Unusual second order isotropic to nematic phase transition behaviour in hyper-swollen lyotropic liquid crystal driven by rod-sphere transition of micelles

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We have investigated the phase transition behavior by DLS measurement in the hyper-swollen lyotropic nematic (LN) phase, formed by a combination of anionic and cationic surfactants (sodium dodecyl sulfate; SDS and dodecyl trimethyl ammonium bromide; C12TAB, respectively) at a total surfactant concentration $f \leq 8$wt%. The mole fraction $\alpha$ between SDS and C12TAB is varied between 2.3 and 2.7. We have found an interesting type of continuous 2nd order isotropic-nematic (I-N) phase transition for some surfactant ratios, as shown in polarizing optical microscope photograph (Fig.1) and investigating the driving mechanism. Director fluctuations observed in depolarized (vertical-to-horizontal polarization rotation; VH) signal, clearly shows critical slowing down on both sides of the phase transition as shown in Fig.2. It should be noted that in all samples which show the 2nd order I-N phase transition, referred as group A in Fig.3, the size of micelles is drastically reduced above the phase transition. In addition, all have the same radius of the micelle, almost equivalent to the length of the surfactant molecules, which can be estimated from translational diffusion constant observed in polarized (vertical-to-vertical polarization rotation; VV) scattering with Einstein-Stokes’s law as shown in Fig.3. It is quite reasonable that the micelle shape becomes spherical in the isotropic phase. We concluded that the 2nd order transition is driven by the decrease in the anisotropy of “building blocks” of the nematic, namely the rod to sphere transition of micelles. The birefringence continuously weakens near the 2nd order I-N phase transition due to the decrease in order parameter as well as in the simultaneous decrease in anisotropy of the building blocks. The latter also strongly affects the excluded volume interaction between micelles and thus the origin of orientational order. We have found a 2nd order I-N phase transition driven by the shape transformation of the building blocks for the first time.

Furthermore, we also identified the conventional first order transition with large I-N phase coexistence region in more symmetric mixtures (lower $\alpha$) of anionic and cationic surfactant. In this mixture the net charge on the micelle surface is more neutralized, increasing the stability of elongated micelles. As shown in Fig.3, the data for these mixtures (group B) indicate longer relaxation time and larger average micelle radius, at all temperatures, also above the I-N phase transition.

Fig.1 Polarizing optical microscope photographs near the second-order I-N transition ($f=8$wt%, $\alpha=2.55$).

Fig.3 $\alpha$ dependence of the translational diffusion mode observed in polarized DLS(VV) and the estimation of the hydrodynamic radius of the micelles from Einstein-Stokes law.

Fig.2 Temperature dependence of relaxation time for two types of fluctuations with the prediction of their respective dispersion relations ($f=8$wt%, $\alpha=2.55$).

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