Nanofabrication in Polymer Solutions

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Dedicated to the Occasion of the 80th Birthday of Prof. HUANG Bao-Tong and Prof. FENG Zhi-Liu

Abstract This review covers recent advances in fabrication of nanomaterials in polymer solutions with emphasis on using the self-assembled amphiphilic block copolymers in solution to fabricate organic/inorganic composites with nanoscale modifications. The phase behavior of block copolymers in water and the use of templates to form ordered nanostructures are reviewed in detail. Modern physical techniques for nanoscale characterization are also introduced. The authors suggested that this approach should provide new routes to create materials with interesting morphologies for many different applications.

Keywords nanostructured material, polymer solution, block copolymer, micelle, self-assembly, review

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Nanostructured materials have drawn a great deal of attention in recent years because of their promising potentials in future applications. The fabrication of nanomaterials has become a highly active research area involving scientists in many different fields, *e.g.*, physics, chemistry, biology and materials science and engineering. The inorganic synthesis including biomineralization by using intermolecular bonds to act in a cooperative manner in order to construct organized supramolecular systems by self-assembly has been of particular interest[1]. The studied inorganic materials have been extended to semiconductors[1f, 1g, 1k], silicon-based materials[1c-1e], super-magnetic materials[1h-1m] and biominerals[1n](*e.g.*, bone, teeth). Some relatively simple inorganic minerals($CaCO_3$, SiO_2, Fe_3O_4, CdS and so on) have been synthesized with controlled, functional architectures[1]. This area has been growing so drastic that it is difficult for us to give a comprehensive review within a few pages. In this paper, we only summarize some representative new works to highlight the current major frontiers.

One very important aspect on the nano-scale synthesis is to form desired supramolecular pre-organization that can be used as a "matrix" for inorganic synthesis[1a]. Some surfactants, including amphiphilic block copolymers[2], can self-associate into organized structures in a selective solvent, *i.e.*, a solvent selectively good for one part of the molecule(*e.g.*, the head group(s) of a surfactant or the hydrophilic block(s) of the block copolymer) and a worse solvent for the other part (*e.g.*, the organic tail(s) of the

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surfactant or the hydrophobic blocks(s) of the block copolymer). The so formed systems include micelles, microemulsions, vesicles, monolayers and some biological macromolecules(*e.g.*, proteins). Then, inorganic reagents are added into the system and are automatically distributed in the favored environment(due to free energy minimization). For example, water-soluble salts will only exist in the hydrophilic regions. Under certain external conditions, chemical reaction can occur at the specific region where the reagents exist and produce stable(*e.g.*, insoluble in water) products that will exist in its new favored environment. Such kind of final products can have very special orders on a nanometer scale, such as the formation of nano-tubes, nano-spheres or nano-cavities[1].

The design of homogeneous nanoscale templates as synthetic matrices often formed one of the key steps during the formation of nanomaterials. Among the templates being investigated, self-assembled nanostructures formed by block copolymer micelles have been widely explored because of their diversity in supramolecular structures(*e.g.*, spherical, cylindrical, lamellar and bicontinuous) that can be tuned by adjusting the block chain lengths or chain architecture.

The self-assembly of block copolymers into micellar structures occurs when they are dissolved in a selective solvent, with the solvent-phobic blocks forming the core and the solvent-philic blocks forming the corona[2]. The formation of spherical micelles with the so-called "core-shell" structure often obeys a close-association mechanism with the formula[3b].

$$nA \leftrightarrow (A)_n \tag{1}$$

The association number, *i.e.*, the number of polymer chains in one micelle, of the micelles is about the same for all of the micelles under fixed external conditions. For tri-block copolymers with two end blocks in a poor or nonsolvent, supramolecular formation with open structures that tend to obey an open-association mechanism can occur[3]:

$$\text{unimer} \leftrightarrow \text{dimer} \leftrightarrow \text{trimer} \leftrightarrow \cdots\cdots \tag{2}$$

Then, broad distributions in the micellar mass and the micellar size can be observed. Furthermore, spherical micelles could change shape to other morphologies, *e.g.*, prolate[4a,4b] or oblate[4c], by changing external conditions, such as temperature or solvent composition.

Numerous physical methods have been utilized in studying block copolymer micelles in solution[2a,3a]. Usually a combination of several physical methods is needed. The most widely used techniques include scattering techniques [static light scattering(SLS), dynamic light scattering(DLS), small-angle X-ray scattering(SAXS) and small-angle neutron scattering(SANS)], viscosity measurements, NMR and pulsed field-gradient spin-echo NMR, gel permeation chromatography, fluorescence spectrophotometry, transmission electron microscopy(TEM), atomic force microscopy(AFM) and scanning electron microscopy(SEM).

The phase behavior of block copolymers in water have been well studied because

most of the applications of copolymers were in aqueous solution[2c]. In aqueous solution, the solubility of block copolymers decreased with increasing temperature and above a certain temperature, phase separation happened so that the copolymer could no longer be dissolved in water to form a homogeneous one-phase region. This temperature is called the "cloud-point temperature"[3c]. At higher polymer concentrations, the entanglement of polymer chains in solution leads to the formation of homogeneous, immobile gel-like structures. The first gel-like structure is usually a cubic structure(body-centered cubic and face-centered cubic), formed by the ordered packing of spherical micelles. At higher polymer concentrations, the arrangement of the hydrophilic and hydrophobic regions leads to the formation of hexagonal or lamellar structures. Bicontinuous cubic structure could also be observed sometimes between the hexagonal and lamellar regions[2]. For the flower-like micelles formed by a block copolymer in a selective solvent for the middle block, an open network without any ordered structure can generally be obtained at high polymer concentrations. A schematic plot is shown in Fig. 1 to demonstrate the general phases and phase transitions of block copolymers in aqueous solution. The most common method to determine the phase structure of the gel-like materials is SAXS. The scattering peaks, which appear in the small-angle region, can reveal the nature of nanostructures, by identifying the relative positions of the higher ordered peaks to the primary peak, with the position of the primary peak being related to the domain size of the nanostructure.

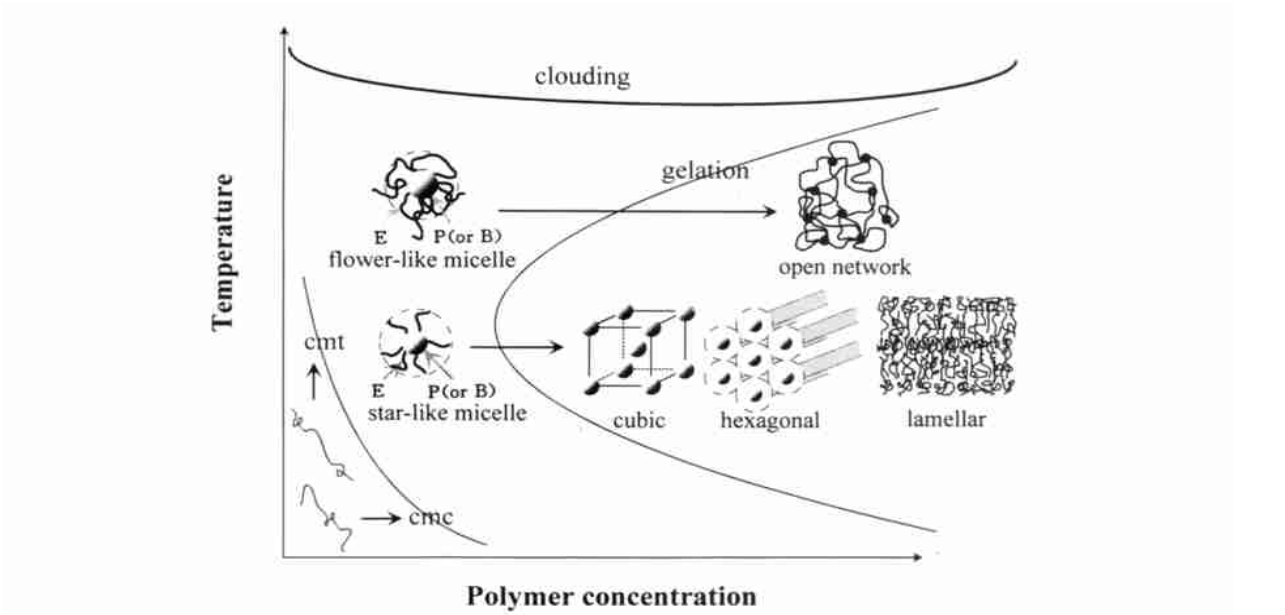

Fig. 1 Schematic plot to show the phase behavior of amphiphilic block copolymers (represented by EBE and BEB-type triblock copolymers) in aqueous solution

Copolymer/water/oil ternary phase diagrams can be much more complicated even at a fixed temperature[6]. Lindman and co-workers did extensive studies on the phase behavior of Pluronics(a group of triblock copolymers containing hydrophilic E blocks and hydrophobic P or B groups, with E, P, B being polyoxyethylene, polyoxypropylene and

polyoxybutylene, respectively) in the presence of water and xylene[6d-6g]. The ternary phase diagram of Pluronic P84($E_{19}P_{44}E_{19}$)/water/*p*-xylene studied by Alexandridis *et al.* at room temperature is cited in Fig. 2 where at least nine different phases can be identified: normal (oil-in-water) micellar solution, cubic, hexagonal, bicontinuous cubic; reversed (water-in-oil) micellar solution, cubic, hexagonal, bicontinuous cubic phases and a lamellar phase[6g].

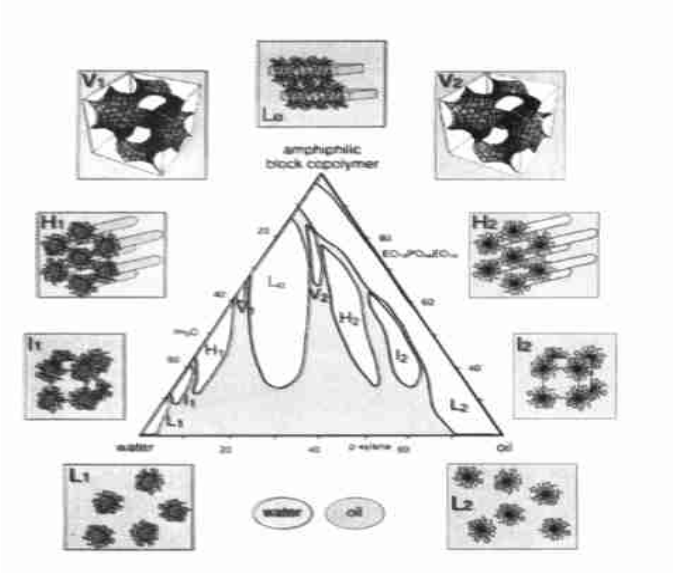

Fig. 2 Ternary phase diagram of Pluronic P84 ($E_{19}P_{44}E_{19}$)/waer/*p*-xylene at room temperature
Nine different phases can be identified: normal(oil-in-water) micellar solution L_1, cubic I_1, hexagonal H_1, bicontinuous cubic V_1; reversed(water-in-oil) micellar solution L_2, cubic I_2, hexagonal H_2, bicontinuous cubic V_2 phases and a lamellar phase L_T(cited from ref. 6g)

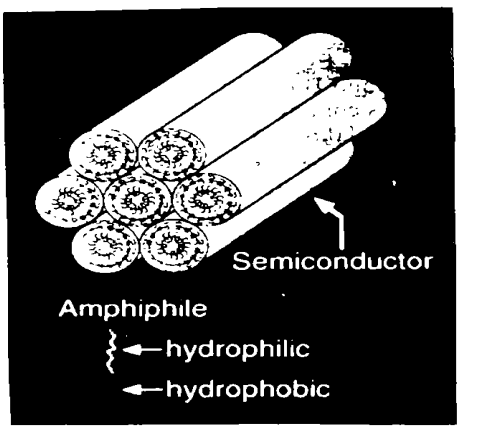

Fig. 3 Schematic representation of an ordered nanocomposite solid in which the organic phase consists of hexagonally closed-packed tubules of self-assembled amphiphiles. Inorganic semiconductor CdS precipitates in the hydrophilic region (cited from ref. 1f)

The ordered nanostructures formed by the self-assembled block copolymers can be used as unique templates for fabricating materials with nano-scale modifications. An example was given by Stupp and co-workers[1f]. They used the two-dimensional hexagonal nano-structure packed by cylindrical amphiphilic micelles as the template to synthesize CdS(an important semiconductor) nanotubes(Fig. 3). CdS was prepared by introducing H_2S into the hydrogel containing water-soluble $CdCl_2$ ions, which should reside only in the hydrophilic region. The water-insoluble CdS was then accumulated in the hydrophilic region. After removing the polymer matrix by calcination at high temperature, pure CdS nanotubes could be obtained. The final product could ever maintain the hexagonal packing, as confirmed by SAXS and TEM measurements.

Stucky and co-workers did extensive work to use different Pluronic PEO-PPO-PEO triblock copolymers as templates to form mesoporous silica[1d]. Compared to short-chain surfactants, the block copolymers provided larger and tunable domain sizes that could be

used for making silica with larger holes, an important parameter for molecular sieves. Different mesoporous silica samples with hexagonal packing and having 5 to 30 nm pores were synthesized. Again, calcination was used after the inorganic reaction to remove the polymer materials. Both TEM and SAXS (with several scattering peaks appearing at small angles) showed that the final products had certain hexagonal order in the nanometer scale (Fig. 4). Besides silica, the same group also extended their exploration to making nanomaterials of other inorganic compounds by using similar approaches, such as the oxides of lead, iron, tungsten, antimony and zinc[1c].

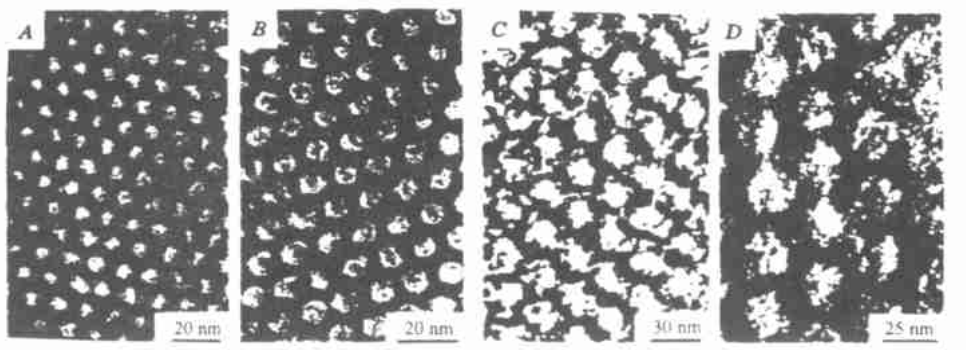

Fig. 4 TEM images of calcined hexagonal mesoporous silica with different average pore sizes (*A*) 6.0 nm, (*B*) 8.9 nm, (*C*) 20.0 nm and (*D*) 26.0 nm (cited from ref. 1d)

By taking advantage of the self-assembly of an amphiphilic polymer, Hanabusa and co-workers synthesized long "macaroni"-like TiO_2 hollow fibers with potential applications as photovoltaic solar cells, photocatalytic devices and rechargeable lithium ion battery electrodes[7]. They designed a special polymer trans-(1*R*, 2*R*)-1, 2-cyclohexanedi (11-aminocarbonylundecylpyridinium) hexafluorophosphate which can self-assemble into rods and interact with $Ti[OCH(CH_3)_2]_4$. TiO_2 would grow on the surface of the polymer rods into a hollow rod structure. The SEM measurements clearly showed the formation of quite uniform TiO_2 hollow fibers with inner diameters between 150~600 nm and lengths of about 200μm, as shown in Fig. 5.

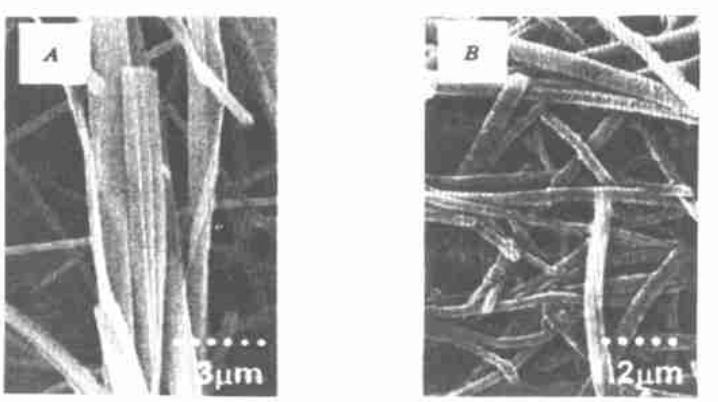

Fig. 5 SEM images of the calcined TiO_2 hollow fibers prepared under acidic (*A*) and basic (*B*) conditions (cited from ref. 7)

Metal nanoparticles possess unique chemical and physical properties that can be exploited in a wide variety of technical applications, such as catalysis, non-linear optics, ultrapurification and microelectronics. Their properties usually depend strongly on their size, size distribution, shape and chemical environment. Therefore, it is important to make uniform metal nanoparticles to narrow size distributions. Bronstein et al[8] reported the use of an amphiphilic polymer matrix formed by poly(octadecylsiloxane) (PODS) to grow noble metal nanoparticles. The nanostructured polymer matrix was used not only to interact with inorganic reagents, but also to stabilize the metal particles and to confine their environments during particle growth. The authors showed that it was successful to prepare noble metal nanoparticles by using this technique.

Another approach to use polymer chains in solution is to form organic/inorganic nanocomposites[9]. Antonietti *et al* reported the use of a triblock copolymer PEO-PMAA-C_{12} [with PMAA being poly(methacrylic acid) and C_{12} being a dodecyl chain] to form inorganic nanoparticles such as $CaCO_3$[9a]. Among the three blocks in the polymer, two blocks are hydrophilic(long chain PEO and short chain PMAA). The polymer chains would form micelles in aqueous solution with PEO and PMAA being micellar shells. The idea was to use the charged PMAA block to interact with inorganic salts and surfaces, and to use PEO to increase the solubility of the system in water. At different acidic pH conditions, two new types of discrete nested structures, consisting of hybrid nanofilaments arranged to give an unusual neuron-like morphology (Fig. 6), were synthesized. The coorperative interactions at a local level between $Ca_3(PO_4)_2$ clusters and the polymer units could be responsible for the highly anisotropic nature of the product. After aging, a second hybrid morphology consisting of compact aggregates appeared, which showed the interlocked layer structure of an ordered inorganic/organic mesophase with a domain size of 3 nm. They proposed that the new materials might be useful as novel ceramics precursors, reinforcing filters or biomedical implants.

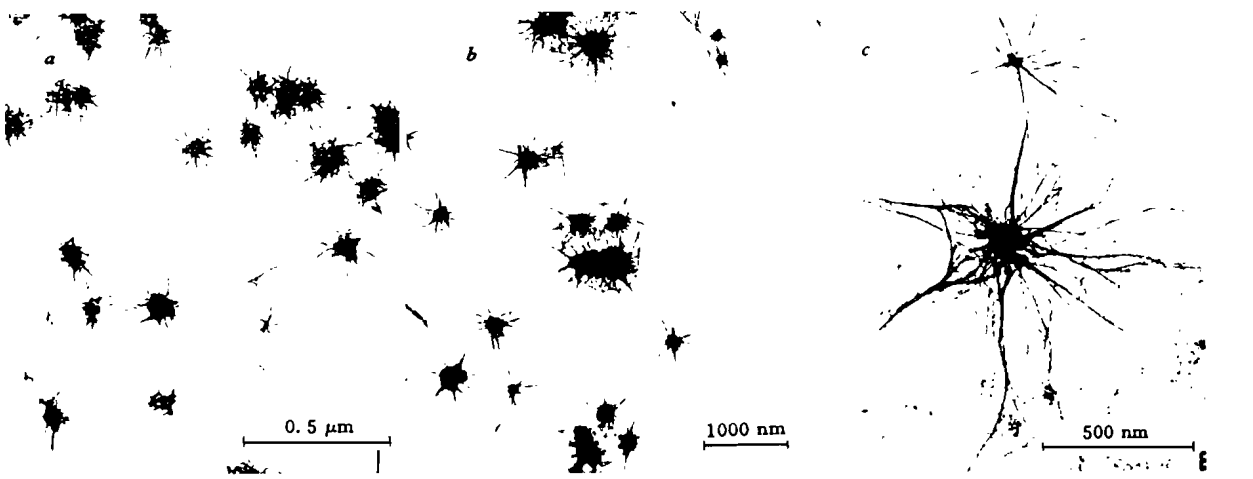

Fig. 6 TEM images(*a*~ *c*) showing the growth of neuron-like calcium phosphate/polymer mesostructures at pH 4.5 and 5.0(cited from ref. 9a)

Recently, our group discovered a new fabrication mechanism where the polymer chains (polyoxyethylene) functioned simultaneously as a weak reducing agent, and a network to hold the final products long enough so that "perfect" hollow nanospheres could be synthesized. A typical example is the formation of Mo oxide "hollow" nanospheres, which can be obtained from the slow decomposition of a water-soluble precursor compound $MoO_2(OH)(OOH)$. Without polymers, normal MoO_3 would be obtained. However, in the presence of PEO-containing polymers, Mo was partially reduced from Mo(Ⅵ) to a mixture of Mo(Ⅴ) and Mo(Ⅵ), by showing a color change from yellow to dark blue. The crystalline structure of MoO_3 basically disappeared, but over 100 new scattering peaks appeared in the small angle region, indicating an extremely ordered simple-cubic packing of 5 nm nanospheres. The Mo oxide nanospheres should be chemically connected in order to produce such a long-range order. This supposition was supported by a high resolution TEM measurement although final confirmation would require further experimental evidence, perhaps by means of surface-to-volume measruements. The new structure was very similar to that of Linde type-A zeolite, but with a much larger domain size(Fig. 7). We can exclude the possibility of the micelle-templating model, because these nanospheres could be obtained in the presence of only long chain PEO homopolymer solutions.

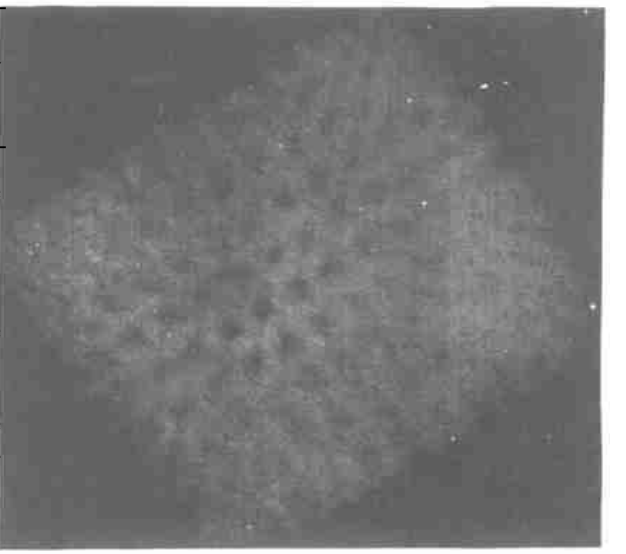

Fig. 7 TEM image of the packing of Mo oxide hollow nanospheres into ordered zeolite-like structure
The distance between two adjacent pores is 5.0 nm

In summary, polymer networks in solution provide a variety of ways to fabricate inorganic materials and organic/inorganic composites with special nanoscale modifications. This dynamic field shall grow vigorously in the near future and create new materials with interesting morphology for different applications, for example, in photonics, electronics, catalysis and microsensors.

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