Feature Article

Versatile Strategies for Fabricating Polymer Nanomaterials with Controlled Size and Morphology

Hyeonseok Yoon, Moonjung Choi, Kyung Jin Lee, and Jyongsik Jang*

School of Chemical and Biological Engineering, Seoul National University, Seoul 151-742, Korea

Abstract: The development of reliable synthetic routes to polymer nanomaterials with well-defined size and morphology is a critical research topic in contemporary materials science. The ability to generate nanometer-sized polymer materials can offer unprecedented, interesting insights into the physical and chemical properties of the corresponding materials. In addition, control over shape and geometry of polymer nanoparticles affords versatile polymer nanostructures, encompassing nanospheres, core-shell nanoparticles, hollow nanoparticles, nanorods/fibers, nanotubes, and nanoporous materials. This review summarizes a diverse range of synthetic methods (broadly, hard template synthesis, soft template synthesis, and template-free synthesis) for fabricating polymer nanomaterials. The basic concepts and significant issues with respect to the synthetic strategies and tools are briefly introduced, and the examples of some of the outstanding research are highlighted. Our aim is to present a comprehensive review of research activities that concentrate on fabrication of various kinds of polymer nanoparticles.

Keywords: nanoparticles, polymers, polymerization, self-assembly, templates.

Introduction

Rapid advances in nanotechnology have brought about a significant paradigm shift in fabricating materials from bulk features of micrometer scale to ultrafine features of nanometer scale. The precise size control of materials at the nanometer level allows the generation of superior chemical and physical properties that are quite different from those of their bulky counterparts.[1,2] Hence, numerous researches on a wide range of nanomaterials consisting of metals, semiconductors, polymers, biomaterials have been extensively carried out all over the world. In particular, there has been noteworthy progress in synthesizing metallic and inorganic semiconductor nanomaterials. A rich variety of chemical and physical techniques have been developed for the size- and shape-control of inorganic nanomaterials. As a typical example, changing the size of an inorganic crystal in the nanometer regime enables the tuning of the frequency it emits when pumped by outside energy.[3,4] Thus quantum dots of specific sizes and components will emit at predictable frequencies, which makes them useful in the application fields of optical devices, displays, sensors, and biomarkers. In the case of organic materials, it has been shown

---

*Corresponding Author. E-mail: jsjang@plaza.snu.ac.kr

that the thickness of thin polymer films considerably affects their physical properties, such as glass transition temperature, melting temperature, chain orientation, and crystallinity.[5-7] However, the advance in preparation of polymer nanomaterials has been relatively slow until now, and little attention has been paid to the study of the characteristics derived from the difference in size or shape of polymer nanomaterials, in contrast to metal and semiconductor nanocrystals.

Polymer nanomaterials with well-defined structures can provide a number of distinct advantages over other materials, including ease of synthesis and processing, structural diversity, tunable surface functionality, light weight, and flexibility. Many efforts have been devoted toward the generation of polymer nanomaterials with the desired characteristics, leading the development of synthetic routes to polymer nanospheres, core-shell nanoparticles, hollow nanoparticles, nanofibers, nanotubes, and nanoporous structures.[8] Of the various synthetic strategies, template synthesis is a very powerful tool to fabricate polymer nanomaterials. This approach is classified into "hard template synthesis" and "soft template synthesis" by kinds of templates used. While colloidal particles, inorganic fibers, porous membranes, and mesoporous silicas can be utilized as hard templates, soft templates include surfactants, block copolymers, polyelectrolytes, liquid crystals, and biomolecules. As a minority, template-free synthesis can also lead to a variety of polymer nanostructures. This approach is mainly based on the self-assembly of nanoscale building blocks. Even though such substantive progress has been made into the synthesis of polymer nanomaterials during the last decade, to the best of our knowledge, there is little useful information on the general overview of this significant and rapidly growing research field. Here, we outline the versatile strategies that have been investigated to fabricate polymer nanomaterials with tailored sizes and shapes. Various techniques toward polymer nanoparticles are highlighted through examples of recent relevant works, including a brief discussion of each methodology.

Polymer Nanostructures

Nanospheres. Spherical polymer nanoparticles have attracted considerable attention because of their unique properties different from those of the bulk materials (e.g, electrical, optical, thermal, mechanical and chemical characteristics).[9-12] To date, diverse synthetic ways to prepare polymer nanoparticles have been continuously developed. In particular, microemulsion polymerization has become one of the most extensively used methods. In terms of droplet size and stability, emulsion systems can

be classified into the following three categories: macroemulsion, miniemulsion, and microemulsion.[13-16] Microemulsion is defined as a thermodynamically stable and transparent dispersion of oil and water containing domains of nanometer dimensions (5–50 nm). In general, microemulsion at least consists of ternary mixtures of oil, water, and surfactant. Surfactant is an amphiphilic molecule consisting of a hydrophilic head-group and a hydrophobic tail-group. The hydrophilic head-group can be cationic, anionic, zwitterionic, or nonionic. In addition, the hydrophobic tail-group is commonly one or two long hydrocarbon chains ($> C_{10}$). Surfactant molecules can be spontaneously assembled into spherical, cylindrical, hexagonal, and bilayered structures. When their concentration is extremely low in an aqueous medium, the surfactant molecules exist at the air/water interface, leading to a monolayer. The hydrophilic head-group of the surfactant is inside the water while the hydrophobic tail-group is outside the water. When the surfactant concentration increases up to the critical micelle concentration (CMC), spherical micelles are formed by the association of hydrophobic tails. Importantly, the self-assembled micelles can serve as nanoreactors for various inorganic/organic reactions and polymerization. Typical examples involve the preparation of polymer nanoparticles with diameters of a few nanometers using low-temperature microemulsion polymerization.[17-20] The low-temperature polymerization is appropriate for reducing the inner space of a micelle due to the deactivated surfactant chain mobility. Therefore, polypyrrole (PPy) nanoparticles with an average diameter as small as 2 nm could be synthesized through chemical oxidation polymerization of the corresponding monomer inside the spherical micelles consisting of cationic surfactant molecules.[17] As the polymerization temperature increased, the nanoparticles grew as a result of the enhanced surfactant chain mobility. In addition, the diameter of the nanoparticles gradually decreased with reducing the hydrocarbon spacer length of the surfactant. The micelle aggregation number is defined as the number of surfactant molecules required to organize a micelle and generally it becomes smaller as the chain length of the surfactant decreases. The reduced micelle aggregation number gives rise to the formation of smaller nanoparticles. On the other hand, the longer surfactant chains provide more free volume inside the micelle, which lead to the increment of particle size. Hence, the formation of polymer nanoparticles in a microemulsion is influenced by synthetic parameters such as the concentration and type of surfactant, ionic strength and pH of solution, and polymerization temperature. Up to now, various kinds of polymer nanospheres have been prepared by microemulsion polymerization,
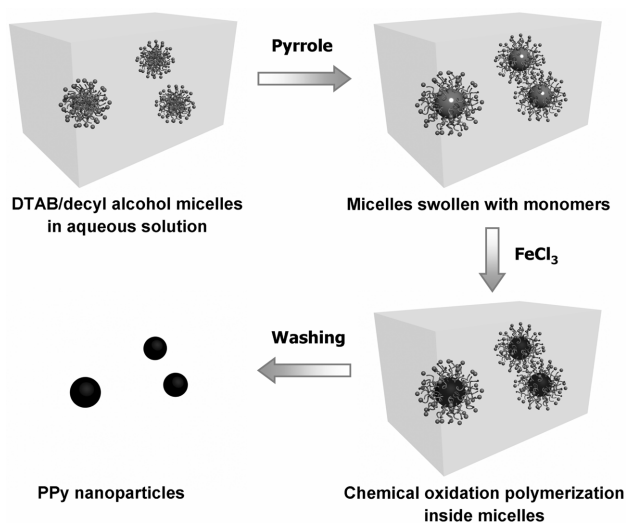
Figure 1. Schematic illustration of the fabrication of PPy nanoparticles in a DTAB/decyl alcohol microemulsion system.

Figure 2. TEM image of monodisperse PPy nanoparticles prepared by micelle templating (inset: photograph showing a Petri dish containing 12 g of PPy nanoparticles prepared in a single polymerization reaction). Reproduced with permission from Ref. 34; Copyright 2005, Wiley-VCH Verlag GmbH & Co. KGaA.

including polystyrene,[21-23] poly(methyl methacrylate) (PMMA),[24,25] poly(glycidyl methacrylate) (PGMA),[26] polyaniline (PANI),[27-31] poly(3,4-ethylenedioxythiophene) (PEDOT),[32,33] and polyacetylene.[33] Recently, the large-scale synthesis of monodisperse polymer nanoparticles has been explored using an effective micelle templating method.[34-36] Figure 1 presents the schematic illustration of the synthetic route to polymer nanoparticles. Dodecyltrimethylammonium bromide (DTAB) was used to form micelles as the nanoreactor, and decyl alcohol was selected as a co-surfactant for improving the stability of the micelles. Figure 2 displays a transmission electron microscopy (TEM) image of monodisperse PPy nanoparticles with an average diameter of ca. 60 nm and a photograph (inset) of a Petri dish containing 12 g of PPy nanoparticles, a very large quantity in a laboratory-scale synthesis. It was considered that the coordination interaction between surfactant and co-surfactant played a crucial role in synthesizing PPy nanoparticles with uniform size. Conventional emulsion polymerization commonly generates polydisperse polymer nanoparticles due to a destabilization mechanism, such as the diffusional degradation of monomers in micelle droplets. The diffusional degradation of monomers is caused by their migration from small droplets to large ones in order to reduce the chemical potential gradient (the Ostwald ripening effect).[37] It is known that this destabilization mechanism can be regulated by the addition of a suitable co-surfactant. The co-surfactant (mostly, an alcohol or alkane) has a strong influence on the stability of micelles and the phase behavior of emulsions. For instance, water-insoluble long-chain alcohols can retard or even prevent the diffusion of monomers through the aqueous phase in the oil/
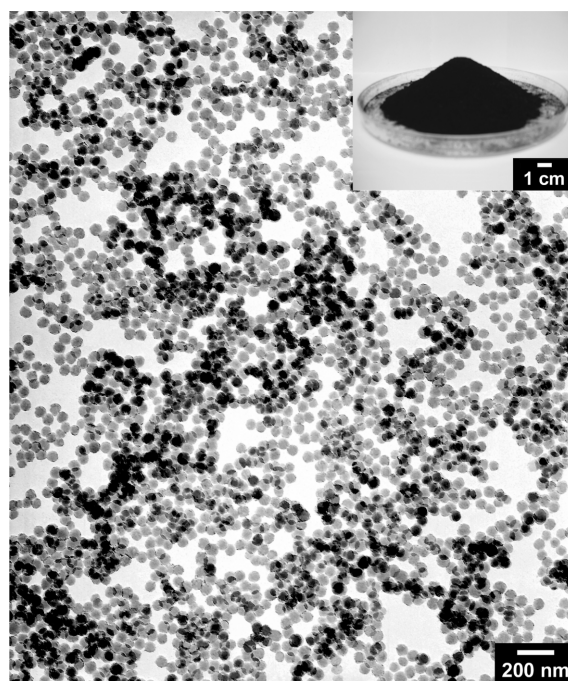
water micelle system due to the osmotic pressure effect.[37]

Dispersion polymerization is a powerful method which affords monodisperse micrometer-sized particles on a batch production scale. The dispersion polymerization can be defined as a type of precipitation polymerization in which one carries out the polymerization of a monomer in the presence of a suitable steric stabilizer.[38] The reaction medium is a solvent for the monomer and stabilizer, while it is a nonsolvent for the resulting polymer. Under precise controlled conditions, dispersion polymerization often yields nanometer-sized polymer particles. Mandal *et al.* have been obtained PPy particles with diameters of 55–250 nm by dispersion polymerization in aqueous media.[39,40] They used ethylhydroxyethylcellulose as a steric stabilizer, and ferric chloride (FeCl$_3$) or ammonium persulfate (APS) was employed as an oxidizing agent. As the polymerization proceeds, PPy segments begin to separate out from the aqueous medium and finally form spherical particles due to their hydrophobicity. The interparticle aggregation is prevented by the adsorption of the polymeric stabilizer on the surface of the nanoparticles. The particle size decreased with increasing molecular weight of the stabilizer at the same stabilizer concentration, and the amount of the stabilizer required decreased with increasing alcohol content of the

medium. Colloidal PANI nanoparticles with diameters of 2–3 nm could be prepared with the aid of poly(sodium 4-styrenesulfonate) (PSS), as an anionic polyelectrolyte, in aqueous phase.[41,42] The nanocolloids were fabricated via the oxidative polymerization of aniline in dilute and semi-dilute solutions of PSS with molecular weight of 6,800 g mol^{-1} or higher. The PSS provided a suitable local environment for the formation of PANI nanoparticles through electrostatic and hydrophobic interactions.

Several research groups have taken advantages of the self-assembly and phase separation of block copolymers in a medium to synthesize polymer nanoparticles.[43-47] Block copolymer amphiphiles self-assemble to organize block copolymer micelles or vesicles, which may then be chemically transformed into crosslinked spherical nano-structures. Generally, this strategy allows the size control of nanoparticles with tuning the block length and ratio of the copolymers. In synthesis of block copolymers, atom-transfer radical polymerization (ATRP) has been widely used, which is a reliable controlled/living radical poly-merization.[48-54] ATRP affords precise control of molecu-lar weight, structures, and functionalities. Rannard and co-workers synthesized amphiphilic block copolymers using ATRP in aqueous phase and then could obtain well-defined block copolymer nanoparticles via a con-trolled branching process.[43] It is noteworthy that the branching strategy can be expanded to the fabrication of more complex nanoscale architectures. Kowalewski and co-workers explored the micellization of block copolymers consisting of polyacrylonitrile (PAN) and poly(acrylic acid) (PAA), followed by the formation of shell-crosslinked nanoparticles.[44] In a mixture of *N,N*-dimethylformamide (DMF) and water, the PAN block constitutes the micellar core while the PAA block forms a water-soluble shell. The carboxylic acid groups of the shell layer were crosslinked with a diamine, resulting in covalently stabi-lized shell-crosslinked PAN nanoparticles.

Another interesting approach to polymer nanoparticles involves aqueous/ionic liquid interfacial polymeriza-tion.[55] PANI nanoparticles with diameters of 30–80 nm were prepared using chemical polymerization at the aqueous/ionic liquid interface where the monomer came into contact with the initiator. Electrochemical routes to fabricate polymer nanoparticles have been also reported in literatures.[56,57] The PANI nanoparticles with a diameter of ca. 80 nm were electropolymerized with erbium(III) chloride under magnetic field.[56] It was reported that there was an electrostatic interaction between erbium(III) and PANI chains and the magnetic field applied had an orien-tation effect on PANI chains. A pulsed potentionstatic method was used to deposit PANI nanoparticles on a highly oriented pyrolytic graphite surface from dilute

PANI acidic solution. The surface concentration and size of PANI nanoparticles were tunable by changing the charge of electropolymerization.[57]

Core-Shell Nanoparticles. Over the last decade, there have been considerable efforts to fabricate core-shell nanoparticles with electrical, optical, magnetic, and cata-lytic functionalities.[58,59] Owing to their exclusive charac-teristics over single-component nanoparticles, extensive investigations have been made into the state-of-the-art applications of core-shell nanoparticles.[60-62] Compared with nanocomposites or copolymer nanoparticles, core-shell nanoparticles have also beneficial properties originating from the well-defined compartments of two distinct polymer phases. For instance, most organic/inorganic nanoparticles without surface protection undergo irre-versible aggregation in media, and the nanoparticles capped with small molecules are also readily degraded by hydrolysis or oxidation of the capping ligands.[63] Therefore, coating of nanoparticles with polymer shells can prevent the interparticle aggregation and further pro-tect the core nanoparticles from oxygen or other chemicals. In addition, the polymer shell enhances the compatibility of inorganic nanoparticles in polymer hosts and provides a platform for chemical/biological functionalization.[64]

In general, inorganic-organic or organic-organic core-shell nanoparticles have been prepared by two-stage emulsion polymerization,[65-69] surfactant-free seeded polymeriza-tion,[70-75] surface-initiated controlled polymerization,[76-81] encapsulation using reactive surfactants,[82-85] and layer-by-layer (LBL) deposition.[86-90] First, two-stage emulsion polymerization has been one of the most common meth-ods for fabricating core-shell nanoparticles. The core nanoparticles are formed inside micelles at first stage and the consecutive polymerization of second-stage mono-mer proceeds around the core nanoparticles. During this process, the formation of core-shell nanoparticles is pri-marily governed by thermodynamic and kinetic factors. In terms of thermodynamic stability, the most important consideration is the interfacial energy between the core and the shell. Suitable surfactants or initiation systems can be employed to control the interfacial energy.[61,62] Kinetic control over phase-separation process via diffu-sion of the polymer chains during particle growth is also necessarily considered. There are a few key factors to control the kinetics of shell formation, such as the con-centration of monomer, molecular weight of the resulting polymer, crosslinking density, and reaction temperature. Several important studies have been reported in litera-tures.[65,66] For example, PPy-PMMA core-shell nanoparti-cles were prepared by microemulsion polymerization using cationic surfactants.[65] The pyrrole monomer was injected into the micellar solution and polymerized with

the initiator, ferric chloride. Consequently, the methyl methacrylate (MMA) monomer and water-soluble radical initiator were introduced into the solution to encapsulate PPy cores with PMMA shells. The PPy-PMMA core-shell nanoparticles were used as a filler in a PMMA matrix for highly transparent conductive thin films. Interestingly, the PMMA shell promoted compatibility of the conductive PPy fillers with the PMMA matrix and improved conductive performance than that of uncoated PPy nanoparticles.

Surfactant-free seeded polymerization is a typical method to fabricate polymeric composite microspheres in industry. Recently, this polymerization method has been often used to prepare functional core-shell particles on a nanometer scale.[70-75] Inorganic cores such as colloid silicas[70,71] and quantum dots[72-74] were encapsulated with polymer shells via *in-situ* surface polymerization by phase separation and electrostatic interaction. As a notable case, monodisperse silica-PANI core-shell nanoparticles were prepared through chemical polymerization of aniline monomer adsorbed on the silica core.[70] Aniline monomers are converted to anilinium cations in acidic conditions with a pH of 3 and adsorbed onto the negatively charged surface of silica nanoparticles. Since aniline has a pK_a of 4.63, it is expected to be positively charged at pHs below this value. The silica nanoparticles possess negative surface charges at pHs above the isoelectric point (pH 2). The aniline monomer electrostatically adsorbed onto the silica surface was then polymerized by APS at room temperature. This simple process allowed the formation of uniform PANI shells as thin as a few nanometers on the silica cores. In the case of polymer-polymer core-shell nanoparticles, the graft copolymerization can be occurred at the core-shell interface, leading the formation of a stable and compact shell. Jang *et al*. reported the graft copolymerization of poly(*N*-vinylcarbazole) (PVK) on the surface of PPy nanoseeds using ceric ammonium nitrate (CAN).[75] By virtue of strong oxidizing power of CAN, the PPy nanoseeds composed of α,α'-linked or α,β-linked pyrrole rings provided the initiation sites for the growth of PVK branches.

As mentioned previously, ATRP is one of the well-known methodology for surface-initiated controlled polymerization on solids.[48,49] This polymerization technique has been extended to the fabrication of core-shell nanoparticles because it can offer polymer shells with low polydispersity and is relatively easy to control. For the synthesis of core-shell nanoparticles, the initiators for ATRP are chemically attached onto the surface of nanoparticles and then the initiator-modified nanoparticles are used as macroinitiators in the subsequent polymerization reaction. Inorganic cores such as silica,[76] gold,[77,78] and iron oxide[79-81]

nanoparticles have been employed, because their preparation and surface chemistry are well-developed. In most cases, the surface of inorganic cores was tailored to link the initiators by ligand exchange or silane coupling reactions. An interesting example is the synthesis of γ-Fe$_2$O$_3$-polystyrene core-shell nanoparticles using solvent-free ATRP.[74] Oleic acid-stabilized γ-Fe$_2$O$_3$ nanoparticles were ligand exchanged with an ATRP initiator (2-bromo-2-methylpropionic acid), and then the modified γ-Fe$_2$O$_3$ nanoparticles (as the macroinitiator) could dissolved in styrene monomer. Accordingly, the formation of polystyrene shells was achieved without the addition of solvent, yielding well-formed γ-Fe$_2$O$_3$-polystyrene core-shell nanoparticles. This solvent-free ATRP technique offers the precise control on the monomer/macroinitiator ratios because the free initiators in solution can be kept to minimum without the use of solvents.

Core-shell nanoparticles can be also prepared by encapsulation methods using reactive surfactants such as crosslinkable block copolymers[82-84] and end-functionalized polymers.[85] In general, amphiphilic block copolymers self-assemble into stable micelles or adsorbed monolayers in proper solutions. Hence, di- or triblock copolymers have been widely utilized to enhance the colloidal stability of various nanoparticles by forming ionic or steric barriers around the nanoparticles. Similarly, under specific conditions, amphiphilic block copolymers can spontaneously form a protective layer for the nanoparticle surface. The soluble block extends into the solution and constitutes an external layer while the insoluble block adsorbs onto the particle surface. The assembled layer is crosslinked to attain a better stability and its thickness is determined by the composition and length of component blocks. Taton *et al*. explained the self-assembly behavior of block copolymers on nanoscopic surfaces by Marques-Joanny-Leibler model.[82] The structure of the core-shell nanoparticles was dependent on a correlation between the nanoparticle size (ρ) and the radius of gyration of block copolymer (R_g). In the case of large nanoparticles ($\rho/R_g > 1$), a single nanoparticle served as a core for adsorption of block copolymers, and the thickness of a block copolymer shell increased in proportion to the copolymer concentration. On the other hand, in the case of smaller nanoparticles ($\rho/R_g \approx 1$), the nanoparticles acted like solutes that were dissolved inside block copolymer micelles. As the copolymer concentration decreased, the number of particles within micelles increased, rather than decreasing copolymer shell thickness. For poly(styrene-*b*-acrylic acid) (PS-*b*-PAA) copolymers ($R_g \approx 3$ nm), gold nanoparticles with diameters of more than 10 nm had a well-defined core-shell structure containing a single nanoparticle core, whereas smaller gold nanoparticles

with a diameter of 4 nm exhibited a core-shell structure containing multiple nanoparticles.

Of the surface engineering methods, LBL deposition technique utilizes electrostatic self-assembly between positive and negative polyelectrolytes.[59,86-88] A typical polyelectrolyte pair is cationic poly(allylamine hydro-chloride) (PAH) and anionic PSS. Shi and co-workers reported the coating of PAH/PSS multilayers on mesoporous hollow silica nanoparticles for stimuli-responsive controlled release.[86] In this case, the silica surface was negatively charged above the isoelectric point (pH 2), which favored a first-layer coating of the positively charged polycation PAH, followed by the negatively charged PSS. The introduction of polyelectrolyte shells increased drug storage capacity of the mesoporous hollow nanoparticles as well as enhanced their mechanical strength. The controlled drug release was also achieved by changing the pH value or the salt concentration of the release medium. Decher *et al.* carried out the spectroscopic analysis of the plasmon absorption band of colloidal gold nanoparticles to monitor the adsorption of a polyelectrolyte layer on the nanoparticle surface.[87] At least twenty PSS/PAH layers could be consecutively deposited without interparticle aggregation. Caruso and co-workers also has reported the polyelectrolyte coating of gold nanoparticles via LBL electrostatic self-assembly.[88,89]

Jang *et al.* have developed a vapor deposition polymerization (VDP) technique as a powerful tool to create a uniform polymer layer on the nanoparticle surface.[90] Typically, silica nanospheres with different diameters (25 and 200 nm) and irregularly shaped titania nanoparticles were coated with vinyl polymers such as PMMA and polydivinylbenzene (PDVB). The overall synthetic procedure is illustrated in Figure 3. First, the inorganic cores were pretreated with a silane coupling agent to improve their chemical affinity to organic monomers. The surface-modified inorganic nanoparticles were placed inside the reaction chamber with a solid initiator, and the inter-
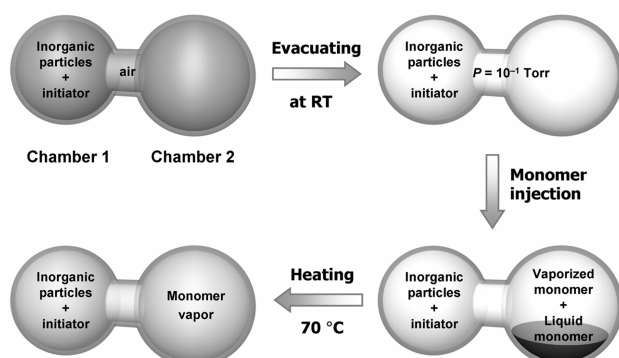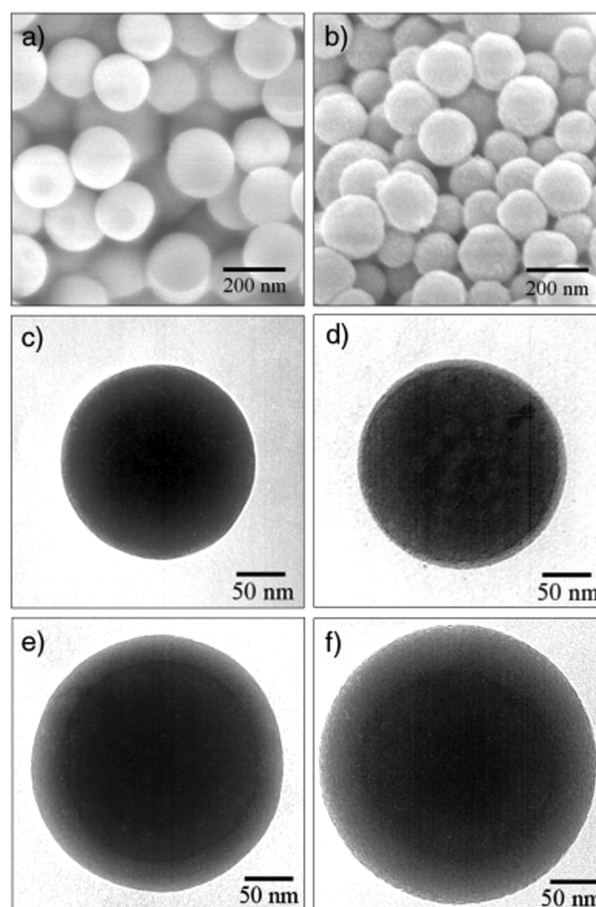

Figure 4. SEM images of a) 200 nm silica particles as synthesized and b) silica particles coated with PMMA. TEM images of c) 200 nm silica particle and d-f) silica-PMMA core-shell nanoparticles with the various shell thickness (MMA/silica weight ratio of 0.25 in d), 0.75 in e), and 1.5 in f)). Reproduced with permission from Ref. 90; Copyright 2003, Wiley-VCH Verlag GmbH & Co. KGaA.

nal pressure was then reduced to 10^{-1} torr. Liquid monomer was injected into the reaction chamber and concurrently vaporized. Polymerization of monomer vapors was proceeded by thermal decomposition of the initiator at 70 °C. The inorganic nanoparticles were magnetically stirred to prevent the interparticle aggregation. Figure 4 shows the typical scanning electron microscopy (SEM) and TEM images of PMMA-coated silica nanoparticles obtained with different weight ratios of MMA to silica. Notably, the PMMA-coated silica nanoparticles had a uniform and thin PMMA layer whose thickness depended on the feeding amount of MMA. Compared with their bulk counterparts, nanoparticles provide considerably enlarged surfaces on which the most of monomers can adsorb from the vapor phase. Therefore, the growth of polymer layers can proceed exclusively in the monomer layers adsorbed on the surface of the nanoparticles, leading the formation of

Figure 3. Schematic representation of the VDP for the encapsulation of the inorganic nanoparticles.

highly uniform polymer shells. The degree of polymerization was primarily dependent on the synthetic variables, including the kind and amount of initiator, reaction time, and reaction temperature. Moreover, the shell thickness could be controlled by changing the monomer/nanoparticle weight ratio. As a result, it is expected that the VDP approach will open a new and general route for the fabrication of various types of core-shell nanostructures.

Hollow Nanoparticles. The growing demand for hollow polymer nanoparticles has expedited the development of various synthetic strategies such as micro-/miniemulsion polymerization, colloidal templating, LBL self-assembly, phase separation of block copolymers, crosslinking of micellar structures, vesicle polymerization.[91] Hollow nanospheres can be utilized for a variety of applications such as controlled release, catalysis, coating, composites, and fillers.

One of the facile methods for fabricating hollow polymer nanoparticles is the encapsulation of a nonsolvent (often called "hydrophobe") on the basis of phase separation during polymerization, because of the differences of interfacial tension.[92-94] In general, a hydrophobic nonsolvent and a monomer constitute an emulsion phase at the initial stage. As the polymerization proceeds, however, the separation of the polymer phase from the nonsolvent phase occurs to generate a hollow polymer structure surrounding the nonsolvent phase. The theoretical prediction of the equilibrium morphology, which was thermodynamically favorable, was investigated by Torza and Mason.[95] They proposed the equilibrium morphology of two immiscible liquid droplets (phase 1 and 3) suspended in a mutually immiscible liquid (phase 2). The resulting morphology is rationalized by the analysis of the interfacial tensions between the phases (γ_{12}, γ_{23}, and γ_{13}) and spreading coefficients for each phase as $S_1 = \gamma_{23} - (\gamma_{12} + \gamma_{13})$. In the cases of $S_1 < 0$ ($\gamma_{12} > \gamma_{23}$), phase 1 is completely encapsulated by phase 3 when $S_2 < 0$ and $S_3 > 0$. On the other hand, partial encapsulation occurs when $S_2, S_3 < 0$ and no encapsulation occurs when $S_2 > 0$ and $S_3 < 0$. The interfacial energies can be also influenced by the type and amount of surfactant and initiator or the use of other additives. One noticeable case involves the fabrication of hollow polystyrene nanocapsules with diameters of less than 20 nm in microemulsions of cationic surfactant/isooctane/water.[96] Isooctane and potassium persulfate were used as a nonsolvent and a water-soluble initiator, respectively. In this system, the water-soluble initiator generated radicals in the aqueous phase, which were adsorbed and anchored to the micelles formed. Owing to the low interfacial energy, the polymerization of styrene monomer occurred primarily at the interface between isooctane and water. The size of the polymer nanocapsules was tunable by using different surfactants.

The core-shell nanostructures have also been used as precursors to prepare hollow nanostructures by the removal of core materials via chemical etching or combustion. The core materials have to fulfill the following requirements: i) they have to be stable during the formation process of polymer shells; ii) the core-removal condition does not affect the structure and stability of polymer shells formed; iii) the etched core components have to readily leave the empty polymer shells. Silica,[97] AgCl,[98] cyclodextrin,[99] PMMA,[100] and soluble PPy[101,102] have been employed as sacrificial core materials. First of all, crosslinked polystyrene hollow nanospheres were obtained using silica nanoparticles as the sacrificial core.[97] The ATRP initiators were immobilized onto the surface of silica nanoparticles with a diameter of ca. 25 nm, and then silica nanoparticles with surface-grafted poly(styrene-*b*-MMA) (PS-*b*-PMMA) were prepared via surface-initiated ATRP of styrene and subsequent ATRP of MMA. PMMA was decomposed via chain scission, whereas PS underwent crosslinking under ultraviolet (UV) irradiation. The silica core was removed by acid etching, and the crosslinked polystyrene hollow nanospheres remained unagglomerated and stable in organic solvents. The shell thickness can be tuned by controlling the PMMA and PS chain lengths during the ATRP process. Another example is the fabrication of PAN nanocapsules using cyclodextrin-mediated microemulsion polymerization.[99] Cyclodextrins are cyclic oligosaccharides with 6–8 glucopyranose units arranged in a way that the exterior surface of a cyclodextrin is covered by hydrophilic groups while the cavity of a cyclodextrin is hydrophobic. Cyclodextrins have been considered as potential pore template materials due to their chemical functionality, high water solubility, low toxicity, and different cavity sizes. The mixture of acrylonitrile and cyclodextrin was added into the micellar solution, and cerium sulfate and nitrilotriacetic acid were used as redox initiators. During the polymerization process, cyclodextrin molecules prefer locating in the core part of the micelles facing the PAN phase, finally giving rise to cyclodextrin-PAN core-shell nanoparticles. Cyclodextrin and residual reagents were readily removed after washing with excess methanol, and the size of hollow interiors was tailored by the feeding amount of cyclodextrin. Recently, an elegant approach to remove the core under mild conditions has recently been demonstrated.[101,102] The soluble PPy core and the crosslinked PPy shell were created by cupric chloride and ferric chloride oxidizing agents, respectively, during two-stage microemulsion polymerization (Figure 5). The cupric chloride with a
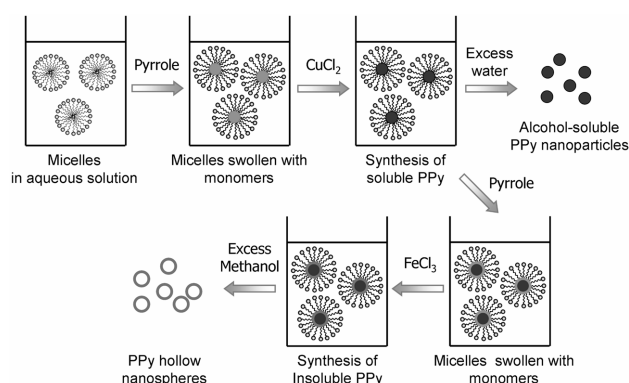
Figure 5. Schematic representation of the fabrication of PPy nanocapsules.

low oxidation potential of +0.16 V rendered linear PPy chains, which was soluble in alcohol, whereas the ferric chloride with a higher oxidation potential of +0.77 V yielded a crosslinked PPy shell. The core part consisting of linear PPy chains could be readily etched out by dissolving in methanol. Figure 6 shows the representative TEM images of soluble PPy nanoparticles and as-formed PPy nanocapsules. PMMA-polystyrene core-shell nanospheres were also synthesized as a precursor for polystyrene hollow nanoparticles by microemulsion polymerization using nonionic poly(alkylene oxide) block copolymer surfactants.[100] The polystyrene shell was crosslinked with divinylbenzene (DVB). Consequently, the PMMA core was dissolved with methylene chloride, resulting in polystyrene hollow nanospheres. The size of the hollow nanospheres was controlled by varying the concentration and type of surfactants and molar ratio of surfactant-to-monomer. The diameters of the hollow nanospheres were ca. 15–30 nm and the shell thickness was ca. 2–5 nm.

Owing to their controllable permeability and surface functionality, polymer capsules with polyelectrolyte shells have attained much interest as new types of carriers and microreactors. LBL self-assembly approach is a typical
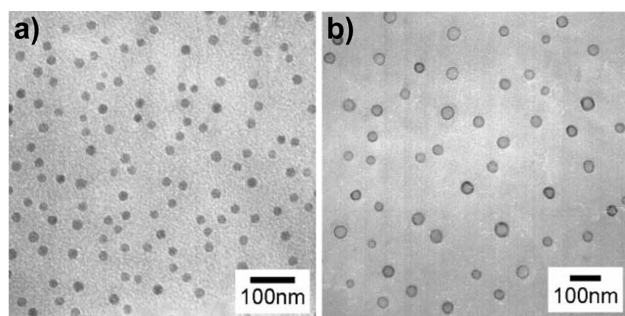

Figure 6. Typical TEM images of a) soluble PPy nanoparticles and b) PPy nanocapsules. Reproduced with permission from Ref. 102; Copyright 2004, Royal Society of Chemistry.

methodology that has been used to generate hollow polyelectrolyte shells.[59,103,104] It has been shown that LBL self-assembly is highly available on flat substrates or on the surface of micron-sized particles. However, there are only a few examples of using LBL techniques for the fabrication of nanometer-sized hollow nanospheres.[87,105] From both theoretical and experimental points of view, significant studies on adsorption of polyelectrolytes on colloidal particles have been reported in literatures.[106,107] Stoll and Chodanowski suggested that the adsorption of polyelectrolytes was favored by increasing particle size and decreasing ionic concentration. Namely, it was considered that the adsorption of polyelectrolytes onto the surface of nanoparticles was limited by the small dimensions and high surface curvature of the nanoparticles. To achieve the successful LBL self-assembly on a nanometer scale, there is a necessity for a better understanding of various parameters such as i) concentration, molecular weight, geometry, and charge density of polyelectrolytes, ii) size, concentration, and surface properties of core particles, iii) ionic strength, pH, and temperature.

Block copolymers can self-assemble to micelles or vesicles with dimensions of 10−100 nm. Hence, they can be also utilized for the controlled formation of hollow nanostructures.[108-110] The general fabrication procedure is as follows: i) synthesis of block copolymer composed of a crosslinkable block and a degradable block; ii) micellization; iii) crosslinking of the shell block; iv) removal of the core block by chemical degradation. Wooley's group has studied the fabrication of hollow nanospheres by ozonolysis of shell-crosslinked micelles consisting of a series of block copolymers. Poly(isoprene-*b*-acrylic acid) (PI-*b*-PAA) diblock copolymers formed micelles with a PI core and a PAA shell in an aqueous solution.[108] The PAA shell was crosslinked with a diamino crosslinker, 2,2′-(ethylenedioxy)bis(ethylamine), and the PI core could be removed by ozonolytic degradation. Similarly, poly(ε-caprolactone-*b*-acrylic acid) (PCL-*b*-PAA) diblock copolymers formed micelles with a PCL core and a PAA shell in an aqueous solution. In this case, the selective hydrolysis of the PCL cores in acidic or basic conditions yielded hollow nanospheres.[109] The diameter of the hollow nanospheres depended strongly on the degree of polymerization of block copolymers and the nature of crosslinking agents.

There are several examples of using the self-assembled micelles organized by interpolymer complexation instead of phase separation of block copolymers.[111-113] The core chains and the shell chains are connected through noncovalent interactions such as hydrogen bonding. To produce hollow nanostructures, this approach affords simple dissolution rather than chemical degradation. Nonco-

valently connected micelles with the hydroxyl-containing polystyrene (PS-OH) core and the poly(4-vinylpyridine) (P4VP) shell could be formed in a selective solvent mixture by hydrogen-bonding complexation.[111] The P4VP was crosslinked with 1,4-dibromobutane under mild conditions, and the PS-OH core was readily dissolved in DMF. Carboxyl-terminated polybutadiene (CPB) and poly(vinyl alcohol) (PVA) also formed spherical micelles driven by hydrogen bonding in aqueous solution. The PVA shell was crosslinked with glutaraldehyde and then the CPB core was removed in tetrahydrofuran (THF)-rich solution.[112]

Vesicle polymerization techniques can be divided into two approaches: i) the direct polymerization of polymerizable units forming a vesicle and ii) the polymerization of monomer within a vesicle.[114-116] A poly(2-methyloxazoline-b-dimethylsiloxane-b-2-methyloxazoline) triblock copolymer formed vesicles in dilute aqueous solution.[114] The UV-induced radical polymerization of the methacrylate end-groups of the triblock copolymer in the vesicular aggregates yielded hollow nanostructures. Chitosan and acrylic acid also formed spherical micelles in aqueous solution due to the ionic bonding between the $-NH_3^+$ groups of chitosan molecules and the negatively charged CH_3COO^- counterions.[115] The outer part of the micelles is mainly composed of positively charged protonated chitosan chains, whereas the inner part is comprised of polyion complexes of chitosan and acrylic acid. The radical polymerization of acrylic acid was performed using potassium persulfate and the crosslinking of chitosan was consecutively carried out with glutaraldehyde. The size of the micelles shrank during the polymerization process and then further decreased after crosslinking. Interestingly, the crosslinking reaction made the chitosan layer denser, yielding hollow nanostructures.

Nanorods & Nanofibers. There has been great interest in the synthesis of polymer nanofibers due to their intriguing properties derived from small dimensions, high aspect ratio, enlarged surface area, and flexibility. Polymer nanofibers have a wide variety of applications such as microelectronic devices, sensors, controlled drug release, bioscaffolding, wound dressing, and filtrations.[117-121] One of the foremost methods for the preparation of polymer nanofibers is electrospinning technique. Electrospinning, also known as electrostatic spinning, is a simple and effective method capable of producing continuous fibers with diameters ranging from the nano- to microscale.[122-124] The electrospinning process uses a high voltage electric field to produce electrically charged jets from polymer solution or melts. An electrical potential on the order of kilovolts is applied to give rise to strong electrostatic field between a capillary, containing a poly-

mer solution or melt, and a grounded collection target. Beyond a critical field strength, the electrostatic forces can overcome the surface tension of the polymer solution or melt at the capillary tip and thus cause the ejection of a thin jet. The charged jet undergoes a stretching and whipping process with solvent evaporation or cooling, yielding continuous fibers. Successful electrospinning requires the judicious choice of polymer/solvent systems to prepare solutions exhibiting the desired viscoelastic behavior. Various electrospinning techniques have been applied to the fabrication of nanofibers consisting of natural and synthetic polymers, polymer blends, and polymer composites.[125-131] Several approaches have been considered for the alignment of electrospun nanofibers,[132,133] and the complex architectures including core-shell,[134] porous,[135] and hollow[136] nanostructures can be also fabricated through modified electrospinning techniques. The diameter of electrospun fibers is susceptible to the concentration of polymer in solution. In general, the diameter of fibers can be reduced by using low concentration polymer solutions. Although this condition sometimes gives rise to the formation of beads rather than fibers, such an undesirable tendency can be suppressed by increasing the electrical conductivity of the solution. Polyamide nanofibers of approximately 50 nm in diameter were produced by electrospinning of low concentration solutions of polyamide/formic acid in the presence of pyridine. In an analogous way, poly(L-lactide) (PLA) nanofibers of approximately 10 nm in diameter were obtained by electrospinning of PLA/dichloromethane in the presence of palladium(II) diacetate.[137] In the case of PANI/poly(ethylene oxide) blends, nanofibers with diameters as small as 20 nm were readily prepared under the optimized condition.[138] It is known that appropriate electrical conductivities range from nano- to microsiemens per centimeter and viscosities range from tens to hundreds of millipascals per second.[122]

The so-called hard template synthesis has been also used for the preparation of polymer nanofibers. This approach includes the infiltration of nanochannels of a solid-state template with an appropriate precursor, followed by the conversion of this precursor to the desired materials.[139-141] A variety of materials with cylindrical pores have been used as hard templates, including porous alumina membrane, track-etched polycarbonate membranes, and mesoporous silicas. The templates are removed by mainly acid or base etching process to retrieve the resulting polymer product. The use of hard templates is of advantage in tailoring the diameter and length of desirable nanomaterials because their dimensions are precisely defined by the template used. In addition, multifunctional nanostructures such as core-shell and segmented

nanofibers can be obtained through controlled deposition techniques.[142,143] Various kinds of polymer nanofibers have been fabricated via chemical or electrochemical polymerization of monomers[144] and wetting of polymer solutions or melts.[145,146] Polydicarbazole nanorods with carboxyl functional groups were chemically polymerized within the cylindrical pores of alumina membranes by a liquid phase polymerization technique,[144] and liquid crystalline epoxy/PANI composite nanorods were prepared inside an alumina membrane by a temperature-gradient curing process.[145] Nanofibers consisting of vinyl polymers such as PMMA and PGMA were obtained through a VDP-mediated template method.[147,148] To prepare the nanofibers, the alumina membrane was wetted by the radical initiator solution and the monomer vapor was then injected for the VDP. The radical polymerization proceeded smoothly inside the pores of the membrane under an inert atmosphere, leading to the formation of well-defined nanofibers. In other cases, PPy-PMMA coaxial nanocables were fabricated via sequential polymerization of pyrrole and MMA inside the channel of mesoporous silica, followed by acid-etching of the silica template.[149] The templating process of ordered mesoporous materials was also successfully used to produce polythiophene nanowire bundles whose individual nanowires had a diameter of as small as 3 nm.[150]

In contrast to hard template synthesis, soft template synthesis employs self-assembled structures composed of soft materials such as surfactants, block copolymers, liquid crystalline polymers, and biomolecules.[151-158] First, above the second critical micelle concentration (CMC II), surfactant molecules spontaneously organize into cylindrical micelles. These micelle structures can serve as templates for the formation of desirable one-dimensional (1D) nanostructures when coupled with appropriate polymerization reactions. A notable example of surfactant templating is the formation of PAN nanofibers by a salt-assisted microemulsion polymerization.[151,152] Spherical micelles consisting of a cationic surfactant were formed in aqueous solution and the acrylonitrile monomer was then added into the micellar solution. The polymerization of monomers was promoted by using redox initiators (ceric sulfate and nitrilotriacetic acid) inside the spherical micelles and subsequently an iron salt (ferric chloride) was introduced into the micellar system. Importantly, spherical micelles containing preformed PAN nanoparticles transformed into cylindrical micelles after the addition of ferric chloride. Namely, it is considered that the iron salt acts as a structure-directing agent in generating the nanofibers. PEDOT nanorods and poly (furfuryl alcohol) nanowires could be also prepared with the aid of surfactant templates.[153,154] In a similar way,

block copolymers and liquid crystalline polymers have been employed as soft templates to generate 1D polymer nanostructures. Under appropriate conditions, self-organization of block copolymers and liquid crystalline polymers may result in hierarchical structures with cylindrical pores, similar to that of self-assembled surfactants. Russell and co-workers prepared the templates for nanowire arrays by using the phase separation of PS-*b*-PMMA under an applied electric field,[155] and Stupp *et al*. achieved the formation of molecularly oriented PEDOT chains on a substrate by using a hexagonal, lyotropic liquid crystalline template.[156] Shinkai and co-workers employed anionic synthetic lipid assemblies to prepare 1D helical PEDOT and PPy superstructures,[157] and Kiriy *et al*. reported the use of single molecules of negatively charged polyelectrolyte to grow continuous PPy nanowires.[158]

Recent studies have verified that seeding approach is an effective method to produce single polymer or polymer composite nanofibers.[159-161] Typically, a facile route to silver nanoparticles-embedded polymer nanofibers was explored on the basis of 1D assembly of silver nanoparticles.[161] The overall synthetic procedure is illustrated in Figure 7. PVA has a lone pair of electrons on the hydroxyl group, which can coordinate with metal ions. Accordingly, the introduction of PVA into aqueous silver nitrate solution results in silver cation-PVA complexes. Vigorous stirring condition gives rise to a high shear flow and PVA became fully oriented with silver ions in the flow direction. To initiate the polymerization of MMA and simultaneously reduce silver cations, 2,2'-azobis (isobutyronitrile) (AIBN) was added into the silver ion-PVA solution. The radicals arising from the decomposition of AIBN reduced silver ions to generate linear silver nanoparticles-PVA assemblies, due to the dipole-dipole interaction between the silver nanoparticles. At this
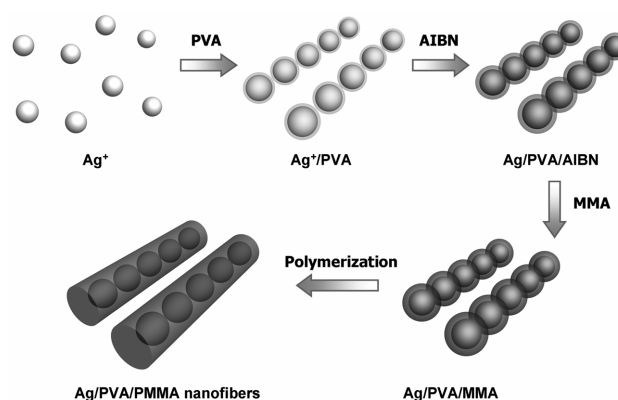

Figure 7. Schematic illustration of the preparation of silver nanoparticles-embedded polymer nanofibers. Reproduced with permission from Ref. 161; Copyright 2006, Royal Society of Chemistry.
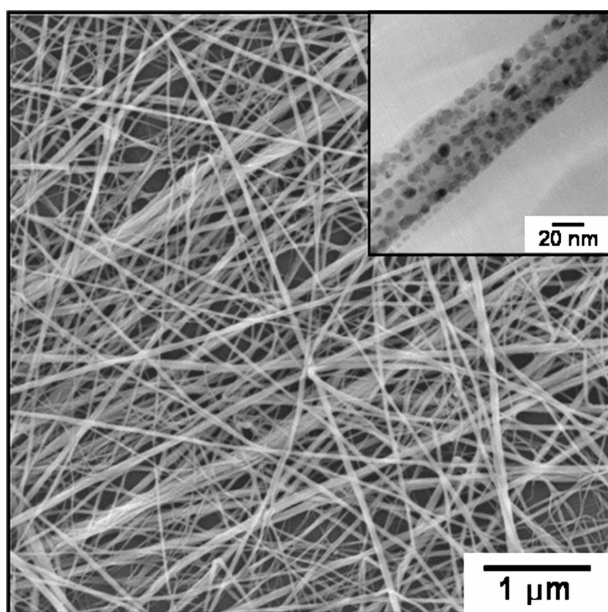
Figure 8. Typical SEM and TEM (inset) images of silver nanoparticles-embedded polymer nanofibers. Reproduced with permission from Ref. 161; Copyright 2006, Royal Society of Chemistry.

stage, it was considered that PVA acted as a gelator as well as a stabilizing agent to prohibit silver clusters sintering. When MMA was injected, the remaining radicals initiated the polymerization of MMA. Figure 8 shows the SEM and TEM (inset) images of as-formed nanofibers. The diameter and length of the nanofibers were approximately 30 nm and 60 μm, respectively. The diameters of embedded silver nanoparticles and polymer nanofibers were controlled by varying the weight ratio of silver ion to PVA.

Several research groups have demonstrated that PANI nanofibers can be synthesized without the aid of any templates.[162-167] It turned out that the nanofibrillar morphology is intrinsic to PANI synthesized in water, and the key to producing nanofibers was effectively suppressing the secondary growth that leads to agglomerated particles. This concept was recently applied to the fabrication of PPy nanofibers in a similar fashion.[168] PPy nanofibers were produced by adding a small amount of bipyrrole into the chemical polymerization reaction of pyrrole. Since bipyrrole (ca. 0.53 V) has a lower oxidation potential than pyrrole (ca. 0.60 V), it can serve as nucleation centers for growing polymer chains. Analogous to the PANI system, therefore, the accelerated reaction rate by bipyrrole promotes homogeneous nucleation of growing polymer chains, yielding fibrillar PPy nanostructures.

Nanotubes. 1D polymer nanostructures with hollow interiors are an important class of materials with diverse applications, ranging from micro- and nanoelectronics,

optics, catalysis, energy storage and conversion, and biomedical science.[169-171] There have been many efforts to fabricated polymer nanotubes from the viewpoint of both fundamental research and practical applications. Strategies for fabricating polymer nanotubes can be divided into two categories: template-assisted synthesis and template-free synthesis. Most polymer nanotubes were produced by template-assisted synthesis using porous membranes, nanofibers, surfactants, and cyclodextrin.

Template synthesis using porous alumina and track-etched polycarbonate membranes is a well-established method for fabricating polymer nanotubes. The elegance of this approach lies in its ability to produce a wide range of polymer nanofibers depending on few physical and chemical parameters.[139] Of course, precise control on these parameters is required for tailoring the shape, size, and properties of final products. Above all, in the case of thermoplastic or soluble polymers, nanotubes can be prepared via wetting of porous membranes.[172,173] When a polymer melt or solution is placed on a porous membrane, it invades the porous membrane and wet rapidly the pore walls due to the high surface energy of the membrane, finally giving rise to tubular nanostructures. The thickness of wetting layer is mainly determined by the polymer-template interaction. Interestingly, thermosetting polyimide nanofibers with tailored wall-thicknesses could be also fabricated by wetting the polymer precursor solution in the channels of the alumina membrane, followed by a curing process.[174] On the other hand, conducting polymer nanotubes have been extensively synthesized by chemical[175,176] and electrochemical[177-179] polymerization using porous membranes. Polyelectrolytes could be deposited within the cylindrical pores of templates to obtain nanotubes.[180,181] VDP-mediated template synthesis has also been proven to be an effective approach for obtaining nanotubes with controlled wall-thicknesses on the scale of a few nanometers.[182-186] Several kinds of polymer nanotubes consisting of PPy, carboxylated PPy, and PAN have been successfully fabricated and applied to carbon precursors, fluorescence resonance energy transfer (FRET) platforms, catalyst supports, signal transducers, molecular probes, and DNA carriers. A nonreactive solvent such as heptane can be introduced into the reaction chamber, making it possible to produce nanotubes with more uniform wall-thickness.[183]

Another well-established route to nanotubes is the so-called "tubes by fiber templates" approach. Soluble or degradable nanofibers are coated with polymer thin layers and then the selective removal of the template nanofibers generates hollow nanofibers, namely nanotubes. As expected, the size and shape of the nanotubes strongly

depended on the nanorod template. In many cases, electrospun nanofibers were utilized as template nanofibers. A particular example is the preparation of poly(*p*-xylylene) (PPX) nanotubes through chemical vapor deposition of PPX onto electrospun PLA nanofibers, followed by subsequent pyrolysis of the PLA nanofibers.[137] Using this approach, PPX nanotubes with inner diameters of less than 10 nm and outer diameters of ca. 50 nm could be obtained. Recently, Xia and co-workers demonstrated a new concept to fabricate polymer nanotubes by using electrospinning combined with VDP.[187] The synthetic procedure involved electrospinning of a PSS nanofiber core, followed by VDP of acrylonitrile, oxidative stabilization of the PAN sheath, and selective removal of the core with water. The outer diameter and wall-thickness of PAN nanotubes obtained were ca. 100 nm and ca. 14 nm, respectively.

As mentioned previously, cylindrical micelles have turned out to be excellent soft templates for 1D nanostructures. The geometry of micelles depends on the molecular structure of surfactants such as the area of head-group, length and volume of tail-group, and kinds of counterion and solvent. From the viewpoint of external macroscopic variables, the thermodynamic conditions, depending on temperature, pressure, and concentration of surfactant and additives, are also critical to the self-assembly and growth of micelles. Recently, there have been a series of studies on the fabrication of conducting polymer nanotubes by cylindrical micelle templating. Sodium bis(2-ethylhexyl) sulfosuccinate (AOT) has employed in order to generate reverse (water-in-oil) cylindrical micelles in an apolar solvent.[188-193] When an

appropriate amount of ferric chloride was added into the AOT solution, spherical AOT micelles were transformed into cylindrical micelles. It can be explained that the incorporation of metal salt into AOT emulsion strongly affects the micelle aggregation number as well as the second CMC. Importantly, iron cations (oxidizing agent) are concentrated in the anionic head-group of AOT due to electrostatic interactions. Therefore, when pyrrole or EDOT monomers were introduced into the AOT cylindrical micelle phase, they were chemically polymerized by iron cations along the surface of the cylindrical micelles. 1D nanostructures of PPy and PEDOT have been successfully fabricated, and the simple synthetic procedure offered a great possibility to produce 1D nanostructures in large quantities. Figure 9 shows the typical SEM and TEM images of PEDOT nanotubes prepared by AOT micelle templating.[192] The photograph shown in the inset of Figure 9(a) exhibits a Petri dish containing ca. 3 g of PEDOT nanotubes obtained from a single polymerization reaction. The TEM image visualized the hollow interior of the nanotubes. The inner surface of the nanotubes was fairly smooth (Figure 9(b) inset), supporting that the chemical oxidation polymerization of monomer proceeded on the surface of the cylindrical micelles. It is possible to control the size and shape of 1D nanostructures by changing synthetic variables such as the amounts of surfactant and oxidizing agent, kind of solvent, and polymerization temperature. This facile and effective approach might be expanded to allow the fabrication of various kinds of nanotubes.[194]

Cyclodextrin was also used as a sacrificial template for creating the hollow interior of 1D nanostructures.[99] The
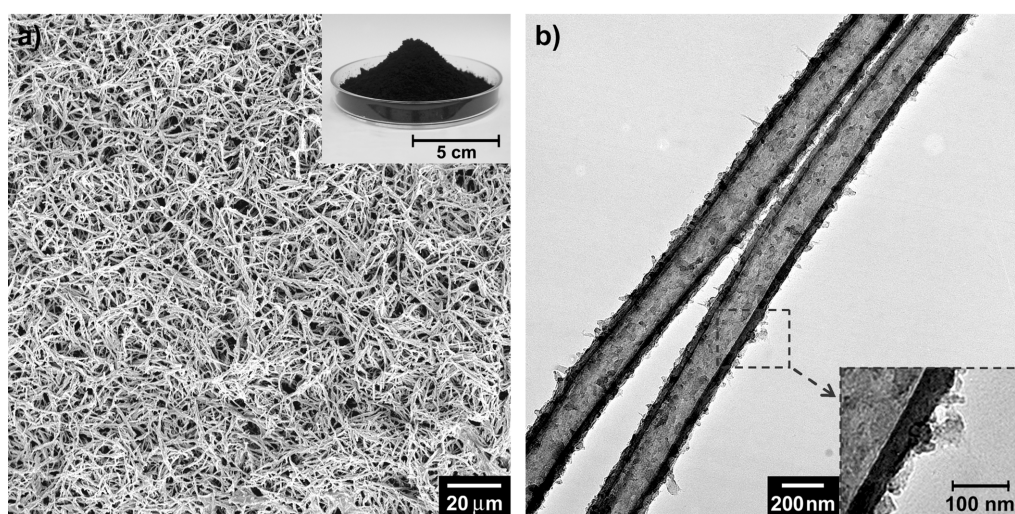

Figure 9. a) Typical SEM and b) TEM images of PEDOT nanotubes synthesized by AOT cylindrical micelle templating. Insets: a) A photograph showing a Petri dish containing ca. 3 g of PEDOT nanotubes fabricated in a single polymerization reaction. b) A magnified image of the selected area. Reproduced with permission from Ref. 192; Copyright 2007, Wiley-VCH Verlag GmbH & Co. KGaA.

cylindrical micelle structure of a cationic surfactant was achieved by the addition of metal salt (ferric chloride). The cluster of cyclodextrin molecules existed in the core part of the cylindrical micelles during the polymerization of acrylonitrile monomer, resulting in cyclodextrin-filled PAN nanotubes. Cyclodextrin was easily removed by alcohol washing.

It has been shown that block copolymer self-assembly is an effective technique to generate nanotubes. The approach comprises design and synthesis of block copolymers, self-assembly of block copolymers, the interlocking of the self-assembled nanostructures, and the selective removal of the core domain. Raez *et al*. demonstrated that the self-assembly of poly(ferrocenyldimethylsilane-*b*-dimethylsiloxane) (PFS-*b*-PDMS) gave tubular nanostructures in nonsolvents for PFS.[195] The PFS blocks aggregate and crystallize to make a shell with a cavity in the middle of the tube, while the PDMS blocks form the corona. The wall-thickness of the nanotubes was 7 nm and their inner diameter was 7–9 nm, depending on kind of solvents. Liu *et al*. described the fabrication of nanotubes using a triblock copolymer, poly(isoprene-*b*-2-cinnamoylethyl methacrylate-*b*-*tert*-butyl acrylate) (PI-*b*-PCEMA-*b*-PBA).[196] This block copolymer self-assembled to cylindrical micelles with a PBA corona, a PCEMA shell and a PI core, respectively, in methanol. Tubular nanostructures were obtained after photo-crosslinking of PCEMA and degradation of PI. A series of similar works have been reported by the same group.[197-199]

A simple self-assembly approach to obtain polymer nanotubes has been reported in literatures. The major contribution to this approach has been made by Wan and co-workers through *in-situ* doping polymerization method.[200-202] Typically, PANI nanotubes were synthesized using APS in the presence of *β*-naphthalene sulfonic acid (NSA) as a dopant.[200] It was found that the NSA played a "template-like" role in creating the tubular nanostructures. The size, morphology, and electrical properties of the resulting nanostructures were strongly dependent on the kind of dopant and the reaction conditions. Similar works related with the formation of polymer nanotubes by self-assembly approach have been achieved on the basis of crystallization of oligomers[203] and aggregation of methyl orange.[204,205]

Nanoporous Materials. Porous polymer materials with feature sizes ranging from a few nanometers to a few tens of nanometers have unique surface, structural, and bulk properties that underline their significant uses in various fields such as ion exchange, separation, catalysis, and sensors.[206] There have been three main approaches to construct nanoporous polymer structures (1–100 nm in pore diameter): direct synthesis of nanoporous structures,

template-mediated synthesis, and introduction of polymers into mesostructured materials. First, direct synthesis of nanoporous polymer structures can be made by controlled foaming,[207,208] ion track etching,[209-211] and phase separation of block copolymers.[212-215] Krause *et al*. have carried out systematic studies on the physical foaming behavior of polymers using CO_2 as physical blowing gas.[207,208] Nanoporous foams consisting of poly(ether imide), poly(ether sulfone), and polysulfone/polyimide blends have been obtained by controlled CO_2 foaming, and these foams had nanoporous bicontinuous structures with pore sizes as small as 40 nm. Nanoporous membranes have been prepared from polycarbonate,[209] poly(ethylene terephthalate),[210] poly(vinylidene fluoride)[211] films via heavy ion irradiation, followed by track etching. The polymer films are bombarded with ions, which produce randomly spaced damage tracks through the films. These tracks are then chemically etched to generate uniform cylindrical pores through the films. During this process, due to the random nature of pore generation, a number of pores may in fact intersect within the resulting membranes. The pore diameters can be tailored in the range of 10–2,000 nm by adjusting etching time and etching solution temperature. The preparation of nanoporous polymers has been achieved from block copolymer precursors as well.[212-215] As a notable case, polystyrene was incorporated into a block copolymer with PLA as the minority component through the combination of living anionic polymerization and controlled coordination insertion polymerization.[212] The resulting materials had a hexagonally packed array of PLA nanocylinders in the functionalized PS matrix, and the hydrolytic degradation of PLA domain allowed the formation of a nanoporous structure without disturbing the remaining polystyrene framework. It was found that the domain sizes of block copolymer precursors dictate the size characteristics of the porous material. The domain sizes were tunable by changing the molecular weight of block copolymers.

The second case has been realized by using a wide variety of soft templates (e.g., surfactants, polyelectrolytes, and liquid crystals)[216-222] and hard templates (e.g., colloidal nanoparticles and porous materials).[223,224] It is usually difficult to create nanoporous polymer structures under polymerization or casting conditions due to thermodynamic instability, in contrast with the case of porous silica families such as MCM-41 and SBA-15.[225] It has been found that the formation of nanoporous polymer materials is mainly affected by thermodynamic considerations such as the compatibility of templates with polymers and the conformation of polymer chains in a confinement.[206] Nevertheless, there have been some successful cases where nonionic surfactants were used as

templates. Recently, nanoporous PAN materials were fabricated by reverse micelle templating in *N*-methyl-2-pyrrolidone (NMP).[216] To create the micelle as a kind of nanoporogen, two nonionic surfactants with different spacer lengths were employed: PPO$_{19}$-PEO$_{33}$-PPO$_{19}$ (Pluronic 25R4) and PPO$_{14}$-PEO$_{23}$-PPO$_{14}$ (Pluronic 17R4), where PPO and PEO indicates poly(propylene oxide) and poly(ethylene oxide), respectively. Acrylonitrile monomer was mixed with nonionic surfactant and then dissolved in NMP. In this state, the relatively hydrophobic monomer was located at the exterior of the micelles and polymerized by a radical initiator (AIBN). Importantly, the resulting nanoporous PANs had fairly monodisperse pores and the pore diameters were tunable by changing the type and concentration of surfactants. The pore diameter of nanoporous PAN prepared with Pluronic 17R4 (6.7 nm) was larger than that of nanoporous PAN prepared with Pluronic 25R4 (8.7 nm). In addition, the pore diameter of nanoporous PAN increased gradually with increasing the weight ratio of surfactant to monomer. The nanoporous PANs had considerably large surface areas of 350–500 m^2 g^{-1}, which depended on the pore size. Another micelle templating method was also developed to obtain highly ordered and stable nanoporous polymers.[217] The nanoporous structures can be obtained by an evaporation-induced self-assembly method, using amphiphilic triblock copolymers (PEO-PPO-PEO) and a soluble low-molecular weight polymer of phenol/formaldehyde (resol), followed by a thermopolymerization process. The abundant hydroxyl groups of phenol/formaldehyde can interact strongly with triblock copolymers through hydrogen bonding, probably leading to the successful organization of polymer precursors and block copolymers. As a result, the thermopolymerization at 100 ℃ yielded a rigid zeolite-like hydrocarbon network with three-connected benzene rings through covalent bonding. The nanoporous polymers exhibited large uniform mesopores (2−50 nm in pore diameter), surface areas, and pore volumes. In addition, various nanoporous textures were readily obtained by changing the kind of surfactant and the weight ratio of surfactant to polymer precursor. Importantly, these nanoporous polymers can be readily converted to functional materials through modifying their organic framework walls.[218] Cationic surfactants have been also exploited to generate nanoporous polymer structures. A recent study demonstrated that the so-called "surfactant-mediated interfacial polymerization" was effective to selective fabrication of PEDOT nanostructures with nanometer-sized cavities.[219] At first stage, cationic ammonium surfactants with different alky chain lengths were used to form micelles in aqueous solution. The micelles were able to capture the redox initiator

(CAN) due to electrostatic interactions between the cerium complex and the surfactant molecules, and the chemical polymerization of EDOT monomer proceeded at the micellar surface. PEDOT nanocapsules were prepared at relatively low surfactant concentrations, just above the CMC of surfactants. At higher surfactant concentrations, on the other hand, nanoporous PEDOT foams were obtained by the coagulation of the micelle-embedded PEDOT nanocapsules. A similar phenomenon could be observed in the synthesis of nanoporous PDVB structures using colloidal silica aggregates as the template.[223] It is expected that these concepts may be expanded to the fabrication of various types of nanoporous materials.[226]

Ordered nanoporous polymers have been often obtained using nanoporous inorganic frameworks.[227-230] In this case, the resistance of the pore structure to heat and solvents is remarkably improved, and the textural properties such as pore sizes and structures can be manipulated easily. For instance, nanoporous polymer-silica composites were obtained through the controlled adsorption of monomers on the silica mesopore walls, followed by the subsequent thermal polymerization.[227] The vinyl monomer, crosslinker, radical initiator were selectively impregnated into the silica mesopore walls under reduced pressure to achieve uniform distribution, and the subsequent thermal polymerization resulted in polymer-silica composites with well-defined porosity. Various vinyl monomers, such as styrene, chloromethyl styrene, 2-hydroxyethyl methacrylate, and methacrylic acid, could be successfully polymerized in the presence of crosslinking agents, such as DVB and ethylene glycol dimethacrylate. Furthermore, the as-formed polymers served as platforms for incorporating versatile functional groups through suitable organic reactions. Similar synthetic strategies toward nanoporous organic polymers have been described with mesoporous carbons.[229,230] Notably, a conducting polymer (PPy) was intercalated into the framework mesopores of a mesostructured carbon.[230] Intercalation of PPy into the mesostructured carbon made a contribution to the improvement of thermal stability of PPy in comparison to their bulk counterparts. In addition, the carbon/PPy mesostructures with different PPy (conductivity: 0.01 S cm^{-1} for bulk PPy) loading amounts exhibited electrical conductivities which were less than an order of magnitude lower than that of the pristine carbon (1.0 S cm^{-1}).

Summary and Outlook

We gave an overview on a variety of methods that have been developed for generating polymer nanostructures.

The synthetic strategies could be classified into three categorizes: hard template synthesis, soft template synthesis, and template-free synthesis. Each methodology has its specific merits as well as weaknesses. For instance, the hard template synthesis is of advantage in tailoring the dimensions of nanomaterials. However, owing to complicated synthetic process and comparatively high cost, the use of hard templates has the significant drawback that scale-up for industrial applications is highly difficult. To overcome this limitation, soft template synthesis has emerged as an alternative strategy against hard template method. Generally, polymer nanoparticles can be prepared in relatively large quantities by using soft templates. On the other hand, it is difficult to achieve precise control over the uniformity and dimensions of the resulting products. Template-free synthesis is very straightforward. However, this approach is limited to particular precursor materials, and extensive efforts are sometimes required to design molecular architectures that are able to assemble into nanostructures with desired functions. In this regard, most of the methods described in this review still need to be improved. Furthermore, there are several critical issues that remain to be addressed before these materials find widespread use in practical applications. First, the size- and shape-dependent properties of polymer nanomaterials need to be thoroughly investigated for better understanding of the structural parameters determining physical and chemical properties. The second issue is to give a careful consideration to the chemical, thermal, and mechanical stability of as-prepared polymer nanoparticles for practical applications. Lastly, the third issue involves an evaluation on how these nanomaterials will impact human health and environment. It is expected that these important issues will be the subject of intense research in this field for many years to come. In parallel, it will become increasingly important to perform interdisciplinary studies for advances in synthesis and application of polymer nanoparticles.

References

(1) E. Roduner, *Chem. Soc. Rev.*, **35**, 583 (2006).
(2) G. Hodes, *Adv. Mater.*, **19**, 639 (2007).
(3) C. Burda, X. Chen, R. Narayanan, and M. A. El-Sayed, *Chem. Rev.*, **105**, 1025 (2005).
(4) K. L. Kelly, E. Coronado, L. L. Zhao, and G. C. Schatz, *J. Phys. Chem. B*, **107**, 668 (2003).
(5) J. H. Kim, J. Jang, D. Y. Lee, and W. C. Zin, *Macromolecules*, **35**, 311 (2002).
(6) J. H. Kim, J. Jang, and W. C. Zin, *Langmuir*, **17**, 2703 (2001).
(7) J. H. Kim, J. Jang, and W. C. Zin, *Macromol. Rapid Commun.*, **22**, 386 (2001).
(8) J. Jang, *Adv. Polym. Sci.*, **199**, 189 (2006).
(9) S. Nayak and L. A. Lyon, *Angew. Chem. Int. Ed.*, **44**, 7686 (2005).
(10) J. Panyam and V. Labhasetwar, *Adv. Drug Deliv. Rev.*, **55**, 329 (2003).
(11) Y. -K. Lee, *Macromol. Res.*, **14**, 387 (2006).
(12) K. Y. Lee, *Macromol. Res.*, **13**, 542 (2005).
(13) P. Y. Chow and L. M. Gan, *Adv. Polym. Sci.*, **175**, 257, (2005).
(14) J. M. Asua, *J. Polym. Sci.; Part A: Polym. Chem.,* **42**, 1025 (2004).
(15) J. Klier, C. J. Tucker, T. H. Kalantar, and D. P. Green, *Adv. Mater.*, **12**, 1751 (2000).
(16) R. Nagarajan and E. Ruckenstein, *Langmuir*, **16**, 6400 (2000).
(17) J. Jang, J. H. Oh, and G. D. Stucky, *Angew. Chem. Int. Ed.*, **41**, 4016 (2002).
(18) J. Jang and J. H. Oh, *Chem. Commun.*, 2200 (2002).
(19) J. Jang and J. H. Oh, *Langmuir*, **20**, 8419 (2004).
(20) J. Jang and J. H. Oh, *Adv. Mater.*, **16**, 1650 (2004).
(21) C. D. Anderson, E. D. Sudol, and M. S. El-Aasser, *Macromolecules*, **35**, 574 (2002).
(22) G. He and Q. Pan, *Macromol. Rapid Commun.*, **25**, 1545 (2004).
(23) J. A. Westbrook, K. L. Manno, and Y. Li, *Chem. Educator.*, **6**, 104 (2001).
(24) S. E. Shim, H. Lee, and S. Choe, *Macromolecules*, **37**, 5565 (2004).
(25) Y. Wang, W. Zhong, N. Jiang, and W. Yang, *Macromol. Rapid Commun.*, **26**, 87 (2005).
(26) J. Jang, J. Bae, and S. Ko, *J. Polym. Sci.; Part A: Polym. Chem.,* **43**, 2258 (2005).
(27) J. Jang, J. Ha, and S. Kim, *Macromol. Res.*, **15**, 154 (2007).
(28) P. A. Hassan, S. N. Sawant, N. C. Bagkar, and J. V. Yakhmi, *Langmuir*, **20**, 4874 (2004).
(29) D. Kim, J. Choi, J.-Y. Kim, Y.-K. Han, and D. Sohn, *Macromolecules*, **35**, 5314 (2002).
(30) M. G. Han, S. K. Cho, S. G. Oh, and S. S. Im, *Synth. Met.*, **126**, 53 (2002).
(31) B.-J. Kim, S.-G. Oh, M.-G. Han, and S.-S. Im, *Synth. Met.,* **122**, 297 (2001).
(32) K. Müller, M.-K. Park, M. Klapper, W. Knoll, and K. Müllen, *Macromol. Chem. Phys.*, **208**, 1394 (2007).
(33) K. Müller, M. Klapper, and K. Müllen, *Macromol. Rapid Commun.*, **27**, 586 (2006).
(34) J. Jang and H. Yoon, *Small*, **1**, 1195 (2005).
(35) H. Yoon, S. Ko, and J. Jang, *Chem. Commun.*, 1468 (2007).
(36) B. Choi, H. Yoon, I.-S. Park, J. Jang, and Y.-E. Sung, *Car-*

bon, **45**, 2496 (2007).

(37) I. Capek and C.-S. Chern, *Adv. Polym. Sci.*, **155**, 101 (2001).

(38) S. Kawaguchi and K. Ito, *Adv. Polym. Sci.*, **175**, 299 (2005).

(39) T. K. Mandal and B. M. Mandal, *J. Polym. Sci.*, **37**, 3723 (1999).

(40) T. K. Mandal and B. M. Mandal, *Polymer*, **36**, 1911 (1995).

(41) J. Jang, J. Ha, and J. Cho, *Adv. Mater.*, **19**, 1772 (2007).

(42) S. Dorey, C. Vasilev, L. Vidal, C. Labbe, and N. Gospodinova, *Polymer*, **46**, 1309 (2005).

(43) C. Tang, K. Qi, K. L. Wooley, K. Matyjaszewski, and T. Kowalewski, *Angew. Chem. Int. Ed.*, **43**, 2783 (2004).

(44) T. He, D. J. Adams, M. F. Butler, C. T. Yeoh, A. I. Copper, and S. P. Rannard, *Angew. Chem. Int. Ed.*, **46**, 9243 (2007).

(45) T. Akagi, M. Baba, and M. Akashi, *Polymer*, **48**, 6729 (2007).

(46) C. Choi, M.-K. Jang, and J.-W. Nah, *Macromol. Res.*, **15**, 623 (2007).

(47) S. Y. Kim, S. H. Cho, Y. M. Lee, and L.-Y. Chu, *Macromol. Res.*, **15**, 646 (2007).

(48) K. Matyjaszewski and J. Xia, *Chem. Rev.*, **101**, 2921 (2001).

(49) T. E. Patten and K. Matyjaszewski, *Adv. Mater.*, **10**, 901 (1998).

(50) A. Hasneen, S. J. Kim, and H.-J. Paik, *Macromol. Res.*, **15**, 541 (2007).

(51) Z. Xue, S. K. Noh, and W. S. Lyoo, *Macromol. Res.*, **15**, 302 (2007).

(52) Y.-J. Kwark, J. Kim, and B. M. Novak, *Macromol. Res.*, **15**, 31 (2007).

(53) H. J. Kim, H. S. Kim, and Y. K. Kwon, *Macromol. Res.*, **13**, 529 (2005).

(54) S. C. Hong, K. E. Shin, S. K. Noh, and W. S. Lyoo, *Macromol. Res.*, **13**, 391 (2005).

(55) H. Gao, T. Jiang, B. Han, Y. Wang, J. Du, Z. Liu, and J. Zhang, *Polymer*, **45**, 3017 (2004).

(56) R. Lv, S. Zhang, Q. Shi, and J. Kan, *Synth. Met.*, **150**, 115 (2005).

(57) Z. Tang, S. Liu, Z. Wang, S. Dong, and E. Wang, *Electrochem. Commun.*, **2**, 32 (2002).

(58) M. A. Khan and S. P. Armes, *Adv. Mater.*, **12**, 671 (2000).

(59) F. Caruso, *Adv. Mater.*, **13**, 11 (2001).

(60) R. M. Crooks, M. Zhao, L. Sun, V. Chechik, and L. K. Yeung, *Acc. Chem. Res.*, **34**, 181 (2001).

(61) C. J. Zhong and M. M. Maye, *Adv. Mater.*, **13**, 1507 (2001).

(62) K. Kim, J.-H. Kim, S. Kim, H. Chung, K. Choi, I. C. Kwon, J. H. Park, Y.-S. Kim, R.-W. Park, I.-S. Kim, and S. Y. Jeong, *Macromol. Res.*, **13**, 167 (2005).

(63) Y. F. Chen and Z. Rosenzweig, *Nano Lett.*, **2**, 1299 (2002).

(64) M. K. Corbierre, N. S. Cameron, M. Sutton, S. G. J. Mochrie, L. B. Lurio, A. Ruehm, and R. B. Lennox, *J. Am. Chem. Soc.*, **123**, 10411 (2001).

(65) J. Jang and J. Oh, *Adv. Funct. Mater.*, **15**, 494 (2005).

(66) J. Jang and H. Ha, *Chem. Mater.*, **15**, 2109 (2003).

(67) D. I. Lee, *J. Polym. Sci.; Part A: Polym. Chem.*, **44**, 2826 (2006).

(68) M. R. Moghbeli, N. Mohammadi, and R. Bagheri, *J. Appl. Polym. Sci.*, **105**, 1412 (2007).

(69) J.-E. Jönsson, O. J. Karlsson, H. Hassander, and B. Törnell, *Macromolecules*, **34**, 1512 (2001).

(70) J. Jang, J. Ha, and B. Lim, *Chem. Commun.*, 1622 (2006).

(71) M. G. Han and S. H. Foulger, *Chem. Commun.*, 2154 (2004).

(72) J. Jang, S. Kim, and K. Lee, *Chem. Commun.*, 2689 (2007).

(73) W. B. Tan and Y. Zhang, *Adv. Mater.*, **17**, 2375 (2005).

(74) J. M. Dubach, D. I. Harjes, and H. A. Clark, *J. Am. Chem. Soc.*, **129**, 8418 (2007).

(75) J. Jang, Y. Nam, and H. Yoon, *Adv. Mater.*, **17**, 1382 (2005).

(76) T. von Werne and T. E. Patten, *J. Am. Chem. Soc.*, **123**, 7497 (2001).

(77) D. Li, Y. Cui, K. Wang, Q. He, X. Yan, and J. Li, *Adv. Funct. Mater.*, **17**, 3134 (2007).

(78) D. J. Kim, S. M. Kang, B. Kong, W.-J. Kim, H.-J. Paik, H. Choi, and I. S. Choi, *Macromol. Chem. Phys.*, **206**, 1941 (2005).

(79) G. Li, J. Fan, R. Jiang, and Y. Gao, *Chem. Mater.*, **16**, 1835 (2004).

(80) C. R. Vestal and Z. J. Zhang, *J. Am. Chem. Soc.*, **124**, 14312 (2002).

(81) Y. Wang, X. Teng, J.-S. Wang, and H. Yang, *Nano Lett.*, **3**, 789 (2003).

(82) Y. Kang and T. A. Taton, *Macromolecules*, **38**, 6115 (2005).

(83) Y. Kang and T. A Taton, *Angew. Chem. Int. Ed.*, **44**, 409 (2005).

(84) G. Liu, X. Yan, Z. Lu, S. A. Curda, and J. Lal, *Chem. Mater.*, **17**, 4985 (2005).

(85) B. D. Korth, P. Keng, I. Shim, S. E. Bowles, C. Tang, T. Kowalewski, K. W. Nebesny, and J. Pyun, *J. Am. Chem. Soc.*, **128**, 6562 (2006).

(86) Y. Zhu, J. Shi, W. Shen, X. Dong, J. Feng, M. Ruan, and Y. Li, *Angew. Chem. Int. Ed.*, **44**, 5083 (2005).

(87) G. Schneider and G. Decher, *Nano Lett.*, **4**, 1833 (2004).

(88) D. I. Gittins and F. Caruso, *J. Phys. Chem. B*, **105**, 6846 (2001).

(89) K. S. Mayya, B. Schoeler, and F. Caruso, *Adv. Funct. Mater.*, **13**, 183 (2003).

(90) J. Jang and B. Lim, *Angew. Chem. Int. Ed.*, **42**, 5600 (2003).

(91) W. Meier, *Chem. Soc. Rev.*, **29**, 295 (2000).

(92) C. J. McDonald, K. J. Bouck, A. B. Chaput, and C. J. Stevens, *Macromolecules*, **33**, 1593 (2000).

(93) F. Tiarks, K. Landfester, and M. Antoietti, *Langmuir*, **17**, 908 (2001).

(94) Y. Luo and X. Zhou, *J. Polym. Sci.; Part A: Polym. Chem.*, **42**, 2145 (2004).

(95) S. Torza and S. G. Mason, *J. Colloid Interface Sci.*, **33**, 67 (1970).

(96) J. Jang and K. Lee, *Chem. Commun.*, 1098 (2002).

(97) G. D. Fu, Z. Shang, L. Hong, E. T. Kang, and K. G. Neoh, *Macromolecules*, **38**, 7867 (2005).

(98) D. Cheng, H. Xia, and H. S. O. Chan, *Langmuir*, **20**, 9909 (2004).

(99) J. Jang and J. Bae, *Macromol. Rapid Commun.*, **26**, 1320 (2005).

(100) J. Jang and H. Ha, *Langmuir*, **18**, 5613 (2002).

(101) J. Jang, X. L. Li, and J. H. OH, *Chem. Commun.*, 794 (2004).

(102) J. Jang, J. H. Oh, and X. L. Li, *J. Mater. Chem.*, **14**, 2872 (2004).

(103) C. S. Peyratout and L. Dähne, *Angew. Chem. Int. Ed.*, **43**, 3762 (2004).

(104) D. G. Shchukin, G. B. Sukhorukov, and H. Möhwald, *Angew. Chem. Int. Ed.*, **42**, 4472 (2003).

(105) D. I. Gittins and F. Caruso, *Adv. Mater.*, **12**, 1947 (2000).

(106) P. Chodanowski and S. Stoll, *J. Chem. Phys.*, **115**, 4951 (2001).

(107) P. Haronska, T. A. Vilgis, R. Grottenmüller, and M. Schmidt, *Macromol. Theory Simul.*, **7**, 241 (1998).

(108) J. L. Turner and K. L. Wooley, *Nano Lett.*, **4**, 683 (2004).

(109) Q. Zhang, E. E. Remsen, and K. L. Wooley, *J. Am. Chem. Soc.*, **122**, 3642 (2000).

(110) T. Sanji, T. Nakatsuka, S. Ohnishi, and H. Sakurai, *Macromolecules*, **33**, 8524 (2000).

(111) M. Wang, M. Jiang, F. Ning, D. Chen, S. Liu, and H. Duan, *Macromolecules*, **35**, 5980 (2002).

(112) Y. Zhang, M. Jiang, J. Zhao, J. Zhou, and D. Chen, *Macromolecules*, **37**, 1537 (2004).

(113) K. Orfanou, D. Topouza, G. Sakellariou, and S. Pispas, *J. Polym. Sci.; Part A: Polym. Chem.*, **41**, 2454 (2003).

(114) C. Nardin, T. Hirt, J. Leukel, and W. Meier, *Langmuir*, **16**, 1035 (2000).

(115) Y. Hu, X. Jiang, Y. Ding, Q. Chen, and C. Yang, *Adv. Mater.*, **16**, 933 (2004).

(116) D. Kim, E. Kim, J. Kim, K. M. Park, J. Baek, M. Jung, Y. H. Ko, W. Sung, H. S. Kim, J. H. Suh, C. H. Park, O. S. Na, D.-K. Lee, K. E. Lee, S. S. Han, and K. Kim, *Angew. Chem. Int. Ed.*, **46**, 3471 (2007).

(117) A. M. Aleshin, *Adv. Mater.*, **18**, 17 (2006).

(118) S. J. Hurst, E. K. Payne, L. Qin, and C. A. Mirkin, *Angew. Chem. Int. Ed.*, **45**, 2672 (2006).

(119) D. O'Carroll, I. Lieberwirth, and G. Redmond, *Nat. Nanotechnol.*, **2**, 180 (2007).

(120) I. S. Lee, O. H. Kwon, W. Meng, and I.-K. Kang, *Macromol. Res.*, **12**, 374 (2004).

(121) H. Park, K. Y. Lee, S. J. Lee, K. E. Park, and W. H. Park, *Macromol. Res.*, **15**, 238 (2007).

(122) A. Greiner and J. H. Wendorff, *Angew. Chem. Int. Ed.*, **46**, 5670 (2007).

(123) T. Subbiah, G. S. Bhat, R. W. Tock, S. Parameswaran, and S. S. Ramkumar, *J. Appl. Polym. Sci.*, **96**, 557 (2005).

(124) D. Li, Y. Wang, and Y. Xia, *Adv. Mater.*, **16**, 361 (2004).

(125) M. Li, J. Zhang, H. Zhang, Y. Liu, C. Wang, X. Xu, Y. Tang, and B. Yang, *Adv. Funct. Mater.*, **17**, 2650 (2007).

(126) D. Sun, C. Chang, S. Li, and L. Lin, *Nano Lett.*, **6**, 839 (2006).

(127) S.-Y. Jang, V. Seshadri, M.-S. Khil, A. Kumar, M. Marquez, P. T. Mather, and G. A. Sotzing, *Adv. Mater.*, **17**, 2177 (2005).

(128) Y. H. Jung, H. Y. Kim, D. R. Lee, S. Y. Park, and M. S. Khil, *Macromol. Res.*, **13**, 385 (2005).

(129) D. Li, A. Babel, S. A. Jenekhe, and Y. Xia, *Adv. Mater.*, **16**, 2062 (2004).

(130) S.-H. Lee, J. W. Yoon, and M. H. Suh, *Macromol. Res.*, **10**, 282 (2002).

(131) D.-K. Kim, S. H. Park, B. C. Kim, B. D. Chin, S. M. Ju, and D. Y. Kim, *Macromol. Res.*, **13**, 521 (2005).

(132) D. Yang, B. Lu, Y. Zhao, and X. Jiang, *Adv. Mater.*, **19**, 3702 (2007).

(133) P. Katta, M. Alessandro, R. D. Ramsier, and G. G. Chase, *Nano Lett.*, **4**, 2215 (2004).

(134) Z. Sun, E. Zussman, A. L. Yarin, J. H. Wendorff, and A. Greiner, *Adv. Mater.*, **15**, 1929 (2003).

(135) M. Bognitzki, W. Czado, T. Frese, A. Schaper, M. Hellwig, M. Steinhart, A. Greiner, and J. H. Wendorff, *Adv. Mater.*, **13**, 70 (2003).

(136) Y. Dror, W. Salalha, R. Avrahami, E. Zussman, A. L. Yarin, R. Dersch, A. Greiner, and J. H. Wendorff, *Small*, **3**, 1064 (2007).

(137) H. Hou, Z. Jun, A. Reuning, A. Schaper, J. H. Wendorff, and A. Greiner, *Macromolecules*, **35**, 2429 (2002).

(138) Y. Zhou, M. Freitag, J. Hone, C. Staii, and A. T. Johnson, N. J. Pinto, and A. G. MacDiarmid, *Appl. Phys. Lett.*, **83**, 3800 (2003).

(139) C. R. Martin, *Chem. Mater.*, **8**, 1739 (1996).

(140) J. C. Hulteen and C. R. Martin, *J. Mater. Chem.*, **7**, 1075 (1997).

(141) S. A. Sapp, D. T. Mitchell, and C. R. Martin, *Chem. Mater.*, **11**, 1183 (1999).

(142) M. Lahav, E. A. Weiss, Q. Xu, and G. M. Whitesides, *Nano Lett.*, **6**, 2166 (2006).

(143) S. Park, J.-H. Lim, S.-W. Chung, and C. Mirkin, *Science*, **303**, 348 (2004).

(144) J.-P. Lellouche, S. Govindaraji, A. Joseph, J. Jang, and K. J. Lee, *Chem. Commun.*, 4357 (2005).

(145) J. Jang and J. Bae, *Adv. Funct. Mater.*, **15**, 1877 (2005).

(146) G. A. O'Brien, A. J. Quinn, D. Iacopino, N. Pauget, and G. Redmond, *J. Mater. Chem.*, **16**, 3237 (2006).

(147) K. J. Lee, J. H. Oh, Y. Kim, and J. Jang, *Adv. Mater.*, **18**, 2216 (2006).

(148) S. Ko and J. Jang, *Biomacromolecules*, **8**, 1400 (2007).

(149) J. Jang, B. K. Lim, J. Lee, and T. Hyeon, *Chem. Commun.*, 83 (2001).

(150) G. Li, S. Bhosale, T. Wang, Y. Zhang, H. Zhu, and J.-H. Fuhrhop, *Angew. Chem. Int. Ed.*, **42**, 3818 (2003).

(151) J. Jang and J. Bae, *Angew. Chem. Int. Ed.*, **43**, 3803 (2004).

(152) J. Jang, J. Bae, and E. Park, *Adv. Funct. Mater.*, **16**, 1400 (2006).

(153) J. Jang, M. Chang, and H. Yoon, *Adv. Mater.*, **17**, 1616 (2005).

(154) Y. Yan, H. Yang, F. Zhang, B. Tu, and D. Zhao, *Small*, **2**, 517 (2006).

(155) T. Thurn-Albrecht, J. Schotter, G. A. Kästle, N. Emley, T. Shibauchi, L. Krusin-Elbaum, K. Guarini, C. T. Black, M. T. Tuominen, and T. P. Russell, *Science*, **290**, 2126 (2000).

(156) J. F. Hulvat and S. I. Stupp, *Adv. Mater.*, **16**, 589 (2004).

(157) T. Hatano, A.-H. Bae, M. Takeuchi, N. Fujita, K. Kaneko, H. Ihara, M. Takafuji, and S. Shinkai, *Angew. Chem. Int. Ed.*, **43**, 465 (2004).

(158) V. Bocharova, A. Kiriy, H. Vinzelberg, I. Mönch, and M. Stamm, *Angew. Chem. Int. Ed.*, **44**, 6391 (2005).

(159) X. Zhang, W. J. Goux, and S. K. Manohar, *J. Am. Chem. Soc.*, **126**, 4502 (2004).

(160) X. Zhang and S. K. Manohar, *J. Am. Chem. Soc.*, **126**, 12714 (2004).

(161) H. Kong and J. Jang, *Chem. Commun.*, 3010 (2006).

(162) J. Huang and R. B. Kaner, *Chem. Commun.*, 367 (2006).

(163) H. Ding, M. Wan, and Y. Wei, *Adv. Mater.*, **19**, 465 (2007).

(164) N. R. Chiou and A. J. Epstein, *Adv. Mater.*, **17**, 1679 (2005).

(165) J. Jang, J. Bae, and K. Lee, *Polymer*, **46**, 3677 (2005).

(166) N.-R. Chiou, C. Lu, J. Guan, L. J. Lee, and A. J. Epstein, *Nat. Nanotechnol.*, **2**, 354 (2007).

(167) L. Liang, J. Liu, C. F. Windisch, Jr., G. J. Exarhos, and Y. Lin, *Angew. Chem. Int. Ed.*, **41**, 3665 (2002).

(168) H. D. Tran, K. Shin, W. G. Hong, J. M. D'Arcy, R. W. Kojima, B. H. Weiller, and R. B. Kaner, *Macromol. Rapid Commun.*, **28**, 2289 (2007).

(169) R. Dersch, M. Steinhart, U. Boudriot, A. Greiner, and J. H. Wendorff, *Polym. Adv. Technol.*, **16**, 276 (2005).

(170) C. R. Martin and P. Kohli, *Nat. Rev.*, **2**, 29 (2003).

(171) M. R. Abidian, D.-H. Kim, and D. C. Martin, *Adv. Mater.*, **18**, 405 (2006).

(172) M. Steinhart, R. B. Wehrspohn, U. Gösele, and J. H. Wendorff, *Angew. Chem. Int. Ed.*, **43**, 1334 (2004).

(173) M. Steinhart, J. H. Wendorff, A. Greiner, R. B. Wehrspohn, K. Nielsch, J. Schilling, J. Choi, and U. Gösele, *Science*, **296**, 1997 (2002).

(174) J. Jang, K. J. Lee, and Y. Kim, *Chem. Commun.*, 3847 (2005).

(175) V. P. Menon, J. Lei, and C. R. Martin, *Chem. Mater.*, **8**, 2382 (1996).

(176) M. G. Han, and S. H. Foulger, *Chem. Commun.*, 3092 (2005).

(177) R. Xiao, S. I. Cho, R. Liu, and S. B. Lee, *J. Am. Chem. Soc.*, **129**, 4483 (2007).

(178) M. Fu, Y. Zhu, R. Tan, and G. Shi, *Adv. Mater.*, **13**, 1874 (2001).

(179) S. Demoustier-Champagne and P.-Y. Stavaux, *Chem. Mater.*, **11**, 829 (1999).

(180) Z. Liang, A. S. Susha, A. Yu, and F. Caruso, *Adv. Mater.*, **15**, 1849 (2003).

(181) S. Ai, G. Lu, Q. He, and J. Li, *J. Am. Chem. Soc.*, **125**, 11140 (2003).

(182) S. Ko and J. Jang *Biomacromolecules,* **8**, 182 (2007).

(183) K. J. Lee, J. H. Oh, Y. Kim, and J. Jang, *Chem. Mater.,* **18**, 5002 (2006).

(184) S. Ko and J. Jang, *Angew. Chem. Int. Ed.,* **118**, 7726 (2006).

(185) J. Jang, S. Ko, and Y. Kim, *Adv. Funct. Mater.,* **16**, 754 (2006).

(186) J. Jang and J. H. Oh, *Chem. Commun.*, 882 (2004).

(187) J. T. McCann, B. Lim, R. Ostermann, M. Rycenga, M. Marquez, and Y. Xia, *Nano Lett.*, **7**, 2470 (2007).

(188) J. Jang and H. Yoon, *Langmuir*, **21**, 11484 (2005).

(189) J. Jang and H. Yoon, *Chem. Commun.*, 720 (2003).

(190) H. Yoon, M. Chang, and J. Jang, *J. Phys. Chem. B,* **110**, 14074 (2006).

(191) J. Jang and H. Yoon, *Adv. Mater.*, **15**, 2088 (2003).

(192) H. Yoon, M. Chang, and J. Jang, *Adv. Funct. Mater.*, **17**, 431 (2007).

(193) H. Yoon, J.-Y. Hong, and J. Jang, *Small*, **3**, 1774 (2007).

(194) J. Jang and H. Yoon, *Adv. Mater.*, **16**, 799 (2004).

(195) J. Raez, I. Manners, and M. A. Winnik, *J. Am. Chem. Soc.*, **124**, 10381 (2002).

(196) S. Stewart and G. Liu, *Angew. Chem. Int. Ed.*, **39**, 340 (2000).

(197) X. Yan, G. Liu, and Z. Li, *J. Am. Chem. Soc.*, **126**, 10059 (2004).

(198) Z. Li and G. Liu, *Langmuir*, **19**, 10480 (2003).

(199) X. Yan, F. Liu, Z. Li, and G. Liu, *Macromolecules*, **34**, 9112 (2001).

(200) Z. Wei, Z. Zhang, and M. Wan, *Langmuir*, **18**, 917 (2002).

(201) Z. Zhang, Z. Wei, and M. Wan, *Macromolecules*, **35**, 5937 (2002).

(202) K. Huang and M. Wan, *Chem. Mater.*, **14**, 3486 (2002).

(203) J. Stejskal, I. Sapurina, M. Trchová, E. N. Konyushenko, and P. Holler, *Polymer*, **47**, 8253 (2006).

(204) X. Yang, T. Dai, Z. Zhu, and Y. Lu, *Polymer*, **48**, 4021 (2007).

(205) X. Yang, Z. Zhu, T. Dai, and Y. Lu, *Macromol. Rapid Commun.*, **26**, 1736 (2005).

(206) H. P. Hentze and M. Antonietti, *Curr. Opin. Solid State Mater. Sci.*, **5**, 343 (2001).

(207) B. Krause, K. Diekmann, N. F. A. van der Vegt, M. Wessling, *Macromolecules*, **35**, 1738 (2002).

(208) B. Krause, H. J. P. Sijbesma, P. Münüjlü, N. F. A. van der Vegt, and M. Wessling, *Macromolecules*, **34**, 8792 (2001).

(209) T. W. Cornelius, P. Y. Apel, B. Schiedt, C. Trautmann, M. E. Toimil-Molares, S. Karim, and R. Neumann, *Nucl. Instrum. Methods Phys. Res., Sect. B*, **265**, 553 (2007).

(210) P. Y. Apel, Y. E. Korchev, Z. Siwy, R. Spohr, and M. Yoshida, *Nucl. Instrum. Methods Phys. Res., Sect. B*, **184**, 337 (2001).

(211) O. Cuscito, M.-C. Clochard, S. Esnouf, N. Betz, and D. Lairez, *Nucl. Instrum. Methods Phys. Res., Sect. B*, **265**, 309 (2007).

(212) A. S. Zalusky, R. Olayo-Valles, J. H. Wolf, and M. A. Hillmyer, *J. Am. Chem. Soc.*, **124**, 12761 (2002).

(213) T. Xu, H.-C. Kim, J. DeRouchey, C. Seney, C. Levesque, P. Martin, C. M. Stafford, and T. P. Russell, *Polymer*, **42**, 9091 (2001).

(214) U. Jeong, D. Y. Ryu, J. K. Kim, D. H. Kim, T. P. Russell, and C. J. Hawker, *Adv. Mater.*, **15**, 1247 (2003).

(215) T. Hayakawa, T. Kouketsu, M.-A. Kakimoto, H. Yokoyama, and S. Horiuchi, *Macromol. Res.*, **14**, 52 (2006).

(216) J. Jang and J. Bae, *Chem. Commun.*, 1200 (2005).

(217) Y. Meng, D. Gu, F. Zhang, Y. Shi, H. Yang, Z. Li, C. Yu, B. Tu, and D. Zhao, *Angew. Chem. Int. Ed.*, **44**, 7053 (2005).

(218) R. Xing, N. Liu, Y. Liu, H. Wu, Y. Jiang, L. Chen, M. He, and P. Wu, *Adv. Funct. Mater.*, **17**, 2455 (2007).

(219) J. Jang, J. Bae, and E. Park, *Adv. Mater.*, **18**, 354 (2006).

(220) Y. Meng, D. Gu, F. Zhang, Y. Shi, L. Cheng, D. Feng, Z. Wu, Z. Chen, Y. Wan, A. Stein, and D. Zhao, *Chem. Mater.*, **18**, 4447 (2006).

(221) Q. Li, F. Quinn, and F. Caruso, *Adv. Mater.*, **17**, 2058 (2005).

(222) H.-K. Lee, H. Lee, Y. H. Ko, Y. J. Chang, N.-K. Oh, W.-C. Zin, and K. Kim, *Angew. Chem. Int. Ed.*, **40**, 2669 (2001).

(223) J. Jang and B. Lim, *Adv. Mater.*, **14**, 1390 (2002).

(224) A. B. Fuertes, M. Sevilla, S. Álvarez, T. Valdés-Solís, and P. Tartaj, *Adv. Funct. Mater.*, **17**, 2321 (2007).

(225) S. Polarz and M. Antonietti, *Chem. Commun.*, 2593 (2002).

(226) G. Kim, H. Kim, Y. Ko, and Y. Kwon, *Macromol. Res.*, **13**, 499 (2005).

(227) M. Choi, F. Kleietz, D. Liu, H. Y. Lee, W. S. Ahn, and R. Ryoo, *J. Am. Chem. Soc.*, **127**, 1924 (2005).

(228) C. H. Kim, S. S. Kim, F. Guo, T. P. Hogan, and T. J. Pinnavaia, *Adv. Mater.*, **16**, 736 (2004).

(229) M. Choi and R. Ryoo, *Nat. Mater.*, **2**, 473 (2003).

(230) Y. S. Choi, S. H. Joo, S.-A. Lee, D. J. You, H. Kim, C. Pak, H. Chang, and D. Seung, *Macromolecules*, **39**, 3275 (2006).