



Preparation and physical properties of a macroscopically aligned lyotropic hexagonal phase templated hydrogel

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ARTICLE INFO

Article history:

Available online 1 March 2013

Keywords:

Hexagonal phase
Diffusion tensor
Lyotropic liquid crystal hydrogel
NMR diffusometry
PGSE NMR
Self-diffusion

ABSTRACT

Lyotropic liquid crystal (LLC) materials, such as lyotropic liquid single crystal hydrogels (LLSCHs) and LLC templated hydrogels, have the potential for a wide range of applications from nanomaterials to drug delivery. Most of the applications are dependent on transport processes through the gels. While powder distribution LLC hydrogels and elastomers have been shown to be alignable by uniaxial stress/strain, LLSCH that are macroscopically aligned can be made by photopolymerisation after alignment of suitable polymerisable surfactants. Cross-linked polyethylene glycol diacrylate (PEG-DA) hydrogels, have previously been templated using powder distribution LLC phases of non-polymerisable surfactants. In this work, a macroscopically aligned LLC hexagonal phase templated PEG-DA hydrogel was made. The alignment was monitored with ^2H NMR quadrupole splitting which showed that the hydrogel retained the macroscopic alignment after photopolymerisation. The effects of compression/deswelling were recorded using optical and polarised optical microscopy (POM). However, the focus of this work was on studying the self-diffusion of water in the hydrogel, which is pertinent not only for the typical applications of these materials but for potentially new applications. Pulsed gradient spin-echo nuclear magnetic resonance (PGSE NMR) provides a way of investigating the self-diffusion easily and non-invasively. Interestingly the measured self-diffusion of water, at least for the sample in this study, was relatively independent of the diffusion time used (i.e., 70 ms to 3 s).

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1. Introduction

Lyotropic liquid crystal (LLC) phases consist of self-assembled ordered structures of amphiphilic molecules in the presence of a solvent [1]. Typically the materials made with LLC phases consist of a powder distribution of director orientations, but certain mesophases, i.e., hexagonal and lamellar, may be macroscopically aligned with external fields such as mechanical shear and magnetic fields [2–6].

Hydrogels are an important class of materials suitable for applications such as gel separations, superabsorbent materials, composite/catalyst materials, drug delivery, and in the purification of waste water [7–13]. In lyotropic liquid single crystal hydrogels (LLSCHs) and LLC templated hydrogels, the properties of the LLC phases are transferred to the hydrogels, e.g., Refs. [12,14,15], and so they have a wide range of applications including lenses, templates for nanoporous materials, drug delivery systems, nanofiltration membranes, gas separation membranes and selective vapour barriers, e.g., Refs. [10,14,16–18]. As most of these applications in-

volve the transport of molecules, clarifying the diffusion in these environments is essential. Pulsed gradient spin-echo (PGSE) NMR, aka NMR diffusometry or DOSY, is a non-invasive technique that is well suited to measuring self-diffusion [19].

Hydrogels with LLC order can be made either by using polymerisable surfactants, e.g., Refs. [14,15,18], or by polymerising non-surfactant monomers in the continuous regions of an LLC phase, e.g., Refs. [10,12,16,20]. LLSCH have been made by aligning a lyotropic lamellar phase of a polymerisable surfactant in a magnetic field prior to polymerisation with or without cross-linker, e.g., Refs. [14,15]. In some cases where monomers are polymerised in LLC phases, the templated polymers may only be loosely dependent on the structure of the LLC phase [8,10,16]. Whether or not the LLC phase structure is retained/templated after polymerisation depends on the type of monomer, e.g., hydrophilic or hydrophobic, the initiator structure, and polymerisation kinetics which is dependent on method of initiation and also on the LLC phase structure with a higher amount of LLC order retained for photopolymerisation [10,16,21–23]. Systems studied by Lester et al. [23,24] retained the phase structure of the surfactants after polymerisation of the monomers. Polarised optical microscopy (POM) images showed the phases were retained with slight blurring of the POM images but with no phase separation [23,24]. Small angle X-ray scattering

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(SAXS) also confirmed the retention of the phase structure but with a slight change in the scattering angle for the hexagonal phases suggesting a change in the d spacing with polymerisation [16,23]. In a recent study by Clapper et al. [12,20], templated hydrogels using lamellar [20] and hexagonal [12] LLC phases were made and the properties of the hydrogel depended on the LLC phase, with minimal disruption to the LLC phase and minimal phase separation during polymerisation. Clapper and Guymon [12] polymerised polyethylene diacrylate (PEG-DA) monomers in the hexagonal phase of the non-ionic surfactant $C_{15}EO_{10}$, but this was only done for a powder distribution sample like in other studies, e.g., Refs. [10,20,22,23]. PEG-DA was chosen since it is hydrophilic and polymerises in a continuous network around the LLC phase [12].

The aim of this work was to prepare a macroscopically aligned lyotropic hexagonal phase templated PEG-DA hydrogel using an aligned hexagonal phase of a non-ionic surfactant and to examine its physical and diffusive properties with the hexagonal phase still present in the hydrogel. The samples were aligned in a magnetic field prior to photopolymerisation since phases of non-ionic surfactants consisting of an alkyl chain and polyethylene oxide chain are readily magnetically alignable [25–27], with the hexagonal phase aligning with the director, i.e., the cylinder axes, of the phase parallel to the magnetic field and the long axis of the surfactant molecules aligning perpendicular to the magnetic field as these surfactants have a negative diamagnetic susceptibility [25–28]. Conversely, surfactants with positive diamagnetic susceptibility align with their long axis parallel to the magnetic field [15,29]. A good description of the effect of negative and positive molecular and aggregate diamagnetic susceptibility can be found in Ref. [3].

The non-ionic surfactant used for this study was decaethylene glycol monododecyl ether ($C_{12}EO_{10}$). The binary phase diagrams for the non-ionic surfactants $C_{12}EO_n$ and water are known [30–32]. $C_{12}EO_{10}$ has a normal hexagonal phase between ~40 and 80 wt.% $C_{12}EO_{10}$ depending on the temperature [33]. The hexagonal phase of $C_{12}EO_{10}$ was found to still form with PEG-DA ($M_n = 700 \text{ g mol}^{-1}$) present, which is similar to in Ref. [12] where $C_{15}EO_{10}$ was used with PEG-DA with molecular weight 575 g mol^{-1} . The hexagonal phase containing PEG-DA was aligned in a high magnetic field and then photopolymerisation resulted in a macroscopically aligned lyotropic hexagonal phase templated hydrogel. The alignment during preparation and after UV curing was monitored with ^2H NMR and POM. Hydrogel discs were made with the alignment perpendicular to the disc axes and observations were made with respect to deswelling and uniaxial compression down the disc axis. The deswelling and elongation with compression of the templated hydrogels occurred along the alignment direction. The self-diffusion of water and its anisotropy in the aligned templated hydrogel containing the surfactant molecules was measured using pulsed gradient stimulated echo (PGSTE) NMR and two kinds of analysis were performed. First the diffusion in each direction was calculated using non-linear regression of a monoexponential function, and secondly the diffusion tensors were calculated using non-linear regression of the entire dataset. No time dependence of the diffusion coefficient was observed for diffusion times up to 3 s. The salient theory for solid state ^2H NMR and NMR diffusion measurements is covered in Section 2.

2. Theory

2.1. Quadrupole splitting

Quadrupolar nuclei, i.e., spin $>1/2$, give rise to quadrupolar coupling and quadrupole splitting ($\Delta\nu_Q$) for systems where there is some restriction on the orientational averaging, e.g., liquid crystals and solids [34]. The exact form of the electric quadrupole interac-

tion can be found elsewhere [34,35]. For ^2H (spin = 1) of D_2O , a single peak is observed for an isotropic phase and a doublet is observed for aligned samples [3,14,25–27]. For aligned cylinders with rotation/motion of the molecules about the cylinder axis the splitting is given by [35],

$$\Delta\nu_{Q,\text{aligned hexagonal}} = \frac{3A_{\text{Hex}}}{8} \left(\frac{e^2qQ}{h} \right) (3 \cos^2 \theta - 1), \quad (1)$$

where θ is the angle between the cylinder axis and the magnetic field direction, A_{Hex} is the residual anisotropy which includes the order parameters and molecular asymmetry parameter [36–38], and e^2qQ/h is the static quadrupolar coupling [35,36,38]. The observed peak separation is also influenced by peak broadening [35,38]. Broadening of the spectra may result from the size of the domains in the sample [39–41]. Quadrupole splitting and the dependence on orientation, makes ^2H NMR useful for monitoring the alignment and orientation of LLC phases and materials, e.g., see Refs. [3,14,15,25,40–42].

2.2. PGSE NMR

PGSE NMR is able to measure the self-diffusion of molecules by using the Larmor frequency as a label for position [19]. The simplest and most common pulse sequences for measuring diffusion are the pulsed gradient spin-echo (PGSE) (the Stejskal and Tanner sequence, a modified Hahn Spin-Echo) [43] and the pulsed gradient stimulated echo (PGSTE) [44] pulse sequences. With square gradient pulses the echo signal and echo attenuation for a single freely diffusing species is given by [19],

$$S(g, t_{\text{aq}}) = S(0, t_{\text{aq}})E(g, \Delta) \quad (2)$$

$$\begin{aligned} \text{where } E(g, \Delta) &= \frac{S(g, t_{\text{aq}})}{S(0, t_{\text{aq}})} = \exp\left(-\gamma^2 g^2 D \delta^2 \left(\Delta - \frac{\delta}{3}\right)\right) \\ &= \exp(-bD), \end{aligned} \quad (3)$$

where $S(g, t_{\text{aq}})$ is the total signal observed with applied magnetic gradient pulses of amplitude $g \text{ T m}^{-1}$, $S(0, t_{\text{aq}})$ is the signal when $g = 0 \text{ T m}^{-1}$ (i.e., 0%), $E(g, \Delta)$ gives the normalised signal with attenuation from diffusion, δ is the duration of the gradient pulse in seconds, γ is the gyromagnetic ratio of the nucleus, Δ is the diffusion time in seconds and t_{aq} is the time of acquisition. Note that the diffusion coefficient, D ($\text{m}^2 \text{ s}^{-1}$), is the diffusion measured along the direction of the gradient vector, \mathbf{g} . For isotropic samples D is the same in every direction measured. For a direction other than along the primary gradient directions (i.e., other than along x , y , and z), g in Eq. (3) is typically a vector sum of the contributing gradient strengths, e.g., diffusion measured along an xy gradient direction has the strength $\sqrt{g_x^2 + g_y^2}$, or g is the gradient value calibrated for that direction if found not to be a vector sum during gradient calibration. D can be obtained by non-linear regression of Eq. (3) onto the attenuation data. Other experimental considerations can be found elsewhere [19,45].

Normally non-linear regression of Eq. (3) is used to calculate the diffusion coefficients, however for the sample in this work the residual surfactant signal and water signal were slightly overlapped. Since the surfactant signal was not decaying or was slowly decaying, and as the contribution to the water signal due to the overlap was small, Eq. (3) was modified to include a 'baseline' type correction, i.e., a monoexponential function with floating amplitude, A , and baseline offset, E_{off} , which accounts for the small overlapped slowly or non-diffusing surfactant molecules as,

$$E(g, \Delta) = E_{\text{off}} + A \exp(-bD), \quad (4)$$

where E_{off} is constrained to be greater than or equal to zero. This 'baseline' type correction has been included for similar systems

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