

Polystyrene-*b*-Poly(oxyethylene methacrylate) 블록 공중합체 막을 이용한 은 나노입자 생성

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Formation of Silver Nanoparticles in Polystyrene-*b*-Poly(oxyethylene methacrylate) Block Copolymer Membranes

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요약: 원자전달 라디칼 중합을 이용하여 polystyrene-*b*-poly(oxyethylene methacrylate) (PS-*b*-POEM) 블록 공중합체를 합성하고, FT-IR을 통해 중합이 성공적으로 이루어졌음을 확인하였다. 또한 자기 조립된 블록 공중합체 막을 제조한 후, 전구체 AgCF₃SO₃ 도입과 UV 조사를 통해 고체상에서 은 나노입자를 성장시켰다. TEM 전자현미경과 UV-visible 분광학 분석을 통해 블록 공중합체 막의 내부에 은 나노입자가 형성된 것을 확인하였고, 또한 친수성 POEM 영역의 함량을 조절함으로써 나노입자의 크기를 조절할 수 있었다. 금속 나노입자를 제조하는 데 있어서 POEM 함량이 적은 블록 공중합체가 더 효과적임을 확인하였다.

Abstract: A diblock copolymer of polystyrene-*b*-poly(oxyethylene methacrylate) (PS-*b*-POEM) was synthesized via atom transfer radical polymerization (ATRP), as revealed by FT-IR spectroscopy. The self-assembled block copolymer membrane was prepared and used to template the growth of silver nanoparticles in the solid state by the introduction of AgCF₃SO₃ precursor and UV irradiation process. Transmission electron microscopy (TEM) and UV-visible spectroscopy confirmed the *in situ* formation of silver nanoparticles within the block copolymer membranes, and the size of nanoparticles were controlled by adjusting the moiety of hydrophilic POEM domains. PS-*b*-POEM block copolymer with a lower POEM content was effective in generating smaller size of metal nanoparticles.

Keywords: atom transfer radical polymerization, block copolymer, nanoparticles, silver, templates

1. Introduction

In recent years, an intense effort has been focused on the preparation of nanoparticles, nanocomposites, and nanostructured materials due to their markedly different optical, electrical, and mechanical properties with respect to bulk materials [1-4]. The nanomaterials that possess such specific, intriguing properties can be ex-

ploited for many applications in various fields such as magnetic resonance imaging [5], electrochemistry [6], and photoluminescence [7]. Therefore, much effort has been devoted to developing advanced functional nanomaterials, with a view toward opening new opportunities for constructing functional nanostructures [8-11].

In particular, more attention has been paid to the preparation and characterization of silver nanoparticles because of their intriguing optical, electronic, magnetic,

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and mechanical properties [12-19]. It is well known that silver nanoparticles are superior to other metal nanoparticles for many reasons such as antimicrobial activity [20], catalysis [21], surface-enhanced Raman spectroscopy [22], and facilitated olefin transport [23]. However, the difficulty of handling of these nano-sized metals has represented a strong limitation for their use. In addition, most metal nanoparticles are unstable and tend to agglomerate to grow due to the high free surface energy that can be oxidized by air, moisture, and other chemicals. The embedding of nanoparticles in a polymeric matrix may provide an effective solution for manipulation and stabilization problems. This method is based on the *in-situ* reduction of metal ions that are dispersed in polymer matrices. Several synthetic routes for the preparation of silver nanoparticles using a template membrane have been reported, e. g. using H₂ gas [24], heat treatment [25], NaBH₄ solution [26], and gamma/ultraviolet irradiation [27,28].

In this study, we report on the *in-situ* preparation of nanocomposite membranes in which silver nanoparticles are embedded. First, we synthesized a microphase-separated block copolymer, i.e. polystyrene-*block*-poly(oxyethylene methacrylate) (abbreviated as PS-*b*-POEM) via atom transfer radical polymerization (ATRP). The block copolymer matrix was selected because of its ability to form well-defined ordered nanostructures. The reduction of silver ions occurred within the block copolymer template membrane via ultraviolet irradiation. The resulting PS-*b*-POEM/Ag materials were characterized using transmission electron microscopy (TEM), UV-visible spectroscopy, and FT-IR spectroscopy.

2. Experimental

2.1. Materials

Silver trifluoromethanesulfonate (AgCF₃SO₃, > 99%), styrene (99%), poly(oxyethylene methacrylate) (POEM, poly(ethylene glycol) methyl ether methacrylate, M_n = 475 g/mol), copper(I) chloride (CuCl, 99%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 99%), and methyl 2-bromopropionate (MBP) were purchased

from Aldrich and used as received. Methanol and tetrahydrofuran (THF) of analytical reagent grade were obtained from J. T. Baker.

2.2. Synthesis of PS-Br

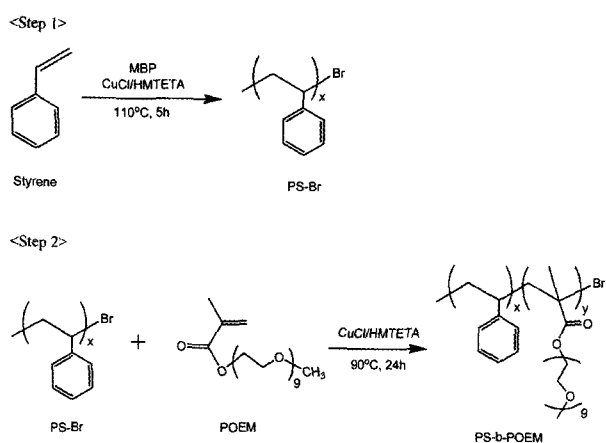
Twenty grams of styrene, 0.296 g CuCl, and 1.24 mL of HMTETA were added in a 250 mL flask. This green mixture was stirred until it formed a homogeneous solution. The solution was purged with nitrogen for 30 min, and then 0.22 mL of MBP was added. The mixture was placed in a 110°C oil bath for 5 h. After polymerization, the polymer product was diluted with THF and passed through an activated Al₂O₃ column to remove the catalyst. The polymer was then precipitated out with methanol. The PS-Br homopolymer was then dried in a vacuum oven overnight at room temperature.

2.3. Synthesis of PS-*b*-POEM block Copolymer

Two grams of PS-Br macroinitiator was dissolved in 20 mL of toluene. And then, 0.037 mL of HMTETA, and 0.0132 g of CuCl were added to the solution with different amounts of POEM (PS-Br : POEM = 1 : 1 and 1 : 2 wt%). The mixture was stirred until forming a homogeneous solution and purged with nitrogen for 30 min. The mixture was placed in a 90°C oil bath for 24 h. After polymerization, the resultant polymer solution was diluted with THF. After passing the solution through a column with activated Al₂O₃ to remove the catalyst, the solution was precipitated into methanol. PS-*b*-POEM diblock copolymer was obtained and dried in a vacuum oven overnight at room temperature.

2.4. Formation of Silver Nanoparticles within Membrane

Predetermined amounts of block copolymer and AgCF₃SO₃ were dissolved in THF to make up polymer solutions of 1 wt%. The concentration of silver salt was fixed at 20 wt% relative to the total amounts of materials. To prepare membrane, polymer/silver salt solutions were dropped and spread with a micropipet on a glass slide, and the samples were dried under nitrogen atmosphere for 2 h at room temperature and further dried



Scheme 1. (Step 1) Synthesis of PS-Br via ATRP, (Step 2) block copolymerization of POEM from PS-Br via ATRP.

in a vacuum oven for 2 days. A UV irradiation was performed using a UV hand lamp (UVlite1, UVitec) at 254 nm with a distance of 1 mm between the membrane and the lamp.

2.5. Characterization of Membranes

FT-IR spectra of the samples were collected using Excalibur Series FTIR (DIGLAB) instrument between the frequency ranges of 4,000~700 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 measurement, the dried membranes were dissolved in THF, and then a drop of this solution was placed onto a standard copper grid. UV-visible spectroscopy was measured with spectrophotometer (Hewlett-Packard) in the range of 300~800 nm.

3. Results and Discussion

Scheme 1 illustrates the two-step reaction for the synthesis of PS-*b*-POEM diblock copolymer by ATRP. The first step involved the homopolymerization of styrene in bulk at 110°C for 5 h in the presence of MBP/CuCl/HMTETA, producing bromine-terminated PS (PS-Br). PS-*b*-POEM diblock copolymer was successively synthesized using PS-Br and CuCl/HMTETA as a macroinitiator and catalyst/ligand complex, respectively.

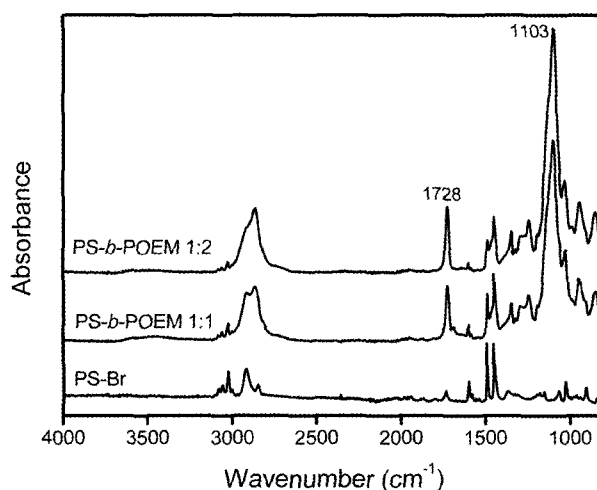


Fig. 1. FT-IR spectra of PS-Br and PS-*b*-POEM diblock copolymers.

Two kinds of PS-*b*-POEM diblock copolymers were synthesized with PS : POEM = 1 : 1 and 1 : 2. These polymers are expected to molecularly self-assemble into the nanophase domains of hydrophilic POEM with the hydrophobic domains of PS block. This morphology is responsible for the effective control of nanoparticle formation.

Block copolymerization with the different amounts of POEM has been confirmed by FT-IR spectroscopy, as shown in Fig. 1. The aromatic C=C stretching bands of pristine PS appeared at 1,630, 1,600, 1,494 and 1,451 cm^{-1} . Upon block copolymerization, the new bands appeared at 1,728 and 1,103 cm^{-1} for both compositions, assigned to the carbonyl (C=O) and ether (C-O-C) stretching bands of POEM, respectively [29]. The absorbance of both peaks increased with the amount of POEM. These FT-IR spectroscopic results confirm the successful synthesis of sequential diblock copolymer via ATRP, and the moiety of POEM domain was controlled by varying the amount of added POEM.

Microphase-separated PS-*b*-POEM diblock copolymers consisting of hydrophobic PS and hydrophilic POEM domains were used as a template membrane. The chemical dissimilarity between the two polymer segments is sufficient to promote self-assembly in a solid membrane. The ether oxygens of the POEM domains are well known to associate with silver ions or complexes

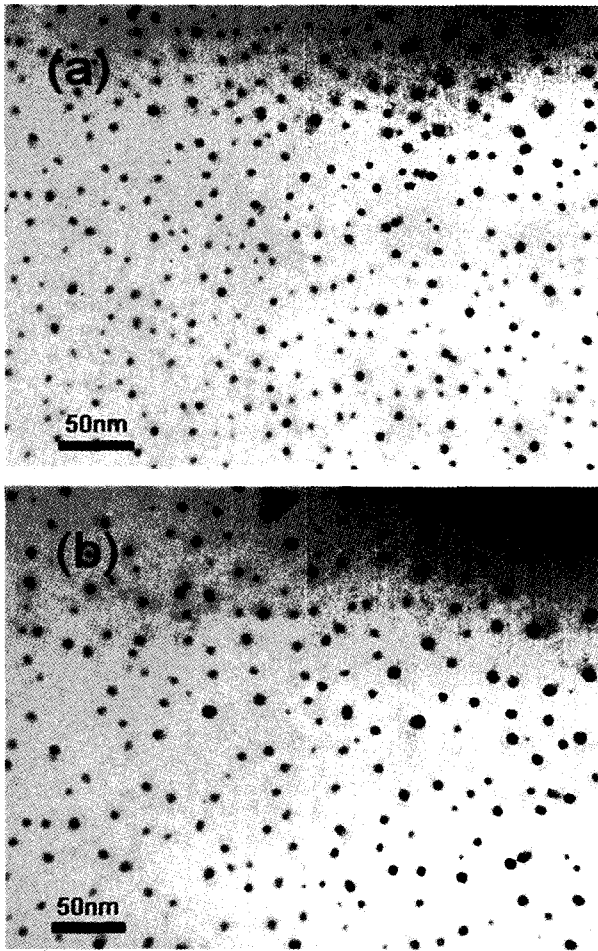


Fig. 2. TEM micrographs and size distribution of silver nanoparticles in (a) PS-*b*-POEM 1 : 1/AgCF₃SO₃ membrane, and (b) PS-*b*-POEM 1 : 2/AgCF₃SO₃ membrane upon UV irradiation for 60 min.

via direct coordination to metal ions [30,31]. In contrast, the PS domains are not expected to confine silver ions, resulting in a microphase separated structure. Since silver salts possess hydrophilic properties, most of the salts are expected to be selectively confined and *in-situ* reduced in the hydrophilic POEM domains only. As a result, silver nanoparticles might be arranged in patterns that reflect the underlying morphologies of the diblock copolymers. It has been reported that the materials containing ethylene oxides can readily reduce metal ions to metal nanoparticles through the oxidation of their oxygen groups, indicating that the POEM domains of the copolymer may play an effective role for the reduction of silver ions [32,33].

The formation of silver nanoparticles created *in situ* in PS-*b*-POEM block copolymer membranes with two different POEM contents under UV irradiation was monitored using TEM micrographs. As shown in Fig. 2, the TEM images of the samples with both compositions indicate that most of silver nanoparticles were created in the PS-*b*-POEM/AgCF₃SO₃ membranes without significant particle agglomeration. Silver nanoparticles were stabilized with 4~6 nm and 5~8 nm in average size within PS-*b*-POEM 1 : 1 and PS-*b*-POEM 1 : 2 template membrane, respectively (Fig. 2(a) and 2(b)). It demonstrates that the PS-*b*-POEM block copolymer with a lower content of POEM plays a role more effectively in generating smaller nanoparticles.

UV-visible spectroscopy is known to be quite effective for monitoring the formation of silver nanoparticles. Fig. 3(a) and 3(b) show the UV-visible absorption spectra of PS-*b*-POEM 1 : 1/AgCF₃SO₃ and PS-*b*-POEM 1 : 2/AgCF₃SO₃ membranes with increasing UV irradiation times, respectively. Before UV irradiation (0 min), there was no distinguishable UV absorption for both compositions. Upon UV irradiation, however, one strong UV absorption peak centered at around 410~450 nm was observed, corresponding to the plasmon excitation of silver nanoparticles. It is generally accepted that the absorption peak whose maximum occurs at around 410~450 nm is related to the formation of silver metal nanoparticles [15-28]. Furthermore, the magnitude of this peak is related to the concentration of silver nanoparticles while the peak position relates to the size of the silver nanoparticles [15-28]. The plasmon peak for the PS-*b*-POEM/AgCF₃SO₃ membrane grew up continuously with UV irradiation time, indicating that the number of silver nanoparticles increased. The plasmon peak of PS-*b*-POEM 1 : 2/AgCF₃SO₃ membrane (449 nm) was red-shifted compared to that of PS-*b*-POEM 1 : 1/AgCF₃SO₃ (417 nm). This is because that silver nanoparticles in PS-*b*-POEM 1 : 2/AgCF₃SO₃ membrane are larger than those of 1 : 1 membrane, as confirmed by TEM. This result demonstrates that POEM plays an important role as a reducing agent for controlling the formation of silver

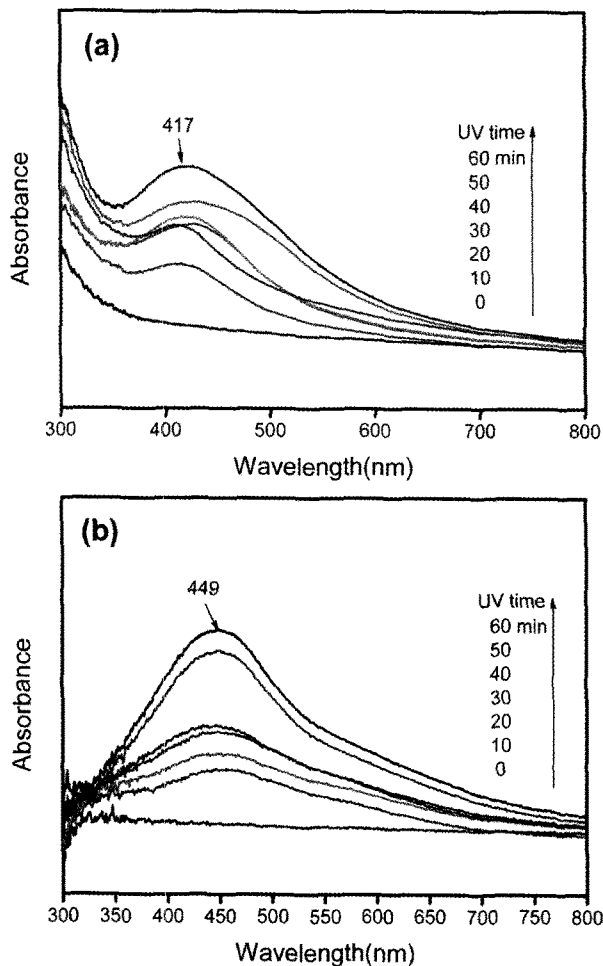


Fig. 3. UV-visible spectra of (a) PS-*b*-POEM 1 : 1/Ag-CF₃SO₃ membrane, and (b) PS-*b*-POEM 1 : 2/ AgCF₃SO₃ membrane with increasing UV irradiation time.

nanoparticles, and the size of silver nanoparticles can be controlled by adjusting the moiety of POEM domain in micro-separated PS-*b*-POEM block copolymer.

4. Conclusions

An amphiphilic PS-*b*-POEM diblock copolymer was successfully synthesized via ATRP technique using PS-Br as a macroinitiator. Successful synthesis of microphase-separated PS-*b*-POEM diblock copolymer with different compositions was confirmed by FT-IR spectroscopy. The diblock copolymer was used as a template membrane for the self-assembled formation of silver nanoparticles in the solid state. Silver nanoparticles

were formed under UV irradiation through in situ reduction of silver ions dissolved in a microphase-separated PS-*g*-POEM template membrane. Silver ions were selectively incorporated in the hydrophilic POEM domains due to their strong interaction with polar ether oxygens of POEM in the block copolymer. TEM images and UV-visible spectroscopy revealed that the silver nanoparticles were grown in situ within the block copolymer template membrane, and the size of silver nanoparticles were controlled by adjusting the moiety of hydrophilic POEM domain in block copolymer.

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