

# Reverse Micelle Formation and Water Solubilization by Polyoxyalkylene Block Copolymers in Organic Solvent

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A systematic investigation of the effects of polymer chemical composition and molecular mass on (i) the micellization of polyoxyalkylene block copolymers [poly(ethylene oxide)/poly(propylene oxide), PEO/PPO, and poly(ethylene oxide)/poly(butylene oxide), PEO/PBO] in an organic solvent (*p*-xylene: selective solvent for the PPO and PBO blocks) in the presence of some water and (ii) the solubilization of water (selective solvent for the PEO blocks) in these systems is presented. The ability of the ("reverse") micelles to solubilize water has been employed for the detection of the critical micellization concentration ("reverse" cmc). The "reverse" cmc values were in the range 0.01–0.1 *m* (5–20 wt %), while the maximum water solubilization values were 0.3–0.5 g of water per g of copolymer. The cmc decreased with increasing copolymer molecular mass for a given copolymer chemical composition. A notable increase (more than doubling) in the water solubilization capacity (expressed in water molecules per EO segment) was observed when the PEO content of PEO–PPO–PEO copolymers decreased from 40 to 20%. A simple model for the reverse micelles is developed (based on the volume fractions of the different components and the effective length of a copolymer molecule) that captures experimental trends and allows the estimation of the (spherical) micelle radius and aggregation number.

## Introduction

Surfactants are well-known to self-assemble in solutions and thus enhance compatibility or segregation between immiscible solvents.<sup>1,2</sup> Parallels can often be drawn between typical (low molecular mass) surfactants and copolymers having both hydrophilic and hydrophobic blocks.<sup>3</sup> One such example is amphiphilic (nonionic) copolymers composed of hydrophilic poly(ethylene oxide) (PEO) and hydrophobic poly(propylene oxide) (PPO) or poly(butylene oxide) (PBO) blocks.<sup>4,5</sup> A number of PEO–PPO–PEO block copolymers (also known as poloxamers) are commercially available (under the trade names Pluronics and Synperonics) in molecular masses ranging from 2000 to 20 000, and 20–80 wt % PEO contents. PEO–PBO–PEO copolymer became commercially available only recently and in relatively limited molecular mass and composition ranges. Many of these block copolymers associate in aqueous solutions into micelles (with a "core" consisting of the water-insoluble PPO or PBO blocks and a "corona" composed by solvated segments of the water-soluble PEO blocks),<sup>6–10</sup> at higher concentrations, the polyoxyalkylene block copolymers can also self-assemble into lyotropic liquid crystals.<sup>11–18</sup>

In addition to their association in aqueous solutions, surfactants form thermodynamically stable "reverse" micellar or "microemulsion" systems<sup>19,20</sup> which find a number of interesting applications.<sup>21,22</sup> Although PEO–PPO–PEO copolymers can solubilize small amounts of organic compounds in aqueous micellar solutions,<sup>23</sup> the solution behavior of polyoxyalkylene block copolymers in oil and the solubilization of water in these solutions (microemulsion formation) have received scant attention in the literature.<sup>24</sup> A notable exception is the recent work

by Chu and co-workers, who reported the water-induced micelle formation of a PEO–PPO–PEO copolymer (Pluronic L64: EO<sub>13</sub>PO<sub>30</sub>EO<sub>13</sub>) in *o*-xylene.<sup>25–28</sup> This copolymer did not form micelles in *o*-xylene in the absence of water or even in the presence of small water amounts (up to ~0.15 water molecules per EO segment). However, "reverse" micelles with a hydrated PEO core and a PPO corona were formed by EO<sub>13</sub>PO<sub>30</sub>EO<sub>13</sub> in *o*-xylene at higher water concentrations, as shown by scattering techniques.<sup>25–28</sup> In our investigation of the complete phase diagram of the EO<sub>13</sub>PO<sub>30</sub>EO<sub>13</sub>–H<sub>2</sub>O–*p*-xylene system at 25 °C, we showed that the copolymer was miscible with *p*-xylene in all proportions and formed an isotropic solution (L<sub>2</sub> region) along the copolymer–oil axis of the ternary phase diagram; up to ~2 water molecules per EO segment could be solubilized in the EO<sub>13</sub>PO<sub>30</sub>EO<sub>13</sub>–*p*-xylene solution.<sup>14</sup> L<sub>2</sub> regions have also been identified in the PO<sub>19</sub>EO<sub>33</sub>PO<sub>19</sub>–water–*p*-xylene<sup>15</sup> and BO<sub>10</sub>EO<sub>17</sub>–water–*p*-xylene ternary systems,<sup>17</sup> but the focus of the studies reported in refs 14, 15, 17 has been on the lyotropic mesophases. Here we turn our attention to the oil-rich, "reverse" micellar, solutions formed by PEO/PPO and PEO/PBO block copolymers (at the oil corner of the ternary phase diagram, as shown schematically in Figure 1).

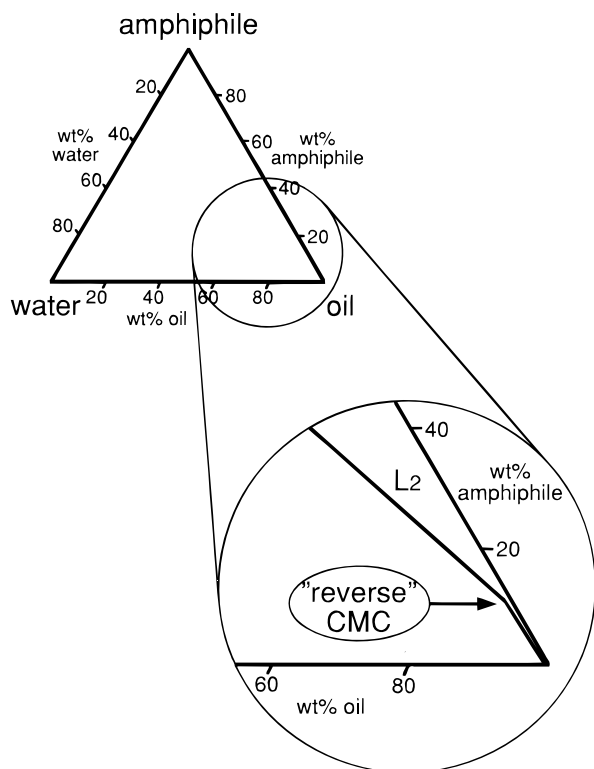
The micellization of polyoxyalkylene block copolymers in an organic solvent (*p*-xylene, selective for the PPO and PBO blocks) and the solubilization of water (selective solvent for the PEO blocks) in these systems are reported in this paper. The ability of the ("reverse") micelles to solubilize water (once they are formed) has been employed for the detection of the micelle formation (see Figure 1). The critical micellization concentration, cmc, of amphiphilic molecules in organic solvents cannot be determined from, for example, surface tension measurements<sup>7</sup> since there is no significant tendency of the amphiphiles to adsorb at the air–oil interface. Instead, water solubilization can prove useful in the determination of cmc in organic solvents,<sup>29</sup> just as solubilization of organic compounds

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**Figure 1.** Schematic of the focus of the present investigation, the oil-rich corner of a ternary amphiphile–water–oil phase diagram. The abrupt increase in the water solubilization capability of the amphiphile-in-oil solution is indicative of the self-association of the amphiphile molecules into “reverse” micelles.

(with suitable spectroscopic properties) has been used for detecting the formation of micelles in aqueous solutions.<sup>6,8,30,31</sup> At the same time, the phase boundary of the ternary copolymer–water–oil “reverse” micellar solution region can be delineated from the determination of the maximum water uptake (see Figure 1). The block copolymers studied have the PEO–PPO–PEO, PEO–PBO–PEO, and PBO–PEO block sequences and cover a range of block sizes. This is the first systematic study of reverse micelle formation and water solubilization capacity by amphiphilic block copolymer in organic solvents and has allowed us to ascertain the effects of the copolymer molecular mass and composition on these processes.

## Materials and Methods

**Materials.** Nine different polyoxyalkylene block copolymers were examined. The commercial notations of the copolymers, together with their nominal molecular masses, polyoxyethylene contents, and chemical formulas (calculated from the molecular masses and PEO contents), are listed in Table 1. Also tabulated there, are the hydrophilic–lipophilic balance (HLB) numbers and the cloud point (CP) temperatures of the copolymers in aqueous solutions. Both HLB and CP are measures of the relative hydrophobicity of the amphiphilic polymers and depend on the copolymer PEO content, architecture, and molecular mass. The Pluronic poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) triblock copolymers were kindly supplied by BASF Corp., Mount Olive, NJ, while the B-series Polyglycol diblock poly(butylene oxide)–poly(ethylene oxide) and triblock poly(ethylene oxide)–poly(butylene oxide)–poly(ethylene oxide) copolymers were obtained as a gift from Dow Chemical Co., Midland, MI. The chemical structure of the polyoxyalkylene block copolymers studied here is shown in Figure 2. All copolymers were used as received. Hydrophobic

impurities (originating from incomplete copolymerization of the middle PPO or PBO block) are known to be present in some of the commercially available polyoxyalkylene block copolymers and to interfere with the detection of micelle formation in aqueous solutions.<sup>4,9</sup> We expect such impurities to be well soluble in the organic solvent and to not affect the reverse micelle formation. To examine the influence of such impurities, we purified Pluronic L64 using extraction with hexane and tested the fractionated copolymer for reverse micelle formation and solubilization. The data thus obtained were indistinguishable from the data obtained from the “as received” copolymer (data not shown). *p*-Xylene (1,4-dimethylbenzene) of purity >99.0% was obtained from Fluka Chemie AG, Switzerland, while <sup>2</sup>H<sub>2</sub>O (99.80 atom % <sup>2</sup>H) was purchased from Dr. Glaser AG, Switzerland. The <sup>1</sup>H<sub>2</sub>O used was treated with a Milli-Q system.

**Water Solubilization Measurements.** Copolymer-in-xylene solutions (2–10 g each) were prepared individually in the 0–50 wt % copolymer concentration range by weighing the two components in glass tubes. The samples were carefully sealed with screw-caps to avoid solvent evaporation. Water was titrated to the copolymer-in-oil solution in increments of ~0.02 g (or less). Following the addition of each water drop, the samples were homogenized by vortex-mixing and left standing for 15–30 min in order to equilibrate. If the resulting solutions were homogeneous and transparent, more water was added. The development in the samples of a (persistently) hazy or milky appearance after the addition of a water drop was an indication that the maximum solubilization was reached, resulting in a phase separation of the sample into a majority oil-rich “reverse” micellar solution and a minority aqueous solution or a lyotropic mesophase; the minority phase remained dispersed in the majority phase (for a time period that depended on the type and concentration of the copolymer used) and eventually precipitated (its density being higher because of the higher water content). Copolymer-in-xylene solutions (of appropriate concentration) were occasionally added to these hazy/milky samples in order to clear them up (by decreasing the water concentration) and ensure the reversibility of the phase separation. Solubilization experiments were done at 25 ± 1 °C for all polyoxyalkylene block copolymers. Heavy water, <sup>2</sup>H<sub>2</sub>O, was primarily used in the solubilization experiments (instead of ordinary water, <sup>1</sup>H<sub>2</sub>O) in order to complement our ternary copolymer–water–oil phase behavior studies and to allow for <sup>2</sup>H NMR measurements in the investigation of phase equilibria.<sup>12–17</sup> <sup>1</sup>H<sub>2</sub>O was also used for some solubilization experiments. Isotopic substitution (from <sup>2</sup>H<sub>2</sub>O to <sup>1</sup>H<sub>2</sub>O) does not seem to influence much either the cmc or the maximum water uptake by L64 (EO<sub>13</sub>–PO<sub>30</sub>EO<sub>13</sub>) in xylene (data not shown). This is similar to what has been observed in the micellization of a PEO–PPO–PEO copolymer in <sup>2</sup>H<sub>2</sub>O and in <sup>1</sup>H<sub>2</sub>O.<sup>31</sup> The results obtained in this work with <sup>2</sup>H<sub>2</sub>O are thus valid also for <sup>1</sup>H<sub>2</sub>O.

## Results and Discussion

**Water Solubilization by Polyoxyalkylene Block Copolymers in Organic Solvents: “Reverse” Micelle Formation and cmc Determination.** The amount of water solubilized in copolymer–oil solutions over a wide range of copolymer concentrations is shown in Figure 3 for three different polyoxyalkylene block copolymers, representative of the ones examined here. Three distinct regions can be identified in the water solubilization curves.

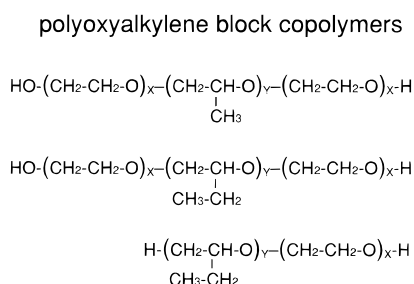
(i) At low copolymer concentrations, the ability of the copolymer–oil solution to take in water is very limited and the water solubilization (expressed in grams of water per grams of copolymer) varies little with the copolymer concentration. The

TABLE 1: Properties of the Polyoxyalkylene Block Copolymers Investigated Here

polymer notation		chemical formula	mol. mass	EO wt %	HLB <sup>a</sup>	cloud point (°C) <sup>b</sup>
(BASF/Dow)	(CFTA)					
Pluronic L62	Poloxamer 182	EO <sub>6</sub> PO <sub>34</sub> EO <sub>6</sub>	2500	20	7	24
Pluronic L92	Poloxamer 282	EO <sub>8</sub> PO <sub>50</sub> EO <sub>8</sub>	3650	20	5.5	16
Pluronic L44	Poloxamer 124	EO <sub>10</sub> PO <sub>23</sub> EO <sub>10</sub>	2200	40	16	73
Pluronic L64	Poloxamer 184	EO <sub>13</sub> PO <sub>30</sub> EO <sub>13</sub>	2900	40	15	60
Pluronic P84	Poloxamer 234	EO <sub>19</sub> PO <sub>44</sub> EO <sub>19</sub>	4200	40	14	73
Pluronic P104	Poloxamer 334	EO <sub>27</sub> PO <sub>61</sub> EO <sub>27</sub>	5900	40	13	78
BL50-1500		R <sup>d</sup> -BO <sub>10</sub> EO <sub>17</sub>	1500	50		48–57 <sup>c</sup>
B40-1900		EO <sub>13</sub> BO <sub>10</sub> EO <sub>13</sub>	1900	60		79–81 <sup>c</sup>
B40-2500		EO <sub>17</sub> BO <sub>14</sub> EO <sub>17</sub>	2500	60		77–83

<sup>a</sup> Hydrophilic–lipophilic balance; the HLB values for the Pluronic copolymers were taken from Schmolka, I. R. *Surfactant Sci. Ser.* **1967**, 1, 300. <sup>b</sup> Determined in 10% aqueous solution for the Pluronic (BASF) copolymers and in 1% aqueous solution for the B-series Polyglycols (Dow).

<sup>c</sup> Cloud point values taken from Nace, V. M. *J. Am. Oil Chem. Soc.* **1996**, 73, 1; the cloud point for B40-2500 was extracted from the manufacturer (Dow) literature. <sup>d</sup> R denotes monobutyl ether (according to the manufacturer, the BL50-1500 diblock copolymer has one terminal primary hydroxyl group).

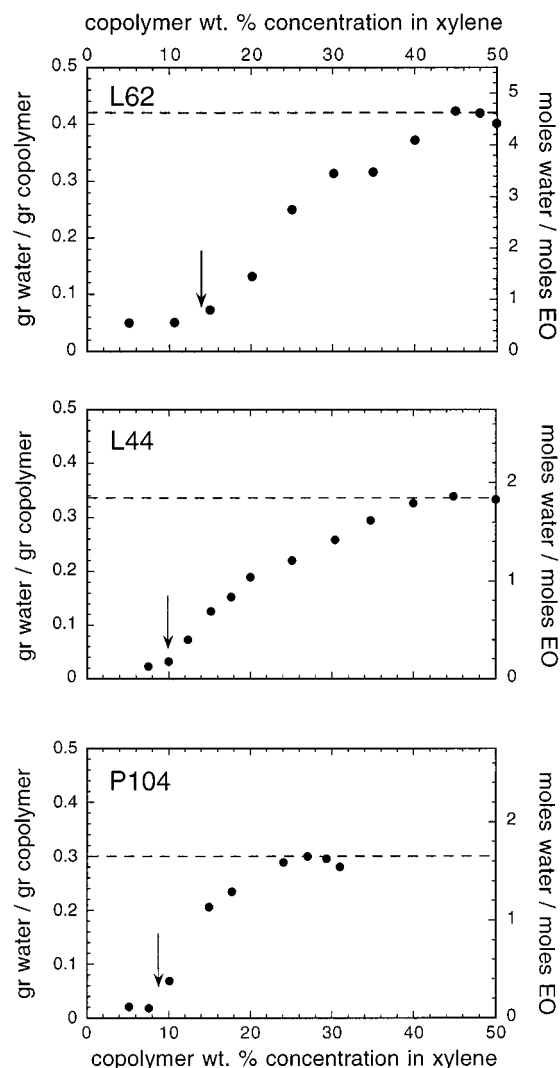


**Figure 2.** Schematic of the chemical structures of the polyoxyalkylene block copolymers used in this study: (top) Pluronic poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) copolymer, (middle) B-series Polyglycol poly(ethylene oxide)-*block*-poly(butylene oxide)-*block*-poly(ethylene oxide) copolymer, and (bottom) BL Polyglycol poly(butylene oxide)-*block*-poly(ethylene oxide) copolymer.

copolymer molecules are molecularly dissolved in oil (unimers) in this concentration range.

(ii) An abrupt increase in the water solubilization capability is noted at a certain copolymer concentration. This increase is a cooperative process and is indicative of the self-association of the copolymer molecules into “reverse” micelles, which provide a hydrophilic microenvironment suitable for water solubilization. The solubilization of water can thus be used in the determination of the cmc of amphiphilic molecules in organic solvents,<sup>29</sup> in a manner similar to the use of the solubilization of organic compounds for detecting micellization in aqueous solutions.<sup>6,8,30,31</sup> The “reverse” critical micellization concentration (cmc) can be determined from the copolymer concentration at which the water solubilization capacity starts increasing (the cmcs in the solubilization curves of Figure 3 are marked by arrows; the cmc values were determined from plots having a logarithmic concentration scale, as commonly used in aqueous surfactant solutions<sup>6</sup>). At copolymer contents higher than the cmc, the amount of water solubilized (expressed in either grams of water per grams of copolymer or wt % water in the ternary copolymer–water–oil system) increases strongly with the copolymer concentration. The magnitude of the water solubilization capability depends on the micelle size, while the rate of its increase is a reflection of the tendency of water to get solubilized in the reverse micelles. In this concentration region, the copolymer molecules that participate in the reverse micelles should be in equilibrium with unimers.

(iii) A plateau is reached at higher copolymer concentrations, where the amount of water solubilized per gram of copolymer does not change further with increasing copolymer concentration. The upper limits to the solubilization capacity for water (maximum water solubilization) are indicated in Figure 3 by



**Figure 3.** Water (<sup>2</sup>H<sub>2</sub>O) solubilization in copolymer-in-xylene solutions for representative polyoxyalkylene block copolymers, plotted as grams water per gram of copolymer (left-hand-side Y axis) and number of water molecules per EO segment (right-hand-side Y axis) vs copolymer wt % concentration in xylene (prior to the addition of water). From top to bottom: L62 (EO<sub>6</sub>PO<sub>34</sub>EO<sub>6</sub>), L44 (EO<sub>10</sub>PO<sub>23</sub>EO<sub>10</sub>), and P104 (EO<sub>27</sub>PO<sub>61</sub>EO<sub>27</sub>). The “reverse” critical micellization concentrations are marked in the solubilization curves by arrows. The upper limits to the solubilization capacity for water are indicated in the graphs by the dotted lines.

the dotted lines. We note that the upper copolymer concentration studied here was limited to ~55 wt %. Above this

**TABLE 2: Summary of "Reverse" Critical Micellization Concentration and Maximum Water Solubilization Values for the Polyoxyalkylene Block Copolymers Studied Here**

polymer notation	chemical formula	"reverse" cmc <sup>a</sup>		max. water solubilization	
		wt %	<i>m</i>	g wtr/ g pol	mol wtr/ mol EO
L62	EO <sub>6</sub> PO <sub>34</sub> EO <sub>6</sub>	14	0.060	0.42	4.60
L92	EO <sub>8</sub> PO <sub>50</sub> EO <sub>8</sub>	5	0.017	0.41	4.50
L44	EO <sub>10</sub> PO <sub>23</sub> EO <sub>10</sub>	10	0.045	0.34	1.85
L64	EO <sub>13</sub> PO <sub>30</sub> EO <sub>13</sub>	9	0.031	0.36	2.00
P84	EO <sub>19</sub> PO <sub>44</sub> EO <sub>19</sub>	14	0.033	0.48	2.60
P104	EO <sub>27</sub> PO <sub>61</sub> EO <sub>27</sub>	9	0.013	0.30	1.65
BL50-1500	BO <sub>10</sub> EO <sub>17</sub>	3	0.020	0.35	1.50
B40-1900	EO <sub>13</sub> BO <sub>10</sub> EO <sub>13</sub>	20	0.10	0.34	1.25
B40-2500	EO <sub>17</sub> BO <sub>14</sub> EO <sub>17</sub>	12	0.050	0.38	1.40

<sup>a</sup> The cmcs are given in mass units (copolymer wt % concentration in xylene + copolymer, prior to the addition of water), and in molal units (copolymer moles in 1000 g xylene + copolymer, prior to the addition of water).

concentration, ordered (lyotropic liquid crystalline) phases are usually formed.<sup>14–17</sup> For some polyoxyalkylene block copolymers, a crystallization of the reverse micelles into a cubic structure has been observed at copolymer contents as low as 40 wt %;<sup>16,17,32,33</sup> the ability of this micellar cubic structure to solubilize water was not investigated further.

While we take advantage of the parallels between hydrophobic dye solubilization for the detection of cmc in aqueous solutions and water solubilization for the determination of ("reverse") cmc in organic solvents, we note that the mechanism responsible for the association of the amphiphiles is different between aqueous and apolar solvents. This difference is reflected in the need for some water to be present in order for reverse micelles to form<sup>25,26</sup> (see related discussion in the following section). Water thus both induces and reports the reverse micelle formation, and the "reverse" cmc values reported here should be evaluated in this context.

We are referring to the microstructure in the copolymer–water–oil *L*<sub>2</sub> solutions as that of "reverse micelles" throughout the paper, but we report no structural information here. However, we have carried out small-angle neutron scattering (SANS) measurements in the *L*<sub>2</sub> solution region for four different PEO–PPO–PEO copolymers which indicate a spherical reverse micellar morphology even at high copolymer and water contents (this SANS investigation will be the subject of a forthcoming publication). Published light, X-ray, and neutron scattering data for Pluronic L64 (EO<sub>13</sub>PO<sub>30</sub>EO<sub>13</sub>) in *o*-xylene in the presence of water are also in support of the spherical micelle picture.<sup>25–28</sup> The formation of the cubic liquid crystalline structures mentioned in the previous paragraph is another indication that the spherical micellar structure is prevalent in the *L*<sub>2</sub> regions.<sup>16</sup>

**Water Solubilization and "Reverse" Micelle Formation in Organic Solvents: General Trends and Comparison with Nonionic Surfactants.** As discussed in the preceding section, the water solubilization curves provide valuable information on the "reverse" critical micellization concentration and the maximum water solubilization capacity; such values are listed in Table 2 for all the polyoxyalkylene block copolymers studied here. This systematic study of PEO–PPO–PEO, PEO–PBO–PEO, and PBO–PEO copolymers allows us to ascertain the effects of copolymer molecular mass (range investigated: 1500–5900) and composition (PEO wt % range investigated: 20–60) on water solubilization and reverse micelle formation. The specific trends with respect to the various copolymer characteristics are presented and discussed in detail in subse-

quent sections; here we address some general trends and compare to other block copolymers and nonionic surfactants.

The cmc values determined for the polyoxyalkylene block copolymers in xylene (at 25 °C) were typically in the range 5–20 wt % or 0.01–0.1 *m* (cmc values for the different copolymers are listed in Table 2). Although such cmc numbers are high compared to cmcs of typical surfactants in aqueous solutions<sup>1</sup> (and may even fall in the semidilute polymer solution regime), they are comparable to the cmcs of "hydrophilic" PEO–PPO–PEO block copolymers in water (for example, the cmcs of Pluronic L64 (EO<sub>13</sub>PO<sub>30</sub>EO<sub>13</sub>) and Pluronic P84 (EO<sub>19</sub>PO<sub>44</sub>EO<sub>19</sub>) at 25 °C are 7 and 2.6 w/v %, respectively<sup>4–6,34</sup>). The free energy of micellization (which is related to the cmc through  $\Delta G^\circ = RT \ln(X_{\text{cmc}})$ , where  $X_{\text{cmc}}$  is the cmc at temperature *T* expressed in mole fraction units) depends strongly on the free energy of transferring the "solvophobic" block from its bulk state (melt) into the (bad) solvent. This transfer free energy is relatively small both for the case of PPO in water<sup>5</sup> and also for the case of PEO in xylene<sup>35</sup> (the presence of small amounts of water may also be required in order for the PEO to become sufficiently "solvophobic"<sup>25,29</sup>) and thus explains the relatively high cmcs of polyoxyalkylene block copolymers.

Micelle formation for a number of block copolymers in selective (organic) solvents has been reported in the literature.<sup>36–38</sup> In most cases the "solvophobic" block had a strong tendency to (micro- or macro-) phase-separate and the cmcs were very low (in fact, in some cases the cmcs were practically zero as the micelles were first formed in a solvent mixture of adequate solvent quality and then dialyzed against the desired solvent<sup>36</sup>). The micelle formation by block copolymers in organic solvents usually does not require the presence of water; in the case of poly(ethylene oxide)–polystyrene diblock copolymers dissolved in cyclopentane, however, small amounts of water were needed to induce micellization.<sup>39</sup>

Coming back to the parallels between amphiphilic copolymers and surfactants, we note that the formation of reverse micelles by nonionic surfactants in "dry" (in the absence of water) organic solvents is ambiguous.<sup>29,40–45</sup> Studies of nonionic poly(ethylene oxide) alkyl ethers in heptane and decane, for example, have shown that the degree of surfactant association is low (cmc ≈ 10 wt %) and that only small aggregates (consisting of 5–15 molecules) are present above the cmc.<sup>42</sup> In the presence of small amounts of water, however, the surfactant–oil–water mixture lowers its free energy by forming micelles in oil.<sup>29,41,46–50</sup> The structure and aggregation number of such micelles were found different from that of micelles formed in aqueous solutions.<sup>21,22,29,41,47,48</sup>

The maximum water solubilization values (listed in Table 2) for the polyoxyalkylene block copolymers studied here were typically 0.3–0.4 grams of water per grams of copolymer at 25 °C, which correspond to roughly 2 water molecules per EO segment for copolymers of ~50 wt % PEO (we note that the values tabulated in Table 2 are based on the total amount of water and copolymer present in the three-component system; if we account for the nonassociated copolymer which does not contribute to the micellar solubilization, for possible hydrophobic impurities which do not form reverse micelles, and for the finite solubility of water in oil + copolymer below the cmc, then the water solubilization values in the micelles would be 10–20% higher than the ones presented in Table 2). Approximately 4 water molecules per EO segment could be solubilized in polyoxyethylene dodecyl ethers + benzene (at 30 °C)<sup>47</sup> and 2.5 in alkyl-phenyl polyoxyethylenes + *p*-xylene (at 25 °C).<sup>49,50</sup>

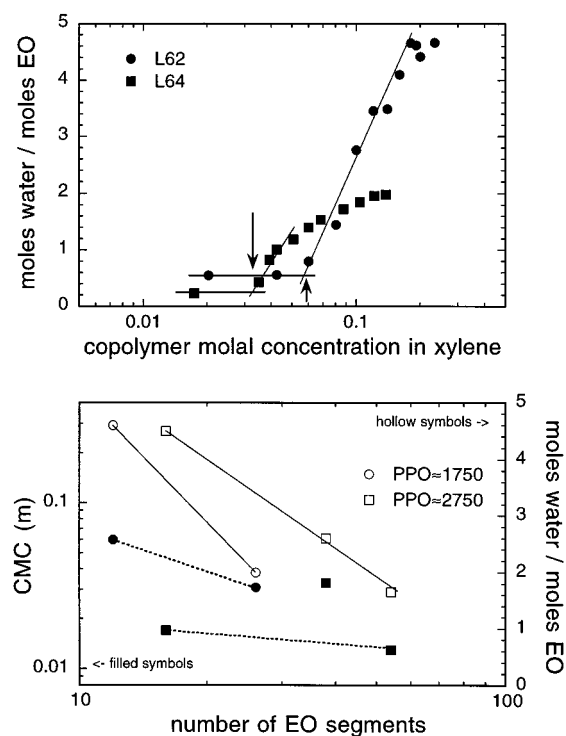
The state (i.e., "bound" or "free") of the water molecules in the reverse micelles is not known. It is probably no coincidence that the average number of water molecules "bound" to each EO segment of PEO homopolymers in aqueous solution (reported to be in the range  $1-3^{51-53}$ ) is similar to the maximum water solubilization for some copolymers (see Table 2). While some of the water molecules in the polyoxyalkylene block copolymer reverse micelles will be hydrating the EO segments, we anticipate some others to behave like "bulk" water and be able to participate in, for example, chemical reactions.<sup>21</sup> The following are in support of this speculation: (i) up to 4.5 water molecules per EO segment can be solubilized in the reverse micelles under certain conditions (e.g., at low PEO content—see Table 2 and related discussion below—or at different temperatures and in the presence of salts, unpublished results), well above that needed for the hydration of EO; (ii) even at 2 water molecules per EO segment, the  $W_0$  value (water/surfactant molar ratio, often used as an attribute of reverse micelles<sup>19,54</sup>) of polyoxyalkylene block copolymer reverse micelles is 60 (considering, for example, a copolymer molecule with 30 EO segments), a relatively high number.<sup>19</sup> Spectroscopic studies (currently in progress in our laboratory) should elucidate the state of water in the polyoxyalkylene block copolymer reverse micelles.

**Effect of Copolymer Composition.** The relative size of the "solvophobic" PEO block (rather than the PPO or PBO block size) should be the controlling parameter in the tendency of the polyoxyalkylene block copolymers to form micelles in organic solvents, just as the size of the hydrophobic PPO block is important to the micellization in aqueous solutions.<sup>4-6</sup> In the case of polyoxyalkylene block copolymers (and generally for nonionic surfactants) in aqueous solutions, the cmc is found to decrease exponentially with increasing solvo(hydro)phobic (PPO, PBO, or alkyl) block size, for a fixed solvo(hydro)philic block size.<sup>4-6</sup>

The effects of the copolymer hydrophilic PEO block size on water solubilization and "reverse" micelle formation by polyoxyalkylene block copolymers in organic solvent are presented in Figure 4 for two groups of copolymers (L62 ( $\text{EO}_6\text{PO}_{34}\text{EO}_6$ )—L64 ( $\text{EO}_{13}\text{PO}_{30}\text{EO}_{13}$ ) and L92 ( $\text{EO}_8\text{PO}_{50}\text{EO}_8$ )—P84 ( $\text{EO}_{19}\text{PO}_{44}\text{EO}_{19}$ )/P104 ( $\text{EO}_{27}\text{PO}_{61}\text{EO}_{27}$ )), each with the same PPO block size and PEO—PPO—PEO triblock architecture but different (20% for L62 and L92, and 40% for L64, P84, and P104) PEO contents (we note that the appropriate comparison for L92 would be P94, but since P94 is not commercially available, we compare L92 with P84 and P104, copolymers with lower and higher molecular mass, respectively, than P94).

The cmc of L92 ( $\text{EO}_8\text{PO}_{50}\text{EO}_8$ ) is half that of P104 ( $\text{EO}_{27}\text{PO}_{61}\text{EO}_{27}$ ) in mass concentration, but there is almost no difference between the cmcs when they are expressed in molal terms (the cmc of P84 is much higher than that of P92 in both mass and molal concentration). The cmc of L62 ( $\text{EO}_6\text{PO}_{34}\text{EO}_6$ ), on the other hand, is 50% and 100% higher than that of L64 ( $\text{EO}_{13}\text{PO}_{30}\text{EO}_{13}$ ) when expressed in mass and molal concentrations, respectively. The cmcs of L62 and L64 follow the anticipated trend of decreasing cmc with increasing PEO size; the "reverse" cmc dependence on the copolymer PEO block size is not that clear for the L92—P84/P104 group.

While the water uptake measured in grams of water per grams of copolymer is comparable for both L62—L64 and L92—P84/P104, a notable increase (more than doubling) in the number of water molecules solubilized per EO segment was observed when the PEO content of PEO—PPO—PEO copolymers decreased from 40 to 20%. This can be simply attributed to more space available for water solubilization in the micelle core for



**Figure 4.** Effect of polyoxyalkylene block copolymer chemical composition on water solubilization and "reverse" micelle formation in organic solvent. (a, top) Water ( $^2\text{H}_2\text{O}$ ) solubilization in xylene solutions of the L62 ( $\text{EO}_6\text{PO}_{34}\text{EO}_6$ ) and L64 ( $\text{EO}_{13}\text{PO}_{30}\text{EO}_{13}$ ) copolymers which have the same (PEO—PPO—PEO) triblock architecture and PPO block length but different PEO block size. The ratio of water molecules solubilized per EO segment is plotted vs the logarithm of the molal copolymer concentration in oil (prior to the addition of water). (b, bottom) "Reverse" critical micellization concentration (given in molal copolymer concentration in oil, left-hand-side Y axis) and maximum water solubilization values (number of water molecules per EO segment, right-hand-side Y axis) in xylene at 25 °C plotted as a function of the number of the copolymer EO segments for the L62—L64 and L92—P84/P104 copolymer groups.

copolymers having low PEO content (see the section "Estimation of the Micelle Core Size...") but could also be related to a more efficient packing of such copolymer molecules in the reverse micelles. Micellization is the result of opposing contributions: an increase in the solvophobic block size increases the tendency for segregation/association, but the solvophobic/solvophilic ratio ("packing" parameter) must be at an optimal value for spherical micelles to be favored. A nonmonotonic dependence of water solubilization on the PEO block size has been observed for poly(ethylene oxide) dodecyl ethers dissolved in benzene:<sup>47</sup> the number of water molecules solubilized per EO segment increased with increasing number of EO segments from 3.5 (at  $N_{\text{EO}} = 3$ ) to 6 (at  $N_{\text{EO}} = 5$ ), but then decreased to 4 (at  $N_{\text{EO}} = 7$ ).

In addition to their chemical composition, the macromolecular architecture (at fixed chemical composition) of the polyoxyalkylene block copolymers is expected to affect their micellization properties.<sup>56</sup> Although we only examined one diblock copolymer (to the best of our knowledge, there are no commercially available diblock PPO—PEO copolymers), BL50-1500 ( $\text{BO}_{10}\text{EO}_{17}$ ), we can still compare its behavior to that of the triblock B40-2500 ( $\text{EO}_{17}\text{BO}_{14}\text{EO}_{17}$ ). The diblock has a much lower (4 times less) cmc than the triblock but comparable water solubilization capability. The cmc trend compares favorably with a theoretical comparison of the micellization of A—B—B—A and A—A—B—B block copolymers in a solvent selective for B which showed a 10-fold lower cmc for the diblock.<sup>56</sup> The

similar domain size predicted for A-B-B-A and A-B copolymers of the same A block size and the same B wt %<sup>57</sup> matches the similar water solubilization capability of BO<sub>10</sub>EO<sub>17</sub> and EO<sub>17</sub>BO<sub>14</sub>EO<sub>17</sub> (presumably originating from a similar micelle size).

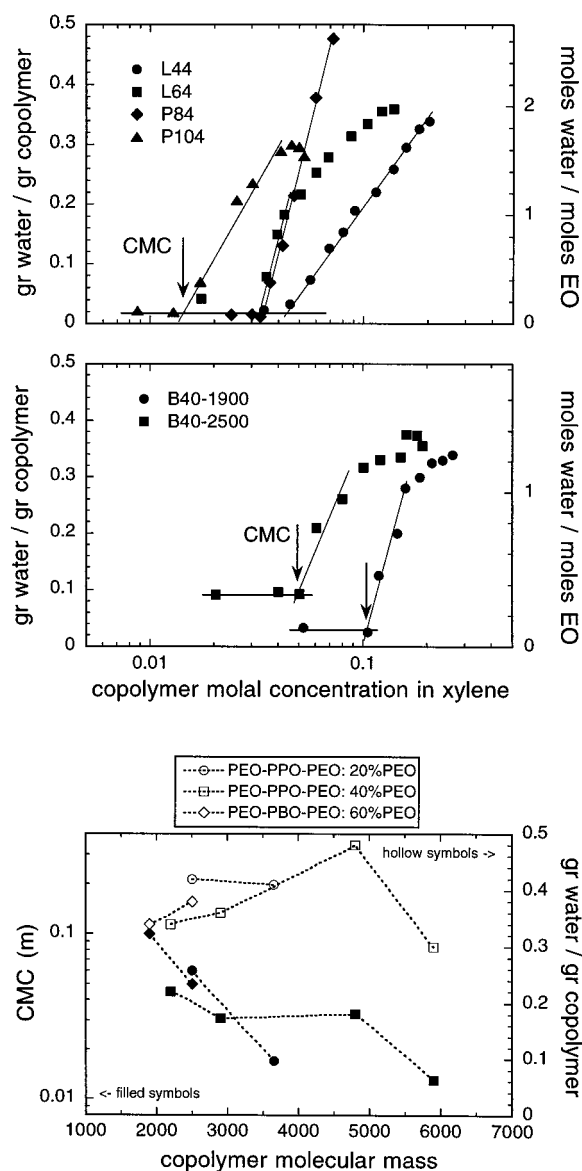
**Effect of Copolymer Molecular Mass.** An increase of the total number of monomer segments *N* (and consequently of the molecular mass) in a block copolymer (at a fixed polymer chemical composition, and thus solvent-polymer interactions) results in an increase of the segregation between the different blocks and facilitates self-organization.<sup>32,58</sup> It is thus appropriate to examine the effect of polyoxyalkylene block copolymer molecular mass on "reverse" micelle formation and water solubilization in xylene.

Our findings are presented in Figure 5a,b for two groups of copolymers of PEO-PPO-PEO and PEO-PBO-PEO triblock architecture, respectively. The copolymer PEO content is the same in each group (40 and 60 wt %, respectively), but the molecular mass increases in the order L44 (EO<sub>10</sub>PO<sub>23</sub>EO<sub>10</sub>) < L64 (EO<sub>13</sub>PO<sub>30</sub>EO<sub>13</sub>) < P84 (EO<sub>19</sub>PO<sub>44</sub>EO<sub>19</sub>) < P104 (EO<sub>27</sub>PO<sub>61</sub>EO<sub>27</sub>) and B40-1900 (EO<sub>13</sub>BO<sub>10</sub>EO<sub>13</sub>) < B40-2500 (EO<sub>17</sub>BO<sub>14</sub>EO<sub>17</sub>). Results for the L62-L92 group (20 wt % EO content) are summarized in Figure 5c. A trend of decreasing cmc with increasing copolymer molecular mass was observed for the B40-1900-B40-2500 and L62-L92 groups (e.g., the cmcs of L62 and L92 are 14 and 5 wt %, respectively). The decreasing cmc with increasing molecular mass dependence has been observed in the micellization of polyoxyalkylene block copolymers in water.<sup>4-6</sup> This trend is also followed by the L44-L64-P84-P104 group when the cmc is expressed in molal concentration (the cmcs of L44 and P104 are 0.045 and 0.013 *m*, respectively). However, when the cmc is expressed in mass concentration, P84 exhibits a higher cmc (14 wt %) than L44, L64, and P104 (cmc ≈ 10 wt %). At this time we are not able to explain this behavior.

The dependence of the water solubilization capacity on the copolymer molecular mass is less clear than that of the cmc (and less striking than the water solubilization capability dependence on the PEO block size presented in the previous section). The maximum water solubilization is approximately the same for L62 and L92 (at 0.42 grams of water per grams of copolymer) and it increases by 10% from B40-1900 to B40-2500. P84 stands out in the group L44-L64-P84-P104 as having the highest solubilization capability (0.48 grams of water per grams of copolymer, as opposed to ~0.35 for L44 and L64, and 0.30 for P104); part of the decrease observed from P84 to P104, though, can be attributed to the formation by P104 of a reverse micellar cubic structure (P. Alexandridis, unpublished data) which limited the P104 copolymer concentration range investigated to 35 wt %.

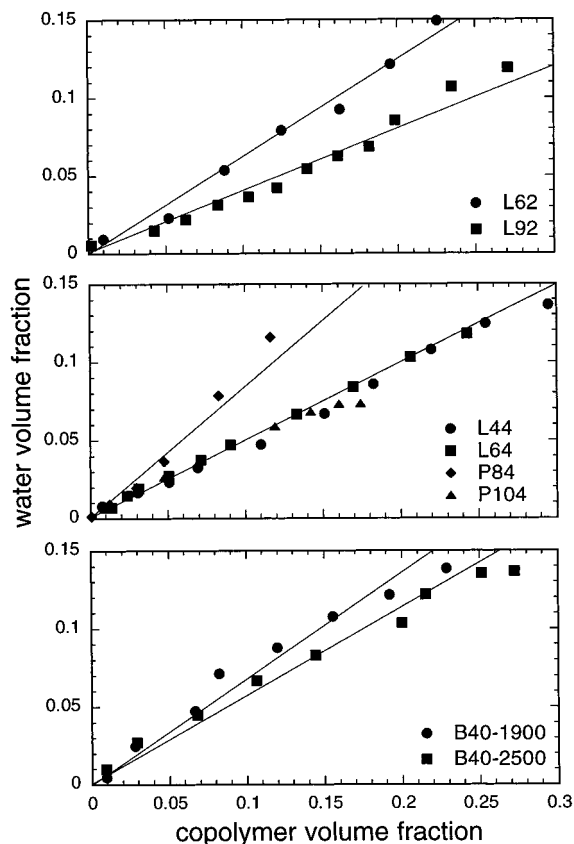
**Estimation of the Micelle Core Size and Aggregation Number.** The characteristics (size and aggregation number) of the water-swollen reverse micelles can be related to the molecular dimensions and block composition of the polyoxyalkylene block copolymers and to the volume fraction of the copolymer and water components in the ternary copolymer-water-oil system, using a model based on simple geometrical arguments. The model validity can then be tested by comparing its predictions to the boundaries of maximum water solubilization determined in this work and to experimentally determined reverse micelle radii.

We consider (i) that the copolymer molecules (of volume fraction  $\Phi_p$ ) that participate in the micelles are in equilibrium with unimers of concentration equal to the "reverse" cmc, (ii) that all water is solubilized in the micelles (a valid postulation



**Figure 5.** Effect of polyoxyalkylene block copolymer molecular mass on water solubilization and "reverse" micelle formation in organic solvent. (a, top) Water ( $\text{H}_2\text{O}$ ) solubilization in xylene solutions of the L44 (EO<sub>10</sub>PO<sub>23</sub>EO<sub>10</sub>), L64 (EO<sub>13</sub>PO<sub>30</sub>EO<sub>13</sub>), P84 (EO<sub>19</sub>PO<sub>44</sub>EO<sub>19</sub>), and P104 (EO<sub>27</sub>PO<sub>61</sub>EO<sub>27</sub>) copolymers which have the same (PEO-PPO-PEO) triblock architecture and PEO content (40 wt %) but different molecular weights. (b, middle) Water ( $\text{H}_2\text{O}$ ) solubilization in xylene solutions of the B40-1900 (EO<sub>13</sub>BO<sub>10</sub>EO<sub>13</sub>) and B40-2500 (EO<sub>17</sub>BO<sub>14</sub>EO<sub>17</sub>) copolymers which have the same (PEO-PBO-PEO) triblock architecture and PEO content (60 wt %) but different molecular weights. In a and b, grams of water per gram of copolymer (left-hand-side Y axis) and number of water molecules per EO segment (right-hand-side Y axis) solubilized are plotted vs the logarithm of the molal copolymer concentration in xylene. (c, bottom) "Reverse" critical micellization concentration (given in molal copolymer concentration in oil, left-hand-side Y axis) and maximum water solubilization values (grams of water per gram of copolymer, right-hand-side Y axis) in xylene at 25 °C plotted as a function of the copolymer molecular mass for the L62-L92, L44-L64-P84-P104, and B40-1900-B40-2500 groups.

since the solubility of water in toluene at 25 °C is ~0.053 wt %, and the solubility of water in xylene should be less than that in toluene), and (iii) that the micelles have a core containing (only) PEO and water and a corona consisting of PPO or PBO and oil (this assumption is borne by SANS measurements on L64 (EO<sub>13</sub>PO<sub>30</sub>EO<sub>13</sub>) in *o*-xylene in the presence of  $\text{H}_2\text{O}$ , which indicated that, while water molecules existed not only in the micellar core but also in the corona, the volume fraction of water



**Figure 6.** Maximum amount of water solubilized by polyoxyalkylene block copolymers in organic solvent plotted as the water volume fraction (in the ternary copolymer–water–oil system) vs the volume fraction of the copolymer which participates in the reverse micelles. Data for three polymer groups, PEO–PPO–PEO copolymers of 20 and 40 EO wt %, and PEO–PBO–PEO copolymers of 60 EO wt %, are shown. As explained in the text, the micelle radius can be estimated from such data and knowledge of the copolymer dimensions.

in the core was 40 times larger than that in the corona<sup>55</sup>). Assuming that the micelles are spherical, the radius,  $R$ , of the micelle core can be calculated from the ratio of the copolymer molecular volume ( $v_p$ ) to the copolymer area at the polar/apolar (see refs 14,15 for definitions) interface ( $\alpha_p$ ):

$$R = \frac{3f v_p}{\Phi_p \alpha_p} = 3l_p \frac{f}{\Phi_p} \quad (1)$$

where  $f = \Phi_w + \varphi_{EO}\Phi_p$ ,  $\Phi_w$  is the volume fraction of water in the ternary copolymer–water–oil mixture,  $\varphi_{EO}$  is the volume fraction of PEO in the copolymer molecule, and  $l_p$  is the characteristic length of a copolymer molecule ( $l_p$  is an effective length, defined by a volume-to-area ratio,  $l_p = v_p/\alpha_p$ ).

After substituting  $f$  into eq 1 and reorganizing we obtain

$$\frac{R}{l_p} = 3 \left( \frac{\Phi_w}{\Phi_p} + \varphi_{EO} \right) \quad (2)$$

$$\frac{\Phi_w}{\Phi_p} = \frac{R}{3l_p} - \varphi_{EO} \quad (3)$$

Equation 3 can be tested against the maximum amount of water solubilized by the polyoxyalkylene block copolymers in xylene.  $\Phi_w$  vs  $\Phi_p$  data are plotted in Figure 6 for three polymer groups, PEO–PPO–PEO copolymers of 20 and 40 EO wt % and PEO–PBO–PEO copolymers of 60 EO wt %. It becomes apparent from the data of Figure 6 that  $\Phi_w$  increases linearly with  $\Phi_p$ ,

**TABLE 3: Characteristics of the Polyoxyalkylene Block Copolymer Reverse Micelles at the Maximum Water Solubilization Boundary**

polymer notation	EO vol. frac.	$\Phi_w/\Phi_p^a$	$R/l_p^b$	$l_p^c$ (Å)	$R^d$ (Å)	$N_{agg}^e$
L62	0.19	0.63	2.4	25	61	290
L92	0.19	0.40	1.8	30	53	190
L44	0.38	0.50	2.6	24	62	330
L64	0.38	0.50	2.6	26	70	350
P84	0.38	0.83	3.6	31	113	750
P104	0.38	0.50	2.6	39	103	560
BL50-1500	0.48	0.38	2.7	32	85	1220
B40-1900	0.57	0.68	3.8	26	96	980
B40-2500	0.57	0.58	3.4	25	85	560

<sup>a</sup> Ratio of the water to copolymer (participating in the reverse micelles) volume fractions, calculated from the data presented in Figure 6. <sup>b</sup> Calculated from eq 3. <sup>c</sup> Length of the copolymer molecules estimated from their molecular volume,  $v_p$ , and molecular area at the polar/apolar interface,  $\alpha_p$  ( $l_p = v_p/\alpha_p$ ). The interfacial area values used were obtained from SAXS measurements in the lamellar lyotropic liquid crystalline region at a copolymer volume fraction of  $\sim 0.7$ . Interfacial areas for L62, L64, and BL50–1500 were taken from data published in refs 12, 14, and 17, respectively.  $\alpha_p$  values for L44, P84, P104, B40–1900, and B40–2500 were taken from SAXS measurements (Alexandridis, P. unpublished data), while  $\alpha_p$  for L92 was estimated from the L62 value via the relationship  $\alpha_p \approx N^{1/2}$  ( $N$ : total number of segments in a copolymer molecule). <sup>d</sup> Maximum radius of the reverse micelle core, calculated from eq 1. <sup>e</sup> Number of copolymer molecules in the reverse micelles, calculated from eq 4.

indicating that the  $R/l_p$  ratio is constant along the stability boundary of the reverse micellar ( $L_2$ ) region for all copolymers examined. The  $R/l_p$  ratio at the maximum water solubilization is a measure of the ability of the copolymer molecules to stretch (by paying an entropic penalty) as they try to accommodate the water (and thus reduce enthalpically unfavorable water–oil contacts) while maintaining the spherical reverse micellar morphology.  $R/l_p$  was found to be roughly 2.5 for the PEO–PPO–PEO copolymers and 3.5 for the PEO–PBO–PEO copolymers (see Table 3). At  $R/l_p$  values higher than the ones listed in Table 2, spherical reverse micelles are no longer capable of minimizing the system free energy and phase separation occurs.

Equation 2 indicates that the ratio  $R/l_p$  should remain constant along a dilution line of varying oil concentration at a fixed water-to-copolymer ( $\Phi_w/\Phi_p$ ) ratio. Indeed, the reverse micelle radius was found from SANS measurements (Svensson, B.; Alexandridis, P.; Olsson, U.; Mortensen, K. Unpublished data) to remain approximately independent of the copolymer + water (or oil) volume fraction at a fixed water-to-copolymer ratio, indicating that  $l_p$  is constant. The micelle size,  $R$ , is expected from eq 2 to increase with increasing the water/copolymer volume fraction,  $\Phi_w/\Phi_p$ , if  $l_p$  is constant. Static and dynamic light scattering measurements in the  $EO_{13}PO_{30}EO_{13}$ – $H_2O$ – $o$ -xylene system, reported in ref 25, show that the micelle radius increases (doubles) with increasing (from 0.5 to 2.0) water/EO molar ratio, in agreement with the prediction of eq 2.  $R/l_p$  is also expected from eq 2 to increase linearly with the copolymer PEO content,  $\varphi_{EO}$ . This could explain the high water solubilization capacity exhibited by L62 (compared to that of L64), since, for copolymers of similar  $R/l_p$  ratios, the higher the copolymer PEO content, the lower the water uptake in the reverse micelles.

The maximum core size attained by the water-swollen reverse micelles can be estimated from the  $\Phi_w$  vs  $\Phi_p$  ( $L_2$  phase boundary) data of Figure 6, provided that the characteristic length of the copolymer molecule is known. Values for the latter can be estimated (from interfacial area values obtained from SAXS measurements in the lamellar lyotropic liquid

crystalline region) for the different copolymers studied here and are listed in Table 3.  $R$  is found to be in the range 60–110 Å. This is comparable to the characteristic lengths measured by SAXS in the lyotropic liquid crystalline regions of such polyoxyalkylene block copolymers.<sup>12–18,32,33</sup> For the group of PEO–PPO–PEO copolymers with 40% EO content, the predicted micelle core radius increases with increasing copolymer molecular mass. On the contrary, for the L62–L92 and B40–1900–B40–2500 groups, the smaller copolymer molecules are expected to have a higher micelle core radius; the higher  $\Phi_w/\Phi_p$  ratios of L62 and B40–1900 can overcome their low  $l_p$  (Table 3).

The number of copolymer molecules per reverse micelle ( $N_{\text{agg}}$ ) can be derived by expressing the micelle core volume (i) as a function of the core radius (given by eq 1) and (ii) as  $N_{\text{agg}}$  multiplied by the molecular volume of the copolymer PEO blocks ( $\varphi_{\text{EO}}v_p$ ) and the molecular volume of the water molecules hydrating the PEO blocks [ $v_w$  times  $(\Phi_w/v_w)/(\Phi_p/v_p)$ , where  $(\Phi_w/v_w)/(\Phi_p/v_p)$  is the number of water molecules per copolymer molecule] and is given by the following equation:

$$N_{\text{agg}} = 36\pi \left( \frac{f}{\Phi_p} \right)^2 \frac{v_p^2}{\alpha_p^3} = 36\pi \frac{l_p^2}{\alpha_p^2} \left( \frac{\Phi_w}{\Phi_p} + \varphi_{\text{EO}} \right)^2 \quad (4)$$

In addition to the maximum  $R$  and  $N_{\text{agg}}$  estimated at the water solubilization boundary and presented in Table 3, eq 2 and eq 4, respectively, can be used to estimate a spherical micelle core size and aggregation number at any given point in the  $L_2$  region (above the cmc). If the micelles were elongated (instead of being spherical), then the prefactor 3 in eq 2 should be replaced by a number in the range 2–3 (2 is valid for infinitely long cylinders).

In general, we expect the solubilization of water in the copolymer–oil solution to be affected by the specific water–copolymer interactions and not just be a simple function of the copolymer molecular mass and chemical composition. The packing considerations we presented above introduce part of the water–copolymer interactions into the experimentally determined  $l_p$  values (which are a measure of the relative swelling of the chains by the solvent). Even without specific knowledge of  $l_p$ , however, insight into the factors affecting the water solubilization in block copolymer reverse micelles is offered by eqs 2 and 3. While our model can assess the conditions at the experimentally determined  $L_2$  phase boundary, it is not appropriate for predicting this phase boundary. The stability of the reverse micelles (maximum water solubilization boundary) is related to the free energy in the  $L_2$  region and in the adjacent (coexisting) liquid crystalline (lc) region (if the latter is of lower free energy, then the reverse micelles will no longer be stable). A model able to capture the free energy in the different morphologies is required in order to predict the boundaries between regions of different morphology.

## Conclusions

The micellization of poly(ethylene oxide)/poly(propylene oxide) and poly(ethylene oxide)/poly(butylene oxide) block copolymers in *p*-xylene (organic solvent selective for the PPO and PBO blocks) in the presence of some water and the solubilization of water (selective solvent for the PEO blocks) in these systems are reported here. The ability of the “reverse” micelles to solubilize water has been employed for the detection of the copolymer cmc in *p*-xylene (“reverse” cmc), just as solubilization of organic compounds is used for detecting micellization in aqueous solutions. Furthermore, the determination of the maximum water uptake by the micelles allowed

the delineation of the phase boundaries of the ternary copolymer–water–oil “reverse” micellar solution ( $L_2$ ) region.

This systematic study of PEO–PPO–PEO, PEO–PBO–PEO, and PBO–PEO block copolymers has proved helpful in ascertaining the effects of copolymer molecular mass (range examined: 1500–5900) and copolymer chemical composition (PEO wt % range examined: 20–60) on the reverse micelle formation and water solubilization processes.

The “reverse” cmc values were in the range 0.01–0.1 *m* (5–20 wt %), while the maximum water solubilization values were 0.3–0.5 grams of water per grams of copolymer.

The cmc (expressed in molal units) decreased with increasing copolymer molecular mass at a given polymer chemical composition, reflecting the increase in block segregation (and tendency toward self-organization) with increasing copolymer chain length. The cmc also decreased with increasing PEO (solvophobic) block size for a fixed PPO block. A diblock PBO–PEO copolymer exhibited much lower cmc than the corresponding PEO–PBO–PEO triblock.

The water uptake was not affected much by the copolymer molecular mass for all copolymers studied. However, a notable increase (more than doubling) in the water solubilization capacity (expressed in water molecules per EO segment) was observed when the PEO content of PEO–PPO–PEO copolymers decreased from 40 to 20% (at fixed PPO block size).

A simple model for the micelles is developed (based on the volume fractions of the different components and the apparent length of a copolymer molecule) that captures this trend (for copolymers of similar  $R/l_p$  ratios, it is expected from eq 2 that the higher the copolymer PEO content, the lower the water uptake in the reverse micelles) as well as other experimental observations ( $R/l_p$  remains constant along a dilution line of varying oil concentration at a fixed water/copolymer ratio;  $R/l_p$  increases with increasing water/copolymer volume fraction) and allows the estimation of the (spherical) micelle radius and aggregation number.

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