

Formation of Silver Nanoparticles Created *In Situ* in an Amphiphilic Block Copolymer Film

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ABSTRACT: In this work, silver nanoparticles were synthesized with an amphiphilic diblock copolymer, polystyrene-*block*-poly(1-vinyl-2-pyrrolidone) (PS-*b*-PVP), as a template film. First, microphase-separated amphiphilic PS-*b*-PVP (70 : 30 wt %) was synthesized through atom transfer radical polymerization. The self-assembled block copolymer film was used to template the growth of silver nanoparticles by the introduction of a silver trifluoromethanesulfonate precursor and an ultraviolet irradiation process. The *in situ* formation of silver nanoparticles with an average size of 4–6 nm within the block copolymer template film was confirmed with transmission electron microscopy, ultraviolet–visible spectroscopy, and wide-angle X-ray

scattering. Fourier transform infrared spectroscopy also demonstrated the selective incorporation and *in situ* formation of silver nanoparticles within the hydrophilic poly(1-vinyl-2-pyrrolidone) domains, which were mostly due to the stronger interaction strength of the silver with the carbonyl oxygens of poly(1-vinyl-2-pyrrolidone) in the block copolymer. This work provides a simple route for the *in situ* synthesis of silver nanoparticles within a polymer film. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2352–2357, 2008

Key words: atom transfer radical polymerization (ATRP); block copolymers; nanocomposites

INTRODUCTION

Interest in nanoparticles and nanostructured materials has been fueled by continuous discoveries of their new and unique properties that are not often present on a larger scale.^{1–3} It has been well recognized that the unique properties of nanomaterials stem from their small size and large specific surface area. These materials are central to fundamental studies in nanotechnology, and they are effectively applied in the fields of catalysis,⁴ electrochemistry,⁵ and photoluminescence.⁶ Thus, much effort has recently been devoted to the development of functional nanoparticles, opening new opportunities for constructing equally functional nanostructures.^{7–11}

Among such materials, silver nanoparticles have been intensively studied because of their intriguing optical, electronic, magnetic, and mechanical properties.^{12–14} In particular, silver nanoparticles play an important role in applications in antimicrobial activity,¹⁵ catalysis,¹⁶ surface-enhanced Raman spectroscopy,¹⁷ and facilitated olefin transport.¹⁸ Many meth-

ods have been developed for synthesizing silver nanoparticles, primarily based on a solution synthesis containing a liquid medium, reductants, and surfactants. A template-assisted nanofabrication strategy based on self-assembled nanostructures is one promising method for macroscopically manipulating nanopatterned surfaces. In this method, metal nanoparticles can be prepared by the *in situ* reduction of metal ions within a polymer template film with H₂ gas,¹⁹ a heat treatment,²⁰ a solution of NaBH₄,²¹ and γ /ultraviolet (UV) irradiation.^{22,23} Recently, the Buriak group^{24,25} described block copolymer templating of semiconductor surface chemistry, using the block copolymer to direct chemical reactions with the surface in a spatially defined manner. The Composto group²⁶ also presented a novel one-step assembly process that encompasses the *in situ* formation of silver nanoparticles, directed assembly of block copolymers into a perpendicular lamellar morphology, and nanoparticle organization into patterned arrays.

In this work, we synthesized a microphase-separated diblock copolymer, that is, polystyrene-*block*-poly(1-vinyl-2-pyrrolidone) (PS-*b*-PVP; 70 : 30 wt %) through atom transfer radical polymerization (ATRP) and detailed the use of the block copolymer as a template film to synthesize silver nanoparticles. Silver nanoparticles were *in situ* prepared within the block copolymer template by the reduction of a silver trifluoromethanesulfonate (AgCF₃SO₃) precursor under UV irradiation. The resultant systems were

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characterized with transmission electron microscopy (TEM), ultraviolet-visible (UV-vis) spectroscopy, wide-angle X-ray scattering (WAXS), and Fourier transform infrared (FTIR) spectroscopy.

EXPERIMENTAL

Materials

AgCF₃SO₃ (>99%), styrene (99%), 1-vinyl-2-pyrrolidone (>99%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA; 99%), copper(I) chloride (CuCl, 99%), and methyl 2-bromopropionate (MBP) were purchased from Aldrich (St. Louis, MO) and used as received without further purification.

Synthesis of the bromine-terminated polystyrene (PS-Br) macroinitiator

In a 250-mL, pear-shaped flask, 20 g of styrene, 0.296 g of CuCl, and 1.24 mL of HMTETA were added, and then the green mixture was stirred until it was a homogeneous solution. Nitrogen was purged to the solution for 30 min, and then 0.22 mL of MBP was added. The mixture was placed in a 110°C oil bath for 5 h. After polymerization, the resultant polymer was diluted with tetrahydrofuran (THF). After the solution was passed through a column with activated Al₂O₃ to remove the catalyst, it was precipitated into methanol. The PS-Br macroinitiator was obtained and dried in a vacuum oven overnight at room temperature.

Synthesis of the PS-*b*-PVP diblock copolymer

PS-Br (6 g) was dissolved in 30 mL of anisole with stirring. 1-Vinyl-2-pyrrolidone (6 g), 0.0888 g of CuCl, and 0.372 mL of HMTETA were added to the solution. The green mixture was stirred until it was a homogeneous solution and then purged with nitrogen for 30 min. The mixture was placed in a 90°C oil bath for 24 h. After polymerization, the resultant block copolymer was diluted with THF. After the passage of the solution through a column with activated Al₂O₃ to remove the catalyst, it was precipitated into methanol. The PS-*b*-PVP diblock copolymer was obtained and dried in a vacuum oven overnight at room temperature.

Formation of silver nanoparticles

Predetermined amounts of the diblock copolymer and AgCF₃SO₃ were dissolved in THF to make up 1 wt % polymer solutions. The concentration of silver salt was fixed at 20 wt % with respect to the polymer. The polymer/silver salt solutions were dropped and spread with a micropipette on the slide

glass. The samples were dried under a nitrogen atmosphere for 2 h at room temperature and further dried in a vacuum oven for 2 days. UV irradiation was performed with a UV hand lamp (UVilite, UVitec, Cambridge, UK) at 254 nm with a distance of 1 mm between the sample and lamp.

Characterization

Proton nuclear magnetic resonance (¹H-NMR) measurements were performed with a 600-MHz, high-resolution NMR spectrometer (Avance 600 MHz FT NMR, Bruker, Ettlingen, Germany). FTIR spectra of the samples were collected with an Excalibur Series FTIR instrument (Digilab Co., Hannover, Germany) in the frequency range of 4000–400 cm⁻¹ with an attenuated total reflection facility. TEM pictures were obtained with a Philips CM30 microscope (Hillsboro, OR) operating at 300 kV to observe silver nanoparticles resulting from the reduction of silver ions. For TEM measurements, the dried films were dissolved in THF, and then a drop of this colloidal silver dispersion was placed on a standard copper grid. UV-vis spectroscopy was measured with a spectrophotometer (Hewlett-Packard, Hayward, CA) in the range of 300–800 nm. The WAXS experiment was carried out on a Rigaku 18-kW rotating-anode X-ray generator (Berlin, Germany) with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) operated at 40 kV and 300 mA. The 2θ range was 4–40° with a scanning speed of 3°/min, and the distance from the sample to the detector was 185 mm.

RESULTS AND DISCUSSION

Synthesis of the block copolymer

Controlled radical polymerization has been firmly established as an efficient method for the synthesis of polymers with a low polydispersity and a degree of polymerization predetermined by the monomer-to-initiator ratio.²⁷ Among living radical polymerizations, ATRP is attractive because of the rapid and reversible exchange between low concentrations of growing radicals and dormant species.²⁸ ATRP for the PS-*b*-PVP diblock copolymer was carried out with a procedure reported in the literature.^{24,25} The first step, which produced PS-Br, involved the homopolymerization of styrene in bulk at 110°C for 5 h in the presence of MBP, CuCl, and HMTETA. The obtained polystyrene (PS) exhibited a narrow molecular distribution (polydispersity index = 1.3) and a molecular weight of 14,000 g/mol, as determined by gel permeation chromatography. The yield of polymerization was as high as 90%. The PS-*b*-PVP diblock copolymer was then synthesized with PS-Br and CuCl/HMTETA as a macroinitiator and catalyst/ligand, respectively. The resultant diblock

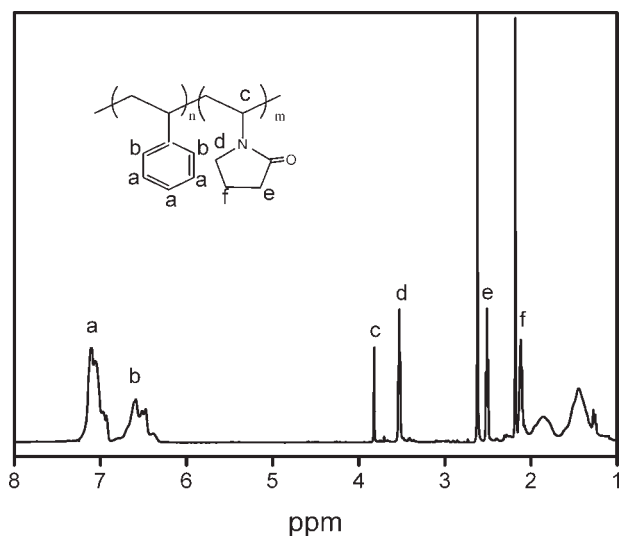


Figure 1 $^1\text{H-NMR}$ spectrum of the PS-*b*-PVP diblock copolymer.

copolymer showed a narrow molecular distribution (polydispersity index = 1.4) and a molecular weight of 20,000 g/mol.

The chemical structure and composition of the diblock copolymer were investigated with $^1\text{H-NMR}$ spectroscopy. Figure 1 shows the $^1\text{H-NMR}$ spectrum of the PS-*b*-PVP diblock copolymer. The signals at 7.1–7.0 (a) and 6.6–6.5 ppm (b) were attributed to benzene groups of PS. The signals at 3.8 (c), 3.5 (d), 2.5 (e), and 2.1 ppm (f) resulted from the poly(1-vinyl-2-pyrrolidone) (PVP) block. The $^1\text{H-NMR}$ spectrum shows that the diblock copolymer PS-*b*-PVP had a composition of 70 : 30 wt % and that the synthesis via ATRP was successful.

Figure 2 presents the FTIR spectra of the PS homopolymer and PS-*b*-PVP diblock copolymer synthe-

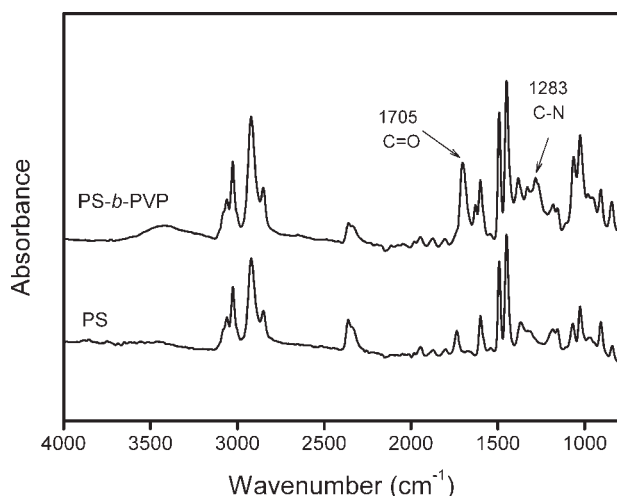


Figure 2 FTIR spectra of the PS homopolymer and PS-*b*-PVP diblock copolymer.

sized by ATRP. The aromatic C=C stretching modes of neat PS produced four peaks at 1630, 1600, 1494, and 1451 cm^{-1} . Upon diblock copolymerization, new stretching bands appeared at 1705 and 1283 cm^{-1} , which were assigned to C=O and C–N of PVP, respectively. These FTIR spectroscopy results are also clear evidence of the sequential synthesis of the triblock copolymer by ATRP.

Formation of the silver nanoparticles

The molecular structure of the block copolymer, that is, PS-*b*-PVP, and a schematic diagram detailing the process of formation of silver nanoparticles created *in situ* in the amphiphilic block copolymer film are provided in Figure 3. The microphase-separated PS-*b*-PVP, consisting of hydrophilic PVP and hydrophobic PS domains, was used as a template film. The chemical dissimilarity between the two polymer segments was sufficient for self-assembly in a solid film. The carbonyl oxygens (C=O) of the PVP domains are well established to associate with silver ions or complexes via direct coordination to metal ions.^{29,30} On the other hand, the PS domains are expected not to confine silver ions, producing a microphase-separated structure. Because silver salts have hydrophilic properties, most of the salts are expected to be selectively reduced in hydrophilic PVP domains. As a

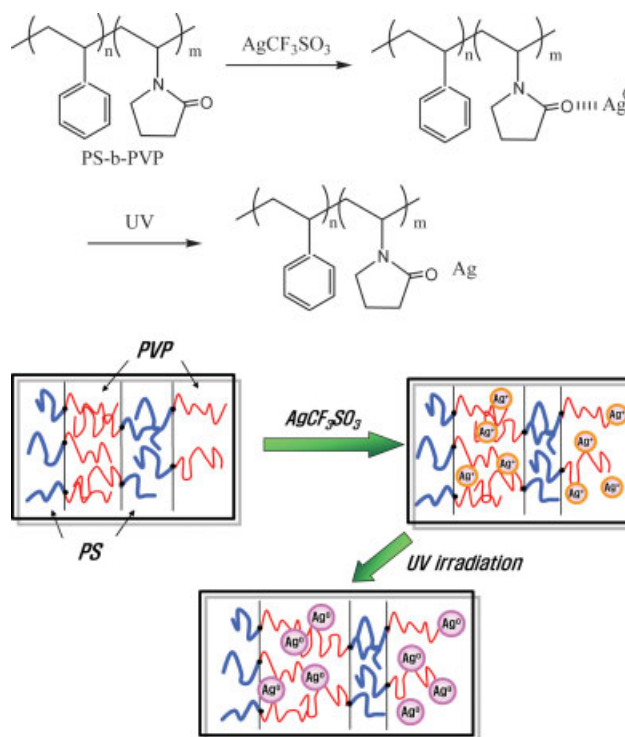


Figure 3 Schematic process of the *in situ* formation of silver nanoparticles created in a PS-*b*-PVP film. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

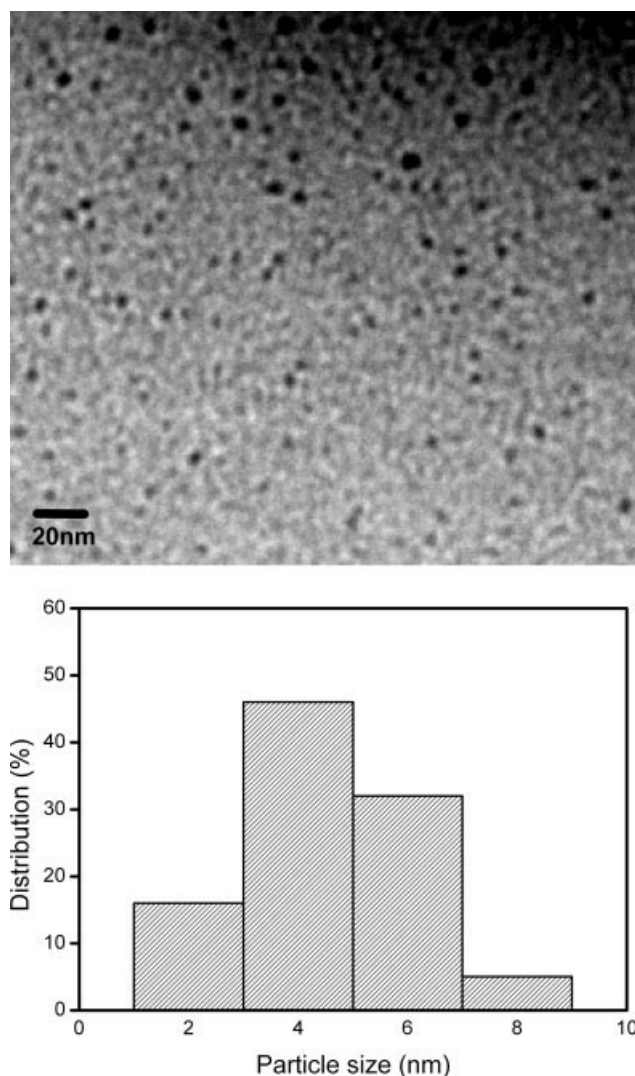


Figure 4 TEM micrograph of silver nanoparticles created *in situ* in a PS-*b*-PVP/AgCF₃SO₃ film by UV irradiation for 60 min.

result, the silver nanoparticles might be arranged in patterns that reflect the underlying morphologies of the block copolymers.

It has been reported that materials containing ethylene oxides or carbonyl oxygens can readily reduce silver ions to silver nanoparticles through the oxidation of their oxygen groups, and this indicates that the PVP domains of the copolymer may play a similar role in the reduction of silver ions.^{31,32} The formation and size of silver nanoparticles created *in situ* in the block copolymer film by UV irradiation were monitored with TEM micrographs. The TEM results of Figure 4 indicate that the silver nanoparticles created in the PS-*b*-PVP/AgCF₃SO₃ film ranged in size from 2 to 8 nm, and the majority of the nanoparticles were 4–6 nm without agglomerated particles. It was also found that the amphiphilic PS-*b*-PVP block copolymer self-assembled molecularly

into continuous hydrophobic nanophase domains of PS (light region) and isolated hydrophilic domains of PVP domains (dark region). Silver nanoparticles with an average size of 4–6 nm remained confined to the hydrophilic PVP domains of the amphiphilic block copolymer, presumably because of the specific interaction between the nanoparticles and the carbonyl oxygens of PVP domains. This result presents the effective control of the graft copolymer film for the formation of silver nanoparticles.

UV-vis absorption spectra are known to be quite effective in monitoring the formation of silver nanoparticles. Figure 5 presents the UV-vis absorption spectra for a PS-*b*-PVP/AgCF₃SO₃ film with increasing UV irradiation times. Before UV irradiation (0 min), there was no distinguishable UV absorption for the PS-*b*-PVP/AgCF₃SO₃ film. However, after UV irradiation, one strong UV absorption peak centered around 415 nm was observed, corresponding to the plasmon excitation of silver nanoparticles. It is generally accepted that the absorption peak whose maximum occurs around 410–420 nm is related to the formation of silver metal nanoparticles.^{19–23} It is also known that its magnitude correlates to the concentration of silver nanoparticles, whereas the peak position is related to the size of the silver nanoparticles.^{19–23} The plasmon peak for the PS-*b*-PVP/AgCF₃SO₃ film continuously grew with the increases in the UV irradiation time, indicating the increase in the silver nanoparticles in number. This result might be due to the effective protecting role of PVP as well as a reducing role, implying that the formation of silver nanoparticles is effectively controlled.

To confirm the formation of silver nanoparticles created in the block copolymer film, WAXS spectra were measured for pristine PS-*b*-PVP and PS-*b*-PVP/AgCF₃SO₃ films after UV irradiation for 60 min, as

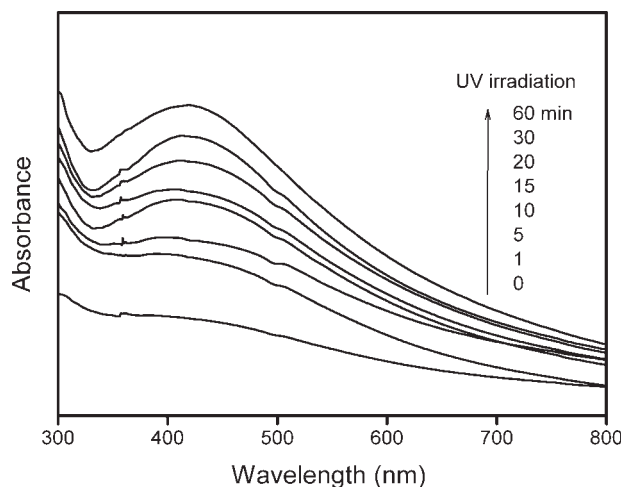


Figure 5 UV-vis spectra for a PS-*b*-PVP/AgCF₃SO₃ film with increasing UV irradiation time.

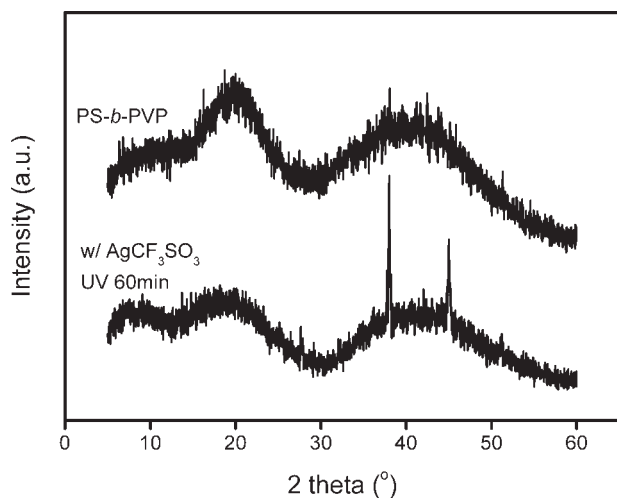


Figure 6 WAXS data for pristine PS-*b*-PVP and PS-*b*-PVP/AgCF₃SO₃ films after UV irradiation for 60 min.

shown in Figure 6. The pristine PS-*b*-PVP block copolymer exhibited two broad, amorphous halos around 19.8 and 39.9°, which showed a lack of crystallinity in the film. Upon UV irradiation of the PS-*b*-PVP/AgCF₃SO₃ film for 60 min, two sharp prominent peaks at 2θ values of about 38 and 44° appeared, which were attributable to the (111) and (200) Bragg's reflections of the face-centered cubic structure of silver metal, respectively.^{33,34} The amorphous halo of the PS-*b*-PVP/AgCF₃SO₃ films was not significantly different from that of the pristine block copolymer, showing that the nanostructure of the block copolymer film was not significantly perturbed by the presence of silver nanoparticles.

Interaction between the polymer and silver

Our previous studies reported that the C=C double bond of PS as well as the carbonyl oxygens of PVP can play a role as coordination sites to silver ions.^{22,32,33} Thus, the interaction between the PS-*b*-PVP block copolymer and silver was investigated with FTIR spectroscopy, as shown in Figure 7. The neat block copolymer exhibited the strong C=O peak of PVP at 1705 cm⁻¹ as well as the aromatic C=C stretching peaks of PS at 1630, 1600, 1494, and 1451 cm⁻¹. Upon the introduction of AgCF₃SO₃, the C=O peak of PVP shifted to 1640 cm⁻¹, probably because of the silver-ion coordination to carbonyl oxygens. The shift of the complexed C=O peak to a lower wave number may have resulted from the coordinative interaction between the silver ions and carbonyl oxygens.^{35,36} Even though the peaks at 1630 and 1600 cm⁻¹ overlapped with the complexed C=O peak at 1640 cm⁻¹ to some degree, it is evident that the aromatic C=C stretching peaks of PS

were hardly changed. Therefore, it is strongly suggested that the coordination of silver ions with the amide C=O of PVP is more favorable than that with the aromatic C=C of PS, and thus the silver ions are selectively incorporated into hydrophilic PVP domains. This presumably originates from the stronger interaction of the amide C=O/silver pair in comparison with that of the C=C/silver pair. Upon UV irradiation of the PS-*b*-PVP/AgCF₃SO₃ film for 60 min, the shoulder peak around 1698 cm⁻¹ appeared, presumably because of the C=O bond interacting with silver nanoparticles. The higher peak position of C=O/silver nanoparticles (1698 cm⁻¹) with respect to C=O/silver ions (1640 cm⁻¹) may come from the fact that the interaction strength of the former is weaker than that of the latter.

CONCLUSIONS

The development of self-assembled silver nanoparticles within a diblock copolymer template film with dry chemical processing has been reported. An amphiphilic PS-*b*-PVP diblock copolymer (70 : 30 wt %) was synthesized through ATRP and used as a template for the synthesis and confinement of silver nanoparticles. Silver nanoparticles with an average size of 4–6 nm were formed under UV irradiation through the *in situ* reduction of silver ions dissolved in the microphase-separated PS-*b*-PVP template film. Silver ions were selectively incorporated into the hydrophilic PVP domains because of their stronger interaction with polar carbonyl oxygens of PVP in the block copolymer, as confirmed by FTIR spectroscopy. TEM images, UV-vis spectroscopy, and WAXS data clearly revealed that the silver nanoparticles

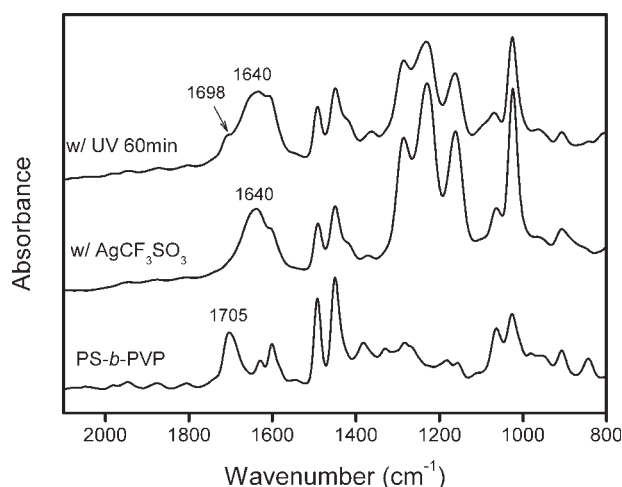


Figure 7 FTIR spectra of pristine PS-*b*-PVP and PS-*b*-PVP/AgCF₃SO₃ films before and after UV irradiation for 60 min.

from the silver ions were grown *in situ* and confined in the template block copolymer film.

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