

Synthesis and Phase Behavior of New Amphiphilic PEG-Based Triblock Copolymers as Gelling Agents for Lamellar Liquid Crystalline Phases

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ABSTRACT: We report the first evidence of the potential of new amphiphilic ABA-triblock copolymers as gelling agents for lamellar liquid crystalline L_{α} phases. Recently, we described a new type of lamellar hydrogels which are not based on a polymer network swollen in water but are obtained by the addition of small amounts of a nonionic polymer surfactant to the fluid lamellar L_{α} phase of the dimyristoyl-phosphatidyl-choline(DMPC)/pentanol/water system. In contrast with these previously reported gelling agents which were all AB-diblock copolymers, the novel ABA-triblock copolymers consist of double chain hydrophobic moieties (A) attached to each end of a poly(ethylene glycol) chain (B). The synthesis of these new macromolecules and their gelation properties are described. The comparison of these novel lamellar hydrogels with those based on the AB-diblock copolymers provides direct evidence for the existence of cross-bridging conformations of the ABA-triblock copolymers between adjacent membranes.

Introduction

Hydrogels of polymer networks constitute a very important class of "soft" matter materials from both scientific and technological viewpoints. Their uses span diverse areas from the food industry to the medical and biotechnological industries in implants, tissue replacements, drug delivery systems, and bioseparations.^{1–6} Poly(ethylene glycol) (PEG) is a nonionic water soluble polymer which has been studied extensively in a broad range of scientifically and technologically important problems in colloidal science and complex fluids.⁷ More recently, because of its extremely low immunogenicity, it has been used to prepare hydrogels for numerous biomedical applications.

We have recently developed a different class of hydrogels which are based on fluid membranes (Figure 1) comprised of the lipid DMPC (dimyristoyl-phosphatidyl-choline) and the cosurfactant pentanol with small amounts of an amphiphilic AB-diblock copolymer.^{8,9} These copolymers, also called PEG-surfactants, consists of a hydrophilic PEG chain covalently linked to a hydrophobic moiety. Such macromolecules are hydrophobically anchored but free to diffuse within the fluid membrane. There are striking differences between these membrane-based liquid crystalline biogels, labeled $L_{\alpha,g}$, and isotropic hydrogels of polymer networks. For example, as the amount of water is increased, less polymer is required for gelation. Furthermore, whereas even concentrated (>50 wt %) free PEG-water mixtures do not gel, gelation occurs in lamellar mixtures contain-

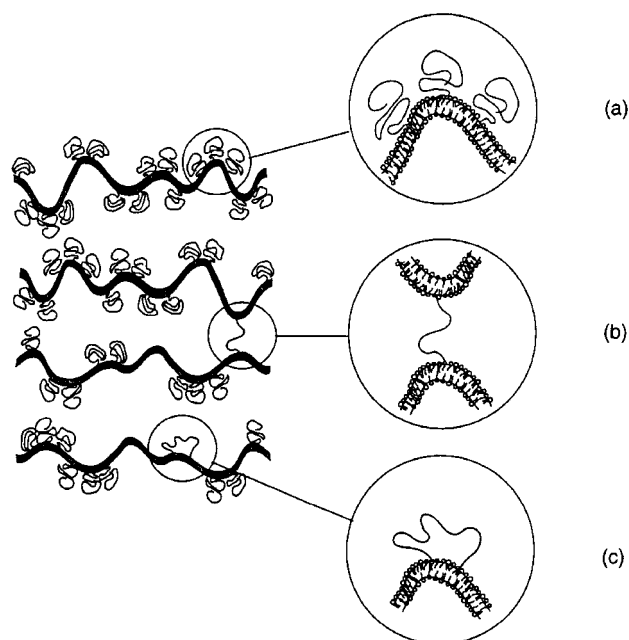


Figure 1. Schematic representation of undulating fluid membranes composed of a lipid (DMPC), a cosurfactant (pentanol) and amphiphilic block copolymers: (a) amphiphilic AB-diblock copolymers in mushroom configurations; (b) ABA-triblock copolymer in a bridging configuration; (c) ABA-triblock copolymer in a looping configuration.

ing as little as 0.5 wt % of PEG-surfactant. The addition of the cosurfactant pentanol to membranes consisting of DMPC thins the bilayer membrane which leads to the decrease of its bending rigidity $k \approx k_B T^{10}$ and allows us to explore the swollen lamellar regime¹¹ where the biogel is stable. The new physical gel phase has the same liquid-crystalline lamellar symmetry as that of the usual fluid L_{α} phase but displays three-dimensional elastic properties.

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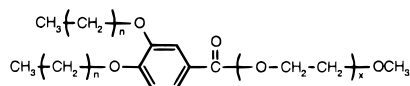
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a) Amphiphilic AB-Diblock Copolymer



b) Amphiphilic ABA-Triblock Copolymer

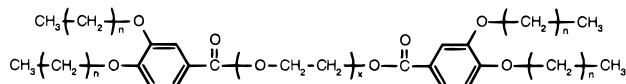


Figure 2. Chemical structures of amphiphilic AB-diblock copolymers **5a–c** and **6a–c** and of amphiphilic ABA-triblock copolymers **8a–e** based on 3,4-(alkoxy)benzoic acid and poly(ethylene glycol) segments.

In this paper, we describe the synthesis of a new series of ABA-triblock copolymers which consist of double chain hydrophobic 3,4-(alkoxy)benzoic acid moieties (A) attached on each end of a PEG chain (B) (Figure 2a). We also describe the synthesis of two series of AB-diblock copolymers consisting of a double chain hydrophobic 3,4-(alkoxy)benzoic acid moiety (A) attached only to one end of a PEG chain (B) which has not been published before (Figure 2b). We demonstrate for the first time the gelation properties of the ABA-triblock copolymers through visual inspection of test tubes, optical microscopy and small-angle X-ray scattering. In principle, these novel macromolecules can adopt not only looping conformations when both end-anchors are in the same membrane but also original cross-bridging conformations with the end-anchors in opposing membranes (Figure 1). The detailed comparison of these new lamellar hydrogels with the previously reported ones based on the AB-diblock copolymers provides direct evidence for the cross-bridging conformations of the ABA-triblock copolymers.

Experimental Section

Materials. Protocatechuic acid ethyl ester (98+ %) (TCI), 1-bromotetradecane (98%) and 1-bromooctadecane (96%) (both Acros), thionyl chloride (97%) (Aldrich), and all other conventional reagents were used as received. Poly(ethylene glycols) of number-average molecular weights (M_n) of 200 ($M_w/M_n = 1.05$, $DP_n = 4$), 600 ($M_w/M_n = 1.12$, $DP_n = 13$), 2000 ($M_w/M_n = 1.04$, $DP_n = 45$), 4600 ($M_w/M_n = 1.06$, $DP_n = 104$), and 8000 ($M_w/M_n = 1.06$, $DP_n = 181$) and poly(ethylene glycol) mono methyl ethers of number-average molecular weights of 750 ($M_w/M_n = 1.07$, $DP_n = 16$), 2000 ($M_w/M_n = 1.11$, $DP_n = 45$), and 5000 ($M_w/M_n = 1.10$, $DP_n = 113$) were purchased from Aldrich. The poly(ethylene glycols) were dried at 110 °C for 2 h in a vacuum prior to use. DMPC of a purity >99% was purchased from Avanti Polar Lipids Inc., and pentanol of >99% purity was purchased from Sigma Chemical Co.; both compounds were used as received. We also used purified 18 MΩ water provided from a Millipore unit.

Characterization. 1H NMR measurements were carried out on a Gemini 200 MHz spectrometer at 20 °C in $CDCl_3$. FT-IR spectra were recorded with a Perkin-Elmer FT-IR 1600 spectrometer. Thermal transitions were determined with a Perkin-Elmer DSC 7. The heating and cooling rates were 10 K/min. Molecular weight determination was performed on a Waters GPC system equipped with a W510 pump (eluent, THF; flow rate, 0.5 mL/min), two PL columns (500 and 1000 Å pore size), a RI detector (W410) and an UV detector (W440, 254 nm). The GPC was calibrated with polystyrene standards (PSS).

Synthesis of Monomers. The synthesis of 3,4-bis(tetra-decyloxy) benzoic acid chloride (**2b**) and 3,4-bis(octadecyloxy) benzoic acid chloride (**3b**) was carried out in analogy to the procedure described by Malthête et al.¹² and Lattermann et al.^{13,14} The reaction sequence is outlined in Figure 3.

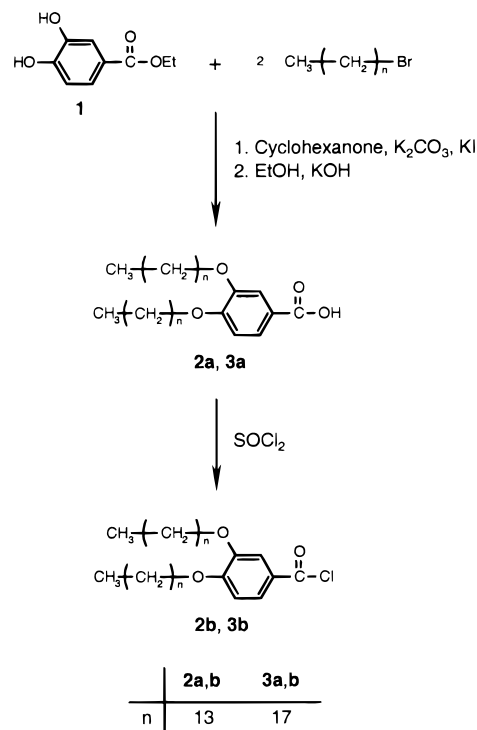


Figure 3. Synthesis of 3,4-(alkoxy)benzoic acid chlorides **2b** and **3b**.

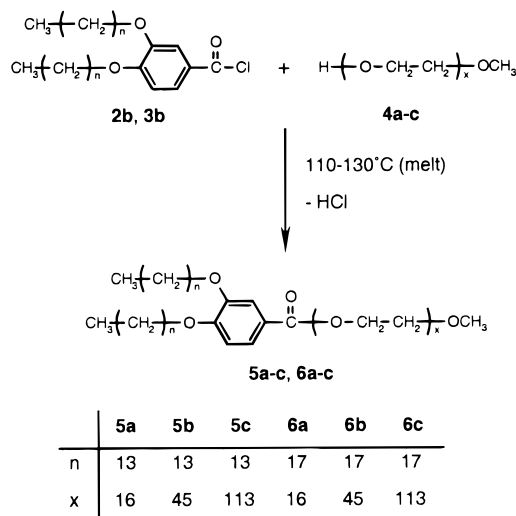


Figure 4. Synthesis of amphiphilic AB-diblock copolymers **5a–c** and **6a–c**.

Synthesis of AB-Diblock and ABA-Triblock Copolymers. Three series of nonionic surfactants were synthesized, two of them based on poly(ethylene glycol) mono methyl ether (AB-diblock copolymers **5a–c**, **6a–c**) and one based on α,ω -dihydroxy-poly(ethylene glycol) (ABA-triblock copolymers **8a–e**). The poly(ethylene glycol) unit was covalently attached to the hydrophobic moiety by a coupling procedure depicted in Figures 4 and 5. As a representative example, the synthesis of triblock copolymer **8c** is described in the following. The syntheses of the other block copolymers are carried out in analogy to this procedure.

ABA-Triblock Copolymer (8c). 6.0 g (3 mmol) of poly(ethylene glycol) (**7c**) ($M_n = 2000$) and 3.39 g (6 mmol) of 3,4-bis(tetradecyloxy) benzoic acid chloride (**2b**) were placed in a Schlenk tube and heated to 120 °C. Instantaneous development of bubbles in the viscous melt indicated the start of the coupling reaction. The melt was stirred for 26 h, and a continuous vacuum was applied to remove gaseous hydrochloric acid. The reaction mixture was cooled to room temperature,

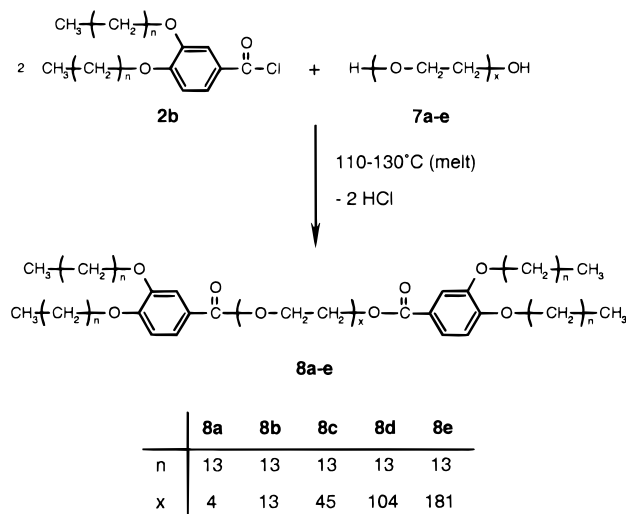


Figure 5. Synthesis of amphiphilic ABA-triblock copolymers **8a–e**.

Table 1. Characteristic Data of AB-Diblock Copolymers 5a–c and 6a–c

polymer	$M_{n,calc}^a$	$M_{n,GPC}^b$	M_w/M_n^c	thermal behavior ^d
5a	1300	1840	1.02	K 40 (156) I
5b	2550	3860	1.04	K ₁ 37 (38) K ₂ 51 K ₃ 54 (308)* I
5c	5550	8850	1.07	K 60 (814) I
6a	1410	1940	1.08	K ₁ 13 (17) K ₂ 32 (41) K ₃ 56 K ₄ 60 (72)* I
6b	2660	3500	1.06	K 51 (372) I
6c	5660	7290	1.08	K 58 (866) I

^a Calculated number-average molecular weight. ^b Number-average molecular weight determined by GPC (polystyrene standards, eluent: THF). ^c Polydispersity index determined by GPC (polystyrene standards, eluent: THF). ^d Transition temperatures are given in °C, enthalpy values (in brackets) are given in kJ/mol; asterisk denotes the sum of enthalpies for **K**₂ + **K**₃ and **K**₃ + **K**₄, respectively (DSC, second heating, 10 K/min).

Table 2. Characteristic Data of ABA-Triblock Copolymers 8a–e

polymer	$M_{n,calc}^a$	$M_{n,GPC}^b$	M_w/M_n^c	thermal behavior ^d
8a	1290	1890	1.02	K 47 (119) I
8b	1690	2310	1.06	K 47 (134) I
8c	3090	4710	1.02	K 46 (262) I
8d	5690	8510	1.05	K ₁ 31 (61) K ₂ 53 (631) I
8e	9090	13230	1.09	K 57 (1160) I

^a Calculated number-average molecular weight. ^b Number-average molecular weight determined by GPC (polystyrene standards, eluent: THF). ^c Polydispersity index determined by GPC (polystyrene standards, eluent: THF). ^d Transition temperatures are given in °C, enthalpy values (in brackets) are given in kJ/mol (DSC, second heating, 10 K/min).

dissolved in 30 mL of THF, filtered and poured into 500 mL of hexane. The polymer was collected, dissolved in 25 mL of THF and finally precipitated into 300 mL of hexane. The compound was dried at 30 °C in a vacuum (yield: 95%). ¹H NMR: δ 7.65 (dd, 2H), 7.54 (d, 2H), 6.85 (d, 2H), 4.43 (t, 4H), 4.04 (t, 8H), 3.80 (t, 4H), 3.65 (m, 172H), 1.83 (m, 8H), 1.15–1.45 (m, 88H), 0.88 (t, 12H).

The ¹H NMR shifts of ABA-triblock copolymers **8a,b** and **8d,e** are identical to the shifts reported above. The integral value of the signal at 3.65 ppm varies due to the different composition of the block copolymers. The ¹H NMR shifts of AB-diblock copolymers **5a–c** and **6a–c** are also identical to the shifts reported above, except an additional peak at 3.35 ppm (s, 3H) which indicates the methoxy endgroup of the PEG segment. Tables 1 and 2 summarize the molecular weight data and the phase transitions of the AB-diblock copolymers **5a–c**, **6a–c** and of the ABA-triblock copolymers **8a–e**. The

polydispersity indices of the AB-diblock copolymers (1.02–1.08) and of the ABA-triblock copolymers (1.02–1.09) are as low as the indices of the pure poly(ethylene glycol) mono methyl ethers (1.07–1.11) and of the pure poly(ethylene glycol)s (1.04–1.12), respectively. This indicates a complete coupling reaction.

Sample Preparation. All samples were prepared as described previously.⁹ A molar ratio of pentanol to surfactant molecules (DMPC + PEG–surfactant) of 4.0 ± 0.5 was maintained for all samples in order to ensure that the surfactant chains would always be in the melted state.

Investigation of Physical Properties. The gel behavior of each sample was determined by the inversion test defined previously.⁹ Samples were examined on a macroscopic scale in natural and polarized light and also on a microscopic scale using optical microscopy and X-ray scattering as described previously.⁹

Results and Discussion

Synthesis. A series of novel ABA-triblock copolymers (**8a–e**) was synthesized by coupling of 3,4-bis(tetradecyloxy) benzoic acid chloride (**2b**) with α,ω -dihydroxy-poly(ethylene glycol) (Figure 5). The molecular weight of the PEG segment ranged between 200 and 8000. The condensation reaction was carried out in the melt and driven to completion by evaporation of the hydrochloric acid in a vacuum. In addition, two series of AB-diblock copolymers (**5a–c**, **6a–c**) were synthesized in a similar way by coupling of poly(ethylene glycol) mono methyl ether with 3,4-bis(tetradecyloxy) benzoic acid chloride (**2b**) and 3,4-bis(octadecyloxy) benzoic acid chloride (**3b**), respectively (Figure 4). The molecular weight of the PEG segment was varied in the range of $M_n = 750–5000$. The molecular weight data as well as the phase transitions for both block copolymer series are summarized in Tables 1 and 2.

Gelling Properties. In this section, we describe the gelation properties of the ABA-triblock copolymers synthesized here. We compare the gels obtained in systems containing the novel triblock copolymers with gels produced in systems containing the diblock copolymers and note the similarities and differences.

We have found, at certain concentrations, that the ABA-triblock copolymers **8c**, **8d**, and **8e** can induce gelation of the fluid L_{α} phase in a manner analogous to the AB-diblock copolymers of the series **5a–c** and **6a–c**. The phase diagram for the amphiphilic ABA-triblock copolymer **8e** showing the L_{α} and $L_{\alpha,g}$ regions is shown in Figure 6 with the water weight fraction Φ_w plotted vs the mol % of amphiphilic ABA-triblock copolymer **8e** (ϕ_{PEG}) in the total lipid content of the membrane. The phase behavior of these ABA-triblock copolymers is qualitatively much like the AB-diblock copolymers.^{8,9} Gels are obtained with very small amounts of ϕ_{PEG} ($\phi_{PEG} \sim 2$) and the amount of amphiphilic ABA-triblock copolymer required for gelation decreases as the amount of water is increased. However, quantitatively, the phase behavior of the ABA-triblock copolymers is different than the diblock copolymers. The one phase region for systems containing the ABA-triblock copolymer is much narrower as a function of water weight fraction and the upper two-phase boundary occurs as a much lower Φ_w . This second point will be discussed more fully later.

Figure 7 shows four different test tubes which have just been tilted in the horizontal position in order to illustrate the similarities in flow properties between the gels obtained by addition of either the ABA-triblock or the AB-diblock copolymer. Sample A and B contain 4

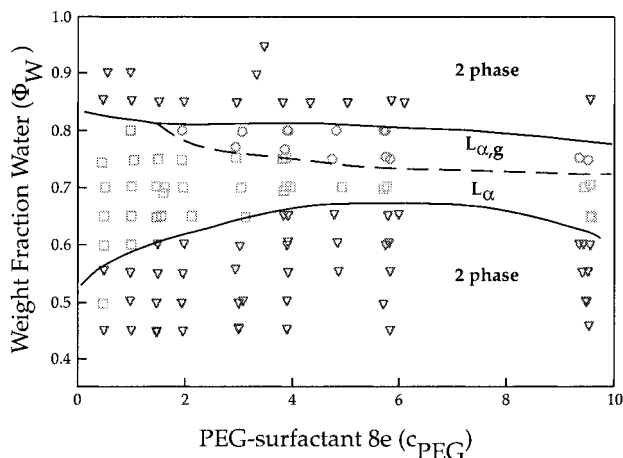


Figure 6. Phase diagram of the quaternary system composed of water, pentanol, DMPC, and the amphiphilic ABA-triblock copolymer **8e**. The water weight fraction Φ_w is plotted vs the concentration of the block copolymer c_{PEG} [$c_{\text{PEG}} = (\text{mol } \mathbf{8e} / (\text{mol } \mathbf{8e} + \text{mol DMPC}))100$]. The transition between the L_α and $L_{\alpha,g}$ phases is denoted by a dashed line and the single phase to two phase transitions are shown as solid lines.

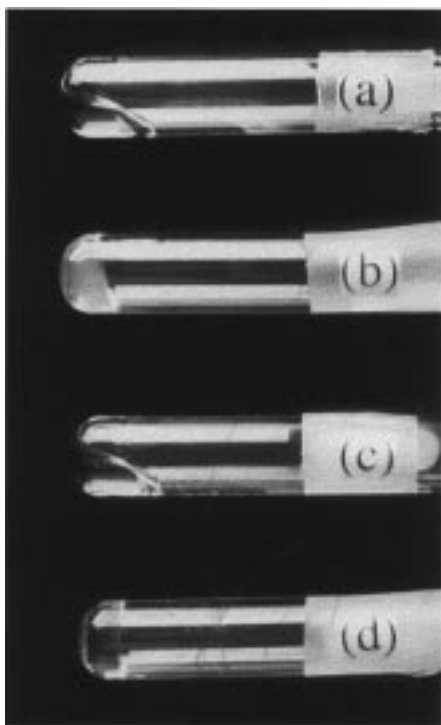


Figure 7. Series of test tubes filled with different mixtures of copolymer, water, cosurfactant, and DMPC tilted horizontally to demonstrate the gelation properties of these novel copolymers: (a) a fluid L_α phase containing the amphiphilic AB-diblock copolymer **6b** of composition $\Phi_w = 74$ wt % and $c_{\text{PEG}} = 4.0\%$; (b) a gel $L_{\alpha,g}$ phase containing the amphiphilic AB-diblock copolymer **6b** of composition $\Phi_w = 80$ wt % and $c_{\text{PEG}} = 4.0\%$; (c) a fluid L_α phase containing the amphiphilic ABA-triblock copolymer **8e** of composition $\Phi_w = 70$ wt % and $c_{\text{PEG}} = 4.9\%$; (d) a gel $L_{\alpha,g}$ phase containing the amphiphilic ABA-triblock copolymer **8e** of composition $\Phi_w = 75$ wt % and $c_{\text{PEG}} = 4.9\%$.

mol % of amphiphilic AB-diblock copolymer **6b** with 74 and 80 wt % water, respectively. Sample C and D contain 4.9 mol % of amphiphilic ABA-triblock copolymer **8e** at 70 and 75 wt % water, respectively. It is obvious that the flow characteristics of the gels produced with either diblock or triblock copolymers are comparable. For systems containing either the diblock or

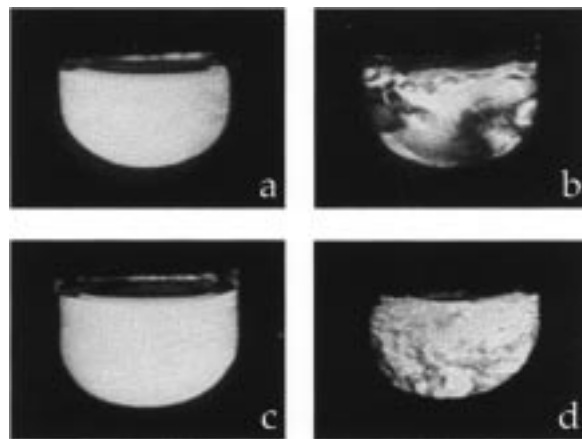


Figure 8. Same test tubes as in Figure 7 viewed between crossed polarizers showing that these samples are birefringent, demonstrating the liquid crystalline nature of the L_α and $L_{\alpha,g}$ phases: (a) a fluid L_α phase containing the amphiphilic AB-diblock copolymer **6b** of composition $\Phi_w = 74$ wt % and $c_{\text{PEG}} = 4.0\%$; (b) a gel $L_{\alpha,g}$ phase containing the amphiphilic AB-diblock copolymer **6b** of composition $\Phi_w = 80$ wt % and $c_{\text{PEG}} = 4.0\%$; (c) a fluid L_α phase containing the amphiphilic ABA-triblock copolymer **8e** of composition $\Phi_w = 70$ wt % and $c_{\text{PEG}} = 4.9\%$; (d) a gel $L_{\alpha,g}$ phase containing the amphiphilic ABA-triblock copolymer **8e** of composition $\Phi_w = 75$ wt % and $c_{\text{PEG}} = 4.9\%$.

triblock copolymers synthesized here, the $L_{\alpha,g}$ phase occurs in water swollen lamellar L_α phases. Although the flow properties of the gels containing the diblock and triblock copolymers are similar, the stability of the gels differs. Gels formed by addition of diblock copolymers to the L_α phase have remained stable up to 2 years. However, the gels formed by addition of the triblock copolymers are metastable and slowly demix on a time scale ranging from several months to a year.

Examination of the same test tubes in polarized light (Figure 8) demonstrates that on a macroscopic scale the L_α and $L_{\alpha,g}$ phases containing either the diblock or triblock copolymers are liquid-crystalline in nature. The L_α phase does not show any texture at this length scale. In contrast, the $L_{\alpha,g}$ phase generally displays a nematic-like texture with a variable density of line defects on a millimeter length scale.

These observations were complemented by the observation of textures by polarized light microscopy. We found that the textures inherent in systems containing the novel ABA-triblock copolymers are analogous to those seen in the AB-diblock copolymer systems.⁹ A defining signature^{8,9} of the biogel $L_{\alpha,g}$ regime as it sets in from the fluid lamellar L_α phase is the proliferation of layer-dislocation type defects which are stabilized by the segregation of the block copolymers to the high membrane curvature defect regions connecting the membranes. This is illustrated in Figure 9 which shows the optical texture of a fluid L_α phase containing a very small amount of an amphiphilic ABA-triblock copolymer and a $L_{\alpha,g}$ biogel containing a larger amount of the same triblock copolymer. The textures of the fluid L_α phase show the usual black homeotropic regions broken by oily streaks which are the typical defects of lyotropic L_α phases.¹⁵ In contrast, the gel texture shows a proliferation of very thin line defects which we call "whisps". The gel phase is then characterized by a highly defected microstructure comprised of a network of connected membrane bilayers with the block copolymers segregated to the high curvature regions. This leads to

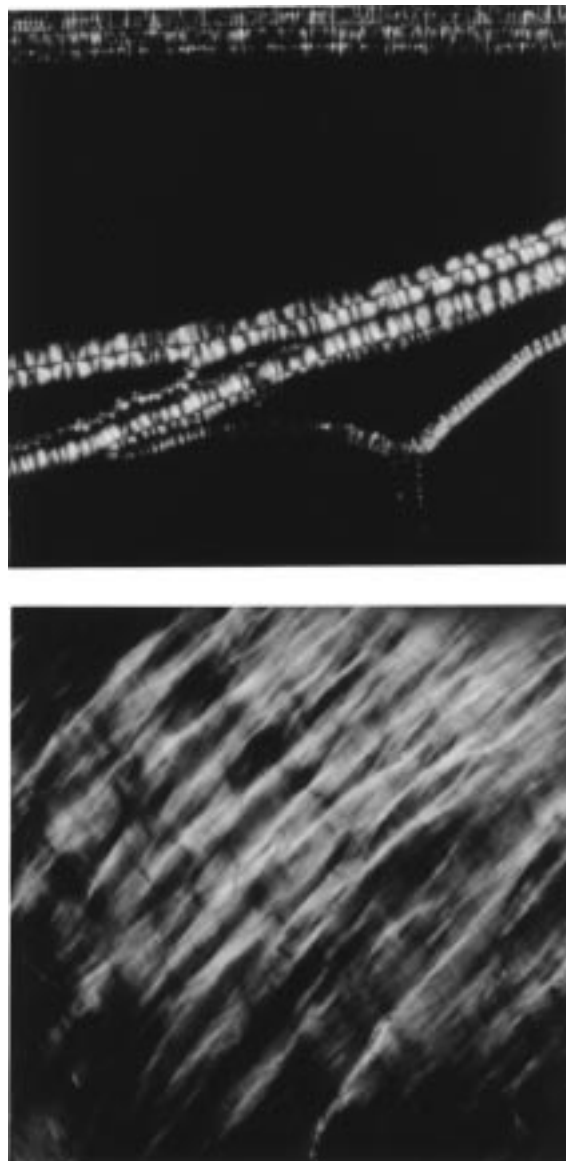


Figure 9. Polarized light microscopy of samples in the L_{α} and $L_{\alpha,g}$ regime showing distinct textures. The fluid L_{α} phase (shown at top) shows oily streak defects while samples in the $L_{\alpha,g}$ phase (shown at bottom) reveal a proliferation of very thin line defects. The fluid L_{α} sample contains the amphiphilic ABA-triblock copolymer **8e** of composition $\Phi_w = 75$ wt % and $c_{PEG} = 0.5\%$. The gel $L_{\alpha,g}$ sample contains the amphiphilic ABA-triblock copolymer **8e** of composition $\Phi_w = 75$ wt % and $c_{PEG} = 4.9\%$.

random layer orientation domains on a semi macroscopic length scale which may induce elasticity and thus gellike behavior because domains which have their layer normals with a finite projection along the flow direction will resist shear to avoid tilting of layers.¹⁶ The same pattern of proliferation of layer-dislocation type defects was seen in samples containing the AB-diblock copolymers synthesized here.⁹

Figure 10 shows small-angle X-ray scattering scans of unoriented samples composed of the amphiphilic ABA-triblock copolymer **8e**, DMPC, pentanol, and water in the fluid and gel phases. The 001 peaks of the lamellar structure are clearly observed for both phases, demonstrating that there is no structural phase transition at this length scale between the fluid and gel phases as was the case for the AB-diblock copolymers. The fluid L_{α} phase sample examined by X-ray scattering

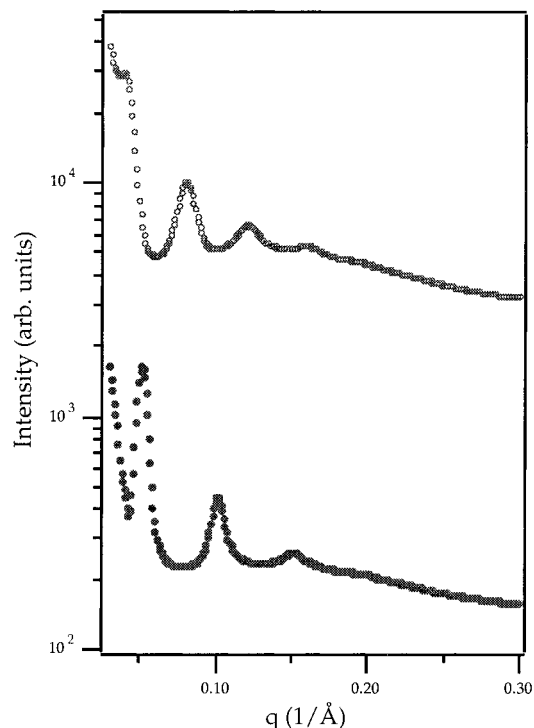


Figure 10. Small-angle X-ray scattering scans of unoriented samples in the fluid and gel phases. Open symbols denote the gel $L_{\alpha,g}$ phase containing the amphiphilic ABA-triblock copolymer **8e** of composition $\Phi_w = 70$ wt % and $c_{PEG} = 4.85\%$. Closed symbols show the fluid L_{α} phase containing the amphiphilic ABA-triblock copolymer **8e** of composition $\Phi_w = 75$ wt % and $c_{PEG} = 4.85\%$. The interlamellar spacing for the gel sample is 155 Å and for the fluid sample is 122 Å ($d = 2\pi/q_1$).

(Figure 10, closed symbols) occurs just above the lower two-phase boundary (Figure 6) and shows an interlamellar spacing of 122 Å. Interestingly, this spacing just allows for the incorporation of the PEG-moiety of the ABA-triblock between the membranes. We can calculate the water spacing between the membranes by first obtaining the membrane thickness from $d = \delta/\phi_m$,⁹ where d = interlamellar spacing, δ = membrane thickness, and ϕ_m = the volume fraction of membrane in the system. For this system, $\delta = 29$ Å. Therefore, the water spacing for the fluid L_{α} sample is $d_w = d - \delta = 93$ Å. The radius of gyration for the PEG chain of amphiphilic ABA-triblock copolymer **8e** is calculated from $R_g = aN^{3/5}$ (a = effective monomer length = 3.6 Å,⁹ N = number of monomers = 181 for PEG M_n of 8000) which gives $R_g = 81.5$ Å. For the PEG segment to insert between the membranes, it is necessary for d_w to be larger than the natural extension of the polymer moiety, R_g . We see that the lower two-phase boundary just fulfills this requirement. This suggests that the system is stable in a lamellar regime only when the PEG segment can be incorporated between the membranes. The AB-diblock copolymers show the same behavior with the lower two-phase boundary occurring at a water spacing just larger than the R_g of the polymer moiety.^{8,9}

In contrast, the upper two-phase boundary of the system containing the novel ABA-triblock copolymer occurs at a water spacing much smaller than that seen in the AB-diblock copolymer systems. The ABA-triblock gel $L_{\alpha,g}$ sample demonstrates an interlamellar spacing of 155 Å corresponding to a water spacing of 126 Å (Figure 10, open symbols). Incorporation of any more water results in phase separation. Therefore, the upper

two-phase boundary in this system occurs at water spacings only slightly larger than 126 Å. This behavior is dramatically different than that seen in systems incorporating the AB-diblock copolymers. In these systems, the lamellar regions remain one phase up to dilutions which correspond to an interlamellar spacing of about 360 Å and a water spacing of 334 Å. This separation is much larger than the radius of gyration R_g of the PEG chain ($R_g = 62$ Å for a PEG M_n of 5000), which suggests a mushroom type conformation for the AB-diblock copolymer (Figure 1a). The behavior seen in the ABA-triblock system is evidence of the cross-bridging configuration (Figure 1b) for the ABA-triblock copolymer where the multilayer membrane cannot support separations much larger than a significantly stretched PEG segment. It also suggests that the looping configuration is not significantly lower in energy cost than the bridging configuration. In this case, the lamellar hydrogel appears to be based on 2-dimensional fluid membranes, but where the membranes have transient cross-links through the 1-dimensional polymers.

Conclusions

We have presented a straightforward method to synthesize ABA-triblock copolymers consisting of hydrophobic A-blocks and a hydrophilic B-block which act as gelling agents for the lamellar liquid crystalline L_α phase. The anchoring strength of these block copolymers can be easily varied by increasing the number of hydrocarbons in the alkyl chains and/or by varying the number of alkyl chains attached to the benzene ring (1–3). The hydrophilic character of these block copolymers depends on the chain length of the poly(ethylene glycol) segment. For future work this will give us a large variety of control parameters for further investigations on the structure–property relationships of these block copolymers. We have shown that the ABA-triblock copolymers presented here can induce gelation of fluid L_α phases in a way similar to that previously reported for the AB-diblock copolymers. However, we have also found that the intermembrane spacing of samples containing the AB-diblock copolymer dilutes to a much greater extent than that of samples containing ABA-triblock copolymers. This strongly suggests that the ABA-triblock copolymers adopt the cross-bridging con-

figuration and that the looping configuration is not a significantly lower energy configuration.

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