Aqueous Solutions and Gels of Diblock Copolymers of 1,2-Butylene Oxide and Ethylene Oxide Studied by Light Scattering and Rheology

Antonis Kelarakis, Vasiliki Havredaki, and Kyriakos Viras
National and Kapodistrian University of Athens, Department of Chemistry, Physical Chemistry Laboratory, Panepistimiopolis, 157 71 Athens, Greece

Withawat Mingvanish, Frank Heatley, and Colin Booth*
Department of Chemistry, University of Manchester, Manchester M13 9PL, U.K.

Shao-Min Mai
Department of Chemistry, University of Sheffield, Sheffield S3 7HF, U.K.

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Copolymers $B_20 E_{430}$, $B_20 E_{510}$, and $B_20 E_{610}$ ($B =$ oxybutylene repeat unit, $E =$ oxyethylene repeat unit, subscripts indicate chain length in repeat units) were synthesized and characterized by gel permeation chromatography (for distribution width) and $^{13}$C NMR spectroscopy (for absolute molar mass and composition). Dynamic and static light scattering were used to determine micellar properties in dilute aqueous solution: e.g., micelle association numbers and radii. A tube-inversion method was used to define the mobile-immobile (hard gel) phase boundary. For copolymer $B_20 E_{610}$, immobile gels form at concentrations as low as 2.9 wt %. Rheological measurements of dynamic modulus and yield stress served to characterize the gel properties and to confirm the phase boundaries. The results are combined with those from previous work on related block copolymers to obtain scaling relationships for the dependence of micellar and gel properties on $E$-block length, thus enabling prediction of the requirements for and properties of very dilute aqueous gels. The validity of treating the micelles as hard spheres is discussed.

1. Introduction

Block copolyethers in dilute aqueous solution readily form micelles, and their concentrated micellar solutions form liquid-crystal mesophases (gels) comprising packed micelles. From a physicochemical viewpoint, the properties of both are of interest. An account of work on micellar solutions of copolymers of ethylene oxide (EO) and 1,2-butylene oxide (BO) has been published recently,1 and reviews summarize related work on triblock copolymers of ethylene oxide and propylene oxide. 2,3 A recent paper 4 draws together a considerable body of work on gels of diblock $E_m B_n$ block copolymers. We use the notation $E =$ oxyethylene, OCH$_2$CH$_2$, and $B =$ oxybutylene, OCH$_2$(C$_2$H$_5$), with $m$ and $n$ denoting block lengths in repeat units.

A recent interest in our laboratory has been the formation and properties of gels of diblock $E_m B_n$ copolymers with long $E$ blocks.4–6 Copolymers with $B$ blocks in the range $n = 17–19$ and $E$ blocks in the range $m = 96–398$ were prepared and shown to form gels, i.e., spherical micelles packed into cubic structures at concentrations as low as 3.5 wt % in the case of copolymer $E_{398} B_{19}$. These copolymers are referred to hereafter as the $B_{18}$ series. Outside the hard gel region, the micellar solutions of the copolymers exhibited a rich rheological behavior, with well-defined regions of soft gel, i.e., Bingham fluids having yield stress and dynamic storage modulus ($G'$) in excess of loss modulus ($G''$). We use the terms “hard” and “soft” gel in the manner introduced by Hvidt and co-workers.7,8 The present work is an extension to copolymers with yet longer $E$ blocks, the aim being to define the $E$-block length necessary to obtain a cubic-packed hard gel at yet lower concentrations, e.g., 2 wt %. Because it was difficult to mix efficiently a small volume of BO with a large volume of viscous poly(oxyethylene) ($M_n = 20 000–30 000 \text{ g mol}^{-1}$), it was convenient to reverse the sequence of anionic polymerization to BO followed by EO. We denote the copolymers so produced as $B_n E_{m}$ to signify this change. The series was based on $B_{20}$, and the copolymers prepared were $B_{20} E_{430}$, $B_{20} E_{510}$, and $B_{20} E_{610}$.

2. Experimental Section

2.1. Copolymers. The diblock copolymers were prepared by sequential anionic polymerization of 1,2-butylene oxide followed by ethylene oxide. The general methods used for their preparation and characterization have been described previously.9,10 The monofunctional initiator was 2-butanol activated by reaction with potassium metal (mole ratio OH/K $\approx 10$). Vacuum line and ampule techniques were used. At the completion of the first
TABLE 1: Molecular Characteristics of the Copolymers®

<table>
<thead>
<tr>
<th>copolymer</th>
<th>wt % E</th>
<th>Mw/10^3 g mol^-1 (NMR)</th>
<th>Mr/Mw (NMR)</th>
<th>wt % poly(E)</th>
<th>Mw/10^3 g mol^-1 (GPC)</th>
<th>Mr/Mw (GPC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B20E430</td>
<td>92.9</td>
<td>20.4</td>
<td>1.06</td>
<td>6</td>
<td>21.6</td>
<td></td>
</tr>
<tr>
<td>B20E510</td>
<td>94.0</td>
<td>23.9</td>
<td>1.06</td>
<td>8</td>
<td>25.3</td>
<td></td>
</tr>
<tr>
<td>B20E610</td>
<td>94.9</td>
<td>28.3</td>
<td>1.09</td>
<td>6</td>
<td>30.8</td>
<td></td>
</tr>
</tbody>
</table>

*Estimated uncertainties: wt % E to ±0.05; Mw and block lengths to ±3%; Mw/Mr to ±0.02. Mw calculated from Mn and Mr/Mw.

stage, the poly(oxybutylene) precursor was divided between four ampules and dried under vacuum before EO was added.

Characterization of the four copolymers by gel permeation chromatography, GPC, calibrated with poly(oxyethylene) standards, indicated narrow chain length distributions for the copolymers, i.e., Mw/Mn < 1.10, where Mw and Mn are the mass-average and number-average molar masses, respectively, plus small shoulders on the low elution volume side attributable to 6-8 wt % poly(oxyethylene) accidentally initiated in the second stage of the polymerization by moisture. Absolute values of Mw of the precursor poly(oxyethylene) and the final copolymers were obtained by 13C NMR spectroscopy by comparison of integrals of resonances from the carbons of end groups, junction groups and backbone groups, based on the assignments of Heatley et al. The spectra also served to confirm the diblock structure and the presence of the poly(oxyethylene) impurity. Relevant molecular characteristics are listed in Table 1, where the formulas are for the copolymer, i.e., corrected for the impurity.

2.2. Light Scattering. Solution clarification and static and dynamic light scattering measurements were carried out as described previously. Static light scattering (SLS) intensities were measured by means of a Brookhaven BI 200S instrument using vertically polarized incident light of wavelength λ = 488 nm supplied by an argon-ion laser (Coherent Innova 90) operated at 500 mW or less. The intensity scale was calibrated against benzene. Dynamic light scattering (DLS) measurements were made under similar conditions, using a Brookhaven BI 9000 AT digital correlator to acquire data. Experiment duration was in the range 5–20 min, and each experiment was repeated two or more times. In both methods, scattered light intensity was usually measured at an angle θ = 90° to the incident beam.

The correlation functions from dynamic light scattering (DLS) were analyzed by the constrained regularized CONTIN method to obtain distributions of decay rates (Γ), and hence distributions of apparent mutual diffusion coefficient, Dapp = Γ/2q^2, q = (4πnλ) sin(θ/2), n is the refractive index of the solvent, and ultimately of apparent hydrodynamic radius (r_h,app, radius of the hydrodynamically equivalent hard sphere corresponding to Dapp) via the Stokes–Einstein equation:

\[ r_{h,\text{app}} = kT/(6\pi\eta D_{\text{app}}) \]  \hspace{1cm} (1)

where \( k \) is the Boltzmann constant and \( \eta \) is the viscosity of the solvent at temperature \( T \). In practice, intensities I(Γ) delivered by the CONTIN program at logarithmically spaced values of decay rate were transformed to \( I(\log \Gamma ) = I(\Gamma)|^{\Gamma \to 0} \) to obtain intensity distributions of log(Γ), and so of log(r_h,app). Normalization of I(log r_h,app) gave the intensity fraction distributions presented in section 3.1. Average values of Γ, delivered by the CONTIN program by integration over the intensity distributions, were similarly converted to intensity-average values of r_h,app. The basis for analysis of static light scattering (SLS) was the Debye equation:

\[ K^*c(I - I_0) = 1/M_w + 2A_Ec + ... \]  \hspace{1cm} (2)

where \( I \) is intensity of light scattering from solution relative to that from benzene, \( I_0 \) is the corresponding quantity for the solvent, \( c \) is the concentration (in g dm⁻³), \( M_w \) is the mass-average molar mass of the solute, \( A_E \) is the second virial coefficient (higher coefficients being neglected in eq 2), and \( K^* \) is the appropriate optical constant. Values of the specific refractive index increment, dn/dc, its temperature increment, and other quantities necessary for the calculations, have been given previously. In fact, values of dn/dc are very similar for poly(oxyethylene) and poly(oxybutylene), making dn/dc insensitive to the exact composition of the copolymers, and making correction for refractive index difference within the copolymer unnecessary.

2.3. Rheometry. The rheological properties of the samples were determined using a Bohlin CS50 rheometer with water-bath temperature control. Couette geometry (bob, 24.5 mm diameter, 27 mm height; cup, 26.5 mm diameter, 29 mm height) was used for all the samples, with 2.5 cm³ sample being added to the cup in the mobile state. A solvent trap maintained a water-saturated atmosphere around the cell, and evaporation was not significant for the temperatures and time scales investigated.

Storage and loss moduli were recorded across the temperature range with the instrument in oscillatory-shear mode, usually at a frequency of 1 Hz, but for certain systems across the range 0.1–10 Hz. In this mode, the samples were heated at 1 deg min⁻¹ in the range 5–92 °C. For all measurements the strain amplitude was low (<0.5%, linear viscoelastic region), thus ensuring that \( G' \) and \( G'' \) were independent of strain.

Measurements of yield stress and viscosity were made at selected temperatures with the instrument in steady-shear mode. The instrument was programmed to increase the shear stress in a series of logarithmically spaced steps, allowing a maximum of 1 min to equilibrate at each step. Usually, a period of 30 min was allowed for temperature equilibration before starting the program at any given temperature.

In related tube-inversion experiments, samples (0.5 g) were enclosed in small tubes (internal diameter ca. 10 mm) and observed while slowly heating (or cooling) the tube in a water bath, usually within the range 0–70 °C. The change from a mobile to an immobile system (or vice versa) was determined by inverting the tube. The heating/cooling rate was normally 0.5 °C min⁻¹; experiments using a slower heating rate (0.15 °C min⁻¹) gave transition temperatures that differed by less than 1 °C. This simple method of detecting gelation, which is sensitive to the yield stress of the gel, has been shown to define the same hard gel phase boundary as rheometry.

3. Micelle Properties by Light Scattering

Solutions of the copolymers did not cloud over the concentration and temperature ranges investigated (c = 16 wt %, T = 90 °C).

Considering the known effect of B-block length on the critical micelle concentrations of oxyethylene/oxybutylene diblock copolymers, it was expected that all three B20E430 copolymers would be completely micellized at room temperature and above. The results obtained for their dilute solutions using dynamic and static light scattering confirmed this, as described below.

3.1. Hydrodynamic Radius. Intensity fraction distributions of apparent hydrodynamic radius [log(r_h,app)] were obtained by DLS for copolymer solutions at 20, 30, and 40 °C and at concentrations up to 12 g dm⁻³. The distributions obtained for 1 g dm⁻³ solutions of the three copolymers at 20 °C are shown.
in Figure 1. The single narrow peaks with maxima in the range \( r_{h,\text{app}} \approx 23-28 \text{ nm} \) indicate micelles formed by closed association. The intensity fraction distributions found at higher concentrations were displaced to lower values of \( \log(r_{h,\text{app}}) \) but were otherwise similar to those shown in Figure 1.

In Figure 2 the reciprocal of the intensity average of \( r_{h,\text{app}} \) is plotted against copolymer concentration for the three copolymers. Through eq 1, \( 1/r_{h,\text{app}} \) is related to \( D_{\text{app}} \) but is compensated for change in temperature and viscosity. Complication is avoided in Figure 2 by fitting a single line to all the data points for a given copolymer irrespective of temperature. Linear extrapolation of the individual data sets to zero concentration gave the values of \( r_b \) listed in Table 2 (where \( r_b \) implies the inverse of the intensity average of \( 1/r_0 \)). The positive slope of \( 1/r_{h,\text{app}} \) as a function of \( c \) is consistent with spherical micelles effectively interacting as hard spheres. This point is discussed in section 5.2.

The temperature dependence of \( r_b \) is small, within the error of determination. It has been known for some time that the hydrodynamic radii of micelles of block copoly(oxyalkylene)s in aqueous solution are insensitive to change in temperature.\(^{1,2} \) The effect, first noted for \( \text{E}_{m}\text{P}_{n}\text{E}_{m} \) copolymers,\(^{15} \) is attributable to compensation between an increase in association number of the micelle and a decrease in swelling of the micelle fringe as temperature is increased.

3.2. Association Number and Thermodynamic Radius. SLS experiments were performed on copolymer solutions at the temperatures and concentrations described for the DLS experiments. Debye plots, see eq 2 of section 2.2, were used to analyze the data. Used for scattering at 90°, the equation assumes small particles relative to the wavelength of the light. Radii of gyration estimated as 0.775\( r_h \) (i.e., as if the micelles were uniform spheres) are in the range 19–23 nm based on the values of \( r_b \) listed in Table 2, and a small effect from intraparticle interference is to be expected at the high end of this range. However, from published tables\(^{16} \) the maximum effect for the largest micelles is to increase \( M_N \) by 4%. Given the likely error from other sources, this correction was ignored.

Equation 2 truncated to the second term could not be used in the present experiments because micellar interaction caused significant curvature of the Debye plot even in the low concentration range. This feature is illustrated in Figure 3, in which the reciprocal of the apparent association number, \( l/\langle l \rangle_{\text{app}} = M_{\text{w,mol}}K'c/(I - I_s) \), is plotted against concentration for the three copolymers in solution at 20 °C. This particular plot is preferred for illustrative purposes as the three curves overlap in the usual Debye plot of \( K'/c(I - I_s) \) versus \( c \). Rather than accommodate the curvature by use of a virial expansion, so introducing a number of adjustable coefficients, we have fitted the data with curves based on Percus–Yevick scattering theory for hard spheres that uses the Carnahan–Starling approximation as proposed by Vrij.\(^{17} \) see Figure 3. The validity of treating the micelles as hard spheres is discussed in section 5.2. The procedure is equivalent to using the virial expansion for the

![Figure 1](image1.png)

![Figure 2](image2.png)

**TABLE 2: Micellar Characteristics from Light Scattering: \( \text{B}_{20}\text{E}_{m} \) Copolymers in Water**

<table>
<thead>
<tr>
<th>copolymer</th>
<th>( T/\degree C )</th>
<th>( r_b/\text{nm} )</th>
<th>( M_{\text{w}}/10^5 \text{ g mol}^{-1} )</th>
<th>( N )</th>
<th>( \delta_i )</th>
<th>( r_t/\text{nm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{B}<em>{20}\text{E}</em>{430} )</td>
<td>20</td>
<td>25.2</td>
<td>13.5</td>
<td>63</td>
<td>19.4</td>
<td>21.0</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>24.9</td>
<td>15.5</td>
<td>72</td>
<td>18.7</td>
<td>21.8</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>24.5</td>
<td>17.4</td>
<td>81</td>
<td>17.8</td>
<td>22.4</td>
</tr>
<tr>
<td>( \text{B}<em>{20}\text{E}</em>{510} )</td>
<td>20</td>
<td>27.8</td>
<td>14.3</td>
<td>57</td>
<td>23.0</td>
<td>22.7</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>28.0</td>
<td>16.8</td>
<td>66</td>
<td>22.5</td>
<td>23.8</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>28.3</td>
<td>18.4</td>
<td>73</td>
<td>23.4</td>
<td>24.2</td>
</tr>
<tr>
<td>( \text{B}<em>{20}\text{E}</em>{610} )</td>
<td>20</td>
<td>30.2</td>
<td>14.6</td>
<td>47</td>
<td>25.7</td>
<td>23.7</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>30.0</td>
<td>16.8</td>
<td>55</td>
<td>25.0</td>
<td>24.7</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>29.5</td>
<td>19.1</td>
<td>62</td>
<td>23.3</td>
<td>25.2</td>
</tr>
</tbody>
</table>

\( r_b \) (hydrodynamic radius) and \( r_t \) (thermodynamic radius), both to \( \pm 5\% \); \( M_{\text{w}} \) (mass-average molar mass of micelles), \( N \) (association number of micelles), and \( \delta_i \) (thermodynamic expansion factor relative to anhydrous volume), all to \( \pm 10\% \).
structure factor for hard spheres taken to its seventh term but requires only two adjustable parameters, \( M_w \) and a new parameter, \( \alpha_t \), related to the volume excluded by one micelle to another, i.e., to the volume fraction occupied by the micelles acting as effective hard spheres. Specifically, \( \alpha_t \) is a thermo-
dynamic expansion parameter defined by

\[
\alpha_t = \frac{V_t}{V_a} \tag{3}
\]

where \( V_t \) is the thermodynamic volume (that is one-eighth of the excluded volume for a micelle acting as an effective hard sphere) and \( V_a \) is the anhydrous volume of the micelle, i.e.,

\[
v_t = \frac{M_w}{N_A \rho_a} \tag{4}
\]

where \( N_A \) is Avogadro’s constant and \( \rho_a \) is the density of the copolymers calculated assuming mass additivity of specific volumes from published values for the component homopolymers.18 Details of the procedure have been described many times previously; see, for example, refs 5, 12, and 19.

Results obtained for the three copolymers at three temperatures are listed in Table 2, together with association numbers of the micelles calculated from

\[
N_w = \frac{M_{w, mic}}{M_{w, mol}} \tag{5}
\]

using the values of \( M_{w, mol} \) listed in Table 1. Also listed is the thermodynamic radius \( (r_t) \) calculated from \( M_w \) and \( \delta_t \) via eqs 3 and 4.

4. Gelation and Gel Properties

4.1. Phase Diagrams by Tube Inversion. Mobile–immobile boundaries determined by tube inversion (under the conditions described in section 2.3) are shown in Figure 4. In keeping with previous work on related copolymers,4–6 and the reports of Hvidt and co-workers,7,8 the immobile gels are referred to as hard gels. Depending on E-block length, the minimum concentration for hard gel formation \( (c^*) \) was in the range 2.9–3.8 wt %, with solutions of copolymer \( B_{30}E_{610} \) gelling at the lowest concentrations: see Table 3.

TABLE 3: Predicted and Observed Values of the Critical Gel Concentration: Micellar Solutions of \( B_{30}E_{610} \) Copolymers at 40 °C

<table>
<thead>
<tr>
<th>copolymer</th>
<th>( c^*/\text{wt} % ) predicted</th>
<th>observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>( B_{30}E_{430} )</td>
<td>3.8</td>
<td>4.2</td>
</tr>
<tr>
<td>( B_{30}E_{510} )</td>
<td>3.3</td>
<td>3.5</td>
</tr>
<tr>
<td>( B_{30}E_{610} )</td>
<td>2.9</td>
<td>3.2</td>
</tr>
</tbody>
</table>

In micellar systems of this type, gelation at any temperature can be understood in terms of solvent-swollen spherical micelles filling space as effective hard spheres.3,5,7,8,12,20–24 The important parameter is the volume fraction of effective hard spheres. As discussed in section 3.2, the effective size of micelles acting as hard spheres can be derived from the concentration dependence of the intensity of scattered light as the thermodynamic volume \( v_t \), which relates to the volume excluded by one micelle to another. The same quantity is available from other scattering techniques, e.g., small-angle neutron scattering.19 It is convenient to use the parameter \( \delta_t \) and write the volume fraction as

\[
cgc = \frac{\phi}{1000 \rho_a} \tag{6}
\]

where \( c \) is the copolymer concentration in g dm\(^{-3} \) and \( \rho_a \) is the density of anhydrous liquid copolymer as defined in section 3.2. In the particular case of a body-centered cubic (bcc) structure, the critical volume fraction for gelation is \( c_{gc} = 0.68 \), and the critical concentration for hard gel formation \( (c_{gc} \text{ in g dm}^{-3}) \) is

\[
cgc/(\text{g dm}^{-3}) = 680 \rho_a / \delta_t \tag{7}
\]

Considering solutions at 40 °C, use of eq 7 leads to the predicted values for the \( c_{gc} \) (in wt %) that are compared with observed values (interpolated from Figure 4) in Table 3. Prediction and experiment are in good agreement.

4.2. Temperature Dependence of Modulus. 4.2.1. Hard Gels. As the micellar properties of the present copolymers closely mirrored those reported earlier for the \( B_{18} \) series, attention was directed toward the very dilute hard gels formed from copolymer \( B_{20}E_{610} \). The effect of concentration and
temperature on the storage modulus measured at frequency $f = 1$ Hz is shown in Figure 5. The temperature at which the storage modulus fell steeply to a low value, arbitrarily defined as $G' \approx 200$ Pa, was used to define the phase boundary. Other realistic choices of $G'$ did not change the temperature by more than $(\pm 2)$ °C. As seen in Figure 6, the phase boundary defined in this way corresponds closely to that defined by tube inversion. In similar experiments carried out at 10 Hz, the hard gel phase boundary was unaffected.

The maximum storage modulus reached by the most dilute hard gel (3 wt %) was only 440 Pa (20 °C, see Figure 5). Nevertheless, the gel remained immobile when held inverted in the tube, indicating a significant yield stress (see section 4.3). However, when subjected to gentle shaking, the gel flowed. A frequency scan for this most dilute solution from 0.1 to 30 Hz (see Figure 7) showed that $G'$ was only weakly dependent on frequency at low values and reached a plateau value at 1 Hz, while $G''$ fell slightly as the frequency was increased, i.e., behavior somewhat similar to that of a Maxwell element with a long relaxation time.²⁵ Dilute hard gels of the other copolymers behaved similarly when tested in this way.

4.2.2. Soft Gels. Examples of plots of log(modulus) against temperature ($f = 1$ Hz) for $B_{20}E_{610}$ solutions are shown in Figure 8. It is seen that the phase transition at high temperature (but not at low, see Figure 8a) is to a fluid with $G'' > G'$. As noted in the Introduction, it is convenient to label this fact by calling such mobile fluids soft gels, in contrast to the sols for which $G'' > G'$.

Examples of plots of log(modulus) against temperature ($f = 1$ Hz) for $B_{20}E_{610}$ solutions below the limiting concentration for hard gel formation are shown in Figure 9. The temperature at which $G'$ obviously exceeds $G''$ was taken as the lower limit of the soft gel region of the phase diagram under the conditions used. In contrast to the hard gel phase boundary, the temperature of the sol/soft gel boundary decreased on increasing the frequency, much as described previously for micellar solutions of copolymers of the $B_{18}$ series, e.g., by some 20 °C for the 2.5 wt % solution of copolymer $B_{20}E_{610}$ on changing the frequency from 1 to 10 Hz.

A further complication in investigating the soft gels was the time dependence of their properties after loading, i.e., after they had been subject to severe flow. This feature is illustrated in Figure 10 for a 3 wt % solution of copolymer $B_{20}E_{610}$ in its soft-gel phase at 30 °C. The storage modulus measured at $f = 1$ Hz (see Figure 10a) increased with time from $G' \approx 1$ Pa measured 2 min after loading to $G' \approx 15$ Pa after 68 min, while the loss modulus remained roughly constant. The frequency dependence of storage modulus changed with time after loading (see Figure 10b) from that characteristic of a liquid with a short relaxation time (2 min) to that characteristic of a gel with long relaxation time (68 min). In making the routine measurements described in this paper, about 30 minutes was allowed for equilibration before measurement.

The sol/soft-gel boundaries ($f = 1$ Hz) found for dilute solutions of copolymer $B_{20}E_{410}$ and for similarly dilute solutions of copolymers $B_{20}E_{430}$ and $B_{20}E_{510}$, are shown in the combined phase diagram in Figure 11. The straight lines, which highlight the sol/soft gel boundaries, are arbitrarily drawn to meet the hard gel boundaries; the actual behavior at low temperature may well be more complex than that depicted. As would be expected,
the form of this diagram resembles closely that found for dilute solutions of the related copolymers of the B\textsubscript{18} series (see Figure 9 of ref 6). A similar phase diagram has also been reported for aqueous solutions of a diblock copolymer of ethylene oxide and styrene oxide, S\textsubscript{13} E\textsubscript{60}.\textsuperscript{26}

4.3. Yield Stress. Examples of the effect of a programmed increase in shear stress on micellar solutions of the copolymers are shown in Figure 12 for 3 and 5 wt % solutions of B\textsubscript{20} E\textsubscript{610}. As indicated in Figure 5, the 3 wt % solution is a sol at low temperature, a hard gel in the interval 15–25 °C, and a soft gel above 30 °C. Figure 12a shows that the sol at 5 °C had zero yield stress, the hard gel at 20 °C had a yield stress of 12 Pa (sufficient to render it immobile in the tube-inversion test provided that it was not shaken), and the soft gel at 35 °C had a low yield stress of 6 Pa. The 5 wt % solution (see Figure 12b) was a stable hard gel at all temperatures below 65 °C, and the yield stresses at 5, 25, and 45 °C were correspondingly high, in the region of 100 Pa. At 65 °C, which is at the boundary between the hard and soft gel (see Figure 5), the yield stress is 5 Pa, characteristic of a soft gel. Other solutions gave similar results: see Table 4. More dilute solutions (3.5 wt % B\textsubscript{20} E\textsubscript{430} and 2 wt % B\textsubscript{20} E\textsubscript{610}) had yield stresses below 2 Pa in their soft gel regions. Parallel to the behavior of the storage modulus, and as noted for the soft gels of the B\textsubscript{18} series of copolymers,\textsuperscript{6} the yield stresses of the soft gels of the present copolymers were reduced to very low values by shearing but recovered after storage for 1 h or more. Given the low levels of yield stress (<2 Pa) found for the dilute gels, and also their shear and time

![Figure 8](image1.png)  
Figure 8. Temperature dependence of logarithmic storage and loss modulus for aqueous solutions of copolymer B\textsubscript{20} E\textsubscript{610} at the concentrations (wt %) indicated. Frequency = 1 Hz. Filled symbols denote G' and unfilled symbols denote G''.

![Figure 9](image2.png)  
Figure 9. Temperature dependence of logarithmic storage and loss modulus for aqueous solutions of copolymer B\textsubscript{20} E\textsubscript{610} at the concentrations (wt %) indicated. Frequency = 1 Hz. Filled symbols denote G' and unfilled symbols denote G'".
dependence, it was impossible to distinguish soft gel from sol on the basis of yield stress alone. However, as demonstrated in section 4.2.2, the criterion $G' > G''$ held.

5. Effect of E Block Length: Comparison of Present and Previous Results

5.1. Micelle Association Number and Radius. From Table 2, it is apparent that values of the radii increase with increase in E-block length while values of the micelle association number decrease. This is illustrated in the log--log plots of Figure 13, where the present results for the $B_{20}E_{m}$ block copolymers in solution at 40 °C are compared with those obtained previously under the same conditions for the four $E_aB_b$ block copolymers of the $B_{18}$ series. The straight lines in Figure 13, which are drawn through the combined data points for both series, emphasize the agreement between the data sets. The apparent insensitivity of micellar properties to B-block length is unexpected in view of Figure 10.

Table 4: Yield Stresses ($\sigma_y$/Pa) of Aqueous Solutions of $B_{20}E_{m}$ Block Copolymers

<table>
<thead>
<tr>
<th>$T$/°C</th>
<th>3 wt %</th>
<th>5 wt %</th>
<th>10 wt %</th>
<th>4 wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0</td>
<td>110$^a$</td>
<td>340$^a$</td>
<td>22$^a$</td>
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<tr>
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<td>8</td>
<td>37$^a$</td>
<td>37$^a$</td>
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<tr>
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<td>20$^a$</td>
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<td>7</td>
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<tr>
<td>85</td>
<td>7</td>
<td>5</td>
<td>3</td>
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</tbody>
</table>

$^a$ Denotes immobile gel in the tube-inversion test. $^b$ Not investigated by tube inversion.

5. Effect of E Block Length: Comparison of Present and Previous Results

5.1. Micelle Association Number and Radius. From Table 2, it is apparent that values of the radii increase with increase in E-block length while values of the micelle association number decrease. This is illustrated in the log--log plots of Figure 13, where the present results for the $B_{20}E_{m}$ block copolymers in solution at 40 °C are compared with those obtained previously under the same conditions for the four $E_aB_b$ block copolymers of the $B_{18}$ series. The straight lines in Figure 13, which are drawn through the combined data points for both series, emphasize the agreement between the data sets. The apparent insensitivity of micellar properties to B-block length is unexpected in view of Figure 10.
of the many results indicating otherwise.\(^1\)
Possibly, it is a consequence of the difference in the order of polymerization
(BE versus EB), which means that the B blocks in the \(B_mE_n\) copolymers
terminate in methyl groups whereas those in the \(E_mB_n\) copolymers terminate
in hydroxyl groups. This possibility will be investigated in the near future.

In Figure 13a, the slope of the best straight line through the combined points
is in agreement with the exponent \(-0.51\) derived theoretically for \(E_mP_n\)
diblock copolymers by Nagarajan and Ganesh.\(^5,7\)
This is an equilibrium treatment based on the Flory–Huggins model in which
the water/polymer interactions are introduced via known values of parameter \(\chi\)
for water/poly(oxyethylene) and water/poly(oxypropylene). The scaling
eponent of \(m^{-0.51}\) is system specific but depends essentially on the
fact that water at low temperatures is a good solvent for poly(oxyethylene).
Accordingly, one might reasonably expect similar behavior for the two systems,
\(E_mP_n\) and \(E_mB_n\), which both have poly(oxyethylene) coronal blocks.

As reviewed by Hamley,\(^28\) and discussed previously in relation to related
copolymers,\(^1,20\) theoretically derived scaling laws for micelle radius of gyration
(or the micelle corona thickness, which is a large part of the micelle radius in the
present systems), place the exponent of \(m\) in the range 0.5–0.8. Of the two radii measured in the present work, the hydrodynamic radius is most closely related to those considered
by theory, but the exponent obtained from the combined plot in Figure 13b
\((r_h \sim m^{0.04 \pm 0.02})\) lies outside the range of predicted values. This value, and the corresponding exponent for the
thermodynamic radius \((r_t \sim m^{0.28 \pm 0.03})\), are similar to values reported previously for related block copolymers.\(^20\)

5.2. \(B_2B_6E_m\) Micelles as Hard Spheres.
A combination of dynamic and static light scattering enables investigation of the
validity of considering the micelles as hard spheres. One approach is to compare directly the values of the effective hard-sphere radii arising from the two methods, as the ratio \(r_t/r_h\)
should be unity for a completely hard sphere. As reviewed by Selser,\(^29\) this parameter is used in investigating the nature of
the coil–coil interaction of polymers in solution. Values of the ratio are plotted against E-block length in Figure 14 and are
seen to be below unity, especially for the copolymer with the longest E blocks, which is consistent with the most expanded
corona giving the softest interaction potential. We have shown previously that micelles of comparable copolymers with signi-
ficantly shorter E blocks have \(r_t/r_h\) closer to unity, e.g., 0.93 for \(E_{30}B_{18}\) in aqueous solution at 20 °C.\(^4\) As the temperature is
raised, the solvent becomes poorer, resulting in an increase in micellar association number (Table 2). This counteracts the
expected increase in interpenetration of the E blocks in the corona of the micelle (i.e., a softening of the interaction
potential), and the overall effect is an increase in \(r_t/r_h:\) see Figure
14. This complication is, of course, peculiar to associating systems.

In a related approach, applied to micelles by Konak et al.,\(^30\)
the second diffusion virial coefficient \((k_D)\) obtained from a plot of the apparent diffusion coefficient against \(c, i.e.
\[ D_{app} = D(1 + k_D c) \]
is expressed in volume fraction units as
\[ k_D(\phi) = k_D / \bar{v} \approx k_D m_w / \bar{v}_h \]
where \(\bar{v}\) is the partial specific volume and \(m_w\) and \(\bar{v}_h\) are respectively the average mass
\((m_w = M_w/N_A)\) and hydrodynamic
The dependence of the micellar properties (i.e., association number and radius) of E/B diblock copolymers on E-block length has been investigated for copolymers with E-block lengths up to $E_{610}$. The behavior is as expected, i.e., related to that of their analogues with shorter chain lengths. The same is true of gelation concentration and gel properties (e.g., modulus), which is a direct consequence of the fact that these properties depend on micelle properties. The scaling relations obtained allow secure prediction of the synthetic requirements for the preparation of extremely dilute aqueous packed gels: for example, formation of a 2 wt % aqueous gel will require synthesis of a micellizable E/B copolymer with an E-block length of ca. 1300 chain units. Parallel scaling relationships enable prediction of gel properties.

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Copolymers of 1,2-Butylene Oxide and Ethylene Oxide

References and Notes

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