# Sulfonated Poly(Ether Ether Ketone)/Poly(Vinyl Alcohol) Sensitizing System for Solution Photogeneration of Small Ag, Au, and Cu Crystallites

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Illumination of air-free aqueous solutions containing sulfonated poly(ether ether ketone) and poly(vinyl alcohol) with 350 nm light results in benzophenone ketyl radicals of the polyketone. The polymer radicals form with a quantum yield 0.02 and decay with a second-order rate constant 6 orders of magnitude lower than that of typical  $\alpha$ -hydroxy radicals. Evidence is presented that the polymeric benzophenone ketyl radicals reduce Ag<sup>+</sup>, Cu<sup>2+</sup>, and AuCl<sub>4</sub><sup>-</sup> to metal particles of nanometer dimensions. Decreases in the reduction rates with increasing Ag<sup>I</sup>, Cu<sup>II</sup>, and Au<sup>III</sup> concentrations are explained using a kinetic model in which the metal ions quench the excited state of the polymeric benzophenone groups, which forms the macromolecular radicals. Quenching is fastest for Ag<sup>+</sup>, whereas Cu<sup>2+</sup> and AuCl<sub>4</sub><sup>-</sup> exhibit similar rate constants. Particle formation becomes more complex as the number of equivalents needed to reduce the metal ions increases; the Au<sup>III</sup> system is an extreme case where the radical reactions operate in parallel with secondary light-initiated and thermal reduction channels. For each metal ion, the polymer-initiated photoreactions produce crystallites possessing distinct properties, such as a very strong plasmon in the Ag case or the narrow size distribution exhibited by Au particles.

## Introduction

Synthesis of metal nanoparticles is an area of constant interest since these particles possess unusual properties and also because of their possible use in the fabrication of arrays with different dimensionalities.<sup>1-6</sup> Light-initiated reduction of metal ions in the presence of electron donors is a known method for the preparation of small metal particles that has found a wide range of applications including synthesis of metallic colloids,<sup>7</sup> imaging,<sup>8</sup> and metallization and patterning of polymer films.<sup>9,10</sup> Given the growing technological significance of metallized polymer films,<sup>11</sup> development of simple photochemical routes for the preparation of metallic structures in these matrixes remains an important goal. Direct excitation by hard UV photons has been employed often to induce photoreduction of metal ions or complexes that absorb strongly below 300 nm,<sup>7,9,12,13</sup> allowing preparation of a variety of metal particles either in solution or in solids. Limitations of this method are the need for matrixes exhibiting some transparency to high-energy light and stability against excessive photochemical degradation. The energetic photons may also induce undesired oxidation of the products, as was found in the case of Ag crystallites.<sup>14</sup>

An alternative procedure involves utilization of metal complexes that absorb photons with  $\lambda > 300$  nm. Silver halides and AuCl<sub>4</sub><sup>-</sup> ions are the best known examples of species that experience photoreduction initiated by near-UV or visible light;<sup>8,15</sup> some Cu<sup>2+</sup> complexes undergo similar photoreactions.<sup>16</sup> This method is less restrictive since a wide range of matrixes are fairly transparent at longer wavelengths, but only a limited number of metallic species experiencing efficient photoreduction have been identified. Metal particles sometimes form via multiphotonic reactions: 17-21 one of their distinctive features is the possibility of inducing such reactions by excitation wavelengths at which the metal ions exhibit no absorption of light. While the feasibility of such processes is hard to anticipate, reductions derived from mutiphoton absorption by photosensitizers offer a more predictable method for producing metal crystallites.<sup>10b</sup> Potential problematic issues of mutiphotonic reactions are nontrivial effects induced by some matrixes.<sup>17,19</sup> Another strategy is based on photoreactions of ketones to initiate formation of metal crystallites. Illumination of ketones results in excited states of the carbonyl group able to abstract H atoms from compounds acting as donors; this process can produce reducing  $\alpha$ -hydroxy (or ketyl) radicals.<sup>22</sup> Reduction of Ag, Au, and Cu complexes to metal particles have been achieved through excitation of acetone,<sup>23</sup> acetophenone,<sup>24</sup> benzophenone (BP),<sup>25,26</sup> and anthraquinone derivatives in the presence of alcohols as H atom donors.27 Benzoin has also been employed to photogenerate metal crystallites,<sup>28</sup> although this compound forms reducing radicals via a different process. An advantage of ketone-initiated photoreactions is their versatility since they are not dependent on the photochemical properties of the metal precursors.

Stable nanometer-sized particles are frequently prepared in solutions containing polymers that can hinder uncontrolled growth of the crystallites. Hence, an alternative method for generating small metallic crystallites in solution is to use macromolecules that function as "particles stabilizers" and that also participate in the photoreduction of metal precursors as either sensitizers or reductants. An example of such a system

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would comprise a polymer acting as a sensitizer and another that performs the donor and particle stabilizer functions at the same time. Because the macromolecules contain a large number of functions that can participate in the photoreactions, changes of a few of such groups during the reactions are not expected to alter significantly the ability of the polymers to perform their tasks. Such systems could offer a high degree of processing flexibility as they may generate not only colloidal solutions but also metallized polymeric films, membranes, or gels upon solvent evaporation from the colloids. Furthermore, solution studies were anticipated to help identify polymer combinations yielding efficient particle generation in insoluble films derived from such macromolecular materials. This expectation was based on earlier results showing that solution experiments were useful as fast tests for optimizing the polymeric compositions of films.18c

The strategy based on polymeric materials as key components for the initiation of particle formation was validated in recent investigations.<sup>29</sup> Efficient generation of nanometer-sized Ag crystallites was demonstrated upon exposure to 350 nm light of insoluble films made from poly(vinyl alcohol) (PVA), sulfonated poly(ether ether ketone) (SPEEK), and Ag<sup>+</sup> ions. Selection of such a combination aimed at mimicking the solution photoreactions of the BP/2-propanol system, which yields reducing α-hydroxy radicals commonly known as benzophenyl ketyl (BPK) radicals.<sup>22</sup> The benzophenone groups of SPEEK were envisioned to act in a way analogous to BP molecules, whereas PVA was intended to fulfill the role of 2-propanol as an H atom donor. Illumination produced reducing species with an absorption band centered at 565 nm, thought to be BPK radicals of the polyketone (hereafter referred to as SPEEK radicals).<sup>29</sup> The long lifetime of the polymer radicals allowed confirmation of their participation in the reduction of Ag<sup>+</sup>. A preliminary report showed that extension of the polymer photoreactions to solutions was possible since PVA and SPEEK are water-soluble.<sup>29b</sup> Examined here are the kinetic features of the SPEEK-sensitized generation of stable Ag, Au, and Cu crystallites in aqueous media. Evidence is presented that the metal ions affect significantly the photoprocesses of SPEEK, altering the rates of particle formation.

## **Experimental Section**

Poly(vinyl alcohol), 99+% hydrolyzed (average molar mass  $= 8.9 - 9.8 \times 10^4$  g/mol), was obtained from Aldrich. Poly-(ether ether ketone) (PEEK) with an average molar mass of 4.5  $\times$  10<sup>4</sup> g/mol was a gift from Victrex, Inc. AgClO<sub>4</sub>·H<sub>2</sub>O (Aldrich), HAuCl<sub>4</sub>·3H<sub>2</sub>O (Alfa), CuSO<sub>4</sub>·5H<sub>2</sub>O, HCl, HClO<sub>4</sub>, NaOH, and H<sub>2</sub>SO<sub>4</sub> (Fisher) were used as received. Glassware employed for colloid synthesis was treated with aqua regia; deionized water from an ion-exchange resin deionizer (U. S. Filter Service) was used in all procedures. Water-soluble SPEEK was obtained by complete sulfonation of PEEK using literature procedures,<sup>30</sup> which will be described only briefly. The polyketone was ground to a fine powder and dried under vacuum at 150 °C. A suspension consisting of 150 g of PEEK per L of 96% H<sub>2</sub>SO<sub>4</sub> was heated at 50 °C for several days under constant stirring, inducing sulfonation followed by dissolution of the resulting SPEEK. Combination of the resulting solution with an H<sub>2</sub>O/HCl mixture (5:1 v/v) precipitated the product. Occluded H<sub>2</sub>SO<sub>4</sub> was extracted from the sulfonic acid derivative via three water washings, followed by neutralization with a 0.02 M NaOH solution, rinsing with H<sub>2</sub>O, and drying at 150 °C under vacuum. Losses of the soluble product were minimized by using icecold liquids. Product characterization via FTIR, NMR, and elementary analysis (Atlantic Microlab) yielded results in good agreement with published SPEEK data.<sup>30b</sup>

Separate solutions of PVA and of the sodium salt of SPEEK were prepared by dissolving each of the polymers in water at 70 °C and combining them under stirring, keeping a PVA/ SPEEK molar ratio of 20:1 in all experiments. The mixture was placed in a glovebag filled with nitrogen and then bubbled slowly with N<sub>2</sub> for 1 h to avoid severe foaming of PVA. Aqueous solutions of the Ag, Au, and Cu metal ions were bubbled with nitrogen for 20 min inside the glovebag. Finally, the polymer solution was combined with one containing a metal precursor, yielding final concentrations of 1.6 wt % PVA and 0.7 wt % SPEEK. In terms of monomer units, these concentrations correspond to 0.36 M in the case of PVA and 0.018 M for SPEEK. Such a polymer combination was identified in preliminary experiments as that enabling the most efficient photogeneration of Ag crystallites. The kinematic viscosity of aqueous solutions containing the 1:20 SPEEK/PVA molar ratio was determined at room temperature by means of a Cannon-Fenske CFRC 9721-1359 glass viscometer. Detection of polymer crosslinking during illumination was not feasible with this technique because of the relatively high solution viscosity and the short illuminations required for completion of the photochemical reactions.

Milton Roy #33-17-80 optical test tubes (path length = 1 cm) that had flattened bottoms served as irradiation vessels. The tubes were sealed with rubber septa after introduction of the solutions, which were stirred throughout the photolysis. Mixtures containing HAuCl<sub>4</sub> were kept at 4–5 °C until shortly before irradiation to prevent the thermal reduction of Au ions by PVA.<sup>31</sup> Uniform illumination of the optical tubes was achieved by positioning them at midheight inside a Rayonet 100 circular illuminator that generated photons with  $\lambda = 350 \pm 15$  nm by means of 16 RPR-3500A lamps. The temperature inside the illuminated Rayonet was 29 °C; an Aberchrome 540 was used to determine the light intensity ( $I_0$ ).<sup>32</sup> Optical densities were measured on a Shimadzu UV—vis PC2501 spectrophotometer. Kinetic data derived from optical determinations were typified by a maximum deviation of 30%.

Transmission electron microscopy (TEM) measurements were carried out by employing a JEOL JEM-2010 microscope with an accelerating voltage of 200 kV or on a Zeiss EM 10CR operating at 60 kV. Specimens were prepared on Cu grids covered with holey-carbon films for Ag and Au colloids. The grids were dipped into the colloidal solutions, excess liquid was removed, and the samples were dried under vacuum. Ni grids were used to image copper colloids; specimen preparation was conducted inside a glovebag to avoid oxidation of Cu particles by air. Characterization of the air-stable Ag and Au crystallites employed X-ray diffraction (XRD) because electron diffraction measurements were hindered by films of the polymers deposited on the TEM grids during sample preparation. Samples for XRD determinations were prepared via colloid centrifugation and dispersion of the precipitates in water. This procedure was repeated twice, and the resulting solids were dried under vacuum, coated onto glass fibers, and fixed with an epoxy resin. The fibers were mounted on a Bruker SMART APEX charge coupled device (CCD) diffractometer that employed Mo Ka radiation. Comparisons of average particle diameters obtained from TEM and XRD determinations were not meaningful given that the method of sample preparation for diffraction experiments induced particle growth.



**Figure 1.** UV-vis spectra of air-free SPEEK/PVA solution: before irradiation, (0); after 1 min of irradiation, (i); and after 3, 5, 10, 20, and 33 min in the dark;  $\lambda = 350$  nm and  $I_0 = 3.4 \times 10^{-5}$  M(*hv*)/s. Inset: Second-order plot for the dark decay of the polymer radical absorption at 565 nm.

#### **Results and Discussion**

Sulfonation of PEEK allowed to use the BP groups of the soluble polymer derivative as initiators of photoreactions in aqueous solutions. Slow transformations accompanied by weak optical signals resulted from illumination of air-free SPEEK solutions, but large absorptions developed fast in the presence of PVA. Figure 1 depicts the optical spectra of such a SPEEK/ PVA solution photolyzed for 1 min, showing a band with  $\lambda_{max}$ = 565 nm. Illumination of films composed of these polymers produced an identical optical signal that was attributed to SPEEK radicals.<sup>30</sup> Short-lived absorptions with similar shape and  $\lambda_{max}$ value (560 nm) have been detected during the photoreduction in the presence of 2-propanol of water-soluble benzophenone derivatives containing alkyl sulfonate functions in the para position.<sup>33</sup> The photogenerated transient species are believed to be BPK radicals of the sulfonated BP derivatives. Interestingly, allowing completion of the radical decay process followed by another illumination step re-forms the absorption with  $\lambda_{max}$ = 565 nm depicted in Figure 1. No such signal results when air-saturated solutions of the polymers are irradiated. These observations and the spectral results from experiments with alkyl sulfonate derivatives of BP support the interpretation that SPEEK radicals are responsible for the band centered at 565 nm.

Photogeneration of BPK radicals in SPEEK/PVA systems can be understood on the basis of the known light-induced transformations of benzophenone.<sup>22</sup> Light absorption by BP yields first a singlet (n,  $\pi^*$ ) excited state, which converts fast through intersystem crossing into a triplet (n,  $\pi^*$ ) excited state able to abstract an H atom from 2-propanol. A similar path for the formation of polymer radicals seems reasonable given the structural analogies between benzophenone molecules and the BP groups of SPEEK as well as those existing between 2-propanol and PVA. Reaction 1 represents the proposed overall electronic transition to the triplet excited state

$$\{\mathbf{R'RC=O}\}_z + hv \rightarrow \{^{3}\mathbf{R'RC=O}\}_z^* \tag{1}$$

where R and R' are the groups attached to the carbonyl function within the SPEEK. The structures of the repeating units of each polymer that undergo changes are presented in reaction 2, which represents the H atom abstraction reaction leading to SPEEK radicals



where the first structure on the left side corresponds the triplet excited state of a BP unit in an SPEEK chain. Abstraction of H atoms from PVA in solution is known to predominantly produce  $\alpha$ -hydroxy radicals that behave as reducing agents.<sup>34</sup> For this reason, only such types of PVA radicals were included as products in reaction 2.

Hydrogen atom abstraction from 2-propanol mainly generates  $(CH_3)_2C^{\bullet}OH$  radicals that reduce benzophenone molecules into BPK radicals,  $(Ph)_2C^{\bullet}OH$ , with a rate constant of  $k = 4 \times 10^5$  M<sup>-1</sup> s<sup>-1</sup>.<sup>35</sup> The similarities in the structures of the  $\alpha$ -hydroxy radicals derived from 2-propanol and from PVA suggest that reduction of the BP groups of SPEEK by the polyol radicals is feasible. This process is represented by reaction 3

{(CH<sub>2</sub>)C<sup>•</sup>OH}<sub>y</sub> + {R'RC=O}<sub>z</sub> 
$$\rightarrow$$
  
{R'RC<sup>•</sup>OH}<sub>z</sub> + {(CH<sub>2</sub>)CO}<sub>y</sub> (3)

The efficiency of this secondary formation path of SPEEK radicals is difficult to estimate because PVA radicals decay in water with rate constants ranging between 1 and  $7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  depending on the radical concentration.<sup>34</sup> Also, the participating macromolecular species in the SPEEK/PVA solutions are anticipated to diffuse slower than benzophenone molecules and (CH<sub>3</sub>)<sub>2</sub>C•OH. However, the high concentration of BP groups from SPEEK (0.018 M) is expected to facilitate the reduction of the polymeric carbonyl groups through reaction 3. Consequently, the optical signal shown in Figure 1 after 1 min of photolysis reflects the total amount of SPEEK radicals produced via reactions 2 and 3.

The extinction coefficient ( $\epsilon$ ) of SPEEK at 350 nm in aqueous solution is 900 M<sup>-1</sup> cm<sup>-1</sup>. This means that most of the incident photons are absorbed by the polyketone at the employed SPEEK concentration because the solutions exhibit an absorbance much larger than 1 at 350 nm. Thus, an initial quantum yield for the formation of SPEEK radicals ( $\phi_i$ (SPEEK•) =  $r_i$ (SPEEK•)/ $I_0$ ) can be evaluated from  $I_0 = 3.4 \times 10^{-5} \text{ M}(hv)/\text{s}$  and the initial rate of radical generation,  $r_i$ (SPEEK•). Correcting the radical signal from the absorbance recorded prior to photolysis yields an initial change in optical density of  $\Delta_i$ OD equal to 2.5  $\times$  10<sup>-3</sup> s<sup>-1</sup> at 565 nm. Considering that  $r_i(\text{SPEEK}^{\bullet}) = \Delta_i \text{OD}/\epsilon$  and assuming that the extinction coefficient of SPEEK radicals is close to the value reported for  $(Ph)_2C^{\bullet}OH$  radicals ( $\epsilon = 3.5 \times 10^3$  $M^{-1}$  cm<sup>-1</sup>),<sup>35</sup> the calculation results in  $\phi_i$ (SPEEK•) = 0.02. This estimate is only a lower limit because, as illustrated in Figure 1, spectral data recorded after photolysis is stopped indicate that the radicals decay in the time range of several minutes. Also,  $\phi_i$ (SPEEK•) will be affected by the cross reaction between polymer radicals similar to the one noticed for (Ph)<sub>2</sub>C<sup>•</sup>-OH and  $(CH_3)_2C^{\bullet}OH$  that occurs with  $k = 8 \times 10^8 \text{ M}^{-1}$ 

 $s^{-1}$  in acetonitrile.<sup>35</sup> Equation 4 represents the cross reaction of SPEEK radicals with PVA radicals

$$\{(CH_2)C^{\bullet}OH\}_v + \{R'RC^{\bullet}OH\}_z \rightarrow \text{products}$$
(4)

for which the rate constant may be even higher as was determined for the decay of PVA radicals in water.<sup>34</sup> Hence, the reaction between SPEEK radicals and PVA radicals is expected to lower the yield of the former species under steady-state photolysis particularly because, as shown below, the polyketone radicals exhibit a rather long lifetime.

Included in the inset of Figure 1 is a second-order plot derived from the corrected OD at 565 nm during the first 20 min of the decay step (3 half-lives). A straight-line relationship is obtained with a slope of 5.02 OD<sup>-1</sup> min<sup>-1</sup> ( $r^2 = 0.995$ ). The use of the above-mentioned extinction coefficient for BPK radicals yields a rate constant for the decay of SPEEK radicals equal to *k*(decay) = 290 M<sup>-1</sup> s<sup>-1</sup>. Essentially the same decay rate constant (within experimental error) results for photolytic periods between 10 and 60 s, followed by monitoring only OD at 565 nm as a function of time. These results indicate that species absorbing at 565 nm decay via radical—radical disproportionation and/or dimerization typical of  $\alpha$ -hydroxy radicals

$$\{R'RC'OH\}_z + \{R'RC'OH\}_z \rightarrow$$
  
dimerization/disproportionation (5)

Moderate stirring of the solutions after photolysis accelerates the radical decay noticeably, yielding in a rate constant 2.5 times higher than the  $k_5$  value obtained in unstirred solutions. This effect arises from the diffusional restrictions that the macromolecules experience since the viscosity of the concentrated polymer solutions is 4 times the value of H<sub>2</sub>O. Nevertheless, the  $k_5$  values for SPEEK radicals are several orders of magnitude smaller than the decay rate constant in water for (Ph)<sub>2</sub>C•OH and (CH<sub>3</sub>)<sub>2</sub>C•OH (1 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> in both cases).<sup>36,37</sup> Negatively charged radicals of poly(acrylic acid) (PAA) formed at pH > p $K_a$  exhibit a much longer lifetime than that of their neutral counterparts generated in acid solution.<sup>38</sup> As for polycarboxylate radicals, electrostatic repulsions between anionic SPEEK chains increase the radical lifetime by hindering reactive collisions between the macromolecules.

Photoreduction of Ag<sup>+</sup> Ions. Illustrated in Figure 2 is the evolution with illumination time of the optical spectra from a SPEEK/PVA solution also containing 60  $\mu$ M Ag<sup>+</sup> ions. The spectra are corrected from the spectrum acquired prior to illumination. A broad absorption with  $\lambda_{max} = 415$  nm is detected initially, but the optical signal increases in strength and blueshifts with irradiation time to reach 395 nm at the end of the photoreaction. This signal corresponds to the surface plasmon of Ag particles with nanometer dimensions.<sup>4</sup> The evolution of this absorption with reaction time has been well-documented<sup>14,18,25,37</sup> and originates from slight changes in the  $\lambda_{max}$ and strength of the plasmon with increasing particle size.<sup>4</sup> Presented in Figure 3a is a TEM image confirming that fairly spherical Ag particles form during the photochemical process. Depicted in Figure 3b is a histogram of crystallite diameters showing that the most frequent particle size is 6 nm whereas the average diameter amounts to 7.4 nm. XRD measurements verified the metallic nature of the particles; the relevant data is presented in the Supporting Information.

As shown in Figure 2, the metal particles present at the end of the photoreaction possess a very strong and narrow plasmon band. Reduction of silver ions in the range of  $18 \ \mu M \le [Ag^+] \le 250 \ \mu M$  yields signal intensities varying linearly with metal



**Figure 2.** Evolution of normalized optical spectra during photolysis of a solution containing  $6 \times 10^{-5}$  M AgClO<sub>4</sub>, PVA, and SPEEK;  $I_0 = 2.4 \times 10^{-5}$  M(*hv*)/s. The irradiation time increases according to 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 60, and 70 s.



**Figure 3.** (a) TEM image of a colloid made by photolysis of a SPEEK/ PVA solution containing  $6 \times 10^{-5}$  M AgClO<sub>4</sub> and the (b) corresponding histogram of particle diameters.

concentration and an  $\epsilon$  value (at 400 nm and per mole of Ag atoms) of 2.4 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>. This extinction coefficient is about 5 times higher than that of particles photogenerated in

PAA/PVA solutions<sup>18c</sup> and more than 3 times the  $\epsilon$  value of Ag crystallites formed in 2-propanol.<sup>14</sup> Particles exhibiting unusually strong plasmons have been made in aqueous solutions of several polymeric stabilizers by means of the acetone/2propanol sensitizing system,<sup>23b</sup> in micelles using benzophenone as photosensitizer,<sup>25a</sup> or via radiolysis in methanol containing PVA.<sup>39</sup> Colloids produced radiolytically consist of crystallites spanning the size range of 2-15 nm, which resembles the diameter distribution depicted in Figure 3b. Thus, the strong plasmon is not a consequence of a specific method of preparation or of a particularly narrow size distribution. Common features of colloids with an intense optical signal are their average particle diameter of about 7 nm and their sensitivity to oxidation by air. The reaction with O<sub>2</sub> diminishes the strength and red-shifts the plasmon, but the signal intensity decreases only by 20% in the case of the SPEEK/PVA system as compared with at least 50% for the colloids studied earlier.<sup>23b,39</sup>

Photochemical generation of Ag crystallites also takes place by irradiation with 350 nm light of solutions containing Ag<sup>+</sup> and PVA in the presence or absence of PAA.<sup>18b</sup> Such a process is not an important contributor to the Ag<sup>+</sup> photoreduction in the presence of SPEEK since the polyketone absorbs most of the impinging photons. This conclusion is supported by the large differences between the plasmon depicted in Figure 2 and those of Ag particles photogenerated in the absence of SPEEK.<sup>18c</sup> Another interesting result shown in Figure 2 is that the band at 565 nm starts being noticed when about 80% of the Ag<sup>+</sup> ions have been reduced. The signal due to SPEEK radicals becomes particularly discernible after particle formation stops, serving as an indicator that the photoreduction of Ag<sup>+</sup> is completed. Further insight about the role of the macromolecular radicals in the reduction process is provided by experiments where the radicals were created (without Ag<sup>+</sup> ions) by illumination of either SPEEK/PVA films or of solutions containing the two polymers.<sup>29</sup> Metal colloids are produced by mixing a photolyzed SPEEK/PVA solution with a nonirradiated solution containing AgClO<sub>4</sub> in the absence of air. Also, Ag particles result inside irradiated films after immersing the polymeric solids into solutions of Ag<sup>+</sup>. In contrast, illumination of solutions containing silver ions and only PVA generates metal crystallites 200 times slower than in the presence of SPEEK. These findings, together with the data of Figures 1 and 2, are indisputable evidence that SPEEK radicals act as reductants toward Ag<sup>+</sup> ions. The simplest representation of the reduction process is

$$\{\mathbf{R'RC^{\bullet}OH}\}_{z} + \mathbf{Ag^{+}} \rightarrow \{\mathbf{R'RC=O}\}_{z} + \mathbf{Ag} + \mathbf{H^{+}} \quad (6)$$

At this point, a relevant issue concerns the oxidation potential of SPEEK radicals, which is expected to be similar to the value for (Ph)<sub>2</sub>C•OH radicals. An estimate of the reducing power of (Ph)<sub>2</sub>C•OH can be derived after considering that BP is reduced in solution by (CH<sub>3</sub>)<sub>2</sub>C•OH whereas the methanol radical (•CH<sub>2</sub>OH) is unable to induce such reduction.<sup>40</sup> The standard oxidation potentials of the two alcohol radicals are  $E^{\circ}[(CH_3)_2C^{\bullet}]$  $OH/(CH_3)_2C=O, H^+$ ] = 1.4 V and  $E^{\circ}[CH_2OH/(H_2C=O, H^+)]$ = 1.2 V.<sup>37</sup> Consequently,  $E^{\circ}[(Ph)_2C \bullet OH/(Ph)_2C = O, H^+]$  is lower than 1.4 V but higher than 1.2 V, which agrees well with the  $E^{\circ}$  value of 1.31 V estimated from half-wave potentials.<sup>41</sup> Failed attempts to detect the reaction between (CH<sub>3</sub>)<sub>2</sub>C•OH and Ag<sup>+</sup> to form Ag atoms with time-resolved methods were considered evidence that such process is not possible since the estimated reduction potential for the [Ag<sup>+</sup>/Ag] couple is very negative,  $E = -1.8 \text{ V}.^{23b}$  This conclusion is at odds with our findings and with the reported photogeneration of Ag crystallites using (CH<sub>3</sub>)<sub>2</sub>CO and (Ph)<sub>2</sub>CO as sensitizers.<sup>23,25</sup> Surprisingly,



**Figure 4.** Extent of reaction as a function of illumination time for SPEEK/PVA solutions containing different AgClO<sub>4</sub> concentrations: 1.8  $\times 10^{-5}$  M ( $\blacksquare$ ); 3.6  $\times 10^{-5}$  M ( $\bullet$ ); 6  $\times 10^{-5}$  M ( $\blacktriangle$ ); 9  $\times 10^{-5}$  M ( $\bullet$ );  $I_0 = 2.4 \times 10^{-5}$  M(hv)/s.

a rate constant of  $k = 4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for the reduction of Ag<sup>+</sup> by BPK radicals in micelles was extracted via multiexponential fitting of data from a recent laser photolysis study.<sup>25a</sup> Such high rate constant is hard to reconcile with earlier unsuccessful efforts to detect the reaction of Ag<sup>+</sup> with the stronger reductant (CH<sub>3</sub>)<sub>2</sub>C•OH.

Inclusion of the H<sup>+</sup> concentration effect on  $E^{\circ}[(CH_3)_2C^{\bullet}OH/$  $(CH_3)_2C=O, H^+$  yields an oxidation potential of 1.8 V at pH  $= 7,^{5}$  demonstrating that reduction of Ag<sup>+</sup> by the radical is not necessarily endergonic. Considering that such a pH is typical of degassed SPEEK/PVA solutions, the corrected standard potential of •CH2OH leads to an oxidation potential for SPEEK radicals smaller than 1.8 V but larger than 1.6 V. Although reaction 4 is slightly endergonic, complexation of Ag atoms with  $Ag^+$  to form  $Ag_2^+$  can provide an additional driving force for the reduction of silver ions by SPEEK radicals. Coupling of the fast complexation step ( $k = 8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) to the  $Ag^+$  reduction by  $(CH_3)_2C^{\bullet}OH$  is thought to enable the redox process.<sup>5</sup> In fact, the data of Figure 1 suggest a kinetic rather than thermodynamic origin for the failed efforts to detect the reaction between Ag<sup>+</sup> and (CH<sub>3</sub>)<sub>2</sub>C•OH. Time-resolved measurements require high radical concentrations, but such conditions accelerate the second-order radical decay. Since  $k(Ag^+ +$  $(CH_3)_2C^{\bullet}OH) \le 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1},^{23b}$  the radical-radical decay channel is significantly faster than the reaction with silver ions. However, the much longer lifetime of SPEEK radicals allows them to reduce silver ions efficiently.

Formation of Ag crystallites in water proceeds via a complex mechanism comprising fast reactions of cationic as well as of neutral silver clusters.<sup>42</sup> Analogous reactions seem to be involved in the SPEEK/PVA system because the spectra exhibits none of the long-lived absorptions from polymer-stabilized Ag clusters found in PAA solutions.<sup>42a</sup> Presented in Figure 4 is the advance of reaction ( $x = OD_t/OD_{\infty}$ ) as a function of illumination time for several metal ion concentrations. Evaluation of *x* used the optical data at 400 nm and assumed a nearly constant  $\epsilon$ value for the particles throughout the reaction. In all cases, the initial stage is characterized by a slow variation of *x* with time, followed by a period of increasing acceleration and a final step of declining rates. The initial rate of particle formation ( $r_i$ ) decreases steadily when the Ag<sup>+</sup> concentration increases between 36 and 500  $\mu$ M. Figure 5 demonstrates that the





**Figure 5.** Dependence of the reciprocal initial reaction rates as a function of the metal concentration:  $Ag^+(\bullet)$ ;  $Cu^{2+}(\blacksquare)$ .

reciprocal of the initial rate varies linearly with metal ion concentration according to the relationship  $1/r_i = 1.1 \times 10^6 + 3.6 \times 10^{10} [\text{Ag}^+]$  ( $r^2 = 0.993$ ). These observations are atypical because the rate of crystallite formation has been frequently found to increase linearly with the Ag<sup>+</sup> concentration.<sup>14,18</sup>

Quenching of excited BP molecules by Ag<sup>+</sup> occurs during the photochemical formation of Ag particles in micellar solutions sensitized by benzophenone.<sup>25a</sup> A similar reaction is expected to take place in the polymer solutions

$$\{{}^{3}\mathbf{R'RC}=\mathbf{O}^{*}\}_{z} \xrightarrow{\mathrm{Ag}^{+}} \{\mathbf{R'RC}=\mathbf{O}\}_{z}$$
(7)

Both energy and electron-transfer mechanisms can be involved during quenching of singlet and triplet excited states of aromatic ketones by metal complexes.<sup>13</sup> Reaction 7 is formulated as an energy-transfer process because the electron-transfer route is expected to produce metal particles via formation of Ag atoms and is unable to explain the data of Figure 5. The decrease in  $r_i$  with increasing Ag<sup>+</sup> concentration is understood in terms of a competition between reactions 2 and 7. Only those excited BP groups of the macromolecules not quenched by Ag<sup>+</sup> are able to form SPEEK radicals that, ultimately, produce Ag crystallites. Equation 8 is obtained from standard competition analysis<sup>13</sup>

$$r_i = r({}^{3}\text{SPEEK*}) k_2[\text{PVA}]/(k_2[\text{PVA}] + k_7[\text{Ag}^+]_i)$$
 (8)

where  $r({}^{3}\text{SPEEK}^{*})$  represents the formation rate of triplet excited states from polymeric BP groups, while  $k_2$  and  $k_7$  are the rate constants for reactions 2 and 7, respectively. Inversion of eq 8 yields an expression matching the relationship obtained from Figure 5

$$1/r_i = 1/r({}^{3}\text{SPEEK}^{*})\{1 + k_7[\text{Ag}^+]_i/k_2[\text{PVA}]\}$$
(9)

Evaluation of  $k_7$  from the slope and intercept of the straight line shown in Figure 5 and the concentration of monomer units present in PVA (0.36 M) requires a  $k_2$  value. In water, the rate constants for H atom abstraction from ethanol and 2-propanol by the triplet state of BP range between 2 and 3 × 10<sup>6</sup> M<sup>-1</sup> s<sup>-1</sup>.<sup>25a,36</sup> The use of similar  $k_2$  values results in  $k_7 = (2-3) \times$ 10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup>, which agrees reasonably with the quenching constant of the BP triplet state by Ag<sup>+</sup> in micellar solutions  $((4-6) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}).^{25a}$  The  $k_7$  values are more than an order of magnitude larger than the quenching constants of benzophenone triplets by O<sub>2</sub> or BP molecules in H<sub>2</sub>O.<sup>36</sup> Such high rate constants are inconsistent with diffusion-controlled processes given the considerable viscosity of the solutions imparted by their high polymer concentrations but can be rationalized in terms of the ionic nature of SPEEK. The solution behavior of polyelectrolytes is influenced by strong Coulombic attractions between charged macromolecular groups and their counterions.<sup>43</sup> For SPEEK, the attractions are expected to keep part of the Ag<sup>+</sup> ions in close proximity of the polymeric sulfonic groups. Fast quenching of BP triplet states by Ag<sup>+</sup> ions located next to the polymeric charges is possible because of the short distance separating the sulfonic groups from their adjacent carbonyl functions.

The experimental intercept results in  $r(^{3}\text{SPEEK}^{*}) = 9.1 \times$  $10^{-7}$  M/s, and division by  $I_0$  yields 0.04 as the quantum yield of excited BP groups, ø(3SPEEK\*). A possible reason for such low quantum yield is that intersystem crossing from a singlet to triplet (n,  $\pi^*$ ) state is less effective for SPEEK than for BP, which is 100% efficient.36a,b For instance, intersystem crossing may partially lead to triplet  $(\pi, \pi^*)$  states, which in the case of 4,4' substituted benzophenones participate less effectively in the generation of BPK radicals via H atom abstraction.36b Alternatively, decay of the (n,  $\pi^*$ ) state may be faster in the case of the polymeric material than for benzophenone molecules, or ground-state BP groups of SPEEK may quench the excited states in a way similar to the self-quenching that the aromatic ketone experiences in H<sub>2</sub>O.<sup>36a</sup> However, self-quenching must be restricted by the considerable entanglement of SPEEK chains with PVA macromolecules that is anticipated at the high polyol concentration. Another possibility is the formation of groundstate complexes of SPEEK analogous to those responsible for the emission exhibited by PEEK.36c In fact, SPEEK exhibits an emission very similar to that of PEEK, which hampered attempts to detect fluorescence signals originating from the Ag particles. A maximum quantum yield of radical formation equal to 0.08 is predicted from  $\phi(^{3}SPEEK^{*})$  after considering reactions 2 and 3, but  $\phi_i$ (SPEEK•) is only 0.02 for solutions without Ag<sup>+</sup> ions. The low radical yield is probably a result of reaction 4 since the cross reaction consumes SPEEK radicals and also prevents their further formation via reaction 3.

An accelerated formation of Ag together with a maximum reaction rate are noticed in Figure 4 at intermediate illumination times. Indeed, the highest initial quantum yield of particle generation is 0.013 at  $[Ag^+] = 18 \ \mu M$ , whereas the quantum yield calculated from the maximum reduction rate  $(\phi(Ag_n))$  is 0.06 for this system. Fairly similar rate maxima were derived from the data of Figure 4; in all cases  $\phi(Ag_n) > \phi_i(SPEEK^{\bullet})$ , meaning that reaction 6 is able to compete with reaction 4. Also, a topmost  $\phi(Ag_n)$  value of 0.07 results from the data for  $[Ag^+]$ = 90  $\mu$ M, which is close to the maximum quantum yield of SPEEK radical formation predicted from ø(3SPEEK\*). The agreement between experimental and extrapolated quantum yields indicates that reaction 3 plays a substantial role in the metal formation. Direct Ag<sup>+</sup> reduction by PVA radicals is deemed less important due to their short lifetime in solution<sup>34</sup> and also because the concentration of polymeric BP groups is over 100 times higher than the Ag<sup>+</sup> concentration.

The rate of reaction 7 gradually decreases as photolysis proceeds due to the concomitant decline in  $Ag^+$  concentration, which favors particle formation. Interestingly, the reduction of  $Ag^+$  by •CH<sub>2</sub>OH radicals is known to be efficient only when the silver ions are bound to metal crystallites or clusters.<sup>39</sup> A



**Figure 6.** Evolution of the optical spectra during photolysis of a solution containing  $2.6 \times 10^{-4}$  M CuSO<sub>4</sub>, PVA, and SPEEK;  $I_0 = 6 \times 10^{-5}$  M(*hv*)/s. The irradiation time increases according to 0, 30, 50, 70, 90, 110, 130, 150, 170, 200, 230, 260, 290, 330, 390, 450, 510, 570, 630, and 780 s.

similar increase in the rate of reaction 6 must take place when metal is present in the SPEEK/PVA solutions because the photoreaction accelerates after at least 20% of the Ag<sup>+</sup> ions have been reduced. Another unusual kinetic feature noticed in Figure 4 is that the rate of metal formation reaches a maximum at  $x \le 0.42$  for  $[Ag^+] \le 36 \,\mu\text{M}$ , which is when the concentration of unreduced metal ions is between 15 and 21  $\mu$ M. In contrast, the maximum photoreduction rate for solutions with  $[Ag^+] \ge$ 60  $\mu$ M occurs at  $x \ge 0.91$ , when about 6  $\mu$ M of metal ions are left unreduced. Thus, significant retardation of the metal ion photoreduction occurs in solutions containing the highest Ag<sup>+</sup> concentrations. Protons are known to quench the triplet state of BP in aqueous solution.<sup>36</sup> Quenching of SPEEK carbonyl triplets by protons seems logical in systems with high Ag<sup>+</sup> concentrations, where large H<sup>+</sup> concentrations are generated through reaction 6. Hence, the shapes of the curves shown in Figure 4 originate from the quenching of polymeric triplet BP states by Ag<sup>+</sup> and H<sup>+</sup>, in conjunction with the accelerating effect induced by metallic clusters/particles.

Photoreduction of Cu<sup>2+</sup> Ions. Exposure of air-free solutions containing 2.5  $\times$   $10^{-4}$  M CuSO4, PVA, and SPEEK to 350 nm photons induces several spectral changes illustrated in Figure 6. Two consecutive steps can be identified from the optical data; the initial process generates a broad absorption with  $\lambda_{max}$ between 460 and 470 nm, which is accompanied by a slightly turbid yellow coloration of the solution. The second transformation produces a signal centered at 575 nm and a simultaneous change in the solution color from yellow to red. Similar observations have been made during the radiolytic reduction of Cu<sup>2+</sup> in aqueous PVA solutions.<sup>44</sup> The initial product is believed to consist of suspended copper(I) hydroxide particles, whereas the material formed during the second process exhibits properties typical of Cu crystallites. Having in mind that Cu<sup>I</sup> and the metallic product are sensitive to air in H<sub>2</sub>O,<sup>44</sup> support for these assignments is provided by the fact that exposure to O<sub>2</sub> of SPEEK/PVA solutions containing either of the chromophores induces fast disappearance of their characteristic absorptions.

Reduction of  $Cu^{II}$  to particles of a yellow  $Cu^{I}$  product, presumed to be CuOH, has been observed only in strongly basic solutions.<sup>45</sup> A similar material is formed when free radicals reduce cupric ions in neutral solutions either through photolysis of SPEEK or via radiolysis.<sup>44</sup> Cu<sup>2+</sup> ions undergo hydrolysis in neutral solution forming Cu(OH)<sup>+</sup> as the main product, but the distribution of hydroxo copper(II) species remains controversial.<sup>46</sup> Thus, the yellow material seems to originate from reduction of hydroxo complexes present in the neutral polymeric solutions. According to Figure 6, development of the signal with  $\lambda_{max} = 460$  nm is completed in about 200 s. This band is less well-defined thereafter as the Cu<sup>I</sup> compound starts transforming into metallic Cu, because the metal particles also absorb strongly below 530 nm. Optical data gathered at 460 and 575 nm when the first formation step ends in solutions with  $15 \leq [Cu^{2+}] \leq$  $50 \,\mu\text{M}$  yields  $\epsilon$  values for the cuprous compound of  $2.7 \times 10^3$ and  $1.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ , respectively. An interesting observation is that the Cu<sup>I</sup> product remains unchanged when illumination is stopped, indicating that the transformation of this material into metal requires the action of light.

Identification of the product from the second step is facilitated by the emergence in Figure 6 of the characteristic surface plasmon of nanometer-sized Cu crystallites centered between 570 and 580 nm.<sup>4</sup> Copper particles photogenerated in SPEEK/ PVA solutions exhibit an extinction coefficient of  $3.2 \times 10^3$ M<sup>-1</sup> cm<sup>-1</sup> at 575 nm. Sequential red and blue shifts of the plasmon similar to those shown in Figure 6 occur frequently during formation of Cu crystallites<sup>44</sup> and probably originate from slight changes in the optical properties of particles with different sizes.<sup>4</sup> The long-term instability of Cu particles in the presence of O<sub>2</sub> and water made their characterization by TEM mandatory, since the absence of air during such measurements prevented oxidation reactions. Very laborious experiments were needed given that only a few particles survived the sample transfer into the microscope and because electron diffraction analysis was restricted to grid regions relatively free of polymer films deposited during sample preparation. Figure 7a is a bright-field image demonstrating that the particles are nearly spherical but with a very broad size distribution of 5-40 nm. The corresponding ring pattern shown in Figure 7b depicts the typical reflections of face-centered cubic (fcc) Cu, confirming the metallic nature of the nanoparticles.

Figure 8 illustrates the evolution of the advance of reaction as a function of photolysis time for solutions containing three different initial concentrations of CuSO<sub>4</sub>. At a first glance, the meaning of the plots seems questionable given that calculation of x employs kinetic data gathered at 575 nm together with  $OD_{\infty}$ values corresponding to the full formation of the Cu crystallites. In fact, the plots aim at depicting the temporal evolution of transformations involving two-electron-transfer processes. Such plots are feasible because the  $\epsilon$  value for Cu<sup>I</sup> at 575 nm is, fortuitously, approximately half of the extinction coefficient of Cu particles. As a consequence of this difference in  $\epsilon$  values, x reaches 0.5 in all plots of Figure 8 upon completion of the first step producing Cu<sup>I</sup> and increases thereafter to a limiting value of 1 as metal formation proceeds. Monitoring the evolution of the signal at 460 nm allowed independent verification that the first step was completed.

Formation of a Cu<sup>I</sup> compound implies that SPEEK radicals act as reducing agents toward Cu<sup>2+</sup> complexes according to

$$\{\mathbf{R'RC^{\bullet}OH}\}_{z} + \mathbf{Cu}^{2+} \rightarrow \{\mathbf{R'RC=O}\}_{z} + \mathbf{Cu}^{+} + \mathbf{H}^{+} \quad (10)$$

where  $Cu^{2+}$  represents all of the  $Cu^{II}$  species present in the polymer solutions and  $Cu^+$  corresponds to the "CuOH" species. Direct evidence for the redox process is provided by the outcome of injecting a CuSO<sub>4</sub> solution into a preirradiated polymeric solution in the absence of air and light. As a result, the absorption of SPEEK radicals decays instantly with concomitant formation of the signal attributed to the Cu<sup>I</sup> compound. Reduction of Cu<sup>2+</sup> by SPEEK radicals is not surprising



**Figure 7.** (a) TEM image of a photochemically obtained copper colloid according to the conditions of Figure 6. (b) Electron diffraction pattern of copper crystallites. The reflections are in good agreement with the data listed in the Joint Committee on Powder Diffraction Standards (card 4-0836).



**Figure 8.** Extent of reaction as a function of illumination time for SPEEK/PVA solutions containing different CuSO<sub>4</sub> concentrations: 1.5  $\times 10^{-4}$  M ( $\blacktriangle$ );  $3 \times 10^{-4}$  M ( $\blacksquare$ );  $5 \times 10^{-4}$  M ( $\blacklozenge$ ).

considering that  $E^{\circ}[Cu^{2+}/Cu^{+}] = 0.168 V^{47}$  and that  $\alpha$ -hydroxyalkyl radicals derived from CH<sub>3</sub>OH, CH<sub>3</sub>CH<sub>2</sub>OH, and (CH<sub>3</sub>)<sub>2</sub>CHOH reduce cupric ions with rate constants between 1.6 and 0.5  $\times 10^{8} M^{-1} s^{-1}$ .<sup>48</sup> These reactions have been interpreted in terms of complexation of the alcohol radicals by Cu<sup>2+</sup> and formation of Cu<sup>III</sup> intermediates; reaction 10 is expected to occur in a similar fashion. Formation of the "CuOH"

species is explained if SPEEK radicals react faster with the hydroxo complexes than with nonhydroxylated cupric ions.

As for the Ag system, the data of Figure 8 indicates that the rates of the initial reaction decrease with increasing Cu<sup>2+</sup> concentration. Included in Figure 5 is a plot of  $1/r_i$  versus [Cu<sup>2+</sup>], where  $r_i$  is the rate of the initial step; the resulting straight line obeys the equation  $1/r_i = 3 \times 10^5 + 7.6 \times 10^8 [Cu^{2+}]$ . Hence, the triplet states of polymeric BP groups are quenched by the Cu<sup>II</sup> complexes via an energy-transfer process similar to reaction 7. Competition between reaction 2 and the quenching process accounts for the inverse dependence of  $r_i$  on Cu<sup>2+</sup> concentration, allowing derivation of expressions analogous to eqs 8 and 9. Quenching constants of  $k_0 = (2-3) \times 10^9 \,\mathrm{M}^{-1} \,\mathrm{s}^{-1}$  are obtained using  $k_2$  values of  $(2-3) \times 10^6 \,\mathrm{M}^{-1} \,\mathrm{s}^{-1}$  together with the slope of the straight-line equation. These constants are 10 times lower than those of Ag<sup>+</sup>, probably reflecting the different contributions from the various Cu<sup>II</sup> species present in the solutions. In agreement with the Ag system, the experimental intercept yields  $\phi(^{3}\text{SPEEK}^{*}) = 0.056$ , and the highest quantum yield of  $Cu^{I}$  generation ( $\phi(Cu^{I}) = 0.04$ ) not only results at the lowest Cu<sup>2+</sup> concentration but is within the maximum predicted from  $\phi(^{3}\text{SPEEK^{*}})$ . Also,  $\phi(\text{Cu}^{\text{I}}) > \phi_{i}(\text{SPEEK^{\bullet}})$  at all  $\text{Cu}^{2+}$  concentrations, meaning that reaction 10 competes effectively with reaction 4. However, the data of Figure 8 indicates that the photoreaction follows an apparent zero-order rate law, which is confirmed by the linear increase of OD at 460 nm with time. Thus, decreases in Cu<sup>2+</sup> concentration during photolysis affects both the quenching process and reaction 10 in a similar fashion because the reduction process is not influenced by the presence of the Cu<sup>I</sup> product.

According to Figure 8, no simple relationship exists between the rate of Cu particle formation and metal ion concentration during the second step. For instance, similar quantum yields of metal formation (0.007) are obtained at  $[Cu^{2+}] \leq 300 \ \mu M$ , but the efficiency drops at the highest metal ion concentration. Also, the kinetics of the metal photogeneration are not entirely reproducible in solutions containing  $[Cu^{2+}] \ge 300 \,\mu\text{M}$ , hinting that heterogeneous processes participate in this transformation. Evidence exists that Cu<sup>+</sup> ions are not reduced to metal atoms by  $\alpha$ -hydroxyalkyl radicals,<sup>48,49</sup> because of the unfavorable redox potential,  $E^{\circ}[Cu^+/Cu(atom)] = -2.7 \text{ V}.^5$  Hence, reduction of the Cu<sup>I</sup> product by SPEEK radicals appears unfeasible. This conclusion is supported by the fact that mixing a solution containing SPEEK radicals with a CuSO<sub>4</sub> solution generates exclusively the "CuOH" product. Cu<sup>+</sup> ions disproportionate in acidic aqueous solutions

$$2Cu^{+} \leftrightarrows Cu + Cu^{2+} \tag{11}$$

and  $K = 5.4 \times 10^5 \text{ M}^{-1}$  was determined from measurements of the equilibrium on Cu electrodes,47 but a constant about 14 times smaller was obtained in the absence of bulk metal.<sup>48b</sup> The results of the present investigation and of previous studies indicate that the yellow Cu<sup>I</sup> product is stable toward disproportionation.44,49 Nevertheless, fast metal formation was observed upon treatment of "CuOH" with a dilute acid solution.44 Figure 9 illustrates the spectral changes occurring in the absence of air when a solution containing the yellow Cu<sup>I</sup> product is acidified with HClO<sub>4</sub> to yield  $[H^+] = 7 \times 10^{-4}$  M. Immediate decay of the signal at 460 nm takes place, with concomitant formation of the plasmon due to Cu crystallites. Comparison of the optical data at 460 and at 575 nm with the spectra shown in Figure 7 provide confirmation that the process involves a 2:1 molar ratio of Cu<sup>I</sup> to metallic Cu, as required by reaction 11.



**Figure 9.** (1) UV-vis spectrum of a solution containing  $2.6 \times 10^{-4}$  M CuSO<sub>4</sub>, PVA and, SPEEK photolyzed for 200 s. (2) After injection of 20  $\mu$ L of 0.1 M HClO<sub>4</sub>.

These observations indicate that bound Cu<sup>+</sup> is unable to disproportionate but that reaction 11 takes place when cuprous ions become free in solution after dissolution of the hydroxide particles by protons. The dynamics of the particle photogeneration depicted in Figure 8 can be rationalized on the basis of these results since protons formed via reaction 10 accumulate in the polymer solutions, and when x approaches 0.5 their concentrations are close to the initial Cu<sup>2+</sup> concentration. Dissolution of the cuprous hydroxide becomes then appreciable, and the resulting Cu<sup>+</sup> ions start disproportionating to Cu<sup>2+</sup> and metal particles. SPEEK radicals continue to reduce cupric ions through reaction 10, although such ions are now those resulting from reaction 11. Coupling of reactions 10 and 11 explains the similar slopes noticed in Figure 8 prior to and after x reaches a value of 0.5; the slope changes noticed thereafter suggest that another process participates in the generation of crystallites. Cu particles are known to catalyze the reduction of Cu<sup>I</sup> species by  $\alpha$ -hydroxyalkyl radicals.<sup>49</sup> Having in mind that the concentration of copper ions left unreduced is very small at x values close to 1 (which makes reaction 11 improbable), a metal-mediated reduction of cuprous ions by SPEEK radicals seems a possible explanation for the last reaction step.

Photoreduction of AuCl<sub>4</sub><sup>-</sup> Ions. Elucidation of the transformations of HAuCl<sub>4</sub> induced by light in SPEEK/PVA solutions faces challenges not encountered in the cases of  $Ag^+$  or  $Cu^{2+}$ . Indeed, radiation with  $\lambda \leq 350$  nm initiates the reduction of AuCl<sub>4</sub><sup>-</sup> ions in the presence of reducing agents, including alcohols.9a,15,17,50 Direct photoreduction of HAuCl<sub>4</sub> seems improbable in our system since the 350 nm photons are overwhelmingly absorbed by SPEEK. Nevertheless, some testing of the photoprocesses taking place in the absence of the polyketone was conducted to assess their impact on the SPEEKinitiated photoreaction. Specifically, the experiments aimed at detecting possible chain reductions of the Au<sup>III</sup> ions similar to those induced by direct excitation of AuCl<sub>4</sub><sup>-</sup> in polymer gels containing methanol.<sup>17</sup> AuCl<sub>4</sub><sup>-</sup> ions are also reduced thermally by PVA molecules with a molar mass similar to that of the polyol used in the present study.<sup>31</sup> Metal formation lasts more than 6 days when 100  $\mu$ M AuCl<sub>4</sub><sup>-</sup> reacts with 3 mM PVA but only a few hours in the SPEEK/PVA solutions where the PVA concentration is approximately 100 times higher than the concentration used earlier. Although the dark reaction is suppressed before photolysis via the method described in the Experimental Section, parallel occurrence of the thermal reduction during illumination is possible.



Figure 10. Dependence of the induction period on HAuCl<sub>4</sub> concentration in the presence of both polymers (**D**),  $I_0 = 5.6 \times 10^{-5} \text{ M}(hv)/\text{s}$  and in the presence of only PVA (**O**),  $I_0 = 3.3 \times 10^{-5} \text{ M}(hv)/\text{s}$ .

Reduction of  $AuCl_4^-$  to the metal usually involves two consecutive processes; the first step forms  $AuCl_2^-$  ( $\lambda_{max} = 246$ nm) in homogeneous solution<sup>51</sup> or species believed to be Au clusters exhibiting signals centered at 350-380 nm in polymeric systems.<sup>15a,17,50,52</sup> The first step occurs with bleaching of the yellow color of AuCl<sub>4</sub><sup>-</sup> ( $\lambda_{max} = 319$  nm),<sup>9a,31</sup> followed by photoreduction of the initial products to metallic Au. A similar two-step transformation takes place during illumination of SPEEK/PVA solutions in the presence of HAuCl<sub>4</sub>. Au crystallites are not detected during the first step (referred to as the induction period), which occurs without any color change for solutions with [HAuCl<sub>4</sub>] < 300  $\mu$ M since SPEEK absorbs most of the light under such conditions. However, bleaching is noticed at higher Au<sup>III</sup> concentrations and in SPEEK-free solutions, where a yellow coloration due to the auric ions can be detected. Metal generation starts once the bleaching process is over; particles are not produced when photolysis is stopped at the end of the induction period, even when irradiated solutions are left in the dark for several hours. These findings indicate that the second step is a light-initiated process that begins after most of the Au<sup>III</sup> ions have been consumed and that this phototransformation involves products from the first reaction.

Illustrated in the curve labeled with squares in Figure 10 is the evolution of the induction period as a function of HAuCl<sub>4</sub> concentration in photolyzed SPEEK/PVA solutions, whereas the circles correspond to data from experiments performed without SPEEK. Considerable uncertainty remains about the true induction period for SPEEK/PVA solutions with 90 µM HAuCl<sub>4</sub> given that the measured value (5 s) is within the time required for the optical determinations. However, the longer induction period (65 s) for the lowest HAuCl<sub>4</sub> concentration (100  $\mu$ M) in the absence of SPEEK is less affected by the experimental constraints. Nevertheless, the data of Figure 10 support the conclusion that direct photoreduction of HAuCl<sub>4</sub> is not significant in SPEEK/PVA solutions because the induction periods of these systems are, in general, considerably shorter than those obtained in the absence of the polyketone. Figure 11 depicts the corresponding quantum yields of photoreduction (ø(-HAuCl<sub>4</sub>)) as a function of Au<sup>III</sup> concentration in the presence of SPEEK and PVA. Evaluation of the quantum yields assumed that the induction periods correspond to the times required to photoreduce all of the auric ions initially present. This assumption is supported by the fact that the induction



**Figure 11.** Variation of the quantum yield for Au<sup>III</sup> reduction as a function of HAuCl<sub>4</sub> concentration,  $I_0 = 5.6 \times 10^{-5} \text{ M}(hv)/\text{s}$ . Inset: Concentration dependence of the reciprocal rate of photoreduction for Au<sup>III</sup> ( $\bullet$ ) and Au<sup>I</sup> ( $\bigcirc$ ).

periods coincide with the times needed for complete bleaching of the Au<sup>III</sup> color. Not included in the figure is the quantum efficiency (0.36) estimated for 90  $\mu$ M HAuCl<sub>4</sub> in the presence of SPEEK due to the uncertainties mentioned above. Although the quantum yields are higher than the efficiencies obtained for the Ag<sup>+</sup> and Cu<sup>2+</sup> systems, the data are not consistent with a chain reaction.

Detection of the optical signals from AuCl2<sup>-</sup> or clusters produced via the Au<sup>III</sup> reduction is impaired by the absorption due to SPEEK. Photoreduction of Au<sup>III</sup> in polymer films or gels produces stable Au clusters,<sup>15,17</sup> but these species exist only as transients when auric ions are reduced in solution.<sup>31</sup> Interestingly, the products of the first step remain unchanged in the dark for times longer than those needed to complete the photogeneration of metal particles. This observation is consistent with the fact that Au<sup>I</sup> disproportionates very slowly to form Au even in the presence of metal.<sup>17,52,53</sup> For simplicity, we have assumed that aurous ions are photogenerated during the first reaction, which means that the quantum yields of Figure 11 correspond to a two-electron transformation. According to this interpretation, the photoreduction of HAuCl<sub>4</sub> is at least 2 times more efficient than those for Ag<sup>+</sup> and Cu<sup>2+</sup>, implying that  $\phi(^{3}SPEEK^{*})$  and the quantum yield of radical formation are higher for the Au<sup>III</sup> system. Such conclusions are hard to justify since the quantum yields of triplet states and of polymer radicals found in  $Ag^+$  and  $Cu^{2+}$  solutions are mutually consistent. Figure 11 shows that ø(-HAuCl<sub>4</sub>) decreases with increasing Au<sup>III</sup> concentration, and the inset demonstrates that the reciprocal of the photoreduction rate  $(r(-HAuCl_4))$  is a linear function of the metal ion concentration with  $1/r(-HAuCl_4) =$  $-1.8 \times 10^5 + 2.6 \times 10^9$ [HAuCl<sub>4</sub>]. Obviously, auric ions quench the triplet states of polymeric BP groups in a way similar to reaction 7. The negative value of the intercept means that  $\phi(^3$ -SPEEK\*) < 0, which has no physical meaning, but supports the notion that the quantum yields depicted in Figure 11 are abnormally high.

Reduction of  $AuCl_4^-$  to  $AuCl_2^-$  is characterized by a positive potential,  $E^\circ = 0.92 \text{ V}.^{54}$  In cationic polymer gels, the reduction of  $Au^{\text{III}}$  by •CH<sub>2</sub>OH (a weaker reductant than SPEEK radicals) generates clusters containing metal atoms bound to  $Au^{\text{I}.17}$  Hence, the polymer radicals are anticipated to reduce  $Au^{\text{III}}$  ions, and several findings corroborate such expectation. For example, no



**Figure 12.** Evolution of the optical spectra during photolysis of a solution containing  $2.7 \times 10^{-4}$  M HAuCl<sub>4</sub>, PVA, and SPEEK;  $I_0 = 5.6 \times 10^{-5}$  M(*hv*)/s. The irradiation time increases according to 0, 3, 4, 5, 6, 7, 8, 9, 11, 12, 13.5, 15, 17, and 20 min.

signal centered at 565 nm is detected throughout the first step, and mixing a solution containing photogenerated SPEEK radicals with another containing HAuCl<sub>4</sub> results in an instantaneous decay of the radical absorption. The large  $\phi$ (-HAuCl<sub>4</sub>) values can be explained if the SPEEK-initiated photoreaction occurs in parallel with the known thermal reduction of Au<sup>III</sup> by PVA.<sup>31</sup> Such an interpretation is supported by the slow roomtemperature bleaching of auric ions detected in solutions that contain only PVA or at high HAuCl<sub>4</sub> concentrations in SPEEK/ PVA mixtures. Another consequence of the negative intercept extracted from Figure 11 is that calculation of  $k_0$  for Au<sup>III</sup> via an expression analogous to eq 9 is not possible. Utilization of the  $k_2$  and  $\phi(^{3}SPEEK^{*})$  values used for Cu<sup>2+</sup> yields a rough estimate of  $k_{\rm Q} \approx 7 \times 10^9 \, {\rm M}^{-1} \, {\rm s}^{-1}$ . This estimate is similar to the  $k_0$  value of the cupric species, probably reflecting the participation of several products from the HAuCl<sub>4</sub> hydrolysis in the quenching process.54

Figure 12 depicts the evolution of the optical spectra recorded during the second step for a SPEEK/PVA solution containing initially 270 µM HAuCl<sub>4</sub>. In this plot, the origin of time corresponds to the end of the induction period; the initial spectrum demonstrates that the first reaction occurs without significant spectral changes above 400 nm. Photolysis beyond the induction period induces a blue coloration of the solutions and a broad absorption centered at about 550 nm. During the first 11 min, the signal increases in strength, followed by a substantial narrowing at longer times as well as a blue-shifting of the maximum to 520 nm. The solutions turn increasingly red, exhibiting the typical surface plasmon of spherical Au particles.<sup>4</sup> Plasmon intensities that vary linearly with Au concentration are obtained upon complete metal ion reduction in the range of 90  $\leq$  [Au<sup>III</sup>]  $\leq$  550 µM. The corresponding extinction coefficient  $(4 \times 10^3 \,\mathrm{M^{-1} \, cm^{-1}})$  is in good agreement with  $\epsilon$  values reported earlier.<sup>53</sup> Figure 13a is a typical TEM image of a gold colloid, confirming that, apart from a few aggregates of crystallites, the photoreaction forms spherical particles. The histogram of crystallite diameters illustrated in Figure 13b is evidence of a very narrow distribution since the most frequent particle size coincides with the average diameter of 3 nm. XRD data verifying the metallic nature of the crystallites are included in the Supporting Information.

According to the spectral changes depicted in Figure 12, photoreduction of Au<sup>I</sup> first produces the chromophores respon-



**Figure 13.** (a) TEM image of gold colloid obtained as indicated in Figure 12 and the (b) corresponding histogram of particle diameters.



**Figure 14.** Extent of reaction as a function of illumination time for SPEEK/PVA solutions containing different HAuCl<sub>4</sub> concentrations: 9  $\times 10^{-5}$  M (O); 1.8  $\times 10^{-4}$  M ( $\bullet$ ); 3  $\times 10^{-4}$  M ( $\blacktriangle$ ); 5.5  $\times 10^{-4}$  M ( $\bullet$ ).

sible for the blue color, followed by their subsequent transformation to Au particles at the later stages of the second step. This transformation is also evident in the plots of Figure 14, depicting the evolution of the advance during the second reaction for solutions containing several initial Au<sup>III</sup> concentrations. Highlighted by arrows are discontinuities corresponding to the starting points of the blue to red change. Evaluation of x used the optical data at 520 nm together with the extinction coefficient of the Au particles. Such a procedure underestimates the advance of reaction at times shorter than those marked by the arrows because the species responsible for the broad signals are known to be weaker light absorbers at that wavelength than Au particles.<sup>55</sup> Despite this shortcoming, the results clearly show a progressively less efficient evolution of x with an increasing Au<sup>I</sup> concentration, signifying that aurous ions produced in the first reaction quench the triplet states of polymeric BP groups.

Only lower limits of the initial photoreduction rates can be obtained from Figure 14 in the absence of the extinction coefficient at 520 nm for the species originating the broad signals. Nevertheless, these rough estimates confirm the validity of a competition expression similar to eq 8 since the plot included in the inset of Figure 11 shows that the inverse of the rate is linearly dependent on the Au<sup>I</sup> concentration with  $1/r_i =$  $4 \times 10^4 + 6 \times 10^9$ [Au<sup>I</sup>]. The intercept yields  $\phi$ (<sup>3</sup>SPEEK\*) = 0.45, which is at least 8 times larger than the quantum efficiencies derived from the Ag<sup>+</sup> and Cu<sup>2+</sup> systems. In fact, the actual  $\phi(^{3}SPEEK^{*})$  must be even larger since the real initial rates are higher than those used for the plot shown in the inset of Figure 11. For the same reason, the corresponding slope is only a lower limit of the true value, making questionable any attempt to evaluate  $k_0$ . As in the case of the initial step, the most probable reason for the large photoreduction rates is the occurrence of a process in parallel with the reaction involving SPEEK radicals. However, this secondary reduction channel is light-initiated because the products of the first step remain unchanged in the dark within the time frame of the photochemical experiments. The exact nature of such reaction is not known, but possible pathways include quenching of the singlet state of excited polymeric BP groups via electron transfer or a chain photoreaction similar to the process noticed in polymer gels.<sup>17</sup>

Metal crystallites form during photolysis from a reaction between SPEEK radicals and the chromophores responsible for the broad signals since the radical absorption at 565 nm is not observed in Figure 12. Generation of Au particles from precursors displaying a blue color has been noticed when AuCl<sub>4</sub><sup>-</sup> is reduced either thermally in some solutions<sup>56,57</sup> or via photolysis inside the channels of porous glasses.<sup>55</sup> The blue coloration originates from scattering of light by very large aggregates containing weakly interacting Au species that do not exhibit metallic diffraction signals. Broad spectra centered at 550 nm are also obtained when a HAuCl<sub>4</sub> solution is mixed with another containing SPEEK radicals. Irrespective of the method of preparation (through direct photolysis or solution mixing), the chromophores remain unchanged for about 100 min, followed by a sluggish emergence of the plasmon from Au crystallites. Identification of the chromophores by TEM was not feasible because of their short lifetime as well as the interfering effects induced by the polymeric components of the solutions. The dark transformation of the species responsible for the blue color resembles the postirradiation reaction found during radiolysis of AuCl<sub>4</sub><sup>-</sup> solutions, where Au<sup>I</sup> ions bound to small metal particles are slowly converted into gold atoms via disproportionation as well as through reduction by PVA.53 Occurrence of the latter reaction is not unreasonable given that aurous ions are known to react with solvent molecules in water/ acetonitrile mixtures with formation of metal.58

The earlier findings suggest that aggregates of small Au particles containing bound aurous ions are the species responsible the blue coloration in SPEEK/PVA solutions. According

to this scenario, part of the aurous ions formed in the first reaction react with SPEEK radicals producing the aggregates. Once this step is completed, Au<sup>I</sup> ions bound to the aggregates are reduced by SPEEK radicals whereas the slower dark metal formation probably results from their reaction with PVA. The transformation of aggregates is envisioned to resemble the process that yields gold particles in citrate solutions.<sup>57</sup> Reduction of the surface-bound Au<sup>I</sup> species induces fusion of the metal particles, which transforms the aggregates into larger metal crystallites with well-defined plasmon bands. Particle formation processes that exhibit different levels of mechanistic complexity have been encountered as well during the reduction of Pd and Pt ions by SPEEK radicals. Kinetic data pertaining to such systems will be present in a forthcoming report, which will also demonstrate that metal colloids made photochemically from SPEEK/PVA solutions can easily be converted into polymer films containing metallic crystallites with nanometer dimensions.

### Conclusions

The present study complements earlier investigations<sup>29</sup> and demonstrates the versatility of the SPEEK/PVA system for the generation of small metal particles in different matrixes. Formation of long-lived BPK radicals derived from SPEEK occurs via illumination with 350 nm photons of solutions containing PVA and the polyketone in the absence of air. Electrostatic repulsions between the anionic SPEEK chains in conjunction with the considerable viscosity of the polymer solutions contribute to the long lifetime of the macromolecular radicals. Their stability at room temperature enables the polymer radicals to efficiently reduce Ag<sup>I</sup>, Cu<sup>II</sup>, and Au<sup>III</sup> ions with the formation of nanometer-sized metal crystallites. Quenching of the triplet excited state of BP groups from SPEEK by the metal ions limits the efficiency of the particle photogeneration processes. However, crystallites form under optimum conditions with efficiencies higher than the quantum yield of polymer radicals measured in the absence of metal ions. This observation implies that the metal ions compete with processes that restrict the effectiveness of the radical production. The dissimilar mechanistic features exhibited by the crystallite formation processes of the three metals are exemplified by the generation of kinetically metastable intermediates that are different for each metal ion.

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**Supporting Information Available:** XRD traces of precipitated metal colloids. This material is available free of charge via the Internet at http://pubs.acs.org.

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