

Photochemical synthesis of crown-shaped platinum nanoparticles using aggregates of G4-NH₂ PAMAM dendrimer as templates

Xuzhong Luo^a and Toyoko Imae^{*ab}

Received 16th August 2006, Accepted 9th November 2006

First published as an Advance Article on the web 21st November 2006

DOI: 10.1039/b611867b

Crown-shaped platinum nanoparticles were synthesized by UV irradiation in the presence of G4-NH₂ PAMAM dendrimers in water. Aggregates of the dendrimers, which were formed in the aqueous solution, served as templates for the formation of such nonspherical nanoparticles. This is the first report on the preparation of structure-controlled platinum nanoparticles by photoreduction. This methodology to use dendrimer aggregates as templates is powerful for the production of shape-controlled nanostructures.

Introduction

The study of noble metal nanomaterials is an active research area in materials science.¹ A significant challenge faced in the application of shape-controlled metal nanoparticles is to fabricate nanoparticles with novel structures and shapes. In comparison with metal nanoparticles with the more common shape (sphere), shape-controlled nanoparticles display novel properties and have wider potential for fabricating electric devices,² biological labels,³ optical devices,⁴ magnetic data storage systems,⁵ and biological sensors.⁶ Recently, many attempts have been made to prepare nanoparticles having nonspherical and controllable shapes, such as tetrahedra,⁷ prisms,³ irregular prisms,⁸ cubics,⁹ polyhedra,⁹ triangles,¹⁰ ribbons,¹¹ disks,¹² triangular nanoframes and nanoplates,¹³ nanorods,^{14a} tadpoles,^{14b} etc. However, the challenge for synthesizing these nanoparticles has been met with limited success. Therefore, the study of developing new methods for synthesis of metal nanoparticles with well-controlled shapes and sizes is of great significant.

Previous studies⁹ revealed that some linear polymers were effective capping reagents for synthesis of certain metal nanoparticles with well-controlled structure. In comparison with linear polymers, high generation poly(amido amine) (PAMAM) dendrimers are oligomeric molecules with quasi-spherical morphology. The specific structures of dendrimers render them useful unimolecular templates for the preparation of metal nanoparticles. Pioneering research on the synthesis of metal nanoclusters was reported at the same time by several groups by using dendrimers as both nanoreactors and stabilizers.¹⁵ Different from the reduction of metal ions by using reducers,^{15a,b,c} Esumi *et al.*^{15c} and Kéki *et al.*^{16a} reported the preparation of gold and silver colloids with UV irradiation in the presence of dendrimers. Kim *et al.*^{16b} reported the photochemical synthesis of gold nanorods with controlled aspect ratios using a surfactant as a capping reagent. UV

irradiation yielded not only spherical but also polygonal silver nanoparticles in the presence of PAMAM dendrons with an anthracenyl focal point.¹⁷ The transformation from spherical gold nanoparticles to polygonal microplates with time was observed under UV irradiation in the presence of PAMAM dendrimers at a low content.¹⁸

In this report, we describe the synthesis of crown-shaped platinum nanoparticles under the UV irradiation in the presence of fourth generation NH₂-terminal (G4-NH₂) PAMAM dendrimers. The formation process of the crown-shaped platinum nanoparticles is also discussed. This is the first report on the preparation of structure-controlled platinum nanoparticles by photoreduction.

Experimental

H₂PtCl₆·6H₂O and a methanol solution of G4-NH₂ PAMAM dendrimer were purchased from Sigma Chemical Co. and Aldrich Chemical Co., respectively. For synthesis of platinum nanoparticles, a mixture of H₂PtCl₆ (0.1 mM) and dendrimer (0.07 mM) in water was UV-irradiated for 7 h with a low-pressure mercury lamp (HOYA-SCHOTT, EX250, λ 200–450 nm) in a dark box at ambient temperature (~25 °C). Then the color of the solution changed from orange to light brown. The obtained particles were collected by centrifugation.

UV-visible absorption spectrum measurement was performed spectrometrically (Shimadzu UV-2200) for solutions and dispersions in a quartz cell (1 cm path length). The transmission electron microscopic (TEM) images and diffraction patterns were taken with a Hitachi H-7000 microscope, operating at an accelerating voltage of 100 kV. Scanning electron microscopic (SEM) imaging and energy-dispersive X-ray (EDX) microanalysis were carried out by using a field emission microscope (JEOL, JSM-6330F) equipped with a JEOL JED-2140 EDX microanalyzer and operated at an accelerating voltage of 10–20 kV. For atomic force microscopic (AFM) observation, specimens were examined on a Digital Instruments Nanoscope III. Images were recorded at the scanning rate of 1 Hz by a tapping mode operating at the height mode. Specimens for microscopic observation were prepared by dropping aqueous dispersions of platinum

^aResearch Center for Materials Science, Nagoya University, Chikusa, Nagoya 464-8602, Japan

^bGraduate School of Science, Nagoya University, Chikusa, Nagoya 464-8602, Japan. E-mail: imae@nano.chem.nagoya-u.ac.jp; Fax: +81-52-789-5912

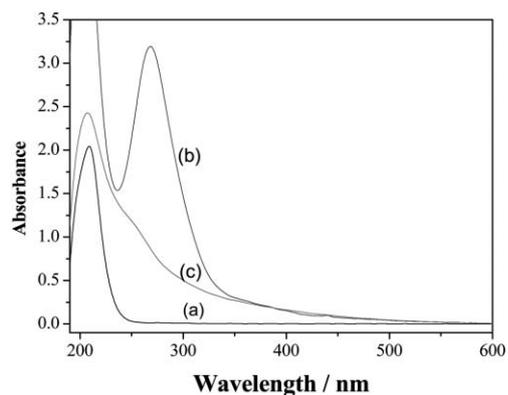


Fig. 1 UV-visible absorption spectra during the preparation of platinum nanoparticles: (a) an aqueous solution of G4-NH₂ PAMAM dendrimer, (b) a mixed solution of G4-NH₂ PAMAM dendrimer and H₂PtCl₆, (c) a mixed solution of G4-NH₂ PAMAM dendrimer and H₂PtCl₆ after UV irradiation for 7 h.

nanoparticles onto a carbon film-coated grid or a freshly cleaved mica surface and drying them quickly.

Results and discussion

UV-visible absorption spectroscopy was used to monitor the photoreduction process of a mixed aqueous solution of

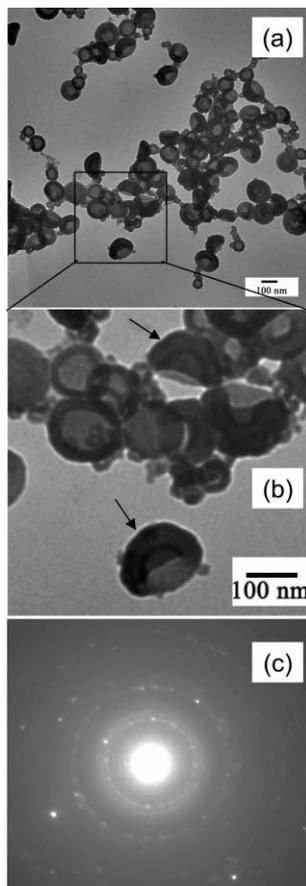


Fig. 2 TEM images of platinum nanoparticles at different magnifications (a and b) and an electron diffraction pattern of particles (c).

H₂PtCl₆ and dendrimer. Variation of the absorption spectra is given in Fig. 1. Before UV irradiation, there are two strong absorption bands: one is a 210 nm band of dendrimer and another is a band at 265 nm that is assigned to the absorption band of a complex of PtCl₆²⁻ and dendrimer (chloride ligands were replaced by the functional groups of dendrimers), since the latter band is not detectable in an absorption spectrum of an aqueous solution of G4-NH₂ PAMAM dendrimer. After UV irradiation for 7 h, the absorption band at 265 nm disappeared, but a broad shoulder band appeared at 250 nm, implying the formation of platinum nanoparticles, because the shoulder band is a characteristic plasmon resonance band of platinum nanoparticles.¹⁹

Fig. 2(a) and (b) show TEM images, at different magnifications, of platinum nanostructures obtained after UV irradiation for 7 h. The particles range from 100 to 130 nm in size and have a shell of around 10–30 nm thickness. Although the possible shapes of the particles can be assumed to be hollow sphere, ring or crown-shape, the most probable shape is “crown-shape”, as presumed from the particle texture in the TEM images (indicated by arrows in Fig. 2(b)). It is noticeable that the concavities of the particles are electron density-less. “Crown-shaped particles” are not “broken fragments of hollow spheres with a hole”, because similarly shaped platinum particles are found in the TEM pictures. Hollow spheres can be fabricated by using polystyrene latex spheres as templates, but they are easily broken into different shapes of fragments or with different sizes of holes.²⁰ The electron

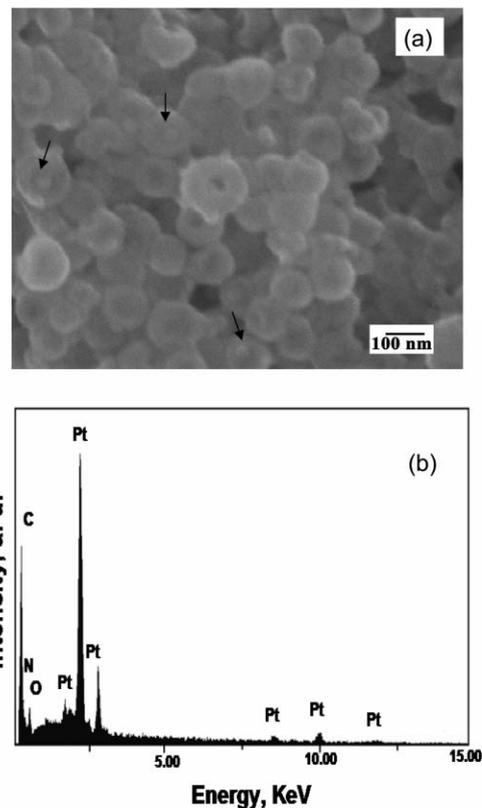


Fig. 3 SEM image (a) and EDX spectrum (b) of the platinum nanoparticles.

diffraction pattern of the particles (Fig. 2(c)) reveals that the platinum particles are in a crystalline state.

The scanning electron microscopic technique was used to characterize the particle structure in detail. Shown in Fig. 3(a) is a SEM image of the particles. It can be seen clearly that most of the particles are a sphere with concavity, that is, crown-shaped. An EDX spectrum of the particles (Fig. 3(b)) presents some peaks assigned to platinum. This reveals that the particles are mainly composed of platinum. It can also be seen from the SEM image that some particles are not concave but hold a small ball in the concavity, as marked by arrows in Fig. 3(a). EDX measurement also reveals that organic compounds coexist with the particles, since there are carbon, nitrogen, and oxygen peaks. Thus, it is reasonable to suppose that the compounds in the concavities of the particles are dendrimers. The size of the concavities was further confirmed by AFM observation, as described below.

For AFM observation, the particles were centrifuged and washed several times with methanol in order to completely remove dendrimers attached to the particles. Shown in Fig. 4 is an AFM image of the platinum particles after removal of dendrimers. The AFM image clearly indicates that there is a concavity on a platinum shell. This is consistent with the crown-shaped model. The section analysis of the AFM image indicates that the height of the crown-shaped platinum

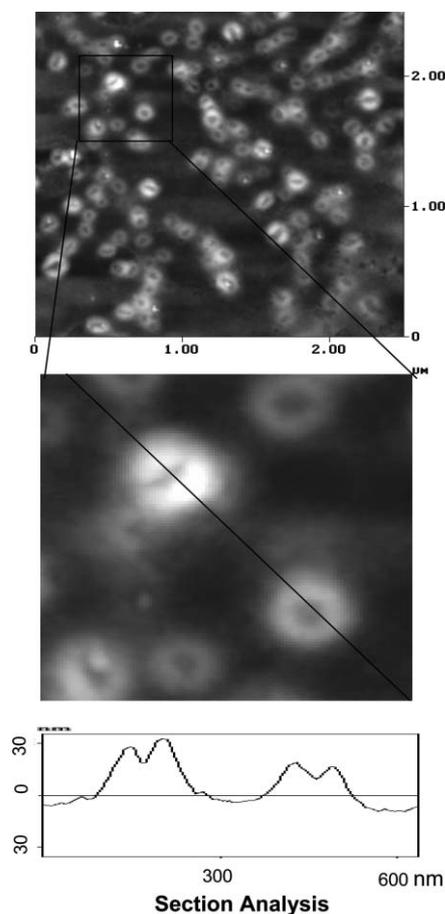


Fig. 4 AFM images of platinum particles after removal of dendrimers and the corresponding section analysis.

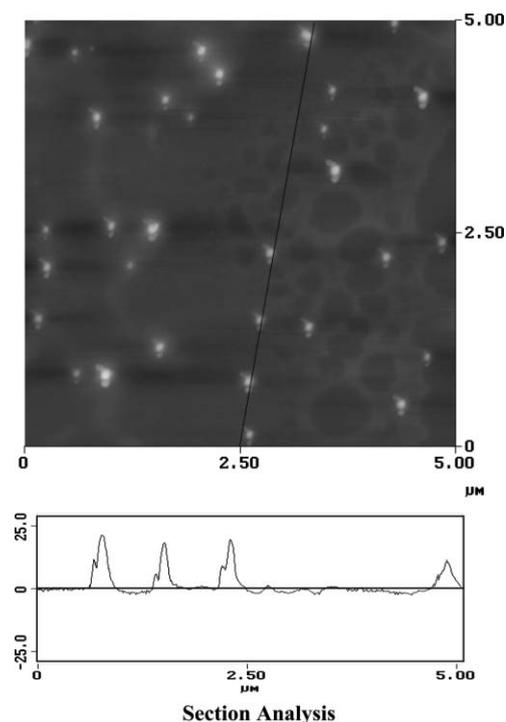


Fig. 5 An AFM image of a specimen prepared from an aqueous solution (0.07 mM) of G4-NH₂ PAMAM dendrimer with the corresponding section analysis.

particles ranges from 30 to 50 nm. It was also found that the particles after removal of dendrimers are not stable but easy coalesce to form bigger particles. This implies that the dendrimers also served as stabilizers for the platinum nanoparticles.

The aperture of a concave, which was evaluated from TEM images and section analysis of AFM images, ranged from 40 to 70 nm. This size is much bigger than the size of a free G4-NH₂ PAMAM dendrimer in solution (*ca.* 4.5 nm in radius²¹). In order to understand the formation process of crown-shaped platinum nanoparticles, an aqueous solution of G4-NH₂ PAMAM dendrimer at the same concentration (0.07 mM) as that used in the preparation of platinum nanoparticles was

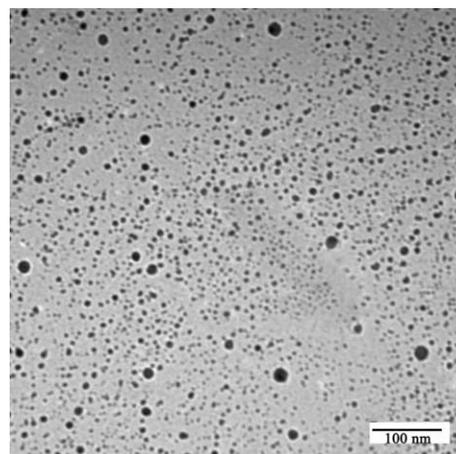
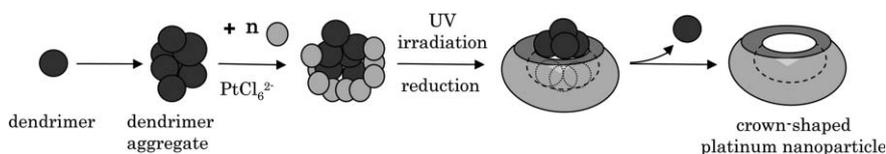


Fig. 6 A TEM image of platinum nanoparticles prepared under UV irradiation in a methanol solution of G4-NH₂ PAMAM dendrimer.



Scheme 1 Schematic illustration of the formation process of crown-shaped platinum nanoparticles.

dropped on a mica substrate, and the specimen was observed after drying. An AFM image (Fig. 5) reveals that there are some particles within the background roughness. This indicates that some dendrimers are not monodispersed but formed aggregates. The height of the aggregates is around 23 nm. The particles of this size can fit within the concavity of the platinum particles. Thus, it can be confirmed that the dendrimer aggregates served as templates in the formation of crown-shaped platinum nanoparticles and they existed in the concavities of the particles, as seen in SEM, although it is difficult to determine their existence from TEM because of the low density of the dendrimers.

The role of dendrimer aggregates as templates can be further confirmed by the following experiment. G4-NH₂ PAMAM dendrimer dissolves monomolecularly in methanol, and no AFM images of dendrimer aggregates were observed in a specimen prepared from a methanol solution at a concentration of 0.07 mM, different from the case in water. (Therefore, the observed aggregates in the specimen from aqueous solution are not attributed to the drying effect.) A methanol solution of the dendrimer and H₂PtCl₆ was prepared at the same concentration as the aqueous solution examined above, and it was irradiated for 7 h with UV light. TEM observation (Fig. 6) reveals that only spherical platinum nanoparticles exist. This implies that no crown-shaped platinum nanoparticles are formed in a methanol solution after UV irradiation due to the absence of dendrimer aggregates in the solution.

Based on the results described above, the proposed process for the formation of crown-shaped platinum nanoparticles is illustrated in Scheme 1. In the aqueous solution, some G4-NH₂ PAMAM dendrimers form aggregates with self-controlled size. In this case, the motive force for the aggregation may be the intermolecular hydrogen bonding among amine and amide groups of the dendrimer. After addition of H₂PtCl₆, Pt(IV) ions coordinate and complexate with dendrimers on the surface of the dendrimer aggregates. With UV irradiation, Pt(IV) ions were reduced to platinum metal, which thus form crown-shaped nanoparticles on the surface of the dendrimer aggregates. Free dendrimers may be adsorbed on the surface of the nanoparticles, giving rise to the stabilization of the particles. Since the dendrimer aggregates are not a real globe, the platinum metal may grow asymmetrically from the crystallization point on the aggregate, forming crown-shaped nanoparticles. The advantage of using dendrimer aggregates as templates is the production of the smaller size of the shape-controlled (crown-shaped) nanoparticles. Such crown-shaped nanoparticles can be utilized as a template for preparing size-controlled ball-like materials of nanometer scale. Especially, if a crown-shaped platinum nanoparticle is immobilized on one edge of a cylindrical particle, a match-shaped platinum catalyst will be fabricated.

Conclusions

Crown-shaped platinum nanoparticles have been produced by UV irradiation in the presence of G4-NH₂ PAMAM dendrimers in water. Some G4-NH₂ PAMAM dendrimers in the aqueous solution form aggregates, which serve as templates for the formation of nanoparticles. The dendrimers also play a role as stabilizers for the particles. The methodology of photoreduction established in the present work is expected to lead to new opportunities for the synthesis of novel metal nanostructures.

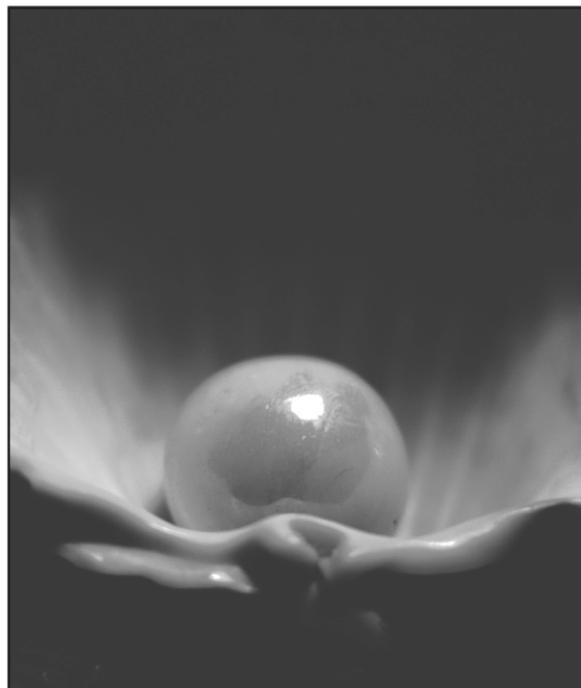
Acknowledgements

XL is thankful to the 21st century COE program (No. 14COEB01-00) in Nagoya University for the financial support. This work was partly supported by a Grant-in-Aid for Scientific Research (B) (15350067) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

References

- (a) G. Schmid, *Chem. Rev.*, 1992, **92**, 1709; (b) M. A. El-Sayed, *Acc. Chem. Res.*, 2001, **34**, 257.
- H. Fissan, M. K. Kennedy, T. J. Krinke and F. E. Kruijs, *J. Nanopart. Res.*, 2003, **5**, 299.
- R. Jin, Y. Cao, C. A. Mirkin, K. L. Kelly, G. C. Schatz and J. G. Zheng, *Science*, 2001, **294**, 1901.
- S. A. Maier, P. G. Kik, H. A. Atwater, S. Meltzer, E. Harel, B. E. Koel and A. A. G. Requicha, *Nat. Mater.*, 2003, **2**, 229.
- S. Sun, C. B. Murray, D. Weller, L. Folks and A. Moser, *Science*, 2000, **287**, 1989.
- (a) M. Bruchez, Jr., M. Moronne, P. Gin, S. Weiss and A. P. Alivisatos, *Science*, 1998, **281**, 2013; (b) J. J. Storhoff, R. Elghanian, R. C. Mucic, C. A. Mirkin and R. L. Letsinger, *J. Am. Chem. Soc.*, 1998, **120**, 1959; (c) L. Yu, I. A. Banerjee and H. Matsui, *J. Am. Chem. Soc.*, 2003, **125**, 14837.
- (a) N. R. Jana, L. Gearheart and C. J. Murphy, *Langmuir*, 2001, **17**, 6782; (b) N. R. Jana and X. Peng, *J. Am. Chem. Soc.*, 2003, **125**, 14280.
- (a) N. R. Jana, L. Gearheart and C. J. Murphy, *J. Phys. Chem. B*, 2001, **105**, 4065; (b) B. Mayers, X. Jiang, D. Sunderland, B. Cattle and Y. Xia, *J. Am. Chem. Soc.*, 2003, **125**, 13364; (c) J. Hu, Q. Chen, Z. Xie, G. Han, R. Wang, B. Ren, Y. Zhang, Z. Yang and Z. Tian, *Adv. Funct. Mater.*, 2004, **14**, 183.
- (a) T. S. Ahmadi, Z. L. Wang, T. C. Green, A. Henglein and M. A. El-Sayed, *Science*, 1996, **272**, 1924; (b) Y. Sun and Y. Xia, *Science*, 2002, **298**, 2176.
- J. S. Bradley, B. Tesche, W. Busser, M. Maase and M. T. Reetz, *J. Am. Chem. Soc.*, 2000, **122**, 4631.
- V. F. Puentes, K. M. Krishnan and A. P. Alivisatos, *Science*, 2001, **291**, 2115.
- (a) S. Chen, Z. Fan and D. L. Carroll, *J. Phys. Chem. B*, 2002, **106**, 10777; (b) Y. Sun and Y. Xia, *Nano Lett.*, 2003, **3**, 1569; (c) M. Maillard, P. Huang and L. Brus, *Nano Lett.*, 2003, **3**, 1611.
- G. S. Metraux, Y. C. Cao, R. Jin and C. A. Mirkin, *Nano Lett.*, 2003, **3**, 519.
- (a) F. Kim, J. H. Song and P. D. Yang, *J. Am. Chem. Soc.*, 2004, **124**, 14316; (b) J. Hu, Y. Zhang, B. Liu, J. Liu, H. Zhou, Y. Xu, Y. Jiang, Z. Yang and Z.-Q. Tian, *J. Am. Chem. Soc.*, 2004, **126**, 9470.

- 15 (a) M. Zhao, L. Sun and R. M. Crooks, *J. Am. Chem. Soc.*, 1998, **120**, 4877; (b) L. Balogh and D. A. Tomalia, *J. Am. Chem. Soc.*, 1998, **120**, 7355; (c) K. Esumi, A. Suzuki, N. Aihara, K. Usui and K. Torigoe, *Langmuir*, 1998, **14**, 3157; (d) R. M. Crook, M. Zhao, L. Sun, V. Chechik and L. Yeung, *Acc. Chem. Res.*, 2001, **34**, 181; (e) A. Manna, T. Imae, K. Aoi, M. Okada and T. Yogo, *Chem. Mater.*, 2001, **13**, 1674.
- 16 (a) S. Kéki, J. Török, G. Deák, L. Daróczy and M. Zsuga, *J. Colloid Interface Sci.*, 2000, **229**, 550; (b) F. Kim, J. H. Song and P. D. Yang, *J. Am. Chem. Soc.*, 2002, **124**, 14316.
- 17 C. Hinano, T. Imae, Y. Yanagimoto and Y. Takaguchi, *Polym. J.*, 2006, **38**, 44.
- 18 D. Wang and T. Imae, *Chem. Lett.*, 2006, **35**, 1152.
- 19 L. Yang, Y. F. Luo, X. R. Jia, Y. Ji, L. P. You and Q. F. Zhou, *J. Phys. Chem. B*, 2004, **108**, 1176.
- 20 H. Shiho and N. Kawahashi, *J. Colloid Interface Sci.*, 2000, **226**, 91; H. Shiho and N. Kawahashi, *Colloid Polym. Sci.*, 2000, **278**, 270.
- 21 D. A. Tomalia, A. M. Naylor and W. A. Goddard, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 138.



Looking for that **special** research paper from applied and technological aspects of the chemical sciences?

TRY this free news service:

Chemical Technology

- highlights of newsworthy and significant advances in chemical technology from across RSC journals
- free online access
- updated daily
- free access to the original research paper from every online article
- also available as a free print supplement in selected RSC journals.*

*A separately issued print subscription is also available.

Registered Charity Number: 207890

RSCPublishing

www.rsc.org/chemicaltechnology

22030683