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Stimuli-responsive one-dimensional copolymer nanostructures fabricated by metallogel template polymerization and their adsorption of aspirin

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pH responsive poly(*N*,*N*′-methylenebisacrylamide-*co*-4-vinylpyridine) (P(MBA-4VP)) one dimensional (1D) nanostructures have been prepared by metallogel template copolymerization, which was carried out in an Ag(I)-coordinated organogel with benzoyl peroxide (BPO) as the initiator. The product has been characterized using infrared spectroscopy, scanning electron microscopy and transmission electron microscopy. The experimental results reveal that the gel fiber is a crucial template for polymerization. Due to the degradation of the template in copolymerization, nanofibers of metallogel were transcribed to copolymer nanowires. The introduction of co-monomer 4-vinylpyridine (4VP) imparts to the 1D copolymer nanostructures pH sensitivity and the possible use as an adsorption material of aspirin. Adsorbed 1D copolymer nanostructures could be regenerated using proton solvent, acid medium and salt solution. In addition, silver nanoparticle loaded copolymer nanowires have been produced from the reduction of silver ions instead of template removal, where silver ions act both as the template and as the nanoparticle growth substrate.

Introduction

The pursuit of stimuli responsive polymers with a desired structure and novel utilization has persisted over many decades,[1] and covers chemistry, physics, biology, and materials science.[2] Stimuli-responsive polymers (also called intelligent,[3] smart,[4,5] or environmentally sensitive[6] polymers) can undergo relatively large and abrupt physical or chemical changes in response to small external environmental stimuli, such as temperature, pH, electrolyte concentration, light, electric or magnetic fields, and a combination of any of them.[7] Among these stimuli, pH is the most intensively investigated in various laboratories and industries[8] due to its rapid response,[9,10] relative effective control[11,12] and a versatile application range.[13] A pH-response can be obtained either by using weakly acidic monomers (*e.g.* acrylic acid) whose ionization status can be changed by pH variation, or by using weakly basic monomers (*e.g.* 4-vinylpyridine) that can be rendered water-soluble by protonation at low pH.[11,14] pH responsive polymers have been widely investigated for drug delivery, separation, and diagnostics applications.[13] Presently, a great deal of work has been dedicated to different physical forms of stimuli responsive polymers, such as nanogels/microgels,[15–17] micelles,[18] brushes,[19] membranes[20] and so on, that can be crafted into new smart materials.[1] However, one dimensional (1D) polymer nanostructures such as stimuli responsive nano-objects have rarely been addressed.

In recent years, the study of 1D polymer nanostructures, such as nanowires, nanoribbons and nanotubes, has attracted considerable attention, and much effort has been focused on the exploration of their unique properties and their synthesis and fabrication. Their 1D morphology and anisotropic nanostructures offer an unlimited amount of potential applications relevant to electromechanical nanoscale devices,[21] separations,[22,23] drug delivery[24,25] and catalyst supports.[26] So far, three different strategies have been developed for the preparation of 1D polymer nanostructures, including electrospinning,[27] self-assembly of block copolymers[28] and template methods. Most of the template methods focus on the polymerization in porous hard templates,[29,30] which are tedious to remove fully after the synthesis. Every strategy has its own advantages and disadvantages. Therefore, it is still required to develop novel and facile approaches for 1D polymer nanostructures from a practical view point.

Recently, our group has reported the fabrication of 1D polymer nanostructures using a metallogel as a soft template, which can be very easily removed.[31] Metallogels, the supramolecular gels in some way incorporating metallic elements,[32] have heat-stable properties and a facile preparation procedure,[33] which have been exploited to fabricate and assemble inorganic nanomaterials,[34] as well as polymer nanostructures.[33] In our previous articles, we have developed a silver metallogel and based on which we managed to fabricate 1D polymer nanostructures by the free radical polymerization of multifunctional

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monomers, such as *N*,*N*′-methylenebisacrylamide (MBA)[31] and diacryloyl-2,6-diaminopyridine (DADAP).[35,36] Heat-initiated polymerization took place on the gel fibers, and the original gel fibers were successively easily removed by using excess ammonia. However, these works were based on the homopolymerization of a cross-linkable monomer bearing coordination groups, which limit the selection of monomers seriously. Therefore, the purpose of this paper is to introduce other monofunctional monomers to copolymerize with MBA to synthesis 1D copolymer nanostructures. That means more selections for co-monomer types, copolymer compositions and functions of 1D copolymer nanostructures.

In this paper, we attempted to fabricate pH responsive 1D copolymer nanostructures *via* copolymerizing MBA with pH sensitive co-monomer 4-vinylpyridine (4VP) using the silver metallogel as a template. Compared to DADAP, 4VP is easy to obtain and renders the copolymer to be sensitive to pH changes.[37] Furthermore, the pyridine group can form the double hydrogen bonding system with carboxylic acid group with the association constant up to 10^7 M^{-1} in chloroform.[38,39] Therefore, the product is capable of 'uptaking' some carboxylic compounds (*e.g.* aspirin) from dilute solution effectively, which makes the 1D copolymer nanostructures to be used as an adsorption material in drug production, extraction and recovery industries. Additionally, we also tried to fabricate silver nanoparticle loaded copolymer nanowires by using the reducing agent to treat the copolymerized product, instead of ammonia treatment to remove the metallogel templates. Different from the traditional method which involves the entrapment and subsequent reduction of silver ions,[40] silver ions originally exist inside the copolymer nanowires without additional incorporation steps in this system. Silver ions act both as the template and as the nanoparticle growth substrate. That means a more deep application of 1D copolymer nanostructures and a simple approach for one dimensional metal–organic hybrid nanomaterials.

The obtained 1D copolymer nanostructures were characterized by Fourier-transform infrared (FT-IR), whereas their morphology was confirmed by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) analyses and the rheological properties of the gel samples were tested by a rheometer. The pH-responsive behaviors of 1D copolymer nanostructures formed at various monomer compositions were investigated as the change of pH values. Their adsorption and desorption of aspirin were detected by a UV-Vis spectrometer. The morphology of silver nanoparticle loaded copolymer nanowires was confirmed by TEM and the silver nanoparticles were characterized using electron dispersive X-ray (EDX) spectroscopy. Based on these results, we think that this simple approach reported herein may be extended to prepare more kinds of functional 1D polymer nanostructures.

Experimental

Materials

Tetrahydrofuran (THF, Tianjin Chemical Reagents) was freshly distilled from sodium prior to use; benzoyl peroxide (BPO) was purchased from Beijing Chemicals and purified by recrystallization using methanol. *N*,*N*′-Methylenebisacrylamide (MBA) purchased from Sigma Aldrich was used as received. Benzene-1,3,5-tricarbonyl trichloride, 3-hydroxyl pyridine, pyridine, 4-vinylpyridine (4VP), $AgNO_3$ and aspirin purchased from Alfa Aesar were used as received. Other solvents and reagents, including deionized water, ethanol, dichloromethane, chloroform and so on, were used without further purification.

Synthesis of tripyridin-3-yl benzene-1,3,5-tricarboxylate (ligand L)

First, 3.81 g (40 mmol) of 3-hydroxyl pyridine and 3.2 g of pyridine (40 mmol) were dissolved in 70 mL dehydrated THF. 2.65 g (10 mmol) benzene-1,3,5-tricarbonyl trichloride dissolved in another 30 mL of dehydrated THF was dropped into the solution in 1 h at room temperature. After addition, the reaction mixture was allowed to stir at 85 °C for 12 h. After that, the cooled resulting solution was evaporated at reduced pressure and 50 mL deionized water was added to dissolve impurities. The resulting white solid was filtered and purified by column chromatography using dichloromethane/THF (5/1) as the eluent to give a 2.91 g product (66% yield). ^{1}H NMR (300 MHz, [D_6] DMSO, δ/ppm): 9.08 (s, 3H, aryl H), 8.70 (d, 3H, 2-pyridyl H), 8.58 (d, 3H, 6-pyridyl H), 7.91(d, 3H, 4-pyridyl H), 7.59 (d × d, 3H, 5-pyridyl H). FT-IR (KBr, cm^{-1}): 3085, 3066 (aryl and pyridyl C–H), 1740 (C=O, strong), 1589, 1578, 1477, 1427 (aryl, pyridyl C=C and pyridyl C=N).

Fabrication of 1D copolymer nanostructures

In a typical process, 10 mg ligand L, 8 mg MBA and a certain molar ratio of 4VP were dissolved in 0.4 g dehydrated THF in a vial, then a 0.4 g THF solution of 6 mg $AgNO_3$ and 2 mg BPO was injected quickly by a needle. A gel (2 wt%) was formed within 10 seconds. The tightly sealed vial containing the gel was put into an oil bath at 63 °C to carry out the radical copolymerization of MBA and 4VP. After a desired period of reaction, excess ammonia was added to remove any remaining templates. The white solid was collected by filtration, washed repeatedly with ammonia and THF, and finally dried in a vacuum.

Characterization of 1D copolymer nanostructures

The resulting copolymer was characterized by a Nicolet 560 Fourier-transform infrared (FT-IR) spectroscope. The morphology of 1D copolymer nanostructures was characterized using transmission electron microscopy (TEM) and scanning electron microscopy (SEM). TEM images were obtained on a JEOL J2010 transmission electron microscope operating at an accelerating voltage of 200 kV by drop casting the sample dispersion on copper grids coated with a carbon film. SEM images were obtained on a JEOL FESEM 6704F electron microscope operating at an accelerating voltage of 20 kV after the sample was coated with a thin layer of gold. The rheological properties of the metallogels and copolymer gels were tested by a Physica MCR300 rheometer with a plate fixture.

pH-responsive behaviors of 1D copolymer nanostructures

The equilibrium swelling ratio was determined to characterize the pH-responsive behavior of 1D copolymer nanostructures. The equilibrium swelling ratio (Q) was determined as follows:

$$Q = (W_s - W_d)/W_d$$

where W_s and W_d are the weights of the swollen and dry gels, respectively.

To determine the equilibrium swelling behavior, known amounts of dried copolymer gels after the ammonia treatment were put into 5 mL buffer solutions at different pH values, until a constant weight was attained. The buffer solutions of different pH values were prepared with 0.2 mol L^{-1} disodium hydrogen phosphate solution, 0.1 mol L^{-1} citric acid solution, 0.05 mol L^{-1} disodium hydrogen phosphate solution and 0.1 mol L^{-1} sodium hydroxide solution.

Adsorption and desorption of aspirin

The rate of guest molecule adsorption was measured by placing 10 mg of dried copolymer gels after the ammonia treatment in 2 mL aspirin–chloroform solution (50 mg L^{-1}). The absorbance spectrum of the solution was recorded with a UV757CRT spectrophotometer, and the characteristic absorbance of aspirin at 242 nm was used to monitor its concentration. For the desorption studies, the aspirin-loaded copolymer gels were immersed in 5 mL solvents including hot (65 °C) ethanol, buffer solution of pH 2.2 and sodium chloride solution respectively, then filtered after a certain time. The absorbance spectra of these filtrates were recorded with a UV757CRT spectrophotometer. After that, new solvents were added again to immerse the aspirin-loaded copolymer gels and then filtered, and the absorbance spectra of these filtrates were recorded. This process was repeated until the absorbance of filtrates in UV-Vis spectra was less than 0.3.

Fabrication and characterization of silver nanoparticle loaded copolymer nanowires

The copolymerization process was the same as that of 1D copolymer nanostructures. After 24 hours of copolymerization, the resulting copolymer gel with the template was dried to remove THF, and then 2 mL ethylene glycol solution was added in the vial to swell the copolymer gel. The tightly sealed vial containing the gel and ethylene glycol solution was put into an oil bath at 120 °C to carry out the reduction reaction of silver ions for 2 hours. The high temperature ethylene glycol solution acted as a reducing agent for the silver ions. After reduction, the yellow solid was collected by filtration, washed repeatedly with deionized water, and finally dried in a vacuum. The morphology of silver nanoparticle loaded copolymer nanowires was characterized using a JEOL J2010 TEM and the silver nanoparticles were characterized using electron dispersive X-ray (EDX) spectroscopy performed on a JEOL J2010 with an Oxford spectrometer.

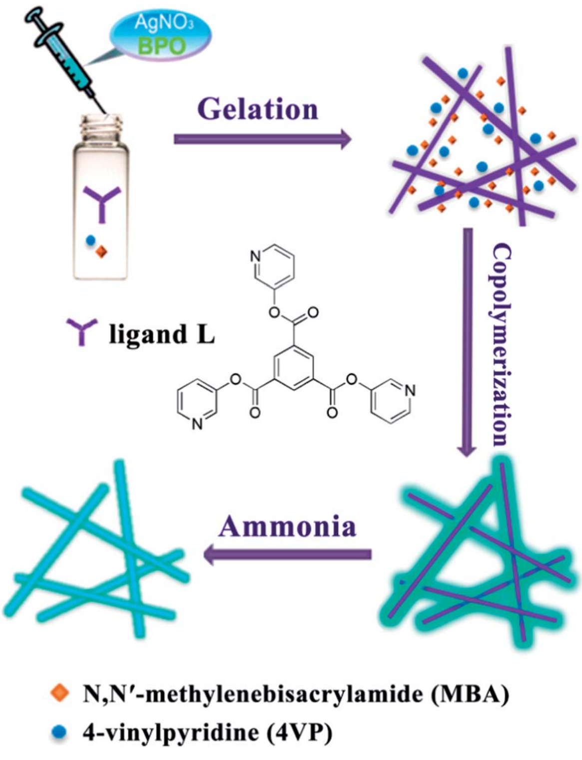
Results and discussion

Fabrication of 1D copolymer nanostructures

As reported in our previous article, the silver ions constituting the metallogel fibers on the surface could adsorb molecules bearing coordination groups.[31] Therefore the monomer used for polymerization should have certain groups that can interact with silver ions, like amide groups of MBA and the pyridine group of DADAP, which make polymerized products adhere onto the surfaces of the template fibers during polymerization.

In this study, six random copolymers poly(*N*,*N*′-methylenebisacrylamide-*co*-4-vinylpyridine) (defined as P(MBA-4VP)) were prepared by the free radical copolymerization of the two monomers within the THF metallogel. The co-monomer 4VP whose pyridine groups can coordinate with silver ions may be responsible for copolymers adhering onto the surfaces of the template, as well as MBA. However, the coordination ability of pyridine groups is stronger than that of amide groups,[35] and thus excess 4VP will affect the gelation time or appearance of the gel. The molar ratios of MBA/4VP in the feed of six copolymers were 1/1, 1/2, 1/3, 1/4, 1/5 and 1/6, and for convenience in the discussion, the corresponding six random copolymers were defined as P(MBA-4VP-1), P(MBA-4VP-2), P(MBA-4VP-3), P(MBA-4VP-4), P(MBA-4VP-5) and P(MBA-4VP-6), respectively.

The preparation procedure is illustrated in Scheme 1. The two co-monomers and BPO were separately added into the THF solutions of ligand L and $AgNO_3$, and the gel was rapidly produced in 10 s by injecting $AgNO_3$ solution into ligand L solution. Afterwards, the gel was treated at 63 °C to carry out the



Scheme 1 Illustration of the procedure for the fabrication of 1D copolymer nanostructures.

radical copolymerization of MBA and 4VP. After polymerization, the resulting gel-like sample was treated with excess ammonia to remove the remaining metallogel templates and then dried in a vacuum oven.

Infrared spectroscopy

The 1D copolymer nanostructures are characterized by FT-IR spectroscopy. Fig. 1A shows the FT-IR spectrum of pure poly(*N*,*N*′-methylenebisacrylamide) (PMBA) nanotubes, where the broad peak at 3269 cm^{-1} represents N–H stretching and 1655, 1529, and 1213 cm^{-1} correspond to amide I, II, and III bands, respectively; the small peak at 3066 cm^{-1} indicates a residual double bond that had not been fully polymerized. Fig. 1B shows the FT-IR spectrum of P(MBA-4VP-2) 1D nanostructures. Except for the peaks corresponding to secondary amide in PMBA, characteristic peaks of pyridine rings of P(MBA-4VP-2) are manifested by 1601 cm^{-1} representing C=N stretching and 1417 cm^{-1} representing C=C stretching.

Morphology characterization

As reported in our previous article, ligand L could form 3D networks of fibers with silver ions in THF, therefore forming the metallogel.[41] In this work, the fibrillar networks of the metallogel (2 wt%) were used as a template to fabricate 1D copolymer nanostructures, and the formation of the metallogel was confirmed by the inverted-test-tube method (Fig. 2A). The TEM image in Fig. 2B reveals the morphology of the metallogel, therein numerous fibers entangle to form a network structure. Most of the fibers have their diameters in the range of 30–50 nm and can extend several micrometers in length, demonstrating their high aspect ratio.

After polymerization, P(MBA-4VP) was synthesized on the template gel fibers, giving 1D copolymer nanostructures as a white gel (Fig. 3A). The SEM image of P(MBA-4VP-2) 1D nanostructures after the ammonia treatment is shown in Fig. 3B. Similar to the original gel fibers, the networks of 1D copolymer nanostructures are branched and interconnected. Lengths of the nanowires can reach tens of micrometres and their uniform diameter is 80 nm.

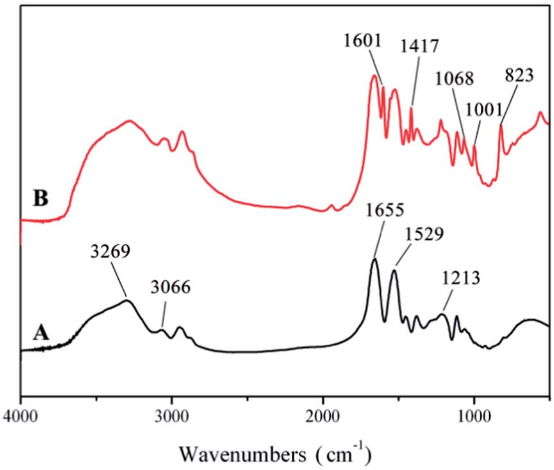


Fig. 1 FT-IR spectra of (A) PMBA and (B) P(MBA-4VP-2).

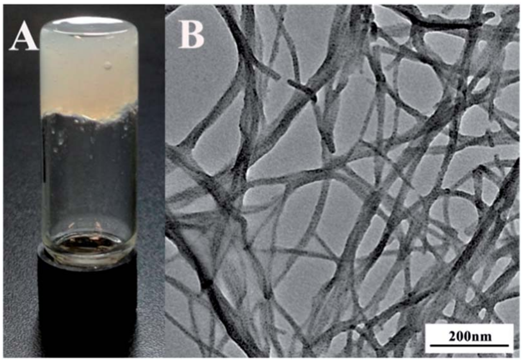


Fig. 2 (A) Photograph of the metallogel as the template. (B) TEM image of metallogel nanofibers.

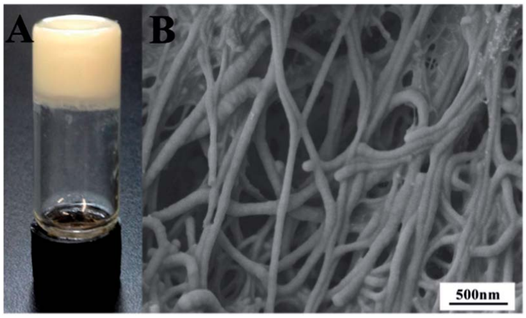


Fig. 3 (A) Photograph of the copolymer gel. (B) SEM image of P(MBA-4VP-2) 1D nanostructures.

The TEM images of P(MBA-4VP) 1D nanostructures after the ammonia treatment with different molar ratios of MBA/4VP are displayed in Fig. 4. In the sample with lower 4VP molar contents, both nanotubes and nanowires appeared (Fig. 4A). The arrows in Fig. 4A point to the hollow nanotubular structures in P(MBA-4VP-1), and the average inner diameter of the nanotubes is 20 nm, slightly smaller than the diameters of the gel template shown in Fig. 2B. With the increase of the MBA/4VP molar ratio from 1/2 to 1/5, only copolymer nanowires were obtained (Fig. 4B–F), and the yield of copolymer nanowires could all be higher than 95%. When the molar ratio of MBA/4VP is further increased to 1/6, coordination between the pyridyl group of 4VP and the silver ions constituting the metallogel will affect the formation of the gel template, resulting in copolymer nanowires with more defects and fracture (as indicated by arrows in Fig. 4F) and the decrease of the yield of copolymer nanowires (below 60%).

In order to investigate the template effect for copolymerization and the fabrication mechanism of copolymer nanowires, we monitored the polymerization process in different stages *via* TEM observation. The TEM images of P(MBA-4VP-2) 1D nanostructures obtained at different polymerization times (without ammonia treatment) are displayed in Fig. 5. In the early stage (Fig. 5A), a core–shell 1D nanostructure was obtained consisting of the copolymer shell and the nanofiber core. As the

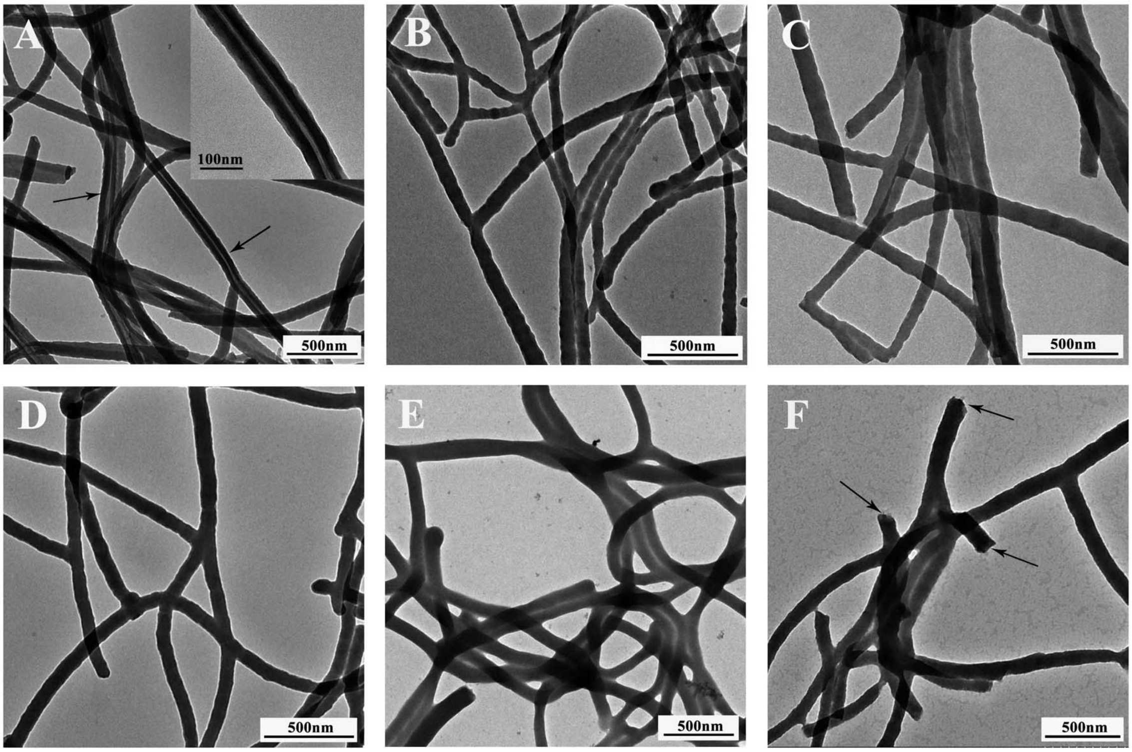


Fig. 4 TEM images of P(MBA-4VP) 1D nanostructures. (A) P(MBA-4VP-1), (B) P(MBA-4VP-2), (C) P(MBA-4VP-3), (D) P(MBA-4VP-4), (E) P(MBA-4VP-5), and (F) P(MBA-4VP-6). The inset of the magnified image shows the hollow nanotubular structures in P(MBA-4VP-1).

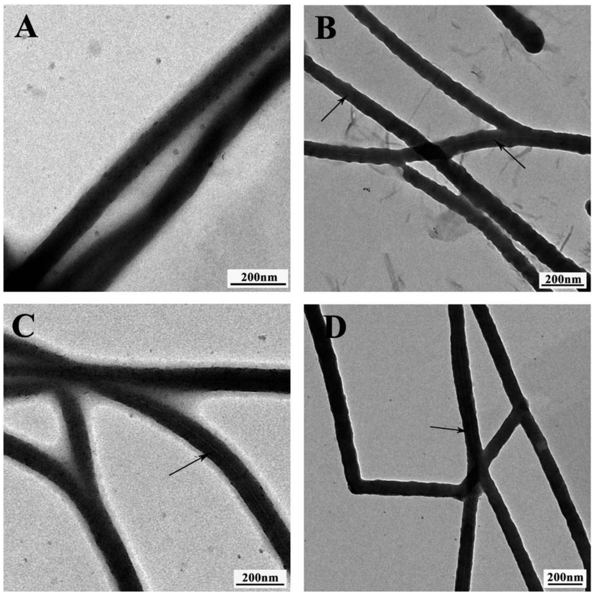


Fig. 5 TEM images of P(MBA-4VP-2) 1D nanostructures after (A) 2 h, (B) 6 h, (C) 14 h and (D) 24 h of copolymerization.

polymerization time gets longer, the metallogel templates were eroded gradually (Fig. 5B–D). The hollow nanotubular structures were obtained even before the ammonia treatment, as indicated by arrows in Fig. 5B–D. Their average inner diameter is 5 nm, smaller than that of P(MBA-4VP-1) nanotubes in Fig. 4A. After removing the template, these nanotubes might collapse quickly resulting in the disappearance of the narrow inner diameter and only nanowires were observed.

The fabrication mechanism of copolymer nanowires could be described by the 'self-degraded template polymerization' mechanism.[35] The metallogel templates were eroded gradually during the polymerization, and the eroding process could be ascribed to the pyridyl groups of 4VP which were inclined to coordinate with the silver ions of the template gel.

Rheological properties

The metallogel is rather fragile and could be destroyed into a free-flowing liquid by shaking or sonication, especially the addition of monomers into the gel could lower the gel strength to some extent.[31] That might be attributed to the coordination interaction between amide groups and pyridyl groups with silver ions, which lowers the density of silver ions as the cross-linker, thus lowering the gel strength. After copolymerization of MBA and 4VP, the product was obtained as a gel which could not be destroyed by shaking or sonication, indicating the formation of a copolymer gel.

The mechanical properties of the metallogel and the copolymer gels were measured by using a rheometer. In Fig. 6, curves of the storage modulus (G') and the loss modulus (G'') against frequency are presented. Obviously, the copolymer gel displays a higher strength than the metallogel. Both G' and G'' of the P(MBA-4VP-2) gel are higher than those of the P(MBA-4VP-4) gel, which indicates that the incorporation of mono-functional monomer 4VP could cause the decrease of crosslinking degree of the copolymer making the gel strength lowered to some

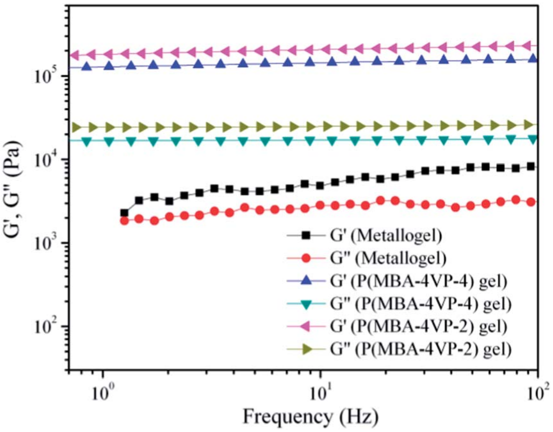


Fig. 6 Storage modulus and loss modulus of the copolymer gels and the metallogel at different frequencies.

extent. In contrast to the metallogel, the copolymer gel shows a typical elastic behavior, and is strong enough to be used as a specific adsorbing material.

pH-responsive behaviors of 1D copolymer nanostructures

4VP is a weak basic monomer, and its polymer or copolymer could show pH-responsive behavior that undergoes a phase transition under pH 5 owing to the protonation of pyridine groups.[11,37] The pyridine groups contribute protons under acidic conditions and accept them under basic conditions, which results in the transition from an expanded state to a collapsed state that can be explained by the osmotic pressure exerted by mobile counterions neutralizing the network charges.[14]

Therefore, P(MBA-4VP) 1D nanostructures could respond to a pH change in buffer solutions. The photographs in Fig. 7 reveal pH-responsive behavior of P(MBA-4VP-4) 1D nanostructures immersed into buffer solutions of pH 2.2 (Fig. 7A) and 11 (Fig. 7B) respectively. The size of the P(MBA-4VP-4) gel decreased as the pH increased from 2.2 (Fig. 7D) to 11 (Fig. 7E), due to the deprotonation of the 4VP pyridine groups. That means P(MBA-4VP-4) 1D nanostructures swell at pH 2.2 while deswell at pH 11.

To investigate the pH-responsive behaviors of P(MBA-4VP) 1D nanostructures with different molar contents of 4VP, a known amount of dried copolymer gels after the ammonia treatment was immersed into 5 mL of different pH buffer solutions at room temperature, and their equilibrium swelling ratio (*Q*) was measured after 1 day. The curves of *Q* against pH are shown in Fig. 8, which is characteristic behavior of the polymer with weakly basic groups.[42] In Fig. 8, the most noticeable feature is the sharp change in the *Q* values between pH 3 and 5, which corresponds to a transition from the charged to uncharged state on the network. Additionally, Fig. 8 shows that the pH sensitivity weakens with the decrease of molar contents of 4VP. The result indicates that the co-monomer 4VP is responsible for the pH sensitivity of P(MBA-4VP) nanostructures, and the increase in crosslinking degree with the decrease in molar contents of 4VP is another cause that limits the copolymer gels from swelling.

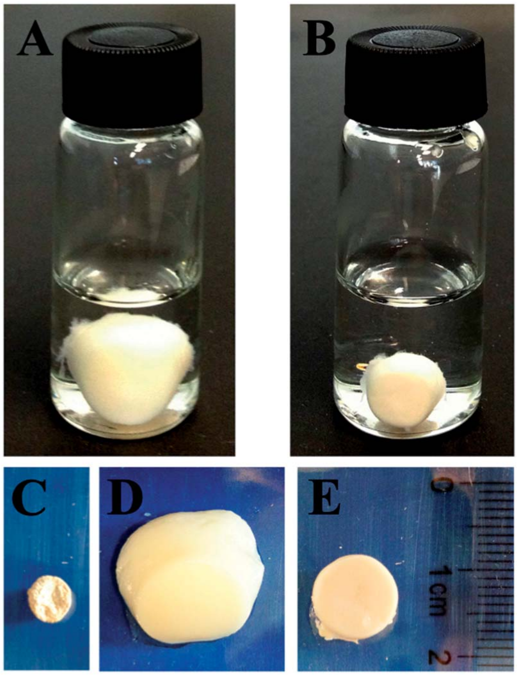


Fig. 7 Photographs of pH-responsive behavior of P(MBA-4VP-4) 1D nanostructures immersed into buffer solutions of pH 2.2 (A) and pH 11 (B) respectively. (C) Dried sample and the same sample saturated by buffer solutions of pH 2.2 (D) and pH 11 (E) respectively.

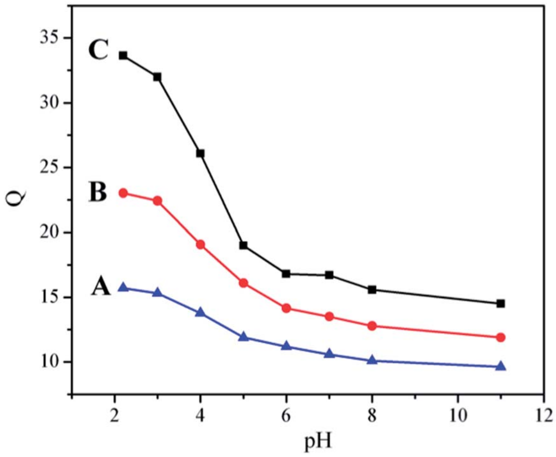


Fig. 8 pH sensitivity of P(MBA-4VP) 1D nanostructures. (A) P(MBA-4VP-1), (B) P(MBA-4VP-2), and (C) P(MBA-4VP-4).

The feature is also noticeable in Fig. 9, which reveals the reversible pH response of P(MBA-4VP) 1D nanostructures alternatively kept at the two extreme pH values. Known amounts of dried copolymer gels with different molar contents of 4VP were alternatively kept in a 5 mL buffer solution of pH values 2.2 and 11 for 12 hours.

Adsorption and desorption of aspirin

Generally, pyridine groups in P(MBA-4VP) nanostructures can form the double hydrogen bonding system with carboxylic acid

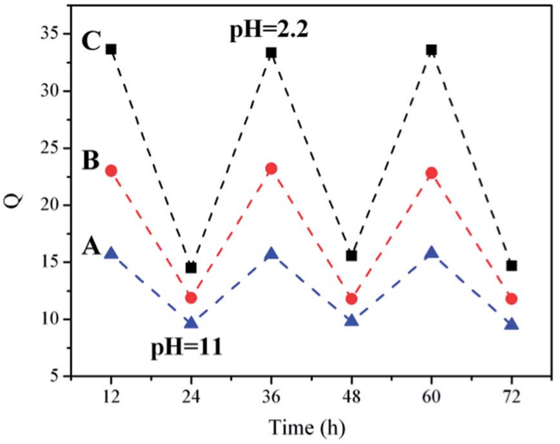


Fig. 9 The reversible pH response of P(MBA-4VP) 1D nanostructures alternatively kept in a buffer solution of pH values 2.2 and 11 for 12 hours. (A) P(MBA-4VP-1), (B) P(MBA-4VP-2), and (C) P(MBA-4VP-4).

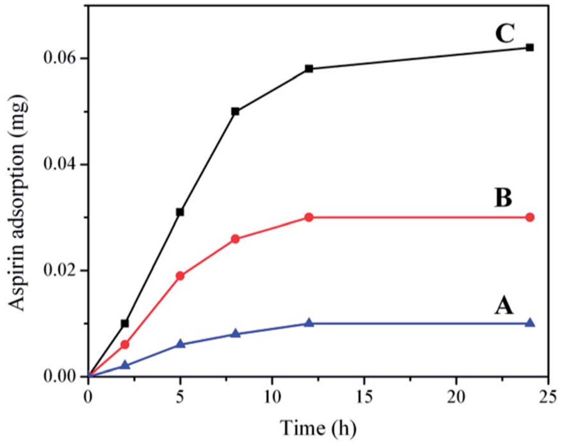


Fig. 11 Mass increase of adsorbed aspirin in P(MBA-4VP) 1D nanostructures with respect to time. (A) P(MBA-4VP-1), (B) P(MBA-4VP-2), and (C) P(MBA-4VP-4).

groups, making the products capable to uptake some carboxylic compounds from dilute solution effectively. That provides the possibility to functionalize the P(MBA-4VP) 1D nanostructures.

Aspirin (chemical name is 2-acetylsalicylic acid) is an important medicine used to reduce fever and to relieve mild to moderate pain from headaches, colds, toothaches, and muscle aches. The carboxylic acid group in the chemical structure makes aspirin possible to be immobilized on P(MBA-4VP) 1D nanostructures. To investigate the adsorption of aspirin, a known amount of dried copolymer gels after the ammonia treatment was immersed into dilute aspirin–chloroform solution (50 mg L^{-1}) for a certain time. Their time-dependent UV-Vis spectra in Fig. 10 show that the intensity of the peaks decreases with respect to time, from 2 h to 12 h, which indicates that all samples are capable of adsorbing aspirin from the organic phase.

The mass of aspirin adsorbed in P(MBA-4VP) 1D nanostructures increased with the adsorption time (shown in Fig. 11), and basically tended to be stable after 24 h to reach the equilibrium. The maximum adsorption increased with molar contents of 4VP which suggests the formation of the double hydrogen bonding system, and the contents of pyridine groups of P(MBA-4VP) 1D nanostructures contribute to the different adsorption amounts of guest aspirin. However, not all pyridine groups of 1D copolymer nanostructures were involved in aspirin adsorption. Take P(MBA-4VP-4) for example, a 10 mg sample used for adsorption contained 0.07 mmol pyridine groups, while the equilibrium molar content of aspirin adsorbed in P(MBA-4VP-4) 1D nanostructures was 0.000344 mmol, much less than the molar content of pyridine groups, indicating that only the pyridine groups distributed on the surface of 1D copolymer nanostructures could participate in adsorption.

The 1D copolymer nanostructures could be regenerated through desorption of aspirin from the copolymer gels, and there are three methods to do this. The first is according to the reversible nature of hydrogen-bonding, desorption of aspirin will take place when a heated proton solvent is used. So we treated the aspirin-loaded sample with heated ethanol repeatedly, then aspirin was removed from the copolymer gels thoroughly. The other is to place the aspirin-loaded sample in a buffer solution of pH 2.2, and the protonation of pyridine groups could destroy the double hydrogen bonding system between the gel sample and aspirin, which is based on the pH sensitivity of P(MBA-4VP) 1D nanostructures. The third is based

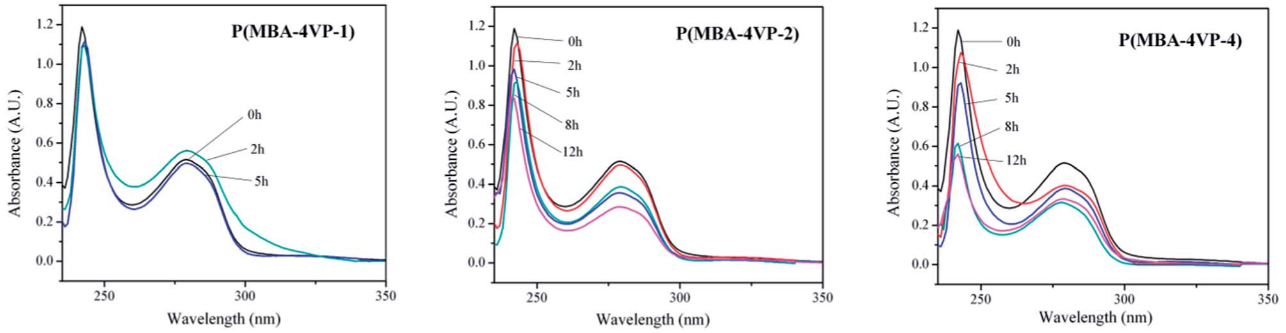


Fig. 10 UV-Vis spectra of time-dependent adsorption of aspirin from chloroform solution by using P(MBA-4VP) 1D nanostructures with different molar contents of 4VP.

on the effect of ionic interaction on hydrogen-bonding. Aspirin was released from the copolymer gels when placed in a 0.1 mol L^{-1} sodium chloride solution, because salt solution could easily break hydrogen bonds. Therefore, we immersed aspirin-loaded P(MBA-4VP-4) and P(MBA-4VP-2) 1D nanostructures in hot ethanol, a buffer solution of pH 2.2 and a 0.1 mol L^{-1} sodium chloride solution respectively. The UV-Vis spectra of ethanol solutions, buffer solutions of pH 2.2 and sodium chloride solutions at different times are presented in Fig. 12–14 respectively. With the increase of times of immersion, the concentration of aspirin released in filtrates decreased, which indicates the removal of guest molecules from the copolymer gels.

After desorption, the aspirin-released sample was placed in initial aspirin–chloroform solution to absorb aspirin again for 12 hours, and then desorbed using hot ethanol. The test was repeated three times. The mass of aspirin adsorbed in P(MBA-4VP-4) 1D nanostructures each time is summarized in Fig. 15, which is basically identical. This suggests that P(MBA-4VP) 1D nanostructures could be regenerated and used as an adsorption material repeatedly.

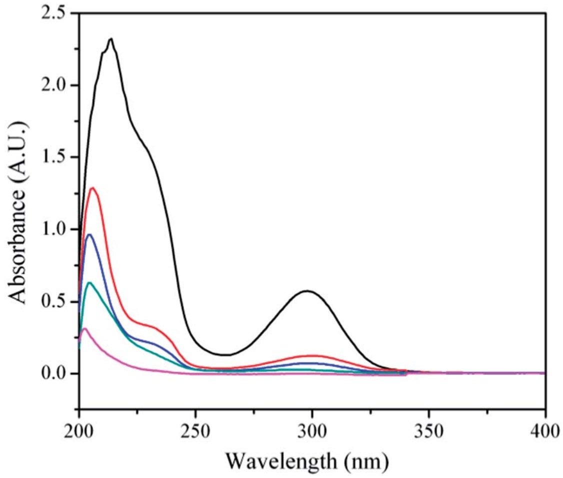


Fig. 12 UV-Vis spectra of ethanol solutions at different times. The curves from up to down correspond to 2 h, 4 h, 6 h, 8 h and 10 h, respectively.

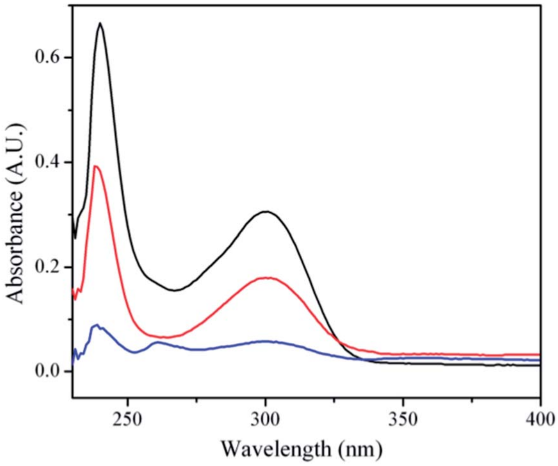


Fig. 13 UV-Vis spectra of buffer solutions of pH 2.2 at different times. The curves from up to down correspond to 2 h, 4 h and 6 h respectively.

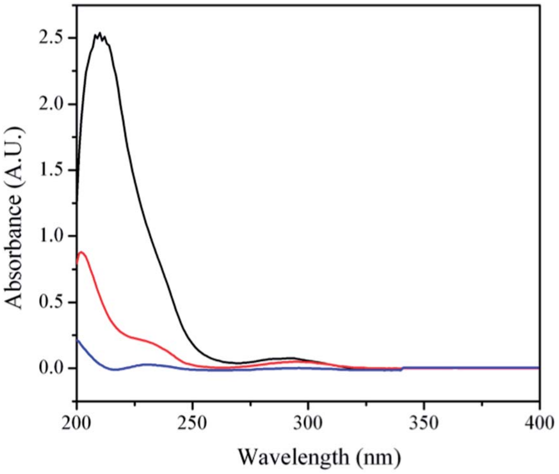


Fig. 14 UV-Vis spectra of 0.1 mol L^{-1} sodium chloride solutions at different times. The curves from up to down correspond to 2 h, 4 h and 6 h respectively.

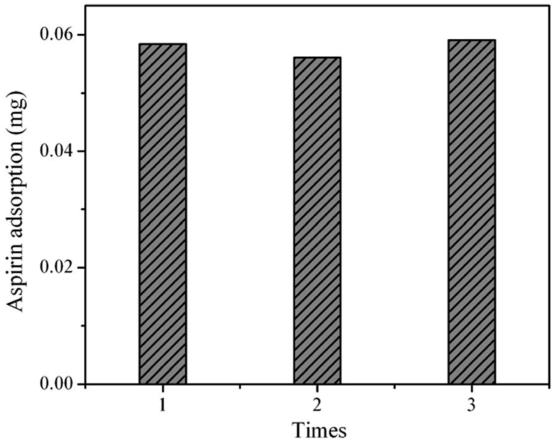


Fig. 15 Mass of aspirin adsorbed in P(MBA-4VP-4) 1D nanostructures at different experimental times.

Fabrication of silver nanoparticle loaded copolymer nanowires

In the fabrication process of P(MBA-4VP) 1D nanostructures using the silver metallogel as a template, silver ions play an important role in the induced deposition of copolymerized products onto the surfaces of the template fibers, which should be removed after copolymerization. However, if we use the reducing agent to treat the copolymerized products, instead of ammonia treatment to remove the metallogel templates, silver nanoparticle loaded copolymer nanowires would be produced from the reduction of silver ions.

There are a variety of reduction methods of silver ions. In this study, we use high temperature ethylene glycol solution as a reducing agent for reducing silver ions to silver nanoparticles, which is a classical method of silver nanowire synthesis.[43]

As the reduction time gets longer, the color transition process of the copolymer gel from light yellow to brown yellow was observed, which indicates the generation of silver nanoparticles.[44] A typical TEM image of silver nanoparticle loaded P(MBA-4VP-2) nanowires is shown in Fig. 16A. The silver nanoparticles rather than silver nanowires are dispersed throughout the P(MBA-4VP-2) nanowires, and they are almost spherical with diameters of about 5–15 nm. However, under the same reduction conditions, the small black particles have not been observed on pure PMBA nanotubes (Fig. 16B). The reason is the leaching of silver ions due to swelling of PMBA during reduction. The introduction of 4VP could improve the coordination ability of copolymerized products with silver ions, so as to enhance the binding capacities of P(MBA-4VP) nanowires for silver nanoparticles to prevent their leaching. These observations indicate that pyridine groups of 4VP play an important role in the immobilization of silver nanoparticles inside copolymer nanowires. EDX analysis of the selected region in Fig. 17 shows the peaks of silver, further proving that silver nanoparticles exist in copolymer nanowires. In this system, silver ions act both as the template and as the nanoparticle growth substrate.

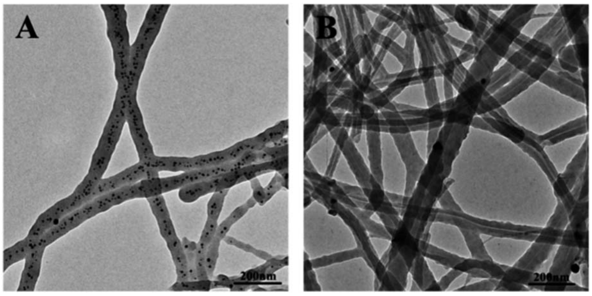


Fig. 16 TEM images of (A) P(MBA-4VP-2) and (B) PMBA 1D nanostructures with the template after the 2 h reduction.

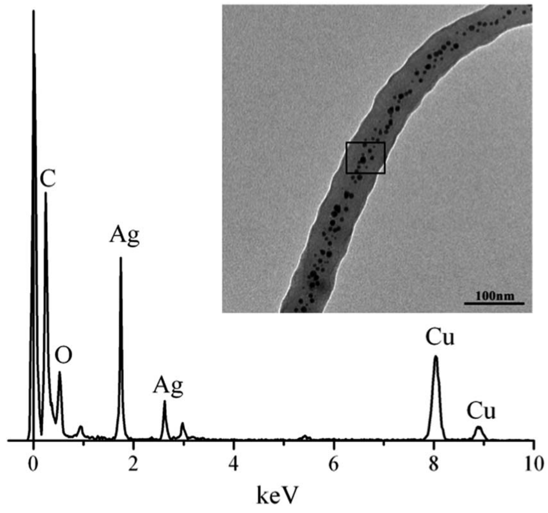


Fig. 17 EDX spectrum of a single P(MBA-4VP-2) nanowire with the template after the 2 h reduction.

Additionally, we have also found that different reduction methods and reduction times have a great influence on the size and distribution of silver nanoparticles. The overall and detailed experimental results will be published in a future article.

Conclusions

In conclusion, using a metallogel as a template, we successfully fabricated pH responsive 1D copolymer nanostructures *via* copolymerizing MBA with pH sensitive co-monomer 4VP. The combination of 1D polymer nanostructures with stimuli responsive polymers could impart to materials the unique structures and smart properties, and broaden their application field. This approach is very simple and efficient, involving copolymerization in a gel system at a moderate temperature. TEM and SEM analyses of the reaction product demonstrate the morphology of 1D copolymer nanostructures including nanowires and nanotubes, which duplicate the networks of nanofibers of the template metallogel. The fabrication mechanism of copolymer nanowires could be described by the 'self-degraded template polymerization' mechanism. The introduction of co-monomer 4VP imparts to the 1D copolymer nanostructures pH sensitivity and the possible use as an adsorption material of special compounds, such as aspirin. Adsorbed 1D copolymer nanostructures could be regenerated using proton solvent, acid medium or salt solution. The pH-responsive behaviors and reversible pH response of various 1D copolymer nanostructures were investigated. Their adsorption and desorption of aspirin were detected by a UV-Vis spectrometer. Using this strategy, a variety of functionalized 1D copolymer nanostructures might be prepared by different kinds of co-monomers. In addition, silver nanoparticle loaded copolymer nanowires have been produced from the reduction of silver ions instead of template removal, where silver ions act both as the template and as the nanoparticle growth substrate.

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