Self-Assembly of Unlike Homopolymers into Hollow Spheres in Nonselective Solvent

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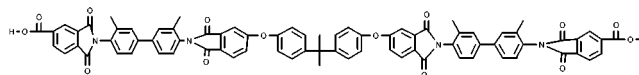Fudan University, Shanghai 200433, China*

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Self-assembly of macromolecules is an efficient and rapid pathway to supramolecular nanometer- or micrometer-sized objects which are almost impossible to synthesize by conventional chemical reactions.[1] Among the variety of self-assembly of polymers, micellization of block and graft copolymers in selective solvents[2,3] has been the most extensively studied. In recent years, great efforts have been made for fabricating supramolecular objects with novel phase morphologies, architectures, and functions.[1,4] One kind of the targeting materials is hollow spherical aggregates which are much in demand for the use as nano- or microcarriers for catalytic particles, molecules with electronic and photonic functions, as well as biological and medical species, and so forth. Such hollow spheres could be obtained from a block copolymer precursor, but it needs complicated physical and chemical procedures.[5,6] Jenekhe and Chen[7] reported that block copolymers composed of both coil and rod blocks could form large hollow spheres directly in selective solvents and further form ordered microstructure in the cast films. In addition, stepwise deposition of polyelectrolytes on a template followed by removing the template was suggested for producing submicrometer hollow spheres.[8]

In our group, efforts have been devoted to produce micelles without the chemical bonds between the core and shell.[9] For example, it was found that mixing polystyrene (PS) oligomers with a carboxyl end-group and poly(4-vinyl pyridine) (PVPy) in their common solvent chloroform, "graft copolymer" with the former as branches and the latter as backbone was formed due to the hydrogen bonding between the carboxyl and pyridine groups. The "graft copolymer" kept soluble in chloroform and formed micelles when a precipitant for one of the blocks was added. These noncovalently connected micelles behaved just like the conventional ones. In these investigations, both the backbone and grafts are flexible polymer coils. In this communication, the work is extended to a combination of rod and coil homopolymers, which leads to entirely new results.

By simply mixing two homopolymers, that is, rodlike low-molecular weight polyimide (PI) (Scheme 1) with two carboxyl end groups and coil-like poly(4-vinyl pyridine) in chloroform,

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Scheme 1. Chemical Structure of Polyimide (PI)

which was their common solvent and not a selective solvent, spherical aggregates with a size in hundreds of nanometers were produced. The number- and weight-average molecular weights of PI were 4600 and 9280 respectively, and the molecular weight of PVPy was 1.4×10^5. Both PI and PVPy were soluble in $CHCl_3$. However, mixing the dilute solutions of PI and PVPy over a broad range of proportions unexpectedly led to faint blue opalescence that indicated the formation of nano- or micro-sized particles. The hydrodynamic radius distributions of the solutions of PI/PVPy in chloroform obtained by light scattering are shown in Figure 1. Except for the case of the lowest concentration, the aggregates show very narrow size distributions as indicated by the low polydispersity index (PDI) values (0.02 and 0.06). This is not expected as there are no chemical bonds between PI and PVPy and both of them are polydispersed homopolymers. The solutions of PI/PVPy form stable aggregates with apparent "molecular weight" (MW) in the range of $6.1–20 \times 10^7$ and average hydrodynamic radius $\langle R_h \rangle$ from 238 to 384 nm. As the root-mean-square of end-to-end distance of PVPy and the fully extended length of PI are estimated to be only 26 and 20 nm, respectively, it is reasonable to think that such large spheres contain a hollow cavity. This argument is supported by the rest of the data in Table 1 as follows. (1) The average density of the micelles (ρ) is only $1.3–1.8 \times 10^{-3} g/cm^3$, which is about 2 orders of magnitude smaller than that of ordinary polymer micelles[10] and surfactant-free dispersed polymer particles.[11] (2) For the spheres with low polydispersity, the $\langle R_g \rangle/\langle R_h \rangle$ values (0.92 and 1.15) are far different from the expected values[12] by theory for a uniform sphere (0.774) and a polymer coil (1.50) but close to that for nondraining thin-layer hollow spheres (1.0). (3) Both the molecular weight and size of the aggregates significantly increase with dilution of the solutions. This behavior is completely different from that found for the ordinary polymeric micelles.

The spherical aggregates of PI/PVPy were confirmed to be hollow by transmission electron microscopy (TEM) and atomic force microscopy (AFM). The morphology of the individual particles without stain is shown in Figure 2A. The remarkable feature of the particles is the obvious contrast between the central and outer part. This is a typical TEM image of hollow spheres, as reported for different kinds of particles with central cavity.[7,8,13] The diameter of the particles in Figure 2A is between 400 and 600 nm, comparable to that measured by LLS. In this micrograph, some irregular mottles can also be observed. It can be attributed to excess PI, which was not attached to PVPy by hydrogen bonding. The 3D-image of the hollow spheres shown in Figure 2B was obtained by tapping-mode AFM for the specimen cast on mica substrate. Instead of perfect spheres, which are often found for ordinary micelles, broken and collapsed particles were observed. Typically, the prominent wall approximately has a peripheral diameter of about 600, a thickness of about 100, and a height of 20 nm. Note that the images in Figure 2, A and B, exhibit morphologies of collapsed hollow spheres. Therefore, the thickness of the prominent wall is not equal to that of the shell of hollow spheres.

As the assembly occurs in a nonselective solvent, we are not able to infer which block composes the inner shell and which

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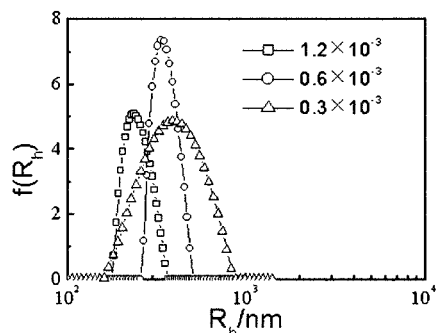(13) Jiang, P.; Bertone, J. E.; Colvin, V. L. *Science* **2001**, *291*, 453.

Figure 1. Hydrodynamic diameter distributions of the PI/PVPy (12/1, w/w) hollow spheres in chloroform with different PI concentrations (g/mL) measured by dynamic light scattering.

Table 1. Characterization Data of the Hollow Spheres of PI/PVPy Measured by Both Dynamic and Static Measurements Which Were Conducted with an LLS Spectrometer (ALV/SP-125) with a Laser Source of Wave-Length 532 nm and CONTIN Analysis Mode

$C \times 10^3$ g·ml^{-1}	$MW \times 10^{-7}$ g·mol^{-1}	$\langle R_h \rangle$ nm	$\langle R_g \rangle / \langle R_h \rangle$	$\rho \times 10^3$ g·cm^{-3}	PD.I.
1.2	6.1	238	1.15	1.8	0.02
0.6	11	322	0.92	1.3	0.06
0.3	20	384	0.85	1.4	0.12

composes the outer shell simply from the knowledge of the solubilities. Since each pyridine unit serves as a proton acceptor, a PVPy chain may carry many, up to 10^2 to 10^3, PI rods. Therefore, the local concentration of PI rods surrounding a PVPy chain is much higher than the average, and consequently the requirement of effective packing of such crowded rods provides the driving force for forming large hollow spheres. This is analogous to the case of lyotropic liquid crystal in solution. If this argument is correct, then PI rods construct the inner shell. A schematic illustration of the self-assembly of the PI rods and PVPy coils into the hollow spheres is shown in Figure 2C. This is, of course, only one of the possible mechanisms for the formation of hollow spheres. The three-layered PVPy−PI−PVPy stucture is also possible. Further research on the detailed structure of the hollow spheres is needed.

As mentioned above, we previously found that PS oligomer with one carboxyl end group and PVPy formed micelles in selective solvent.[9b] However, in this case of coil−coil combination, no micelle formation occurred in common solvents. It is reasonable to think that grafts with enough stiffness are necessary for the formation of hollow spheres in nonselective solvents. Besides, here both ends of the PI oligomer are carboxyl groups, which did not lead to "cross-links" as no microgel was observed. When one carboxyl end is attached to PVPy, the other may form self-association with another PI chain. Such hydrogen bonding between like polymer chains could be useful for stabilizing the micellar structure as reported for the micelles based on block copolymers.[7a]

Further direct self-assembly of the PI/PVPy hollow spheres results in solvent-cast films with a layered, hexagonal close-packing lattice of circular air holes in the polymer matrix, similar to that obtained from coil−rod block copolymers.[7(b)] We will report it in our forthcoming papers.

In short, we have demonstrated a homopolymer strategy for fabricating large hollow spheres by self-assembly. This new approach avoids the use of block copolymers, which is of course
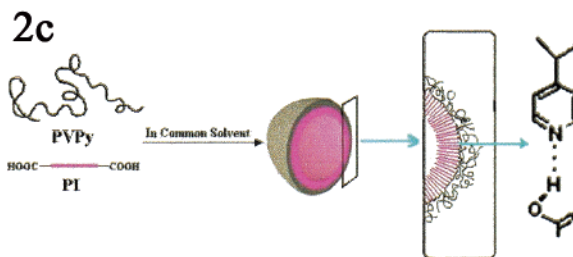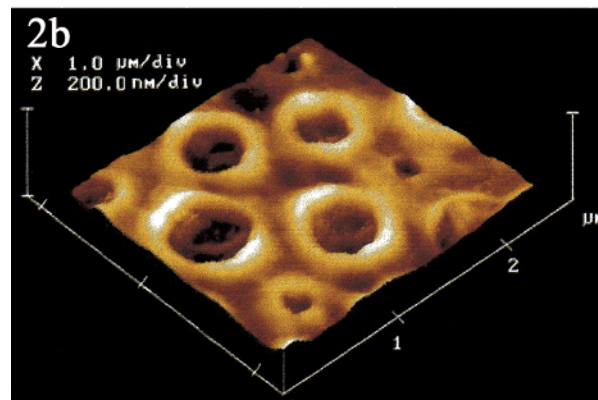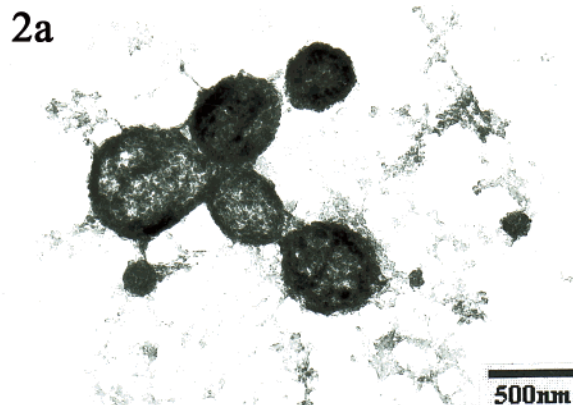

Figure 2. Morphologies of discrete hollow spheres observed by (A) TEM, where scale bar = 500 nm, and (B) by AFM and (C) a schematic illustration of the formation of the hollow spheres.

beneficial for realizing practical applications of such suprastructural materials. Besides, as no theory has expected such kind of assembly of homopolymers, particularly in common solvents, driven by intermolecular hydrogen bonding and efficient packing of rodlike polymers,[14] the findings here are quite challenging to the relevant theories.

Supporting Information Available: Experimental details for the synthesis of PI and PVPy, preparation of the hollow spheres, and characterization methods (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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