



The effect of poly(propylene glycol) on the formation of lyotropic liquid crystalline phases of amphiphiles containing glycerol head groups



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ABSTRACT

In order to prepare a nonlamellar lyotropic liquid crystalline structure, amphiphiles (PPG-Gly 340 and 1000) containing poly(propylene glycol)s of different molecular weights, 340 and 1000 respectively, as hydrophobic chains and glycerol as head groups were synthesized and investigated by optical microscopy and small angle X-ray scattering. The effect of poly(propylene glycol) on the developments of reverse bicontinuous cubic phase (V_2) and reverse hexagonal phase (H_2) was examined by the mixing of PPG-Gly with glyceryl monooleate (GMO). The addition of PPG-Gly to GMO expedites the lamellar- $Ia3d$ (V_2)- $Pn3m$ (V_2) transformation of the hydrated GMO. Poly(propylene glycol)s of different chain lengths show rather different effects on both the phase behavior and the dimension of the structure. The $Pn3m$ lattice parameter can be reduced by more than 20% on the addition of PPG-Gly1000. In contrast, the addition of PPG-Gly 340 increases the dimension by less than 5%. This result is explained by the hydrophobic chain splay. From polarizing optical microscopy, the addition of PPG-Gly 1000 to GMO enhances the formation of H_2 phase substantially. The appearance of the H_2 phase lasts for a temperature range of ca. 23 °C. It was also found that the H_2 phase coexists with the $Pn3m$ phase and does not disappear at the same temperature, indicating a distribution of compositions of the hydrated PPG-Gly 1000/GMO mixtures.

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1. Introduction

It has been recognized for several decades that lyotropic liquid crystalline phases, especially reverse hexagonal (H_2) and reverse bicontinuous cubic (V_2) phases, can provide unique matrices for various biomedical applications such as drug delivery, biosensors, membrane protein crystallization, etc. [1,2]. For the formation of reverse phases, an amphiphile with a small hydrophilic head and a bulky hydrophobic chain, which has a more negative interfacial curvature, is preferred from the viewpoint of geometric packing [3]. Therefore the concept of increasing the cross-sectional area of hydrophobic region by the employment of kink structure such as cis double bonds [4,5], branching structure such as phytanyl groups [6–8], or two hydrophobic chains in one amphiphile molecule [9–11] has been adopted to prepare amphiphiles able to form reverse phases.

In this study, a different approach was exploited: using poly(propylene glycol) (PPG) as hydrophobic chains. Poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol) triblock copolymers, known as Pluronic or Pluronic, have been reported to exhibit versatile lyotropic liquid crystalline phases [12,13].

Pluronic have been used for the preparations of cubosomes and hexosomes from the existing V_2 and H_2 systems respectively [14,15]. The aqueous phase behaviors of amphiphiles containing poly(ethylene glycol) as head groups have been extensively studied [16,17]. Nevertheless, the effect of PPG on the formation of lyotropic liquid crystalline phases remains to be understood. First of all, the methyl branching structure of PPG appears to be suitable for the formation of reverse phases. Secondly, lyotropic liquid crystalline phases are affected by hydrophobic chain length [9,10]. Longer chain length may increase the bulkiness of hydrophobic region and thus favors the formation of reverse phases [18]. Poly(propylene glycol)s of different molecular weights are commercially available and the technique of polymerization is well established. By adjusting the molecular weight, one might be able to manipulate the liquid crystalline phase behavior and the dimension of the structure. Thirdly, the formation of H_2 phase is restricted by the packing constraint in the hydrophobic region. The relief of packing constraint can be realized through the addition of low alkanes or extra long hydrophobic chains [19,20]. The employment of flexible PPG with suitable chain length may be able to effectively fill the energetically unfavorable space of reverse hexagonal structure with less energy cost and facilitate the formation of H_2 phase.

PPGs of molecular weights 340 and 1000 were employed as the hydrophobic chains of amphiphiles, using glycerol as the hydrophilic head

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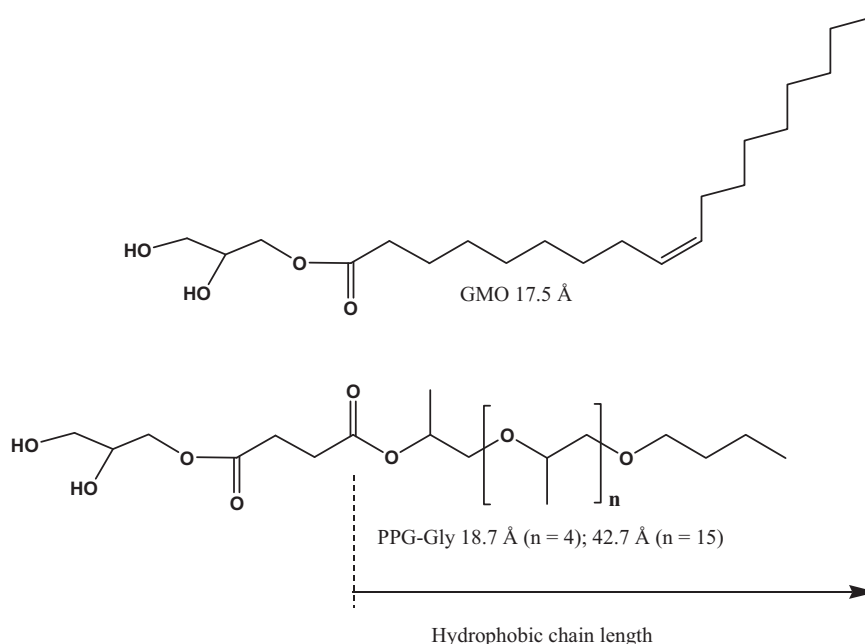


Fig. 1. Molecular structure and estimated dimensions of GMO and PPG-Glys. The dimensions were modeled and estimated by 'the Package Discover in Materials Studio Software'. PPG-Gly 340 was approximated by $n = 4$ and PPG-Gly 1000 by $n = 15$.

group. The structure of the synthesized amphiphiles (PPG-Gly 340 and 1000) is shown in Fig. 1. The lyotropic liquid crystalline behavior of the synthesized PPG-Glys was characterized by the use of polarizing optical microscopy and small angle X-ray scattering (SAXS). The effect of PPG was further exploited by the mixing of PPG-Gly with glyceryl monooleate (GMO) since the lyotropic liquid crystalline behavior of GMO is well characterized [21]. Although, the head group of the designed amphiphiles is not exactly the same as GMO due to the difficulty involved in the synthesis, the effect of PPG can still be identified by the use of different chain lengths.

2. Experimental

2.1. Materials

All chemicals were of reagent grade and were used without further purification. Water was purified by a Millipore Rios 50 system.

2.2. Instruments

^1H NMR spectra were taken by a Bruker Avance III 400 MHz NMR spectrometer. A Nikon Eclipse ME600 polarizing optical microscope equipped with a LinKam LNP hot stage was used. SAXS measurements were performed on a Nanostar U System (Bruker AXS GmbH, Karlsruhe, Germany) equipped with an μS generator (30 W, 50 kV, and 600 mA), a Vantec-2000 area detector, and a TCPU heating/cooling unit. Vantec-2000 area detector is a xenon-based gaseous avalanche detector with an active area of $14\text{ cm} \times 14\text{ cm}$ ($2048\text{ pixel} \times 2048\text{ pixel}$) with a spatial resolution of $68\text{ }\mu\text{m}^2$ on the area detector. The sample-to-detector distance was 1070 mm.

2.3. Synthesis

The following procedure describes the synthesis of PPG-Gly 340. PPG-Gly 1000 and GMO were synthesized in the same way.

2.3.1. Synthesis of 3-(poly(propylene glycol) monobutyl ether)carbonyl propanoic acid, (PPG-acid) [22]

Poly(propylene glycol) monobutyl ether (10 g, 29.4 mmole), succinic anhydride (5.884 g, 0.0588 mole), and triethylamine (5.95 g, 58.8 mmole) were dissolved in dry methylene chloride at room temperature. 4-(Dimethylamino)pyridine (3.592 g, 29.4 mmole) was then added to the solution. The reaction mixture was stirred for 24 h at room temperature. After the reaction, the solution was washed by 1% HCl aqueous solution and water, respectively, several times. Anhydrous magnesium sulfate was added to the organic solution and then was filtered. The filtrate was vacuum evaporated by a rotary evaporator. The resulting viscous liquid was further dissolved by 300 ml hexane and was washed by 1% HCl aqueous solution and water several times. Anhydrous magnesium sulfate was added to the organic solution and then was filtered. The filtrate was vacuum evaporated by a rotary evaporator. The purified liquid was examined to be one-spot by basic-alumina TLC using ethyl acetate as an elution solvent. The yield is 55%. ^1H -NMR (CDCl_3 , δ , ppm): 0.90 (t, 3H, $\text{CH}_3\text{-CH}_2\text{-}$), 1.13 (m, $\text{-CH}_2\text{-CH}(\text{CH}_3)\text{-O-}$), 1.21 (d, 3H, $\text{-CH}_2\text{-CH}(\text{CH}_3)\text{-O-C(O)-}$), 1.35 (m, 2H, $\text{CH}_3\text{-CH}_2\text{-}$), 1.53 (m, 2H, $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-}$), 2.62 (s, 4H, $\text{-O-C(O)-CH}_2\text{-CH}_2\text{-C(O)-OH}$), 3.28–3.65 (m, $\text{-CH}_2\text{-CH}(\text{CH}_3)\text{-O-}$), 5.04 (m, 1H, $\text{-CH}_2\text{-CH}(\text{CH}_3)\text{-O-C(O)-}$).

2.3.2. Synthesis of poly(propylene glycol) monobutyl ether (2,2'-dimethyl-1,3-dioxolan-4-yl)methyl succinate, (PPG-solketal)

PPG-acid (1.76 g, 4 mmole), solketal (1.06 g, 8 mmole) and 4-(dimethylamino)pyridine (0.5 g, 4 mmole) were dissolved in 20 ml dry ethyl acetate and then placed in an iced bath. N,N' -dicyclohexylcarbodiimide (0.8 g, 4.0 mmole) was dissolved in 10 ml dry ethyl acetate and the solution was added dropwise to the prepared PPG-acid solution at $0\text{ }^\circ\text{C}$ in 2 h. The reaction mixture was stirred at room temperature for 24 h and then filtered. The filtrate was vacuum evaporated by a rotary evaporator. The resulting liquid was redissolved by 100 ml *n*-hexane and was washed by 1% HCl aqueous solution and water several times. Anhydrous magnesium sulfate was added to the organic solution and then was filtered. The filtrate was vacuum evaporated by a rotary evaporator. The yield is

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