

Photogeneration Kinetics of Ag Nanoparticles in Light Sensitive Polymer Films

A. S. Korchev*, K. Foti*, M. Sartin*, B. L. Slaten**, W. Gale*** and G. Mills*

* Department of Chemistry, University, AL, 36849

** Department of Consumer Affairs, University, AL, 36849

*** Materials Engineering Program, Auburn University, AL, 36849

ABSTRACT

The kinetics of Ag nanoparticle photogeneration inside optically transparent thin polymer films was studied. Light sensitive polymer films able to initiate the reduction of Ag^+ ions were prepared by blending poly(vinyl alcohol), PVA, and sulphonated poly(ether etherketone), SPEEK. Photolysis of such films with 350 nm photons produced benzophenyl ketyl (BPK) radicals of SPEEK, which are strong reducing agents able to transform silver ions into metal particles. Photoreduction of Ag^+ ions proceeds in the films through a monophotonic process which is not affected by the presence of oxygen. The photogeneration of small Ag crystallites is characterized by an activation energy typical of free radical reactions. At temperatures higher than the glass transition temperature of PVA a second reaction channel becomes important. This high temperature process occurs in the dark and is a self-accelerated reaction catalyzed by Ag nanoparticles present in the films.

Keywords: Ag nanoparticles, photochemistry, free radicals, autocatalysis

1 INTRODUCTION

Research on metallized polymers is an area of current interest in view of the technological importance of these materials.[1] For example, metal-containing polymers play significant roles in the microcircuits and automotive industries.[2,3] Furthermore, formation of nanometer-sized metal particles within polymers is also of interest because these crystallites exhibit size-induced changes in their properties,[4] and macromolecular matrices can be used to control the undesirable spontaneous growth of metal crystallites.[5] Another reason for the interest in polymer-stabilized metal nanoparticles is based on the fact that most of the resulting macromolecular composites can be processed into materials with distinct physicomechanical properties such as flexible films, gels, porous solid and fibers. The properties of the resulting metal-polymer matrices depend on the nature of the metal and polymer as well as on particle size, shape, spatial distribution and, often, preparation method.[6] Generation of metallic crystallites and structures within solid polymers using light as the energy source is an attractive method that can eliminate problems associated with inhomogeneous reactions that are typical of the solid state. This photochemical procedure requires composites, consisting of

metal ion precursors present inside appropriate macromolecular solids, which respond effectively to illumination. Earlier studies have shown that systems based on poly(vinyl alcohol), PVA, are interesting candidates as host materials because this polymer can act as a reducing agent and can be manufactured as transparent films and fibers.[7] For instance, light-induced formation of silver nanoparticles has been achieved in blends of PVA and poly(acrylic acid), PAA, doped with Ag^+ ions.[8,9] However, an important drawback of the PVA/PAA systems is that they require the presence of light-sensitive metal ions (such as Ag(I) or Au(III) complexes) that can initiate the photochemical formation of metal crystallites.

A different approach was recently developed in our laboratories, which involved preparation of polymer matrices that are sensitive to 350 nm light. The polymer composites consist of PVA, which is a defining component in the case of the films framework, and also acts the H-atom donating macromolecule in the photochemical process. Another component is sulphonated poly(ether etherketone), SPEEK, which is the origin for the photosensitivity of the composites. Blends of SPEEK and PVA are not only highly photosensitive but also readily bind metal cations, for instance Ag^+ , from aqueous solutions due to the ion-exchange capabilities of $-\text{SO}_3\text{H}$ groups present in SPEEK. As was shown earlier,[10-13] light initiates reactions of polymers when present either in aqueous solutions or as films, producing macromolecular benzophenyl ketyl (BPK) radicals capable of reducing silver ions. Evidence of silver nanoparticles formation via scavenging of the polymer radicals by Ag^+ was obtained from UV-Vis, EPR, XPS, TEM and FT-IR measurements. Presented here are kinetic data that revealed several mechanistic peculiarities of the metal photogeneration process in SPEEK/PVA polymer films.

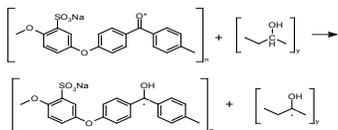
2 EXPERIMENTAL SECTION

Preparation of crosslinked SPEEK/PVA films and doping of the polymer matrices with Ag^+ ions was carried out as described before.[10-13] During photolysis experiments the films were placed into 2 mm quartz cells sealed with stopcocks, which allowed to saturate the polymer matrices with different gases. Illumination took place inside a circular Rayonet photoreactor; in experiments performed at different temperatures the quartz cell were immersed into a water bath located inside the illuminator. The extend of the Ag^+ photoreduction was followed

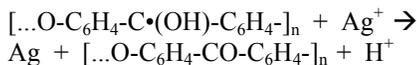
spectrophotometrically via monitoring the formation of the plasmon absorption centered at 400 nm that is characteristic of spherical Ag particles with nanometer dimensions.[4]

3 RESULTS AND DISCUSSION

Earlier studies have shown that photolysis of SPEEK with 350 nm photons results in the formation of reducing polymeric BPK radicals exhibiting an absorption signal with a maximum at 565 nm.[10-13] Excitation of the benzophenone (BP) function yields a triplet excited state able to abstract H-atoms from alcohols, generating a BPK radical and an α -hydroxy alcohol radical.[14] The analogous process for our blends is illustrated in scheme shown below, where the top-left structure represents an excited SPEEK macromolecule and the top-right structure corresponds to PVA. Shown on the bottom are the structures of the SPEEK and PVA radicals, respectively. Alcohol radicals reduce BP groups forming BPK radicals and a similar reduction of the BP groups by PVA radicals is expected to occur, which is consistent with EPR data showing that only SPEEK radicals are present after photolysis.[10]



Binding studies showed that the maximum amount of Ag^+ ions ion-exchanged into the films corresponded to one half of the sulfonic groups present in SPEEK. The high concentration of metal ions present in the films together with the long lifetimes (tens of min) of the BPK radicals of SPEEK allows them to reduce Ag^+ ions yielding Ag particles and reforming the BP functions:



which enabled continuous photogeneration of radicals and metal crystallites. As anticipated, the signal of the BPK radicals centered at 565 nm was not detected during photolysis of films doped with silver ions. Instead, the optical spectra showed the typical plasmon band of Ag crystallites with a maximum at 400 nm, demonstrating that the polymeric BPK radicals are oxidized by Ag^+ ions forming metal particles. TEM images of a microtomed sample of irradiated, Ag^+ -doped films showed the presence of spherical silver particles (average size = 10 nm) uniformly distributed throughout the polymer matrices.

Plots of the optical density at 400 nm as a function of illumination time were nearly linear for about 30 min, indicating that particle formation obeyed initially a zero-order rate law. This kinetic feature allowed the use of

initial rates to characterize the photoreduction of Ag^+ ions. Kinetic data obtained at different intensities of light (I_0) showed that the initial rates increased linearly with increasing photon flux. This means that the reaction order with respect to I_0 is one, implying that photogeneration of Ag particle is a monophotonic process different from the biphotonic reaction observed in PVA/PAA films.[9] Similar rates of particle formation were obtained in the presence or absence of oxygen, indicating that scavenging of the BPK radicals by O_2 was not important in the macromolecular matrices.

Initial rates obtained between 10 and 95 °C yielded an activation energy of $E_a = 32$ kJ/mol, which is a typical value for free radical induced reactions. Thermal reduction of Ag^+ ions in the dark was not observed below the glass transition temperature of PVA (86 °C). However, metal formation was noticed in the dark above the T_g of PVA via a thermal reaction with $E_a = 141$ kJ/mol. Interestingly, this process took place only when Ag crystallites were present in the films. In fact, the thermal reaction became very fast in films that had been exposed to light in order to generate known amounts of Ag crystallites. These findings are clear evidence that the thermal process is self-accelerating, where the metal particles act as catalysts for the Ag^+ reduction.

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