

Polymer-Initiated Photogeneration of Silver Nanoparticles in SPEEK/PVA Films: Direct Metal Photopatterning

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Fabrication of hybrid systems consisting of metal nanoparticles and organic polymers is of considerable interest. These materials exhibit novel combinations of particle and polymer properties that are attractive for applications in nonlinear optics,¹ photoimaging and patterning,² glazing elements for sunlight control and magnetic devices,^{3,4} sensor fabrication,⁵ and catalysis.⁶

Efficient light-induced formation of metal particles in polymers is a required first step in efforts to develop photoadaptive polymer films and fibers. Earlier studies have shown that formation of Ag crystallites can be achieved with 350 nm photons in films made from blends of poly(vinyl alcohol), PVA, and poly(acrylic acid), PAA.⁷ However, these systems required light-sensitive metal ions (such as Ag(I) or Au(III) complexes) to obtain metal crystallites using photochemical methods.

A different approach was employed in the present study, which involved preparation of polymer matrices that are sensitive to light of 350 nm. The polymer systems consist of PVA, that acts as an electron donor in the photoreduction process, and sulfonated poly(ether-ether)ketone, SPEEK (Scheme 1). Under illumination, benzophenone present in PVA films abstracts hydrogen atoms from the polymer.⁸ Benzophenone groups of SPEEK are shown herein to undergo a similar reaction with PVA. The resulting polymeric benzophenone ketyl (BPK) radicals were found to reduce Ag⁺ ions, generating small silver particles in the polymer film. Evidence of silver nanoparticles formation via scavenging of the polymer radicals by Ag⁺ was obtained from UV-vis measurements. This significant finding is the basis for strategies to control metal growth in the solid films by manipulating the amount of polymer BPK radicals formed. From a practical point of view, this approach was anticipated to permit direct metal photopatterning of the polymer surface with mild UV photons.

PVA was from Aldrich ($M_w = (8.9-9.8) \times 10^4$ g/mol), and SPEEK was obtained by sulfonation of PEEK (Victrex, $M_w = 4.5 \times 10^4$ g/mol) in sulfuric acid.⁹ SPEEK-PVA films were made by casting acidic solutions of the polymers and glutaraldehyde (GA) on glass plates using a Gardner knife, followed by drying at 55 °C. Under these conditions, PVA is cross-linked by GA,¹⁰ resulting in water-insoluble, 50 μm thick flexible films containing entrapped SPEEK macromolecules. The films were doped with Ag⁺ through ion-exchange procedures using AgClO₄ solutions, washed, and dried in vacuo. Finally, the films were placed on quartz plates/metal frame holders and irradiated in a circular Rayonet 100 illuminator with 350 nm light.

The color of Ag⁺-doped SPEEK-PVA film develops into a sharp yellow upon photolysis and transforms into dark brown with noticeable reflectivity after about 4-6 h of irradiation. UV-vis spectra of the film recorded during the first 90 min of irradiation

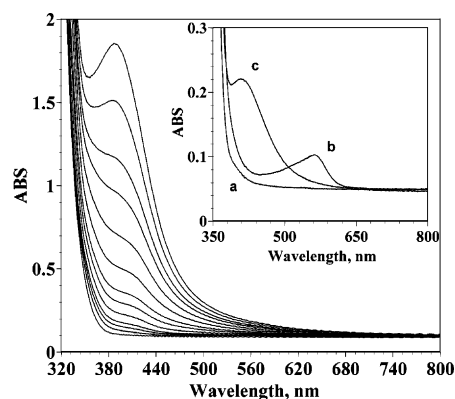
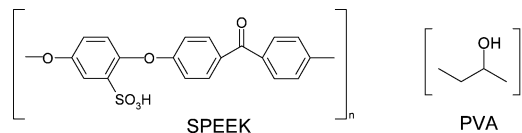


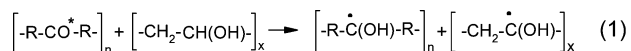
Figure 1. Evolution of spectra during Ag nanoparticle formation in films upon 350 nm light exposure ($I_0 = 2.2 \times 10^{16}$ $h\nu/s$) for 0, 2, 4, 6, 10, 15, 20, 30, 40, 51, 62, 75, and 90 min. Inset: Reaction of SPEEK radicals in films free of Ag⁺ ions; (a) before irradiation; (b) after 5 min of photolysis; (c) after immersing the film into a 10 mM AgClO₄ solution.

Scheme 1. Chemical Structures of the Polymers



are depicted in Figure 1. An absorption centered at 395 nm develops with time, which corresponds to the surface plasmon of spherical silver nanoparticles.¹¹

The light-sensitive nature of Ag⁺ ions is well known, as well as their ability to undergo photoreduction in the presence of alcohols including PVA.^{7,12} However, silver forms in the SPEEK-PVA films via a different mechanism, based on the photosensitivity of benzophenone groups of the SPEEK backbone. It is well known that irradiation of benzophenone generates n,π* type triplet states, which possess high activity for hydrogen abstraction.¹³ Poly(vinyl alcohol) is a suitable H-donor, and, therefore, the reaction between the two polymers leads to the production of polymeric alcohol radicals according to reaction 1.



Evidence that this reaction occurs in the solid matrices was obtained optically: the spectrum of an irradiated Ag⁺-free SPEEK-PVA film, shown in the inset (curve b) of Figure 1, indicates the development of a band centered at 565 nm. This signal is very similar to the absorption of BPK radicals in PVA films or in solution.^{8,14} Thus, we assign the 565 nm absorption to polymeric BPK radicals, hereafter referred to as SPEEK radicals.

The lifetime of generated SPEEK radicals is about 30 min at room temperature. If an irradiated film is immediately immersed

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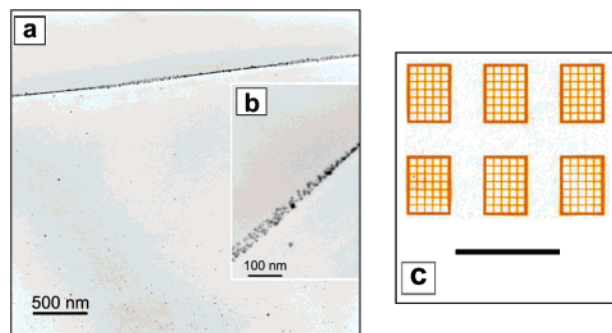
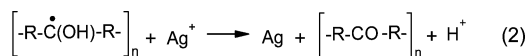


Figure 2. (a) TEM image of a cross-sectioned SPEEK–PVA film doped with Ag^+ after 8 h of light exposure ($\lambda = 350 \text{ nm}$, $I_0 = 3.2 \times 10^{16} \text{ hv/s}$); (b) high magnification image of the surface silver-rich layer; (c) silver patterned polymer surface (the marker represents 2 μm).

in a degassed aqueous AgClO_4 solution, the decay of the 565 nm signal is accompanied by the appearance of the silver crystallite band at 400 nm shown in the inset (curve c) of Figure 1. This result proves that SPEEK radicals participate in the reduction of Ag^+ ions according to reaction 2.



In addition, the absence of the signal at 565 nm during the irradiation of the Ag^+ -doped film (Figure 1) is consistent with the occurrence of reaction 2.

Evidence exists that Ag^+ ions are reduced in solution by BPK and by isopropyl alcohol radicals.^{15,16} Therefore, reduction of Ag^+ by poly(vinyl alcohol) radicals in a way similar to reaction 2 appears feasible, which would also contribute to the formation of metal. Current studies are centered on the photoreduction mechanism of Ag^+ by SPEEK–PVA blends as well as on the reduction of Au^{3+} , Cu^{2+} , Pd^{2+} , and Pt^{4+} ions.

The consequence of reaction 2 is re-formation of the chromophore groups and generation of silver atoms. Ag atoms are anticipated to diffuse within the film, followed by aggregation into metal clusters and subsequent formation of nanosized silver particles. Longer light exposures (more than 4 h) yield layers rich in metal particles on both film surfaces, inducing a dark brown coloration of the polymer matrix. This phenomenon is illustrated in Figure 2a, which is a TEM image of a photolyzed cross-sectioned film. According to the magnified image presented in Figure 2b, the metal layer is about 50 nm thick and is composed of silver nanoparticles.

Formation of particle layers can be understood in terms of diffusion of mobile metal atoms or clusters generated within the film to the surface, where they agglomerate into Ag crystallites. Supporting this hypothesis is the fact that a zone of $\sim 1 \mu\text{m}$ thickness containing only a few nanoparticles is apparent in Figure 2a underneath the film surface. Similar “depletion zones” have been noticed when polymers containing metal precursors are metalized by heating above 300 $^\circ\text{C}$,¹⁷ and during the formation of Ag crystallites in silver carboxylates by light or heat.¹⁸ Analysis of TEM images has indicated that, except for the region directly underneath the surface, Ag particles are randomly distributed throughout the film with a significantly higher concentration than that of the “depletion zone”. This finding demonstrates that the photoreduction of Ag^+ occurs not only in the region under the surface but across the entire film.

The presence of silver on the film surface after exposure to light has been confirmed by means of XPS. Silver has been identified

by the detection of the $\text{Ag}3d_{3/2}$ and $\text{Ag}3d_{5/2}$ photoemission lines at 374.3 and 368.5 eV, respectively, which disappeared upon Ar^+ sputtering to a depth of $\sim 50 \text{ nm}$.

Finally, irradiation with 350 nm light of Ag^+ -doped SPEEK–PVA films using a mask resulted in direct photopatterning. The ultimate resolution of this patterning method remains unknown; so far, 40 μm wide Ag lines (and more complex architectures shown in Figure 2c) can be imaged on the film surface.

In conclusion, a new strategy for metal patterning of polymer surfaces with mild UV light is presented here. The basis for this process is a light-induced reaction between functionalities of different polymers that leads to the generation of macromolecular alcohol radicals. Reaction of the polymeric alcohol radicals with Ag^+ induces formation of silver nanoparticles and regeneration of the SPEEK chromophores. Ag particles are initially randomly distributed across the film, but development of particle-rich layers on the film surfaces and of “depletion zones” occurs as photolysis irradiation proceeds. The method was applied for patterning the polymer surface with silver particles via photolysis with 350 nm light.

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Supporting Information Available: XPS spectrum of the polymer film with the formed silver particle layer (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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