Threading-unthreading equilibrium in solution of molecular nanotubes and linear flexible polymer chains

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Using the Flory–Huggins lattice model, we investigate the threading-unthreading equilibrium in a solution of linear flexible polymer chains and *molecular nanotubes* formed by covalently bonding the ringlike molecules, such as cyclodextrins (CDs). It is found that the threading-unthreading equilibrium depends on the temperature and the molar concentrations of the ringlike molecules and polymer chain segments but is independent of the polymer chain length, which agrees with the experimental observations. By fitting the experimental data of α-CD and poly(ethylene glycol) (PEG), the inclusion energy between α-CD and PEG, which includes the conformation energy loss of PEG resulted from the inclusion, is calculated to be ~ -20.45 kJ/mol per PEG unit. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1851982]

I. INTRODUCTION

Ringlike molecules, such as cyclodextrins (CDs) (a series of cyclic oligosaccharides consisting of six to eight glucose units, called α-, β-, and γ-CDs, respectively), have received great interest from scientists of various disciplines because of the peculiar form and the inclusion property of the cavity.[1,2] Harada *et al.* have reported that CDs can be threaded by more than ten kinds of linear polymers, such as poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG), etc., and form rodlike inclusion complexes called molecular necklaces, in which the CDs form a laterally stacked *molecular nanotube* via hydrogen bonding.[3–6] It has also been reported that β-CD and a conductive polymer, polyaniline, can form an inclusion complex, i.e., a molecular wire insulated by β-CD.[7]

Through the threaded CDs (molecular necklace), Harada *et al.* have synthesized a molecular nanotube by covalently bonding the CDs laterally.[8] Recently, the inclusion-dissociation (or threading-unthreading) equilibrium between molecular nanotubes and polymer chains has also been studied experimentally by Saito *et al.*[9]

As the inner diameters of the CDs and the molecular nanotube are small, a polymer chain included in a molecular nanotube is supposed to be in an extended conformation with no degree of freedom other than the sliding motion along the tube axis. Therefore, the included polymer chain loses its conformational entropy and thus the conformational energy. Therefore, the inclusion of a polymer chain in a molecular nanotube is entropically unfavorable and is driven by the competing hydrophobic inclusion interaction energy between the polymer chain and the cavity of the molecular nanotube. In order to make the threading process occur spontaneously, the drastic loss of the chain conformation entropy accompanied with the inclusion of the long polymer chain must be compensated by the gain of the attractive interaction energy between the polymer chain and the cavity. In other words, by increasing the temperature the polymer chain dissociates from the molecular nanotubes and recovers its intrinsic conformational entropy. Therefore, interesting temperature dependence of the inclusion-dissociation behavior can be expected.

The peculiar threading behavior in the complex formation between molecular nanotubes and linear polymer chains has been investigated by using the Flory–Huggins lattice model.[10,11] However, the obvious disadvantage of the molecular nanotube model used in Refs. 10 and 11 is that the nanotubes are phantom molecules, i.e., they have no excluded volume and do not occupy lattice site. Therefore, their configurational entropy has not been accounted for and their volume fraction cannot be defined. In fact, the excluded volume of the molecular nanotubes is not small compared to the size of chain segment and thus it is not always reasonable to neglect it.

The main objective of this work is to investigate theoretically the threading-unthreading equilibrium behavior between molecular nanotubes and linear polymer chains in solution.

The paper is organized as follows: In Sec. II, detailed theoretical derivations about the ternary solution of molecular nanotubes with fixed length, polymers, and solvents are presented. In Sec. III, the theory is tested by the experimental data existing in the literatures. Besides that, the difference between our theory and the previous theory is also discussed. In Sec. IV, the main conclusions drawn from the present investigation are given and the problems deserving further study are also suggested.

II. THEORY

The lattice model adopted in this work is schematically sketched in Fig. 1. We assume that the ringlike molecules are laterally fused together via covalent bonds to form molecular

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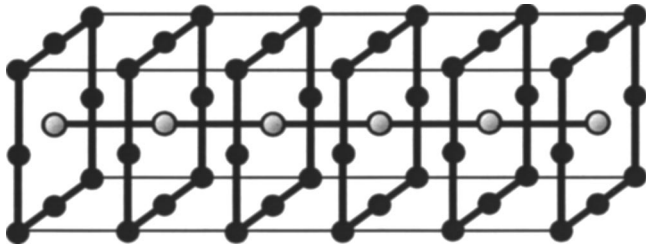
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FIG. 1. The schematic drawing of a molecular nanotube on a simple cubic lattice, formed by laterally fusing the ringlike molecules and threaded by a polymer linear chain.

nanotubes with fixed length of x (see Fig. 2). The polymer chain segments intercalated in the channel of the molecular nanotubes are highly constrained and can only take the *trans*-conformation, while the segments outside the channel can realize their free conformations. We further assume that each ringlike molecule occupies n_c lattice sites (for the cubic lattice model shown in Fig. 1, $n_c=8$) and is completely rigid with no internal degree of conformational freedom. The system is composed of n_x molecular nanotubes of length x (the total segment number of ringlike molecules is $N_t=xn_cn_x$) and n_p polymer chains of length y (the total number of polymer segments is $N_p=yn_p$). The rest of the lattices are occupied by N_s solvent molecules. Therefore, the total number of the lattices in the system is $\Omega=N_t+N_s+N_p$.

   In order to calculate the configurational entropy, we first calculate the number of ways of inserting the molecular nanotubes into the lattices. Following the basic procedure of Ref. 12, we call the ringlike (CD) molecules as the *submolecules* of the molecular nanotubes. We assume that j molecular nanotubes have been inserted into the lattices. Then, the number of ways of inserting the $(j+1)$th molecular nanotube of length x into the lattices can be calculated as follows. It is obvious that the number of ways of inserting the first segment of the first submolecule in the $(j+1)$th molecular nanotube of length x is $(\Omega-jn_cx)$. It is a bit tricky to insert the rest n_c-1 segments of the first submolecule into the lattices. In order to do so, we need an array of n_c-1 lattices that fits into the rigid ringlike submolecule.[12] Assuming that the submolecules and the vacancies are distributed randomly, the probability that the next lattice in the array is unoccupied is proportional to the mole fraction of the vacancies available,
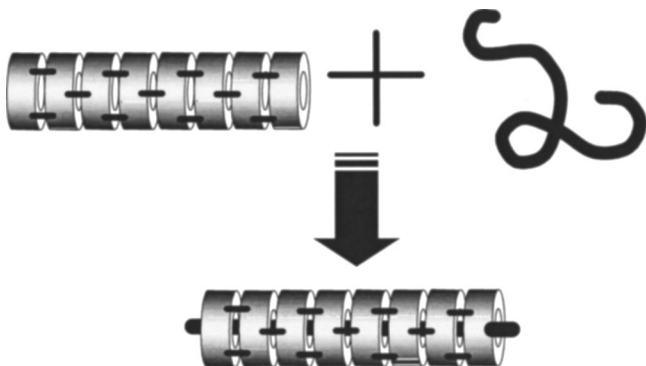

FIG. 2. The schematic drawing of the threading-unthreading transition of the molecular nanotube formed by covalently bonding the ringlike molecules and then threaded by a linear polymer chain.

i.e., $(\Omega-jn_cx)/[\Omega-jx(n_c-1)]$. Here we should mention that, as has already been indicated by Flory,[12] the mole fraction required here follows immediately from the consideration of the vacancies and the *rigid object* as two sets of particles arranged in random linear sequences, and the probability that any particle of the arrangement is succeeded in a given direction by a vacancy obviously equal to the mole fraction of the vacancies. Therefore, the probability of placing the rest segments of the first submolecule of the nanotube with stacking length x can be written as $\{(\Omega-jn_cx)/[\Omega-jx(n_c-1)]\}^{n_c-1}$. Now, we consider the insertion of the second submolecule. Noticing that the second submolecule is laterally attached to the first submolecule, the probability of inserting the first segment of the second submolecule in the molecular nanotube is $(\Omega-jn_cx)/\Omega$, and the probability of inserting the rest n_c-1 segments of the second submolecule can be calculated following the same procedure as discussed previously. In this way, we obtain the ways of inserting the $(j+1)$th molecular nanotube of length x as the following:

$$
\begin{aligned}
v_{j+1} &= z\cdot(\Omega-jn_cx)\\
&\times\left(\frac{\Omega-jn_cx}{\Omega}\right)^{x-1}\left[\frac{\Omega-jn_cx}{\Omega-jx(n_c-1)}\right]^{(n_c-1)x}\\
&= \frac{z}{\Omega^{(x-1)}}\frac{(\Omega-jn_cx)!}{[\Omega-(j+1)n_cx]!}\cdot\frac{[\Omega-(j+1)x(n_c-1)]!}{[\Omega-jx(n_c-1)]!},
\end{aligned}
$$
(1)

where z is the lattice coordination number. In obtaining the second equality, the following approximation has been used:

$$
\begin{aligned}
a^b &= \underbrace{a\ldots a}_{b} \approx a(a-1)(a-2)(a-3)\cdots(a-b+1)\\
&= \frac{a!}{(a-b)!},
\end{aligned}
$$
(2)

with $a\gg b$. Therefore, the total number of ways of inserting all n_x molecular nanotubes of length x can be finally written as

$$
\begin{aligned}
\Xi_t &= \frac{1}{n_x!}\prod_{j=0}^{n_x-1}v_{j+1}\\
&= \frac{z^{n_x}}{\Omega^{n_x(x-1)}}\frac{1}{n_x!}\prod_{j=0}^{n_x-1}\frac{(\Omega-jn_cx)!}{[\Omega-(j+1)n_cx]!}\frac{[\Omega-(j+1)(n_c-1)x]!}{[\Omega-j(n_c-1)x]!}\\
&= \frac{z^{n_x}}{\Omega^{n_x(x-1)}}\frac{[\Omega-n_x(n_c-1)x]!}{(\Omega-xn_xn_c)!\,n_x!}.
\end{aligned}
$$
(3)

   Now, we start to insert the polymer chains. We first assume that j polymer chains of length y have already been inserted into the system. Thus, the number of ways of inserting the first segment of the $(j+1)$th polymer chain into the system is $(\Omega-N_t-jn_py)$. Assuming that the fraction of segments of the $(j+1)$th chain included in the molecular nanotube is f_{j+1}, the rest of the chain segments should be divided

into two parts: one part of the segments, $f_{j+1}y$, is inside the molecular nanotubes and the other part of the segments, $(1-f_{j+1})y$, is outside the molecular nanotubes. The probability of inserting a segment into the molecular nanotube is $(N_t/n_c - y\Sigma_{m=1}^j f_m)/\Omega$ and that of inserting a segment outside the molecular nanotube is $[\Omega - N_t(1+1/n_c) - y\Sigma_{m=1}^j(1-f_m)]/\Omega$. Therefore, the number of ways of inserting the $(j+1)$th polymer chain can be written as

$$v_{j+1} = \frac{\left(N_c/n_c - y\sum_{m=1}^j f_m\right)^{f_{j+1}y}}{\Omega^{f_{j+1}y}}(z-1)^{(1-f_{j+1})y}\frac{\left[\Omega - N_c(1+1/n_c) - y\sum_{m=1}^j (1-f_m)\right]^{(1-f_{j+1})y}}{\Omega^{(1-f_{j+1})y}}$$

$$= \frac{(z-1)^{(1-f_{j+1})y}}{\Omega^y}\frac{\left(N_c/n_c - y\sum_{m=1}^j f_m\right)!\left[\Omega - N_c(1+1/n_c) - y\sum_{m=1}^j (1-f_m)\right]!}{\left(N_c/n_c - y\sum_{m=1}^{j+1} f_m\right)!\left[\Omega - N_c(1+1/n_c) - y\sum_{m=1}^{j+1} (1-f_m)\right]!}. \tag{4}$$

Thus, the number of ways of inserting all n_p polymer chains is

$$\Xi_p = \frac{1}{n_p!\, 2^{n_p}}\left(\frac{yn_p}{fyn_p}\right)^{n_p-1}\prod_{j=0}^{n_p} v_{j+1}$$

$$= \frac{(z-1)^{n_p - y\sum_{j=t}^{n_p} f_j}}{n_p!\, 2^{n_p}\Omega^{n_p y}}\frac{(n_p y)!}{(fn_p y)!\,[(1-f)n_p y]!}$$

$$\times \frac{(xN_t)!}{(xN_t - yfn_p)!}\frac{[\Omega - xN_t(1+1/n_c)]!}{(N_s - xN_t + yfn_p)!}. \tag{5}$$

In obtaining the above result, the relations of $y\Sigma_{j=1}^{n_p}f_j = fyn_p$, with f as the average fraction of threaded polymer segments, and $N_c/n_c = xN_t$ have been used. In addition to that, the term of 2^{n_p} accounts for reverse symmetry of the polymer chains and the term of $\binom{yn_p}{fyn_p}$ accounts for the ways of randomly selecting fyn_p segments out of yn_p of polymer segments.[13] Finally, the total number of ways of inserting all the molecular nanotubes and the polymer chains is written as

$$\Xi = \Xi_t\Xi_p = \frac{z^{N_t}(z-1)^{n_p - fyn_p}}{2^{n_p}\Omega^{n_p y + N_t(x-1)}}\frac{(\Omega - (n_c-1)xN_t)!}{n_p!\,(\Omega - n_c xN_t)!\, N_t!}$$

$$\cdot \frac{(n_p y)!}{(fn_p y)!\,[(1-f)n_p y]!}\cdot\frac{(xN_t)!}{(xN_t - yfn_p)!}$$

$$\cdot \frac{[\Omega - xN_t(1+1/n_c)]!}{(N_s - xN_t + yfn_p)!}. \tag{6}$$

Now, we turn to the calculation of the interaction energies. First, the inclusion energy can be easily defined as

$$\frac{\Delta E_{inc}}{kT} = z\frac{\Delta\varepsilon_{inc}}{kT}fyn_p = z\varepsilon_{inc}fyn_p, \tag{7}$$

where $\Delta\varepsilon_{inc}$ is the energy change for the inclusion of one polymer segment into the cavity of the molecule nanotube and $\varepsilon_{inc} = \Delta\varepsilon_{inc}/kT$. It should be mentioned that, for the case

of spontaneous threading, we must have $\Delta\varepsilon_{inc} < 0$.

The conformation energy of the polymer chains can be calculated as follows. The chain segments that are included in ringlike molecules can only take the *trans*-conformations with the conformation energy $E_t/kT = \varepsilon_t fN_p$. The rest of $(1-f)N_p$ segments have $g(1-f)N_p$ *gauch*-conformations and $(1-g)(1-f)N_p$ *trans*-conformations with g as the fraction of segments of *gauch*-conformation among $(1-f)N_p$ polymer segments that are not included in the cavities of the rings. Therefore, the total conformation energy of the polymer chains can be written as

$$E_{conf} = E_t + E_g = \varepsilon_t[f + (1-g)(1-f)]N_p + \varepsilon_g g(1-f)N_p. \tag{8}$$

Here, g has to be determined in the following way. It is known that $g(1-f)N_p$ *gauch*-conformations can be randomly selected from $(1-f)N_p$ segments and thus the number of ways of arranging these *gauch*-conformations can be calculated as $[(1-f)N_p]!/[g(1-f)N_p]![(1-g)(1-f)N_p]!$. Then, the conformation partition function of the polymer segments not included in the cavity of the rings can be written as

$$Z_{conf} = (z-2)^{g(1-f)N_p}\frac{[(1-f)N_p]!}{[g(1-f)N_p]!\,[(1-g)(1-f)N_p]!}$$

$$\times\exp\{-\varepsilon_t[f + (1-g)(1-f)]N_p - \varepsilon_g g(1-f)N_p\}. \tag{9}$$

Using the Stirling's approximation, the free energy for the chain conformation can be easily obtained. After minimizing the free energy with respect to g, we finally arrived at

$$g = \frac{(z-2)\exp(\varepsilon_t - \varepsilon_g)}{1 + (z-2)\exp(\varepsilon_t - \varepsilon_g)}. \tag{10}$$

The result of Eq. (10) has already been obtained by Flory.[13]

Now, we are well equipped to calculate the free energy of the system. By assembling the results derived above, the partition function of the whole system can be written as
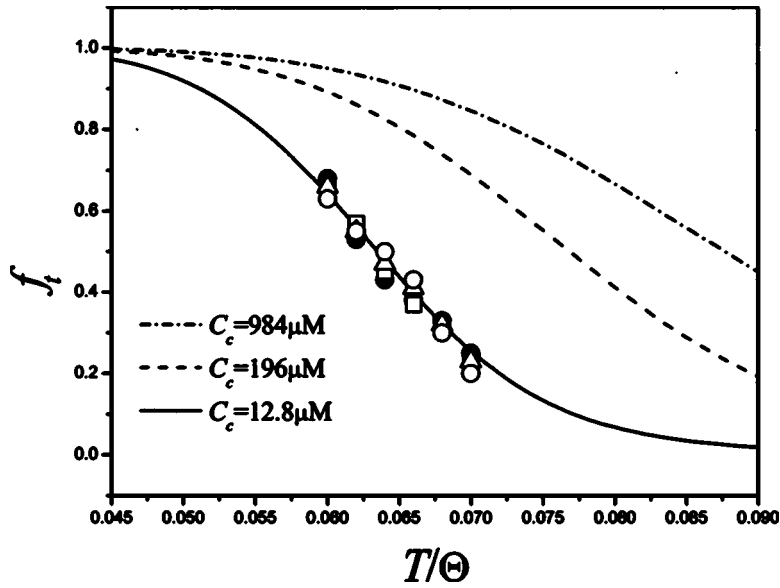
FIG. 3. The threaded fraction of the *molecular nanotubes* f_t as a function of Θ/T. The lines are calculated by Eq. (16) for various concentrations indicated in the figure. In the calculation, the concentrations of the α-CD units of the molecular nanotube and the PEG-Az segment are stoichiometrically matched. The volume fractions of the solvent are indicated in the figure. For simplicity, the equal density for all the components has been assumed in calculating the volume fractions. The experimental data are taken from Ref. 9. The symbols represent PEG-Az600 (●), PEG-Az1000 (□), PEG-Az2000 (▲), and PEG-Az4000 (■), respectively. The experimental data clearly shows the independence of the threaded fraction of the α-CD molecules on the polymer chain length.

$$Z = \frac{z^{N_t}(z-1)^{n_p - fyn_p}}{2^{n_p}\Omega^{n_p y + N_t(x-1)}} \frac{[\Omega - (n_c - 1)xN_t]!}{n_p!\,(\Omega - n_c xN_t)!\,N_t!} \frac{(n_p y)!}{(fn_p y)!\,[(1-f)n_p y]!} \frac{(xN_t)!}{(xN_t - yfn_p)!} \cdot \frac{[\Omega - xN_t(1 + 1/n_c)]!}{(N_s - xN_t + yfn_p)!}$$
$$\times \exp\{-z\varepsilon_{\text{inc}}fyn_p - \varepsilon_t[f + (1-g)(1-f)]yn_p - \varepsilon_g g(1-f)yn_p\}. \tag{11}$$

Finally, using the Stirling's approximation and $(z-1) \approx z$, the free energy per lattice site can be written as

$$\frac{F}{\Omega kT} \approx -\frac{\phi_c}{xn_c}\ln z - \left(\frac{\phi_p}{y} - f\phi_p\right)\ln(z-1) + \frac{\phi_p}{y}\ln 2 + \left[\frac{\phi_p}{y} - \phi_c\left(1 - \frac{1}{n_c^2}\right)\right]\ln\Omega - \phi_p\ln\phi_p + f\phi_p\ln f\phi_p + \phi_p\left(1 - \frac{1}{y}\right)$$
$$+ \frac{\phi_c}{n_c}\left(1 - \frac{1}{x} - \frac{1}{n_c} + n_c\right) + (1-f)\phi_p\ln(1-f)\phi_p + \frac{\phi_p}{y}\ln\frac{\phi_p}{y} - \left[1 - (n_c - 1)\frac{\phi_c}{n_c}\right]\ln\left[1 - (n_c - 1)\frac{\phi_c}{n_c}\right] + (1-\phi_c)$$
$$\times \ln(1-\phi_c) + \frac{\phi_c}{xn_c}\ln\frac{\phi_c}{xn_c} - \frac{\phi_c}{n_c}\ln\frac{\phi_c}{n_c} + \left(\frac{\phi_c}{n_c} - f\phi_p\right)\ln\left(\frac{\phi_c}{n_c} - f\phi_p\right) - \left[1 - \frac{\phi_c}{n_c}\left(1 + \frac{1}{n_c}\right)\right]\ln\left[1 - \frac{\phi_c}{n_c}\left(1 + \frac{1}{n_c}\right)\right]$$
$$+ \left(\phi_s - \frac{\phi_c}{n_c} + f\phi_p\right)\ln\left(\phi_s - \frac{\phi_c}{n_c} + f\phi_p\right) + z\varepsilon_{\text{inc}}f\phi_p - \varepsilon_t[f + (1-g)(1-f)]\phi_p - \varepsilon_g g(1-f)\phi_p. \tag{12}$$

The above free energy is minimized with respect to f and we arrive at

$$\left(\frac{f}{1-f}\right)\left[\frac{\phi_s - (\phi_t/n_c - f\phi_p)}{\phi_t/n_c - f\phi_p}\right] = \frac{\exp\{-[z\varepsilon_{\text{inc}} + (\varepsilon_t - \varepsilon_g)g]\}}{(z-1)} = q. \tag{13}$$

By defining $q = 1/(z-1)\exp\{-[z\varepsilon_{\text{inc}} + (\varepsilon_t - \varepsilon_g)g]\}$, Eq. (13) is then transformed to

$$-\frac{\phi_t}{n_c}q + f\left[\phi_s + \phi_p q - \frac{\phi_t}{n_c}(1-q)\right] + f^2\phi_p(1-q) = 0. \tag{14}$$

Here, the roots of Eq. (14) can be solved as

$$f = \frac{-\phi_s - \phi_p q + \phi_t(1-q)/n_c \pm \sqrt{[\phi_s + \phi_p q - \phi_t(1-q)/n_c]^2 + 4\phi_p(1-q)q\phi_t/n_c}}{2\phi_p(1-q)}, \tag{15}$$

where we should take the "+" sign since f must be positive.

In Eq. (15), f is defined as the fraction of the threaded polymer chain segments. This definition has, however, some disadvantages, i.e., the maximum value of f is $f_{max} = N_c/n_p y n_c = \phi_c/\phi_p n_c \lesssim 1$ when $\phi_p \gtrsim \phi_c/n_c$ and thus it is only convenient for the case of $\phi_p \lesssim \phi_c/n_c$. For the case of $\phi_p \gtrsim \phi_c/n_c$, it is better to define the fraction of the threaded submolecules of the molecular nanotubes, i.e., $f_t = f/f_{max} = f\phi_p (n_c/\phi_c)$ or $f = f_t (\phi_c/\phi_p n_c)$. Following this new definition, Eq. (15) can be rewritten as

$$f_t = \frac{-\left[\phi_s + \phi_p q - \dfrac{\phi_c}{n_c}(1-q)\right] \pm \sqrt{\left[\phi_s + \phi_p q - \dfrac{\phi_c}{n_c}(1-q)\right]^2 + 4\dfrac{\phi_c}{n_c}\phi_p(1-q)q}}{2\dfrac{\phi_c}{n_c}(1-q)}. \tag{16}$$

The inclusion fractions f_t as a function of reduced temperatures T/Θ shown in Fig. 3 are calculated according to Eq. (16) with "+" sign, which is the physical solution. Here, the characteristic temperature is defined as $\Theta/T = -[(\varepsilon_t - \varepsilon_g)g + \varepsilon_{inc}]$ with g defined in Eq. (10) but assumed to be constant in the fitting procedure for the sake of simplicity. The inclusion fraction as a function of molar ratio of the molecular nanotubes to polymer segments is shown in Fig. 4. It is worth of mentioning that the results in Figs. 3 and 4 are very much different from the theoretical results obtained by Okumura, Ito, and Hayakawa.[10] For example, the first-order transition and the molecular nanotube length x dependence and/or polymer chain length y dependence of the transition predicted by Okumura, Ito, and Hayakawa are not seen here. These discrepancies will be discussed in detail in Sec. III by comparing the theoretical predictions with the experimental observations.

III. COMPARING WITH THE EXPERIMENTAL RESULTS

Before we compare our theoretical results with the experimental observations, we should mention that there are basically two kinds of experiments.

The first kind of experiment was designed to prepare threaded molecular nanotubes. The polymer chain threaded molecular nanotubes were obtained by dropping polymer solutions into a saturated solution of CDs (or other ringlike molecules). In this process, the threaded molecular nanotubes were precipitated due to the formation of the long, rodlike molecular nanotubes.[3–6,8] It should be mentioned that, as the longer chains are added, longer molecular nanotubes will be formed and thus will be easier to be precipitated according to the solution theory of rodlike solute.[14,15] Increasing the polymer chain length further, however, the threading of the ringlike molecules becomes more difficult due to the drastic loss of the conformation entropy. Therefore, these two factors cause the chain length dependence of the precipitation. Obviously, the yield of the precipitation in the experiment was related to the phase equilibrium between the precipitated phase and the solution phase. Therefore, the statistical thermodynamics of phase equilibrium in these experiments has to be investigated to clarify these issues. We note that it is straightforward for the present theory to be extended to deal with this special phase equilibrium. However, in order to keep the reasonable length of this paper, we leave it for the next publication.

In another kind of experiment the threading-unthreading transition was investigated in a homogeneous solution (dilute solution) by changing the temperature or varying the concentration and the molar ratios of the molecular nanotubes formed by covalently bonding α-CD molecules and PEG-Az which is PEG modified with azobenzene groups at both ends.[9] In this case, no precipitation has occurred due to the low concentration of the molecular nanotubes. Obviously, our present theory could be tested by this kind of experiment. Therefore, in this section, the comparison between our theoretical calculation and the experimental results would be made. By fitting the experimental data, one can obtain the inclusion and conformation energies.

First, we fit the experimental data on the temperature dependence of the inclusion fraction of the molecular nanotubes, which is formed by covalently bonding α-CDs, by PEG in aqueous solution according to Eq. (16) (see Fig. 3). From the fitting procedure, we obtain the reduced temperature $\Theta/T = -z\Delta\varepsilon_{inc} + (\Delta\varepsilon_t - \Delta\varepsilon_g)g/kT \approx 16.5$. Therefore, the inclusion and the conformation energies for each α-CD can be calculated as $z\Delta\varepsilon_{inc} + (\Delta\varepsilon_t - \Delta\varepsilon_g)g = -16.5 \times 8.314 \times 303$ J/mol ≈ -40.9 kJ/mol. It should be noted that the stoichiometries of the complex are always nearly 2:1 (ethylene glycol units to α-CD). Therefore, the inclusion energy is ~ 20.45 kJ/mol per ethylene glycol units. Although we do not have more well defined experimental data for further quantitative confirmation of the theoretical results, the inclusion energy obtained here is qualitatively reasonable.

Another confirmation of the correctness of the theoretical results obtained here can be made by the following procedure. The inclusion energy obtained from the above fitting procedure is then directly used to calculate the inclusion fraction of the molecular nanotubes of α-CDs as a function of the molar ratio of the α-CD units to the PEG segments without any other fitting parameters. The comparison between the theory and experiment is shown in Fig. 4. Here, we should mention that, instead of the molar ratio of the molecular nanotubes and PEG-Az chains, we have replotted
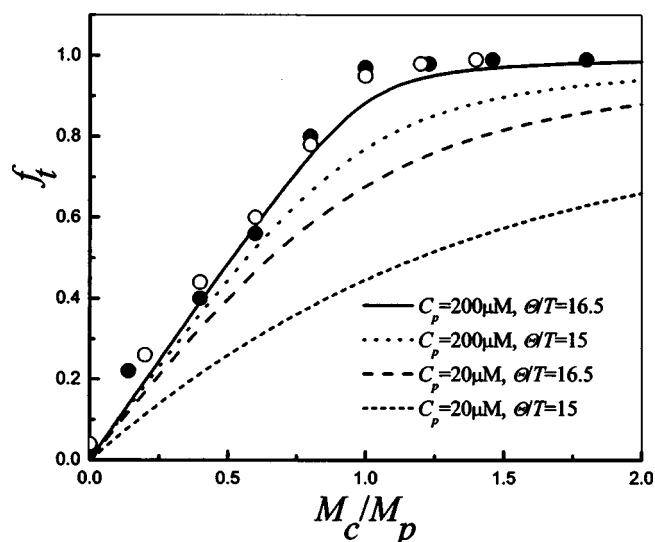
FIG. 4. The threaded fraction of the molecular nanotubes f_t as a function of the molar ratio between the α-CD units of the molecular nanotubes and the PEG segments. The line is calculated by Eq. (16). In the calculation, we have set $x = M_c/M_p$, which is the molar ratio of the stoichiometrically matched numbers of PEG segments and the *submolecules* (α-CD unit) of the molecular nanotubes. The experimental volume fractions of the solvent and the values of Θ/T obtained from Fig. 3 are given here. The experimental data are taken from Ref. 9, where (●) represents the results for PEG-Az2000 and (○) for PEG-Az1000, respectively. Again, the experimental data shows the independence of the threaded fraction of the α-CD molecules on the polymer chain length.

the experimental data presented in Ref. 9 according to the stoichiometric molar ratio of the α-CD units to the PEG segments. The result shows that the experimental data for different PEG-Az chain lengths are all collapsed into one line in the new plot. It is clearly seen from Fig. 4 that, as predicted by our theory, the inclusion molar fraction is independent of the polymer chain length. It is clearly demonstrated in Fig. 4 that the theoretically calculated result based on the fitted inclusion energy agrees with the experimental results quite well.

IV. CONCLUSIONS AND REMARKS

In this paper, the Flory–Huggins lattice model has been used to investigate the threading-unthreading equilibrium in the solution of molecular nanotubes and linear polymer chains. It is found that the threading-unthreading transition occurs as a continuous transition and depends on the molar fractions of the molecular nanotube units and the polymer segments. In other words, the threading-unthreading transi-

tion is independent of the polymer chain length. These findings agree with the experiments quite well. However, we should also mention that, in the frame of the present model, the quantities obtained from fitting the experimental data contain the following possible uncertainties.

(1) It is estimated experimentally that there are nearly six water molecules included in an α-CD.[2] Therefore, when an α-CD molecule is threaded by a PEG segment, six water molecules will be released from its cavity. However, in the present model, only one water molecule is included in the cavity of a rigid ringlike molecule. Certainly, this will introduce some uncertainty in the estimation of the inclusion energy and entropy.

(2) Second, the coordination number in the lattice model is intrinsically difficult to be estimated, which will also introduce some error in the estimation of the inclusion energy.

Fine corrections to overcome the above uncertainties and extensions to deal with the precipitation equilibrium of the solution of molecular nanotubes will be published in later papers.

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