

M98-A10 Photoadaptive Fibers for Textile Materials

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Goals

The aim of this project is to develop photoadaptive fibers that can undergo photoinduced reversible optical and heat reflectivity changes. Thin and optically transparent polymer films were prepared to study the kinetics of the particle evolution that occurs in the photosensitive fibers developed during the first year. The goal of the second year was accomplished since the films were optimized for speed in metal particle formation and were metallized exclusively at high light intensities.

Abstract

Polymeric films that are optically transparent and water-insoluble were made by crosslinking poly(vinyl alcohol) with dimethylsulfoxide in the presence of poly(acrylic acid). Swelling the polymeric materials with solutions of Ag^+ and AuCl_4^- ions allowed uniform incorporation of the metal ions into the polymer matrices. The high optical quality of these films enabled direct detection of photo-generated metal particles utilizing UV-Visible spectroscopy. Speed of metal particle formation was optimized by systematic variations of the preparation conditions. Ag particles of nanometer size were detected within seconds of illumination and particle growth took place via metal deposition on existing particles. Generation of Au particles was about ten times slower and occurred through a chain reaction. In both cases the metal crystallites formed only upon exposure with high intensity artificial light or sun light, but not under ambient light. The fast photochemical metallization occurring exclusively under high photon flux is one of the desired properties of the materials that are being developed. High metal loading can be achieved in these systems, making them interesting materials for applications where stable metal particles are required, such as flexible shields for electromagnetic radiation and resistive heating elements.

Introduction

Polymeric systems containing small metal particles are attractive systems since they are expected to exhibit properties that are of scientific as well as of practical interest. The most interesting systems are those with a photoadaptive (or "smart") behavior, where metal crystallites are generated by the action of light but decay in the dark. Hence, these systems experience desirable and predictable reversible changes in their physical and chemical properties in response to illumination. Conceptually these systems should operate in a fashion similar to the simpler oxide photochromic glasses, where photo-reduction of silver halides yields Ag particles that undergo a dark oxidation reaction to reform the metal halides. The photoadaptive polymeric systems that are envisioned should be of practical interest for the reflection of intense infrared radiation. Currently available polymeric photochromic glasses based on dyes cannot be used for these applications because of the poor reflectivity toward infrared radiation and lack of long term thermal stability of the dyes. A model photoadaptive system was developed recently by us; in

this system AuCl_4^- or PdCl_4^{2-} ions incorporated into methanol-swollen, crosslinked polymers of diallyldimethylammonium chloride (DADMAC) are photo-reduced to form nanometer-sized Au or Ag particles. However, oxidation of the metal crystallites in a dark room temperature reforms the starting metal complexes.

In the present project the research results of gel systems were utilized as a starting point for developing photoadaptive infrared reflecting polymer fibers that operate in a fashion similar to photochromic glasses, that is, metal particles being exclusively formed upon exposure to high intensity visible light, followed by particle decay once the photon intensity decreases to ambient light levels. Light-sensitive fibers of poly(vinyl alcohol), or PVA, that are insoluble in water and contain Ag^+ or AuCl_4^- ions were made during the first year of this study. Illumination of the dry fibers yielded metal particles only under high photon fluxes. Figure 1a is a picture of a PVA fiber made by crosslinking this polymer with dimethylsulfoxide (DMSO) in the presence of poly(acrylic acid), or PAA. Shown in Figure 1b is a fiber containing AgNO_3 after exposure to sunlight for several minutes, an image of the fiber after cross-sectional cutting is presented in Figure 1c. The brown coloration of the exposed fibers indicates that Ag particles with diameters in the nanometer range were generated throughout the fiber. Similar results were obtained when PVA fibers containing poly(DADMAC) and AuCl_4^- ions were irradiated. Particle decay was not detected since no attempt was made to optimize conditions leading to corrosion of the crystallites. It should be noted that formation of stable metal particles inside the polymer systems is also of interest for potential applications such as 3D storage of optical data, shielding of electromagnetic radiation and flexible elements for resistive heating.

The goal of the second year was to investigate the dynamics of particle evolution in the polymer systems. This was a necessary requirement to optimize the speed of the particle formation and oxidation processes. UV-Visible optical detection is the preferred method for such measurements since the crystallites exhibit strong plasmon bands centered between 380 and 500 nm for Ag, and 520 to 650 nm for Au. Polymer films were needed because quantitative optical spectroscopy of single fibers is not feasible with the current technology. Obviously high optical quality and transparent films were mandatory, and the films needed to possess the same photochemical properties that were achieved in the case of the PVA fibers.

Results

Reaction of PVA with DMSO in the presence of PAA yielded gels that were initially employed for fiber formation, the same gels were employed for film preparation. While poly(DADMAC) was used for preparation of fibers loaded with Au(III) ions, it was found that loading of gold ions improved when this polymer was substituted by PAA. After melting the gels at 70°C , films were made by spin coating the solutions onto quartz disks at 300 rpm. The films were then briefly exposed to water or methanol at several temperatures to achieve uniform shrinking, which allowed separation of the films from the quartz support. Best results were obtained utilizing methanol cooled with liquid nitrogen. The films were cleaned by a 19 hour immersion in methanol; incorporation of metal ions into the polymers was accomplished by exposing them to aqueous or methanolic solutions of AgNO_3 or NaAuCl_4 . The films were then briefly cleaned with methanol, placed between 2 quartz disks and dried under vacuum at room temperature. The following parameters were systematically varied in order to optimize film properties: molar mass of PAA ($2\text{-}170 \times 10^3$ g/mol), length of reaction time for gel formation (10-30 min), length of gel aging (0-17 days) and concentrations of metal ions in the solutions

used to load the films (0.1-10 mM). Optimum results were obtained using the following conditions: PAA (Na⁺ salt) with a molar mass of 2.0×10^5 g/mol, 10 min for the crosslinking reaction between PVA with DMSO and PAA, 3 days of gel aging at room temperature, and metal ion concentrations of 10 mM.

Photolysis experiments were performed after drying the fibers using either photons of 350 nm, with a light intensity of 7.0×10^{17} mol (photons)/min, from a Rayonet circular illuminator or direct sunlight. Figure 2 shows the optical spectrum of films containing Ag particles after irradiation for 12 min, the strong signals centered at 460 nm correspond to the plasmon band of the crystallites. Curve C corresponds to a film shrank in methanol at low temperature and then exposed to a methanolic Ag⁺ solution. Lower optical densities were detected for films shrank at room temperature in methanol when exposed to either aqueous (curve B) or methanolic (curve A) solutions of the silver ions. The films turn yellow-brown during the photochemical formation of the particles. Figure 3 is a kinetic plot of the optical data with increasing irradiation time; straight lines are obtained by plotting the cubic root of the optical density at 460 nm. These data are indicative of formation processes where crystallites grow by deposition of metal atoms on small Ag clusters that cannot be detected by optical means. Thus, new particles are detected only after they become large enough to develop a plasmon band. The kinetic results indicate that particle generation in films obtained after shrinking with low-temperature methanol was twice as fast as in cases where shrinking was performed at room temperature. Aging of the gels for 17 days yielded fast particle formation processes, but broad plasmon bands are detected indicating that the resulting particles have a broad size distribution and are probably agglomerated.

Photo-generation of Au particles in films is faster than in fibers but is still ten times slower than formation of Ag crystallites in films. This is not surprising because three electrons are needed to reduce a Au(III) complex whereas only one electron is required to reduce Ag⁺ ions. However, post-irradiation formation of Au particles occurs and is typical of processes involving free radical chain reactions. A similar process takes place during formation of Au crystallites in poly(DADMAC) gels, where the excited state of AuCl₄⁻ reacts with methanol forming free radicals. These radicals diffuse within the gel and further reduce AuCl₄⁻ ions. We have recently demonstrated that particle formation in the poly(DADMAC) gels is a biphotonic process. The fact that formation of Au particles takes place only at high light intensities in these gels and as well as in the PVA films suggests that a similar biphotonic particle formation reaction occurs in the latter systems. Considering that generation of silver particles is faster in the films, it appears that formation of Ag crystallites also proceeds via a biphotonic chain reaction. Such a mechanism is a reasonable explanation for the light sensitivity of the films only under high light intensities.

Preliminary results indicate that Ag particles present in the PVA/PAA films are sensitive toward oxidation upon exposure to peroxide solutions. Interestingly, particle formation takes place again when the treated samples are reirradiated. These results suggest that reversible particle formation can be achieved by incorporation of mild oxidants in the films.

Future Plans

Films of uniform thickness will be spun in order to quantify photonic efficiency. These films will be used to study the chemistry of the interfacial regions, which seem to have different optical properties than the bulk film. These properties are believed to be similar to that of the fibers. Processes to enhance the reversibility of the reactions in the films and fibers will be further explored with the incorporation of mild oxidants into the films and fibers. This is not trivial because we do not want to alter the physical properties of the films or fibers. We will also investigate the effect of the polymer orientation on particle size and distribution. We will employ X-Ray Diffraction to determine the particle size and distribution. Differential Scanning Calorimetry and Reflective Infrared Spectroscopy will be used to further characterize the polymeric films and fibers.

Figure 1a. Poly (vinyl alcohol) fibers, PVA, crosslinked with dimethylsulfoxide in the presence of poly (acrylic acid), PAA.



Figure 1b. PVA/PAA fibers containing AgNO_3 after irradiation.



Figure 1c. Cross-sectional cut of an illuminated PVA/PAA fiber containing AgNO_3 .

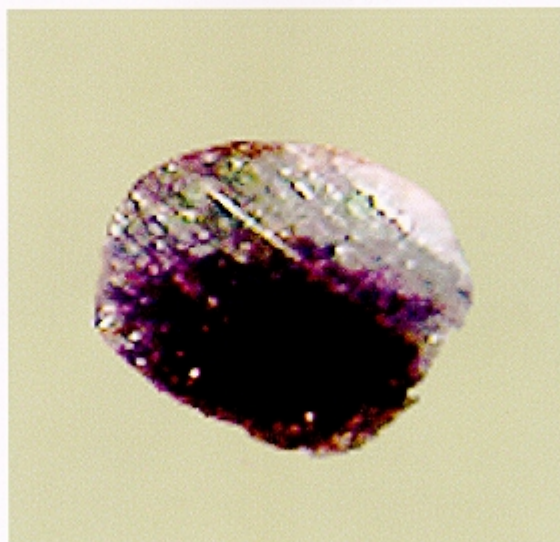
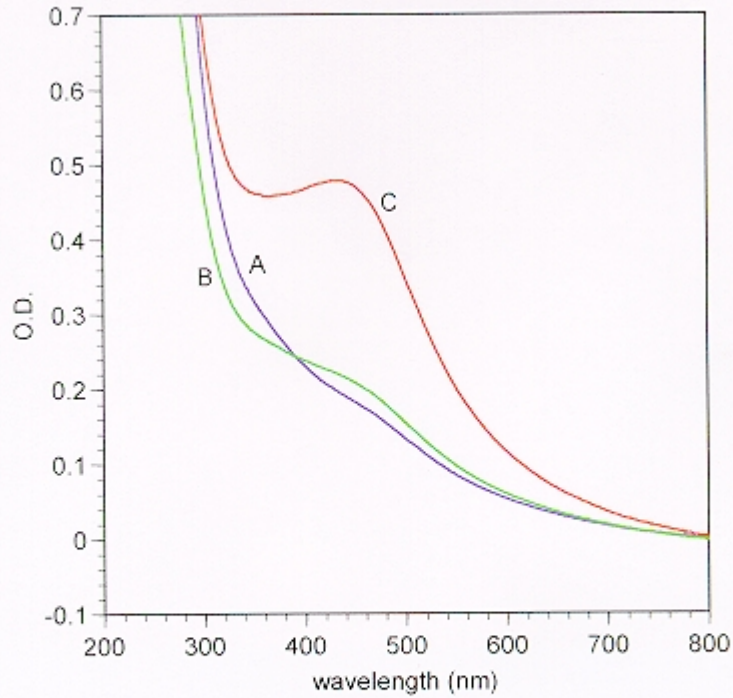
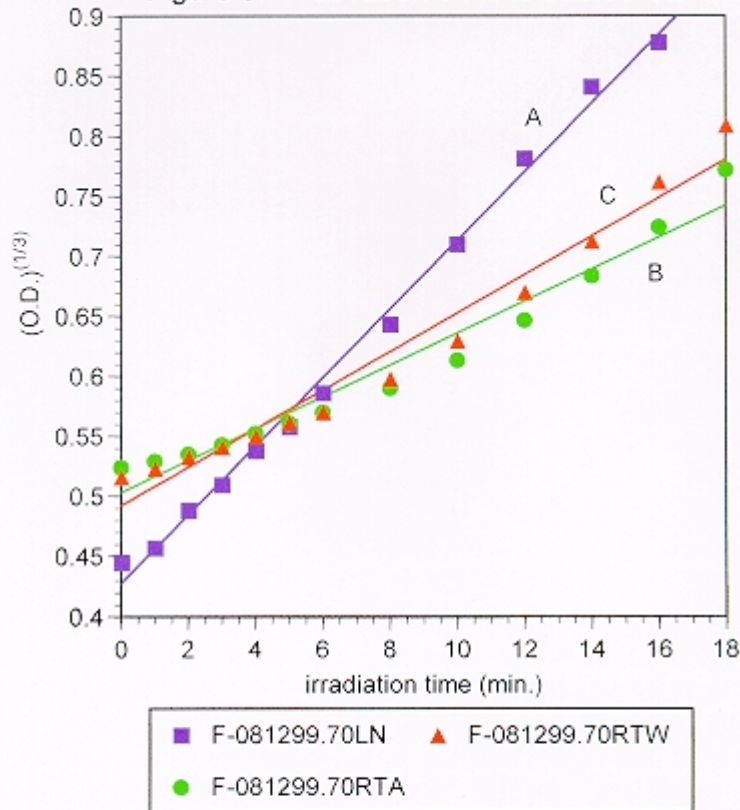


Figure 2. Silver Particle Formation in PVA/PAA Films After 12 Minutes Irradiation, Coagulant Series: Sample F-081299.70



- A-Room Temperature Methanol - Methanol
- B-Room Temperature Methanol - Water
- C-Liquid Nitrogen Cooled Methanol - Methanol

Figure 3. F-081299.70 Films Cubic Plots



A: F-081299.70LN

$$f(x) = 2.854219E-2 \cdot x + 4.275245E-1$$

$$R^2 = 9.952018E-1$$

B: F-081299.RTA

$$f(x) = 1.330147E-2 \cdot x + 5.030305E-1$$

$$R^2 = 9.610748E-1$$

C: F-081299.70RTW

$$f(x) = 1.605031E-2 \cdot x + 4.920699E-1$$

$$R^2 = 9.679004E-1$$