-1})_P$ . Such relaxation behaviour is indeed observed for the 5CB spherical droplets dispersed in the epoxy polymer (Bostik brand) at 86.6 MHz as shown in figure 1. The temperature dependence of the spin–lattice relaxation rates for the bulk 5CB liquid crystal, the bulk epoxy polymer, and the 5CB droplets is presented. Whereas the thin lines serve only as a guide to the eye, the thick solid line is calculated according to equation (4) as the weighted average of the bulk 5CB and bulk polymer relaxation rates. It fits satisfactorily the measured  $T_1^{-1}$  for droplet protons within the limits of experimental error (about 5%). In the fit, the weight factors  $p_{LC} = 0.3$  and  $p_P = 0.7$  have been used, according to the composition of the dispersion, and the 5CB bulk relaxation rate has been increased in the nematic phase by  $\sim 30\%$  to take into account the random director orientation in the confined state [21]. It should be mentioned that the spin–lattice relaxation time  $T_1$  of droplet protons can be observed separately from the polymer protons due to a large difference in the spin–spin relaxation times  $T_2$ . The measured spin–lattice relaxation time, however, does not depend at all on the position in the free induction decay signal. This is again in complete agreement with equation (3) which predicts the same relaxation rate for either spin system. The standard spin–

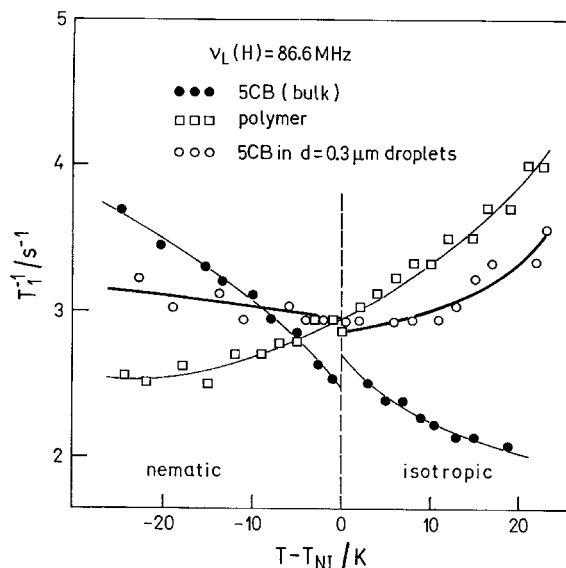


Figure 1. Proton spin–lattice relaxation rates of 5CB droplets with diameter 0.3  $\mu\text{m}$ , 5CB bulk, and pure epoxy polymer at 86.6 MHz. The thick solid line denotes the fit of equation (4) to the experimental data showing the effect of the fast proton cross-relaxation on  $T_1^{-1}$  in the PDLC material.

lattice relaxation data in the MHz range thus clearly demonstrate a fast proton cross-relaxation in the 5CB–epoxy polymer dispersion. This fact confirms the existence of a partially ordered layer of liquid crystal molecules at the boundary and their exchange at a rate which is small compared to the Larmor frequency 86.6 MHz.

It is not possible, however, to find the magnitude of the cross-relaxation without performing additional measurements. We find the selective magnetization inversion technique [2] as the most straightforward way to measure the cross-relaxation rate directly in the high frequency regime. The method is based on the fact that the lengthening of  $\pi$  and  $\pi/2$  pulses beyond  $T_2$  of the polymer leads to an almost complete inversion of liquid crystal magnetization, whereas that of the polymer spins is only partially inverted. As a consequence, the weight factor  $\alpha_{LC}$  increases with respect to  $\alpha_C$  and the reduced magnetization decay of either system is bi-exponential as predicted by equation (1). In figure 2, the time dependence of  $m_{LC}(t)$  in the droplets is plotted for three different lengths  $2\tau$  of the  $\pi$  pulse. The deviation from the mono-exponential decay is clearly visible for  $\tau = 60$  and  $220 \mu\text{s}$ . The solid lines in figure 2 were obtained by fitting equation (1) to the experimental data. The values of the parameters  $(T_1^{-1})^+$  and  $(T_1^{-1})^-$ , obtained by this fit, are  $(T_1^{-1})^+ = (360 \pm 50) \text{s}^{-1}$  and  $(T_1^{-1})^- = (3.9 \pm 0.5) \text{s}^{-1}$ . The latter is identified with the standard spin–lattice relaxation rate at  $T - T_{NI} = 23 \text{K}$ , shown in figure 1, and represents the weighted average of the bulk liquid crystal and polymer relaxation rates. It is independent of  $k_e$ . On the other hand,  $(T_1^{-1})^+$ , which is larger by two

orders of magnitude, is related to  $k_e$  in the limit of fast cross-relaxation by

$$(T_1^{-1})^+ = k_e \left( 1 + \frac{p_{LC}}{p_P} \right), \quad (5)$$

as can be deduced from equation (2). The selective magnetization inversion technique thus yields directly the value of  $k_e$  in the limit  $k_e \gg (T_1^{-1})_{LC}, (T_1^{-1})_P$ . It should be mentioned that the extension of the pulses does not affect the mono-exponential magnetization decay in the bulk 5CB (broken line in figure 2). The value of the spin–lattice relaxation rate measured with extended pulses is the same as that obtained by the standard short pulse technique, though the inhomogeneities in the r.f. magnetic field reduce the initial magnetization to somewhat less than 1.

Using the fitted value  $(T_1^{-1})^+ = 360 \text{s}^{-1}$  for the 5CB droplets dispersed in the epoxy polymer, with  $p_{LC} = 0.3$  and  $p_P = 0.7$ , the effective cross-relaxation rate  $k_e \sim 250 \text{s}^{-1}$  is obtained from equation (5). It is related to the rate  $k$  at which the bound fraction of liquid crystal molecules transfers spin energy between the two proton phases by  $k = k_e/x$ , where  $x$  denotes the relative fraction of the liquid crystal molecules at the surface layer.  $x$  is roughly given by the thickness of the surface layer  $d$  and the radius of the droplets  $R$  as  $\sim 3d/R$ . For  $d \sim 0.8 \text{nm}$  (well above  $T_{NI}$ ) and  $R = 150 \text{nm}$ ,  $k \sim (15 \pm 4) \times 10^3 \text{s}^{-1}$ . This value is in good agreement with that,  $18 \times 10^3 \text{s}^{-1}$ , obtained recently from field-cycling NMR studies on the same material, where the cross-relaxation rate was determined indirectly from the low-frequency relaxation data [20].

#### 4. Discussion

It is astonishing that  $k$  is more than ten times larger in 5CB droplets than in E7 droplets dispersed in the same polymer. E7 is a eutectic mixture of constituents with chemical structure similar to 5CB, and both types of droplet have the same bipolar structure with tangential molecular anchoring at the walls. In order to explain the difference, it should be taken into account that  $k^{-1}$  is determined by the slowest of several processes which include the average dwell-time of molecules at the surface layer  $\tau_s$ , the time of transfer of spin energy across the phase boundary  $\tau_{\text{cross}}$  and  $\tau_P$ , the time within which the magnetization spreads through the polymer. In the isotropic phase of 5CB droplets, it is reasonable to ascribe  $k^{-1} \sim 6 \times 10^{-5} \text{s}$  predominantly to the polymer  $\tau_P$ , the NMR linewidth of the polymer being of the same order of magnitude as  $k$ , and with  $\tau_s$  being considerably shorter as pointed out in ref. [20]. On the other hand,  $k^{-1}$  of E7 droplets, which is about  $8 \times 10^{-4} \text{s}$  both in the nematic and isotropic phases [17], should then be

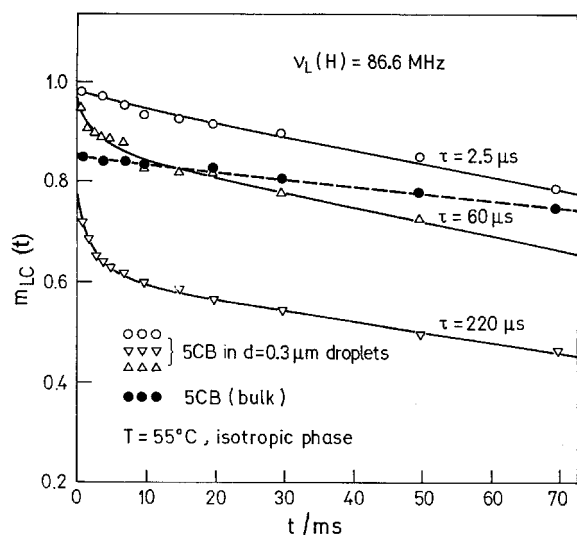


Figure 2. Time decay of reduced proton magnetization in 5CB droplets for three different lengths  $2\tau$  of the preparation  $\pi$ -pulse. Solid lines are calculated according to equation (1). The dashed line is for the bulk 5CB data.

determined either by  $\tau_S$  or  $\tau_{\text{cross}}$ . From the knowledge of  $k^{-1}$  alone, it is not possible to distinguish between these two possibilities. A weaker interaction between liquid crystal and polymer molecules at the boundary (probably due to the diversity of liquid crystal molecules in E7) might reduce the order parameter and the life-time of molecules in the surface layer. In this case  $\tau_{\text{cross}}$  would prevail over  $\tau_S$ . An estimate of  $\tau_{\text{cross}}$  is obtained from  $\tau_{\text{cross}} \sim (2\sigma^2\tau_S/9)^{-1}$  where  $\sigma$  denotes the dipolar interaction between a liquid crystal proton and polymer protons [2]. For example,  $\tau_S \sim 10^{-6}$  s and the effective distance between the two protons 0.2 nm yield  $\tau_{\text{cross}}$  as large as  $5 \times 10^{-4}$  s, a value rather close to  $k^{-1}$  in E7 droplets. The possibility of  $\tau_S$  determining  $k^{-1}$  in the isotropic phase of E7, which was proposed earlier [17], seems less probable in view of the recent measurements on similar systems, where rather short correlation times of the order  $10^{-6}$  s have been reported as  $\tau_S$  [16, 20]. Additional deuterium NMR relaxation studies, which are sensitive to  $\tau_S$  in particular, would be helpful in considering the above problem.

### 5. Summary

We have shown that a simple selective magnetization inversion NMR technique can be applied to determine the proton cross-relaxation in liquid crystal-polymer dispersions. It is useful in particular in the MHz frequency regime where the cross-relaxation is usually much faster than the spin-lattice relaxation and cannot be evaluated from the standard  $T_1$  measurements. The selective magnetization inversion technique can be applied both for the nematic and isotropic phases, though it is more convenient for the latter. Our results show that there is a large difference between the proton cross-relaxation rates in two rather similar PDLC systems. The cross-relaxation rate is thus a quantity which is sensitive to the delicate interplay of different dynamic processes at the liquid crystal-polymer boundary and can be used in the study of surface phenomena. A small change in the strength of surface interaction is undoubtedly reflected in the cross-relaxation effectiveness.

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