Inclusion-Dissociation Transition in the Complex Formation between Molecular Nanotubes and Linear Polymer Chains in Solutions

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The inclusion-dissociation behavior in the complex formation between molecular nanotubes and linear polymer chains in solutions is theoretically investigated by using the Flory-Huggins lattice model. While, in a good solvent, the polymer chains are gradually dissociated from or included into the tubes with varying temperature, the inclusion-dissociation transition occurs sharply in a poor solvent with a hysteresis loop. [S0031-9007(98)06240-1]

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Nanotubes which are fine capillaries with an inside diameter of nm order have attracted a great interest of many physicists because of their peculiar structures. A typical example is a carbon nanotube formed by an arc-discharge method [1]. Recently, a new series of nanotubes with diameters smaller than carbon nanotubes have been chemically synthesized from cyclodextrin (CD) molecules of cyclic form by Harada *et al.* [2–4]. They prepared a polyrotaxane supramolecule in which CDs were threaded on a polymer chain with bulky ends and obtained a molecular tube by cross-linking the adjacent CD units in the polyrotaxane [4]. By removing the bulky ends of the polymer thread, the tube was unthreaded and acted as a host for reversible binding of small molecules. This molecular nanotube, which is soluble in several kinds of solvents such as water, has a constant inside diameter (e.g., 0.45, 0.70, and 0.85 nm for α-, β-, and γ-CD, respectively) and a longitudinal length of submicron order, controllable by varying the length of the polymer chain as a mold, and can form an inclusion complex with a linear polymer chain as shown in Fig. 1(a).

Owing to the infinitesimal inside diameter of a molecular nanotube, a polymer chain forming an inclusion complex with the nanotube has an extended conformation, such as a planar zigzag one, with no degrees of freedom other than a translational motion along its longitudinal axis, which is reminiscent of a well-known "tube" model for the entanglement effect of polymer chains [5]. Thus, the inclusion of a polymer chain into a molecular nanotube is entropically unfavorable and is promoted by an attractive interaction between the chain and the nanotube. In other words, as the temperature increases, the polymer chain dissociates from the nanotube and recovers its intrinsic entropy of a random conformation in solution. The entropy increases linearly with increasing the contour length of the chain if the chain has a random conformation. Accordingly, a drastic change of entropy occurs with the inclusion or dissociation of a long polymer chain and may lead to a transitional behavior in the complex formation between the nanotube and the chain.

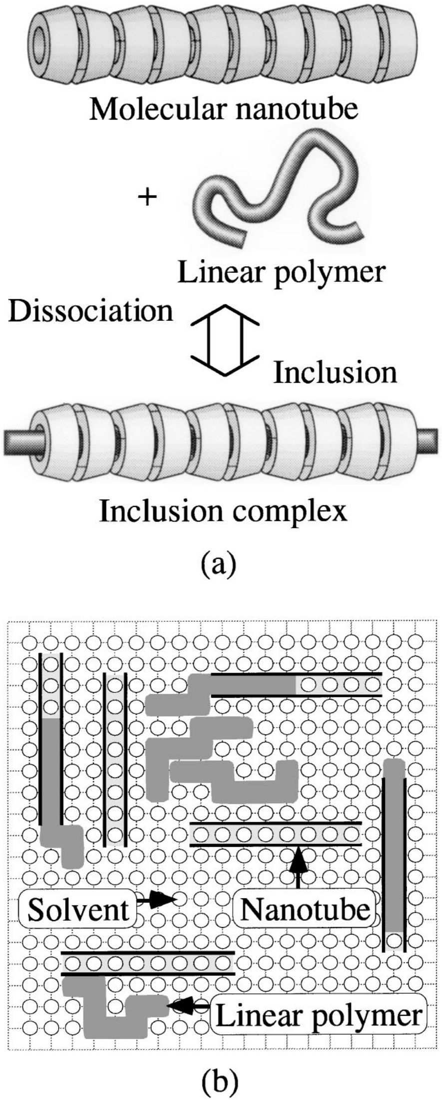

FIG. 1. An inclusion complex formation of a molecular nanotube and a linear polymer chain. (b) A lattice model for the system consisting of molecular nanotubes, polymer chains, and solvent molecules. The dissociated chains interact with each other.

The purpose of this Letter is to investigate theoretically the inclusion-dissociation behavior of the complex between the molecular nanotube and the linear polymer chain in solutions. In addition to the conformational entropy and the tube-chain interaction energy, the property of solvents, good or poor, is another important factor dominating the inclusion-dissociation behavior. This effect is incorporated into the present theory by using the Flory-Huggins lattice model [6].

To evaluate the free energy of a system consisting of molecular nanotubes, polymer chains, and solvent molecules, we adopt a lattice model assuming that the tube and the chain are composed of segments with the same size as the solvent molecule occupying one site on the lattice. In this system, let Ω be the total number of lattice sites and z be the coordination number of the lattice. For simplicity, we further assume that the tube is fully rigid and has a longitudinal length equal to the contour length of the chain; namely, both the tube and the chain consist of N segments occupying N connected lattice points. The inside of the tube is filled with chain segments or solvent molecules, so that the tube segment also occupies one lattice site together with the chain segment or the solvent molecule. While the chain dissociated from the tube has a flexible or coiled conformation with many internal degrees of freedom, the inclusion into the tube drastically changes the chain conformation to a rigid rodlike one. Then the number of ways of placing the rodlike chain fully included into a tube is estimated to be Ωz, which is much smaller than $\Omega z(z-1)^{N-2}$ for a dissociated flexible chain.

Let N_t and N_c be the total numbers of tubes and polymer chains, respectively, and i be the number of tubes forming inclusion complexes with polymer chains. Then $p = i/N_t$ and $\alpha = N_c/N_t$ denote the number ratios of the inclusion tubes to the total ones and of the total polymer chains to the total tubes. By using the Flory-Huggins theory, we estimate the p and α dependences of the free energy F of the system, in which part of the polymer chains is dissociated from the tubes and interact with each other as shown in Fig. 1(b). First, we calculate the energy difference ΔE of the system from the full dissociation state that all of the chains without interaction are dissociated from the tubes.

Let us consider that i chains are fully included into i tubes and the other chains remain dissociated. The inclusion of a chain segment into a tube means that $z-2$ chain segment–solvent molecule pairs and $z-2$ tube segment–solvent molecule pairs are replaced by $z-2$ connections between the chain segment and the inside of the tube. Consequently, the inclusion energy ΔE_{in} of a chain into a tube is given by

$$\begin{aligned}\Delta E_{\mathrm{in}} &= -(z-2)(\epsilon_{\mathrm{ci}} - \epsilon_{\mathrm{si}} + \epsilon_{\mathrm{ss}} - \epsilon_{\mathrm{cs}})Ni \\ &\equiv -\Delta\epsilon_{\mathrm{in}} Ni\,, \end{aligned} \tag{1}$$

where ϵ_{ci}, ϵ_{si}, ϵ_{ss}, and ϵ_{cs} are, respectively, the interaction energies of chain segment–tube inside; solvent molecule–tube inside; solvent molecule–solvent molecule; and chain segment–solvent molecule. ΔE_{in} represents the inclusion-dissociation energy per chain segment. On the other hand, the dissociated chains interact with each other and with the outside of the tubes as shown in Fig. 1(b). According to the Flory-Huggins theory [4], the interaction energy ΔE_{int} of the chains is evaluated to be

$$\begin{aligned}\Delta E_{\mathrm{int}} &= -(\epsilon_{\mathrm{cc}} + \epsilon_{\mathrm{ss}} - 2\epsilon_{\mathrm{cs}})\frac{zN^2(N_c-i)^2}{2\Omega} - (\epsilon_{\mathrm{oo}} + \epsilon_{\mathrm{ss}} - 2\epsilon_{\mathrm{so}})\frac{zN^2N_t^2}{2\Omega} \\ &\quad - (\epsilon_{\mathrm{co}} + \epsilon_{\mathrm{ss}} - \epsilon_{\mathrm{cs}} - \epsilon_{\mathrm{so}})\frac{zN^2N_t(N_c-i)}{\Omega} \\ &\equiv -\Delta\epsilon_{\mathrm{cc}}\frac{N^2(N_c-i)^2}{\Omega} - \Delta\epsilon_{\mathrm{oo}}\frac{N^2N_t^2}{\Omega} - \Delta\epsilon_{\mathrm{co}}\frac{N^2N_t(N_c-i)}{\Omega}\,, \end{aligned} \tag{2}$$

where ϵ_{cc}, ϵ_{oo}, ϵ_{so}, and ϵ_{co} are, respectively, the interaction energies of chain segment–chain segment; tube outside–tube outside; solvent molecule–tube outside; and chain segment–tube outside. Here $\Delta\epsilon_{\mathrm{cc}}, \Delta\epsilon_{\mathrm{oo}}$, and $\Delta\epsilon_{\mathrm{co}}$ are defined as follows:

$$\begin{aligned}\Delta\epsilon_{\mathrm{cc}} &= \frac{z}{2}(\epsilon_{\mathrm{cc}} + \epsilon_{\mathrm{ss}} - 2\epsilon_{\mathrm{cs}})\,, \\ \Delta\epsilon_{\mathrm{oo}} &= \frac{z}{2}(\epsilon_{\mathrm{oo}} + \epsilon_{\mathrm{ss}} - 2\epsilon_{\mathrm{so}})\,, \\ \Delta\epsilon_{\mathrm{co}} &= z(\epsilon_{\mathrm{co}} + \epsilon_{\mathrm{ss}} - \epsilon_{\mathrm{cs}} - \epsilon_{\mathrm{so}})\,. \end{aligned} \tag{3}$$

Therefore, the total energy difference ΔE due to the inclusion of chains and the interactions among chains and tube outsides is given by

$$\begin{aligned}\Delta E(i) = \Delta E_{\mathrm{in}} + \Delta E_{\mathrm{int}} &= -\Delta\epsilon_{\mathrm{in}} Ni - \Delta\epsilon_{\mathrm{cc}}\frac{N^2(N_c-i)^2}{\Omega} \\ &\quad - \Delta\epsilon_{\mathrm{oo}}\frac{N^2N_t^2}{\Omega} - \Delta\epsilon_{\mathrm{co}}\frac{N^2N_t(N_c-i)}{\Omega}\,, \end{aligned} \tag{4}$$

By omitting the third term independent of i, Eq. (4) is rewritten with the volume fraction $\Phi_t = NN_t/\Omega$ of tubes, the inclusion fraction $p = i/N_t$ of tubes, and the ratio $\alpha = N_c/N_t$ of the total chains to the total tubes in the solution as

$$\begin{aligned}E(p) = NN_t[&-\Delta\epsilon_{\mathrm{in}} p - \Phi_t\Delta\epsilon_{\mathrm{co}}(\alpha - p) \\ &- \Phi_t\Delta\epsilon_{\mathrm{cc}}(\alpha - p)^2]\,. \end{aligned} \tag{5}$$

Next we focus on i chains forming the inclusion complexes with tubes. These chains are not necessarily included fully into the tubes, i.e., they can partially dissociate from the tubes as shown in Fig. 1(b). For simplicity, we assume that the chain segments extruding from the tube have no interactions with each other but interact with the fully dissociated other chains. Then, the partition function B of a fully or partially included chain is given by

$$B(p) = \sum_{n=0}^{N-1} (z-1)^n [1 - \Phi_t(\alpha - p)]^n \times \exp\left[\frac{-n[\Delta\epsilon_{\text{in}} - 2\Phi_t \Delta\epsilon_{\text{cc}}(\alpha - p)]}{k_B T}\right], \tag{6}$$

where n is the number of segments extruding from the tube, and $k_B T$ is the thermal energy. Here we introduce the temperature T_c defined by

$$T_c = \Delta\epsilon_{\text{in}}/[k_B \ln(z-1)] \equiv \Delta\epsilon_{\text{in}}/\Delta S, \tag{7}$$

where ΔS represents the inclusion-dissociation entropy per chain segment based on the free rotation around covalent bonds. It is to be noted that, when $T = T_c$, the inclusion energy and the polymer entropy are balancing. Equation (6) is rewritten to a simpler form,

$$B(p) = \frac{1 - \exp[NC(p)]}{1 - \exp[C(p)]}, \tag{8}$$

where

$$C(p) = (1 - 1/\overline{T})\Delta S/k_B - \Phi_t(\alpha - p)(1 - \overline{\Theta}_{cc}/\overline{T}). \tag{9}$$

Here we introduced the reduced temperature $\overline{T} = T/T_c$ and the reduced Θ temperature $\overline{\Theta}_{\text{cc}} = 2\Delta\epsilon_{\text{cc}}/k_B T_c$. Since the chains in the inclusion state are independent of each other, the partition function of the included chains as a whole is given as B^i.

By calculating the total number of ways for arranging dissociated $N_c - i$ chains, $N_t - i$ tubes, and i inclusion complexes, we have the partition function $Z(i)$ of the total system as

$$Z(i) = \frac{(\Omega z)^{N_c - i}}{(N_c - i)!} \frac{(\Omega z)^{N_t - i}}{(N_t - i)!} \frac{(\Omega z)^i}{i!} \prod_{j=0}^{N_t + N_c - i - 1} \left(1 - \frac{Nj}{\Omega}\right)^N \times B^i (z-1)^{N(N_c - i)} \exp\left(-\frac{\Delta E(i)}{k_B T}\right). \tag{10}$$

Here the first two factors on the right-hand side represent the number of ways for placing the fully dissociated polymer chains and tubes on the lattice. The third factor comes from the arrangement of the inclusion complexes on the lattice, and the fourth indicates the excluded volume effect.

By using a proper approximation and taking the logarithm of Eq. (10), we have the reduced (i.e., dimensionless) free energy $\overline{F}(p)$ per tube as a function of the inclusion fraction $p = i/N_t$:

$$\overline{F}(p) \equiv \frac{F(p)}{N_t k_B T} = \left[\frac{N\Delta S}{k_B}\left(1 - \frac{1}{\overline{T}}\right) - N\Phi_t\left(1 - \frac{\overline{\Theta}_{\text{co}}}{\overline{T}}\right) + \ln\frac{Nze}{\Phi_t}\right]p + \frac{N\Phi_t(\alpha - p)^2}{2}\left(1 - \frac{\overline{\Theta}_{\text{cc}}}{\overline{T}}\right) - p\ln B(p) + (\alpha - p)\ln(\alpha - p) + (1 - p)\ln(1 - p) + p\ln p, \tag{11}$$

where the terms independent of p have been omitted and $\overline{\Theta}_{\text{co}}$ is the reduced temperature defined by $\overline{\Theta}_{\text{co}} = \Delta\epsilon_{\text{co}}/k_B T_c$.

Figures 2(a) and 2(b) show the p dependence of $\overline{F}(p)$ for different values of the reduced temperature $\overline{T}$ in a good solvent region ($\overline{T} > \overline{\Theta}_{\text{cc}}$) and in a poor solvent region ($\overline{T} < \overline{\Theta}_{\text{cc}}$), respectively. Figure 2(a) indicates that the free energy curve is always concave upwards for $0 \leq p \leq 1$, so that, as $\overline{T}$ changes, the polymer chains are gradually dissociated from or included into the tubes in a good solvent. On the other hand, a poor solvent produces two local minima of the free energy as shown in Fig. 2(b) owing to the second term on the right-hand side of Eq. (11). Then, there are two stable inclusion fractions, and an inclusion-dissociation transition is expected to occur between them with varying $\overline{T}$.

Figure 3 shows the $\overline{T}$ dependence of equilibrium value of p, which has been obtained from the condition $\partial\overline{F}(p)/\partial p = 0$ for different values of N in the good solvent. As N increases, the inclusion-dissociation behavior becomes sharp and approaches a transitional one without hysteresis at the transition temperature $\overline{T} = 1$ in the limit of $N \to \infty$. On the other hand, the p-$\overline{T}$ curve shown in Fig. 4 indicates that the inclusion-dissociation transition occurs with a hysteresis loop at $\overline{T} \ll \overline{\Theta}_{\text{cc}}$, i.e., in the poor solvent region.

Figure 5 shows the p-α curves for different values of $\overline{\Theta}_{\text{cc}}$. The inclusion fraction p increases linearly and saturates with increasing α in the good solvent region. On the other hand, the dissociation transition can occur after the continuous inclusion in the poor solvent.

In summary, the inclusion-dissociation behavior in the complex formation between the molecular nanotubes and the linear polymer chains in solutions was investigated theoretically by using the Flory-Huggins lattice model. In a good solvent, the polymer chains are continuously dissociated from or included into the tubes as T or α varies. On the other hand, the inclusion-dissociation transition occurs in a poor solvent with a hysteresis loop. These theoretical results are useful for the control of supramolecular structures formed by nanotubes and polymer chains.

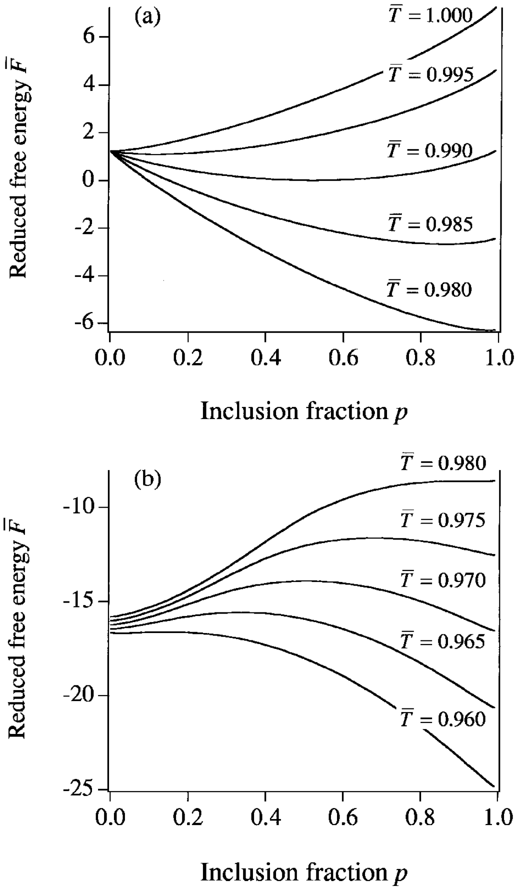

FIG. 2. The reduced free energy $\overline{F}(p)$ of the total system per tube as a function of the inclusion fraction p of the tubes for different values of $\overline{T}$ in (a) good and (b) poor solvent regions. The solid curves are calculated from Eq. (11) for $N = 500$ and $z = 6$; $\Phi_t = 0.01$ and $\overline{\Theta}_{cc} = 0.66$ in case (a), $\Phi_t = 0.1$ and $\overline{\Theta}_{cc} = 1.33$ in case (b).

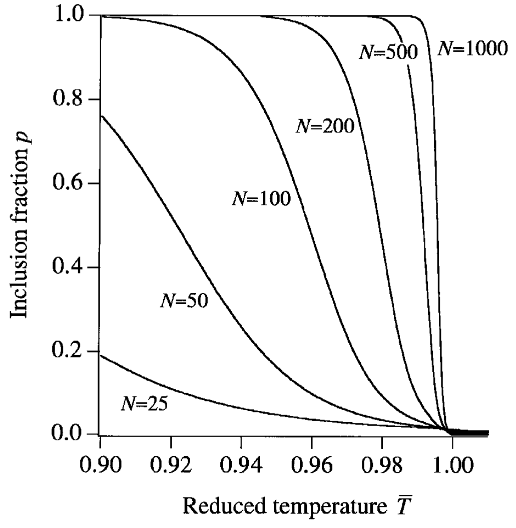

FIG. 3. The $\overline{T}$ dependence of the inclusion fraction p for different values of N in the good solvent. The solid curves are obtained from the condition $\partial\overline{F}(p)/\partial p = 0$ for $z = 6$, $\Phi_t = 0.01$, and $\overline{\Theta}_{cc} = 1.00$.

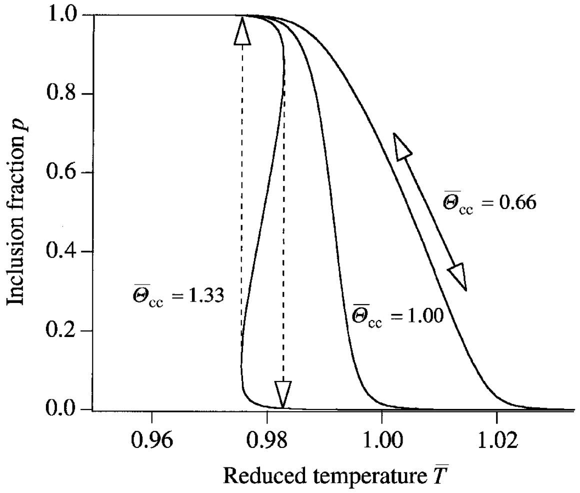

FIG. 4. The $\overline{T}$ dependence of the inclusion fraction p for different values of the reduced theta temperature $\overline{\Theta}_{cc}$. The solid curves are obtained from the condition $\partial\overline{F}(p)/\partial p = 0$ for $N = 500$, $z = 6$, and $\Phi_t = 0.1$.

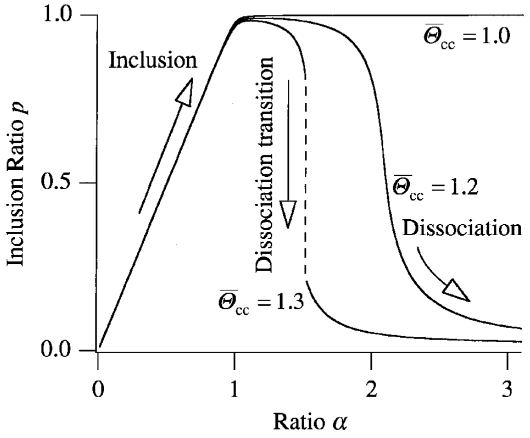

FIG. 5. The dependence of the inclusion fraction p on the ratio $\alpha = N_c/N_t$ for different values of the reduced theta temperature $\overline{\Theta}_{cc}$. The solid curves are obtained from the condition $\partial\overline{F}(p)/\partial p = 0$ for $N = 500$, $z = 6$, $\overline{T} = 0.985$, and $\Phi_t = 0.05$.

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