Novel polymer nanowires with triple hydrogen-bonding sites fabricated by metallogel template polymerization and their adsorption of thymidine†

Botian Li, Liming Tang,* Lu Qiang and Kai Chen

Received 25th August 2010, Accepted 19th October 2010
DOI: 10.1039/c0sm00857e

Novel polymer nanowires with triple hydrogen-bonding sites have been prepared by a one-pot procedure based on metallogel template polymerization, which was carried out in an Ag(I)-coordinated organogel with benzoyl peroxide (BPO) as 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 the polymerization, nanofibers of metallogel were transcribed to polymer nanowires. Polymer nanowires synthesized by this method contain triple hydrogen-bonding sites introduced by the monomer diacryloyl-2,6-diaminopyridine (DADAP); they are used as adsorbing agents for the 'uptake' of thymidine from dilute THF solution. The efficient adsorbing performance and reusable properties will render them ideal candidates for applications relating to biological adsorption.

Introduction

In the past several years, polymer nanowires and nanotubes have attracted considerable attention, since their one-dimensional morphology and structural versatility impart to them great application potential in different areas, such as electronic devices,[1] separations,[2] drug delivery,[3] and catalyst supports.[4] Generally, polymer nanowires can be fabricated by a self-assembly process[5,6] or by template polymerization. Template-assisted synthesis is an efficient, controllable, and conventional route to achieve well-shaped nanowires. Several kinds of materials have been designed as 'hard templates', for example, porous polycarbonate films,[7] porous alumina[8,9] and silver nanowires.[10] However, the removal of the templates is tedious when these hard templates are used.

Supramolecular gels consisting of nanofiber networks have been developed as 'soft templates' to fabricate a variety of inorganic nanotubes;[11–13] in these gel templates, organic fibrous structures could be transcribed to inorganic hollow tubes after '*in situ*' polymerization and calcination. Besides inorganics, organic polymer structure have also been achieved using metallogel templates,[14] although these gels just acted as inverse templates in monomeric solvents for producing porous polymers, their utility for template fabrication was revealed. Owing to their excellent heat-stable properties and facile preparation procedure,[15] these gels display potential applications as templates for polymer nanowires. Recently, our group has developed a silver metallogel based on which we managed to fabricate polymer nanotubes.[16] Heat-initiated polymerization took place on the gel fibers, the original gel fibers were successively easily removed by using excess ammonia, resulting in polymer nanotubes.

Multiple hydrogen-bonding interactions, which are the most important noncovalent forces in biological systems,[17] have been widely employed in copolymer self-assembly,[18,19] surface recognition.[20,21] Compared to single hydrogen bonding groups, the incorporation of multiple acceptor and donor units significantly enhances the strength of a hydrogen-bonding interaction.[17] Some reports have integrated multiple hydrogen-bonding interactions into nanoparticles by surface modification, and studied the capability of reversibly attaching polymers to solid surfaces. For example, Vancso *et al.* investigated the self-complementary molecular assembly between Au nanoparticles modified with quadruple hydrogen-bonding and pyrimidinone moieties,[22] while Rotello and co-workers used Au nanoparticles and polymers functionalized with complementary hydrogen bonding groups such as thymine and triazine to form extended nanoparticle aggregates.[23] In those studies, however, the procedures of synthesis were always complicated, which restricted the application of multiple hydrogen-bonding interaction in these systems. Also, organic polymer nanostructures with multiple hydrogen-bonding sites are limited or undeveloped.

In this paper, we focused on the template fabrication of polymer nanowires with triple hydrogen-bonding sites on the surface by a one-pot procedure. The resulting polymer nanowires were confirmed by TEM and SEM analysis and their adsorption properties in thymidine THF solution were detected by a UV-Vis spectrometer. Thanks to the hydrogen-bonding interactions and huge specific surface area, the product is capable of 'uptaking' thymidine molecules from dilute solution effectively. That makes the polymer nanowires excellent sorbents for specific biological molecules. To the best of our knowledge, this is the first example of novel polymer nanowires with triple hydrogen-bonding sites prepared using metallogel nanofibers as the template. This simple approach might be extended to synthesize some other polymer nanostructures bearing multiple hydrogen-bonding sites.

Experimental

Materials

Tetrahydrofuran (THF, Tianjin Chemical Reagents) was freshly distilled from sodium prior to use; dichloromethane was refluxed

---

Laboratory of Advanced Materials, Department of Chemical Engineering, Tsinghua University, Beijing, 100084, P. R. China. E-mail: tanglm@mail.tsinghua.edu.cn; Fax: (+86) 10-6278-0304

† Electronic supplementary information (ESI) available: Experimental details and additional images. See DOI: 10.1039/c0sm00857e

with calcium hydride and distilled before use. Benzoyl peroxide (BPO) and 2,6-diaminopyridine were purchased from Beijing Chemicals and purified by recrystallization using methanol. Benzene-1,3,5-tricarbonyl trichloride, 3-hydroxyl pyridine and acryloyl chloride purchased from Alfa Aesar were used as received. Other solvents and reagents, including $AgNO_3$, deionized water, ethanol, pyridine and so on were used without further purification.

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

Firstly, 2.86 g (30 mmol) 3-hydroxyl pyridine and 3.2 g pyridine (40 mmol) was dissolved in 30 mL dehydrated dichloromethane. 2.65 g (10 mmol) benzene-1,3,5-tricarbonyl trichloride dissolved in another 30 mL of dehydrated dichloromethane was dropped into the solution in 1 h at room temperature. After addition, the solution was refluxed at 45 °C for 15 h. After that, 20 mL deionized water was added to the resulting solution after cooling, and the aqueous phase was extracted twice with dichloromethane. After evaporation of dichloromethane at reduced pressure, the remaining white solid was recrystallized using ethanol to give 3.42 g product (78% yield).

^1H NMR (300 MHz, [D_6]DMSO, TMS, δ (ppm)): 9.04 (s, 3H, aryl H), 8.60 (d, 3H, 2-pyridyl H), 8.55 (d, 3H, 6-pyridyl H), 7.86 (d, 3H, 4-pyridyl H), 7.61 (d*d, 3H, 5-pyridyl H).

FT-IR (KBr, cm^{-1}): 3076, 3061 (aryl and pyridyl C–H), 1732 (CO, strong), 1577, 1473, 1424 (aryl, pyridyl C=C and pyridyl C=N).

Synthesis of diacryloyl-2,6-diaminopyridine (DADAP)

To an aqueous solution (60 mL) of 2.29 g (21 mmol) 2,6-diaminopyridine and 1.68 g (42 mmol) NaOH, 4.43 g (49 mmol) acryloyl chloride dissolved in 10 mL dichloromethane was added slowly over 15 min. The round-bottomed flask was cooled in an ice-water bath and stirred for 2 h. After removal of solvent in organic layer by rotary evaporation, the yellow solid was filtered and purified by column chromatography using ethyl acetate as eluent to give 2.98 g product (66% yield).

^1H NMR (300 MHz, $CDCl_3$, TMS, δ (ppm)): 8.00 (d, 2H, 3-pyridyl H), 7.74 (t, 1H, 4-pyridyl H), 6.47 (d, 2H, 3-acryloyl *cis* H), 6.24 (d, 2H, 2-acryloyl H), 5.82 (d, 2H, 3-acryloyl *trans* H), 4.28 (s, b, 2H, amide H).

FT-IR (KBr, cm^{-1}): 3327 (N–H stretch), 3033, 2984 (pyridyl and acryloyl C–H), 1679 (C=O stretch), 1592, 1450 (pyridyl C=C and pyridyl C=N).

Synthesis of polymer nanowires

In a typical process, 30 mg (0.068 mmol) of ligand L and 30 mg DADAP was dissolved in 1.5 g THF in a vial, then a 1.5 g THF solution of $AgNO_3$ (18 mg, 0.106 mmol) and BPO (3 mg) was injected. A gel (1.6 wt%) was produced in 10 s, and subsequently kept at 65 °C for 10 h. After polymerization, excess ammonia was added. The white solid was collected by filtration, washed repeatedly with deionized water (20 mL) and ethanol (20 mL) for three times, and finally dried at 40 °C in vacuum.

Characterization

^1H NMR spectra were obtained on a JEOL JNM-ECA300 spectrometer. Fourier-transform infrared (FT-IR) spectroscopy experiments were performed using a Nicolet 560 instrument. Field emission scanning electron microscopy (SEM) measurements were carried out with a JEOL FESEM 6704F electron microscope operating at an accelerating voltage of 20 kV by drop casting the sample dispersed in ethanol on a silicon slice. Transmission electron microscopy (TEM) images were obtained on a JEOL J2010 transmission electron microscope with an accelerating voltage of 200 kV by drop casting the sample dispersion on copper grids coated with carbon film. Electron dispersive X-ray spectroscopy (EDS) was performed on JEOL J2010 with an Oxford spectrometer. The mechanical properties of samples were investigated using a Physica MCR300 rheometer. The rate of guest molecule adsorption was measured by placing 100 mg of polymer nanowires in thymidine THF solution (100 mg L^{-1}). The absorbance spectrum of the solution was recorded with a UV757CRT spectrophotometer, and the characteristic absorbance of thymidine at 267 nm was used to monitor its concentration.

Results and disscusion

In our work, we attempted to achieve functional polymer nanowires with triple hydrogen-bonding sites *via* metallogel template polymerization. The metallogel utilized in experiments denotes an organogel in which a metal ion is included to induce gelation.[24] According to the studies by Xu's group,[25] crosslinking of multidentate ligands by transitional metal ions can form 3D networks responsible for gelation. Herein we synthesized ligand L, a compound with three pyridyl groups, and found that a L/Ag^+ complex can gelate THF solvent by forming crosslinking nanofibers.

The triple hydrogen-bonding interaction is introduced by the monomer DADAP, which could be considered as a kind of DAD (donor–acceptor–donor) monomer with a diaminopyridine group.[26] The synthesis routes of both ligand and monomer are facile and suitable for large-scale production.

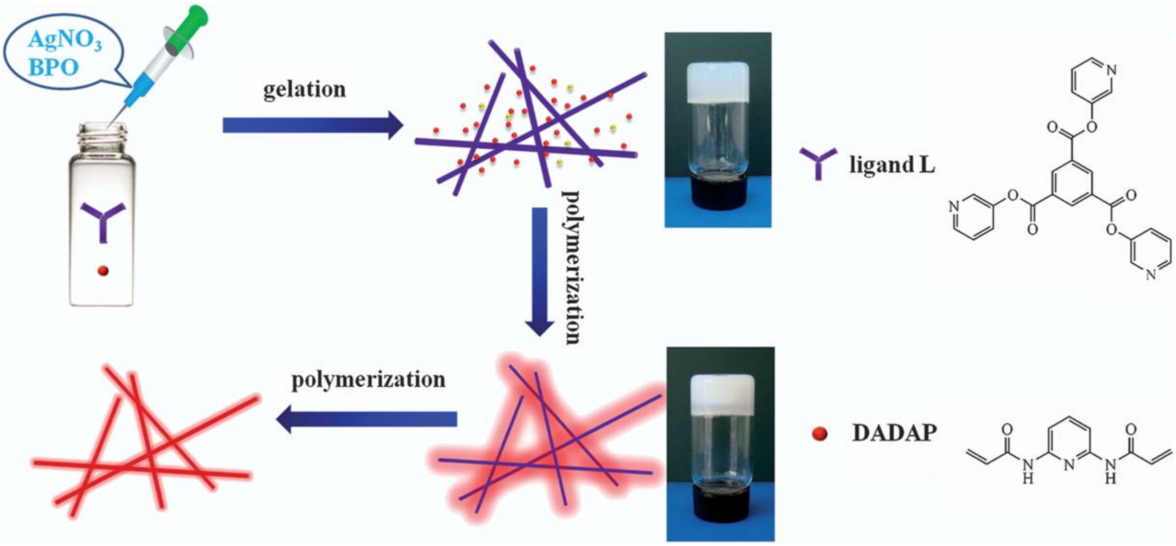
Synthesis of polymer nanowires

The preparation procedure is illustrated in Scheme 1. In the first step, a metallogel was prepared by injecting $AgNO_3$ solution into ligand solution, while the monomer DADAP and the initiator BPO were also mixed simultaneously. The gel was rapidly produced in 10 s, and formation of gel was confirmed by the inverted-test-tube method.[27]

Afterwards, the gel was treated at 65 °C for 10 h to carry out the radical polymerization of DADAP. Poly(diacryloyl-2,6-diaminopyridine) (PDADAP) was synthesized on the template gel fiber, giving polymer nanowires as a white gel. After polymerization, excess ammonia was added to remove the remaining metallogel template; the products were finally obtained after filtration and drying in a vacuum.

Infrared spectroscopy

The polymer nanowires are investigated by FT-IR spectroscopy. In Fig. 1, the FT-IR spectra of the monomer DADAP (a) and



Scheme 1 Illustration of the procedure for fabrication of polymer nanowires.

polymer nanowires (b) both show the characteristic vibrations of pyridyl amide. The broad peak at 3278 cm^{-1} is ascribed to the typical N–H stretching vibration, and the absorptions at 1583 cm^{-1}, 1449 cm^{-1} are assigned as fundamental vibrations of pyridine rings, peaks at 1693 cm^{-1}, 1519 cm^{-1}, 1287 cm^{-1} are attributed to band I, band II, band III of amide absorption respectively. The spectrum of the monomer (Fig. 1a) exhibits unsaturated C–H stretching absorption at 3025 cm^{-1}. After polymerization, alkyl absorptions arise at 2923 cm^{-1}, 2849 cm^{-1} (Fig. 1b), and all of the peaks become broader.

Morphology characterization

Ligand L can be dissolved in polar solvent such as THF and ethanol; its tripodal structure is designed to "catch" silver ions in order to build a coordination polymer,[28;29] the 3D network structure of which could be employed to gelate a solvent. In this work, the fibrillar networks of the metallogel (1.6 wt%) is used as a template to fabricate polymer nanowires. As shown in Fig. 2, the diameters of gel nanofibers are about 30–50 nm, and the average diameter is 40 nm.

In order to investigate the template effect for polymerization and the fabrication mechanism, we monitored the polymerization process in different stages *via* TEM observation. Fig. 3 gives the morphology changes of polymer nanowires with shell/core structure: In the early stage (Fig. 3A), the polymer formed a thin layer on the surface of the gel nanofibers; in the middle stage (Fig. 3B–C), more and more DADAP monomers were polymerized and the polymer layer (as indicated by arrow a) became thicker and thicker, meanwhile the dark nanofiber core denoted by arrow b got thinner. In Fig. 3D, we cannot find gel fiber in the core of the sample which was obtained after 24 h polymerization; this means that the template gel fibers were destroyed during polymerization. We also performed another polymerization experiment without a gel template, and found that almost no polymer was produced at the same concentration of DADAP (1 wt%).

According to the results of our experiments, a possible mechanism can be proposed as depicted in Fig. 4. Because of coordination between the pyridyl group of DADAP and the silver ions constituting the metallogel, the monomer was adsorbed on to the closest surface of gel the fibers, where heat-initiated

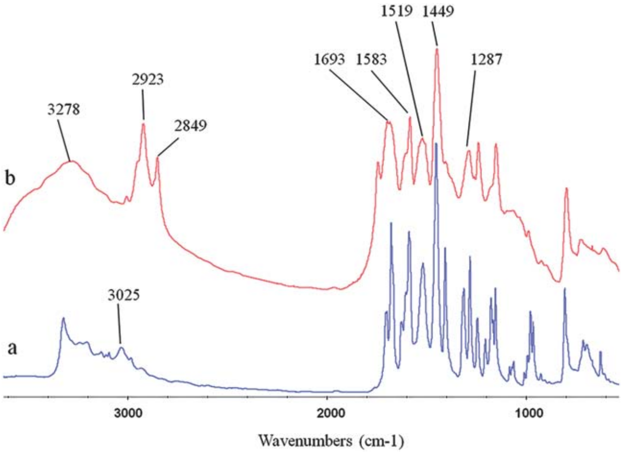


Fig. 1 IR spectra of (a) DADAP and (b) polymer nanowires.

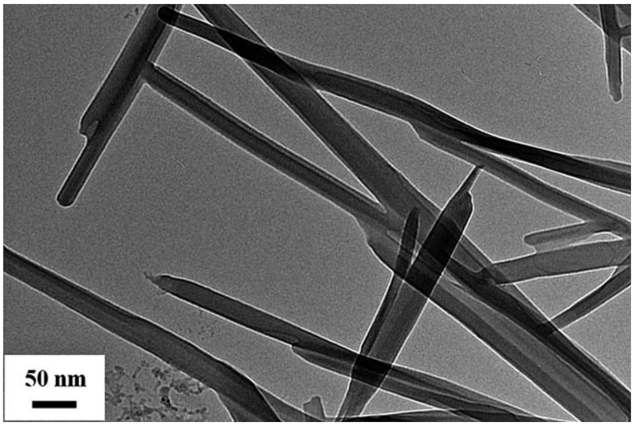


Fig. 2 TEM image of metallogel nanofibers as template.

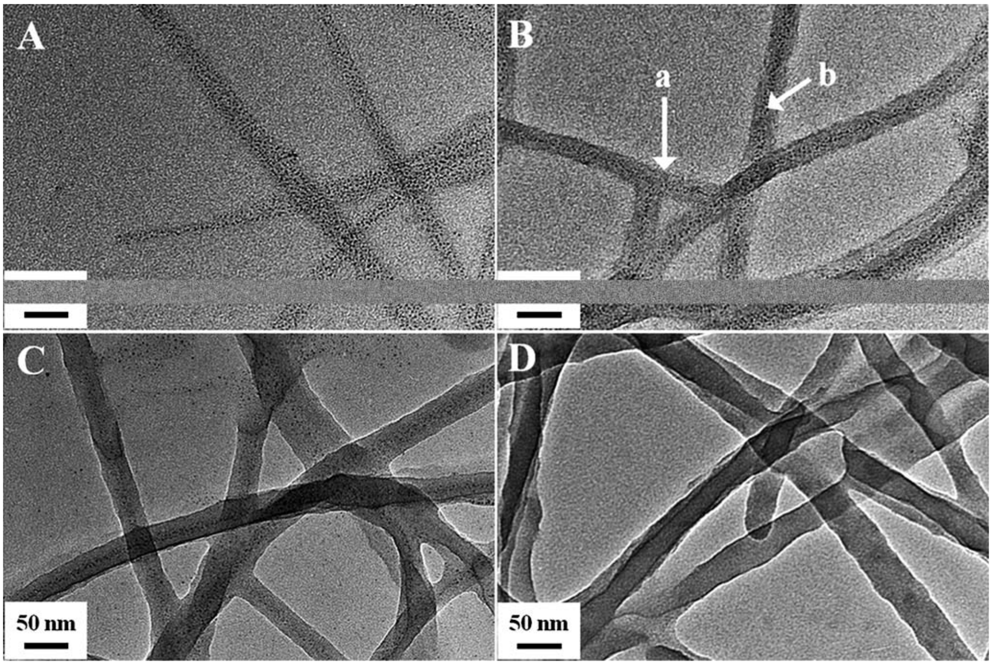


Fig. 3 TEM images of PDADAP nanowires after (A) 4 h; (B) 10 h; (C) 16 h; and (D) 24 h polymerization.

polymerization took place; gel fibers acted as the template in this process. The polymer layer was thickened as polymerization time was prolonged. Simultaneously, metallogel fibers were eroded by polymer from the surface, causing degradation of the template. At last, the whole gel fiber was replaced by a polymer nanowire. This destruction process could be ascribed to the pyridyl groups of the polymer, which were inclined to coordinate with the silver ions of template gel. Prolonging the reaction time (24 h) resulted in solid nanowires instead of hollow nanotubes. Since the template degraded spontaneously in polymerization, we may describe the mechanism as ‘self-degraded template polymerization’.

The SEM image of the sample of polymer nanowires reveals a network structure in Fig. 5. Similar to the original gel fibers, the networks of polymer nanowires are branched and interconnected. Lengths of the nanowires can reach tens of micrometres and their uniform diameter is 50 nm, consistent with the result from the TEM image shown in Fig. 3D.

EDS analysis of the selected region of nanowires in Fig. 6A presents the peaks of silver ions, proving that silver metallogel fibers are still existent in the core of the nanowire. The small black particles scattered throughout the fiber should be silver nanoparticles; they were produced from reducing reaction of silver ions. In contrast, after removal of template nanofiber core, the silver peaks disappear (Fig. 6B).

Ammonia treatment can quickly remove the metallogel template and it seems that the polymer obtained in the middle stage should form nanotubes with the addition of excess ammonia. However, most of them are nanowires—only a small part of product exhibits a hollow structure (Fig. 7) with a narrow

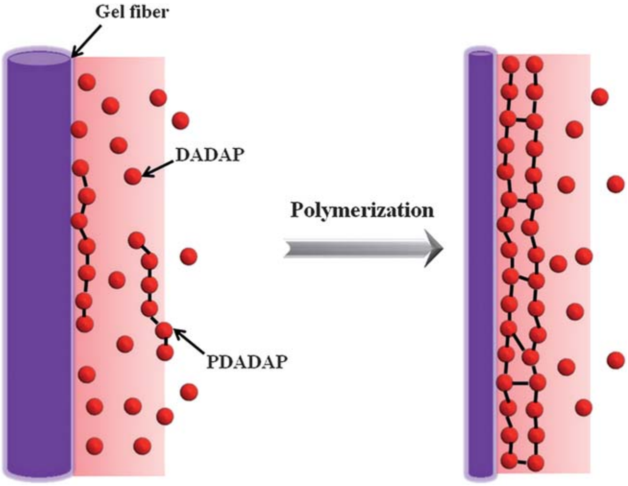


Fig. 4 Template fabrication mechanism of polymer nanowires.

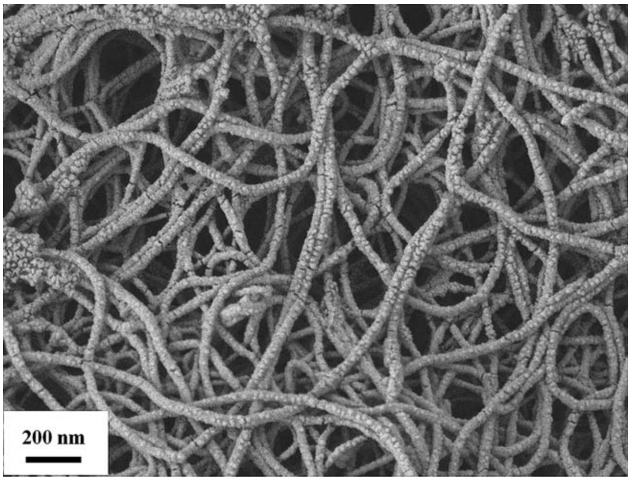


Fig. 5 SEM image of polymer nanowires.

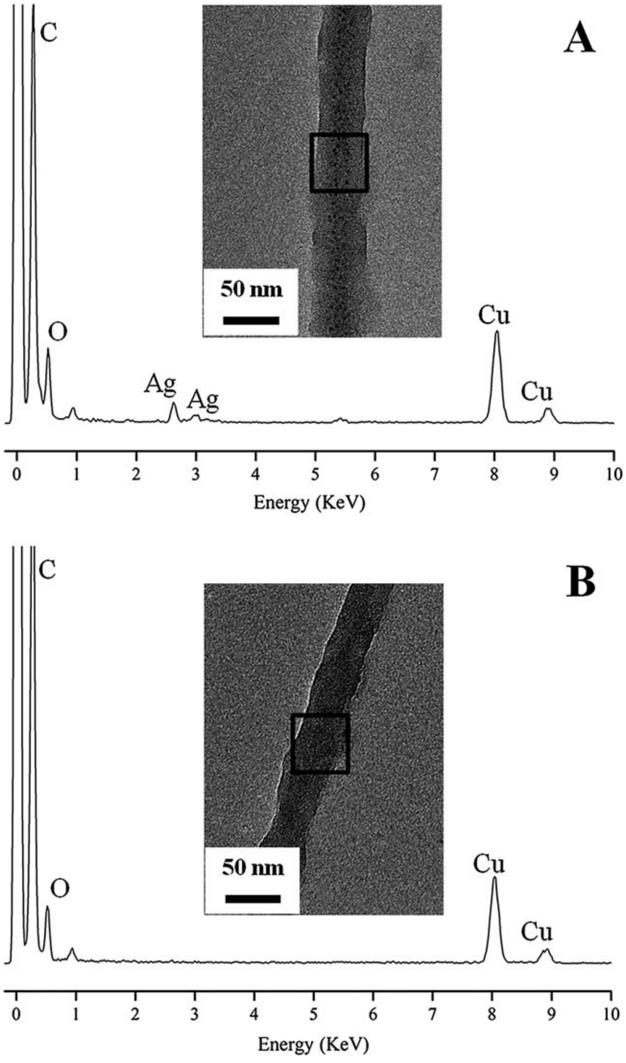


Fig. 6 EDS of a single nanowire obtained after 10 h polymerization: (A) with template; (B) after removal of the metallogel template.

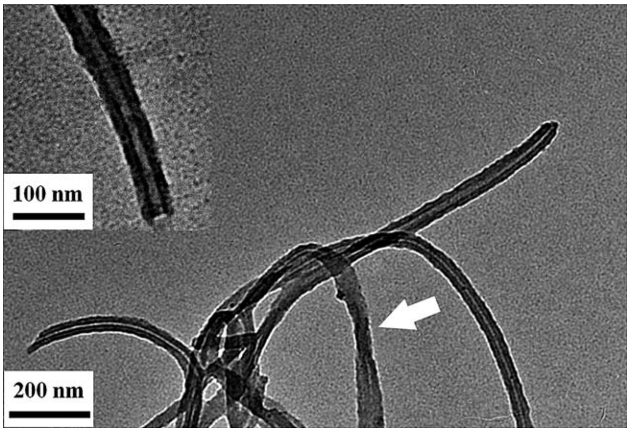


Fig. 7 Polymer nanotubes obtained after removal of the template.

inner diameter, and sometimes a ribbon structure could also be seen (denoted by the white arrow). These results could be ascribed to the flexible mechanical properties of PDADAP; when template nanofibers were removed, these nanowires might collapse quickly, and the minority of them with larger interspaces remained nanotubes. If the polymer layer is too weak to support the tube structure, nanotubes will be squashed into ribbons.

Mechanical properties

In the experiment, we found that the Ag(I) metallogel formed by mixing solutions of silver ions and ligands interestingly exhibits pronounced thixotropic behavior. Shaking or sonication could destroy the fragile gel, resulting in a free-flowing liquid which reformed into a white gel upon standing for several hours. The reversible gel–sol transformation of the metallogel has been reported before as a gel mechano-responsive property.[30] After polymerization of DADAP, the product was obtained as a gel which could not be destroyed by shaking or sonication, indicating the formation of a polymer gel. We can take the white gel out of the vial (Fig. 8A), and it exhibits excellent self-supporting ability. In the saturated gel, networks of polymer nanowires trapped lots of solvent molecules. When dried in air for 3 days, the polymer gel shrinks severely because of the volatilization of the solvent, as shown in Fig. 8B.

The mechanical properties were measured by rheometer. In Fig. 9, curves of the storage modulus (G') and the loss modulus (G'') against frequency are presented. Obviously, the polymer gel displays a higher strength (G' of the polymer gel is about 25 000 Pa, 20 times that of the metallogel, while G'' is more than 10 times larger). In contrast to the metallogel, the polymer gel shows typical elastic behavior, and is strong enough to be used as a specific adsorbing material.

Adsorption of thymidine

To functionalize polymer nanowires prepared by metallogel template fabrication, we introduce hydrogen bonding recognition on the surface of nanowires. Our design is based on the use of a biologically inspired, well-defined, triple hydrogen-bonding motif formed by the complex between thymine and 2,6-diacyldiaminopyridine moieties shown in Fig. 10. This motif provides a robust recognition unit with binding characteristics that are well known in solution.[31;32] The polymer nanowires with triple hydrogen-bonding sites can be utilized for adsorption in solution.

The polymer nanowires have been tested for adsorbing thymidine, a kind of biologically important nucleoside, from

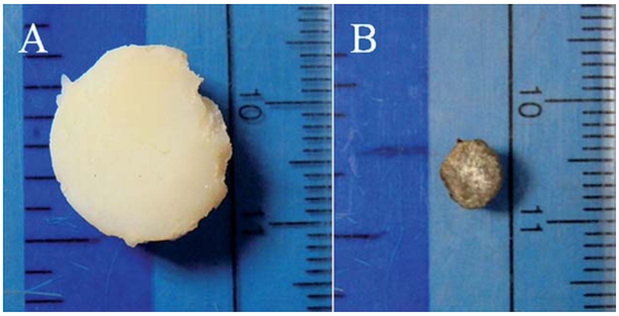


Fig. 8 Macroscopic images of polymer gel: (A) the sample saturated by THF; (B) dried sample.

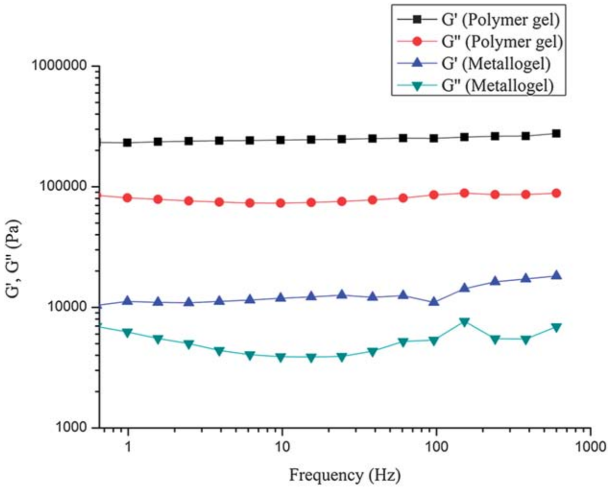


Fig. 9 Storage modulus and loss modulus of the polymer gel and the metallogel at different frequencies.

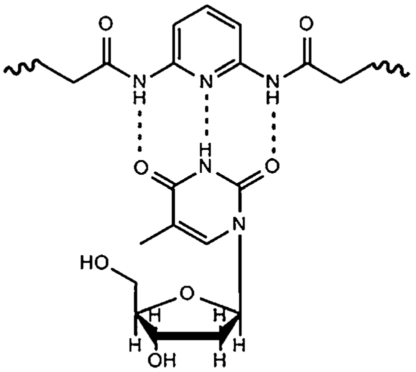


Fig. 10 Triple hydrogen-bonding recognition dyad, based on thymine and 2,6-diacyldiaminopyridine, used in this study.

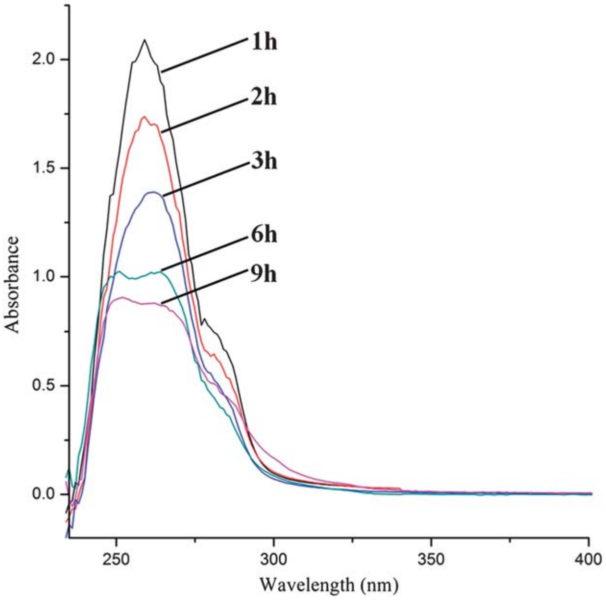


Fig. 11 UV-Vis spectra of time-dependent adsorption of thymidine from THF solution by the application of polymer nanowires.

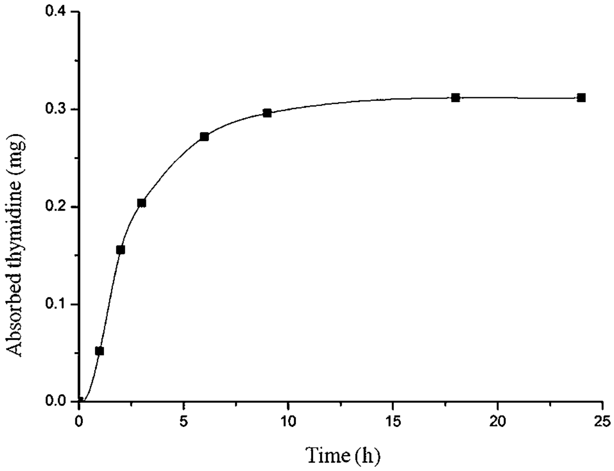


Fig. 12 Mass increase of adsorbed thymidine in polymer nanowires with respect to time.

dilute THF solution (100 mg L^{-1}). When the dry powder of polymer nanowires has been submerged in a solution of thymidine, within a few hours it is capable of removing guest molecules from the organic phase efficiently. It has been observed from the time-dependent UV-Vis spectra (Fig. 11) that the intensity of the peak decreases with respect to time, from 1 h to 9 h, and after 24 h it reaches equilibrium. We investigated the mass of thymidine adsorbed in the polymer nanowires as the adsorption time increased; as shown in Fig. 12, the curve obtained apparently follows first-order kinetics, similar to most surface adsorption procedures. Such result suggests the formation of a triple hydrogen-bonding motif, and the high specific surface area of the nanowires contributes to the adsorption of guest molecules, making the polymer nanowires good sorbents for biological molecules.

According to the reversible nature of hydrogen-bonding, desorption of thymidine will take place when a heated proton solvent is used. So we treated the polymer nanowires adsorbed thymidine with 12 h Soxhlet extraction using ethanol as solvent, then thymidine was removed from sorbents thoroughly. The polymer nanowires could be regenerated in this way and used as sorbents repeatedly which is a great advantage for nucleoside-adsorbing materials.

Conclusions

In conclusion, using a metallogel as a template, we successfully fabricated polymer nanowires with triple hydrogen-bonding sites. This approach is very simple and efficient, involving polymerization in a gel system at a moderate temperature. Triple hydrogen-bonding sites are introduced directly by the monomer. TEM and SEM analyses of the reaction product demonstrate the morphology of polymer nanowires which duplicate the networks of nanofibers of template metallogel. The mechanism of the template polymerization is also illustrated clearly. The polymer nanowires prepared by this method could be used as adsorbing agents of biological molecules, such as thymidine, by immersing in dilute THF solution and the adsorption procedure accords with first-order kinetics. Adsorbed polymer nanowires could be regenerated by Soxhlet extraction. Our study has introduced multiple hydrogen-bonding sites into polymer nanowires. Using this strategy, a variety of functionalized polymer nanowires for biological application might be prepared under appropriate conditions.

Acknowledgements

The financial support from the National Natural Science Foundation of China (Nos. 20574041 and 20874055) and Hi-tech Research and Development Program (863 plan) of China (No. 2009AA062903) is gratefully acknowledged.

Notes and references

1 (*a*) Il Cho and S. B. Lee, *Acc. Chem. Res.*, 2008, **41**, 699–707; (*b*) Aleshin, *Adv. Mater.*, 2006, **18**, 17–27; (*c*) H. X. Chang, Y. Yuan, N. L. Shi and Y. F. Guan, *Anal. Chem.*, 2007, **79**, 5111–5115.

2 (*a*) H. J. Wang, W. H. Zhou, X. F. Yin, Z. X. Zhuang, H. H. Yang and X. R. Wang, *J. Am. Chem. Soc.*, 2006, **128**, 15954–15955; (*b*) E. N. Savariar, K. Krishnamoorthy and S. Thayumanavan, *Nat. Nanotechnol.*, 2008, **3**, 112–117.

3 M. R. Abidian, D. H. Kim and D. C. Martin, *Adv. Mater.*, 2006, **18**, 405.

4 S. Ko and J. Jang, *Angew. Chem., Int. Ed.*, 2006, **45**, 7564–7567.

5 I. W. Hamley, *Soft Matter*, 2005, **1**, 36–43.

6 T. Shimizu, M. Masuda and H. Minamikawa, *Chem. Rev.*, 2005, **105**, 1401–1443.

7 C. Schonenberger, B. M. I. vanderZande, L. G. J. Fokkink, M. Henny, C. Schmid, M. Kruger, A. Bachtold, R. Huber, H. Birk and U. Staufer, *J. Phys. Chem. B*, 1997, **101**, 5497–5505.

8 M. Steinhart, R. B. Wehrspohn, U. Gosele and J. H. Wendorff, *Angew. Chem., Int. Ed.*, 2004, **43**, 1334–1344.

9 K. J. Lee, J. H. Oh, Y. Kim and J. Jang, *Chem. Mater.*, 2006, **18**, 5002–5008.

10 A. H. Chen, H. X. Xie, H. Q. Wang, H. Y. Li and X. Y. Li, *Synth. Met.*, 2006, **156**, 346–350.

11 S. Kawano, S. Tamaru, N. Fujita and S. Shinkai, *Chem.–Eur. J.*, 2004, **10**, 343–351.

12 J. H. Jung, K. Nakashima and S. Shinkai, *Nano Lett.*, 2001, **1**, 145–148.

13 S. Kobayashi, N. Hamasaki, M. Suzuki, M. Kimura, H. Shirai and K. Hanabusa, *J. Am. Chem. Soc.*, 2002, **124**, 6550–6551.

14 Q. Wei and S. L. James, *Chem. Commun.*, 2005, 1555–1556.

15 B. A. Xing, M. F. Choi, Z. Y. Zhou and B. Xu, *Langmuir*, 2002, **18**, 9654–9658.

16 K. Chen, L. M. Tang, Y. Xia and Y. J. Wang, *Langmuir*, 2008, **24**, 13838–13841.

17 L. J. Prins, D. N. Reinhoudt and P. Timmerman, *Angew. Chem., Int. Ed.*, 2001, **40**, 2382–2426.

18 U. Drechsler, R. J. Thibault and V. M. Rotello, *Macromolecules*, 2002, **35**, 9621–9623.

19 H. S. Bazzi and H. F. Sleiman, *Macromolecules*, 2002, **35**, 9617–9620.

20 K. Viswanathan, H. Ozhalici, C. L. Elkins, C. Heisey, T. C. Ward and T. E. Long, *Langmuir*, 2006, **22**, 1099–1105.

21 J. T. Han, D. H. Lee, C. Y. Ryu and K. W. Cho, *J. Am. Chem. Soc.*, 2004, **126**, 4796–4797.

22 S. Zou, Z. H. Zhang, R. Forch, W. Knoll, H. Schonherr and G. J. Vancso, *Langmuir*, 2003, **19**, 8618–8621.

23 A. K. Boal, M. Gray, F. Ilhan, G. M. Clavier, L. Kapitzky and V. M. Rotello, *Tetrahedron*, 2002, **58**, 765–770.

24 J. K. H. Hui, Z. Yu and M. J. MacLachlan, *Angew. Chem., Int. Ed.*, 2007, **46**, 7980–7983.

25 B. G. Xing, M. F. Choi and B. Xu, *Chem.–Eur. J.*, 2002, **8**, 5028–5032.

26 L. Brunsveld, B. J. B. Folmer, E. W. Meijer and R. P. Sijbesma, *Chem. Rev.*, 2001, **101**, 4071–4097.

27 L. A. Estroff and A. D. Hamilton, *Chem. Rev.*, 2004, **104**, 1201–1217.

28 M. Oh and C. A. Mirkin, *Angew. Chem., Int. Ed.*, 2006, **45**, 5492–5494.

29 Y. M. Jeon, J. Heo and C. A. Mirkin, *J. Am. Chem. Soc.*, 2007, **129**, 7480.

30 W. G. Weng, J. B. Beck, A. M. Jamieson and S. J. Rowan, *J. Am. Chem. Soc.*, 2006, **128**, 11663–11672.

31 Z. Li, J. F. Ding, M. Day and Y. Tao, *Macromolecules*, 2006, **39**, 2629–2636.

32 D. J. Duffy, K. Das, S. L. Hsu, J. Penelle, V. M. Rotello and H. D. Stidham, *J. Am. Chem. Soc.*, 2002, **124**, 8290–8296.