

Poly(vinyl chloride)-g-poly(styrene sulfonic acid) 가지형 공중합체막을 이용한 은 나노입자 제조

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Preparation of Ag Nanoparticles by Templating Poly(vinyl chloride)-g-poly(styrene sulfonic acid) Graft Copolymer Membrane

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요약: 원자전달 라디칼 중합(ATRP)에 의해 poly(vinyl chloride) (PVC) 주사슬과 poly(styrene sulfonic acid) (PSSA) 곁사슬로 되어있는 양쪽성 PVC-g-PSSA 가지형 공중합체를 합성하였다. 합성된 고분자 전해질막을 10 wt% AgNO₃ 수용액에 담가 은이온으로 이온교환을 하였으며, 환원제를 통하여 은 나노입자를 성장시켰다. UV분광학과 XRD 분석을 통해 은 나노입자 성장을 확인하였다. 투과전자현미경(TEM) 분석결과 NaBH₄를 사용하였을 때 10~20 nm 크기의 은 나노입자를 얻는데 가장 효과적임을 알 수 있었다. 또한 은 나노입자의 성장은 환원제의 농도와 환원 시간에 크게 영향을 받았다.

Abstract: An amphiphilic graft copolymer consisting of a poly(vinyl chloride) (PVC) backbone and poly(styrene sulfonic acid) (PSSA) side chains (PVC-g-PSSA) was synthesized via atom transfer radical polymerization (ATRP). This polymer electrolyte membrane was ion-exchanged to Ag ions by immersing in 10 wt% AgNO₃ aqueous solution and templated the growth of Ag nanoparticles by a reducing agent. The formation of Ag nanoparticles was confirmed using UV-visible spectroscopy and X-ray diffraction (XRD). Transmission electron microscopy (TEM) revealed that utilization of NaBH₄ was the most effective in the formation of Ag nanoparticles with 10~15 nm in size. The formation of Ag nanoparticles was also strongly affected by the concentration of reducing agent and reduction time.

Keywords: nanoparticles, silver, atom transfer radical polymerization (ATRP), nanomaterials graft copolymer

1. Introduction

Polymer electrolytes include a polymer/salt complex and a polyelectrolyte. The former consists of a solvent-free polymer and a metal salt, which are prepared by dissolving salt in high molecular weight polymer host. The latter is a polymer whose repeating units bear ionically charged groups. Polymer electrolyte membranes have received much attention as their successful use in lithium secondary batteries [1], electro-

chromic devices [2], polymer electrolyte membrane fuel cells [3], dye-sensitized solar cells [4] and facilitated olefin transport membranes [5]. Solid polymer electrolyte membranes are advantageous over liquid-based counterparts in terms of good mechanical properties, ease of fabrication thin film fabrication with desirable sizes and proper electrode/electrolyte contact in various electrochemical devices.

Incorporation of metal nanoparticles into a polymer matrix produces nanocomposite materials, which is an effective method for enhancing the functions of neat

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polymer. These nanocomposites have been recently investigated because they combine the attractive functional properties of nanoparticles with the advantages of polymers. Important advances have been achieved in the areas of electrochemistry, photoluminescence, catalysis and separation membranes [6-9]. In particular, silver nanoparticles have been investigated because of their capability for increasing electrical, mechanical and antibacterial properties of polymer [10-12]. Conventional method for synthesizing nanoparticles is based on the chemical reduction of metal ions in liquid medium. Several synthetic methods using a template polymer membrane have been also reported recently, for example, H₂ gas [13], heat treatment [14], NaBH₄ solution [15], and ultraviolet irradiation [16] was utilized.

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 amphiphilic graft copolymer consisting of a poly(vinyl chloride) (PVC) backbone and poly(styrene sulfonic acid) (PSSA) side chains (PVC-*g*-PSSA) via atom transfer radical polymerization (ATRP). The graft copolymer matrix was selected because of its ability to form well-defined ordered nanostructures. Silver ions within the graft copolymer were *in-situ* reduced to form silver nanoparticles using various reducing agents. In particular, the kinetics for the formation of nanoparticles is reported here. The resulting PVC-*g*-PSSA/Ag nanocomposites were characterized using UV-visible spectroscopy and transmission electron microscopy (TEM).

2. Experimental

2.1. Material

PVC ($M_n = 55,000$ g/mol, $M_w = 97,000$ g/mol), 4-styrene sulfonic acid (SSA), copper (I) chloride (CuCl), 1,1,4,7,10,10-hexamethyl triethylene tetramine (HMTETA), silver nitrate (AgNO₃, > 99%), sodium borohydride (NaBH₄) and 1-methyl-2-pyrrolidinone (NMP) were purchased from Aldrich. Methanol and dimethyl sulfoxide (DMSO) were purchased from J. T. Baker. All

solvent and chemicals were reagent grade and used as received.

2.2. Synthesis of PVC-*g*-PSSA Graft Copolymer

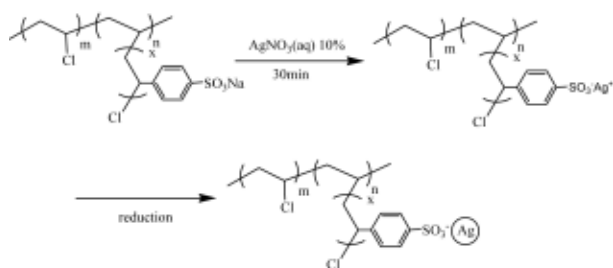
PVC-*g*-PSSA polymer electrolyte membrane was synthesized via ATRP, according to the previously reported method [17]. In brief, two grams of PVC was dissolved in 18 mL NMP in a round flask at 70°C. Separately, 14 g of SSA was dissolved in 18 mL DMSO at 70°C and added to PVC solution. After producing homogeneous solution, 0.04 g of CuCl and 0.1 mL of HMTETA were added and the reaction flask was sealed with a rubber septum. After N₂ purging for 30 min, the reaction vessel was immersed in an oil bath at 90°C. The reaction was allowed to proceed for 24 h. After passing the solution through a column with activated Al₂O₃ to remove the catalyst, it was precipitated into methanol. The polymer was purified by redissolving in DMSO and reprecipitating in methanol. Finally, the polymer was dried in a vacuum oven overnight at room temperature.

2.3. Formation of Silver Nanoparticles

First, 2 g of PVC-*g*-PSSA was dissolved in 20 mL of DMSO with stirring for 2 h. Then, the solution was cast on a slide glass by drop casting method and dried in an oven for a day at 80°C. After drying the solvent completely, the films were immersed into 10 wt% AgNO₃ aqueous solution for 30 min and then dried in the hood for overnight. Three kinds of reducing agent, 0.2 M NaBH₄ (aq), 0.2 M formamide (HCONH₂) (aq) and 0.2 M DMF (HCON(CH₃)₂) were utilized. The immersion time in 0.05 M NaBH₄ and the concentration of NaBH₄ were changed to investigate their effects on the formation of silver nanoparticles.

2.4. Characterization

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 DMSO, and then a drop of this colloidal sil-



Scheme 1. Schematic process for the *in-situ* formation of silver nanoparticles created in a PVC-g-PSSA graft copolymer film.

ver 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 XRD experiment was carried out on a Rigaku 18 kW rotating anode x-ray generator with CuK radiation ($\lambda = 1.5406 \text{ \AA}$) operated at 40 kV and 300 mA. The 2θ range was from 5 to 60° with a scanning speed of $3^\circ/\text{min}$, and the distance from the sample to detector was 185 mm.

3. Results and Discussion

The reaction scheme for the synthesis of silver nanoparticles within the PVC-g-PSSA graft copolymer is illustrated in Scheme 1. PVC-g-PSSA polymer electrolyte membrane was synthesized via one-step ATRP process [17]. This graft copolymer membrane is expected to molecularly self-assemble into continuous nanophase domains of semicrystalline PVC interweaved with hydrophilic domains of PSSA brush layer due to the chemical dissimilarity between the two polymer segments. The polymer electrolyte was ion exchanged to silver ions by immersing 10 wt% AgNO_3 aqueous solution and templated the growth of Ag nanoparticles by a reducing agent.

Fig. 1 shows the UV-visible absorption spectra for as-synthesized PVC-g-PSSA and PVC-g-PSSA/Ag films after reduction reaction. Three kinds of reducing agents were utilized and compared at the same concentration. In the Na^+ form without reduction process, there was no distinguishable UV absorption for

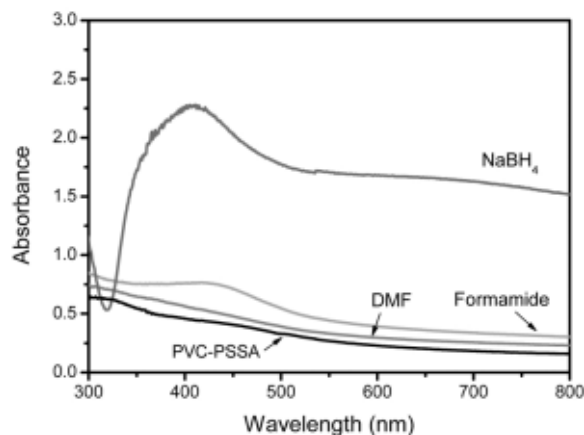


Fig. 1. UV-visible spectra for PVC-g-PSSA and PVC-g-PSSA/Ag film with different reducing agent. The concentration of reducing agent was fixed at 0.2 M.

PVC-g-PSSA film. Upon ion exchange to silver ions and subsequent reduction process by NaBH_4 , a strong UV absorption peak centered at 415 nm was observed corresponding to the plasmon excitation of Ag nanoparticles [18-20]. The absorption peak whose maximum occurs at around 410~450 nm is related to the formation of silver metal nanoparticles [18-20]. 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. In the formamide treated sample, the peak intensity was much smaller than NaBH_4 treated sample at the same concentration. In contrast, there was no significant absorption for the DMF treated sample. As a result, it is found that the reducing power is arranged in the order: $\text{NaBH}_4 > \text{formamide} > \text{DMF}$. Thus, the kinetics for the formation of silver nanoparticles was investigated on the NaBH_4 system by changing the concentration of reducing agent and reduction time.

Fig. 2(a) shows change in UV-visible spectra for PVC-g-PSSA/Ag film depending on the NaBH_4 concentration. The absorbance at 415 nm was normalized by considering the value at 330 nm for all the data and presented in Fig. 2(b). The absorbance sharply increased with NaBH_4 concentration up to 0.005 M, above which it did not increase significantly. Thus, the critical concentration of NaBH_4 was found to be near

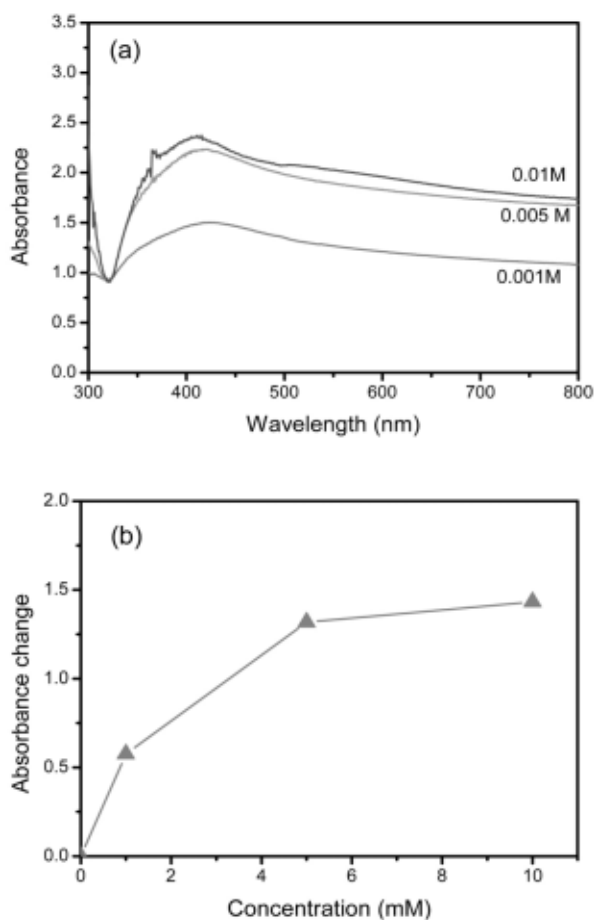


Fig. 2. (a) Change in UV-visible spectra for PVC-g-PSSA/Ag film depending on the NaBH_4 concentration, (b) Change in absorbance at 415 nm by normalizing the value at 330 nm.

0.01 M in the PVC-g-PSSA graft copolymer membrane. Change in UV-visible spectra for PVC-g-PSSA/Ag film was also monitored by changing the contact time with NaBH_4 solution and presented in Fig. 3. The absorbance sharply and linearly increased with contact time with NaBH_4 solution up to 600 sec, above which it increased less sharply.

TEM analysis was carried out to characterize the morphology of PVC-g-PSSA graft copolymer and PVC-g-PSSA/Ag film after reduction. Fig. 4(a) presents the TEM image of unstained PVC-g-PSSA graft copolymer. The difference of electron densities between the PVC main chains and the PSSA side chains provides image contrast between two domains [17].

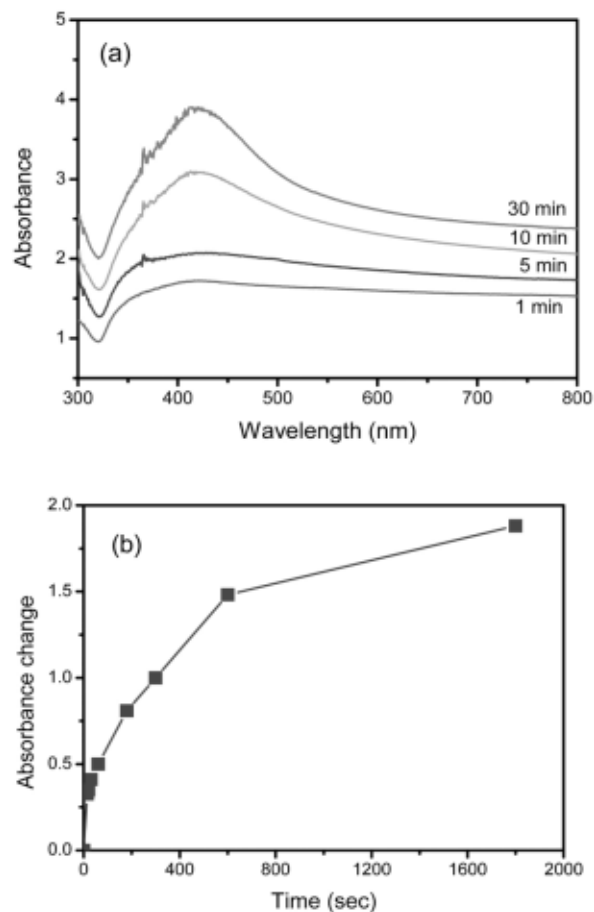


Fig. 3. (a) Change in UV-visible spectra for PVC-g-PSSA/Ag film depending on the contact time with 0.005 M NaBH_4 solution, (b) Change in absorbance at 415 nm by normalizing the value at 330 nm.

Dark regions represent the hydrophobic domains of PVC main chains whereas lighter regions do the PSSA side chains. Thus, the amphiphilic PVC-g-PSSA graft copolymer molecularly self-assembled into continuous nanophase domains of PVC interweaved with hydrophilic domains of PSSA brush layer.

The formation and size of silver nanoparticles created *in-situ* in the PVC-g-PSSA graft copolymer film were monitored using TEM micrograph, as shown in Fig. 4(b). The concentration of NaBH_4 solution and contact time were fixed at 0.005 M and 30 min, respectively. It is because there was no peak shift in UV-visible spectroscopy of Fig. 2, indicating no significant change in particle sizes. TEM images of the

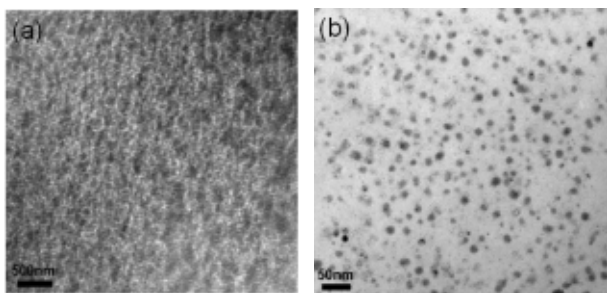


Fig. 4. TEM images of a) pristine PVC-g-PSSA graft copolymer and b) Ag nanoparticles created *in-situ* in PVC-g-PSSA film by 0.005 M NaBH₄ solution for 30 min.

samples showed that the silver nanoparticles created in the PVC-g-PSSA film were stabilized with 10~15 nm in average size without agglomeration. It strongly represents the effective control of graft copolymer film for the formation of silver nanoparticles [21].

XRD were measured for the silver nanoparticles created in the PVC-g-PSSA film to confirm the formation of silver nanoparticles. The results are shown in Fig. 5, where the intensity of X-ray scattering is plotted against the diffraction angle, 2θ . Sharp crystalline peaks at 2θ values of about 38 and 44° appeared, attributable to the (111) and (200) Bragg's reflections of face-centered cubic structure of silver metal, respectively [22]. The amorphous halo at around 20° was also observed, indicating the presence of PVC-g-PSSA film without being perturbed by the presence of silver nanoparticles.

4. Conclusions

Amphiphilic PVC-g-PSSA graft copolymer was synthesized via ATRP technique using PVC backbone as a macroinitiator and used as a template film for the *in-situ* formation of silver nanoparticles in the solid state. Synthesis of microphase-separated PVC-g-PSSA graft copolymer was successful via "grafting from" method using ATRP. The graft copolymer molecularly self-assembled into continuous nanophase domains of PVC interweaved with hydrophilic domains of PSSA brush layer, as revealed by TEM. Nanocomposite films

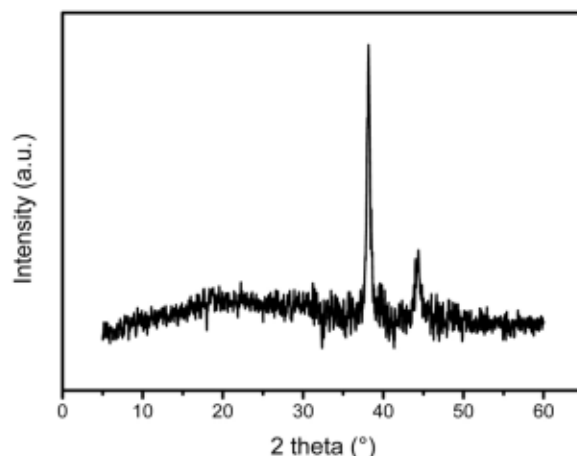


Fig. 5. XRD data of Ag nanoparticles created *in-situ* in PVC-g-PSSA film by 0.005 M NaBH₄ solution for 30 min.

comprising the amphiphilic graft copolymer and the silver nanoparticles were prepared by reduction process. UV-visible spectroscopy, XRD and TEM analysis revealed that the silver nanoparticles with 10~15 nm in average size were *in-situ* grown from the silver ions in the templated graft copolymer film. NaBH₄ was more effective in the formation of Ag nanoparticles than formamide or DMF. The absorbance at 415 nm sharply increased with NaBH₄ concentration up to 0.005 M, above which it did not increase significantly. The absorbance at 415 nm also sharply increased with contact time with NaBH₄ solution up to 600 sec, above which it increased less sharply. Thus, 0.005 M NaBH₄ concentration and 600 sec contact time were found to be sufficient for the preparation of silver nanoparticles in the PVC-g-PSSA graft copolymer.

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