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REENTRANT UNIAXIAL-BIAXIAL TRANSITION IN POLY-ETHYLENE-GLYCOL DOPED LYOTROPIC LIQUID CRYSTALS

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Abstract Interferometric measurements of the effect of a polymer gradativelly added in a lyotropic liquid crystal is reported here. Studies of the phase diagram, birefringence and critical exponents as a function of the polymer concentration are presented. Measurements of the optical birefringence as a function of temperature are performed with the micellar system potassium laurate, 1-decanol, and water doped with variable quantities of the polymer poly-ethylene-glycol (PEG). The transitions from the calamitic nematic phase to a reentrant discotic-biaxial-discotic phase were observed when increasing the PEG molar concentration. Our results confirm the critical properties of the uniaxial-to-biaxial nematic transition. The critical exponent for the order parameter ($\beta = 0.38$) obtained for the sample without PEG is in good agreement with the value calculated for the XY model. Some results with higher PEG doping concentration indicate that β is higher than 0.38 leading to the mean-field value.

INTRODUCTION

Phase transitions of lyotropic liquid crystals have been extensively studied[1–4] due to its rich different phases as a function of temperature, the concentrations of amphiphilic molecules and the solvent, as well. Interferometric measurements of the optical birefringences of the potassium laurate (KL)/Decanol (DeOH)/water lyotropic system have shown that the transitions from the uniaxial to the biaxial phase are mean-field second-order transitions[3]. The critical properties of the

uniaxial-biaxial transition were studied for the same lyotropic system[4], where it was observed deviations from the mean-field behavior. The value obtained for the critical exponent of the order parameter (β) in the uniaxial range is in good agreement with the values calculated for the XY model.

In this paper we report the interferometric measurements of a lyotropic liquid crystal doped with variable quantities of the polymer poly-ethylene-glycol (PEG). Phase transitions were observed when increasing the PEG molar concentration. The topology of the phase diagram as a function of temperature and PEG concentration is shown. The order parameter values of samples with different PEG concentrations are studied to investigate the biaxial domain and its transitions to the uniaxial phases.

EXPERIMENT

The nematic sample[5] is a mixture of potassium laurate/1-decanol/water (KL/ DeOH/ H_2O), with the concentration in weight percent of 33.13/6.51 /60.36, respectively. Variable quantities of the polymer poly-ethylene-glycol (PEG), which has molecular weight of 10000g-MERCK, were added to this lyotropic liquid crystal. The molar concentration of PEG varied from zero to 2.0 x 10^{-3} mols %.

In order to avoid important drifts of the transition temperatures, we restrict ourselves to small doping concentrations of PEG. A small quantity of a water base ferrofluid is added to the samples in order to help their orientation in the presence of a weak magnetic field (H $\sim$ 100 G).

The samples are encapsulated inside microslides 0.1mm thickness, placed in a INSTEC HS1-i hot stage system positioned in a Leitz orthoplan-pol microscope. The smallest temperature steps used were 0.02°C.

The samples were aligned by the combination of a small magnetic field and the walls of the microslide. With this procedure, a homogeneous pseudo-isotropic texture is obtained in the discotic nematic (N_D) phase with the director paralell to the light propagation direction. After the transition to the biaxial (N_{BX}) phase, a homogeneous planar texture is achieved. The birefringence is measured with a Berek compensator.

The experimental set-up is presented in detail in reference 6. The magnetic field (H) is at 45° from the polarizer and the analysis. Special care is taken to reach

an equilibrium state before each measurement. After temperature being changed between each point, there is a waiting period of about 20 min.. Five measurements of the birefringence (Δn) are made at each temperature and a mean value of Δn is obtained.

RESULTS AND DISCUSSION

Figure 1 gives the birefringence data as a function of temperature for the same sample doped with three different PEG molar concentration ([PEG]). The sample with no polymer concentration has the highest birefringence (Δn) values observed (sample S1). At high temperature this sample presents a transition from the calamitic nematic (N_C) to isotropic phase. As the PEG concentration increases Δn decreases for the entire temperature range, leading from a N_{BX} (biaxial nematic) to N_D (discotic nematic) transition at high temperature as observed (samples S2 and S3). At the third sample S3, the one with the highest [PEG], we observed that a reentrant transition occurs, in which the N_D phase appears at low temperature changing to a N_{BX} phase as the temperature increases and to a N_D phase for higher temperature.

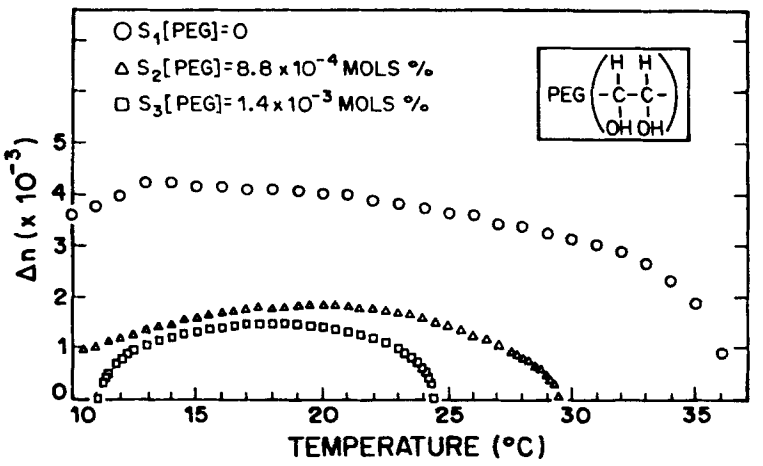

Figure 1: Birefringence vs. temperature for a nematic sample with three different poly-ethylene-glycol (PEG) concentration. The PEG monomer is shown at the inset box.

Figure 2 shows the phase diagram as a function of the [PEG] of the ternary system KL-1-decanol-H_2O lyotropic liquid crystal. The range of N_C wides on decreasing [PEG] and its region extends from 10 to 35°C. The transition from N_C to isotropic micellar solution takes place around 35°C. For PEG concentration higher than 7.0 x 10^{-4} mols %, the N_D and N_{BX} phases are formed. We observe that as [PEG] increases the phase diagram approaches from the transition of $N_C - N_{BX} - N_D$ phases to a reentrant $N_D - N_{BX} - N_D$ phases, which takes place around 1.1 x 10^{-3} mols % of [PEG]. For values of [PEG] higher than 2.0 x 10^{-3} mols %, only the N_D phase is observed, except for temperatures higher than 35°C, where transition to the isotropic phase is observed.

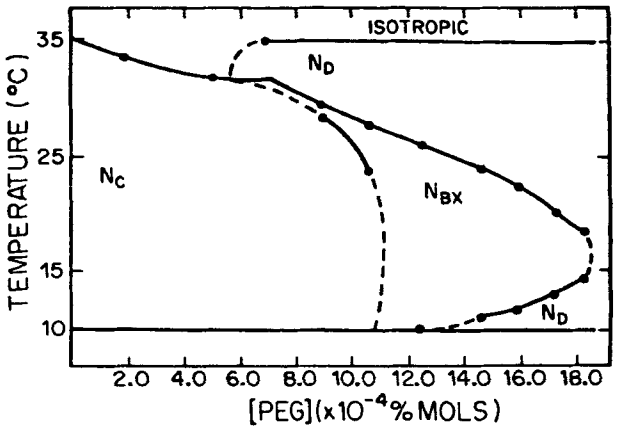

Figure 2: Phase diagram of the potassium laurate-1-decanol-water system doped with polyethylene-glycol (PEG), plotted temperature vs PEG molar concentration. The solid lines are the measured points separating the calamitic (N_C), discotic (N_D), and biaxial (N_{BX}) nematic phases and isotropic phase.

The higher transition temperatures were also observed on decreasing from around 35 to 25.5°C at the biaxial-discotic nematic ($N_{BX} - N_D$) transition, for increasing values of [PEG], as shown in Figure 3. At the discotic-biaxial nematic ($N_D - N_{BX}$) transition region, there is an increase in the low transition temperature from 11.5 to 13.5°C, for a range of 1.45 x 10^{-3} to 1.73 x 10^{-3} mols % of [PEG]. Both temperatures values go indeed in opposite directions leading gradually to shorter regions of the N_{BX} phase until it reaches a new topology of the

phase diagram, becoming a discotic nematic (N_D) phase for the entire range of temperature, as seen in Fig. 2.

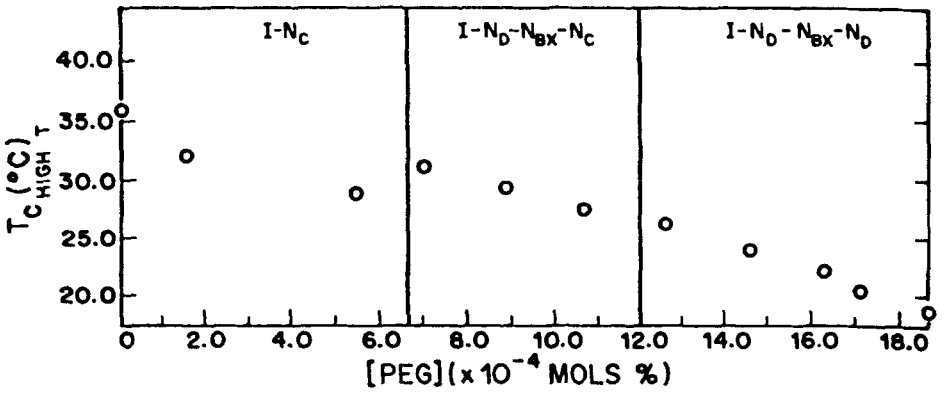

Figure 3: Transition temperature (T_c) at the biaxial-discotic transition side vs. [PEG] for the same sample as in Fig. 2.

From logarithmic plots of the birefringence data (N_D - N_{BX} transition) as a function of reduced temperature for samples with variable PEG quantities, we have determined the critical exponent of the order parameter (β)[4,7]. The transition temperature was adjusted in order to give the best linear fit in the range of 0.10°C, with the measurements taken at each 0.02°C. We have obtained that for the sample without any PEG, the critical exponent for the order parameter is

$$\beta = 0.38 \pm 0.02 \ ,$$

which is in good agreement with the theoretical results for XY model[8,9].

Figure 4 shows the measured order parameter exponent for samples with PEG molar concentration normalized by the amphiphilic mixture concentration. We observed that for the sample with 6.0×10^{-5} normalized [PEG], β increases to 0.40 which is within error limits and still in agreement with the XY model. Meanwhile, the samples with higher PEG doping concentration indicate that β values are 0.53 and 0.56, respectively, which is closer to the mean field value.

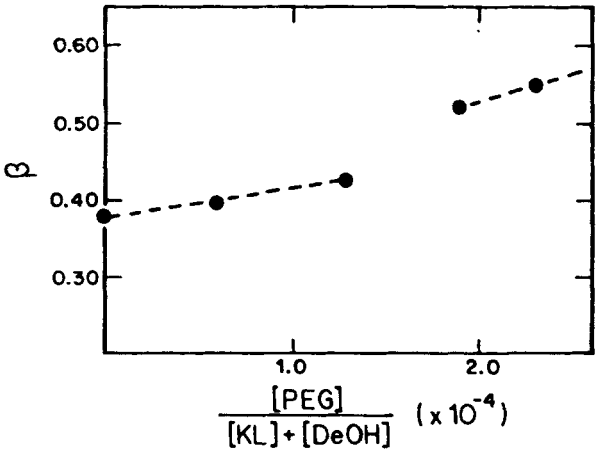

Figure 4: Critical exponent of order parameter (β) vs. PEG molar concentration normalised by the amphiphilic mixture concentration.

CONCLUSION

We have studied the effect of a poly-ethylene-glycol (PEG) polymer added in variable quantities to a lyotropic liquid crystal. From the phase diagram of these samples, we have clearly obtained a gradual transition from the calamitic nematic phase to a reentrant discotic-biaxial-discotic phases and also to a discotic nematic phase, for PEG molar concentration varying from zero to 2.0 x 10^{-3} mols %. We have also observed that the addition of PEG in our lyotropic liquid crystal induces a change in the statistical model, which describes the critical properties of the uniaxial-to-biaxial nematic transition, from the XY model ($\beta = 0.38$) to the mean field theory ($\beta = 0.5$).

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