Osmotic Stress Measurements of Intermolecular Forces in Ordered Assemblies Formed by Solvated Block Copolymers

Zhiyong Gu and Paschalis Alexandridis*

Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York, Buffalo, New York 14260-4200

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ABSTRACT: Intermolecular interactions in ordered (lyotropic liquid crystalline) assemblies formed by hydrated poly(ethylene oxide)−poly(propylene oxide) (PEO−PPO) block copolymers (Pluronics or Poloxamers) have been probed using the osmotic stress method. This method involves the equilibration, following the removal or the addition of an appropriate amount of water, of hydrated block copolymer samples with a system (aqueous polymer solution or water vapor) of known osmotic pressure (in the range 0.05−3000 atm). The primary result from such an experiment is a relationship between osmotic pressure (and consequently the corresponding chemical potential and activity of the solvent water) and block copolymer volume fraction. The osmotic pressure of the two PEO−PPO block copolymer−water systems examined here increased exponentially from 5×10^3 to 3×10^8 Pa over the 6−99.9 wt % block copolymer concentration range. The osmotic pressure of the PEO−PPO block copolymer−water systems in the block copolymer concentration range 6−50 wt % can be well represented by an empirical scaling law for semidilute polymer solutions. A change in the scaling exponent occurs at concentrations close to the disorder−order transition. The activity of water obtained from PEO−PPO block copolymer solutions and gels was fitted well by the Flory−Huggins equation up to 70 wt % block copolymer using an interaction parameter that represents the interactions between the PEO segments and water. The work of dehydration was estimated within each ordered phase and for phase transitions between different ordered structures. Finally, the combination of osmotic force data with data on the distance (spacing) between assemblies in the ordered block copolymer samples (determined via small-angle X-ray scattering), allowed us to construct a force vs distance curve, which reveals that interactions occur at two levels, that of the PEO coil and that of the PEO segment.

Introduction

Amphiphilic molecules (surfactants, lipids, block copolymers) in the presence of selective solvents (e.g., water for ionic and PEO-containing surfactants or block copolymers) are known to form a variety of ordered (lyotropic liquid crystalline) structures, such as cubic, hexagonal, and lamellar.[1−4] The structural elements of these structures are micelles (spherical, cylindrical, and planar, respectively), which generally consist of a solvent-incompatible (hydrophobic) core and a solvated (hydrated) shell (corona) dominated by solvent-compatible (hydrophilic) segments, and have a diameter of 4−20 nm (depending on the amphiphile molecular dimensions).

The structural elements (micelles) attain their thermodynamic stability from a delicate balance between interactions that promote the micelle formation, e.g., minimization of contact between the solvent and the solvent-immiscible part of the amphiphile, and interactions that oppose micelle formation, e.g., repulsion between the solvated parts of the amphiphile.[4−6] Similar considerations govern the thermodynamic stability of ordered block copolymers melts[7] and of solvated block copolymers.[8,9] The long-range (lyotropic liquid crystalline) order is related to repulsive interactions (steric and/or electrostatic) between adjacent assemblies.

Such intermolecular interactions can be quantified by direct force measurements (obtained by surface force apparatus or scanning force microscopy[10−16]) and/or by indirect force measurements (obtained by osmotic stress experiments[17−24]). The surface force method was developed in the 1970s and was initially used to measure forces between solid surfaces.[10,11] Osmotic stress measurements were first developed to study systems of biological relevance, like lipid bilayers,[17,18,23] DNA helices,[22] or proteins. The basic principle of this method is the equilibration of the sample of interest with systems of known osmotic pressure, generally aqueous polymer solutions or saturated salt solutions. When combined with structure determination by X-ray diffraction, a force−distance curve can be obtained, thus providing an opportunity to study repulsive intermolecular forces occurring in well-defined structures via the equation of state. Following extensive studies, a "hydration force" has been proposed to explain the short-range strong repulsive force observed experimentally in such systems because a pure double-layer electrostatic force cannot generate such high force.[23,24] The osmotic stress method has been extended to study polymer solutions[20,25−27] (e.g., hydroxypropylcellulose,[26] xanthan,[20] galactomannan[27]), lamellar phases formed by surfactants (ammonium acetate,[28] dihexadecyldimethylammonium acetate,[29] polyoxyethylene nonionic surfactants[30]), colloids[31−35] (e.g., polystyrene latex dispersions,[32−34] ceramic particle suspensions[35]), and microemulsions (e.g., oil/water microemulsion,[36] bicontinuous microemulsion[37]). However, this method has not yet been applied to block copolymers self-assembled in selective solvents.

Our group has devoted a significant amount of effort toward the study of phase behavior, structure, and dynamics of block copolymers in selective solvents.[1−3,9,38−45] In particular, we have explored the self-

* To whom correspondence should be addressed: e-mail palexand@eng.buffalo.edu; fax (716) 645-3822.

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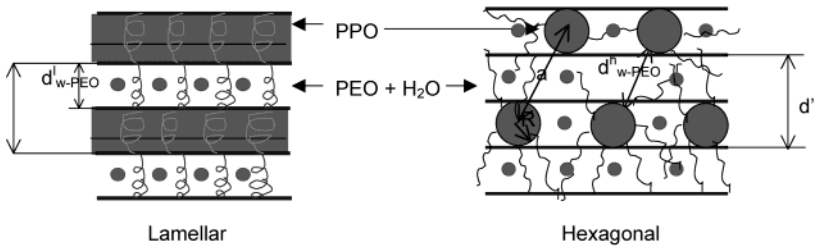

Figure 1. Definition of lattice spacing and lattice separation in lamellar and hexagonal phases. d or d' is the lattice parameter (lattice spacing) between lamellar bilayers or cylinder layers, d^{l}_{w-PEO} is the lattice separation in the lamellar structure, and d^{h}_{w-PEO} is the lattice separation in the hexagonal structure. Both water and PEO segments are present in the d^{l}_{w-PEO} and d^{h}_{w-PEO} regions.

assembly properties of Poloxamer (or Pluronic) poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) (PEO−PPO−PEO) block copolymers in water (selective solvent for PEO) and in mixtures of water with polar organic solvents. Such amphiphilic block copolymers exhibit a remarkable variety of ordered nanostructures in selective solvents, the morphology and characteristic dimensions of which can be readily tuned by the quality and quantity of the solvent. At the same time, they find numerous applications in waterborne coatings and personal care formulations and also in the areas of biomaterials and drug delivery.[46−54]

In this work we investigate the thermodynamic state (chemical potential) of PEO−PPO−PEO block copolymer−water binary systems, across the entire composition spectrum (from disordered micellar solution, to ordered liquid crystalline structures of cubic, hexagonal, and lamellar symmetry, and to systems containing semicrystalline PEO), by means of osmotic stress measurements. We further relate osmotic pressure data to spacings obtained by SAXS (for given block copolymer compositions) in order to obtain force vs distance curves. To the best of our knowledge, this is the first report of such data for ordered block copolymers. Our results aid the understanding of interactions in self-assembled media as well as at surfaces modified by solvated polymers (synthetic or biopolymers).

Materials and Methods

Materials. The Pluronic P105 and Pluronic F127 NF poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) block copolymers were obtained from BASF Corp. and were used as received. The Pluronic P105 and F127 copolymers have nominal molecular weights of 6500 and 12 600, respectively, and PEO contents 50 and 70 wt %, respectively (according to the manufacturer). On the basis of their molecular weights and chemical compositions, Pluronics P105 and F127 can be represented by the formulas $(EO)_{37}(PO)_{58}(EO)_{37}$ and $(EO)_{100}(PO)_{70}(EO)_{100}$, respectively. The bulk density of Pluronic P105 and F127 is approximately 1.05 g/cm^3. 1.0 g/cm^3 was assumed for the density of Pluronic P105 and Pluronic F127 solutions/gels, except indicated otherwise. The moisture content in "as-received" Pluronic P105 was measured by the Karl Fischer titration method and was found below 0.1 wt %. The Pluronic P105 block copolymer is well studied and can thus serve as a "model" system.[39,42,55] Pluronic F127, also known as Poloxamer 407, is a block copolymer which, because of its thermoreversible gelation behavior in aqueous solutions, is widely used in the pharmaceutical field, for example, in drug formulations,[43,56,57] drug delivery,[48,51−53] and treatment of skin burns.[54] Dextran T500 was purchased from Amersham Pharmacia Biotech AB, Uppsala, Sweden (lot number 17-0320-02, M_w = 482 000, M_w/M_n = 2.9). Poly(ethylene glycol) (PEG) 20000 ($M_r \approx$ 16 000−24 000) was obtained from Fluka Chemie GmbH, Switzerland. Samples were prepared individually by weighing appropriate amount of polymer and water with a Mettler AG245 (Toledo) electronic balance with ±0.1 mg accuracy. Lithium chloride (LiCl), sodium iodide (NaI), sodium bromide (NaBr), sodium chloride (NaCl), potassium chloride (KCl), potassium nitrate (KNO_3), and potassium sulfate (K_2SO_4) were purchased from Fisher Scientific Co., L.L.C., Georgia. All salts were analytical grade. Saturated aqueous salt solutions were prepared by dissolving an excess amount of pure salt in water. Millipore-filtered water was used for all sample preparations.

Block Copolymer Phase Behavior and Structure Characterization. *Determination of Phase Diagrams.*[39,55,56] Samples were prepared individually by weighing appropriate amounts of polymer and water into 8 mm (i.d.) glass tubes, which were immediately flame-sealed. Effort has been made to speed the mixing and to ensure the homogenization of the samples. Following equilibration, the phase diagram was determined by inspecting the samples for birefringence between crossed polaroids.[39,55] The block copolymer molecules can self-organize in different topologies depending both on the block copolymer concentration (lyotropic behavior) and on the temperature (thermotropic behavior). In the Pluronic P105−water system, high-water-content solution (L_1, <21 wt % block copolymer), micellar cubic phase (I_1, 25−44 wt %), hexagonal phase (H_1, 48−67 wt %), lamellar phase (L_α, 73−87 wt %), and high-polymer-content paste (L_2, >87 wt %) are thermodynamically stable at room temperature (25 °C).[39,55] In the Pluronic F127−water system, high-water-content solution (L_1, <18 wt % block copolymer), micellar cubic phase (I_1, 19−63 wt %), hexagonal phase (H_1, 65−75 wt %), and high-polymer-content paste (L_2, >75 wt %) are present at 25 °C.[43,56]

Small-Angle X-ray Scattering (SAXS) Measurements. SAXS measurements were performed on a Kratky compact small-angle system equipped with a position-sensitive detector (for detailed information see refs 39 and 55−57). The obtained Bragg diffraction peaks are relatively sharp, in which case the peak position can be evaluated directly from the slit-smeared data.[39,55−57] The structure of the lyotropic liquid crystalline phases was determined from the relative positions of the SAXS diffraction peaks.[39,55−57] The lattice parameter d (the spacing between the lamellar layers), d' (the distance between adjacent rows of cylinders in the hexagonal structure), and a (the distance between the centers of adjacent cylinders) were obtained from the position (q^*) of the first (and most intense) diffraction peak.

$$\text{lamellar: } q^* = \frac{2\pi}{d} \qquad \text{hexagonal: } q^* = \frac{4\pi}{a\sqrt{3}} = \frac{2\pi}{d'} \quad (1)$$

A schematic of the lattice parameter and lattice separation (refer to eqs 15 and 17 for definitions) is shown in Figure 1.

Osmotic Pressure Measurements. Three main methods are normally used to generate osmotic pressure over a wide pressure range.[18,19] One is to place the sample of interest in contact with a polymer solution of known osmotic pressure, using a semipermeable membrane to separate the polymer solution from the test gel sample. This method can generate osmotic pressures from 0.01 to about 50 atm. The second method is to exert physical pressure via a piston acting on the sample through a strong, supported, semipermeable

membrane. This method can be used to generate pressures higher than the polymer solution method.[18,19] However, this method may be dangerous because of the high pressure involved. In the third method, very high (~3000 atm or higher) osmotic pressure can be achieved by exposing the test samples to atmospheres of known water (with water being the solvent in the test sample) vapor pressures, which can be attained in the presence of saturated aqueous salt solutions. In each of the above methods, the osmotic pressure of the test sample is obtained by equilibrating it with the pressure applied externally. Vapor pressure (VP) osmometry is another method to measure the osmotic pressure of a solution.[58] The VP osmometer measures the difference between the vapor pressure of the test solution and that of the pure solvent (the vapor pressure of a solution being lower than that of the pure solvent). However, the VP osmometer works well only in dilute solutions. For example, the operating concentration range is 1−100 mmol/kg (osmotic pressure about 0.0224−2.24 atm) for the Gonotec 070 vapor pressure osmometer (Gonotec GmbH, Berlin, Germany). In this study, the first (polymer solution) and third (saturated salt solution) methods mentioned above were used to set the osmotic pressures of the PEO−PPO−PEO block copolymer−water systems.

Polymer Solution Osmotic Stress Method. In this method, the block copolymer solution or gel (lyotropic liquid crystal) sample was placed in contact with an aqueous polymer (dextran or PEG) solution of known osmotic pressure, using a semipermeable membrane that ensures separation between the equilibrating polymer and the sample, while the water molecules can pass freely through the membrane. A cellulose ester (CE) dialysis membrane (SPECTRUM, Spectrum Laboratories, Inc., Rancho Dominguez, CA) was used to separate the polymer solutions and test samples. The membrane was rinsed thoroughly with Millipore-filtered water before use. The molecular weight cutoff of the CE membrane was 500 g/mol. The equilibrating polymer solutions were checked for possible presence of Pluronic block copolymer, which might have leaked through the CE membrane after the osmotic stress experiment, using a colorimetric method.[47,59] No Pluronic block copolymer was detected in the polymer solutions.

The polymers that we used to generate known osmotic pressure were dextran or poly(ethylene glycol) (PEG), which have very stable osmotic pressures.[19] It has been shown[19] that the osmotic pressures of high molecular weight (between 250 000 and 2 000 000) dextran aqueous solutions are almost the same over a large temperature range. The following equation[19] provides the osmotic pressure (dyn/cm^2) of aqueous dextran solutions as a function of the dextran weight fraction, w:

$$\log [\Pi_{dex}] = 2.75 + 1.03w^{0.383} \quad (2)$$

The temperature effect on the osmotic pressure of PEG solutions is normally larger than that of dextran solutions. The following equation[19] for the osmotic pressure, $\Pi_{PEG20000}$ (dyn/cm^2), of PEG20000 was originally obtained at 30 °C; however, it was directly used in our system (24 °C):

$$\log [\Pi_{PEG20000}] = 1.61 + 2.72w^{0.21} \quad (3)$$

Solutions of known osmotic pressure were prepared individually by weighing appropriate amounts of polymer and water. The Pluronic P105 and Pluronic F127 block copolymer solutions or gels were prepared in the same way. At higher block copolymer concentrations (>30 wt % Pluronic P105 or >20 wt % Pluronic F127), the gels were difficult to handle because the viscosity increased dramatically. A syringe was then used to pump the high concentration gel into the dialysis bag. After the sample was successfully injected into the dialysis bag, a closure was used to seal the bag. The concentration of block copolymer inside the dialysis bag was determined by mass balance (mass change of the sample). The samples were weighed at different time intervals until no mass change was observed, thus establishing the equilibrium state. The equilibration time was about (or less than) 1 month, depending on the concentration of the samples. To speed up the process, dextran (or PEG) solutions were equilibrated with block copolymer−water samples whose initial concentrations were close to the equilibrium concentrations. The osmotic pressure method is a simple but rather tedious method. To ensure the equilibrium states, different initial concentrations of samples were tested. At the same osmotic pressure (polymer concentration), the same results were obtained when starting from different initial block copolymer concentrations. A large excess of equilibrating polymer solution (about 50 times the weight of the block copolymer sample) was used in order to ensure there was no obvious change of the equilibrating polymer concentration (and ensuing osmotic pressure).

Table 1. Relative Humidity (R_H), Osmotic Pressure (π), and Water Chemical Potential (μ) of Saturated Aqueous Salt Solutions at 24 °C

salt	LiCl	NaI	NaBr	NaCl	KCl	KNO_3	K_2SO_4
R_H, %[a]	11.3	38.4	57.9	75.4	84.6	93.8	97.4
π, atm	2951	1295	740	383	226	86	36
log(π) (Pa)	8.48	8.12	7.88	7.59	7.36	6.94	6.57
μ, J/mol	−5382	−2362	−1350	−699	−413	−157	−66

[a] These values are interpolated to 24 °C from ref 61, which reports the relative humidity of saturated aqueous salt solutions as a function of temperature.

Saturated Salt Solution Osmotic Stress Method. Very high osmotic pressure can be achieved by exposing the test samples to known water vapor pressures generated by saturated aqueous salt solutions. Different saturated aqueous salt solutions have different water vapor pressure p at a given temperature.[60,61] The ratio of p to the saturated vapor pressure p_0 is designated as the relative humidity (R_H) and can be related to water chemical potential by the following equation:

$$\Delta\mu = RT \ln\left(\frac{p}{p_0}\right) = RT \ln(R_H) \quad (4)$$

$$\Delta\mu = -\pi v_1 \quad (5)$$

where $\Delta\mu$ is the chemical potential of water vapor, π is the osmotic pressure, and v_1 is the molar volume of water.

Table 1 lists the salts used in order to generate a series of relative humidities. The PEO−PPO block copolymer samples were equilibrated with these salt solutions in a sealed dish, with no direct contact between the sample and the salt solutions. The sealed dishes with higher relative humidities (75%, 85%, 94%, and 97%) were placed in an incubator whose temperature was kept at 24 ± 0.1 °C, and the surrounding relative humidity was in the range 70−90%. For the lower relative humidity conditions (11%, 38%, and 58%), the sealed dishes were left in an air-conditioned room with temperature at 24± 1 °C and ambient relative humidity ranging from 10% to 60%. In this way the disturbance of opening the system to take measurements of the sample weight was greatly reduced. The approximate time for the system to reach the desired relative humidity following a perturbation was less than half hour. The time required for attaining equilibrium was up to 60 days, depending on the relative humidity. A digital hygrometer (±1.5% relative humidity accuracy, Fisher Scientific) was used to check the relative humidity of the air in contact with the saturated salt solutions. We thus confirmed that the relative humidity imposed by the salt solutions was at the prescribed value.

Results and Discussion

Osmotic Pressure of PEO−PPO−PEO Block Copolymer−Water Systems. The osmotic pressure of Pluronic P105 and Pluronic F127 solution/gel is plotted as a function of block copolymer concentration at 24 °C in parts a and b of Figure 2, respectively. The osmotic pressure data shown in Figure 2a,b were obtained from

different methods. Above 60 wt % Pluronic P105 and 45 wt % Pluronic F127, the results were from saturated salt solution osmotic stress measurements. Below these concentrations, the results were obtained from the polymer solution osmotic stress method, in which either PEG20000 or Dextran T500 was used as equilibration solution. The dextran and PEG solutions gave data that overlapped, indicating good agreement between the two different polymer solutions. The osmotic pressure increases from 5×10^3 to 3×10^8 Pa over the 6−99.9 wt % block copolymer concentration range. In general, the osmotic pressure increases exponentially as the block copolymer concentration increases. At very high block copolymer concentrations (above 95 wt %), the osmotic pressure increase is steeper compared to the lower concentration region (as judged by different slopes in the plot of logarithm of osmotic pressure vs block copolymer concentration shown in Figure 2a,b). The boundaries between phases of different structure are indicated in the figures by dotted lines.

At block copolymer concentrations below 30 wt %, the osmotic pressures of Pluronic P105 and F127 are very similar to each other. At concentrations between 30 and 80 wt %, the osmotic pressure of Pluronic F127 is higher than that of Pluronic P105. However, when the block copolymer concentration is above 80 wt %, the reverse trend is observed, i.e., the osmotic pressure of Pluronic F127 becomes lower than that of Pluronic P105. Because in the wide concentration range examined here the PPO block in the PEO−PPO block copolymer−water system will try to minimize the contact with the solvent−water, it is reasonable to assume that the interactions between PEO and water are the ones that contribute mostly to the osmotic pressure. On the basis of this supposition, the data in Figure 2a,b were replotted, with the corresponding PEO concentration as the new *x*-axis as shown in Figure 2c. The PEO concentration was calculated on the basis of the block copolymer concentration and PEO content in the block copolymer molecules. Osmotic pressure data for homopolymer PEO (PEG20000 and PEG6000) are also included in Figure 2c. When plotted against the PEO concentration, the osmotic pressure of Pluronic P105 becomes almost the same as that of Pluronic F127 in the concentration range 30−80 wt % PEO and is also very comparable to the osmotic pressure of PEG20000. This indicates that the osmotic pressure indeed originates mainly from the interactions between PEO and water. Below 30 wt % PEO, the osmotic pressure of Pluronic F127 is lower than that of Pluronic P105, which is due to the fact that the number of particles (micelles), instead of the number of PEO segments, plays an important role in this region.

From Figure 2a,b we can see that the shape of the log(osmotic pressure) vs block copolymer concentration curve is sigmoidal. The sigmoidal shape can be explained qualitatively as follows. When the block copolymer concentration is in the dilute region (below the critical micelle concentration, when there is no micelle formation), the osmotic pressure of the block copolymer solution should follow the law of ideal gases; i.e., the osmotic pressure of block copolymer solution should be proportional to the number density of the particles (block copolymer unimers) and increase rapidly with increased block copolymer concentration. However, when the block copolymer concentration is above the critical micelle concentration (cmc), block copolymer molecules self-assemble into micelles and the number

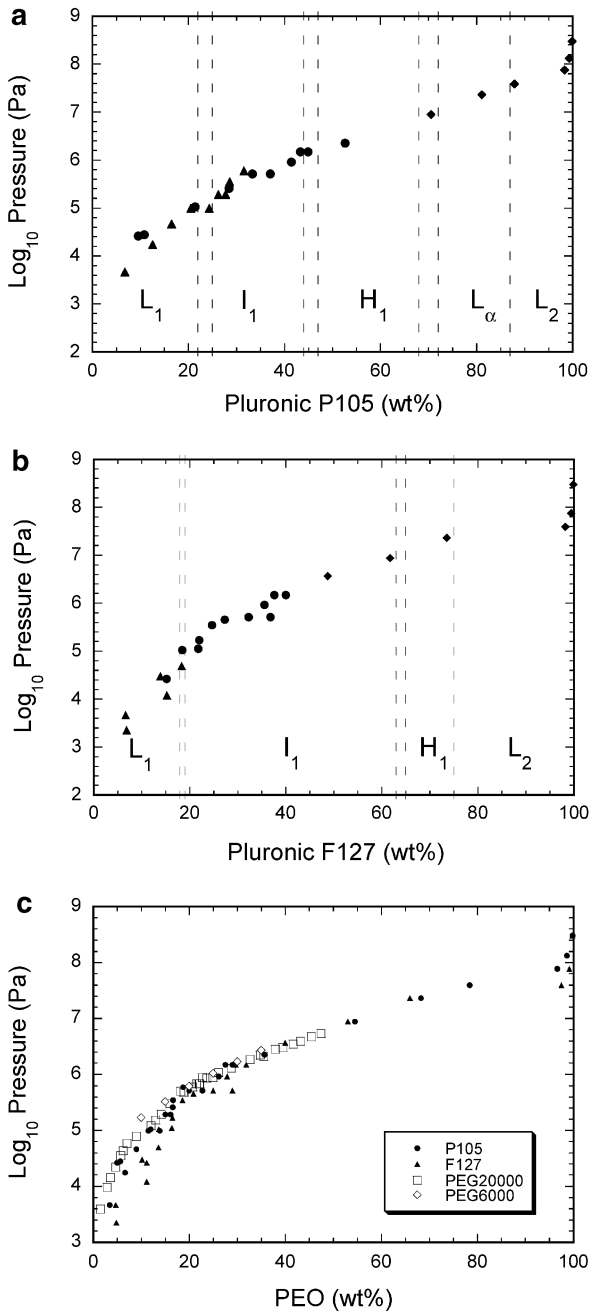

Figure 2. Osmotic pressure of (a) Pluronic P105 and (b) Pluronic F127 aqueous solution/gel at 24 °C: ◆, results from relative humidity osmotic stress measurements; ●, results from osmotic pressure measurements by PEG20000 aqueous solution; ▲, results from osmotic pressure measurements by Dextran T500 aqueous solution. The dotted lines separate regions of different self-assembled structure of the block copolymer. L_1 = high-water-content solution; I_1 = micellar cubic phase; H_1 = hexagonal phase; L_α = lamellar phase; L_2 = high-polymer-content solution (paste). The regions separated by two dotted lines and without any label correspond to compositions where the samples are two-phase. (c) Osmotic pressure of Pluronic block copolymer−water systems plotted as a function of PEO weight fraction at 24 °C. Also shown in Figure 2c are osmotic pressure data for PEG6000 and PEG20000.

of particles (including both unimers and micelles) decreases dramatically, which has a negative effect on the increase of osmotic pressure. On the other hand, the interactions between micelles also contribute to the osmotic pressure: when the block copolymer concentration increases, the interactions (repulsion) between

micelles become stronger. Thus, the overall effect is that the osmotic pressure increases slowly in this regime. Similar considerations apply to the osmotic pressure of block copolymer solutions/gels in the hexagonal and lamellar phases. When the block copolymer concentration is very high, e.g., above 95 wt % block copolymer, a steep rise is observed in the osmotic pressure. This is because the block copolymer is partly hydrated and partly crystalline, so the number of the particles (block copolymer segments) is very large. Moreover, because the water content in this region is very small, the interactions between the particles are very strong, thus contributing to a very high osmotic pressure. This strong repulsion corresponds to short-range interactions at the polymer segment level.

A similar sigmoidal shape has also been observed in the osmotic pressure data of polystyrene (PS) latex dispersions (particle diameter 61 nm, surface charge density 0.14 e/nm^2) in water at pH = 7 and ionic strength 3×10^{-5} M.[32] The osmotic pressure of this latex dispersion increased exponentially when the volume fraction increased from 0 to 0.7.[32] When the volume fraction of PS latex was 0.6, the osmotic pressure was on the order of 10^4 Pa (much lower than that observed in Pluronics gels of similar volume fraction). The exponential increase of osmotic pressure with the polymer concentration indicates that a strong repulsion in these systems is crucial for the stability of both latex dispersions and block copolymer self-assembled structures.

Figure 3a,b gives the osmotic pressure of Pluronic P105 and Pluronic F127 as a function of average water volume per block copolymer. The water volume per block copolymer was calculated on the basis of the block copolymer concentration. It is shown that the osmotic pressure (and chemical potential) exhibits a different dependency on water volume per block copolymer (different slope) at different phases. This kind of pressure vs volume curve can be treated empirically to obtain the free energy or work of block copolymer hydration/dehydration between phase transitions and also the work of hydration/dehydration in each phase examined here (see section on "Work of Hydration/Dehydration at Phase Transitions and within Different Phases"). However, we note that the resolution of the osmotic pressure data and the fewer data points available at higher osmotic pressure do not allow us to draw accurate conclusions on what happens in the vicinity of the phase transitions.

Scaling of the Osmotic Pressure of PEO−PPO−PEO Solution/Gel in the Semidilute Regime. The osmotic pressures of linear polymers in good solvents have been studied, and the following scaling law has been obtained for semidilute solutions[62,63]

$$\frac{\pi M}{CRT} = K_\pi \left(\frac{C}{C^*}\right)^{1/(3\nu-1)} \quad \text{for } C^* < C \ll 1 \qquad (6)$$

where M is the polymer molecular weight, C is the polymer concentration (g/cm^3), R is the gas constant, K_π is a constant, ν is the excluded-volume exponent defined in the radius of gyration−molecular weight relationship: $R_g \propto M^\nu$. ν is 0.6 (3/5) from Flory−Huggins theory[64] and 0.588 from renormalization group theory[65] and has been reported to be 0.585−0.595 for polystyrene in toluene.[62,63] C^* is the critical concentration at which polymer coils begin to overlap, as defined by eq 7. The ratio of the polymer concentration C to C^* indicates the degree of coil overlap.

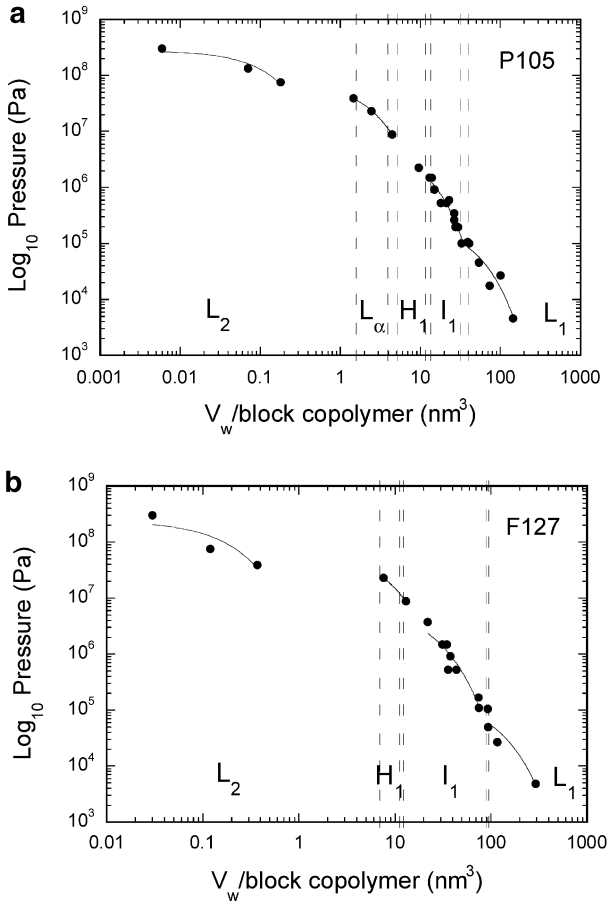

Figure 3. Osmotic pressure of (a) Pluronic P105 and (b) Pluronic F127 aqueous solution/gel as a function of water volume per block copolymer molecule at 24 °C. The dotted lines separate regions of different self-assembled structure. The solid line that passes through the data in each ordered phase is obtained by fitting the experimental data with an exponential function applied in that region.

$$C^* = \frac{3M}{4\pi {R_g}^3 N_A} \qquad (7)$$

where N_A is Avogadro's number.

We tested eqs 6 and 7 for their ability to fit (predict) the osmotic pressure of the Pluronic P105−water and Pluronic F127−water systems of concentrations up to 50 wt % (see dashed lines in Figure 4a,b). The values $K_\pi = 2.2$[63,70] and $\nu = 0.6$ were used in the calculations. Because the basic structural unit in the block copolymer−water system is a micelle when the block copolymer concentration is above the cmc (0.3% (w/v) for Pluronic P105 and 0.7% (w/v) for Pluronic F127 aqueous solutions at 25 °C[66]), the molecular weight and radius of a block copolymer micelle were used in eqs 6 and 7. The molecular weight of a micelle was obtained by multiplying the block copolymer molecular weight with the micelle association number (average number of block copolymer molecules in one micelle, 50 for Pluronic P105).[67] The radius of Pluronic P105 micelle used for this calculation (as an adjustable parameter) was 180 Å, which is about 2 times the hard-sphere interaction radius found in 8 wt % Pluronic P105 aqueous solution at 30 °C.[67] The critical overlap concentration C^* thus

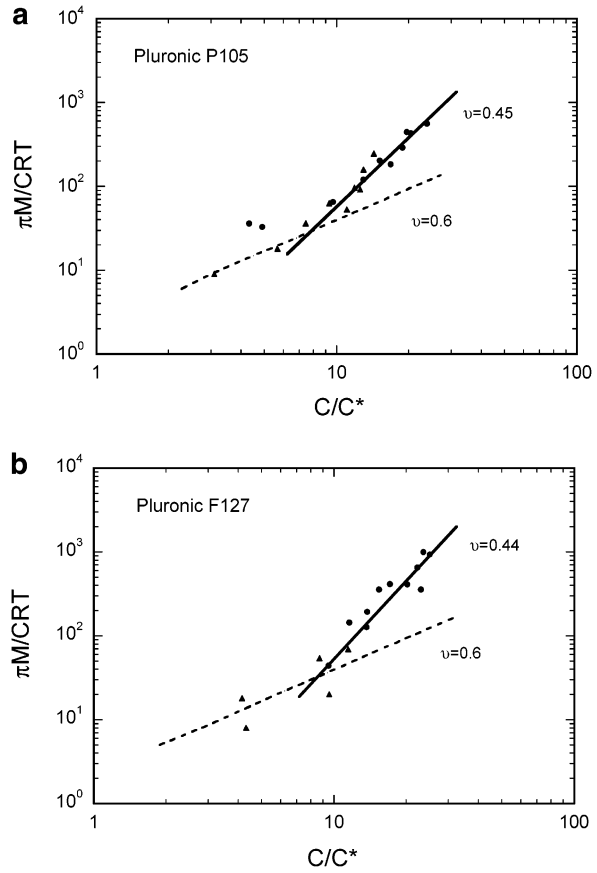

Figure 4. Scaling of the osmotic pressure of (a) Pluronic P105 and (b) Pluronic F127 solution/gel at 24 °C plotted as logarithm ($\pi M/CRT$) vs logarithm (C/C^*): ●, results from osmotic pressure measurements by PEG20000 aqueous solution; ▲, results from osmotic pressure measurements by Dextran T500 aqueous solution. The dashed line is the result from empirical scaling law for the semidilute polymer solution using micelle parameters. The solid line is the linear correlation (in double-logarithm coordinates) used to get the scaling exponent for the Pluronic P105−water system at 17 wt % < C < 50 wt % and for the Pluronic F127−water system at 14 wt % < C < 50 wt %.

obtained for Pluronic P105 is 0.022 g/cm^3 (about 2 wt % Pluronic P105).

From Figure 4a, one can see that the scaling law of eq 6 with $\nu = 0.6$ fits the experimental data well below 17 wt % Pluronic P105 ($C/C^* \approx 8$). However, above 17 wt % Pluronic P105, the differences between the predicted values (dashed line) and the experimental values become increasingly large. When the block copolymer concentration is above 17 wt %, the same scaling law (eq 6) can still be used to fit the experimental data but with a different ν value (0.45) and K_π value (0.1). This decrease of the ν value indicates that the solvent (water) becomes worse for Pluronic P105 when the block copolymer concentration increases: it is known that for a polymer coil under θ conditions $R_g \propto M^{1/2}$, while for globular polymers $R_g \propto M^{1/3}$. It is notable that the change of ν at approximately 17 wt % block copolymer occurs in the vicinity of a phase change in the Pluronic P105−water system. Below 21 wt % block copolymer (and above cmc), a micellar solution forms in the Pluronic P105−water system, whereas when the block copolymer concentrations exceeds 25 wt %, a micellar cubic (ordered) phase forms.[39,55]

Similar results were obtained for the Pluronic F127−water system (see Figure 4b). The critical overlap concentration C^* is 0.022 g/cm^3, and the radius of Pluronic F127 micelle is 190 Å (using association number = 30).[68] Below 14 wt % Pluronic F127, the scaling law fitted well the experimental data with $K_\pi = 2.2$ and $\nu = 0.6$; however, above 14 wt %, a different ν value ($\nu = 0.44$ and $K_\pi = 0.08$) was obtained, which is almost identical to the ν value obtained in the Pluronic P105−water system. The change of the ν value around 14 wt % Pluronic F127 also coincides with the phase change from a disordered micellar solution to an ordered micellar cubic phase.

Polymer brushes are tethered polymer chains attached to a surface (or microstructure) by their ends.[69−71] The forces between polymer brush surfaces have been extensively studied. It has been shown that the osmotic pressure in a polymer brush system exhibits the same scaling law as in a semidilute polymer solution, but the magnitude is 2 times higher in a brush than in a solution with the same polymer concentration.[70] Because the polymer brush description should be closer to our system, we used the same scaling law (eq 6, $\nu = 0.6$, and $K_\pi = 2.2$, but with the osmotic pressure of a polymer brush twice that of the polymer solution) for a polymer brush to refit the osmotic pressure of the Pluronic P105−water system. The radius of the Pluronic P105 micelle thus obtained changes to 150 Å when a polymer brush is considered, which is smaller than the value obtained by the polymer solution equation (180 Å) and closer to the micelle radius obtained experimentally.[67] Similarly, the radius of Pluronic F127 micelle decreased from 190 to 160 Å when the polymer brush model was used for the fitting.

It should be noted that, while we used above the micelle as a structural unit to fit the osmotic pressure of the Pluronic−water system in the concentration range of 6−50 wt %, the parameters of Pluronic unimer (nonassociated polymer) can also be used to fit the osmotic pressure by the same scaling law. When the Pluronic P105 unimer is used in eqs 6 and 7, the radius obtained from the dashed line fit is 17 Å (comparable to the unimer $R_g = 29$ Å[67]); however, the critical overlap concentration becomes $C^* = 0.52$ g/cm^3 (about 52 wt %), which is unrealistically high. We thus consider the micelle as a better descriptor of the osmotic pressure scaling.

Determination of Solvent Activity and Polymer−Solvent Interaction Parameter. The activity of the solvent, a_1, can be related to the osmotic pressure, π, through

$$\Delta\mu = RT \ln a_1 = -\pi v_1 \qquad (8)$$

where v_1 is the molar volume of the solvent; for the solvent used here, water, $v_1 = 18$ cm^3/mol.

The determination of the solvent activity is important in the modeling of the thermodynamic properties of the block copolymer−selective solvent systems. The Flory−Huggins theory is widely used for describing the thermodynamics of polymer solutions.[64] In the framework of the Flory−Huggins theory, the activity of solvent (in our case, water) in polymer solution can be obtained from the following equation:

$$\ln(a_1) = \ln(1 - \varphi_2) + \left(1 - \frac{1}{r_2}\right)\varphi_2 + \chi_{12}\varphi_2^2 \qquad (9)$$

where φ_2 is the volume fraction of polymer, r_2 is the

number of polymer segments, and χ_{12} is the polymer−solvent interaction parameter.

While eq 9 is derived for a system where no phase changes take place, we decided to test its applicability in fitting the activity data obtained for the PEO−PPO block copolymer−water systems. In addition to practical considerations (e.g., prediction of solvent activity), such fits provide us with information on the apparent interaction parameter and the polymer volume fraction effective in our system.

In the Flory−Huggins model, only one parameter, χ_{12}, is needed to fit the activity of water in the PEO−PPO block copolymer aqueous solution/gel over the whole concentration range. We first fitted the data using the Pluronic block copolymer concentration for φ_2. The Flory−Huggins equation (eq 9) described the systems fairly well up to 50 wt % block copolymer. The interaction parameters thus obtained were 0.62 for the Pluronic P105−water system and 0.58 for the Pluronic F127−water system. Because the basic structural unit of the Pluronic solution/gel in the concentration range examined here is a micelle, it may be reasonable to also fit the activity of water in the Pluronic block copolymer system focusing on the interaction parameter between PEO and water. This is because the hydrophilic PEO located in the corona interacts with the solvent water, while the PPO located in the core avoids contact with water. The appropriate polymer volume fraction used in eq 9 in this case is that of PEO, which was obtained from the following equation:

$$\text{PEO vol \%} = \frac{w_{\text{PEO}} v_{\text{PEO}}}{w_{\text{PEO}} v_{\text{PEO}} + w_{\text{H}_2\text{O}} v_{\text{H}_2\text{O}}} \times 100\% \qquad (10)$$

where w_{PEO} and $w_{\text{H}_2\text{O}}$ are the weight fractions of PEO and water in the PEO−PPO block copolymer solution/gel, respectively. The density of PEO was assumed to be 1.05 g/cm^3, the same as that of the Pluronic block copolymer.

The fittings were improved when using the PEO volume fractions calculated based on eq 10. Moreover, the same interaction parameter $\chi_{12} = 0.55$ was obtained for both Pluronic P105 and F127 systems after minimizing the sum of errors between the experimental values and predicted values in the concentration range up to 70 wt % block copolymer (about 54 wt % PEO in the Pluronic P105−water system and 62 wt % PEO in the Pluronic F127−water system). The experimental values of water activity and predicted values (lines) are shown in Figure 5. In this concentration range the differences between the experimental and fitted values are less than 1.6% for the Pluronic P105−water system and 0.5% for the Pluronic F127−water system, much smaller than those from the fits based on the block copolymer concentration. However, when the block copolymer concentration becomes higher than 70 wt %, the difference between the experimental and fitted values increases quickly, as the model becomes less applicable to these conditions.

The activity of water in poly(ethylene glycol) (PEG)−water solutions has been studied using the vapor pressure osmometry method,[72,73] and the Flory−Huggins equation was used to obtain the interaction parameter in such systems.[73] The values of the χ_{12} interaction parameters ranged from 0.4148 to 0.5147 depending on the PEG molecular weight and temperature. χ_{12} increased with increasing temperature, which means that the interaction of PEG and water becomes unfavorable when the temperature increases; the concentration dependency was negligible in the concentration range studied (up to 40 wt %).[73] Higher molecular weight PEG (PEG4000) has a higher χ_{12} compared to PEG400; e.g., χ_{12} is 0.4857 for PEG4000 aqueous solution at 35 °C compared with 0.4148 for PEG400 solution at that temperature. Low molecular weight (water-soluble) poly(propylene glycol) (PPG) has a higher χ_{12} than PEG of similar molecular weight at the same temperature (0.5766 for PPG425 vs 0.4148 for PEG400 at 35 °C) because PPG is more hydrophobic than PEG.[73] The interaction parameter obtained for the Pluronic−water systems considered here ($\chi_{12} = 0.55$) is comparable to the parameter reported for PEG4000−water solutions. The fact that χ_{12} is higher than $^1/_2$ for the Pluronic block copolymer−water system indicates that water is not a good solvent for both Pluronic P105 and Pluronic F127. This is consistent with the segregation that leads to the formation of different self-assembled structures over the block copolymer concentration range examined.

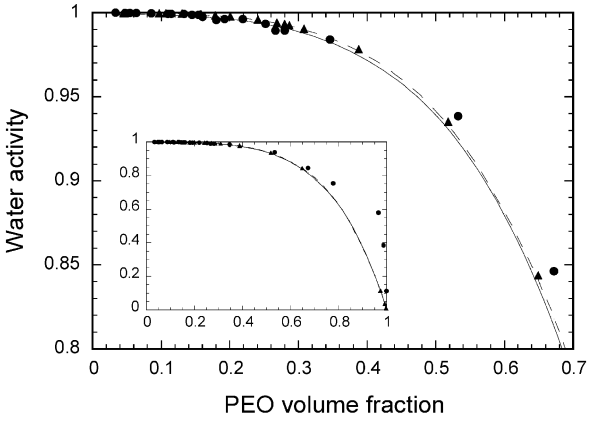

Figure 5. Activity of water in Pluronic block copolymer aqueous solution/gel plotted as a function of PEO volume fraction (obtained by eq 10) at 24 °C: ●, experimental values of Pluronic P105; ▲, experimental values of Pluronic F127; solid line, values predicted using Flory−Huggins equation with $\chi_{12} = 0.55$ for the Pluronic P105−water system; dashed line, values predicted using Flory−Huggins equation with $\chi_{12} = 0.55$ for the Pluronic F127−water system. (The small difference of the two fitted lines is due to the different number of polymer segments used in eq 9.)

Work of Hydration/Dehydration at Phase Transitions and within Different Phases. As alluded to earlier, the osmotic pressure vs water volume per block copolymer data (Figure 3) can be used to obtain the work of hydration/dehydration of block copolymers. Because the Pluronic block copolymers exhibit a variety of ordered phases in the presence of water, it is important to know how much work is needed for the block copolymer to dehydrate at each hydration level (correspondingly each ordered phase). Further, if the temperature effect on the osmotic pressure was to be measured, the entropy and enthalpy of hydration/dehydration could be obtained.[77] In the present study all the experiments were done at constant temperature so the work of hydration/dehydration is estimated at isothermal conditions as described below.

In a two-phase coexistence region, the Gibbs free energy change of phase transition can be obtained by the water volume change multiplied by the osmotic pressure in this region (eq 11).[18,77] This free energy change represents the work of moving water molecules

from one ordered phase to another—a hydration/dehydration process.

$$W = \Delta G = -P\Delta V_w \tag{11}$$

On the basis of eq 11, we estimated the work of dehydration at phase boundaries of different ordered structures of PEO−PPO block copolymer−water systems. The water volume per EO segment is calculated from the block copolymer weight fraction and chemical formula. The volume of one water molecule is 30 Å^3. The phase boundaries used for calculation were described in the "Materials and Method" section. The work of dehydration for the Pluronic P105 system when it transitions from a micellar solutions to a micellar cubic phase is about $0.0026k_BT$ per EO segment, which is equivalent to 0.48 kJ per mole of block copolymer and about 3 times higher than the corresponding value for the Pluronic F127 system ($0.0008k_BT$ per EO). When the ordered phase transforms from the micellar cubic phase to the hexagonal phase, the work of dehydration increases to about $0.01k_BT$ per EO segment for Pluronic P105, about 3−4 times higher than that from the micellar solution to micellar cubic phase transition in the same system. Similarly, when the phase transition is from hexagonal to lamellar phase, the dehydration work for Pluronic P105 increases another 3−4-fold, to about $0.038k_BT$ per EO segment. The dehydration work for Pluronic F127 from the micellar cubic phase to the hexagonal phase is $0.011k_BT$ per EO segment, which is almost the same as that of Pluronic P105. This large difference for the Pluronic P105 and F127 values at phase transition from the micellar solution to the micellar cubic phase is possibly due to the uncertainties in the width of the phase boundaries used for the calculation of the dehydration work.

Within each ordered or disordered phase, the work of hydration/dehydration can be obtained by eq 12.[18,77]

$$W = \Delta G = -\int P \, dV_w \tag{12}$$

We used the following procedure to calculate the work of block copolymer dehydration in each phase. The osmotic pressure shown in each phase region in Figure 3 was fitted by an exponential function, and then the exponential function thus obtained was substituted into eq 12 and integrated with respect to the water volume per EO segment to get the integration expression in this phase region. The work of dehydration in the micellar solution phase was obtained by using the integration expression in this region directly, assuming that the water volume per EO segment is infinitely large at infinite dilute micellar solution. For the work of dehydration in the micellar cubic phase, in addition to the work that is from the integration expression in the micellar cubic region, two other contributions must be used in order to calculate the total work that is needed to remove water from the micellar cubic phases to the bulk solution (here refers to infinite dilute micellar solution): (i) the work of dehydration for the phase transitions from the micellar solution to the micellar cubic phase and (ii) the work that is needed to remove water from the micellar solution at its highest concentration (the lower boundary of the two-phase region from the micellar solution to the micellar cubic phase). A similar approach was applied to the hexagonal, lamellar, and high-polymer-content phases. Figure 6a,b reports the work of dehydration in all the phases. When the hydration level (water volume per EO segment) becomes lower, the work of block copolymer dehydration becomes much higher, which means that it is more difficult to remove water from the ordered phase at low hydration level. This is especially true in the high-polymer-content region, where there are less than 7 water molecules (below 58% RH) for each Pluronic P105 molecule and less than 9 water molecules (below 75% RH) for each Pluronic F127 molecule.

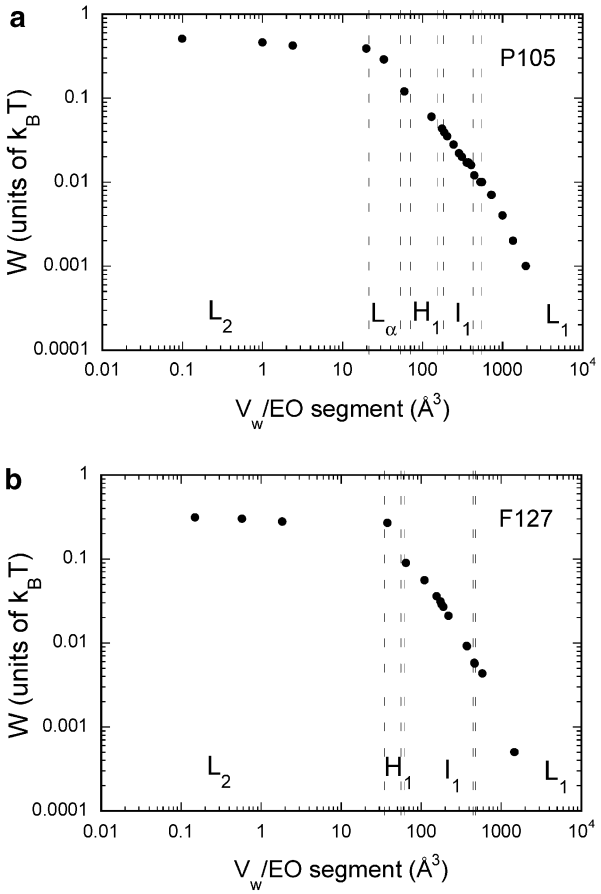

Figure 6. Work of dehydration (in the units of k_BT per EO segment) of (a) Pluronic P105 and (b) Pluronic F127 plotted as a function of water volume per EO segment at 24 °C. Similar to other figures, the dotted lines separate regions of different self-assembled structure of the block copolymer.

To the best of our knowledge, there is no relevant literature on the work of dehydration for systems that exhibit many ordered phases, so it is not possible to compare our results to the literature values. The work of DNA double-helix dehydration has been reported.[77] A comparison of our data with that of DNA dehydration shows that the work of block copolymer dehydration in the micellar cubic and hexagonal phases as shown in Figure 6 is comparable to that of DNA dehydration. Although PEO−PPO block copolymers and DNA are totally different systems, such comparison can still give us a rough idea the magnitude of the dehydration work.

Osmotic Force vs Distance Analysis. Osmotic stress measurements combined with structure characterization are a useful tool for probing the intermolecular interactions in ordered structures.[17−37] The force vs distance curves obtained from this method can help elucidate the formation and stability of ordered assemblies. In the hexagonal phase of the Pluronic P105−

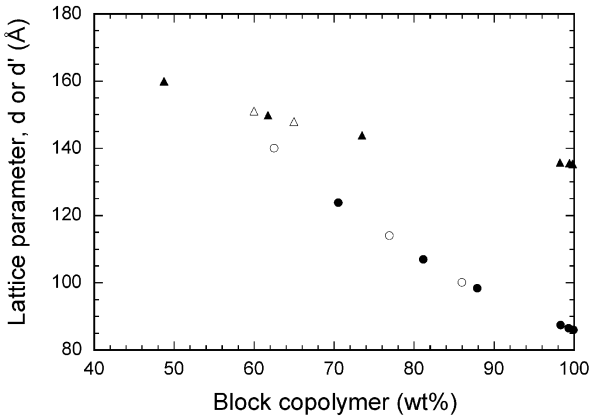

Figure 7. Lattice parameter, d or d', as a function of block copolymer concentration (wt %) for the Pluronic P105−water and Pluronic F127−water systems: ○, experimental results for the Pluronic P105−water system; ●, values obtained assuming one-dimensional swelling for the Pluronic P105−water system; △, experimental results for the Pluronic F127−water system; ▲, values obtained assuming one-dimensional swelling for the Pluronic F127−water system.

water system, the lattice parameter d' (distance between nearest layers of cylinders, see Figure 1) is 140 Å at concentration 62.5 wt % Pluronic P105.[39,55] In the lamellar phase, the lattice parameter d (nearest lamellar bilayers) is 114 Å at 76.9 wt % Pluronic P105[39,55] and 100 Å at 86 wt % Pluronic P105.[57] One-dimensional swelling[4] has been assumed in order to interpolate and to extrapolate the lattice parameters at higher concentrations (Figure 7). One-dimensional swelling in a surfactant/lipid bilayer system represents a case where the added solvent (water) is localized between the bilayers formed by the surfactant/lipid, and the lattice parameter is a linear function of the inverse surfactant volume fraction, $d \sim \varphi_2^{-1}$. In the block copolymer system examined here, the volume fraction φ_2 corresponds to PPO, $d \sim \varphi_{\mathrm{PPO}}^{-1}$, because PPO is located in the core of both lamellar and hexagonal structures and does not swell with water. In the case of one-dimensional swelling, the thickness of the PPO core is assumed to be constant, while the thickness of the hydrated PEO layer will swell with the increase of water concentration. The ● data points reported in Figure 7 correspond to block copolymer concentrations at equilibrium with the values of air relative humidity considered in our experiments. When the Pluronic P105 concentration is above 90 wt %, the structure is not lamellar, but the block copolymer is partly hydrated and partly crystalline in terms of PEO. So the lattice parameters in this region are just an extrapolation. For the Pluronic F127−water system at 25 °C,[41,56] the lattice parameters are 151 Å at 60 wt % and 148 Å at 65 wt % (higher compared with the Pluronic P105−water system). One-dimensional swelling[4] is also used for the extrapolation of lattice parameters for Pluronic F127−water systems (see Figure 7). When the Pluronic F127 concentration is above 75 wt %, the block copolymer is also partly hydrated and partly crystalline.

From the lattice parameter data shown in Figure 7, we can obtain the lattice separation data ($d^{\mathrm{l}}_{\mathrm{w-PEO}}$ or $d^{\mathrm{h}}_{\mathrm{w-PEO}}$) using the equations shown below. Unlike systems such as lipid bilayers and DNA helices, where only water and ions are present between the bilayers,[17,18,22−24] in the block copolymer systems of interest here both water and PEO segments are present in the hydrated PEO domains.

$$\varphi_{\mathrm{PPO}} = \frac{c_{\mathrm{PPO}} v_{\mathrm{PPO}}}{c_{\mathrm{PPO}} v_{\mathrm{PPO}} + (1 - c_{\mathrm{PPO}}) v_{\mathrm{w+PEO}}} \tag{13}$$

$$\text{lamellar:} \quad d_{\mathrm{PPO}} = \varphi_{\mathrm{PPO}} d \tag{14}$$

$$\text{lamellar:} \quad d^{\mathrm{l}}_{\mathrm{w+PEO}} = d - d_{\mathrm{PPO}} \tag{15}$$

$$\text{hexagonal:} \quad R_{\mathrm{PPO}} = a\left(\frac{\sqrt{3}}{2\pi}\varphi_{\mathrm{PPO}}\right)^{1/2} \tag{16}$$

$$\text{hexagonal:} \quad d^{\mathrm{h}}_{\mathrm{w+PEO}} = a - 2R_{\mathrm{PPO}} \tag{17}$$

where φ_{PPO} is the volume fraction of PPO segments, c_{PPO} is the weight percentage of the PPO segments (of the block copolymer) in the sample, v_{PPO} is the specific volume of the PPO segments, d_{PPO} is the thickness of PPO layers in lamellar phase, $d^{\mathrm{l}}_{\mathrm{w+PEO}}$ is the thickness of hydrated PEO layers in the lamellar structure (see Figure 1), $v_{\mathrm{w+PEO}}$ is the specific volume of hydrated PEO segments (assuming ideal mixing of PEO segments and water), R_{PPO} is the radius of the PPO core in the hexagonal structure, and $d^{\mathrm{h}}_{\mathrm{w+PEO}}$ is the thickness of the hydrated PEO corona shell in the hexagonal structure (see Figure 1). For simplicity, the specific volume of PPO and PEO segment is assumed to be the same as that of Pluronic block copolymer, 0.952 $\mathrm{cm^3/g}$; the specific volume of water is 1.0 $\mathrm{cm^3/g}$.

Tables 2 and 3 list the osmotic stress analysis results for the Pluronic P105−water and Pluronic F127−water systems, respectively, from which the force vs distance curves shown in Figure 8 were obtained. In the high concentration region (over 70 wt % P105 and 45 wt % F127), two different slopes were observed in the logarithmic curve, showing that the osmotic pressure decays over distance via two different constants (called "decay lengths"[28]). On the basis of this, a double-exponential function[28] was used to correlate the decay lengths (λ_{h} and λ_{p} in eq 18) and the preexponential parameters (π_{h} and π_{p} in eq 18) to the experimental data (one exponential term was used in each region).

$$\pi = \pi_{\mathrm{h}} \exp\left(-\frac{d}{\lambda_{\mathrm{h}}}\right) + \pi_{\mathrm{p}} \exp\left(-\frac{d}{\lambda_{\mathrm{p}}}\right) \tag{18}$$

where d is $d^{\mathrm{l}}_{\mathrm{w+PEO}}$ for the lamellar structure and $d^{\mathrm{h}}_{\mathrm{w+PEO}}$ for the hexagonal structure and λ is the decay length (Å); the subscript h denotes hydration and p denotes polymer coil.

Interactions at the Polymer Coil Level. When the lattice separation is in the range 55 Å < $d^{\mathrm{l}}_{\mathrm{w+PEO}}$ < 81 Å for the Pluronic P105−water system, the decay length λ_{p} is 17.0 Å, which is much larger than the well-known decay lengths for "hydration force" (generally 1−3 Å)[19,23,24] but corresponds to the radius of gyration of the PEO block (as shown next). The unimer (nonassociated polymer) radius of gyration in 1 wt % Pluronic P105 aqueous solution is about 29 Å at 10 °C.[67] The radius of gyration of the PEO block in the Pluronic P105 unimer coil can be estimated from the following equation:

$$\frac{R_{\mathrm{PEO}}}{R_{\mathrm{g}}} = \left(\frac{N_{\mathrm{EO}}}{N_{\mathrm{P105}}}\right)^{1/2} \tag{19}$$

where R_{PEO} is the radius of gyration of PEO block, R_{g}

Table 2. Osmotic Stress Analysis Results for Pluronic P105

P105, wt %	φ_{PPO}	d, lattice spacing, Å	d_{PPO}, lattice thickness, Å	d^{l}_{w-PEO}, lattice separation, Å	π, Pa	log(π) (Pa)	μ_w, J/mol	H_2O/EO ratio
99.94	0.500	85.9	42.9	43.0	3.0×10^8	8.48	−5382	0.003
99.34	0.496	86.5	42.9	43.5	1.3×10^8	8.12	−2362	0.032
98.33	0.491	87.4	42.9	44.5	7.5×10^7	7.88	−1350	0.083
87.91	0.437	98.3	43.0	55.4	3.9×10^7	7.59	−699	0.67
81.16	0.402	106.9	43.0	63.9	2.3×10^7	7.36	−413	1.1
70.55	0.348	123.7	43.0	80.7	8.7×10^6	6.94	−157	2.0

Table 3. Osmotic Stress Analysis Results for Pluronic F127

F127, wt %	φ_{PPO}	d', lattice spacing, Å	R_{PPO}, core radius, Å	d^{h}_{w-PEO}, lattice separation, Å	π, Pa	log(π) (Pa)	μ_w, J/mol	H_2O/EO ratio
99.86	0.300	135.4	44.9	66.5	3.0×10^8	8.48	−5382	0.005
99.45	0.298	135.5	44.9	66.8	7.5×10^7	7.88	−1350	0.019
98.26	0.294	135.8	44.7	67.5	3.9×10^7	7.59	−699	0.062
73.53	0.218	143.8	40.7	84.7	2.3×10^7	7.36	−413	1.3
61.75	0.182	149.9	38.7	95.6	8.7×10^6	6.94	−157	2.2
48.75	0.143	160.0	36.6	111.5	3.7×10^6	6.57	−66	3.7

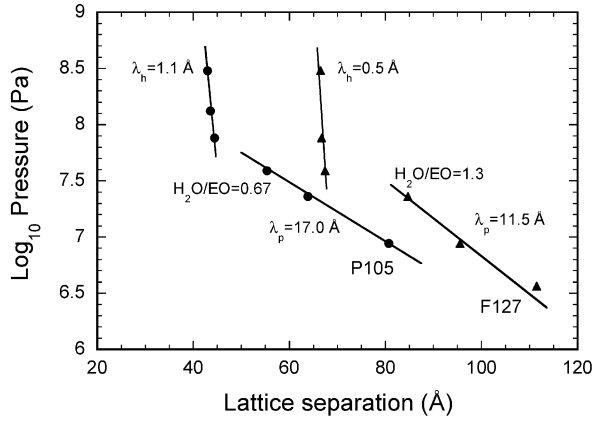

Figure 8. Force vs distance curve: ●, Pluronic P105−water system; ▲, Pluronic F127−water system. Two different decay lengths are observed. The lines connecting the points indicate the range of the power law expressions used to obtain the decay lengths λ_p and λ_h. The numbers listed close to the data points in the figure indicate the number of water molecules per EO segment.

is the unimer radius of gyration, N_{EO} is the number of EO segments in a PEO block, and N_{P105} is the total number of segments in the block copolymer. On the basis of the Pluronic P105 molecular formula (N_{EO} = 37 and N_{P105} = 132) and eq 19, the radius of gyration of PEO block is estimated to 15.4 Å. The decay length λ_p obtained for the Pluronic P105−water system is close to the above-reported value. The radius of gyration of a PEO block was reported to be 17.5 Å in a good solvent in a separate paper,[57] in which the relationship $R_g = aN^{3/5}$ was used to make the estimation (effective monomer size a = 2 Å and N = 37). If the PEO blocks of Pluronic P105 were treated as a polymer brush, then the thickness of the brush was estimated to be 31 Å in a good solvent.[57] The thickness of the polymer brush was given by $L = aN(a/D)^{2/3}$, where D is the distance between the anchoring points of the brush.[57] The difference between the decay length λ_p and the thickness of the brush may come from the fact that, although the lamellar structure in our system is very similar to a polymer brush, water is only a slightly good solvent for PEO so the PEO blocks are not fully extended in the solvent. In addition, because the repulsion between the hydrated PEO blocks in this regime is very large, the extension of the PEO block should be greatly prevented; thus, we expect the thickness of PEO block will be smaller. For the Pluronic F127−water system, the decay length λ_p is found 11.5 Å in the range 84 Å < d^{h}_{w+PEO} < 112 Å. The decay lengths for two different systems are very similar, indicating that the same mechanisms are effective.

In addition to comparing λ_p to the PEO block radius of gyration, we can compare λ_p to the thickness of the PEO-rich corona in Pluronic P105 micelles. The radius of Pluronic P105 micelles in aqueous solution (8 wt %) is 71 Å at 30 °C,[67] while the radius of PPO-rich core is 40 Å.[67] The corona (hydrated PEO blocks) thickness is thus 31 Å. The λ_p obtained above is about half of the micelle corona thickness; however, they are still comparable to each other, indicating that the interaction (repulsion) takes place at the PEO coil level. Another relevant value to compare to λ_p is the shortest distance between nearest-neighbor polar/apolar interfaces in ordered PEO−PPO−PEO block copolymers. The PEO layer thickness is usually a function of polymer concentration and temperature.[74] The presence of another solvent or additive can also change the PEO layer thickness.[74] The PEO layer thickness decreased significantly with increasing Pluronic F127 concentration in the Pluronic F127−butanol (or xylene, butyl acetate)−water system, i.e., from 125 to 70 Å when the block copolymer concentration increased from 20 to 70 wt %.[74] No data were obtained at higher concentrations; however, we expect the PEO thickness values to be much smaller there and closer to the decay length λ_p.

The preexponential factors (π_p) of the decay length λ_p, 1×10^9 Pa (about 1×10^4 atm) for the Pluronic P105−water system and 4×10^{10} Pa (about 4×10^5 atm) for the Pluronic F127−water system, show that the repulsive force in this region (55 Å < d^{l}_{w+PEO} < 81 Å for Pluronic 105 and 84 Å < d^{h}_{w+PEO} < 112 Å for Pluronic 127) is very large. These two preexponential factors represent the extrapolated force when the lamellar or hexagonal structure contacts with each other. They are very comparable to the magnitude of hydration force found in lipid bilayers and other systems;[19,23,24] however, the much larger decay lengths in the block copolymers indicate that another mechanism (interaction at the polymer coil level) is in effect. In this lattice separation region, the water/EO molar ratio is relatively high. At 94% RH, there are about 2 water molecules for each EO segment for both the Pluronic P105−water and Pluronic F127−water systems. The water/EO molar ratios at different air relative humidity conditions are listed in Tables 2 and 3.

The repulsive forces between poly(ethylene oxide) (two molecular weights, 4×10^4 and 1.6×10^5 g/mol) layers adsorbed on mica surfaces in aqueous solvent have been measured by the surface force apparatus.[75] The forces commenced at a surface separation of $(6 \pm 1)R_g$ (R_g is the radius of gyration, $R_g = 6.5$ nm for PEO with MW $= 4 \times 10^4$, and $R_g = 13$ nm for PEO with MW $= 1.6 \times 10^5$) and increased monotonically until to about 6 ± 1 nm separation (comparable to the polymer coil R_g). The force−distance curve suggested an effective extension of PEO from each mica surface of about $3R_g$. The monotonically increasing repulsive forces observed between PEO layers adsorbed on mica are similar to the repulsive forces in the block copolymer−water systems examined here. The forces were also measured between two mica surfaces with PEO adsorbed (MW = 148 000) in 0.04 M $MgSO_4$ aqueous solution.[11] Three regimes were observed for the repulsion forces, depending on the surface distance and also on the rate of surface approach.[11] When the mica surfaces were very close (below 5 nm), the repulsion increased more steeply compared to large separation regime, and the PEO coils were even forced out from the gap between the surfaces.[11] The sharp increase of repulsion force at very short distances observed in these PEO-adsorbed mica surfaces is also very similar to what has been observed for the PEO−PPO−PEO block copolymer systems examined here. A recent report[76] showed that the repulsive forces between PEO-adsorbed mica surfaces in a good solvent increased exponentially with decreasing surface separation. More remarkably, the decay length is linearly proportional to the radius gyration of polymer coil, $\lambda = 0.8R_g$, in the regime of large separation and weak interactions.[76] Although one might expect a higher repulsion when the surface separation decreases and this relation may not hold, it still indicates that in certain regions the repulsive force decays via a characteristic length related to the polymer coil, as is the case in our study.

Interactions at the Polymer Segment Level. When the lattice separation is very small, the decay lengths change significantly compared to the decay length obtained at large lattice separations. The decay length is $\lambda_h = 1.1$ Å when the lattice separation 43 Å < d^l_{w+PEO} < 45 Å for the Pluronic P105−water system; $\lambda_h = 0.5$ Å when the lattice separation 66 Å < d^h_{w+PEO} < 68 Å for the Pluronic F127−water system. This low decay length is very similar to the values observed in biological systems. For example, the decay length is normally 2.5−3.5 Å in DNA double helices and polysaccharides.[19,21,77] For the DNA system, λ is 1.5 Å at very short distances (3−7 Å).[77] Decay lengths smaller than 1 Å have been observed in some systems, such as $\lambda =$ 0.6 Å for a self-assembled protein.[78] Decay lengths of 0.31 and 0.63 Å have been observed for cetyltrimethylammonium bromide (CTAB) cylinders in poly(acrylic acid)−cetyltrimethylammonium bromide (PAA−CTAB) complexes bathed in 10 and 100 mM NaBr at 25 °C.[25] This repulsive force is short-range but very strong. The preexponential factor (π_h) for the Pluronic P105−water system at very short distances is 3×10^{25} Pa (about 1×10^{20} atm), while for the Pluronic F127−water system, π_h is 3×10^{62} Pa (this may be unrealistically high). This strong repulsive force can be attributed to the so-called hydration force.[22−24] In this region, the equilibrium water/EO molar ratio is very small, e.g., 0. 083 at 58% RH and only 0.003 at 11% RH for the Pluronic P105−water system, which means the block copolymer is almost "dry". For the Pluronic F127−water system, the equilibrium water/EO molar ratio is 0.064 at 75% RH and 0.005 at 11% RH. At such conditions, the PEO segments will be very close so that the interactions are very strong. Evidence has been reported that the structure of water inside surfactant lamellar structures can be modified.[79,80] For example, the hydrogen bonding in the water layer confined in lamellar structures formed by the amphiphile tetra(ethylene glycol) *n*-dodecyl ether ($C_{12}E_4$) can be enhanced at distances very close to the surfactant surface, i.e., 2.5−8 Å.[80] The enhanced hydrogen bonding in the water layers at such short distances may also contribute to the strong repulsion in this region. We should point out, however, that, while the λ_h obtained here has a very reasonable value, the lattice parameter values on which it is based are extrapolated and not directly measured.

Conclusions

The osmotic pressures of Pluronic PEO−PPO−PEO block copolymers in water across the 6−99.9% block copolymer composition range were measured directly by the osmotic stress method over a very wide pressure range (0.05−3000 atm). The osmotic pressure increases exponentially with increasing block copolymer concentration. In the region where PEO can be crystalline because of the low (<0.1) water/EO molar ratio (above 95 wt % block copolymer), the osmotic pressure increase is more pronounced.

The osmotic pressure of Pluronic block copolymer solutions/gels in the concentration range 6−50 wt % block copolymer can be represented by the scaling law for semidilute polymer solutions, $\pi M/CRT \propto (C/C^*)^{1/(3\nu-1)}$, with two different ν exponents. At concentrations less than 17 wt % Pluronic P105 and 14 wt % Pluronic F127, $\nu = 0.6$; at higher concentrations $\nu = 0.45$ for Pluronic P105 and $\nu = 0.44$ for Pluronic F127. The change (decrease) of the ν value indicates worsening of the solvent conditions and occurs in the vicinity of the disorder−order transition from disordered micellar solution to ordered micellar cubic phase.

The Flory−Huggins theory was used to fit the activity of water obtained experimentally in Pluronic block copolymer solution/gel. From a dilute micellar solution up to about 70 wt % block copolymer (both block copolymers are in the hexagonal liquid crystalline phase at this concentration), the Flory−Huggins theory fits very well the water activity with interaction parameter $\chi_{12} = 0.55$ for both Pluronic P105 and Pluronic F127. Above 70 wt % block copolymer, the differences between the experimental and fitted values become increasingly large. The fact that χ_{12} is higher than $^1/_2$ is consistent with the segregation in the self-assembled system that we considered.

The work of dehydration for different phase transitions was estimated for both Pluronic P105− and Pluronic F127−water systems. The phase transition from hexagonal to lamellar structure requires more work (energy) in order to dehydrate than that from micellar cubic to hexagonal strucutre. Similarly, the dehydration work is higher from the micellar cubic phase to the hexagonal phase than that from the micellar solution to the micellar cubic phase. The lower the hydration level in block copolymer−water systems, the more energy is needed to remove water from the ordered phases.

Force vs distance curves were obtained for both PEO−PPO−PEO block copolymer−water systems examined

on the basis of the osmotic stress measurements reported here and the structural information obtained by SAXS. Two different decay lengths are observed in highly concentrated block polymer gels. The decay length λ_p is 17.0 Å for the Pluronic P105−water system at lattice separation 55 Å < d^l_{w+PEO} < 81 Å; a similar decay length (11.5 Å) is observed in the Pluronic F127−water system at lattice separation 84 Å < d^h_{w+PEO} < 112 Å. This decay length is comparable to the radius of gyration of a PEO block; thus, the repulsion force acts at the PEO coil level. This is in agreement with surface force measurements between surfaces with adsorbed PEO homopolymer in aqueous solutions.

The decay length λ_h is 1.1 Å for the Pluronic P105−water system when the lattice separation is small, 43 Å < d^l_{w+PEO} < 45 Å. The decay length is 0.5 Å for the Pluronic F127−water system when 66 Å < d^h_{w+PEO} < 68 Å, smaller than that of the Pluronic P105 system. The small decay lengths observed at short distances can be attributed to a hydration force that acts at the PEO segment level. This hydration force is short range but very strong, similar to the hydration forces observed in other polymers, surfactants, or biological systems.

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