

## Templated Formation of Silver Nanoparticles Using Amphiphilic Poly(epichlorohydrine-*g*-styrene) Film

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**Abstract:** This work has demonstrated that a novel amphiphilic poly(epichlorohydrine)-*graft*-polystyrene (PECH-*g*-PS) copolymer at 34:66 wt% was synthesized via atom transfer radical polymerization (ATRP) of styrene using PECH as a macroinitiator. The structure of the graft copolymer was characterized by nuclear magnetic resonance (<sup>1</sup>H NMR) and FTIR spectroscopy, demonstrating that the “grafting from” method using ATRP was successful. The self-assembled graft copolymer was used as a template film for the *in-situ* growth of silver nanoparticles from AgCF<sub>3</sub>SO<sub>3</sub> precursor under UV irradiation. The *in situ* formation of silver nanoparticles with 6–8 nm in average size in the *solid state* template film was confirmed by transmission electron microscopy (TEM), UV-visible spectroscopy and wide angle X-ray scattering (WAXS). Differential scanning calorimetry (DSC) also displayed the selective incorporation and the *in situ* formation of silver nanoparticles within the hydrophilic PECH domains, probably due to stronger interaction of the silvers with the ether oxygens of PECH backbone than that with hydrophobic PS side chains.

**Keywords:** nanocomposite, silver, nanoparticle, graft copolymer, ATRP.

### Introduction

Nanocomposite polymeric films combine the attractive functional properties of nanoparticles with the advantages of polymers.<sup>1–3</sup> Due to the novel properties that are not present in the bulk, nanoparticles and nanostructural materials have received great attention in a wide variety of material science and engineering. Important technological advances have been achieved in the field of catalysis,<sup>4</sup> electrochemistry,<sup>5</sup> photoluminescence<sup>6</sup> and separation membranes.<sup>7,8</sup> In recent years, the development of functional nanoparticles and nanocomposites has attracted much attention because it allows the formation of nanostructures of well-defined physical properties.

Among many inorganic nanoparticles, silver nanoparticles have been intensively studied because electrical,<sup>9</sup> mechanical,<sup>10</sup> and antibacterial properties<sup>11</sup> can be enhanced by adding nanoparticles to polymers. Nanocomposite films containing silver nanoparticles have potential as surface conductive polymeric tapes, and metal contacts for VLSI circuits.<sup>3</sup> These films are also candidates for integral capacitors because they are easy to process at low temperature and exhibit high dielectric constant. In particular, they play important roles for the possible applications to catalysis,<sup>12</sup> surface-enhanced Raman spectroscopy (SERS)<sup>13</sup> and facili-

tated olefin transport.<sup>14</sup> Many methods have been developed for synthesizing silver nanoparticles, mostly based on the solution synthesis using liquid medium, a reductant and a surfactant. In recent years, however, the solid state *in situ* reduction method within a polymer template film has been also developed using H<sub>2</sub> gas,<sup>15</sup> heat treatment,<sup>16</sup> NaBH<sub>4</sub> solution<sup>17,18</sup> and gamma/ultraviolet irradiation.<sup>19–21</sup> This technology can prevent the agglomeration of nanoparticles and allow the nanocrystals to be uniformly dispersed, which results in the highly ordered arrays of functional nanostructures.

In this work, we synthesized amphiphilic graft copolymer, i.e. poly(epichlorohydrine)-*graft*-polystyrene (abbreviated as PECH-*g*-PS) at 34:66 wt% via atom transfer radical polymerization (ATRP) and detailed the use of the graft copolymer as a template film to synthesize silver nanoparticles *at solid state*. Silver nanoparticles were *in situ* prepared within the graft copolymer template film by the reduction of a AgCF<sub>3</sub>SO<sub>3</sub> precursor under a UV irradiation. The resultant materials were characterized using transmission electron microscopy (TEM), UV-visible spectroscopy, wide angle X-ray scattering (WAXS) and differential scanning calorimetry (DSC).

### Experimental

**Materials.** Silver trifluoromethanesulfonate (AgCF<sub>3</sub>SO<sub>3</sub>, >99%), poly(epichlorohydrine) (PECH, *M<sub>w</sub>*~97,000 g/mol,

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$M_n \sim 55,000$  g/mol), styrene (99%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 99%) and copper (I) chloride (CuCl, 99%) were purchased from Aldrich and used as received without further purification.

**Synthesis of PECH-g-PS Graft Copolymer.** 2 g of PECH was dissolved in 25 mL of toluene with stirring at 70 °C for 3 h. After cooling the solution to room temperature, 12 g of styrene, 0.16 g of CuCl and 0.48 mL of HMTETA were added to the solution. The green mixture was stirred until homogeneous solution and purged with nitrogen for 30 min. The mixture was placed in a 100 °C oil bath for 8 h. After polymerization, the resultant polymer solution was diluted with THF. After passing the solution through a column with activated  $\text{Al}_2\text{O}_3$  to remove the catalyst, the solution was precipitated into methanol. PECH-g-PS graft copolymer was obtained and dried in a vacuum oven overnight at room temperature.

**Formation of Silver Nanoparticles.** Predetermined amounts of graft copolymer and  $\text{AgCF}_3\text{SO}_3$  were dissolved in THF to make up polymer solutions of 1 wt%. The concentration of silver salt was fixed at 20 w% relative to the total amounts of materials. The polymer/silver salt solutions were dropped and spread with micropipet on a slide glass. The samples were dried under nitrogen atmosphere for 2 h at room temperature and further dried in a vacuum oven for two days. UV irradiation was performed using a UV hand lamp (UVllite®, UVitec) at 254 nm with the distance of 1 mm between sample and lamp.

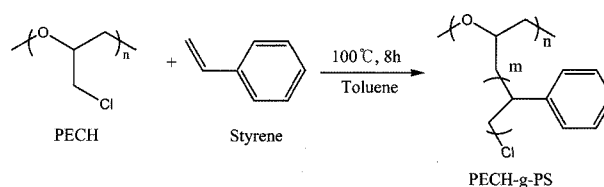
**Characterization.** Nuclear magnetic resonance ( $^1\text{H}$  NMR) measurements were performed with 600 MHz, high resolution NMR spectrometer (AVANCE 600 MHz FT-NMR, Germany, Bruker). FTIR spectra of the samples were collected using Excalibur Series FTIR (DIGLAB Co.) instrument between the frequency ranges of 4000 to 400  $\text{cm}^{-1}$  using ATR facility. TEM pictures were obtained from a Philips CM30 microscope 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 onto a standard copper grid. UV-visible spectroscopy was measured with spectrophotometer (Hewlett Packard) in the range of 300 to 800 nm. The WAXS experiment was carried out on a Rigaku 18kw rotating anode x-ray generator with  $\text{CuK}_\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) operated at 40 kV and 300 mA. The  $2\theta$  range was from 4° to 60° with a scanning speed of 3°/min, and the distance from the sample to detector was 185 mm. Differential scanning calorimeter (DSC 2920, TA Instruments, Inc.) was used to characterize the materials at a heating rate of 10 °C/min under  $\text{N}_2$  environment.

## Results and Discussion

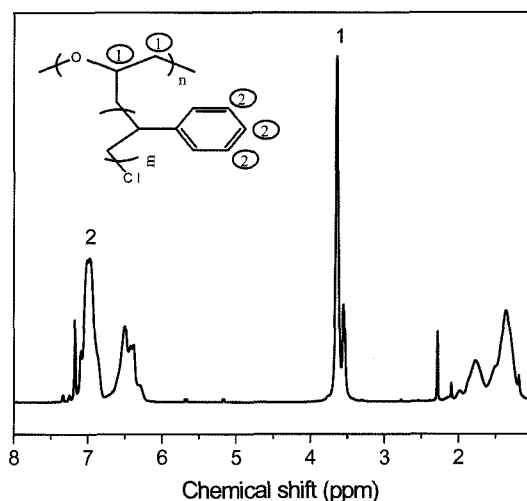
Scheme I illustrates the reaction scheme for the synthesis

of PECH-g-PS graft copolymer by ATRP using direct initiation of the chlorine atoms of PECH. The “grafting from” method based on ATRP technique has been widely used as an efficient polymerization for preparing well-defined graft copolymer. Here, the hydrophobic PS side chains were grafted from the hydrophilic PECH backbone via ATRP initiated by the pendant chlorine atoms.<sup>22,23</sup> Thus the amphiphilic PECH-g-PS graft copolymer is expected to molecularly self-assemble into the nanophase domains of PS brush layers interweaved with the hydrophilic domains of PECH main chains, providing the effective controlling for the formation of silver nanoparticles.

The graft copolymerization of PS side chains from PECH backbone via ATRP has been confirmed by  $^1\text{H}$  NMR spectroscopy, as shown in Figure 1. The  $^1\text{H}$  NMR spectrum revealed the presence of the strong peaks at around 3.7 ppm, attributed to CH and  $\text{CH}_2$  of PECH main chains.<sup>24</sup> Grafting of PS from PECH main chains produced additionally peaks in the region of 7.0 and 6.5 ppm, possibly assigned to the aromatic C=C units of PS. By comparing the integral area of the peak at 7.0 ppm (or 6.5 ppm) for PS with that of the peak at 3.7 ppm for PECH, the grafting ratio of PS in the PECH-g-PS copolymer was calculated and it was 66% on a mass basis. This represents that PS side chains are a major component forming continuous phase in the nanostructure. It should be noted that 30-40% of hydrophilic moiety is appropriate in effective controlling for the formation of sil-



**Scheme I.** Graft copolymerization of styrene from PECH via ATRP.

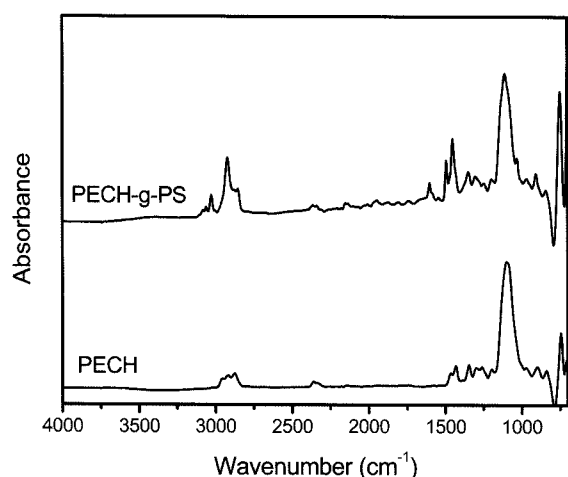


**Figure 1.**  $^1\text{H}$  NMR spectrum of PECH-g-PS graft copolymer.

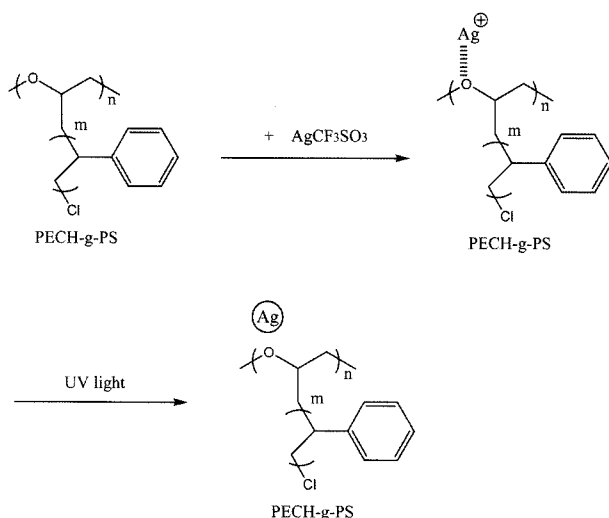
ver nanoparticles.<sup>25,26</sup>

FTIR spectra in Figure 2 display the characterization of graft copolymerization of PS brushes from PECH main chains via ATRP. There is a strong ether stretching band at  $1102\text{ cm}^{-1}$  in the neat PECH. Upon graft copolymerization, the absorption band at  $1650$ ,  $1604$ ,  $1500$  and  $1454\text{ cm}^{-1}$  were additionally observed in PECH-g-PS, attributable to the aromatic C=C stretching modes of PS.<sup>27</sup> The results of the FTIR characterization of the products confirm the successful graft copolymerization via ATRP from the chlorine atoms on the PECH backbone.

The schematic synthesis route for the formation of silver nanoparticles created *in situ* in the graft copolymer film *at solid state* is provided in Scheme II. The amphiphilic, microphase-separated PECH-g-PS film, consisting of hydrophobic PS and hydrophilic PECH domains, was used as a template for the *in situ* formation of nanoparticles. The



**Figure 2.** FTIR spectra of PECH and PECH-g-PS graft copolymer.



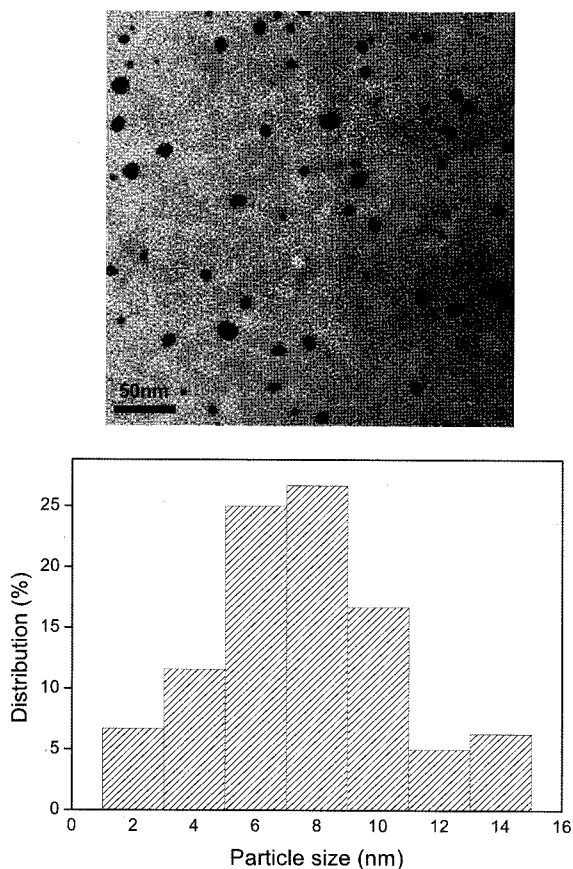
**Scheme II.** Schematic process for the *in situ* formation of silver nanoparticles created in a PECH-g-PS film.

chemical dissimilarity between the two polymer segments is sufficient to self-assemble in a solid film. It has been well known that the ether oxygens of the PECH domains are complexed to metal ions via direct coordinative interaction.<sup>28,29</sup> On the other hand, the PS domains are expected not to confine silver ions because of relatively weaker interaction strength of silver ions with aromatic C=C bonds of styrene. Thus most of the salts would be selectively confined and reduced in the hydrophilic PECH domains. As a result, the silver nanoparticles might be arranged in patterns that reflect the underlying morphologies of the graft copolymers.

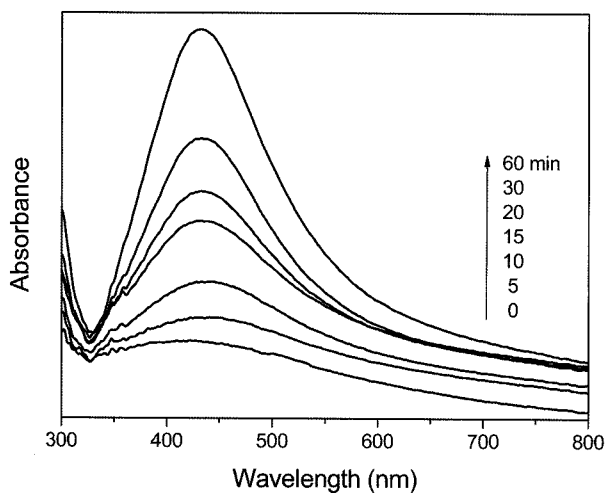
It has been reported that the materials containing ether oxygens can readily reduce metal ions to metal nanoparticles through the oxidation of the oxygen groups, implying that the PECH domains could play an effective role for the reduction of silver ions.<sup>30,31</sup> The formation and size of silver nanoparticles created *in situ* in the PECH-g-PS graft copolymer film under a UV irradiation were monitored using TEM micrograph, as shown in Figure 3. TEM image of the samples showed that the silver nanoparticles *in-situ* created in the PECH-g-PS film ranged 2-14 nm in size without agglomeration but were mostly stabilized with 6-8 nm in average size. This result can be explained in terms of the effective control of graft copolymer film for the formation of silver nanoparticles. More importantly, silver nanoparticles were remained confined to the nanoscale PECH domains (bright region) of the amphiphilic graft copolymer presumably due to specific interaction between the nanoparticles and the PECH domains.

Figure 4 presents the UV-visible absorption spectra for PECH-g-PS/AgCF<sub>3</sub>SO<sub>3</sub> film with increasing UV irradiation times. UV-visible absorption spectra are known to be quite effective in monitoring the formation of silver nanoparticles. The yellow color which appears at 410-430 nm is known as a characteristic absorption of silver nanoparticles, originated from the surface plasmon resonance of silver. It is also known that its magnitude correlates to the concentration of silver nanoparticles while the peak position is related to the size of silver nanoparticles.<sup>15-21,32,33</sup> Before UV irradiation (0 min), there was weak UV absorption for PECH-g-PS/AgCF<sub>3</sub>SO<sub>3</sub> film, implying slight reduction process for silver nanoparticles without UV irradiation. After UV irradiation, however, one strong UV absorption peak centered at around 425 nm appeared, corresponding to the plasmon excitation of silver nanoparticles. The plasmon peak for PECH-g-PS/AgCF<sub>3</sub>SO<sub>3</sub> film continuously grew up with the increase of UV irradiation time, indicating the increase of silver nanoparticles in number. This result represents that PECH plays an important role as a reducing agent for controlling the formation of silver nanoparticles.

To confirm the formation of silver nanoparticles *in-situ* created in the graft copolymer film, WAXS spectra were measured for pristine PECH-g-PS and PECH-g-PS/AgCF<sub>3</sub>SO<sub>3</sub> film after UV irradiation for 60 min, as seen in

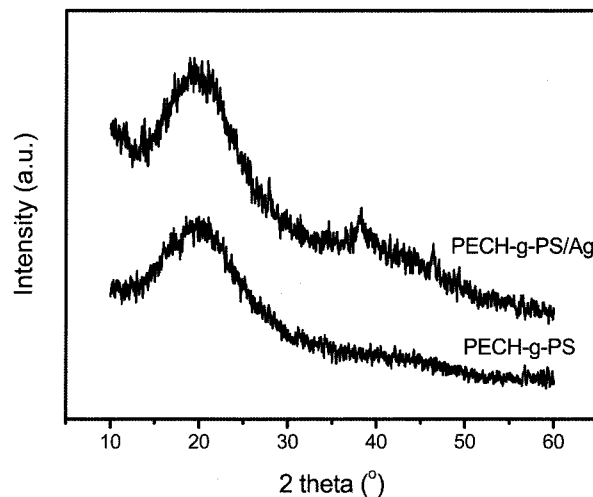


**Figure 3.** TEM micrograph and the size distribution of silver nanoparticles created *in situ* in PECH-g-PS/AgCF<sub>3</sub>SO<sub>3</sub> film by UV irradiation for 60 min.



**Figure 4.** UV-visible spectra for PECH-g-PS/AgCF<sub>3</sub>SO<sub>3</sub> film with increasing UV irradiation time.

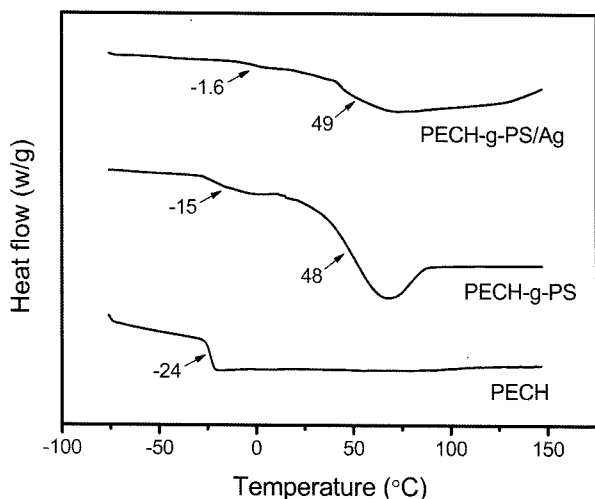
Figure 5. The pristine PECH-g-PS graft copolymer exhibited broad amorphous halos centered at around 19.8°, presenting lack of crystallinity in the film. Upon UV irradiation to PECH-g-PS/AgCF<sub>3</sub>SO<sub>3</sub> film for 60 min, two peaks at



**Figure 5.** WAXS data for pristine PECH-g-PS and PECH-g-PS/AgCF<sub>3</sub>SO<sub>3</sub> film after UV irradiation for 60 min.

$2\theta$  values of about 38° and 44° appeared, attributable to the (1 1 1) and (2 0 0) Bragg's reflections of face-centered cubic structure of silver metal, respectively.<sup>34,35</sup> The average crystallite sizes of the silver nanoparticles were determined by analyzing the most intense (1 1 1) peak and using the well-known Scherrer's equation,  $L=0.9\lambda/(\beta \cos\theta)$ , where  $L$  is particle size,  $\lambda$  is the wavelength of the X-ray (nm), and  $\beta$  is the full width (radians) at half maximum of the signal.<sup>36</sup> Crystallite size determination using Scherrer's equation revealed average particle size of 5.3 nm, which is somewhat lower than that determined from TEM image. This result indicates that the silver nanoparticles are sufficiently remained confined to the nanoscale PECH domains of the amphiphilic graft copolymer. In addition, the amorphous hollow of the PECH-g-PS/AgCF<sub>3</sub>SO<sub>3</sub> film was not greatly different from that of the pristine graft copolymer, representing that the nanostructure of the graft copolymer film was not significantly perturbed by the presence of silver nanoparticles.

The DSC thermograms of pristine PECH, PECH-g-PS graft copolymer and its nanocomposites with silver nanoparticles were presented in Figure 6. The pristine PECH exhibited glass transition temperature ( $T_g$ ) at -24 °C and no melting temperature ( $T_m$ ), presenting its rubbery amorphous state. Two  $T_g$ s at -15 and 48 °C were observed in the PECH-g-PS graft copolymer corresponding to microphase separation of the PECH and PS segments, respectively, representing successful graft copolymerization via ATRP technique. The appearance of two  $T_g$ s in DSC curve presents the microphase-separated structure of amphiphilic graft copolymer into hydrophilic rubbery PECH domains and hydrophobic glassy PS domains.<sup>37</sup> It is also found that the  $T_g$  value associated with the PS segments is lower than expected for neat PS (100 °C), which may reflect partial mixing between PECH and PS segments at their interfaces.<sup>38,39</sup> Upon the *in situ* growth of silver nanoparticles by UV irradiation, the  $T_g$  of



**Figure 6.** DSC data of pristine PECH, PECH-g-PS and PECH-g-PS/AgCF<sub>3</sub>SO<sub>3</sub> film after UV irradiation for 60 min.

PS remained almost invariant at 49 °C whereas that of PECH increased from -15 to -1.6 °C. This result strongly demonstrates that silver nanoparticles selectively interact with ethylene oxide moiety of PECH domains, leading to the restricted chain mobility and  $T_g$  elevation of nanocomposites.<sup>40,41</sup>

## Conclusions

Amphiphilic PECH-g-PS graft copolymer with 34:66 wt% was successfully synthesized via ATRP technique using PECH backbone as a macroinitiator and used as a template film for the self-assembled formation of silver nanoparticles *at solid state*. The nanocomposites consisting of amphiphilic graft copolymer and silver nanoparticles were constructed under UV irradiation through an *in situ* reduction of silver ions dissolved in microphase-separated PECH-g-PS template film. Silver ions were selectively incorporated in the hydrophilic PECH domains due to their strong interaction with polar ether oxygens of PECH in the graft copolymer, as confirmed by DSC result. TEM image, UV-visible spectroscopy and WAXS data clearly revealed that the silver nanoparticles were *in situ* grown from the silver ions and confined in the templated graft copolymer film.

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