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Nanostructures Formed by Combination of Nanotube and Polymer Chain

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Summary: We have investigated polymeric supramolecular systems of inclusion complexes between molecular nanotube and polymer chains theoretically and experimentally. This system indicates inclusion-dissociation behavior much sharper than the inclusion complex between cyclic molecule and small compounds. And we propose some functional supramolecules utilizing the combination of the nanotube or nanoring and polymer chains such as insulated molecular wire and topological gel.

Keywords: conducting polymer, cyclodextrin, gel, inclusion complex, nanotube, polyaniline, supramolecule

Introduction

Various organic supramolecules with unique structures have attracted great interests of many scientists.[1-5] As an example, Harada et al. prepared a polyrotaxane supramolecule in which cyclodextrin (CD) molecules of cyclic form were threaded on a polymer chain with bulky ends[6,7] and then synthesized molecular nanotubes with the diameter smaller than carbon nanotubes by crosslinking the adjacent CD units in the polyrotaxane.[8] This molecular nanotube, highly soluble in several kinds of solvents such as water, has a constant inside diameter (0.45nm) and a longitudinal length of submicron order controllable by varying the length of the polyrotaxane.

Owing to the infinitesimal inside diameter of the molecular nanotube, a polymer chain included in 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. Therefore, the inclusion of a polymer chain into a molecular nanotube is entropically unfavorable and promoted by attractive interaction such as hydrophobic one between the chain and the nanotube. In other

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words, heating results in the dissociation of the polymer chain from the nanotube with recovery of the intrinsic entropy of random coiled conformation. Moreover the conformational entropy and inclusion interaction are roughly evaluated to be proportional to the length of the nanotube and polymer chain. Consequently, the free energy changes drastically with inclusion or dissociation between a long molecular nanotube and polymer chain, which leads to phase transitional behavior.

We have recently investigated the inclusion complex formation between molecular nanotubes and polymer chains theoretically[9,10,14] and experimentally.[11-13,16-19] As mentioned above, this polymeric supramolecular system indicates the inclusion-dissociation behavior more cooperative and sharper than the inclusion complex formation between cyclic molecule and small molecular compounds.[10] And we have proposed some functional supramolecules utilizing the combination of nanotube or nanoring and polymer chains such as insulated molecular wire[16,19] and topological gel.[18] In this report, we will introduce these polymeric supramolecular systems.

Insulated Molecular Wire

Much attention has recently been paid to molecular devices.[20,21] Conjugated conducting polymers were regarded as a promising candidate for molecular wire connecting among electrodes and functional organic molecules such as molecular diode. However, it is quite difficult to actually use conducting polymers for molecular wire and measure the conductivity of a long single chain of conducting polymer. This is mainly because conducting polymer chains generally form fibrils entangled complicatedly. Certainly, some conducting polymer chains with alkyl side chains are soluble in organic solvents and can be isolated in very dilute solution. However, the polymer chain then forms coiled conformation because of the large conformational entropy. The coiled conformation consists of randomly distributed trans and gauche configurations. The trans configuration, namely, the planar zigzag or coplanar one, delocalised electron due to π conjugation while the gauche configuration breaks the conjugation to form defect. This indicates that high conductivity is not expected in the coiled conformation of the conducting polymer but in the all trans configuration, rodlike conformation. Consequently, to use a conducting polymer chain for molecular wire, we have to isolate a single chain and extend it to rodlike conformation. Incidentally, we can somewhat stretch a conducting polymer chain by adding poor solvent or doping, but then the extended polymer chain rapidly aggregates to become insoluble.

To resolve the difficulty in using the conducting polymer for molecular wire, we applied the inclusion complex formation with cyclodextrin (CD) to a conducting polymer chain.[16] What is the advantage of covering the conducting polymer chain with CDs? The coverage should reduce the attractive interaction between polymer chains considerably because CD has hydrophilic outside and highly soluble in various organic solvents. This means that one can easily isolate a single conducting polymer chain by covering with CDs. Next it is also expected that the conducting polymer chain forming the inclusion complex with CDs would be confined to rodlike conformation because the inside diameter of CD is extremely small. This means that the polymer chain has all trans, planar zigzag or coplanar configuration. Therefore, the π conjugation system should spread over a whole chain of the conducting polymer, which results in high conductivity. This inclusion complex has a molecular wire as an axis, which is covered with insulating cyclic molecules. Therefore it can be regarded as insulated molecular wire. Incidentally, there were some other approaches to form insulated molecular wires such as the chemical coupling of several conjugated monomer units threaded through β-CD,[22] the complex formation of camphorsulfonic acid and polianiline[23] and so on.

A conducting polymer used in the inclusion complex formation is emeraldine base polyaniline (PANI), which is highly soluble in n-methyl-2-pyrrolidone (MP) and has the average contour length of 300nm. Other soluble conducting polymers have too bulky side chains such as hexyl one to be included into the fine nanotube. We mixed MP solution of PANI with aqueous solution of α-, β- and γ-CDs at various temperatures. Then blue precipitation appeared in only the solution with β-CD at low temperature below ca. 275K. It has been reported that very high concentration of rodlike inclusion complexes yields precipitation, which is therefore used as an evidence of the inclusion complex formation. Accordingly, the experimental results suggested that only β-CD formed the inclusion complex with PANI because of a close fit in size. This is consistent with a report that aniline molecule, monomer of PANI, forms the inclusion complex with β-CD only. Furthermore, it is another important point of the experimental results that the precipitation was observed at low temperature. This is in qualitative agreement with the theoretical prediction that the inclusion behavior should be promoted at low temperature as mentioned before.

Next we investigated the structure of the inclusion complex by the electric birefringence spectroscopy and STM. The electric birefringence appears in solution containing rodlike molecules.[16] The experimental results of the electric birefringence showed that large electric birefringence was observed in the solution of β-CD and PANI at low temperature below ca. 275K and drastically decreased down to zero with increasing temperature. This means that β-CD and PANI forms rodlike inclusion complex at lower temperature while β-CD is dissociated from PANI at higher temperature. On the other hand, the STM image of HOPG substrate, on which low-temperature solution of β-CD and PANI was dropped and spincoated, showed a rodlike structure caught by an exfoliation of step on HOPG. The length is almost equal to the average contour length 300nm of PANI and the height is close to the outside diameter of β-CD. Consequently, we concluded that the rodlike structure was identified as the inclusion complex of β-CD and PANI, namely, the insulated molecular wire.

Moreover, we investigated the insulation effect of β-CD on oxidization of PANI by iodine.[17] It was reported that when iodine was added to MP solution of emeraldine base PANI, the solution color changed from blue to violet owing to the oxidization of PANI by iodine. Accordingly, the optical absorption spectroscopy determines whether PANI is oxidized or not. When we added iodine to solution of β-CD and PANI at 275K, the solution color did not change although the solution color of PANI alone at 275K changed to violet by addition of iodine. This indicates that β-CD fully covers PANI and prevents oxidization of PANI by iodine at low temperature. Next we heated up the solution of the insulated molecular wire and iodine to 288K. Then the solution color shifted to violet ca. 4 hours after heating. This suggests that β-CD was slowly dissociated from PANI at 288K and then PANI was oxidized by iodine. Namely, PANI is not oxidized by iodine as long as β-CD covers PANI perfectly.

Very recently, we formed another insulated molecular wire consisting of the α-cyclodextrin nanotube and PANI. In this case, we observed some precipitation of the nanotube and PANI even at room temperature.[19] This indicates that the inclusion interaction between the nanotube and PANI is stronger than that of β-CD and PANI. Figure 1 shows the AFM image of the insulated molecular wire on a mica substrate where the mixture of the nanotube and PANI was spin-coated. The height of the rodlike structure is nearly equal to the outside diameter of the nanotube. As mentioned above, PANI could not form inclusion complex with α-CD. This may seem to be inconsistent with the experimental results that the nanotube consiting of α-CD includes PANI.

Fig. 1. AFM topographic image (200nmX200nm) of an insulated molecular wire formed by the α-CD nanotube and PANI. The length is almost equal to the average contour length 300nm of PANI and the height is close to the outside diameter of α-CD.

However, it was reported that the α-CD nanotube included some low molecular compounds such as diphenylhexatriene, which could not form the inclusion complex with α-CD. [24] This is ascribed to some structural change by the cross-linkage of adjacent α-CDs. The same change is considered to occur in the present case of the inclusion complex between the α-CD nanotube nad PANI.

Topological Gel

Polymeric system shows self-assembled higher-order structures formed by a variety of intramolecular and intermolecular interactions. The structures and physical properties in nanoscale exert a great influence on the macroscopic properties. Very recently, we have reported a novel kind of gel other than the conventional physical and chemical gels.[18] The gel has high modulus, transparency and swellability arising from the nanoscale peculiar structure.

First of all let me introduce the hystorical background of the topological gel. Such a supramolecular gel with a polyrotaxane architecture was first formed by Harada's group in 1993.[25] They formed a physical gel having crosslinking points due to the hydrogen bond between α-CDs threaded onto polyethylene glycol (PEG). In 2000, Yui et al. synthesized biodegradable hydrogel having crosslinking points of the polyrotaxane of α-CD and PEG.[26] The biodegradation of the bulky end groups of the polyrotaxane resulted in the liquefaction of the gel, so that the hydrogel is applicable to the regenerative medicine. At almost the same time, we formed the topological gel having figure-of-eight crosslinks moveing freely in a polymer network.

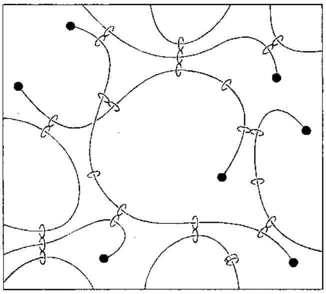

Fig. 2. Schematic diagram of the topological gel. The gel has figure-of-eight crosslinks freely moving in a polymer network.

We first synthesized a polyrotaxane in which a PEG chain with large molecular weight (Mw=20,000 and more) is sparsely included by α-CD. By chemically cross-linking α-cyclodextrins contained in the polyrotaxanes in solutions, we got transparent gels with good tensibility, low viscosity and large swellability in water. In this gel, the polymer chains with bulky end groups are neither covalently cross-linked like chemical gels nor attractively interacted like physical gels, but are topologically interlocked by figure-of-eight cross-links. It is expected that the figure-of-eight cross-links can pass the polymer chains freely to equalize the 'tension' of the threading polymer chains just like pulleys. Therefore, the nanoscopic heterogeneity in structure and stress may be automatically relaxed in the gel. Then we call this topological gel by figure-of-eight cross-links a 'topological gel'.

On tensile deformation, the polymer chains in the chemical gel are broken gradually due to the heterogeneous polymer length between fixed cross-links. On the other hand, the polymer chain in the polyrotaxane gel can pass through the figure-of-eight cross-links acting like pulleys to equalize the tension of the polymer chains cooperatively. Note that the equalization of tensions can occur not only in a single polymer chain, but also among adjacent polymers interlocked by the figure-of-eight cross-links. We call this 'pulley effect'. The physical properties of the topological gel are supposed to mainly result from the pulley effect.

The topological gel is a real example of the sliding gel theoretically considered so far and can be regarded as the third gel other than the chemical and physical gels, where the polymer network is interlocked by topological restrictions. The concept of the topological gel is important not only in the creation of high-performance gels or rubbers, but also as a new framework of artificial molecular motors based on the sliding motion just like the actin and the myosin.

Conclusion

We have so far introduced the polymeric supramolecules of the inclusion complex between the molecular nanotubes and polymer chains. The fundamental feature of the polymeric inclusion complex is transitional behavior different from the inclusion complex between small molecules. We have proposed some applications of the polymeric inclusion complex such as the insulated molecular wire and the topological gel. They are expected to develop into nanoscale electronic devices and nanomachines.

It may be stressed that there are many tools consisting of a string and ring or tube. This means that they are excellent combination and produce novel functions which are not given by each of them. On the other hand, we have not sufficiently applied it to functional materials in nanoscopic scale yet. This report indicates that we can control the nanoscopic structure and macroscopic properties by utilizing the combination between a polymer chain and nanoring or naotube.

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