Deuterium NMR studies of Cellulosic Networks doped with 5CB

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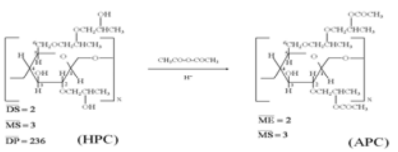
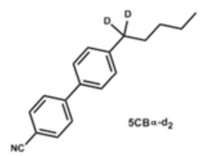
Abstract: *In this work we have used Deuterium NMR to investigate the orientational order in a composite system formed by liquid crystalline APC and deuterated 5CB in the percentages 85% to 15% by weight. The measurements have been done on three different forms of the composite material that include bulk samples, thin film samples and electro spun fibers micro fibers. The NMR results initially suggest two alternative scenarios, one where the LC is confined to small droplets with dimensions smaller than the wave length of visible light and the other were the LC molecules uniformly distributed in the polymer are attached and aligned with the APC polymer chains. Further evaluation of all the NMR results seem to point for the presence of LC droplets in the composite systems with a nematic wetting layer that experiences a order disorder transition driven by the polymer matrix I-N transition*

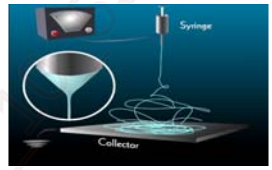
MATERIALS:





EXPERIMENTAL:

We have prepared solutions of [APC (85% wt/wt)+5CB(d$_2$) (15% wt/wt)] (30% wt/wt) in Acetone (70% wt/wt) (Aldrich – without further purification) at room temperature and the contents was allowed to mix for several weeks. The fibers have been prepared from that solution by electrospinning. After diluting the solution with more acetone a cast film has also been prepared and then it has been rolled in a small galss slide for NMR experiment. Part of the mother solution has also been used as bulk sample. In all the cases the samples have been dried in vaccum for 2days. NMR studies were performed for all the samples with variation of temperature.



Discussion of the Results

Recently micro and nano fibers of liquid crystalline cellulose networks were prepared by the electro-spinning method [1]. Particular mechanical properties were detected in these fibers motivating the study of the polymer chains alignment in these systems. Deuterium NMR is particularly suited to study molecular orientational order and was thus used with the introduction of a deuterated nematic probe 5CBα-d2 in the network. DNMR spectra were obtained in the APC cellulose networks doped with deuterated 5CB and prepared in the form of micro and nano fibers, and film and bulk samples for comparison, in the temperature range of 300K to 400K. The spectra recorded are composed of a superposition of an isotropic component (originating a central peak) and an ordered component with a characteristic Pake shape. From these spectra shown in figures 1 and 2 the temperature dependence of the averaged quadrupolar coupling constant ($<\nu_Q>$) was obtained (figure 3) along with the relative intensity of the ordered and disordered components (figure 4) through a fitting procedure (figure 5) to a Pake function (figure 6). While the pure deuterated probe used (5CBα-d2) shows a nematic to isotropic transition at 306 K, the DNMR spectra obtained show that the cellulose networks exhibit the presence of and ordered component almost up to 400K with small differences in between the different samples analyzed. This indicates that the order of the 5CB molecules is strongly determined by the network chains order. Two scenarios may be considered to account for this behavior; one where the 5CB molecules are uniformly distributed through the cellulose network and align with the network chains, and another where the 5CB molecules have phase separate out of the network and form small 5CB reach regions dispersed through the elastomer. Bothe scenarios are compatible with the results obtained with the non oriented samples but the results obtained with the fibers deposited in a glass plate and mainly oriented along a common direction parallel to the X axis (figures 7,8) do not agree with a uniform distribution of the 5CB molecules in the elastomer. It is found that in the case of the oriented fibers the nematic directors are distributed almost uniformly in the XY plane (figure 9) and absent of the Z direction, a situation only compatible with the presence of 5CB droplets deformed by the fiber deposition process.

Considering the presence of 5CB droplets we have applied the model developed by I. Amimori and co-workers [2] for studying stretched PDLC systems to obtain the order parameter S_S imposed on the 5CB molecules at the 5CB-network interface, and shown in a relative form in figure 10. Figure 11 gives the S_S value at N-I transition of the network as a function of the droplets average radius which has not been determined experimentally yet.

In the I. Amimori model the averaged quadrupolar coupling constant ($<\nu_Q>$) is calculated considering complete diffusional averaging in the droplets and is given by:

$$< \nu_Q > = \frac{\nu_{QB}}{S_B} \frac{\int_V S(r,z)\left(\frac{3}{2}\cos(\theta)^2 - \frac{1}{2}\right)dv}{V}$$

The order parameter S(r,z) is calculated in the context of the Landau-de Gennes formalism:

$$S(r,z) = \begin{cases} S_0, & R(z) \ge r \ge R_N(z) \\ S_0 e^{-(R_N(z)-r)/\xi(z)}, & R_N(z) \ge r \end{cases}$$

The order parameter S_0 is a function of the order parameter S_S imposed by the network on the 5CB molecules at the network interface:

$$S_0 = \frac{S_S(T)}{1 + \frac{1}{2g}\sqrt{a(T-T^*)L}}$$

Using the values for $<\nu_Q>$ reported in figure 3 and equations 1, 2 and 3 we have obtained the results reported in figures 10 and 11 for S_S. We have also estimated l_0=15 nm and g > 0.35 J/m^2 .

Deuterium spectra in aligned fibers

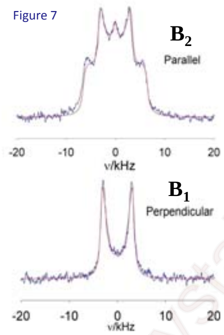


Figure 7

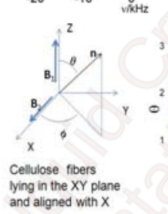


Figure 8

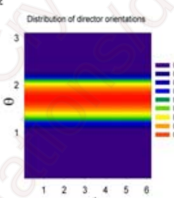


Figure 9

5CB droplet in the I. Amimori model with a isotropic center and an outer nematic layer with a width l_0 and a constant order parameter S_0. In the core the order parameter decays exponentially from S_o on approaching the droplet center. For simplicity we have considered R_0=Z_0.

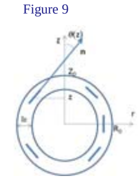


Figure 12

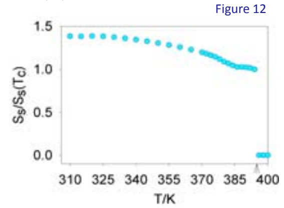


Figure 10

Deuterium Spectra from non oriented samples

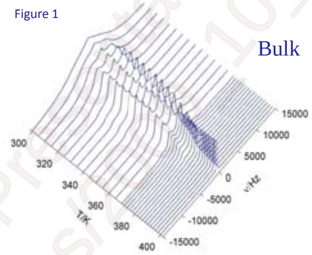


Figure 1

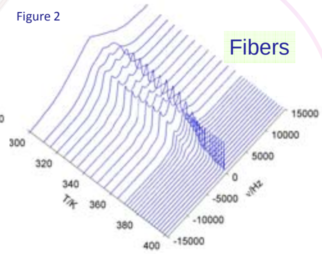


Figure 2

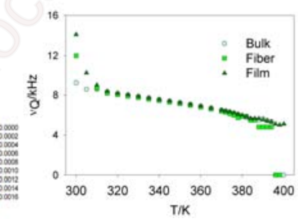


Figure 3

Pake spectrum 3D powder sample

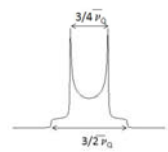


Figure 6

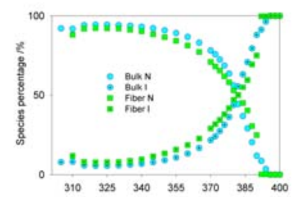


Figure 4

Fibers' spectra with fits

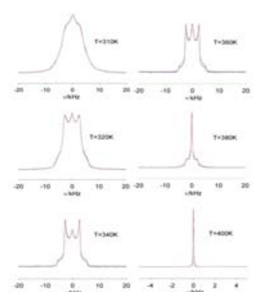


Figure 5

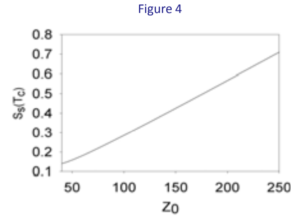


Figure 11

Conclusions: The deuterium nmr study on the liquid crystalline cellulose network indicates that the 5CB molecules are not uniformly distributed in the network but have phase separated out to small 5CB rich regions uniformly distributed. The study also shows the presence of a strong interaction between the 5CB NMR probe and the network . With an independent measurement of the 5CB droplets average radius it is possible to obtain the imposed order parameter at the 5CB-network interface. It was not possible to access the network chains director orientation in the oriented fibers sample. The presence of an isotropic peak along with the Pake pattern indicates that a small percentage of large 5CB droplets is present where complete e diffusional averaging has not occurred.

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References:[1] J.P. Canejo, J.P. Borges, M.H. Godinho, P. Brogueira, P.I.C. Teixeira, E.M. Terentjev, Helical twisting of electrospun liquid crystalline cellulose micro- and nanofibers, **Advanced Materials**, 20(24), 4821-4825 (2008). [2] I. Amimori, J.N. Eakin, Jun Qi, G.Skacej, S. Zumer and G. Crawford **Phys. Rev. E 71,** 031702 (2005)

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