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ARTICLE

A Facile and Efficient Route for Coating Polyaniline onto Positively Charged Substrate

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ABSTRACT: By means of the "swelling−diffusion−interfacial polymerization method" (SDIPM), we successfully coated polyaniline (PANi) onto the positively charged polystyrene (PS) particles, which electrostatically repulse each other. After initially forming aniline-swollen PS particles, diffusion of the monomer toward the aqueous phase was controlled through a slow addition of hydrochloric acid, eventually leading to its polymerization on the particle surface. It is an unique, facile, and efficient approach based on raw substrate particles with cationic surface, in comparison with the previous efforts focusing on laborious surface modification or customized design of the substrate particles. The synthesized composite particles have been extensively characterized using scanning electron microscope, transmission electron microscope, Fourier transform infrared, Raman spectroscopy, and thermogravimetry. The resultant PS/PANi core/shell conductive composites possessed a uniform, intact PANi overlayer, and furthermore, their mophology can be well controlled by simply changing weight ratio of aniline/PS. The importance of the results just consists in the fact that the limitation of constructing an overlayer on similarly charged substrate particles should be overcome by adopting the unique SDIPM.

Introduction

Over the last 15 years or so, there has been considerable research activity centered on conducting polymers.[1−6] Among conducting polymers, polyaniline (PANi) is the most attractive because of its electronic, optical and magnetic properties, environmental stability as well as promising technological applications in electrical devices.[7−14] However, PANi is difficult to process as a result of its insolubility in common solvents and its infusibility. To overcome this drawback, one of the effective methods is to synthesize conducting colloidal composites, for example, PANi micro- or nanocomposite particles with core/shell-like structures. Conducting composite colloidal particles not only could improve the processability of conducting polymers, but also achieve high conductivity with low loading of conducting polymers. Moreover, utilizing a low T_g latex core particles lead to composite colloidal particles with good film-forming properties.[15]

Up to now, large numbers of papers dealing with the coating of PANi onto various colloidal/particulate substrates to afford composite colloidal particles have been reported.[16−23] As a rule, polystyrene particle was selected as a model substrate since it could be easily prepared with narrow size distributions over a wide size range. The surface of adopted PS particles was always functionalized and modified with various functional groups or surfactants to enhance the interactions between PANi oligomers and the PS surface, and therefore improve the coating of PANi. Reynaud and co-workers reported a relatively high coverage of PANi based on cross-linked PS particles stabilized by a surfactant bearing an amide group, which allows the formation of hydrogen bonds with the PANi backbone.[16] Yang's group utilized the inward sulfonation of PS particles to primarily absorb aniline in sulfonated polystyrene shell through the electrostatic interaction, and then PANi was formed by polymerization in situ.[17]

It is perceptibly difficult to directly coat PANi onto positively charged substrate because of the electrostatic repulsion between the positive PANi oligomers and positive surface of substrate. Shi et al. definitely indicated that PANi cannot be coated onto positively charged substrates based on their investigations.[24−26] Wang and co-workers successfully coated PANi onto cationic PS latex, but a negatively charged sulfate surfactant was adopted to change the electrostatic nature of the PS seed particles prior to the coating process.[18] Liu et al. also studied the coating of PANi onto PS particles with imidazolium cations on their surface, and just as was said by them, the oxidant immobilized on the PS surface and weak interactions existing between PANi oligomers and imidazolium cations played critical roles in successfully fabricating PS/PANi composite particles. Besides, in order to increase thickness of the PANi shell, the seeded growth method was applied repeatedly by them.[19]

Obviously, time-consuming surface modification complicates the synthetic procedure, even though it could generally optimize the deposition architecture of the PANi overlayer. A versatile approach of controlling over the PANi coating onto substrate with different surface properties, independent of any other assistance, is still a scientific challenge. Recently, we proposed a distinctly novel, so-called "swelling−diffusion−interfacial−polymerization method" (SDIPM) for preparing PS/PANi composite spheres, regardless of the "naked" PS seed particles used.[20] Compared to the widely used conventional synthetic protocol, the SDIPM developed an unique, new approach, namely, an "inside-out" process, which has been confirmed by a series of experimental results, to afford much more effective control over the structure and morphology of the resultant PS/PANi composites by simply changing the aniline/PS weight ratio or the rate of addition of the doping acid.

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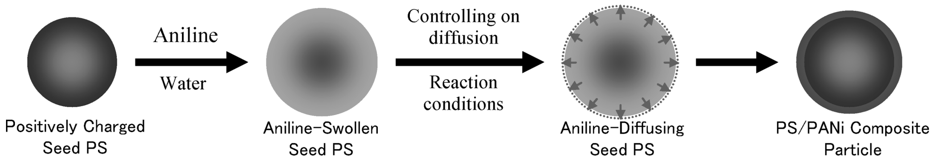

Figure 1. Schematic representation of the proposed swelling–diffusion–interfacial–polymerization method.

In the present paper, PS particles with cationic surface, derived from the decomposition of the used initiator 2,2′-azobisisobutyramidine dihydrochloride (AIBA), were chosen as the model particulate substrate. By means of the SDIPM, we successfully coated PANi onto the positively charged particles independent of any other assistance, to fabricate PS/PANi core/shell conductive composites with uniform size and well-defined shape, and significantly, to further explore the wide applicability of the SDIPM to particulate substrates with any surface properties, even electrostatic repulsion with coated components.

Experimental Section

Materials. Styrene and aniline (AR, Shanghai Chemical Reagent Co.) were purified by distillation under reduced pressure. 2,2′-Azobisisobutyramidine dihydrochloride (AIBA) was purchased from Aldrich (USA) and used as received. Ammonium persulfate (APS) of analytical reagent grade (Shanghai Chemical Reagent Co.) was purified by recrystallization in water. Hydrochloric acid and tetrahydrofuran (THF) were purchased from Nanjing Chemical Reagent Co., and used as received. Distilled water was applied for all polymerization and treatment processes.

Synthesis of Polystyrene Particles. Polystyrene (PS) particles were prepared by emulsifier-free emulsion polymerization. Water (180 mL) and styrene (9 g) were added to a 250 mL four-necked round flask and heated up to 70 °C. It was purged with nitrogen to eliminate the inhibiting effect of oxygen before the addition of initiator under mechanical stirring. Following the attainment of a uniform dispersion, AIBA dissolved in water (0.18 g/15 mL) was added. The polymerization was allowed to proceed under N_2 atmosphere for 24 h before cooling to room temperature.

Preparation of Polystyrene/Polyaniline Composite Particles. First, aniline was added to water (15 mL) at 0 °C and under ultrasonic treatment for 15 min and followed by the addition of the PS seed particles (1.2 g). The mixture was stirred with ultrasonic assistance for 30 min at 0 °C to allow sufficient swell of aniline into PS seed particles. The dispersion of aniline-swollen PS particles was transferred to a three-necked round-bottom flask in an ice bath. The aqueous solution of APS was added to the dispersion in one batch and the initial oxidant/monomer molar ration was fixed at 1:1. This was followed by the addition of hydrochloric acid (1 mol/L), also in an equimolar amount relative to aniline, dropwisely via syringe. The temperature was maintained at 0 °C for the first 5 h of the polymerization, after which the polymerization was carried out for 18 h at room temperature. The solid content of the PS latexes was kept constant at 4 wt %, and the weight ration of aniline monomer to the seed latex was varied from 1:12 to 1:3. The resulting green PS/PANi composite particles were washed repeatedly by centrifugation until the filtrate became colorless. Finally, the products were dried in a vacuum oven for 48 h at 50 °C.

Extraction of the PS Core. Excess THF (10 mL) was added into 50 mg of the dried PS/PANi particles at room temperature. This dispersion was left overnight. The resulting black residue was filtered, washed with THF, and redispersed in water.

Characterization. The morphology of the PS seed particles and the resultant PS/PANi composite particles were observed both by scanning electron microscope (SEM) using an S-4800 instrument (Hitachi Co., Japan) operated at an accelerating voltage of 5 kV (samples sputter coated with gold prior to examination) and transmission electron microscopy (TEM) using a JEM-100 CX (JEOL Co., Japan) microscope. Fourier transform infrared (FTIR) analysis was performed with a Bruker VECTORTM 22 FT-IR spectrometer (Bruker Co., Germany). Raman spectra were measured by use of the MultiRam spectrometer (Bruker Co., Germany). A continuous wave Nd:YAG laser working at 1064 nm was employed for Raman excitation. A total of 200 scans were averaged in each spectrum obtained with laser power 10 mW. Aqueous electrophoresis measurements of PS seed particles and PS/PANi composite particles were carried out using a Malvern Zetasizer Nano Z instrument. The solution pH was adjusted by the addition of HCl or NaOH. Thermogravimetric analysis (TGA) was conducted with a Pyris 1 TGA instrument (PerkinElmer Co., USA) at a heating rate of 20 °C per min in N_2 from room temperature up to 600 °C.

Results and Discussion

The schematic process for "swelling–diffusion–interfacial–polymerization method" is displayed in Figure 1. In the initial stage, upon mixing the monomer (i.e., aniline) with the original seed latex, the former would be enriched inside the seed particles after a certain period according to their good affinity, eventually forming monomer-swollen seed particles. That is, the monomer is distributed mainly in the solid seed particles while the other, which is an integral component participating in the polymerization of the monomer, exists in the continuous phase, and hence the reaction is almost restrained at this stage. Following the change on factors of controlling the diffusion of the monomer from the seed particles toward the aqueous phase, the original thermodynamic equilibrium of the reactants between the two phases will be broken. During diffusing toward the aqueous phase, the monomer could encounter the other reactants existing in the water, such as oxidant APS in present system, to initiate interfacial reaction, i.e., chemical oxidation polymerization of the aniline at the external surface of the seed particles. Thus, it would yield readily coats on the seed particles simultaneously. As the formation proceeds, the swollen seed particles act as reservoirs that constantly release monomer under control to the external surface to keep the processes of diffusion and interface reaction going. In brief, the incorporation of second component, i.e., PANi, with the seed particles can be carried out with an unique "inside-out" way, in contrast to the prevalent thinking toward random deposition or induced deposition. In the process, the outer surface of the seed particles is the necessary path where the diffusing monomer passes through. As a result, an overlayer of the PANi can form more efficiently and be well controllable, moreover, with a homogeneous distribution regardless of the surface modification of the seed latex.

On the basis of the strategic considerations for SDIPM, systems have to meet following requirements: first, at least one of reactants participating in the chemical reaction, preferably of the monomer, can be swelled into the selected seed beads whereas another involving initiator, catalyst etc. must exist in continuous phase. Second, effective manners of governing the absorbate diffusion from the seed beads toward the continuous phase can be found.

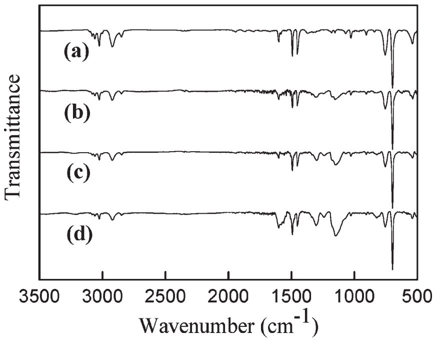

Figure 2. FTIR spectra of PS seed particles (a) and PANi/PS composite particles with different aniline/PS weight ratio: (b) 12:1, (c) 6:1, (d) 3:1.

In the present work, the original PS particles were synthesized by using a cationic initiator (AIBA) and had a ζ potential of 44 mV at pH = 6. Hence, the PS particles, used as particulate substrates, had positively charged surface. By varying the aniline/PS weight ratio (i.e., 1:12 to 1:3), a series of PS/PANi nanocomposites was obtained. The FTIR spectra of this series and PS seed particles are displayed in Figure 2. For the PS seed particles (a), the main absorption bands are at 1498, 1465, 750, and 698 cm^{-1}. In the spectra of PS/PANi composite particles, three additional absorption bands attributed to the PANi component are notably observed at 1303, 1242, and 1150 cm^{-1} (b, c, and d).[27,28] The arisen band intensities of the PANi component could be regarded as supporting evidence for core/shell morphology. Furthermore, it is clear that the intensity of the characteristic peaks of PANi enhances proportionally to increase of the initial amount of added monomer, suggesting that the amount of PANi coating was increased. On the other hand, the ζ potentials of PS/PANi composite particles prepared with aniline/PS weight ratios of 1:12 and 1:3 were 61.3 mV and 66.7 mV, respectively, under the same condition as PS measured. Remarkably, both the original PS particles and the resultant composite particles had positively charged surface, but there was a different level of ζ potentials. It demonstrated plainly the change of the particle surface, and especially, fully proved the successful incorporation of the two similarly charged components. In addition, the ζ potentials for the two composite particles were close each other, which reflected their similar surface and furthermore suggested that the intact PANi overlayer was obtained even at low aniline/PS weight ratio.

Transmission electron microscope (TEM) images of this series and the PS seed particles as shown in Figure 3 demonstrated the formation of the PANi overlayer and their morphology more directly. When the lowest aniline/PS weight ratio of 1:12 was used, a thin PANi overlayer was formed with uniform distribution (Figure 3b). With an increase in the amount of aniline, for example, aniline/PS weight ratio of 1:6 (Figure 3c), the thick and uniform PANi overlayer was obtained remarkably. At still higher concentration of monomer (aniline/PS weight ratio of 1:3), all of the composite particles still maintained their perfectly spherical outline and simultaneously possessed of thicker PANi overlayer (Figure 3d). By comparing these samples, a smooth edge was prepared by adding the lowest concentration of aniline, and then distinct burrlike overlayers were obtained when the concentration of aniline was increased. The variation of PANi overlayers observed in the TEM images is well corresponding to their FTIR spectra. These results allow us to conclude that increasing the PANi loading, i.e., the thickness of PANi shell, can be conveniently achieved by changing the weight ratio of aniline/PS based on the SDIPM, rather than repeated seeded polymerizations.

Scanning electron microscope (SEM) images of PS/PANi composite particles prepared with aniline/PS weight ratio of 1:12 and 1:3 are displayed in Figure 4. In comparison with PS seed particles (see the inset) given in Figure 4a, it is evident that the PS particles are uniformly and entirely coated with PANi overlayer almost without any granular or fibriform morphology. Additionally, the PS/PANi composite particles had visibly rough surface as increased with the aniline/PS weight ratio (e.g., 1:3) and nevertheless, they still maintained their perfectly spherical outline even at high PANi loading. PS extraction experiments were also carried out to further examine the morphology of the PS/PANi composite particles. Parts c and d of Figure 4 show the TEM images of the PANi residue after immersing the corresponding composites in tetrahydrofuran overnight. At a lower aniline/PS weight ratio, the thin PANi shell made it weak and breakable, but it still revealed good uniformity. The intact and uniform hollow structure as using a higher aniline concentration shown in Figure 4d, more clearly demonstrates the advantage of the proposed SDIPM even though applied to the positively charged substrate particles. It is further confirmed by using Raman spectrum that the integrality of PANi overlayer prepared by SDIPM is very excellent even at low weight ratio of aniline/PS. The Raman spectra of a series of samples are depicted in Figure 5. The PS component has a very strong signal at about 1002 cm^{-1} (curve a, ν_1 ring-breathing mode), which is excellently similar to the Raman spectra of PS reported by previous workers.[29]

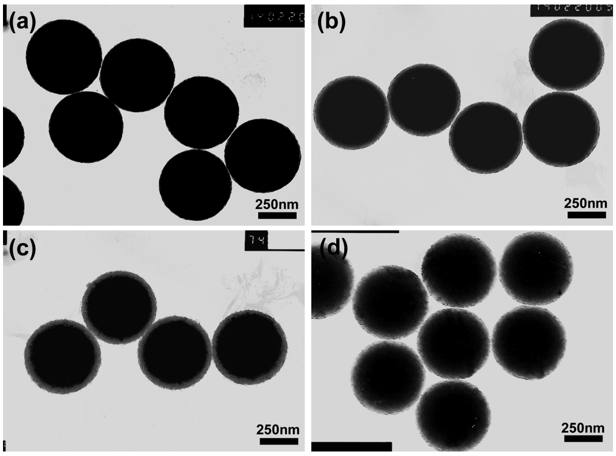

Figure 3. TEM images of PS seed particles (a), and PS/PANi composite particles prepared by using different aniline/PS weight ratio: (b) 1:12, (c) 1:6, (d) 1:3.

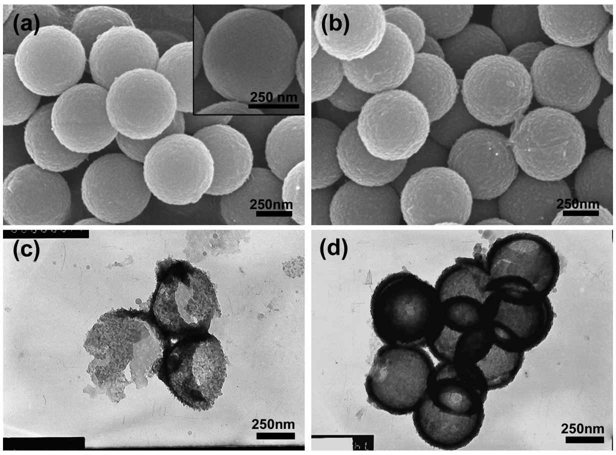

Figure 4. SEM images of PS/PANi composite particles prepared with different aniline/PS weight ratios, (a) 1:12 and (b) 1:3. The inset in part a is a PS seed particle. TEM images of remaining PANi residues after tetrahydrofuran extraction of PS from PS/PANi composite particles prepared with different aniline/PS weight ratios, (c) 1:12 and (d) 1:3.

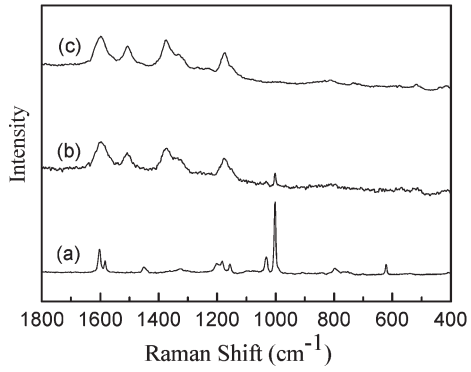

Figure 5. Raman spectra of dried PS particles (a), a heterogeneous admixture of 10 wt % PANi with 90 wt % PS (b), and PS/PANi composite particles with aniline/PS weight ratio of 1:12 (c).

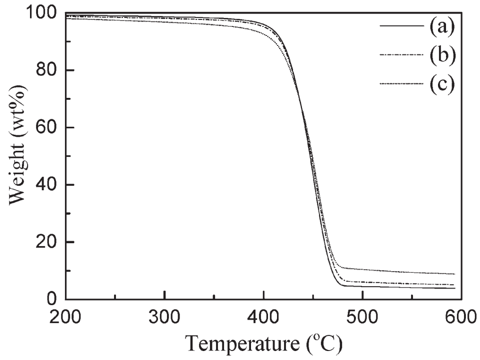

Figure 6. TGA curves of PS/PANi composite particles with different aniline/PS weight ratio: (a) 1:12, (b) 1:6, (c) 1:3.

However, this strong signal completely disappears (curve c) when the PS was covered by a thin PANi overlayer as the composite particles shown in Figure 3c. It is in sharp contrast with control experiment, which was carried out using a heterogeneous admixture with a mass composition of 10 wt % polyaniline chloride bulk powder and 90 wt % PS latex. In the latter case, the signal belonged to the PS is readily observed (curve b), even though it has much higher PANi weight percentage content than the PS/PANi composite particles. This phenomenon can be regarded as a powerful evidence for PS/PANi core/shell morphology, because the Raman signal belonging to PS core could be attenuated or absorbed when the PANi overlayer is perfectly existed and simultaneously has a certain thickness.[22]

Figure 6 represents the thermogravimetric analysis results of the PS/PANi composite particles with different aniline/PS weight ratio. The major weight losses were observed below 475 °C because of the thermal decomposition of PS. The residual fraction refers to the weight percentage content of PANi in the composite particles. According to the TGA curves, the loading efficiency of PANi onto PS seed particles, namely, a ratio of PANi actual content and theoretical content incorporated into the composite particles, can be determined to be 80.5%, 58.0%, and 56.5%, respectively. At the lowest aniline amount, there was a much higher loading efficiency of aniline to transform to the resultant composite particles, which is the prominent feature of the SDIPM in sharp contrast with the conventional deposition method.[20] On the basis of the formation mechanism of diffusion and subsequent polymerization on the interface of seed particles, when the aniline/PS weight ratio is relatively high, there might be an excess of aniline escaping into the aqueous solution and no longer participating in the polymerization at the interface, and thus, impairing the efficiency of converting the monomer into the PANi overlayer of the composite. This impact became more obvious especially when an electrostatic repulsion existed between the particle surface and the aniline hydrochloride.

Conclusions

In summary, we successfully prepared the monodisperse PS/PANi composite particles using positively charged PS particles as model substrate for the first time according to the proposed SDIPM. The resultant morphology of composite particles could be easily controlled by the initial addition amount of aniline. The limitation of coating PANi onto a similarly charged surface of the seed particles was overcome via a "inside-out" forming process on the basis of the unique SDIPM. It should be of considerable interest that the SDIPM will open a versatile way for fabricating an overlayer onto any substrate particles, even existing electrostatic repulsion between them.

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References and Notes

(1) Gangopadhyay, R.; De, A. *Chem. Mater.* **2000**, *12*, 608–622.
(2) Gomez-Romero, P. *Adv. Mater.* **2001**, *13*, 163–174.
(3) Roux, S.; Soler-Illia, G. J. A. A. *Adv. Mater.* **2003**, *15*, 217–221.
(4) Percy, M. J.; Michailidou, V.; Armes, S. P. *Langmuir* **2003**, *19*, 2072–2079.
(5) Li, W.; McCarthy, P. A.; Liu, D.; Huang, J.; Yang, S.; Wang, H. *Macromolecules* **2002**, *35*, 9975–9982.
(6) Thiyagarajan, M.; Samuelson, L. A.; Kumar, J.; Cholli, A. L. *J. Am. Chem. Soc.* **2003**, *125*, 11502–11503.
(7) Huang, J.; Virji, S.; Weiller, B. H.; Kaner, R. B. *J. Am. Chem. Soc.* **2003**, *125*, 314–315.
(8) MacDiarmid, A. G. *Synth. Met.* **1997**, *84*, 27–34.
(9) MacDiarmid, A. G. *Angew. Chem., Int. Ed.* **2001**, *40*, 2581–2590.
(10) Long, Y.; Luo, J.; Xu, J.; Chen, Z.; Zhang, L.; Li, J.; Wan, M. *J. Phys.: Condens. Matter* **2004**, *16*, 1123–1130.
(11) Virji, S.; Kaner, R. B.; Weiller, B. H. *J. Phys. Chem. B* **2006**, *110*, 22266–22270.
(12) Kahol, P. K.; Ho, J. C.; Chen, Y. Y.; Wang, C. R.; Neeleshwar, S.; Tsai, C. B.; Wessling, B. *Synth. Met.* **2005**, *151*, 65–72.
(13) Tan, S.; Zhai, J.; Xue, B.; Wan, M.; Meng, Q.; Jiang, Y. L.; Zhu, D. *Langmuir* **2004**, *20*, 2934–2937.
(14) Levon, K.; Nasybulin, E.; Menshikova, I.; Sergeyev, V.; Zezin, A. *Polymer Science, Ser. A* **2009**, *51*, 701–707.
(15) Khan, M. A.; Armes, S. P. *Adv. Mater.* **2000**, *12*, 671–674.
(16) Kohut-Svelko, N.; Reynaud, S.; Dedryvere, R.; Martinez, H.; Gonbeau, D.; Francois, J. *Langmuir* **2005**, *21*, 1575–1583.
(17) Niu, Z. W.; Yang, Z. Z.; Hu, Z. B.; Lu, Y. F.; Han, C. C. *Adv. Funct. Mater.* **2003**, *12*, 949–954.
(18) Wang, L. Y.; Lin, Y. J.; Chiu, W. Y. *Synth. Met.* **2001**, *119*, 155–156.
(19) Ding, K. L.; Miao, Z. J.; Liu, Z. M.; An, G. M.; Xie, Y.; Tao, R. T.; Han, B. X. *J. Mater. Chem.* **2008**, *18*, 5406–5411.
(20) Wu, Q.; Wang, Z. Q.; Xue, G. *Adv. Funct. Mater.* **2007**, *17*, 1784–1789.
(21) Jang, J. *Adv. Polym. Sci.* **2006**, *199*, 189–259.
(22) Barthet, C.; Armes, S. P.; Lascelles, S. F.; Luk, S. Y.; Stanley, H. M. E. *Langmuir* **1998**, *14*, 2032–2041.
(23) Caruso, F. *Adv. Mater.* **2001**, *13*, 11–22.
(24) Shi, X. Y.; Han, S.; Sanedrin, R. J.; Zhou, F. M.; Selke, M. *Chem. Mater.* **2002**, *14*, 1897–1902.
(25) Shi, X. Y.; Briseno, A. L.; Sanedrin, R. J.; Zhou, F. M. *Macromolecules* **2003**, *36*, 4093–4098.
(26) Shi, X. Y.; Shen, M. W.; Möhwald, H. *Prog. Polym. Sci.* **2004**, *29*, 987–1019.
(27) Chen, S. A.; Lee, H. T. *Macromolecules* **1995**, *28*, 2858–2866.
(28) Park, M. K.; Onishi, K.; Locklin, J.; Caruso, F.; Advincula, R. C. *Langmuir* **2003**, *19*, 8550–8554.
(29) Lascelles, S. F.; Armes, S. P.; Zhdan, P. A.; Greaves, S. J.; Brown, A. M.; Watts, J. F.; Leadley, S. R.; Luk, S. Y. *J. Mater. Chem.* **1997**, *7*, 1349–1355.