

Thermodynamically stable, size selective solubilization of carbon nanotubes in aqueous solutions of amphiphilic block copolymers

R. Nagarajan,^{a)} R. Ashton Bradley,^{b)} and Bindu R. Nair

Molecular Sciences and Engineering Team, Natick Soldier Research, Development and Engineering Center, Kansas Street, Natick Massachusetts 01760, USA

(Received 26 May 2009; accepted 12 August 2009; published online 14 September 2009)

Two molecular modes of amphiphilic block copolymer-carbon nanotube interactions have been identified in the literature, one involving the adsorption of individual block copolymer molecules on the carbon nanotubes and the other involving the adsorption of multimolecular, spherical micelles. In both cases, the nature of stability imparted to the dispersion of carbon nanotubes in the aqueous medium is kinetic, controlled by the steric barrier imposed by the adsorbed individual block copolymer molecules or the adsorbed micelles. In this study, we propose another mode of molecular interaction, wherein the block copolymer molecules self-assemble around the nanotube, generating aggregates in which the nanotubes are solubilized. In this case, the resulting system is a thermodynamically stable nanocolloidal solution, similar to aqueous surfactant solutions, in contrast to the kinetically stabilized nanotube dispersions. To examine whether such solubilization of nanotubes is possible, we have constructed a simple phenomenological theory for the free energy change associated with solubilization and have performed illustrative numerical simulations based on the theory. The calculated results for the commercially available symmetric PEO-PPO-PEO triblock copolymers and for the PEO-PPO diblock copolymers having the same composition and molecular weight as the triblocks show that indeed the block copolymer molecules are capable of solubilizing the carbon nanotubes. While the block copolymers whose natural curvature is cylindrical are the best candidates to solubilize the nanotubes, other block copolymers whose natural curvature is spherical or lamellar, are also found capable of solubilizing the nanotubes. Most interestingly, the solubilization is found to be size specific suggesting that this can be developed into a practical method to fractionate carbon nanotubes by their diameter. These results are applicable to both single-walled and multiwalled carbon nanotubes and the general conclusions are valid also for other diblock and triblock copolymers. © 2009 American Institute of Physics.
[doi:10.1063/1.3216569]

I. INTRODUCTION

Carbon nanotubes (CNTs) are hollow graphitic nanomaterials with diameters ranging from 0.4 to 2 nm for single-walled nanotubes (SWNTs) and from 2 to 100 nm for concentric multiwalled nanotubes (MWNTs). CNTs possess high aspect ratios of the order of 1000 s, very high specific surface areas, high mechanical strength, rich electronic and conductive properties, excellent chemical and thermal stability, and ultralight weight. Because of these superior properties, numerous mechanical, electronic, optical, sensing and biological applications based on CNTs are currently being visualized.¹ It is well recognized that effective dispersion of nanoparticles and the retention of their large aspect ratios are essential for attaining many of their superior properties.^{2,3} However, because of the strong van der Waals attractions between the nanotubes, the freshly synthesized SWNTs do not exist as individual nanotubes but are aggregated into bundle of nanotubes. Extensive research in the last 5 years

has focused on two general approaches to dispersing CNTs.²⁻²¹ One is surface treatment of the nanotubes coupled with covalent functionalization. The main disadvantages of this approach are the disruption of the extended π conjugation in nanotubes and the reduction in nanotube lengths, both of which severely undermine the electrical and mechanical properties of the nanotubes. The second approach is electrostatic or steric stabilization of dispersions by noncovalent adsorption of surfactants or polymers onto the nanotube surface. The main disadvantages of this approach are that only kinetically stable dispersions are obtained, with the stability limited in time, and perturbations to system conditions during processing can lead to dispersion instability and aggregation of nanotubes. Despite their limitations, both of these approaches represent the current compromise between the adverse features intrinsic to the dispersion method and the advantages gained from being able to disperse the nanotubes. To overcome the limitations of the above two approaches, we propose a third approach based on *noncovalent, molecular assembly* to produce a *thermodynamically stable nanocolloidal solution* containing amphiphilic polymers that undergo molecular assembly with and thereby, solubilize the CNTs.

The first attempt at using polymers to stabilize nanotube

^{a)}Author to whom correspondence should be addressed. Electronic mail: ramanathan.nagarajan@us.army.mil.

^{b)}Co-op Intern from the Northeastern University, Department of Chemical Engineering.

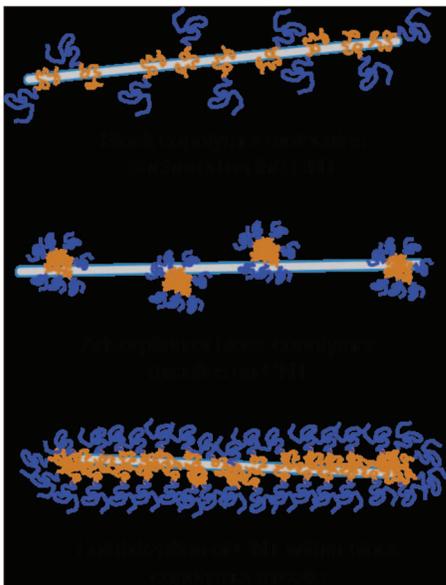


FIG. 1. Schematic representation of the different molecular modes of block copolymer-CNT interactions. The first two modes describe simple adsorption of either singly dispersed block copolymer molecules or spherical block copolymer micelles on the nanotube. The third mode describes the self-assembly of block copolymer molecules around the nanotube, solubilizing the nanotube.

dispersions involved water soluble, linear homopolymers and the mechanism of stabilization was suggested to be based on the polymer wrapping around the nanotubes.² In the case of amphiphilic copolymers, two molecular visualizations of how they interact with the nanotubes have been suggested in the literature (Fig. 1). In the first model, the hydrophobic block of the individual block copolymer adsorbs strongly on the nanotube surface, serving as the anchor, while the hydrophilic block extends and swells in the aqueous domain, imparting steric stabilization to the nanotube dispersion. This is referred to as a nonwrapping model,¹⁸ differentiating it from the polymer wrapping model proposed for the homopolymers.^{2,22} In the second model, spherical micelles (rather than individual molecules) of block copolymers adsorb on the nanotube surface and the steric stabilization is provided by the interactions involving these micellar aggregates.¹⁴ Both of these structural descriptions are quite reasonable and indeed are expected to occur for many amphiphilic block copolymers. In contrast, we propose a third structural description (also shown in Fig. 1) where the block copolymer molecules self-assemble around the CNTs to generate micelles solubilizing the nanotubes. In this case, the nature of stability imparted is thermodynamic and the system can be viewed as not a dispersion, but a thermodynamically stable, aqueous, and nanocolloidal solution. In this paper, we develop a simple phenomenological theory for the molecular assembly of CNT-block copolymer system in aqueous solution, in order to examine whether our proposed structure is thermodynamically favored to occur or not. The theory is formulated such as to apply to diblock and symmetric triblock copolymers. The illustrative numerical simulations based on the theory have been carried out for the

symmetric triblock polyethylene oxide-polypropylene oxide-polyethylene oxide (PEO-PPO-PEO) copolymers since they are commercially available (with the trade name of Pluronics[®]) and for comparison purposes, also for PEO-PPO diblock copolymers having the same block composition and molecular weight as the triblocks. We consider the solubilization of single nanotubes as well as cluster of nanotubes, the cluster being treated simply as a nanotube of larger diameter. The approach and the computational results are applicable to both single wall and multiwall CNTs.

II. THEORY OF SOLUBILIZATION OF CNTS

We consider a system consisting of solvent water, amphiphilic block copolymers and CNTs. The amphiphilic block copolymers exist as singly dispersed molecules as well as aggregates in the aqueous solution. The aggregates may incorporate individual CNT or clusters of CNTs (treated as a cylinder of larger diameter) via micellar solubilization; or alternatively, the block copolymer aggregates may be free of any nanotubes. We assume that there are no individual CNTs in the solution unless they are solubilized by the block copolymer aggregates as described above, since the aqueous solubility of the nanotubes can be considered practically zero. The aqueous solution coexists with a phase of CNTs, consisting of aggregates or bundles of nanotubes, which are merely suspended in the aqueous medium. The question we seek to answer is whether the CNTs will prefer to remain in their own phase because of the strong cohesive nanotube-nanotube interactions or will they be solubilized by the block copolymer micelles to generate a truly nanocolloidal, thermodynamically stable solution. We answer this question by combining a general thermodynamic treatment of self-assembly²³ [Sec. II A] with a phenomenological free energy model for the solubilization of nanotubes within block copolymer aggregates [Sec. II C], which takes into account the geometrical features of the self-assembled aggregates [Sec. II B].

A. Description of equilibrium self-assembly

The chemical potential of molecules in a dilute solution which contains water, singly dispersed block copolymer molecules and block copolymer aggregates of all shapes, with aggregation numbers denoted by g , can be obtained by treating aggregates of each shape and size as distinct chemical species. For block copolymer aggregates, with aggregation number g , including $g=1$ (namely, the singly dispersed molecule), the chemical potential can be expressed²³ in the form

$$\mu_g = \mu_g^o + kT \ln X_g, \quad (1)$$

where μ_g^o is the standard state chemical potential of the specie g , X_g is its mole fraction in solution, k is the Boltzmann constant, and T is the absolute temperature (expressed in K). The standard states for all the aggregates and the singly dispersed copolymer molecule are taken to be infinitely dilute solution conditions. Solvent water and the phase of CNTs are represented by pure component reference states. Note that in Eq. (1), it is possible to consider alternate expressions for the translational entropy (or cratic) term^{24,25} but

TABLE I. Geometrical properties of aggregates. (The variables V_C , V_S , and g are defined per unit length for cylinders and per unit area for lamella. R_T is the radius of the nanotube, either a single tube or a cluster of tubes.)

Property	Nanotube-free aggregates			Cylindrical aggregate solubilizing nanotubes
	Sphere	Cylinder	Lamella	
Volume of hydrophobic A domain V_C	$4\pi R^3/3$	πR^2	$2R$	$\pi[(R+R_T)^2-(R_T)^2]$
Volume of hydrophilic B domain V_S	$V_C[(1+D/R)^3-1]$	$V_C[(1+D/R)^2-1]$	$V_C[(1+D/R)-1]$	$\pi[(D+R+R_T)^2-(R+R_T)^2]$
Aggregation number of micelle g	$V_C/(N_A v_A)$	$V_C/(N_A v_A)$	$V_C/(N_A v_A)$	$V_C/(N_A v_A)$
Area per molecule at domain A-domain B interface a	$4\pi R^2/g=3N_A v_A/R$	$2\pi R/g=2N_A v_A/R$	$2/g=N_A v_A/R$	$2\pi(R_T+R)/g$
Area per molecule at nanotube-domain A interface a_T				$2\pi R_T/g$
Volume fraction of B in corona φ_B	$(V_C/V_S)(N_B v_B)/(N_A v_A)$	$(V_C/V_S)(N_B v_B)/(N_A v_A)$	$(V_C/V_S)(N_B v_B)/(N_A v_A)$	$(V_C/V_S)(N_B v_B)/(N_A v_A)$

the choice is not critical to the purposes of this paper and has no effect on the main conclusions. From the condition of equality of chemical potentials at equilibrium, $\mu_g = g \mu_1$, we get²³ the aggregate size distribution

$$X_g = X_1^g \exp\left(-\frac{\{\mu_g^o - g \mu_1^o\}}{kT}\right) = X_1^g \exp\left(-\frac{g\Delta\mu_g^o}{kT}\right), \quad (2)$$

where $\Delta\mu_g^o$ is the difference in the standard state chemical potentials between a block copolymer molecule present in an aggregate of size g and a singly dispersed block copolymer in water. The critical micelle concentration (CMC) at which the aggregates come into existence is approximately given²³ by

$$X_{\text{CMC}} = \exp\left(\frac{\Delta\mu_g^o}{kT}\right), \quad (3)$$

As is well known, block copolymer molecules can form spherical, cylindrical, or lamellar aggregates in aqueous solutions.²⁶ We can compare the standard state free energy change ($\Delta\mu_g^o$) on the formation of these equilibrium aggregates of different shapes against the standard state free energy change on the formation of cylindrical aggregates solubilizing CNTs and based on minimum energy considerations, determine whether the block copolymer would form a nanotube-free aggregate or a cylindrical micelle solubilizing a single nanotube or a cluster of nanotubes.

To perform predictive calculations of the aggregation behavior, specific expressions for $\Delta\mu_g^o$ are needed. Since $\Delta\mu_g^o$ depends on the shape and size of the aggregates, the geometrical relations governing the aggregates are first defined. All of the equations developed here are in a form applicable to AB diblock copolymers and symmetric BAB triblock copolymers, where A refers to the hydrophobic block and B to the hydrophilic block.

B. Geometrical relations for aggregates

The geometrical relations describing nanotube-free spherical, cylindrical and lamellar block copolymer aggregates as well as cylindrical aggregates in which either a single nanotube or a nanotube cluster is solubilized are summarized in Table I. The variables N_A and N_B refer to the number of segments of block A and block B for the AB diblock as well as the BAB triblock copolymers, implying that the BAB triblock copolymer has two terminal blocks of size $N_B/2$ attached to a middle block of size N_A . We denote the molecular volumes of the A and the B segments, and the solvent water by v_A , v_B , and v_w , respectively. The characteristic lengths of the A and the B segments are denoted by $L_A = v_A^{1/3}$ and $L_B = v_B^{1/3}$.

The hydrophobic domain of the aggregate consists only of block A and we use the variable R to denote the dimension of the A domain. Thus, R is the core radius for sphere or cylinder and the half bilayer thickness for lamella, in the case of nanotube-free aggregates; and R is the thickness of the cylindrical shell of A surrounding the nanotube, in the case of aggregates with solubilized nanotube. The hydrophilic domain consists of block B and solvent water and we use the variable D to denote the dimension of the B domain. Thus, D is the thickness of the shell containing B blocks and solvent water in nanotube-free aggregates as well as nanotubes solubilized aggregates. The variable a is used to denote the interfacial area of the aggregate per constituent block copolymer molecule, at the domain A-domain B interface. The variable R_T denotes the radius of the single nanotube or the nanotube cluster. The variable a_T denotes the interfacial area of the aggregate per constituent block copolymer molecule, at the nanotube-domain A interface.

The number of block copolymer molecules g in the aggregate, the volume V_C of the hydrophobic A domain, and the volume V_S of the hydrophilic B domain, all refer to the

total quantities in the case of spherical aggregates, quantities per unit length in the case of cylindrical aggregates, and quantities per unit area in the case of lamellar aggregates. The hydrophobic A domain volume is calculated as the sum of the volumes of the A blocks constituting the aggregate $V_C = gN_A v_A$. In both the hydrophobic A and hydrophilic B domains, the concentrations of the A and the B segments are assumed to be uniform, with ϕ_A denoting the volume fraction of the A segments in the hydrophobic domain (ϕ_A being unity) and ϕ_B representing the volume fraction of the B segments in the hydrophilic domain. If any two structural variables are specified, all the remaining geometrical variables can be calculated through the relations given in Table I. For convenience, we choose R and D as the independent variables.

C. Contributions to the standard free energy change on of aggregation

The expression for the standard free energy change on aggregation is formulated by identifying all physicochemical changes accompanying micelle formation around a single nanotube or a cluster of nanotubes. A number of contributions have to be considered including changes in the dilution and deformation states of A and B blocks, the formation of domain A -domain B interface, the localization of the copolymer, the backfolding in the case of the triblock copolymer and the transfer of the nanotube from a pure nanotube phase to the interior of the micelle in the aqueous phase. Thus

$$\begin{aligned} \Delta\mu_g^o = & (\Delta\mu_g^o)_{A,dil} + (\Delta\mu_g^o)_{A,def} + (\Delta\mu_g^o)_{int} + (\Delta\mu_g^o)_{B,dil} \\ & + (\Delta\mu_g^o)_{B,def} + (\Delta\mu_g^o)_{loc} + (\Delta\mu_g^o)_{loop} + (\Delta\mu_g^o)_{CNT}, \end{aligned} \quad (4)$$

Expressions for each of these contributions, in the absence of solubilization of nanotubes, have been developed in detail in our previous treatments²⁴⁻²⁶ of aggregation in amphiphilic block copolymer solutions and therefore, are only briefly presented below. The modifications necessary to account for the solubilization of nanotubes are discussed in more detail here.

- (i) Change in state of dilution of block A : In the singly dispersed copolymer, the hydrophobic A block is in a collapsed state, possibly with some solvent trapped in the collapsed globule, and this state is described using the de Gennes theory²⁷ for the conformation of a collapsed polymer

$$\ln(1 - \phi_{A1}) + \phi_{A1} + \chi_{AW} \phi_{A1}^2 = 0, \quad (5)$$

$$\alpha_A = (6/\pi)^{1/3} N_A^{-1/6} \phi_{A1}^{-1/3},$$

where ϕ_{A1} is the segment volume fraction within the collapsed polymer, χ_{AW} is the Flory interaction parameter between block A and the solvent W , and α_A is the chain expansion parameter. The globule surface is interacting with the water medium and the characteristic interfacial tension σ_{AW} is calculated from knowledge of the Flory interaction parameter between block A and the solvent W .

$$\sigma_{AW} = \left(\frac{\chi_{AW}}{6} \right)^{1/2} \frac{kT}{L_W^2}, \quad L_W = v_W^{1/3}, \quad (6)$$

Considering now the aggregated state, the A block is in a domain of its own, equivalent to a pure A polymer. Therefore, the free energy change corresponding to this change in dilution state of A block can be calculated using the Flory theory for polymer solutions²⁸ as:

$$\begin{aligned} \frac{(\Delta\mu_g^o)_{A,dil}}{kT} = & -N_A \left[\frac{v_A}{v_W} \frac{1 - \phi_{A1}}{\phi_{A1}} \ln(1 - \phi_{A1}) \right. \\ & \left. + \frac{v_A}{v_W} (1 - \phi_{A1}) \chi_{AW} \right] - \left(\frac{\sigma_{AW} L_A^2}{kT} \right) \frac{6N_A^{1/2}}{\alpha_A}, \end{aligned} \quad (7)$$

where the first term accounts for the interactions between A segments and water within the collapsed globule and the second term accounts for the interfacial energy between the collapsed globule and water.

- (ii) Change in state of deformation of block A : In the singly dispersed copolymer, the A block deformation is determined by the chain expansion parameter α_A and the free energy of this state is represented by the Flory theory for an isolated polymer molecule.²⁸ In the aggregate, the hydrophobic domain dimension R determines the elastic deformation of the A blocks and the free energy of this state is described by Semenov's theory for elastic deformation in constrained systems.²⁹ On this basis, the free energy change corresponding to the change in elastic deformation states of the A block can be calculated.^{23,26} In nanotube-free aggregates, the hydrophobic block A fills the entire core of the aggregate. For this case

$$\begin{aligned} \frac{(\Delta\mu_g^o)_{A,def}}{kT} = & \left[q \left(\frac{p\pi^2}{80} \right) \frac{R^2}{(N_A/q)L_A^2} \right] \\ & - \left[\frac{3}{2} (\alpha_A^2 - 1) - \ln \alpha_A^3 \right], \end{aligned} \quad (8)$$

where $q=1$ for AB diblock and 2 for symmetric BAB triblock copolymers and p is the shape-dependent molecular packing parameter, equal to 3 for spheres, 5 for cylinders, and 10 for lamellae. The first term accounts for the A block in the aggregated state while the second term corresponds to the A block in the singly dispersed state. When nanotubes are solubilized, the A blocks are confined to the region between the nanotubes and the hydrophilic B blocks. In this case, the deformation free energy in the aggregated state is again calculated using the Semenov theory valid for such a constraint²⁹ and is given by the modified expression²³

$$\frac{(\Delta\mu_g^o)_{A,\text{def}}}{kT} = q \left[\frac{3}{2} \frac{L_A R}{(a_T/q)P} \right] - \left[\frac{3}{2} (\alpha_A^2 - 1) - \ln \alpha_A^3 \right], \quad (9)$$

where a_T is the interfacial area per molecule of the aggregate at the nanotube-domain A interface and P is a shape-dependent function given by $P = \ln[1 + (R/R_T)]$ for the cylindrical aggregates.

- (iii) Change in state of dilution of block B : In the singly dispersed copolymer, the B block is swollen with water and its conformational state is defined by the segment volume fraction ϕ_{B1} within the swollen unimer treated as a sphere and the chain expansion parameter α_B . The segment volume fraction ϕ_{B1} and the corresponding chain expansion parameter α_B are calculated using the Flory theory for a swollen isolated polymer molecule,²⁸ incorporating in it a correction for the coefficient suggested by Stockmayer:³⁰

$$\phi_{B1} = (6/\pi)(N_B/q)^{-1/2} \alpha_B^{-3}, \quad (10)$$

$$\alpha_B^5 - \alpha_B^3 = 0.88(1/2 - \chi_{BW})(N_B/q)^{1/2},$$

where χ_{BW} is the Flory interaction parameter between block B and the solvent W . The free energy of dilution in this state is described by the Flory theory for polymer solutions.²⁸ In the aggregate, the B blocks are again swollen with water but the state of dilution is different compared to that in the singly dispersed state. The free energy of dilution of the B blocks in the aggregate is also described by the Flory theory for polymer solutions.²⁸ On this basis, the free energy contribution to account for the change in the dilution state of B block is written as

$$\begin{aligned} \frac{(\Delta\mu_g^o)_{B,\text{dil}}}{kT} = N_B & \left[\frac{v_B}{v_W} \frac{1 - \phi_B}{\phi_B} \ln(1 - \phi_B) \right. \\ & \left. + \frac{v_B}{v_W} (1 - \phi_B) \chi_{BW} \right] \\ & - N_B \left[\frac{v_B}{v_W} \frac{1 - \phi_{B1}}{\phi_{B1}} \ln(1 - \phi_{B1}) \right. \\ & \left. + \frac{v_B}{v_W} (1 - \phi_{B1}) \chi_{BW} \right], \quad (11) \end{aligned}$$

- (iv) Change in state of deformation of block B : In the singly dispersed copolymer, the B block conformation is described by the chain expansion parameter α_B and the free energy of deformation of this state is represented by the Flory theory for an isolated polymer molecule.²⁸ In the aggregate, the hydrophilic domain dimension D determines the conformation of the B blocks and the chain deformation in this state is described by Semenov's theory.²⁹ On this basis, the free energy change corresponding to the change in elastic deformation states of the B block can be calculated.²³ In nanotubes-free aggregates, the hydrophilic block B

extends from the core domain defined by R to the overall aggregate domain defined by $R+D$. For this case

$$\frac{(\Delta\mu_g^o)_{B,\text{def}}}{kT} = q \left[\frac{3}{2} \frac{L_B R}{(a/q)\phi_B} P \right] - q \left[\frac{3}{2} (\alpha_B^2 - 1) - \ln \alpha_B^3 \right], \quad (12)$$

where a is the surface area per molecule of the aggregate at the domain A -domain B interface, $q=1$ for AB diblock and 2 for BAB triblock, and P is a shape-dependent function given by $P=(D/R)/[1+(D/R)]$ for spheres, $P=\ln[1+(D/R)]$ for cylinders and $P=D/R$ for the lamellae.²³ For cylindrical aggregates in which nanotubes are solubilized, the hydrophilic block B extends from the position $R+R_T$ to the position $R+R_T+D$. For this case

$$\begin{aligned} \frac{(\Delta\mu_g^o)_{B,\text{def}}}{kT} = q & \left[\frac{3}{2} \frac{L_B(R+R_T)}{(a/q)\phi_B} P \right] \\ & - q \left[\frac{3}{2} (\alpha_B^2 - 1) - \ln \alpha_B^3 \right]. \quad (13) \end{aligned}$$

Again, a is the surface area per molecule of the aggregate at the domain A -domain B interface, $q=1$ for AB diblock and 2 for BAB triblock, and P is a shape-dependent function now given by $P=\ln[1+(D/\{R+R_T\})]$.

- (v) Formation of domain A -domain B interface: The formation of an aggregate is associated with the generation of an interface between the hydrophobic domain made up of A blocks and the hydrophilic domain consisting of B blocks and water (W). The characteristic interfacial tension σ_{agg} between the two domains can be calculated based on the Prigogine theory for interfacial tension between two solutions^{31,32} or by approximate composition averaging approaches,²⁶ as is done here.

$$\frac{(\Delta\mu_g^o)_{\text{int}}}{kT} = \frac{\sigma_{\text{agg}}}{kT} a, \quad \sigma_{\text{agg}} = \sigma_{AW}(1 - \phi_B) + \sigma_{AB}\phi_B, \quad (14)$$

where σ_{AB} can be estimated from the Flory interaction parameter χ_{AB} . However, since σ_{AB} is expected to be much smaller than σ_{AW} and ϕ_B is expected to be much smaller than 1, the second term can usually be neglected without any significant consequence and we make this approximation for simplicity. Certainly, it is possible to avoid such a simplification but this does not affect the main results arrived at in this work.

- (vi) Localization of block copolymer: The A - B link in every copolymer molecule is confined to a narrow volume of the aggregate. The corresponding free energy change is calculated using a configurational volume restriction model.^{24,26} For nanotubes-free aggregates

$$\frac{(\Delta\mu_g^o)_{loc}}{kT} = -q \ln \left[\frac{dL_B}{R(1+D/R)^d} \right], \quad (15)$$

where $d=3$ for spheres, 2 for cylinders, and 1 for lamellae. For cylindrical aggregates in which nanotubes are solubilized

$$\frac{(\Delta\mu_g^o)_{loc}}{kT} = -q \ln \left[\frac{2(R+R_T)L_B}{(R_T+R+D)^2 - (R_T)^2} \right]. \quad (16)$$

- (vii) Backfolding for a BAB block copolymer: In the case of a BAB triblock copolymer, the molecule has to fold back to ensure that the B blocks at the two ends are in the hydrophilic domain. The corresponding free energy contribution due to backfolding or loop formation of the A block is calculated using the Jacobson-Stockmayer model³³

$$\frac{(\Delta\mu_g^o)_{loop}}{kT} = \frac{3}{2}\beta \ln[N_A], \quad (17)$$

taking the excluded volume parameter β to be unity.³³

- (viii) Transfer of nanotubes from bulk phase to aggregate in water: All free energy contributions discussed above are only indirectly influenced by the solubilization of the nanotube. A direct and important free energy contribution comes from the transfer of the nanotube from a bulk nanotube phase to the micelle interior. When the nanotubes are transferred from a bulk nanotube phase to an aggregate in aqueous solution, the cohesive nanotube-nanotube and A block- A block interactions are replaced by adhesive nanotube- A block interactions. Such an interchange free energy is represented by the Flory interaction parameter χ_{AT} (subscript T denoting the nanotube or nanotube cluster), which can be used to calculate the free energy change corresponding to this transfer process. Alternately, the transfer process can be viewed as one involving changes in the interfacial states for the nanotubes. In the initial state, the interface of the nanotube or the nanotube cluster is characterized by the interfacial tension $\sigma_{TT}=0$, since each tube is interacting with other identical tubes, that is, the interface is that between identical surfaces. In the aggregate, the nanotubes (or the nanotubes cluster) has an interface in contact with the hydrophobic block A , characterized by the interfacial tension σ_{AT} . Correspondingly, the free energy change for this transfer process can be written as,

$$\frac{(\Delta\mu_g^o)_{CNT}}{kT} = \frac{(\sigma_{AT} - \sigma_{TT})}{kT} a_T = \frac{\sigma_{AT}}{kT} a_T \quad (18)$$

where a_T is the interfacial area of the aggregate per block copolymer molecule, at the nanotube-domain A interface and the free energy change is expressed per molecule of the amphiphilic block copolymer in the aggregate solubilizing the nanotubes. The interfacial tension σ_{AT} can be related to the Flory interaction parameter χ_{AT} using the usual relation

$$\sigma_{AT} = \left(\frac{\chi_{AT}}{6} \right)^{1/2} \frac{kT}{L_A^2}, \quad L_A = v_A^{1/3}. \quad (19)$$

Therefore, the calculations of this free energy contribution using the interfacial free energy consideration or a change in cohesive energy consideration are both equivalent. The magnitude of the Flory parameter χ_{AT} can be expected to be of the order of 0–1, depending on the compatibility between the hydrophobic A block and the nanotubes. This would roughly correspond to interfacial tension σ_{AT} values of 0 to 10 mN/m. Indeed, a value of about 1 for χ_{AT} has been suggested when polypropylene oxide is the hydrophobic block¹⁸ which in view of Eq. (19) would correspond to $\sigma_{AT} = 8.3$ mN/m at 300 K and $\sigma_{AT} = 10$ mN/m at 362 K. Since this is a positive free energy contribution, the smaller the magnitude of σ_{AT} , the larger the likelihood of solubilization of nanotubes within the block copolymer aggregates. In this paper, we will take the variable σ_{AT} as a parameter to perform the illustrative calculations, selecting $\sigma_{AT} = 0, 5$ and 10 mN/m, for the numerical simulations corresponding respectively to χ_{AT} values of about 0, 0.36 and 1.46. Clearly, such variations in the values for χ_{AT} or σ_{AT} can be achieved when the hydrophobic block of the copolymer is chosen to be different from polypropylene oxide.

III. COMPUTATIONAL RESULTS AND DISCUSSION

A. Estimation of molecular constants

Illustrative calculations have been carried out for polyethylene oxide-polypropylene oxide-polyethylene oxide (PEO-PPO-PEO, $E_X P_Y E_X$) symmetric triblock copolymers and PEO-PPO ($E_X P_Y$) diblock copolymers. The molecular volumes of the repeating units are estimated^{24–26} to be $v_A = 0.0965$ nm³ for propylene oxide and $v_B = 0.0646$ nm³ for ethylene oxide while the molecular volume of water is $v_W = 0.030$ nm³. The molecular weights of the PO and EO segments are 58 and 44 Daltons, respectively. The Flory interaction parameters χ_{AW} between PPO and water and χ_{BW} between PEO and water are estimated from available experimental activity data for polymer solutions.³⁴ These data display a concentration dependence for the interaction parameter as has been observed for a number of polymer solutions reflecting the inadequacies of the Flory theory. Since the hydrophilic domain of the aggregate is a dilute solution of PEO in water, χ_{BW} is taken from the dilute region of the activity data as equal to 0.2. The hydrophobic region of the aggregate is made of pure PPO and hence, χ_{AW} is taken from the concentrated region of the activity data as equal to 2.1. The corresponding value for the PPO-water interfacial tension is estimated using Eq. (6) to be $\sigma_{AW} = 25.9$ mN/m.

The interfacial tension between CNT and the hydrophobic block A is a key model parameter. The condition of $\sigma_{AT} < 0$ mN/m can occur if specific interactions are present between the nanotube surface and the A domain. In the most

general case, when nonspecific interactions dominate the polymer-nanotube interactions, we expect $\sigma_{AT} > 0$ mN/m. Such would be the case for the polypropylene oxide block selected in this work for illustrative calculations. In this work, the numerical calculations have been performed taking the interfacial tension between the nanotube surface and the A domain to be $\sigma_{AT} = 0, 5$ and 10 mN/m, respectively. The first choice implies that the block A-nanotube interactions are practically identical to the nanotube-nanotube interactions and this maximizes the probability of solubilization of nanotubes within the block copolymer micelles. The larger the magnitude of σ_{AT} , the greater the incompatibility between block A and the nanotube and consequently, the probability of solubilizing the nanotubes within the micelles decreases.

The free energy minimizations are carried out using the FORTRAN IMSL Subroutine ZXMWD which has been used in our previous theoretical studies dealing with surfactant micelles, mixed micelles, solubilization, and microemulsions.^{23,35} This minimization routine has performed robustly for all of these problems where the number of independent variables over which the minimization is performed has ranged between 1 and 5. In the present case, the minimization is done with respect to the two independent variables R and D . In nanotube-free solutions, the aggregate shape that yields the lowest standard state free energy change on aggregation is taken to be the equilibrium shape. If the standard state free energy change on the formation of the cylindrical aggregate solubilizing the nanotube is lower than that for the formation of the nanotube-free aggregate (sphere, cylinder, or lamella), then the solubilization of the nanotubes is considered favorable.

B. Aggregation behavior in nanotube-free solutions

The equilibrium aggregate morphologies predicted for the PEO-PPO-PEO triblock copolymers of various block compositions and molecular weights are summarized in Fig. 2. The calculated morphologies correspond to concentrations above the CMC and for dilute solutions, namely, no intermicelle interactions are considered. The CMCs for most of the block copolymers shown on Fig. 2 are well below experimentally measurable values and only for the block copolymers that are rich in polyethylene oxide, the CMCs become measurable. Each entry in Fig. 2 corresponds to a commercially available triblock copolymer. The entries in the figure are arranged such that the weight fraction of PEO in the block copolymer increases from top to bottom and the molecular weight of the block copolymer increases from left to right. The calculated results predict that at room temperature, in nanotube-free solutions, the block copolymers with 20 wt % PEO (L62, L72, L92, and L122) form lamellar aggregates, those with 30 wt % PEO form either lamellae (L63) or cylinders (P103 and P123) while molecules containing 40 wt % or more of PEO form spherical aggregates. Lamellar aggregates are favored when the ratio of PEO to PPO is small whereas spherical aggregates are favored when the PEO to PPO ratio is large.

For comparison, the equilibrium aggregate morphologies

L62 E ₂ P ₃₅ E ₆ 2523 Lamella	L72 E ₃ P ₃₅ E ₆ 2750 Lamella	L92 E ₃ P ₃₅ E ₆ 3650 Lamella	L122 E ₁₁ P ₃₅ E ₁₁ 5000 Lamella
L63 E ₃ P ₂₄ E ₅ 2616 Lamella			P103 E ₂ P ₁₀ E ₁₇ 4916 Cylinder
L64 E ₁₃ P ₃₀ E ₁₃ 2854 Sphere		P84 E ₁₃ P ₄₃ E ₁₉ 4123 Sphere	P104 E ₂ P ₁₀ E ₂₇ 5853 Sphere
P65 E ₁₉ P ₂₉ E ₁₉ 3325 Sphere	P75 E ₂₄ P ₃₁ E ₂₄ 4200 Sphere	P85 E ₂₃ P ₄₂ E ₂₃ 4568 Sphere	P105 E ₃ P ₁₀ E ₃₇ 6448 Sphere
	F77 E ₂₄ P ₃₁ E ₂₂ 6600 Sphere	F87 E ₃₁ P ₄₃ E ₆₁ 7700 Sphere	F127 E ₁₀ P ₃₄ E ₁₀₀ 12448 Sphere
F68 E ₇ P ₂₉ E ₇ 8429 Sphere		F88 E ₁₀ P ₃₀ E ₁₀₄ 11375 Sphere	F98 E ₁₁₉ P ₄₃ E ₁₁₈ 12949 Sphere
			F108 E ₁₃ P ₃₀ E ₁₃₃ 14554 Sphere

FIG. 2. Representation of equilibrium aggregate shapes for a number of PEO-PPO-PEO symmetric triblock copolymers, in nanotube-free aqueous solutions. For each block copolymer, the entries include the trade name, block composition (the number of ethylene oxide units E and propylene oxide units P), molecular weight and the equilibrium aggregate shape in dilute aqueous solution.

predicted for the PEO-PPO diblock copolymers of various compositions and molecular weights are summarized in Fig. 3. The block compositions and molecular weights are kept identical to those of the commercially available pluronic triblock copolymer and the entries in Fig. 3 are identified with the same trade names but with a prefix Di to indicate they are diblock copolymers. The general pattern of aggregation for the diblock copolymers follows the same trend as for the triblock copolymers. At room temperature, in nanotube-free solutions, the block copolymers with 20 wt % PEO (Di-L62, Di-L72, Di-L92, and Di-L122) form lamellar aggregates, Di-L63 with 30 wt % PEO forms cylinders, while the other

Di-L62 E ₂ P ₃₅ 2523 Lamella	Di-L72 E ₃ P ₃₅ 2750 Lamella	Di-L92 E ₃ P ₃₅ 3650 Lamella	Di-L122 E ₁₁ P ₃₅ 5000 Lamella
Di-L63 E ₃ P ₂₄ 2616 Cylinder			Di-P103 E ₂ P ₁₀ 4916 Sphere
Di-L64 E ₁₃ P ₃₀ 2854 Sphere		Di-P84 E ₁₃ P ₄₃ 4123 Sphere	Di-P104 E ₂ P ₁₀ 5853 Sphere
Di-P65 E ₁₉ P ₂₉ 3325 Sphere	Di-P75 E ₂₄ P ₃₁ 4200 Sphere	Di-P85 E ₂₃ P ₄₂ 4568 Sphere	Di-P105 E ₃ P ₁₀ 6448 Sphere
	Di-F77 E ₂₄ P ₃₁ 6600 Sphere	Di-F87 E ₃₁ P ₄₃ 7700 Sphere	Di-F127 E ₁₀ P ₃₄ 12448 Sphere
Di-F68 E ₇ P ₂₉ 8429 Sphere		Di-F88 E ₁₀ P ₃₀ 11375 Sphere	Di-F98 E ₁₁₉ P ₄₃ 12949 Sphere
			Di-F108 E ₁₃ P ₃₀ 14554 Sphere

FIG. 3. Representation of equilibrium aggregate shapes for a number of PEO-PPO diblock copolymers, in nanotube-free aqueous solutions. For each block copolymer, the entries include a molecular designation (which is the trade name of the triblock of the same molecular weight and composition preceded by the prefix Di), block composition (the number of ethylene oxide units E and propylene oxide units P), molecular weight and the equilibrium aggregate shape in dilute aqueous solution.

TABLE II. Predicted structural properties of nanotube-free aggregates (R is the size of the hydrophobic A domain, D is the size of the hydrophilic B domain, a is the area per molecule of the domain A-domain B interface, g is the aggregation number defined as the total number of molecules in a micelle in the case of sphere, the number of molecules per nm length in the case of cylinder and the number of molecules per nm² area in the case of lamella.)

Trade Name	Block copolymer description	R (nm)	D (nm)	a (nm ²)	g	Aggregate shape
L62	$E_6P_{35}E_6$	1.75	0.96	1.93	1.04	Lamella
L72	$E_6P_{38}E_6$	1.87	0.96	1.96	1.02	Lamella
L92	$E_8P_{50}E_8$	2.19	1.22	2.20	0.91	Lamella
L122	$E_{11}P_{69}E_{11}$	2.65	1.60	2.52	0.80	Lamella
L63	$E_9P_{32}E_9$	1.45	1.39	2.13	0.94	Lamella
P103	$E_{17}P_{60}E_{17}$	3.86	2.15	2.99	8.1	Cylinder
P123	$E_{20}P_{70}E_{20}$	4.21	2.44	3.21	8.3	Cylinder
L64	$E_{13}P_{30}E_{13}$	3.41	1.66	2.54	57	Sphere
P84	$E_{19}P_{43}E_{19}$	4.22	2.25	2.97	75	Sphere
P104	$E_{27}P_{61}E_{27}$	5.10	2.98	3.47	94	Sphere
P65	$E_{19}P_{29}E_{19}$	3.07	2.21	2.74	43	Sphere
P85	$E_{26}P_{40}E_{26}$	3.63	2.83	3.16	53	Sphere
F127	$E_{100}P_{64}E_{100}$	3.75	7.02	5.00	35	Sphere
F98	$E_{118}P_{45}E_{118}$	2.67	7.03	4.86	18	Sphere
F108	$E_{133}P_{50}E_{133}$	2.83	7.66	5.14	20	Sphere

diblocks with 30 or larger weight percent PEO form spheres. As for the triblocks, lamellar aggregates are favored when the ratio of PEO to PPO is small whereas spherical aggregates are favored when the PEO to PPO ratio is large.

Experimental phase diagrams for PEO-PPO-PEO block copolymers corroborate the aggregation patterns described above corresponding to room temperature and dilute solution conditions.³⁶ Similar experimental phase behavior data where the block copolymer composition is systematically changed over an extensive range are not available for other block copolymers. Limited data³⁷ available for polyethylene oxide-polydimethylsiloxane-polyethylene oxide (PEO-PDMS-PEO) are consistent with the above described dependence of the aggregate shape on block copolymer composition. Previous theoretical studies³⁸ on some diblock copolymers also predicted the same dependence of aggregate shapes on the block copolymer composition.

The predicted aggregation pattern as a function of the block copolymer composition follows the well-known geometrical packing concepts proposed for small surfactant aggregates based on the interplay between the interfacial free energy for the formation of the aggregate core-water interface and the free energy of surfactant head group repulsions.^{39,40} According to this molecular packing concept, when the head group repulsions are weak, lamellar aggregates are favored while for strong head group repulsions, spherical aggregates are formed. Cylindrical aggregates result for intermediate values of head group repulsions. In the block copolymer aggregates considered here, the free energy contributions associated with the hydrophilic B domain are analogous to the head group repulsions in classical surfactant micelles. Therefore the pattern of aggregation observed for increasing head group repulsions in surfactants is reproduced in the case of block copolymers with increasing size of the hydrophilic block.

The predicted hydrophobic and hydrophilic domain dimensions and the aggregation numbers for a number of PEO-PPO-PEO triblock copolymers are listed in Table II. The aggregation number g is the total number of block copolymer molecules in the micelle in the case of spheres, the number of block copolymer molecules per nm length in the case of cylinders, and the number of block copolymer molecules per nm² area in the case of lamellae. For a given size of the hydrophobic block, the hydrophobic domain size R increases from lamellar to cylindrical to spherical aggregate. In contrast, the hydrophilic domain size D is mainly controlled by the size of the B block and less dependent on the shape of the aggregate. The equilibrium area per molecule a increases from lamellar to cylindrical to spherical aggregate.

C. Predicted solubilization behavior of nanotubes in solutions of triblock copolymer

For each of the 21 triblock copolymers shown on Fig. 2, the standard state free energy change on the formation of a cylindrical aggregate solubilizing the nanotube has been computed and compared against the standard state free energy change on the formation of a nanotube-free aggregate (which can be a sphere, cylinder or a lamella, depending on the block copolymer). The difference between these two computed free energy changes on aggregation is plotted in Fig. 4 as a function of the diameter of the nanotube or nanotube cluster, for the model parameter $\sigma_{AT}=0$ mN/m for a number of triblock copolymers. If the difference between the two standard state free energy changes is negative, then it would imply the preferential formation of cylindrical aggregate solubilizing nanotubes compared to the formation of a nanotube-free aggregate. Of the 21 triblock copolymer molecules listed on Fig. 2, nine molecules (six of which are shown on Fig. 4) are found capable of solubilizing the CNTs

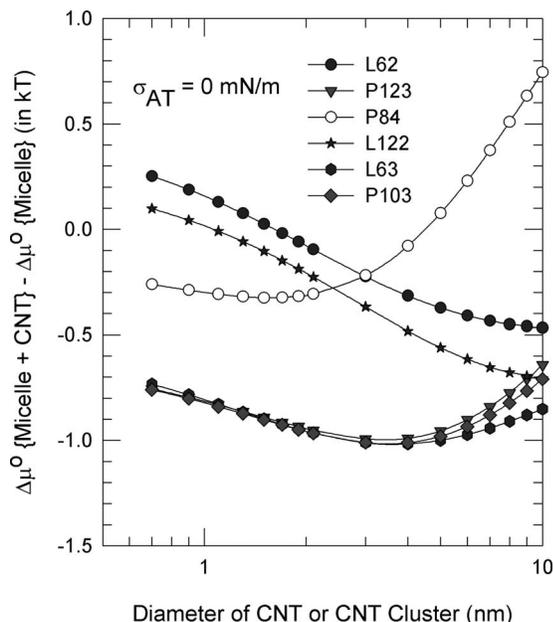


FIG. 4. The difference between the standard state free energy change on forming a cylindrical aggregate with solubilized nanotube and the standard state free energy change on forming a nanotube-free aggregate as a function of the diameter of the nanotube or nanotube cluster for the parameter $\sigma_{AT} = 0$ mN/m. In nanotube-free solutions, these molecules have preferred natural curvatures of sphere (P84), cylinder (P103 and P123) or lamella (L62, L122, and L63). Negative values correspond to preference for nanotube solubilized aggregates over nanotube-free aggregates.

or nanotube clusters. Of these, P103 and P123 are block copolymers whose natural curvature is a cylinder (as can be seen from Fig. 2), while L62, L72, L92, L122, and L63 have lamella as the natural curvature and L64 and P84 have sphere as the natural curvature. All these molecules occur contiguously in Fig. 2 corresponding to continually changing values for the molecular packing parameter. We can conclude that the molecules with cylinder as the natural curvature are the obvious choices to solubilize the nanotube or nanotube cluster while the molecules whose properties are close to the cylinder formers (as can be seen from their location on Fig. 2) are also capable of solubilizing the nanotubes or clusters, in spite of their natural curvature being spherical or lamellar. These conclusions are valid for all concentrations of block copolymers in dilute solutions since the CMCs for all of these block copolymers are negligibly small.

D. Prediction of size selectivity in solubilization

The diameter of the nanotube preferentially solubilized by the aggregates is also consistent with the natural curvature of the block copolymer. Those with sphere as the natural curvatures solubilize the smallest nanotubes; while those with lamella as the natural curvature solubilize the larger nanotube or more likely the nanotube cluster. The block copolymers with cylinder as the natural curvature preferentially solubilize nanotubes or clusters in the intermediate size range. For all block copolymers, the plotted difference in the free energy changes on aggregation show dependence on the size of the nanotube solubilized. Clearly, this implies that the solubilization process is size selective. The results imply that when the block copolymer solution is contacted with the

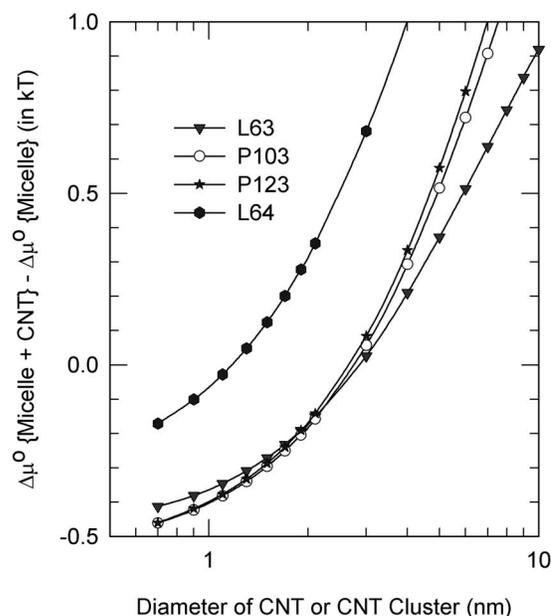


FIG. 5. The difference between the standard state free energy change on forming a cylindrical aggregate with solubilized nanotube and the standard state free energy change on forming a nanotube-free aggregate as a function of the diameter of the nanotube or nanotube cluster for the parameter $\sigma_{AT} = 5$ mN/m. In nanotube-free solutions, these molecules have preferred natural curvatures of sphere (P64), cylinder (P103 and P123) or lamella (L63). Negative values correspond to preference for nanotube solubilized aggregates.

nanotubes, first, the nanotubes for which the free energy change on solubilization is the lowest will be preferentially solubilized. Once all of these nanotubes are solubilized and if free block copolymer micelles are still available, then nanotubes with a higher free energy change on solubilization will be taken up by the micelles. Further, there is a cutoff value for the diameter of the nanotube or nanotube cluster that can be solubilized by a given block copolymer. In this manner a size dependent extraction process for the uptake of nanotubes into micelles can be developed.

E. Impact of nanotube-domain A interactions

As mentioned earlier, an increase in the magnitude of σ_{AT} indicates the adhesive attractions between the nanotube and the hydrophobic A block are weaker than the cohesive nanotube-nanotube attractions. Correspondingly, one would expect a decrease in the probability of solubilization. The solubilization of nanotubes is examined in Figs. 5 and 6 for larger values of the model parameter $\sigma_{AT} = 5$ and 10 mN/m, respectively. Predicted results show that of the 21 triblock copolymer molecules, only four molecules are capable of solubilizing the nanotubes or nanotube clusters when $\sigma_{AT} = 5$ mN/m. These include the lamella former L63, the cylinder formers P103 and P123 and the sphere former L64 (Fig. 5). When $\sigma_{AT} = 10$ mN/m, only the lamella former L63 and the two cylinder formers P103 and P123 are found to solubilize the nanotubes (Fig. 6). The results shown on Figs. 4–6 are independent of the concentration of the block copolymer and are valid for dilute solutions. In all cases, the solubilization is size specific. For the larger values of σ_{AT} ,

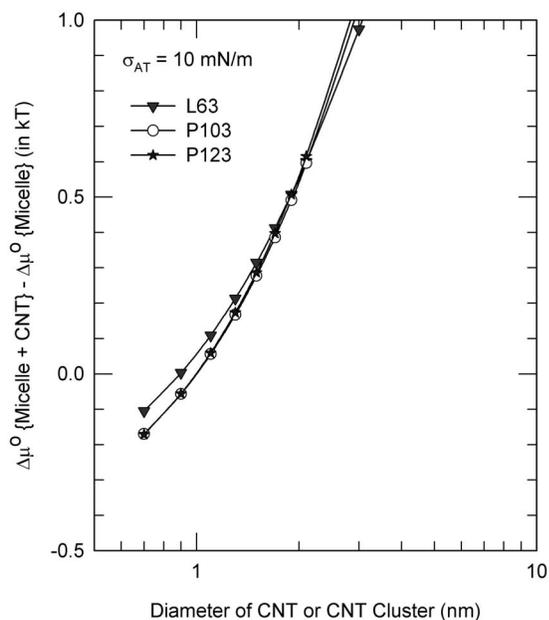


FIG. 6. The difference between the standard state free energy change on forming a cylindrical aggregate with solubilized nanotube and the standard state free energy change on forming a nanotube-free aggregate as a function of the diameter of the nanotube or nanotube cluster for the parameter $\sigma_{AT} = 10$ mN/m. In nanotube-free solutions, these molecules have preferred natural curvatures of cylinder (P103 and P123) or lamella (L63). Negative values correspond to preference for nanotube solubilized aggregates.

the smallest nanotube is always preferentially solubilized compared to the larger diameter tubes (Figs. 5 and 6).

All of the PEO-PPO-PEO triblock copolymers and the PEO-PPO diblock copolymers capable of solubilizing nanotubes are shown on Fig. 7 for different values of the domain A-nanotube interfacial tension σ_{AT} . The figure also indicates the shape of the aggregates formed by these block copolymers in nanotube-free solutions. For both triblock and diblock copolymers, the number of molecules that are capable of solubilizing the nanotubes decreases as the magnitude of σ_{AT} is increased. For $\sigma_{AT} > 14$ mN/m, none of the PEO-PPO-PEO triblocks solubilize any nanotubes and for $\sigma_{AT} > 16$ mN/m, none of the PEO-PPO diblocks solubilize any of the nanotubes. In all cases, as σ_{AT} increases from 0, the block copolymers showing a natural preference for cylinders and other block copolymers whose properties are closest to the cylinder formers are the molecules most likely to solubilize the nanotubes.

F. Influence of various free energy contributions on solubilization of nanotubes

First we examine how the size selectivity of solubilization is influenced by various free energy contributions. All but one of the free energy contributions controlling the formation of cylindrical aggregates solubilizing nanotubes are shown on Fig. 8 for the P103 block copolymer (whose natural curvature is cylinder) corresponding to the model parameter $\sigma_{AT} = 5$ mN/m. These contributions are essentially similar to those associated with the formation of nanotube-free aggregates.^{24–26} Not shown on Fig. 8 is the large negative contribution associated with the transfer of the hydrophobic

PEO-PPO-PEO Triblock Copolymers									
0 mN/m	L 62	L 72	L 92	L 122	L 63	P 103	P 123	L 64	P 84
5 mN/m					L 63	P 103	P 123	L 64	
10 mN/m					L 63	P 103	P 123		
13 mN/m							P 123		
PEO-PPO Diblock Copolymers									
0 mN/m	Di-L 62	Di-L 72	Di-L 92	Di-L 122	Di-L 63	Di-P 103	Di-P 123	Di-L 64	
5 mN/m			Di-L 92	Di-L 122	Di-L 63	Di-P 103			
10 mN/m				Di-L 122	Di-L 63				
15 mN/m				Di-L 122					

FIG. 7. The influence of the nanotube-domain A interfacial tension parameter σ_{AT} on the solubilization of nanotubes. For four different values of σ_{AT} , the triblock copolymers capable of solubilizing the nanotubes are indicated on the upper part of the figure and the diblock copolymers capable of solubilizing the nanotubes are shown on the lower part of the figure. For the triblocks, P103 and P123 are cylinder formers while the molecules to the left are lamella formers and those on the right are sphere formers. Similarly for diblocks, L63 is the cylinder former and those to its left are lamella formers and those on the right are sphere formers.

A block from a singly dispersed molecule to an aggregate. Indeed, this is the primary contribution driving the self-assembly to occur as a spontaneous process. All of the remaining free energy contributions are shown on the figure and are positive. Of these, the localization and backfolding contributions are practically independent of the size of the solubilized nanotube or cluster; hence, they do not affect the size selectivity of solubilization. The interfacial free energy at the domain A-domain B interface decreases strongly with increasing nanotube size while the A block deformation free energy also shows a weak decrease with increasing nanotube size. Consequently, these contributions favor the solubilization of larger diameter tubes or clusters. In contrast, the free energy contributions arising from the dilution and deformation of the B block and the interfacial free energy at the nanotube-domain A interface, all increase the magnitude with increasing diameter of the nanotube or cluster. Therefore, these contributions favor the solubilization of the smaller diameter nanotubes.

Next we compare how the various free energy contributions affect the solubilization of a given nanotube for block copolymer molecules with different natural curvatures. The

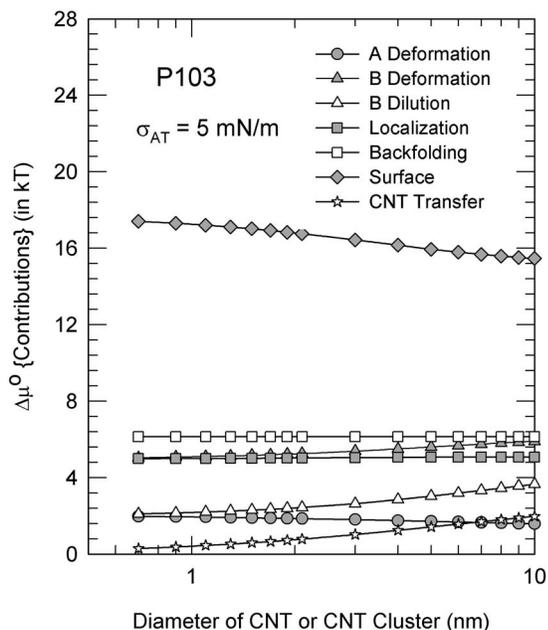


FIG. 8. The contributions to the standard state free energy change on forming a cylindrical aggregate with solubilized nanotube, for the P103 block copolymer as a function of the diameter of the nanotube or nanotube cluster, for the parameter $\sigma_{AT}=5$ mN/m.

calculated difference between the free energy change on formation of a cylindrical micelle incorporating the nanotube, and that for the formation of a nanotube-free micelle of optimal shape (lamella, cylinder, or sphere), $(\Delta\mu_g^0/kT)_{\text{With CNT}} - (\Delta\mu_g^0/kT)_{\text{No CNT}}$, are listed on Table III, in terms of various free energy contributions to aggregation, for three different values of σ_{AT} . The three block copolymers chosen are the lamella former (L122), the cylinder former (P123), and the sphere former (L64) and the nanotube solubilized is taken to be 1.1 nm in diameter. For all block copolymers, the increase in σ_{AT} increases in magnitude of the free energy of formation of the domain A-nanotube interface making solubilization of nanotubes unfavorable. Although this is the largest contribution unfavorable to the solubilization of nanotubes, the A block deformation, the B block deformation and the B block dilution free energy contributions also increase making the solubilization of the nanotubes unfavorable. For all block

copolymers, the free energy of formation of the domain A-domain B interface decreases favoring the solubilization of nanotubes. However, the increase in free energy contributions always dominates over the decrease in free energy contributions and as a result, the increase in σ_{AT} diminishes the capability of the block copolymers to solubilize the nanotubes.

As mentioned earlier, for $\sigma_{AT} > 14$ mN/m, none of the PEO-PPO-PEO triblocks solubilize any nanotubes and for $\sigma_{AT} > 16$ mN/m, none of the PEO-PPO diblocks solubilize any of the nanotubes. Obviously, when the adhesive interactions of the A domain with the nanotube becomes much weaker than the cohesive interactions between the nanotubes, the solubilization is not favored at all. One can conceive of ways to lower σ_{AT} and promote the solubilization of nanotubes into the micelles. One approach is the surface functionalization of the nanotube to cause a reduction in σ_{AT} , including the possibility of a negative σ_{AT} . This is not a favored approach since it requires covalent modifications to the nanotube. The preferred alternative is to change the hydrophobic block A from polypropylene oxide to other hydrophobic polymers for which σ_{AT} will be smaller.

G. Microstructural features of aggregates on solubilization of nanotubes

The microstructural features of the cylindrical aggregates solubilizing the nanotubes are shown on Figs. 9–11 for three block copolymers: The lamella former L63, the cylinder former P103 and the sphere former L64. As discussed previously, their structural features in nanotube-free solutions are listed in Table II. The dimensions R and D of the hydrophobic and hydrophilic domains are plotted on Fig. 9. Since the lamellar aggregate of L63 in the nanotube-free solution becomes a cylinder solubilizing the nanotubes, the size R is increased compared to the nanotube-free solution. Similarly, the spherical aggregate of L64 in the nanotube-free solution becomes a cylinder solubilizing the nanotubes and therefore the size R is decreased compared to the nanotube-free solution. For P103, since the shape remains cylindrical always, the size R is not very much altered. For all three block copolymers, the size R of the A domain decreases significantly with increasing diameter of the solubilized nano-

TABLE III. Influence of various free energy contributions on the solubilization of CNT. (The calculated results are for a single wall CNT with a diameter of 1.1 nm.)

$(\Delta\mu_g^0/kT)_{\text{With CNT}} - (\Delta\mu_g^0/kT)_{\text{No CNT}}$	L122 (Lamella preferring)			P103 (Cylinder preferring)			L64 (Sphere preferring)		
	σ_{AT} in mN/m								
	0	5	10	0	5	10	0	5	10
Block A dilution	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Block A deformation	0.73	0.85	0.96	-0.66	-0.55	-0.44	-1.17	-1.04	-0.92
Domain A-domain B interface	0.89	0.59	0.33	-0.72	-1.12	-1.49	-1.09	-1.60	-2.03
Block B dilution	-1.20	-1.12	-1.04	0.29	0.45	0.59	1.11	1.31	1.49
Block B deformation	-0.42	-0.36	-0.30	0.20	0.32	0.43	0.57	0.73	0.88
Localization	0.00	0.02	0.05	0.04	0.07	0.10	-0.04	0.00	0.04
Backfolding	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Domain A-nanotube interface	0.00	0.34	0.66	0.00	0.45	0.86	0.00	0.57	1.08

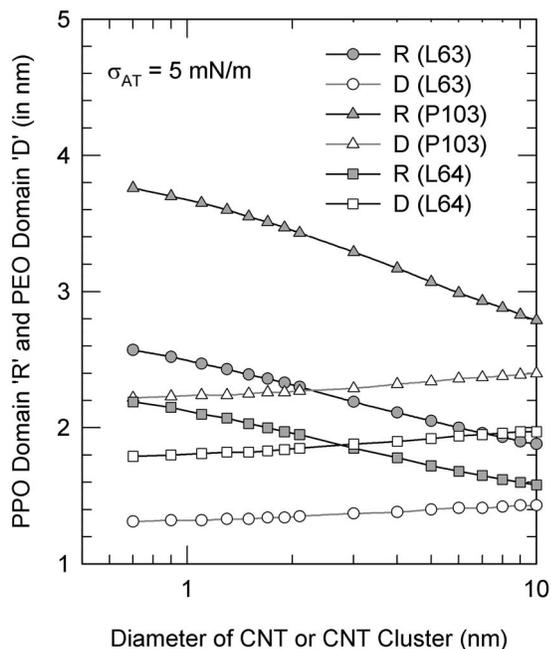


FIG. 9. Dimensions of the hydrophobic domain R and the hydrophilic domain D for nanotube solubilized cylindrical aggregates for the parameter $\sigma_{AT}=5$ mN/m. In nanotube-free solutions, L64 forms spheres, P103 forms cylinders, and L63 forms lamella.

tube or cluster. This is because of the decreasing curvature when the diameter of the solubilized nanotube or cluster increases and is entirely consistent with the similar decrease in R seen when the aggregate shape changes from spherical to cylindrical to lamellar, in the order of decreasing curvature. For all three block copolymers, the size D of the B domain increases slightly with increasing diameter of the solubilized nanotube or cluster. This is again consistent with the finding

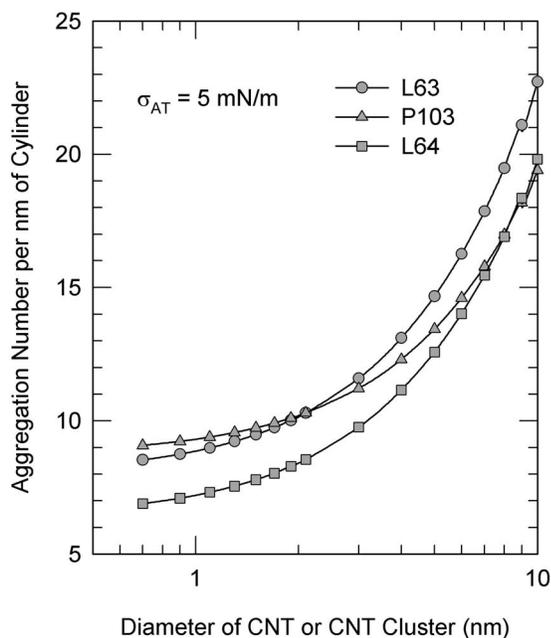


FIG. 10. Aggregation number g per nm length for the nanotube solubilized cylindrical aggregates corresponding to $\sigma_{AT}=5$ mN/m. In nanotube-free solutions, L64 forms spheres, P103 forms cylinders, and L63 forms lamella.

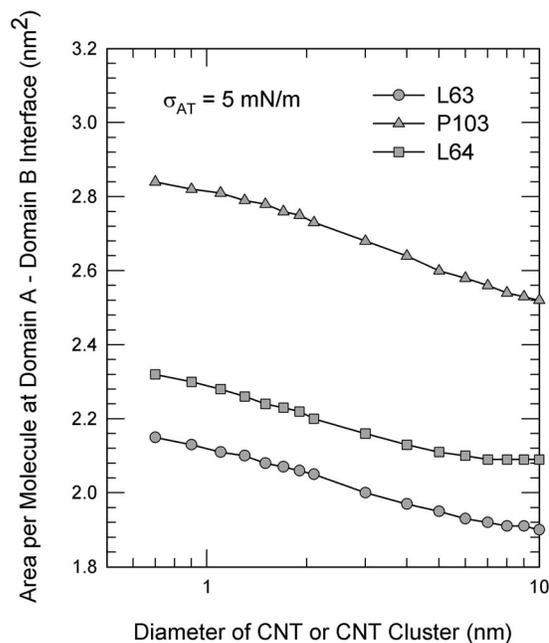


FIG. 11. The interfacial area of the aggregate per block copolymer molecule at the hydrophobic domain A -hydrophilic domain B interface, for the nanotube solubilized cylindrical aggregates, corresponding to $\sigma_{AT}=5$ mN/m. In nanotube-free solutions, L64 forms spheres, P103 forms cylinders, and L63 forms lamella.

that the size D is practically unaffected by the shape of the aggregate and is primarily controlled by the size of the block B .

The number of block copolymer molecules per nm length of the cylindrical aggregate is shown on Fig. 10 for all three block copolymers: the lamella former L63, the cylinder former P103 and the sphere former L64. In all cases, the aggregation number increases as the diameter of the solubilized nanotube increases. This can be anticipated from molecular packing requirements since the area of the aggregate per unit length increases when the diameter of the solubilized nanotube or cluster increases. For a given molecular packing, the increased area will call for an increased number of molecules to occupy the space.

The area per molecule of the aggregate at the domain A -domain B interface is plotted on Fig. 11 for all three block copolymer molecules: the lamella former L63, the cylinder former P103 and the sphere former L64. In all cases, this area per molecule decreases with increasing diameter of the solubilized nanotube. This is because of the decreasing curvature when the diameter of the solubilized nanotube or cluster increases and is entirely consistent with the similar decrease in area per molecule seen when the aggregate shape changes from spherical to cylindrical to lamellar, in the order of decreasing curvature.

IV. CONCLUSIONS

We have developed a simple molecular scale theory to describe the solubilization of CNTs or nanotube clusters by amphiphilic block copolymers in aqueous solutions. The theory is applicable to both single wall and multiwall nanotubes since the physics of the tubes is represented by a single

interfacial tension parameter, σ_{AT} . Numerical simulations based on the theory have been carried out for the commercially available family of symmetric triblock copolymers, PEO-PPO-PEO and also for diblock copolymers of PEO-PPO having the same molecular weight and block composition as the triblock copolymers. The theoretical predictions show that it is possible to solubilize nanotubes or nanotube clusters to generate a thermodynamically stable aqueous nanocolloidal solution, in contrast to the aqueous dispersions of limited kinetic stability generated by simple adsorption of surfactants and polymers on the nanotube. The calculated results show that the block copolymer molecules with cylinder as the natural curvature are the obvious choices to solubilize the nanotube or nanotube cluster while the molecules whose properties are close to the cylinder formers are also capable of solubilizing the nanotubes, in spite of their natural curvature being spherical or lamellar. Increasing magnitude of the interfacial tension parameter σ_{AT} (characterizing the difference between the adhesive energy between the nanotube and the A block and the cohesive energy among the nanotubes) decreases the propensity of the block copolymers to solubilize the nanotubes. However, σ_{AT} can be potentially manipulated by the choice of the hydrophobic block of the block copolymer, thus allowing a variety of diblock and triblock copolymers to solubilize nanotubes and creating a thermodynamically stable nanocolloidal solution. Most interestingly, the solubilization shows size selectivity that can be exploited for a potential nanotube size fractionation process.

ACKNOWLEDGMENTS

The research was supported by an In-House Laboratory Independent Research (ILIR) award from the Natick Soldier Research, Development and Engineering Center.

¹W. A. de Heer, MRS Bull. **29**, 281 (2004).

²M. J. O'Connell, P. Boul, L. M. Ericson, C. Huffman, Y. Wang, E. Haroz, C. Kuper, J. Tour, K. D. Ausman, and R. E. Smalley, *Chem. Phys. Lett.* **342**, 265 (2001).

³V. C. Moore, M. S. Strano, E. H. Haroz, R. H. Hauge, R. E. Smalley, J. Schmidt, and Y. Talmon, *Nano Lett.* **3**, 1379 (2003).

⁴M. Moniruzzaman and K. I. Winey, *Macromolecules* **39**, 5194 (2006).

⁵N. Grossiord, J. Loos, O. Regev, and C. E. Koning, *Chem. Mater.* **18**, 1089 (2006).

⁶R. Bandyopadhyaya, E. Nativ-Roth, O. Regev, and R. Yerushalmi-Rozen, *Nano Lett.* **2**, 25 (2002).

⁷R. Shvartzman-Cohen, E. Nativ-Roth, E. Baskaran, Y. Levi-Kalishman, I. Szeleifer, and R. Yerushalmi-Rozen, *J. Am. Chem. Soc.* **126**, 14850 (2004).

⁸R. S. Shvartzman-Cohen, Y. Levi-Kalishman, E. Nativ-Roth, and R. Yerushalmi-Rozen, *Langmuir* **20**, 6085 (2004).

⁹M. F. Islam, E. Rojas, D. M. Bergey, A. T. Johnson, and A. G. Yodh, *Nano Lett.* **3**, 269 (2003).

¹⁰Y. Kang and T. A. Taton, *J. Am. Chem. Soc.* **125**, 5650 (2003).

¹¹S. S. Karajanagi, H. Yang, P. Asuri, E. Sellitto, J. S. Dordick, and R. S. Kane, *Langmuir* **22**, 1392 (2006).

¹²S. T. Lin, K. L. Wei, T. M. Lee, K. C. Chiou, and J. J. Lin, *Nanotechnology* **17**, 3197 (2006).

¹³O. Matarredona, H. Rhoads, Z. Li, J. H. Harwell, L. Balzano, and D. E. Resasco, *J. Phys. Chem. B* **107**, 13357 (2003).

¹⁴H. Shin, B. G. Min, W. Jeong, and C. Park, *Macromol. Rapid Commun.* **26**, 1451.

¹⁵W. Wenseleers, I. I. Vlasov, E. Goovaerts, E. D. Obraztsova, A. S. Lobach, and A. Bouwen, *Adv. Funct. Mater.* **14**, 1105 (2004).

¹⁶Y. Wu, J. S. Hudson, Q. Lu, J. M. Moore, A. S. Mount, A. M. Rao, E. Alexov, and P. C. Ke, *J. Phys. Chem. B* **110**, 2475 (2006).

¹⁷M. S. Arnold, M. O. Guler, M. C. Hersam, and S. I. Stupp, *Langmuir* **21**, 4705 (2005).

¹⁸E. Nativ-Roth, R. Shvartzman-Cohen, C. Bounioux, M. Florent, D. Zhang, I. Szeleifer, and R. Yerushalmi-Rozen, *Macromolecules* **40**, 3676 (2007).

¹⁹Y. Liu, P. Liang, H. Y. Zhang, and D. S. Guo, *Small* **2**, 874 (2006).

²⁰H. Kitano, K. Tachimoto, T. N. Hirabayashi, and H. Shinohara, *Macromol. Chem. Phys.* **205**, 2064 (2004).

²¹S. Wang, E. S. Humphreys, S. Y. Chung, D. F. Delduco, S. R. Lustig, H. Wang, K. N. Parker, N. W. Rizzo, S. Subramoney, Y. M. Chaing, and A. Jagota, *Nature Mater.* **2**, 196 (2003).

²²V. V. Didenko, V. C. Moore, D. S. Baskin, and R. E. Smalley, *Nano Lett.* **5**, 1563 (2005).

²³R. Nagarajan and E. Ruckenstein, *Langmuir* **7**, 2934 (1991).

²⁴R. Nagarajan and K. Ganesh, *J. Chem. Phys.* **90**, 5843 (1989).

²⁵R. Nagarajan and K. Ganesh, *Macromolecules* **22**, 4312 (1989).

²⁶R. Nagarajan, *Colloids Surf., B* **16**, 55 (1999).

²⁷P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).

²⁸P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, 1962).

²⁹A. N. Semenov, *Sov. Phys. JETP* **61**, 733 (1985).

³⁰W. H. Stockmayer, *J. Polym. Sci.* **15**, 595 (1955).

³¹R. Defay, I. Prigogine, A. Bellemans, and D. H. Everett, *Surface Tension and Adsorption* (Wiley, New York, 1966).

³²K. S. Siow and D. Patterson, *J. Phys. Chem.* **77**, 356 (1973).

³³H. Jacobson and W. H. Stockmayer, *J. Chem. Phys.* **18**, 1600 (1950).

³⁴G. N. Malcolm and J. S. Rowlinson, *Trans. Faraday Soc.* **53**, 921 (1957).

³⁵R. Nagarajan and E. Ruckenstein, *Langmuir* **16**, 6400 (2000).

³⁶B. Chu and Z. Zhou, in *Nonionic Surfactants. Polyoxyalkylene Block Copolymers*, edited by V. M. Nace (Dekker, New York, 1996), Chap. 3.

³⁷J. Yang, G. Wegner, and R. Koningsveld, *Colloid Polym. Sci.* **270**, 1080 (1992).

³⁸R. Nagarajan, in *Solvents and Self-Organization of Polymers*, NATO Advanced Studies Institute Series Vol. 327, edited by S. E. Webber, P. Munk, and Z. Tuzar (Kluwer Academic Publishers, Dordrecht, The Netherlands, 1996) p. 121.

³⁹J. N. Israelachvili, D. J. Mitchell, and B. W. Ninham, *J. Chem. Soc., Faraday Trans.* **72**, 1525 (1976).

⁴⁰R. Nagarajan, *Langmuir* **18**, 31 (2002).