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Field-induced Director Alignment of MCM-41/liquid crystals

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ABSTRACT

We report on the random disorder effect of MCM-41 on the order of the 3β-DOXYL-5α-cholestane (CLS) spin probe in the ZLI-4792 liquid crystal using Electron Spin Resonance (ESR) technique. In different MCM-41 concentrations, the temperature dependence of the director orientational order parameter, $\tilde{P}_2^d$ are studied as well. We have found that increasing the MCM-41 concentration up to 5.0 wt% does depress the director orientational order parameter. The temperature effect on the director orientational order parameter is rather complicated. Besides, in isotropic phase, the concentration effect on the director orientational order parameter is negligible.

| Liquid crystals | MCM-41 | Orientational order | ESR |

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1. INTRODUCTION

The earliest discovery of liquid crystals started in 1888. Since its discovery, director orientational order of liquid crystal has received a considerable attention especially from the theoretical point of view. Research has been expanded from bulk liquid crystal to liquid crystal confined in simple geometries and even porous media with large pore. Typical examples are Vycor glass, Anopore, Nuclepore, controlled porous glass (CPG) [1, 2, 3] etc.

In our present work, mesoporous MCM-41 which has hexagonal structure of the cylindrical pores and high internal surface gains our interest. MCM-41 porous structure is believed can produce random disorder effect to the director orientational order of liquid crystal.

Previously, various experimental methods are used to investigate the liquid crystal director orientational. For example, Nuclear Magnetic Resonance (NMR) spectroscopy. However, Electron Spin Resonance (ESR) complied with spectral simulation that was created by G. R. Luckhurst and colleagues is especially powerful for the investigation of liquid crystal director orientational order.

Spectral simulation is based on the analytical equation that was derived from torque-balance equation [4, 5, 6, 7]. Orientational distribution function for the director $f(\beta)$ is described using a single parameter, λ as shown in equation (1).

$$f(\beta) = \lambda^2/(\lambda^2 - (\lambda^2 - 1)\cos^2\beta)^{3/2} \quad (1)$$

λ is ranged from 1 to infinity. When λ is 1, orientational distribution function becomes 0 and the orientation inside filled system is considered has been perfectly randomized. When λ increases, nematic directors inside filled system are slowly aligned parallel to magnetic field. Finally, second rank director order parameter can be calculated analytically using equation (2).

$$P = (\lambda^2/2)(((2\lambda^2 + 1)/\lambda^2(\lambda^2 - 1)) - 3\arctan(\lambda^2 - 1)^{3/2}) \quad (2)$$

2. EXPERIMENTAL

2.1 Materials, method and instruments

The ZLI-4792 nematic liquid crystal was purchased from Merck. The nitroxide spin probe was the 3β-DOXYL-5α-cholestane (CLS) free radical from Acros. It was chosen because it is well-ordered by the liquid crystal host and has been used in a number of studies. MCM-41 was synthesis by Assoc. Prof. Dr. Salasiah Endud and student from UTM. MCM-41/ZLI-4792 samples were prepared in five concentration including 0.5 wt%, 1.5 wt%, 3.0 wt%, 4.5 wt% and 5.0 wt%. Each sample was analyzed using JOEL JES-FA 100 ESR Spectrometer at 25.0 ºC, 50.0 ºC, 70.0 ºC, 90.0ºC and 110.0ºC. Finally, director orientational order of each sample was generated using equation (2).

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3. RESULTS & DISCUSSION

3.1 Concentration dependence study on MCM-41/ZLI-4792

In concentration dependence study, six samples were studied, either without MCM-41 or with 0.5, 1.5, 3.0, 4.5 and 5.0 wt% MCM-41. Experimental and simulated spectra are shown in Figure **1**. For sample without MCM-41, ESR spectrum contains three sharp peaks which is a typical spectrum for Cholestane nitroxide spin probe in monodomain sample. Director orientational order parameter, $\widetilde{P}_2^d$ is close to unity (0.9), indicates that liquid crystal directors are well aligned by the magnetic field.

Obviously, lineshape of ESR spectrum changes accordingly as MCM-41 concentration increases from 0.5 wt% to 5.0 wt%, suggesting that mesopores of MCM-41 is affecting the director orientational order of ZLI-4792. The most significant changes belong to the growth of peak **4** and **5** and the weakening of peak **1** and **3** intensity. Peak **1** and peak **3** are parallel hyperfine tensors which start to appear in the ESR spectrum of monodomain bulk ZLI-4792 system. Reduce in intensity means the parallel alignment of directors to the magnetic field has been gradually destroyed. Peak **4** and **5** are definitely the symbol of disorder alignment of liquid crystal directors and hence are getting intense as MCM-41 concentration increases.

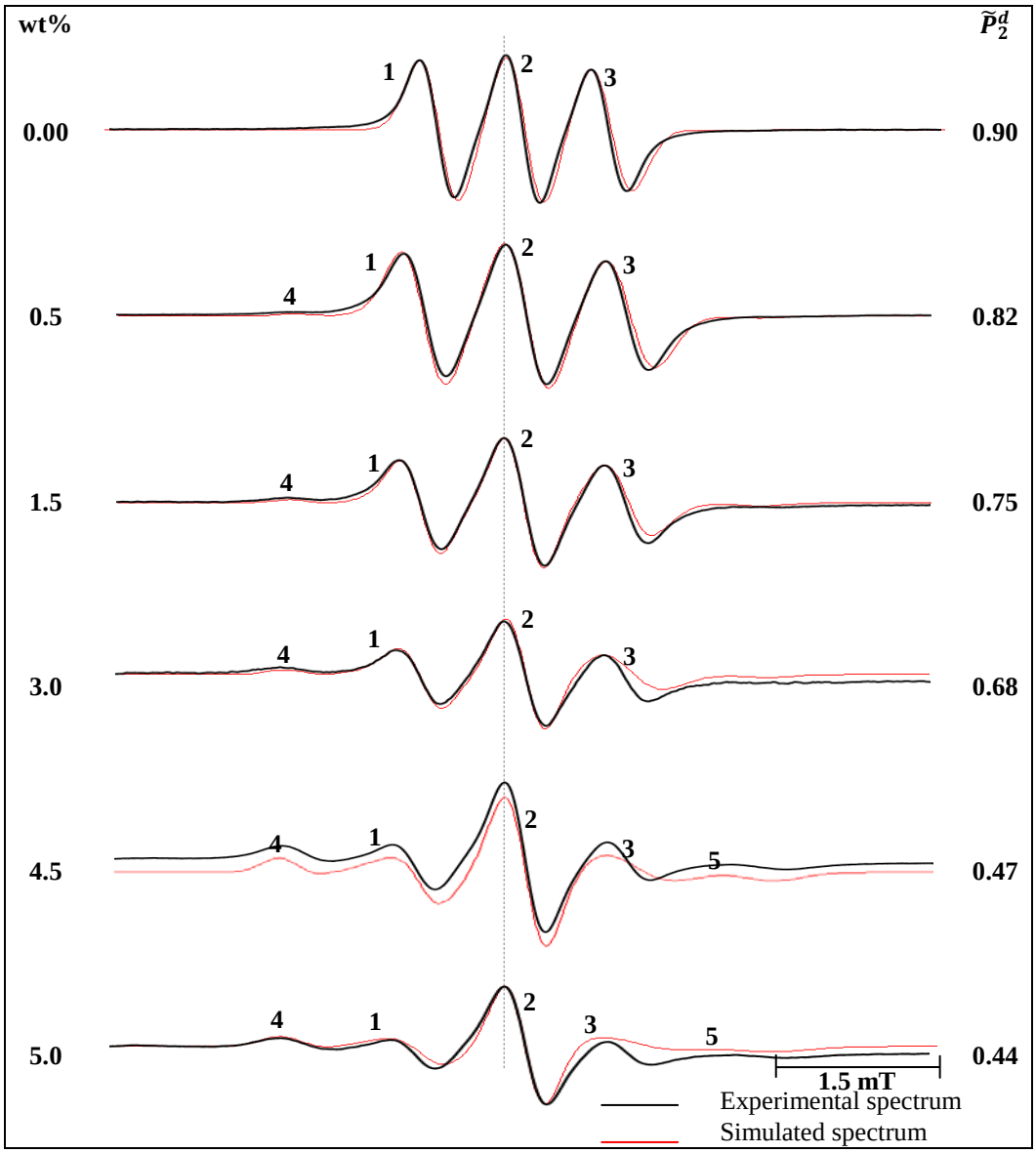

Fig. 1 Experimental and simulated spectra of Cholestane in MCM-41/ZLI-4792 in 0.5 wt%, 1.5 wt%, 3.0 wt%, 4.5 wt% and 5.0 wt%.

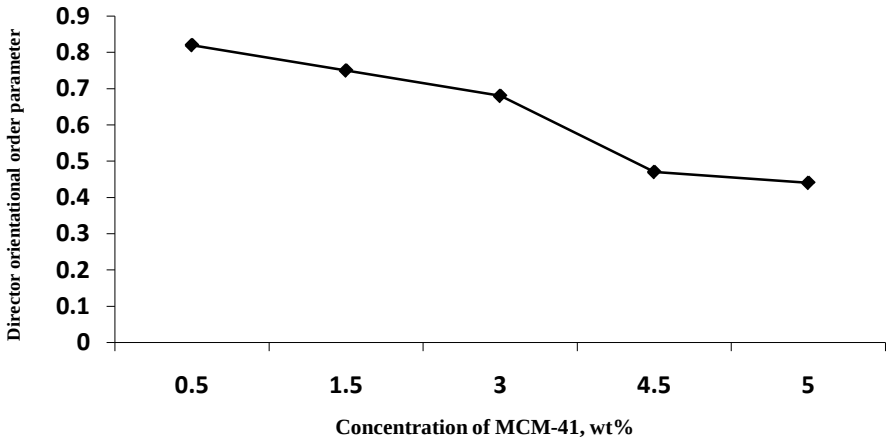

Fig. 2 Concentration dependence director orientational order of MCM-41/ZLI-4792.

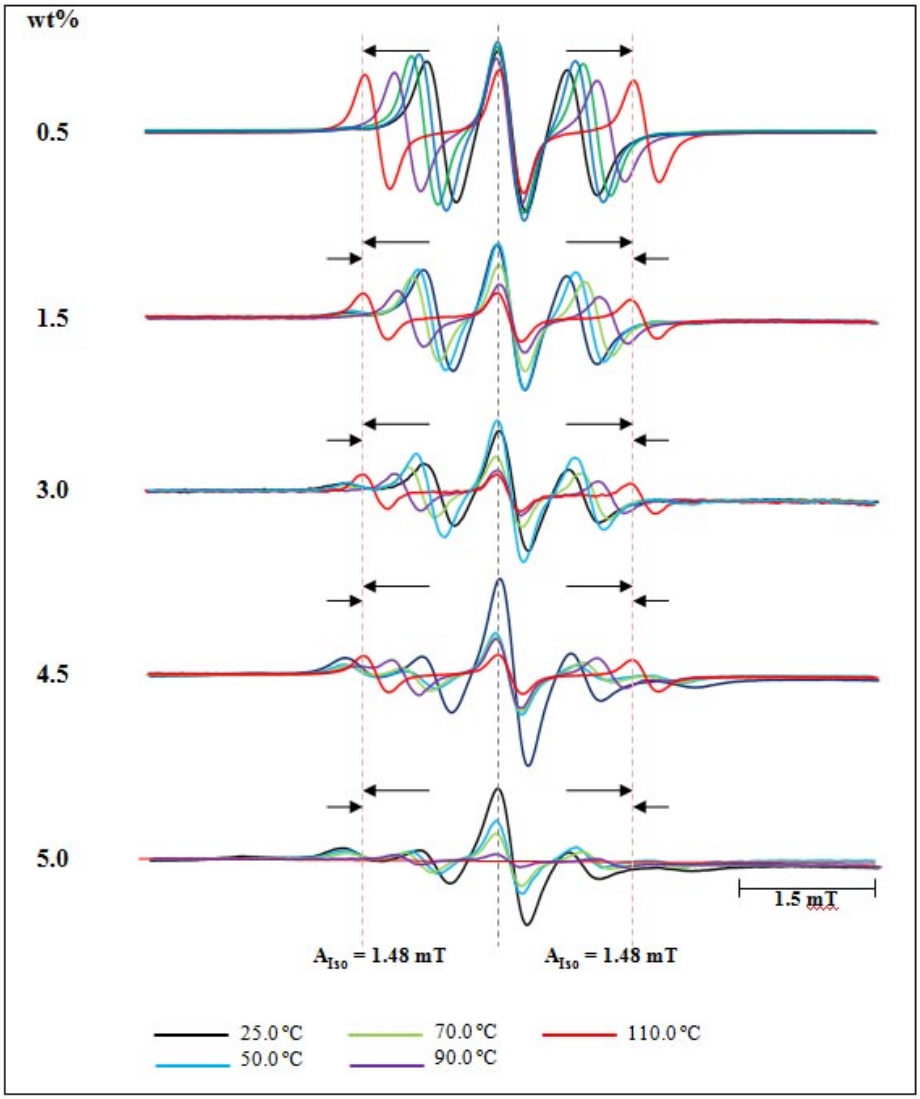

Fig. 3 Temperature dependence ESR spectra of Cholestane in MCM-41/ZLI-4792 of various weight percentages

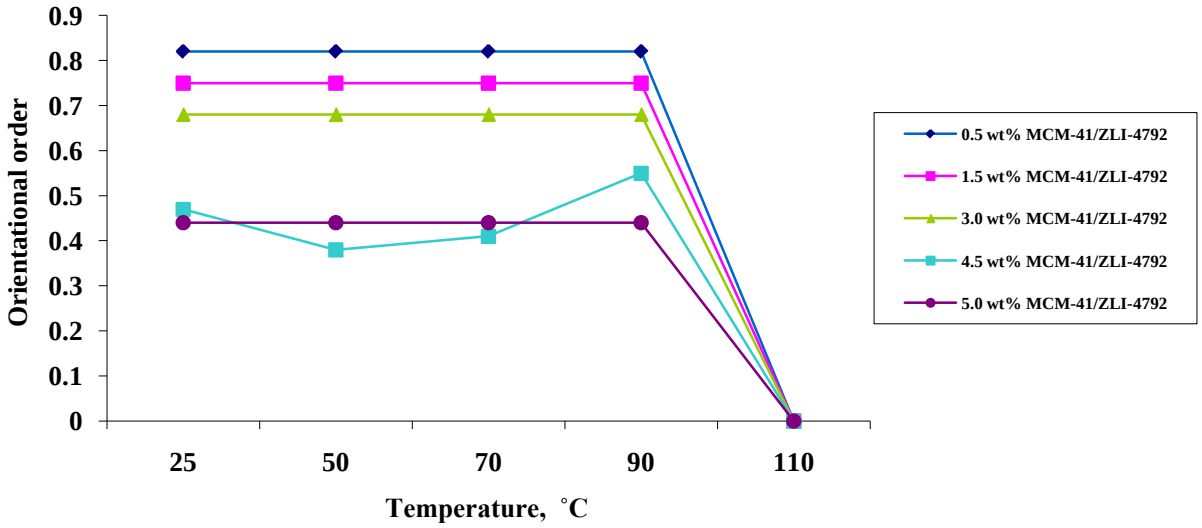

Fig. 4 Temperature dependence director orientational order of MCM-41/ZLI-4792 of various weight percentages

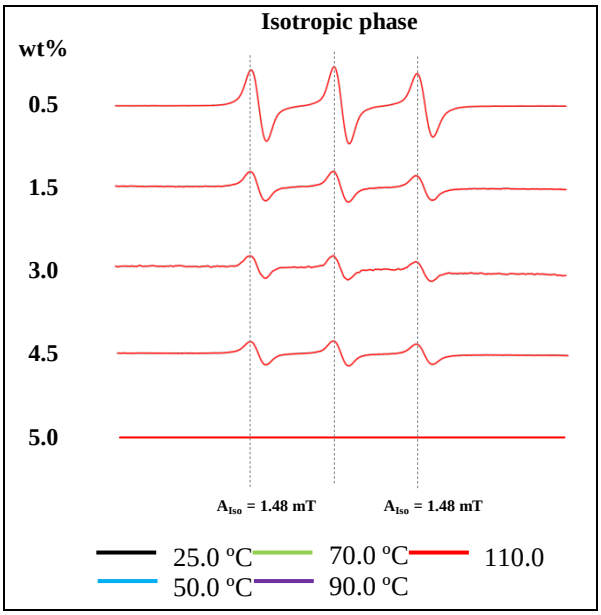

Fig. 5 ESR spectra of Cholestane in MCM-41/ZLI-4792 of various weight percentages in isotropic phase

The disorder effect is believed to be strongest at the layer closest to the MCM-41 pore surface. Within this layer, liquid crystal director might be weakly immobilized by the MCM-41 surface torque into random direction. In spacious area without MCM-41, liquid crystals directors remain aligned by the magnetic field. Therefore, it is reasonable that the disorder effect is increasing as MCM-41 concentration increasing because more liquid crystal molecules will stay inside the porous structure of MCM-41 and hence disordered. Our explanation is compatible to the generated director orientational order as shown in Figure **2**. Director orientational order is gradually depressed as MCM-41 concentration increases from 0.5 to 5.0 wt%. However, the disorder rate is quite slow even concentration of MCM-41 is increased up to 5.0 wt%. This can be explained by the small pore size of MCM-41 at where only limited amount of liquid crystals can enter the pore and being weakly immobilized and affected by the porous surface torque.

3.2 Temperature dependence study on MCM-41/ZLI-4792

In temperature dependence study, ESR spectrum for each sample are recorded at 25.0 ºC, 50.0 ºC, 70.0 ºC, 90.0 ºC and 110.0 ºC and are shown in Figure **3**. Overall, temperature dependence spectra of each sample share a trend. As temperature increases, all hyperfine tensors are shifting toward the position of isotropic hyperfine tensors. Explanation is that energy gained from higher temperature makes ZLI-4792 molecules tend to behave like in isotropic phase.

In the range from 25.0 ºC to 90.0 ºC, director orientational order of all samples remain constant except for 4.5 wt% MCM-41/ZLI-4792 as shown in Figure **4**. This finding tells that MCM-41 has the ability to retain the director orientational order of ZLI-4792 as temperature increases. At 110.0 ºC, every sample shows only isotropic hyperfine tensors with hyperfine spacing of 1.48 mT as shown in Figure **5**. Increasing of MCM-41 concentration does not change the lineshape of the spectrum except for line intensity. Besides, director orientational order is found to be zero for each sample at this isotropic phase (T_{NI} ZLI-4792 = 92.6 ºC). The drop of line intensity is possibly due to the instability of the CLS free radical. Therefore, it is quite clear that director orientational order in isotropic phase is independence on MCM-41 concentration.

4. CONCLUSION

In conclusion, MCM-41 mesoporous structure does misalignment ZLI-4792 director alignment. The disorder effect depends on the MCM-41 concentration. As MCM-41 concentration increases, director orientational order of ZLI-4792 liquid crystal decreases. However, the temperature effect on the director orientational order parameter is rather complicated. Lastly, director orientational order of isotropic phase ZLI-4792 liquid crystal is independence of MCM-41 concentration.free radical scavenging activity against DPPH measured by ESR technique.

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