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

Nelle L. Slack,¹ Mathias Schellhorn,‡,§ Petra Eiselt,¹ Michael A. Chibbaro,† Uwe Schulze,† Heidi E. Warriner,† Patrick Davidson,†,∥ Hans-Werner Schmidt,*,‡ and C. R. Safinya*,†

Materials Department, Physics Department, and Biochemistry and Molecular Biology Program, University of California, Santa Barbara, California 93106, and Makromolekulare Chemie I and Bayreuther Institut für Makromolekülforchung (BIMF), Universität Bayreuth, 95440 Bayreuth, Germany

Received June 8, 1998; Revised Manuscript Received September 14, 1998

ABSTRACT: We report the first evidence of the potential of new amphiphilic ABA-triblock copolymers as gelling agents for lamellar liquid crystalline LR 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 LR 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, consist 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 LRg, 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 containing 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 ≈ kBT¹⁰ and allows us to explore the swollen lamellar regime where the biogel is stable. The new physical gel phase has the same liquid-crystalline lamellar symmetry as that of the usual fluid LR phase but displays three-dimensional elastic properties.

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.
In this paper, we describe the synthesis of a new series of ABA-triblock copolymers which consist of double chain hydrophobic 3,4-(alkyloxy)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-(alkyloxy)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 glycol)s of number-average molecular weights (Mn) of 200 (Mn/Mw = 1.05, DPn = 4), 600 (Mn/Mw = 1.12, DPn = 13), 2000 (Mn/Mw = 1.04, DPn = 45), 4600 (Mn/Mw = 1.06, DPn = 104), and 8000 (Mn/Mw = 1.06, DPn = 181) and poly(ethylene glycol) mono methyl ethers of number-average molecular weights of 750 (Mn/Mw = 1.07, DPn = 16), 2000 (Mn/Mw = 1.11, DPn = 45), and 5000 (Mn/Mw = 1.10, DPn = 113) were purchased from Aldrich. The poly(ethylene glycol)s 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 CDCl3. 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 (elucent, 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(tetradecyloxy) 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 2. Chemical structures of amphiphilic AB-diblock copolymers 5a–c and 6a–c and of amphiphilic ABA-triblock copolymers 8a–e.](image)

**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-(alkyloxy)benzoic acid and poly(ethylene glycol) segments.

**Figure 3.** Synthesis of 3,4-(alkyloxy)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) (Mn = 2000) and 3.39 g (6 mmol) of 3,4-bis(tetradecyloxy) benzoyl 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,
8a and finally precipitated into 300 mL of hexane. The dissolved in 30 mL of THF, filtered and poured into 500 mL

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

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

<table>
<thead>
<tr>
<th>polymer</th>
<th>M_n,calc</th>
<th>M_n,GPC</th>
<th>M_w,M_n</th>
<th>thermal behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>1300</td>
<td>1840</td>
<td>1.02</td>
<td>K 40 (156) I</td>
</tr>
<tr>
<td>5b</td>
<td>2550</td>
<td>3860</td>
<td>1.04</td>
<td>K_37 (38) K_15 (51) K_34 (308)* I</td>
</tr>
<tr>
<td>5c</td>
<td>5550</td>
<td>8850</td>
<td>1.07</td>
<td>K 60 (814) I</td>
</tr>
<tr>
<td>6a</td>
<td>1410</td>
<td>1940</td>
<td>1.08</td>
<td>K_13 (17) K_32 (41) K_36 K_105 (62) (72)* I</td>
</tr>
<tr>
<td>6b</td>
<td>2660</td>
<td>3500</td>
<td>1.06</td>
<td>K 51 (372) I</td>
</tr>
<tr>
<td>6c</td>
<td>5660</td>
<td>7290</td>
<td>1.08</td>
<td>K 58 (866) I</td>
</tr>
</tbody>
</table>

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. Transition temperatures are given in °C, enthalpy values (in brackets) are given in kJ/mol. The integral

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

<table>
<thead>
<tr>
<th>polymer</th>
<th>M_n,calc</th>
<th>M_n,GPC</th>
<th>M_w,M_n</th>
<th>thermal behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td>8a</td>
<td>1290</td>
<td>1890</td>
<td>1.02</td>
<td>K 47 (119) I</td>
</tr>
<tr>
<td>8b</td>
<td>1690</td>
<td>2310</td>
<td>1.06</td>
<td>K 47 (134) I</td>
</tr>
<tr>
<td>8c</td>
<td>3090</td>
<td>4710</td>
<td>1.02</td>
<td>K 46 (262) I</td>
</tr>
<tr>
<td>8d</td>
<td>5690</td>
<td>8510</td>
<td>1.05</td>
<td>K_51 (61) K_53 (631) I</td>
</tr>
<tr>
<td>8e</td>
<td>9090</td>
<td>13230</td>
<td>1.09</td>
<td>K 57 (1160) I</td>
</tr>
</tbody>
</table>

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. Transition temperatures are given in °C, enthalpy values (in brackets) are given in kJ/mol. The integral

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 hexene. 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) is (1.04–1.12), respectively. This indicates a complete coupling reaction.

Sample Preparation. All samples were prepared as described previously. 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. 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.

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(ocytadeoxy) 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\(_w\) 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 \( L_o \) and \( L_{o,r} \) regions is shown in Figure 6 with the water weight fraction \( \phi_w \) plotted vs the mol % of amphiphilic ABA-triblock copolymer 8e (8PEG) 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 \( \phi_{8PEG} \) (\( \phi_{8PEG} \sim 2 \)) 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 from 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 \( \phi_w \). 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
contain 4.9 mol % of amphiphilic ABA-triblock copolymer. The weight fraction of water, pentanol, DMPC, and the amphiphilic ABA-triblock copolymer 8e is plotted vs the concentration of the block copolymer [PEG] [PEG] = (mol 8e/(mol 8e + mol DMPC))100. The transition between the L, and L,, 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, phase containing the amphiphilic AB-diblock copolymer 6b of composition Φw = 74 wt % and c_{PEG} = 4.0%; (b) a gel L, phase containing the amphiphilic AB-diblock copolymer 6b of composition Φw = 80 wt % and c_{PEG} = 4.0%; (c) a fluid L, phase containing the amphiphilic ABA-triblock copolymer 8e of composition Φw = 70 wt % and c_{PEG} = 4.9%; (d) a gel L, phase containing the amphiphilic ABA-triblock copolymer 8e of composition Φw = 75 wt % and c_{PEG} = 4.9%.

**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, and L,, phases: (a) a fluid L, phase containing the amphiphilic AB-diblock copolymer 6b of composition Φw = 74 wt % and c_{PEG} = 4.0%; (b) a gel L, phase containing the amphiphilic AB-diblock copolymer 6b of composition Φw = 80 wt % and c_{PEG} = 4.0%; (c) a fluid L, phase containing the amphiphilic ABA-triblock copolymer 8e of composition Φw = 70 wt % and c_{PEG} = 4.9%; (d) a gel L, phase containing the amphiphilic ABA-triblock copolymer 8e of composition Φw = 75 wt % and c_{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 triblock copolymers synthesized here, the L,, phase occurs in water swollen lamellar L, 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, 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, and L,, phases containing either the diblock or triblock copolymers are liquid-crystalline in nature. The L, phase does not show any texture at this length scale. In contrast, the L,, 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. A defining signature of the biogel L,, regime as it sets in from the fluid lamellar L, 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, phase containing a very small amount of an amphiphilic ABA-triblock copolymer and a L,, biogel containing a larger amount of the same triblock copolymer. The textures of the fluid L, phase show the usual black homeotropic regions broken by oily streaks which are the typical defects of lyotropic L, phases. In contrast, the gel texture shows a proliferation of very thin line defects which we call "whips". 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...
random layer orientation domains on a semi macro-
noscopic 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 copoly-
mers synthesized here.9

Figure 10 shows small-angle X-ray scattering scans of unoriented
samples in the fluid and gel phases. Open symbols denote the
gel LRG phase containing the amphiphilic ABA-tri
block copolymer 8e of composition \( \Phi_w = 70 \text{ wt } \% \) and \( c_{PEG} = 4.85 \text{ wt } \% \). Closed
symbols show the fluid Lc phase containing the amphiphilic
ABA-tri block copolymer 8c of composition \( \Phi_w = 75 \text{ wt } \% \) and \( c_{PEG} = 4.85 \text{ wt } \% \). The interlamellar spacing for the gel sample is
155 Å and for the fluid sample is 122 Å (\( d = 2\pi/q_0 \)).

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

Figure 10. Small-angle X-ray scattering scans of unoriented
samples in the fluid and gel phases. Open symbols denote the
gel LRG phase containing the amphiphilic ABA-tri block copoly-
mer 8e of composition \( \Phi_w = 70 \text{ wt } \% \) and \( c_{PEG} = 4.85 \text{ wt } \% \). Closed
symbols show the fluid Lc phase containing the amphiphilic
ABA-tri block copolymer 8e of composition \( \Phi_w = 75 \text{ wt } \% \) and \( c_{PEG} = 4.85 \text{ wt } \% \). The interlamellar spacing for the gel sample is
155 Å and for the fluid sample is 122 Å (\( d = 2\pi/q_0 \)).

(Figure 10, closed symbols) occurs just above the lower
two-phase boundary (Figure 6) and shows an inter-
lamellar spacing of 122 Å. Interestingly, this spacing
just allows for the incorporation of the PEG-moiey of
the ABA-tri block between the membranes. We can
calculate the water spacing between the membranes by
first obtaining the membrane thickness from \( d = \delta + \delta_m \),
where \( d \) = interlamellar spacing, \( \delta \) = membrane thick-
ness, and \( \delta_m \) = the volume fraction of membrane in the
system. For this system, \( \delta = 29 \text{ Å} \). Therefore, the water
spacing for the fluid Lc sample is \( d_w = d - \delta = 93 \text{ Å} \)

The radius of gyration for the PEG chain of amphiphilic
ABA-tri block copolymer 8e is calculated from
\( R_g = aN^{3/5} \)

where \( a \) = effective monomer length = 3.6 Å, \( N \) = number of
monomers = 181 for PEG M, of 8000) which gives \( R_g = 81.5 \text{ Å} \). 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-
di block 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-tri block copolymer
occurs at a water spacing much smaller than that seen
in the AB-di block copolymer systems. The ABA-tri block
gel LRG 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 copolymer 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 and that the looping configuration is not a significantly lower energy configuration.

Acknowledgment. The authors gratefully acknowledge Y. Heischt and (University of Bayreuth) for her help with the GPC measurements. U.S. acknowledges the support of the Deutsche Forschungsgemeinschaft (DFG) for a postdoctoral fellowship (Schu 1247/1-3). This research is supported by NSF Grant No. DMR-9624091, the donors of the Petroleum Research Fund, administered by the American Chemical Society, Grant No. 31352-AC7, and Los Alamos Grant STB/UC:96-108.

References and Notes