RAPID COMMUNICATIONS

PHYSICAL REVIEW E VOLUME 59, NUMBER 4 APRIL 1999

Switching transition of molecular nanotubes forming an inclusion complex with block copolymers in solutions

Yasushi Okumura,* Kohzo Ito, and Reinosuke Hayakawa

Department of Applied Physics, Graduate School of Engineering, University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan

(Received 2 November 1998)

Switching behavior of molecular nanotubes forming an inclusion complex with block copolymers in solutions is theoretically investigated. As temperature changes, a nanotube including a miscible block copolymer gradually moves from one polymer chain to the other, while a switching transition sharply occurs with a hysteresis loop in an immiscible block copolymer. In a recurrent block copolymer comprising linear polymers of four different types, a nanotube travels on the copolymer rail stepwise with undulating temperature: a molecular motor operated by temperature undulation. [S1063-651X(99)51504-3]

PACS number(s): 61.25.Hq

Nanotubes, fine capillaries with an inside diameter of nm order, have attracted great interest among many physicists because of their peculiar structures. As a typical example, a carbon nanotube formed by an arc-discharge method has been investigated intensively so far. Recently, a new series of nanotubes with diameters smaller than carbon nanotubes were chemically synthesized from cyclodextrin (CD) molecules of cyclic form by Harada, Li, and Kamachi [1,2]. They prepared a polyrotaxane supramolecule in which CDs were threaded on a polymer chain with bulky ends and obtained a molecular tube by crosslinking the adjacent CD units in the polyrotaxane. By removing the bulky ends of the polymer thread, the tube was unthreaded and acted as a host for reversible inclusion of small molecules [2] and a linear polymer chain [3]. 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 used as a mold.

Owing to the infinitesimal inside diameter of the molecular nanotube, a polymer chain included in the nanotube has an extended conformation, such as planar zigzag with no degrees of freedom other than a translational motion along its longitudinal axis. Therefore, the inclusion of a polymer chain in a molecular nanotube is entropically unfavorable and is promoted by an attractive interaction such as a hydrophobic one between the chain and the nanotube, so that a drastic change of entropy occurs with the inclusion or dissociation of a long polymer chain. In our previous paper, we theoretically treated the inclusion-dissociation behavior of the nanotubes and the linear polymer chains in solutions [4]. The theory predicts that the polymer chains in a good solvent are gradually either dissociated from or incorporated into the tubes with varying temperature, while the inclusion-dissociation transition occurs sharply in a poor solvent with a hysteresis loop. Because the attractive inclusion energy and the conformational entropy varies with the species of the polymer chain, the transitional temperature strongly depends on the polymer species.

Now let us consider an inclusion complex of the molecular nanotube and a block copolymer comprising linear polymer chains of two types *A*, *B* as shown in Fig. 1(a). Like the polyrotaxane prepared by Harada, Li, and Kamachi [1], both ends of the block copolymer are terminated with bulky ends of large substitutional groups so that the block copolymer cannot dissociate from the nanotube. If the *A* chain has inclusion energy and entropy larger than the *B* chain, the nanotube includes the *A* chain at low temperature or the *B* chain at high temperature. In other words, the nanotube switches

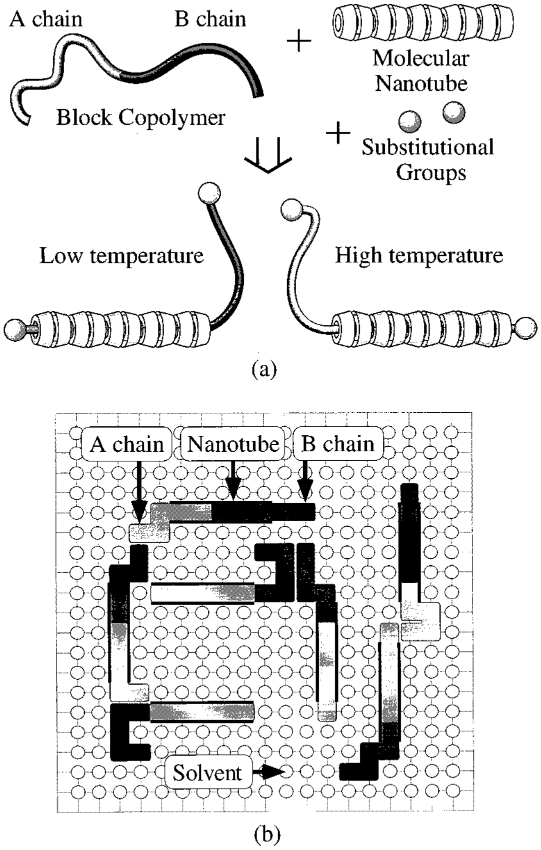

FIG. 1. (a) A switching complex formation of a molecular nanotube and a block polymer. (b) A lattice model for the system consisting of switching complexes and solvent molecules. The protruded chains interact with each other.

---

*Author to whom correspondence should be addressed.

1063-651X/99/59(4)/3823(4)/$15.00 PRE 59

back and forth between the *A* and *B* chains as temperature varies. Thus, we call such an inclusion complex ''switching complex.''

The purpose of this Rapid Communication is to investigate theoretically the switching behavior of the molecular nanotubes in the switching complexes in solutions. In addition to the conformational entropy and the tube-chain interaction energy, the property of miscibility between *A* and *B* chains is another important factor dominating the switching behavior. This effect is incorporated into the present theory by using the Flory-Huggins lattice model [5].

We adopt a lattice model assuming that a molecular nanotube and an *A*-*B* block copolymer are composed of segments with the same size as a solvent molecule occupying one site on the lattice as shown in Fig. 1(b). In this system, let Ω be the total number of lattice sites, *z* the coordination number of the lattice, and N_c the number of switching complexes. The inside of the tube is filled with either *A* or *B* chain segment, so that the tube segment also occupies one lattice site together with the chain segment. For simplicity, we assume that the tube is fully rigid and has a longitudinal length equal to the contour length of the *A* or *B* chain, namely, each of the tubes and the *A* and *B* chains consists of *N* segments occupying *N* connected lattice points. Therefore, the nanotube can move by *N* segments on the block copolymer.

First, let us evaluate the free-energy difference of the switching complex from the full inclusion state with the *A* chain. When the tube moves by a segment towards the *B* chain on the block copolymer, $z-2$ ''*A* segment–tube inside'' pairs and $z-2$ ''*B* segment–solvent molecule'' pairs are replaced by $z-2$ ''*B* segment–tube inside'' pairs and $z-2$ ''*A* chain–solvent molecule'' pairs. Let *n* be the number of *B* segments included in the nanotube, corresponding to the displacement of the tube from the full inclusion state with the *A* chain. Then the free-energy difference $F_s(n,T)$ is given by

$$F_s(n,T)=n[(z-2)(\varepsilon_{ai}-\varepsilon_{as}-\varepsilon_{bi}+\varepsilon_{bs})-T(S_a-S_b)] \equiv n(\Delta\varepsilon_s-T\Delta S_s), \tag{1}$$

where ε_{ai}, ε_{as}, ε_{bi}, and ε_{bs} are, respectively, the interaction energy of *A* segment–tube inside pairs, *A* segment–solvent molecule pairs, *B* segment–tube inside pairs, and *B* segment–solvent molecule pairs. In Eq. (1), S_a and S_b represent the conformational entropy per segment of the *A* and *B* chains, respectively, based on the free rotation around covalent bonds. Therefore, $\Delta\varepsilon_s$ and ΔS_s indicate the differences in inclusion energy and entropy between *A* and *B* segments. If *N* is large enough, the free-energy difference $F_s(N,T)$ between the full inclusion states with the *A* and *B* chains changes drastically with varying temperature *T*. It is to be noted that when $T=T_s\equiv\Delta\varepsilon_s/\Delta S_s$, inclusion forces toward the *A* and *B* chains are balanced.

On the other hand, linear polymer chains extruding from the tubes interact with each other. Next, we focus on miscibility between *A* and *B* chains. Let us consider that a switching complex including *n* of *B* segments interact with the other switching complexes including $\overline{n}$ of *B* segments in the solution, where $\overline{n}$ is the average value of *n*, namely, the average number of *B* segments incorporated into the tube per switching complex. With a mean-field approximation [5], the interaction energy $E_i(n,T)$ is given by

$$E_i(n,T)=-np\Phi\Delta\varepsilon_{aa}-n(1-p)\Phi\Delta\varepsilon_{ab} -(N-n)(1-p)\Phi\Delta\varepsilon_{bb}-(N-n)p\Phi\Delta\varepsilon_{ab}, \tag{2}$$

where *p* is the switching ratio defined by $p=\overline{n}/N$ and $\Phi=NN_c/\Omega$ denotes the volume fraction of polymer chains of each type or tubes. In Eq. (2), $\Delta\varepsilon_{aa}$, $\Delta\varepsilon_{bb}$, and $\Delta\varepsilon_{ab}$ are defined by

$$\begin{aligned}\Delta\varepsilon_{aa}&=(z-2)(\varepsilon_{aa}+\varepsilon_{ss}-2\varepsilon_{as}),\\ \Delta\varepsilon_{bb}&=(z-2)(\varepsilon_{bb}+\varepsilon_{ss}-2\varepsilon_{bs}),\\ \Delta\varepsilon_{ab}&=(z-2)(\varepsilon_{ab}+\varepsilon_{ss}-\varepsilon_{as}-\varepsilon_{bs}),\end{aligned} \tag{3}$$

where ε_{aa}, ε_{bb}, ε_{ab}, and ε_{ss} are, respectively, the interaction energy of *A* segment–*A* segment, *B* segment–*B* segment, *A* segment–*B* segment, and solvent molecule–solvent molecule. Accordingly, the total free energy $F(n,T)$ of the switching complex is given by

$$\begin{aligned}F(n,T)&=F_s(n,T)+E_i(n,T)\\ &=n\Delta\varepsilon_s\left(1-\frac{T}{T_s}\right)-np\Phi\Delta\varepsilon_{aa}-n(1-p)\Phi\Delta\varepsilon_{ab}\\ &\quad-(N-n)(1-p)\Phi\Delta\varepsilon_{bb}-(N-n)p\Phi\Delta\varepsilon_{ab}.\end{aligned} \tag{4}$$

When the tube moves by a segment towards the *B* chain, a change in the free energy is given by

$$\begin{aligned}\Delta F&=\frac{dF(n,T)}{dn}\\ &=k_BT_s[\Delta\overline{\varepsilon_s}(1-\overline{T})+\Phi[(2p-1)\overline{\Theta}_m-\overline{\Theta}_s]].\end{aligned} \tag{5}$$

Here we introduce a reduced energy $\Delta\overline{\varepsilon_s}=\Delta\varepsilon_s/(k_BT_s)$ and reduced temperatures $\overline{T}=T/T_s$, $\overline{\Theta}_m=(2\Delta\varepsilon_{ab}-\Delta\varepsilon_{aa}-\Delta\varepsilon_{bb})/(2k_BT_s)$ and $\overline{\Theta}_s=(\Delta\varepsilon_{aa}-\Delta\varepsilon_{bb})/(2k_BT_s)$, where k_B is the Boltzmann constant. Θ_m and Θ_s represent, respectively, the miscibility and the difference in solubility between *A* and *B* chains.

The partition function of a switching complex is given by

$$B=\sum_{n=0}^{N}K^n=(1-K^{N+1})/(1-K), \tag{6}$$

where

$$K=\exp[-\Delta F/(k_BT)]. \tag{7}$$

Therefore, we obtain the switching ratio *p* of the complex as

$$p(K)=\frac{1}{NB}\sum_{n=0}^{N}nK^n=\frac{-K}{1-K^{N+1}}\left(K^N-\frac{1-K^N}{N(1-K)}\right). \tag{8}$$

Since *K* depends on *p* as shown in Eqs. (5) and (7), we determine *p* from Eq. (8) self-consistently.

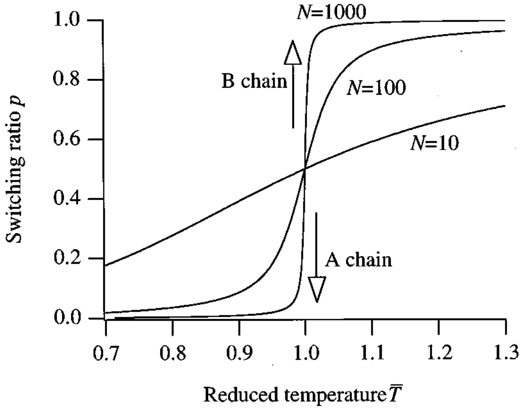

FIG. 2. $\overline{T}$ dependence of the switching ratio p for different values of N for miscible block copolymers. The solid curves are calculated from Eq. (8) with $\overline{\Theta}_m=0$, $\Phi=0.01$, $\overline{\Theta}_s=0$, and $\Delta\overline{\varepsilon}_s=1.00$. This behavior is equivalent to that of a single switching complex because the interaction energy E_i is constant.

Figure 2 shows the $\overline{T}$ dependence of p for different values of N at $\overline{\Theta}_m=0$, i.e., in the case of miscible block copolymers. As N increases, the switching behavior becomes sharp and approaches a transitional behavior without hysteresis at the transitional temperature $\overline{T}=1$ in the limit of $N\rightarrow\infty$.

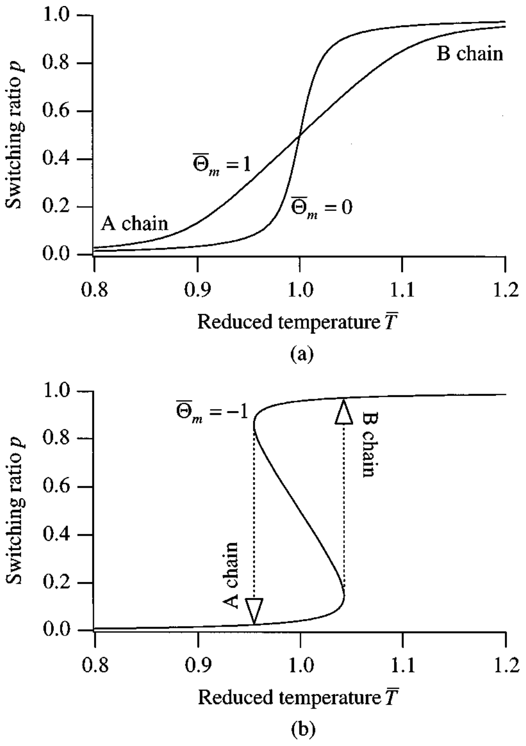

FIG. 3. $\overline{T}$ dependence of the switching ratio p for different values of $\overline{\Theta}_m$ for (a) miscible and (b) immiscible block copolymers. The solid curves are calculated from Eq. (8) with $N=500$, $\Phi=0.05$, $\overline{\Theta}_s=0$, and $\Delta\overline{\varepsilon}_s=0.5$.

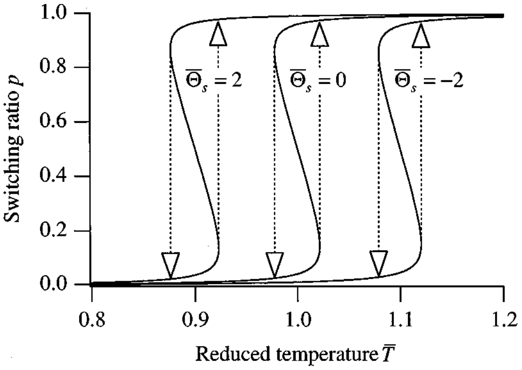

FIG. 4. $\overline{T}$ dependence of the switching ratio p for different values of $\overline{\Theta}_s$ for immiscible block copolymers. The solid curves are calculated from Eq. (8) with $N=500$, $\Phi=0.05$, $\overline{\Theta}_m=-1$, and $\Delta\overline{\varepsilon}_s=0.5$.

Figures 3(a) and 3(b) show the $\overline{T}$ dependence of p for miscible block copolymers $(\overline{\Theta}_m\geqslant 0)$ and for immiscible block copolymers $(\overline{\Theta}_m<0)$, respectively. Figure 3(a) shows that as $\overline{\Theta}_m$ increases, the nanotubes shift gradually with varying temperature on miscible block copolymers. Conversely, the p-$\overline{T}$ curve shown in Fig. 3(b) indicates that the switching transition occurs with a hysteresis in immiscible block copolymers. Figure 4 shows the p-$\overline{T}$ curve for different values of $\overline{\Theta}_s$ at $\overline{\Theta}_m<0$. It is seen that the transition temperature strongly depends on $\overline{\Theta}_s$, the solubility difference between A and B chains.

Finally, let us consider switching behavior of the nanotube including a recurrent block copolymer comprising linear polymer chains of four different types A, B, C, D with the same contour length L as shown in Fig. 5(a). Each polymer chain has the inclusion energy and entropy of $(-\varepsilon_a, S_a)$,

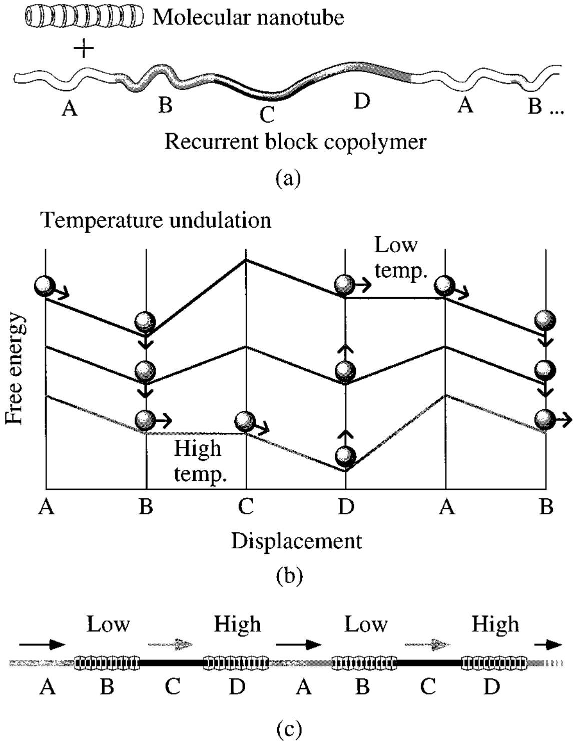

FIG. 5. (a) Nanotube and recurrent block copolymer comprising linear polymer chains of four different types. (b) Schematic free-energy map along the block copolymer for different temperatures. The ball represents the location of the nanotube on the block copolymer. (c) Stepwise motion of the nanotube, induced by temperature undulation, on the block copolymer in one direction.

$(-\varepsilon_b, S_b)$, $(-\varepsilon_c, S_c)$, and $(-\varepsilon_d, S_d)$, respectively. Here we assume $\varepsilon_b > \varepsilon_a \gg \varepsilon_d > \varepsilon_c$ and $S_a \approx S_b \gg S_c \approx S_d$, namely, that the *A* and *B* chains are more flexible and energetically more stable than the *C* and *D* chains, and the *B* and *D* chains have larger inclusion energies than the *A* and *C* chains, respectively. When the nanotube with length *L* includes the block copolymer, the free-energy map along the contour of the block copolymer is given as Fig. 5(b) and changes drastically with varying temperature. At a low temperature, including the *A* chain at the end of the block copolymer, the tube passes the *A* chain and stays at the *B* chain. As temperature rises, the free-energy level at the *B* chain becomes equal to that at the *C* chain at the temperature $T_{bc} = (\varepsilon_b - \varepsilon_c)/(S_b - S_c)$, so that the tube moves toward the *C* chain, passes the *C* chain, and stays at the *D* chain. It is to be noted that the tube does not travel backward, since the *B* chain is more stable than the *A* chain at any temperature. When temperature falls to $T_{da} = (\varepsilon_d - \varepsilon_a)/(S_d - S_a)$, the free energy level at the *D* chain becomes equal to that at the *A* chain, and the tube at the *D* chain moves to the *B* chain. That is, the temperature undulation between T_{bc} and T_{da} moves the tube stepwise in one direction on the block copolymer as schematically shown in Fig. 5(c). In other words, we can control the displacement of the tube on the block polymer, which can be regarded as a molecular motor ‘‘nano-rail.’’ The amplitude of the recurrent free energy, which produces the driving force of the nano-rail, is in proportion to the length *L* of the nanotube. Therefore, if *L* is long enough, the nanotube does not diffuse in either direction by the thermal agitation on the block copolymer, unlike small cyclic molecules such as cyclodextrins. The transitional behavior is a common feature of the supramolecular system comprising nanotubes and linear polymer chains [4].

In summary, the switching behavior of the molecular nanotube in the switching complexes in solutions was investigated theoretically using the Flory-Huggins lattice model. For miscible block copolymers, the nanotubes continuously move back and forth between the *A* and *B* chains as temperature varies. On the other hand, the switching transition occurs for immiscible block copolymers with a hysteresis loop. When a recurrent block copolymer made of four kinds of polymer chains is used, the molecular motor where the displacement of the nanotube is controllable by the temperature undulation can be realized. These theoretical results suggest high function of the supramolecular system consisting of the molecular nanotubes and the block copolymers.

---

[1] A. Harada, J. Li, and M. Kamachi, Nature (London) **356**, 325 (1992).

[2] A. Harada, J. Li, and M. Kamachi, Nature (London) **364**, 516 (1993).

[3] E. Ikeda, Y. Okumura, T. Shimomura, K. Ito, and R. Hayakawa (unpublished).

[4] Y. Okumura, K. Ito, and R. Hayakawa, Phys. Rev. Lett. **80**, 5003 (1998).

[5] P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, 1953).