Macromolecular Research, Vol. 16, No. 2, pp 163-168 (2008)

Fabrication and Characterization of Polystyrene/Gold Nanoparticle Composite Nanofibers

Jung Kil Kim and Heejoon Ahn*

Department of Fiber and Polymer Engineering, Hanyang University, Seoul 133-791, Korea

Received September 21, 2007; Revised November 6, 2007

Abstract: Polystyrene/gold nanoparticle (PS/AuNP) composite fibers were fabricated using an electrospinning technique. Transmission electron microscopy (TEM) showed that the diameters of the naphthalenethiol-capped gold nanoparticles (prior to incorporation into the PS fibers) ranged from 2 to 5 nm. UV-vis spectroscopy revealed the surface plasmon peaks of the gold nanoparticles centered at approximately 512 nm, indicating that nano-sized Au particles are well-dispersed in solution. This was consistent with the TEM observations. The electrospun nanofibers of PS/AuNP composites were approximately 60-3,000 nm in diameter. The surface morphology of the PS/AuNP composite and the dispersability of the Au nanoparticles inside of PS after electrospinning process were investigated by SEM and TEM. The thermal behavior of the pure PS and PS/AuNP nanocomposites and fibers were examined by DSC.

Keywords: electrospinning, gold nanoparticle, nanofibers, polystyrene/gold nanocomposite.

Introduction

Metal nanoparticles are attractive because of their unique electronic, magnetic, optical, thermal, and catalytic properties.[1,2] These properties differ from those of the corresponding bulk materials because of quantum-confinement effects and their very large specific surface area. Gold presents one of the most remarkable cases. Traditionally considered catalytically inactive because it is very stable in the bulk state, it becomes chemically very active when it is dispersed as nanometer-sized particles.[1] The explosion of metal nanoparticle research is driven by extensive technological applications such as magnetic data storage,[3] magneto-optical switches,[4-6] catalysis,[1] quantum electronics,[7-9] molecular sensors,[10,11] biology and biomimetics.[12,13]

Nanoparticles have a tendency to aggregate since they are metastable relative to the equivalent bulk materials due to the positive excess interfacial free energy.[14] Thus, stabilization of nanoparticles against aggregation is a fundamental pre-requisite in nanoparticle science and technology. Nanoparticles may be stabilized by capping with molecular ligands[15] or by protecting them in polymer matrices[16,17] or micellar assemblies.[18] In general, gold nanoparticles can be synthesized by reduction of a gold salt in the presence of an alkanethiol as a capping reagent. This method provides a simple way for the direct synthesis of surface functionalized nanoparticles by using the alkanethiols with various functional groups as stabilizing agents. In terms of functionality, polymer matrices are interesting as an embedding phase because they have a variety of characteristics such as hydrophilic vs. hydrophobic natures, electrical and thermal insulating or conducting properties, and mechanically hard, soft, plastic, or rubbery properties. Thus formation of a polymer-metal nanocomposite is the easiest and most convenient method for gold nanoparticle stabilization and its handling and use.

Polymer-metal nanoparticle composites have been synthesized by the condensation of metal vapors into liquid monomers and subsequent polymerization,[19,20] by emulsion polymerization in the presence of nanoparticles,[21] and by electrosynthesis at liquid-liquid interfaces.[22] Sarma *et al.* synthesized gold nanoparticle-polyaniline composites using H_2O_2 as a reducing agent for gold salts and an oxidizing agent for aniline.[23] Polymer-metal nanoparticle composites have found potential applications in catalysts, photonic and electric sensors, filters, and artificial tissue engineering.[24]

Electrospinning is a novel processing technique for the production of fibers with diameters in the range of a few nanometers to tens of micrometers.[25-27] This technique is very simple and cost effective. The formation of electrospun fibers can be initiated by applying high voltages between a needle and a target electrode. The needle is connected to a syringe containing the polymer solution. If the applied voltage overcomes the surface tension of the poly-

*Corresponding Author. E-mail: ahn@hanyang.ac.kr

mer solution droplet which is formed at the tip of the needle, then the polymer solution jet is launched from the tip and accelerated towards the target electrode. As the jet travels through air, the jet is elongated and fibers are solidified by solvent evaporation, then the dried electro-spun fibers are collected on the target. Many types of polymers have been successfully electro-spun into micro- and nanofibers. Recently, electrospinning technology has been used for fabricating polymer/inorganic nanoparticle composite fibers.[28] Preparation of metal nanoparticles dispersed in polymer fibers is of particular interest because the metal/polymer nanocomposite fibers can achieve the combined distinctive properties of polymer fibers and metal nanoparticles. Silver nanoparticle-embedded polymer nanofibers have been intensively studied due to their potential applications in biomedical field such as tissue scaffolds, antimicrobial filters, and wound dressing materials.[29-31] However, there are limited numbers of reports about gold nanoparticle/polymer composite fibers. Kim *et al.* fabricated one-dimensional arrays of dodecanethiol-capped gold nanoparticles within semicrystalline poly(ethylene oxide) (PEO) nanofibers.[32] Yang *et al.* prepared poly(vinyl alcohol) (PVA) and poly(vinyl pyrrolidone) (PVP) nanofibers embedded with gold nanoparticles without any capping molecules.[33,34]

In this study, we have fabricated polystyrene/gold nanoparticle (PS/AuNP) composite nanofibers using electrospinning method. The optical properties of naphthalenethiol-capped gold nanoparticle are measured by UV-vis spectroscopy. The morphology of and size distribution of nanocomposite fibers and gold nanoparticles are observed by scanning and transmission electron microscopies (SEM and TEM), respectively. The effect of the concentration of the gold nanoparticles on the thermal properties of PS fibers is investigated using differential scanning calorimetry (DSC).

Experimental

Materials. Polystyrene (PS, M_w=230,000), naphthalenethiol, hydrogen tetrachloroaurate ($HAuCl_4$), tetraoctylammonium bromide, sodium borohydride ($NaBH_4$), *N,N*-dimethylformamide (DMF), chloroform, toluene, and dichloromethane (DCM) were purchased from Aldrich and used as received. For electrospinning, the polystyrene/gold nanoparticle composite solutions (20 wt%) were prepared in DMF at room temperature. The weight ratios of gold nanoparticle to polystyrene were 1/10, 1/100, 1/1,000, and 1/10,000.

Synthesis of the Naphthalenethiol-capped Gold Nanoparticle. The synthesis of the naphthalenethiol-capped gold nanoparticle was performed by modifying Brust's method.[35] Briefly, hydrogen tetrachloroaurate ($HAuCl_4$) was transferred by a phase-transfer reagent, tetraoctylammonium bromide, into a dichloromethane solution of naphthalenethiol and was subsequently reduced by adding aqueous sodium borohydride ($NaBH_4$). The naphthalenethiol reacts with the neutral gold surfaces to form gold-sulfur thiolate bonds, and the growth of the Au nanoparticles is terminated when their surfaces are completely covered by naphthalenethiol molecules. The naphthalenethiol-capped Au nanoparticles were precipitated with methanol and redissolved in DMF to prepare PS/AuNP nanocomposites.

Electrospinning. The electrospinning equipment consisted of three major parts: a high voltage power supply, a spinneret, and an electrically conductive collector. In a typical procedure, the polymer solution was loaded into a plastic syringe which was assembled with a stainless steel connector and a needle (30 gauge). The stainless steel connector was connected to a high voltage power supply that is capable of generating DC voltages up to 30 kV. The polymer solution was continuously supplied using a syringe pump (KDS-200, Stoelting, Wood Dale, IL) at various flow rates. The distance between the needle tip and the collector was 20 cm. The syringe pump, needle, electrode, and grounded target were all enclosed in order to reduce the effect of air currents on the trajectory of the electro-spun jet.

Characterization. TEM studies were performed using a field-emission transmission electron microscope (FE-TEM) (JEM2100F, JEOL) fitted with a LaB6 filament at 200 kV. The naphthalenethiol-capped gold nanoparticles were deposited onto a carbon-coated copper grid by drop casting from a 0.1 mg/mL dichloromethane solution. Electro-spun PS and PS/AuNP composite nanofibers were collected on carbon-coated copper grids and aluminum foils for TEM and SEM measurements, respectively. The collected fibers were dried at 30 °C under vacuum for one day to evaporate any residual solvent. SEM images were acquired using a field-emission scanning electron microscope (JSM-6700F FE-SEM, JEOL) operated at accelerating voltages of 5 and 15 kV, and the samples were coated with Au/Pd before imaging. UV-visible spectroscopy was performed using a Shimadzu UV-1650PC spectrometer. DSC measurements were conducted with a TA Instruments DSC-2910 under a nitrogen atmosphere. The samples were sealed in aluminum pans and heated and cooled at a rate of 10 °C/min.

Results and Discussion

The size and shape of the naphthalenethiol-capped Au nanoparticles were characterized by TEM. Figure 1 shows representative TEM images of the naphthalenethiol-capped Au nanoparticles on a carbon-coated copper grid. As shown in Figure 1(a), the Au nanoparticles are spherical shape and exhibit a narrow distribution. The mean size and standard deviation of the Au nanoparticles are 2.5 and 0.25 nm, respectively. The crystal lattice fringes of an individual Au nanoparticle also can be observed by FE-TEM. The crystal lattice fringes of the Au nanoparticle calculated from Figure 1(b) is about 0.24 nm which corresponds to the (111) lattice planes of the face centered cubic (fcc) crystal. An interest-

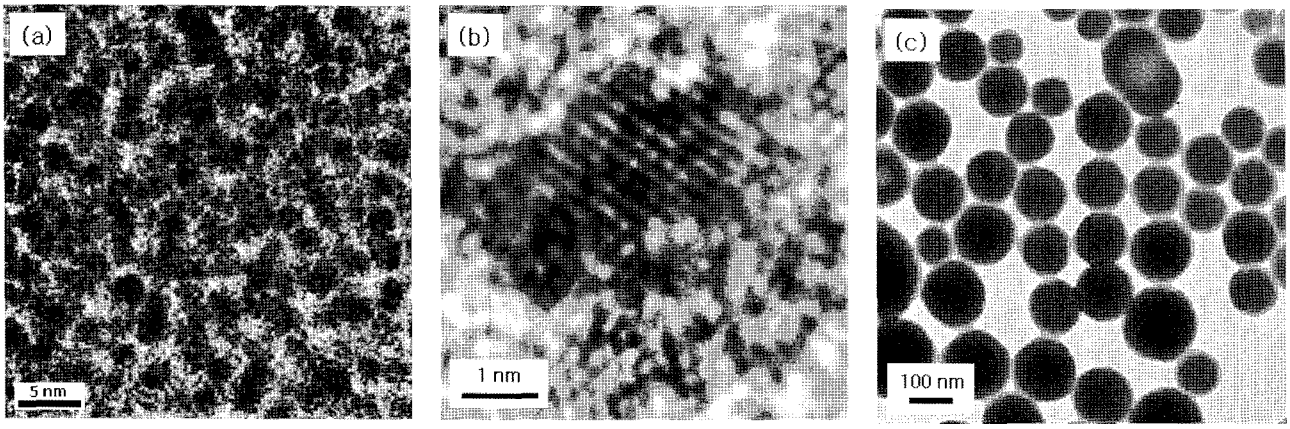

Figure 1. FE-TEM images of naphthalenethiol-capped Au nanoparticles at different magnifications.

ing feature observed on naphthalenethiol-capped Au nanoparticles at lower TEM magnification is that individual Au nanoparticles aggregate and form larger spheres with diameters of 118±45 nm, as shown in Figure 1(c). Note that Figures 1(a)-1(c) are obtained from same sample. Only the magnifications are different. During drying of the gold solution for TEM analysis, the individual gold nanoparticle which was well-dispersed in dichloromethane solution has aggregated on the copper grid. This explains why we observe lager size of agglomerated Au nanoparticles.

Figure 2 displays UV-visible absorption spectra of the naphthalenethiol-capped Au nanoparticle solutions in chloroform, toluene, and *N,N*-dimethylformamide. The absorption spectra exhibit maximum peaks at about 512 nm. These absorption peaks correspond to the surface plasmon band of Au nanoparticles, suggesting that the isolated nanometer-sized Au particles are well-dispersed in the solutions.[36] This observation is consistent with the TEM results.

The effect of the concentration of the gold nanoparticles in polymer solution on the morphology of the electro-spun nanofibers has been characterized using scanning electron microscopy (SEM). Figure 3 shows SEM images of the PS/AuNP composite nanofibers electro-spun from PS/AuNP nanocomposite solutions with various concentrations of naphthalenethiol-capped Au nanoparticles. The nanoparticle-to-polystyrene weight ratios (Au/PS) are 1/10, 1/100, 1/1,000, and 1/10,000. The fibers were electro-spun from a 20 wt.% nanocomposite solution in DMF at 25 kV, and the dis-

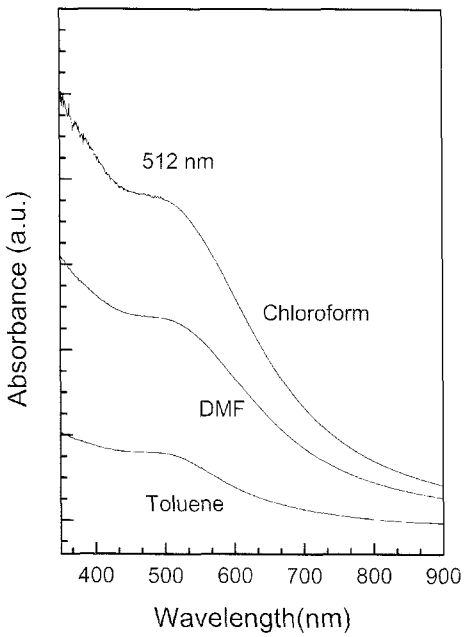

Figure 2. UV-vis absorption spectra of naphthalenethiol-capped Au nanoparticle solutions in chloroform, toluene, and dichloromethane.

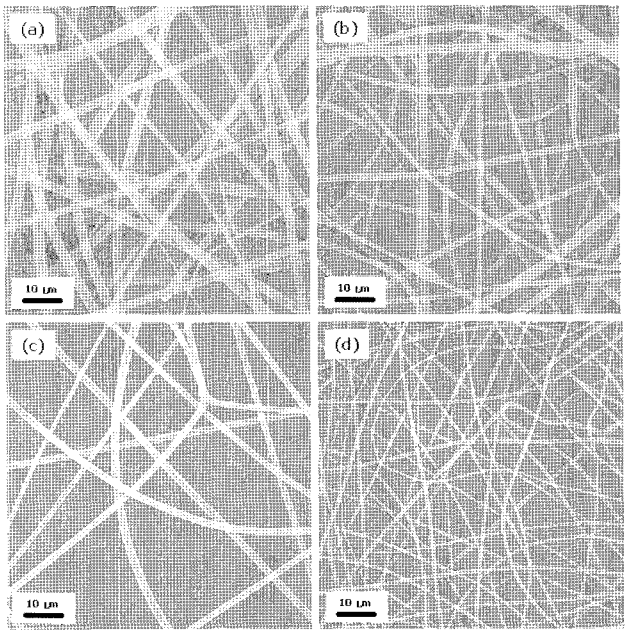

Figure 3. SEM images of electro-spun PS/AuNP composite nanofibers. The weight ratios of Au/PS are (a) 1/10,000, (b) 1/1,000, (c) 1/100, and (d) 1/10.

tance from tip to collector was kept at 20 cm. The average diameters of the electro-spun nanofibers are 2.8, 1.9, 1.7, and 0.9 μm for the nanocomposites with the Au/PS ratios of 1/10,000, 1/1,000, 1/100, and 1/10, respectively. The observed decrease in diameter of the PS/AuNP composite nanofibers with increasing Au nanoparticle content may be due to the increased conductivity of the nanocomposite solutions. Yang *et al.* reported that the conductivity of PVA solutions was enhanced with increasing content of gold nanoparticles in solution.[34] It is known that the charge density of a solution increases with addition of metal nanoparticles. The resultant polymer nanocomposite solution forms thinner electro-spun fibers because stronger elongation forces are imposed on the ejected jets in the electric field.[37] These reports consistently suggest that the addition of gold nanoparticles in a PS solution plays a predominant role in the increased conductivity, resulting in thinner electro-spun fibers. If the content of the gold in the PS could be made high enough to exhibit adequate conductivity, it is possible that the Au/PS composite could be used as a new type of electromagnetic shielding material, based on fibrous mats, for sensitive electronic equipment.

The surface morphology of the electro-spun PS/AuNP composite nanofibers has been analyzed with SEM. Figure 4 shows high magnification SEM images of the same composite nanofibers shown in Figure 3. The composite nanofibers with Au/PS ratios of 1/10,000 and 1/1,000 (Figures 4(a) and 4(b)) exhibit smooth surfaces. However, the surfaces of the composite nanofibers with the ratios of 1/100 and 1/10 (Figures 4(c) and 4(d)) are rather rough. In the case of Au/PS ratios of 1/100 and 1/10, it is also observed that the Au nanoparticles reside on the PS fiber surfaces.

Figure 5 shows TEM images of the electro-spun PS/AuNP composite nanofibers with various concentrations of gold nanoparticles in the polymer solutions. As shown in the figures, the Au nanoparticles appear as small dark spots. In the case of Au/PS ratios of 1/10,000 and 1/1,000, the density of the Au nanoparticles is very low. However, the density of the Au nanoparticles in the PS fibers increases as the Au/PS ratio increases, as shown in Figures 5(c) and 5(d). It is also observed in the TEM images that the Au nanoparticles are well-dispersed in the PS fibers. Kim *et al.* observed one-dimensionally arranged Au nanoparticles within electro-spun poly(ethylene oxide) (PEO) fibers.[32] In this case, semicrystalline PEO was employed as a template for the arranged Au nanoparticles. In contrast, for the PS/AuNP nanocomposite system, the naphthalenethiol-capped Au nanoparticles are almost homogeneously distributed into PS fibers (without any arrangement), as shown in Figures 5(c) and 5(d). DSC has been performed to verify the presence of crystalline structures in pure PS or PS/AuNP nanocomposites in the form of film and electrospun fibers. No endo- or exothermal peaks are observed for any samples during the heating and cooling stages of DSC. This indicates that all samples are completely amorphous rather than crystalline. This result is consistent with the Au nanoparticles being almost homogeneously dispersed (with no order) into the PS fibers.

Additional thermal properties of the PS/AuNP composite films and fibers have been investigated by DSC. Table I summarizes the glass transition temperatures (T_g) for PS and

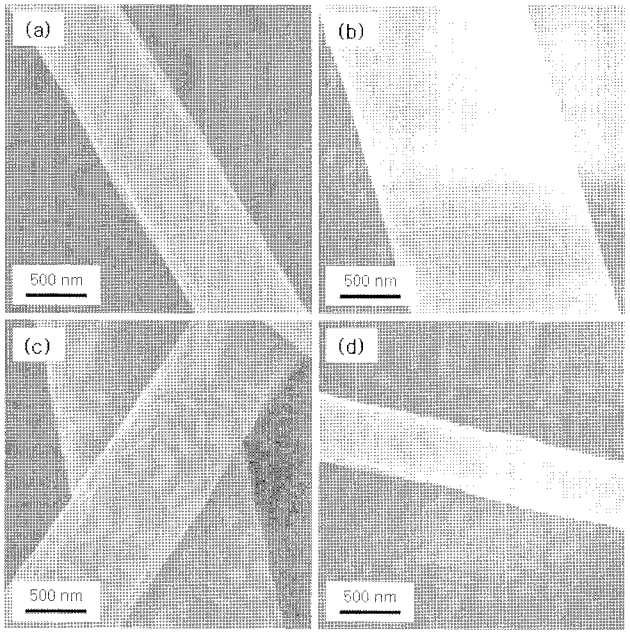

Figure 4. High magnification SEM images of electro-spun PS/AuNP composite nanofibers. The weight ratios of Au/PS are (a) 1/10,000, (b) 1/1,000, (c) 1/100, and (d) 1/10.

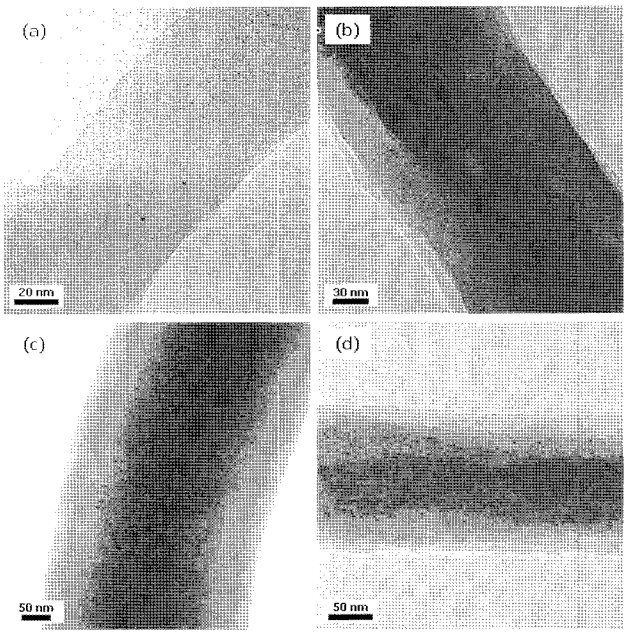

Figure 5. TEM images of electro-spun PS/AuNP composite nanofibers. The weight ratios of Au/PS are (a) 1/10,000, (b) 1/1,000, (c) 1/100, and (d) 1/10.

Table I. Glass Transition Temperatures for PS/AuNP Nanocomposites and Electro-Spun PS/AuNP Nanocomposite Nanofibers with Various Au Concentrations in the Composites

Au/PS Ratio	Glass Transition Temperature (°C)	
	Nanocomposite	Nanocomposite Fiber
Pure PS	102.33	98.03
1/10,000	99.80	96.78
1/1,000	99.63	96.16
1/100	96.44	95.12
1/10	92.41	92.96

PS/AuNP composite films and electro-spun fibers. It is interesting to note that the T_g of PS decreases as the amount of the Au nanoparticle in PS increases for both films and fibers. Balan *et al.* reported that the T_g of acrylic polymers slightly increased with additions of bismuth nanoparticles up to 0.5 wt%, but the T_g for the composite with 1 wt% Bi was lower than that for pure acrylic polymer.[38] The decrease of the T_g of polymers with addition of metal nanoparticles can be explained if it is assumed that the metal nanoparticles behave as plasticizers. In general, plasticizers act as a low molecular weight fraction in a high molecular weight polymer and can contribute to raising the free volume of the total plasticized polymers, which results in a decrease in the T_g of the polymer. In addition to acting as a low molecular weight fraction, the plasticizers may also reduce intermolecular forces between polymer molecules. Thus, the lower T_g values for PS/AuNP nanocomposites, compared to that for pure PS, might be due to the increased free volume of the polymer and reduced intermolecular force between PS molecules caused by the addition of Au nanoparticle into PS. It is also interesting to notice that the T_g values for PS and PS/AuNP nanocomposites shift slightly to lower values after the electrospinning process.

Conclusions

Polystyrene and naphthalenethiol-capped Au nanoparticle composite nanofibers have been fabricated using an electrospinning technique. The Au nanoparticles, with an average diameter of 2.5 nm, are homogeneously dispersed inside and on the surface of PS fibers after electrospinning. The surface of the PS fibers becomes rougher as the Au content increases. Electro-spun composite nanofibers have a broad range of diameters from tens of nanometers to several micrometers. The diameters of the PS/AuNP composite nanofibers gradually decrease with increasing Au content in the nanocomposite due to the increased conductivity of PS/Au solutions. The glass transition temperature of PS shifts to lower values with increasing Au content, which may be due to the fact that the naphthalenethiol-capped gold nanoparticles reduce the interaction between PS molecules.

Acknowledgements. This work was financially supported by KOSEF (grant No. R01-2006-000-10489-0), Seoul City (R&BD Program: 10919) and KICOS (No. K20501000002-07-E0100-00210). H. A. acknowledges the assistance of Dr. Dong Wook Kim for DSC measurement.

References

(1) U. Heiz and U. Landman, *Nanocatalysis*, Springer, Berlin, 2007.
(2) K. H. A. Lau, W. Knoll, and D. H. Kim, *Macromol. Res.*, **15**, 211 (2007).
(3) G. I. Frolov, *Tech. Phys.*, **46**, 1537 (2001).
(4) G. Shemer and G. Markovich, *J. Phys. Chem. B*, **106**, 9195 (2002).
(5) O. A. Aktsipetrov, *Coll. Surf. A*, **202**, 165 (2002).
(6) J. L. Menéndez, B. Bescós, G. Armelles, R. Serna, J. Gonzalo, R. Doole, A. K. Petford-Long, and M. I. Alonso, *Phys. Rev. B*, **65**, 205413 (2002).
(7) A. B. Kharitonov, A. N. Shipway, and I. Willner, *Anal. Chem.*, **71**, 5441, (1999).
(8) A. B. Kharitonov, A. N. Shipway, E. Katz, and I. Willner, *Rev. Anal. Chem.*, **18**, 255, (1999).
(9) V. Pardo-Yissar, R. Gabai, A. N. Shipway, T. Bourenko, and I. Willner, *Adv. Mater.*, **13**, 1320, (2001).
(10) A. K. Boal and V. M. Rotello, *J. Am. Chem. Soc.*, **124**, 5019 (2002).
(11) A. K. Boal and V. M. Rotello, *J. Am. Chem. Soc.*, **122**, 734 (2000).
(12) S.-D. Oh, B.-S. Byun, S. Lee, and S. H. Choi, *Macromol. Res.*, **14**, 194 (2006).
(13) S.-D. Oh, B.-S. Byun, S. Lee, S. H. Choi, M. I. Kim, and H. J. Park, *Macromol. Res.*, **15**, 285 (2007).
(14) Z. Lin, B. Gilbert, Q. Liu, G. Ren, and F. Huang, *J. Am. Chem. Soc.*, **128**, 6126 (2006).
(15) G. Schmid, B. Morun, and J. -O. Malm, *Angew. Chem. Int. Ed. Engl.*, **28**, 778 (1989).
(16) S. V. Manorama, K. M. Reddy, C. V. G. Reddy, S. Narayanan, P. R. Paja, and P. R. Chatterji, *J. Phys. Chem. Solids*, **63**, 135 (2002).
(17) Y. Zhou, H. Itoh, T. Uemura, K. Naka, and Y. Chujo, *Langmuir*, **18**, 5287 (2002).
(18) C. Park, M. Rhue, J. Lim, and C. Kim, *Macromol. Res.*, **15**, 39 (2007).
(19) K. J. Klabunde, J. Habdas, and G. Cárdenas-Triviño, *Chem. Mater.*, **1**, 481 (1989).
(20) M. S. El-Shall and W. Slack, *Macromolecules*, **28**, 8456 (1995).
(21) L. Quaroni and G. Chumanov, *J. Am. Chem. Soc.*, **121**, 10642 (1999).
(22) C. Johans, J. Clohessy, S. Fantini, K. Kontturi, and V. J. Cunnane, *Electrochem. Commun.*, **4**, 227 (2002).
(23) T. K. Sarma, D. Chowdhury, A. Paul, and A. Chattopadhyay, *Chem. Commun.*, 1048 (2002).
(24) L. Nicolais and G. Carotenuto, *Metal-polymer nanocompos-*

ites, Wiley, New Jersey, 2005.
(25) D. I. Cha, K. W. Kim, G. H. Chu, H. Y. Kim, K. H. Lee, and N. Bhattarai, *Macromol. Res.*, **14**, 331 (2006).
(26) K. Park, H. J. Jung, J. J. Kim, K.-D. Ahn, D. K. Han, and Y. M. Ju, *Macromol. Res.*, **14**, 552 (2006).
(27) Y. H. Jung, H. Y. Kim, D. R. Lee, S. Y. Park, and M. S. Khil, *Macromol. Res.*, **13**, 385 (2005).
(28) Z.-M. Auang, Y.-Z. Zhang, M. Kotaki, and S. Ramakrishna, *Composites Sci. Tech.*, **63**, 2223 (2003).
(29) W. K. Son, J. H. Youk, T. S. Lee, and W. H. Park, *Macromol. Rapid Commun.*, **25**, 1632 (2004).
(30) H. Park, K. Y. Lee, S. J. Lee, K. E. Park, and W. H. Park, *Macromol. Res.*, **15**, 238 (2007).
(31) Q. L. Feng, J. Wu, G. Q. Chen, F. Z. Cui, T. N. Kim, and J. O. Kim, *J. Biomed. Mater. Res.*, **52**, 662 (2000).
(32) G.-M. Kim, A. Wutzler, H.-J. Radusch, G. H. Michler, P. Simon, R. A. Sperling, and W. J. Parak, *Chem. Mater.*, **17**, 4949 (2005).
(33) J. Bai, Y. Li, S. Yang, J. Du, S. Wang, J. Zheng, Y. Wang, Q. Yang, X. Chen, and X. Jing, *Solid State Commun.*, **141**, 292 (2007).
(34) Y. Wang, Y. Li, G. Sun, G. Zhang, H. Liu, J. Du, S. Yang, J. Bai, and Q. Yang, *J. Appl. Polym. Sci.*, **105**, 3618 (2007).
(35) M. Brust, M. Walker, D. Bethell, D. J. Schiffrin, and R. Whyman, *J. Chem. Soc., Chem. Commun.*, 801 (1994).
(36) P. Mulvaney, *Langmuir*, **12**, 788 (1996).
(37) W. K. Son, J. H. Youk, T. S. Lee, and W. H. Park, *Polymer*, **45**, 2959 (2004).
(38) L. Balan and D. Burget, *Eur. Polym. J.*, **42**, 3180 (2006).