Reduction and Agglomeration of Silver in the Course of Formation of Silver Nano Cluster in Poly(methyl methacrylate)

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(Received December 25, 1997; CL-970976)

Characterization of Ag nanocluster in poly(methyl methacrylate), PMMA, and kinetic observation on the polymerization of MMA in the presence of silver(I) complex have been investigated. On the basis of these studies, it was revealed that the growing polymer radical is responsible for the reduction of Ag ion and the heat-treatment appears to play an important role for the agglomeration and the formation of Ag cluster.

Because of the drastic size effects that display specific properties being different from the bulk metals, nanoscopic metal particles are of great importance, and have a bright prospect of developing the new field of application in technology.[1]

Although there are a variety of preparative methods to obtain metallic nanoclusters, because of the ease in the preparation of well characterized and stable nanoclusters of narrow size distribution, it seems that the radiolytic method[2] and the chemical method are prominent and powerful means of producing metal aggregates. In the latter method, in general, the metal particles are traditionally obtained by chemical reduction of simple metal salts, using such reducing reagents as sodium borohydride,[3] sodium citrate,[4] amine[5] or ethanol[6], or also adding intentionally some chemicals[7] that generate radicals that are capable to reduce metal ions.

In contrast to these well known methodologies, Nakao[8] has found a method for preparing metal solid sols such as palladium, platinum, silver and gold in poly(methyl methacrylate) (PMMA), which can be obtained simply by polymerizing the mixture of monomer and corresponding metal compound, followed by the post-heating. Peculiar in this preparative procedure is the fact that metal ions are reduced to form zero valent metal clusters, in spite of the absence of specific reducing reagent. For this reason, we decided to reinvestigate the procedure for the preparation of silver clusters in PMMA, in order to elucidate the chemical species that can act as a reducing agent.

The preparation of silver solid sol in PMMA (Ag/PMMA) was essentially identical to that described previously,[8] except that silver(I) trifluoroacetate ($AgCF_3CO_2$, AgTfa) was used as a source of Ag ions, because we knew that this complex can readily dissolve in non-polar polymers such as poly(methylphenylsiloxane).[9] In the course of preparation, the concentrations of the radical initiator AIBN (2,2'-azobisisobutyronitrile), and Agtfa were changed over a wide range. The temperature of the post-heating was 120 °C and the duration was also changed. The Ag/PMMA samples were obtained as film with the following dimensions (3 x 5 cm, 1 mm of thickness). Optical absorption spectra of the colored Ag/PMMA films were measured with the aid of a visible spectrophotometer.

Figure 1 shows the effect of the AIBN concentration on the absorption spectra. An absorption peak is observed around 420 nm, which is due to the characteristic surface plasmon resonance of Ag particles. The absorbance shown in Figure 1 increases as

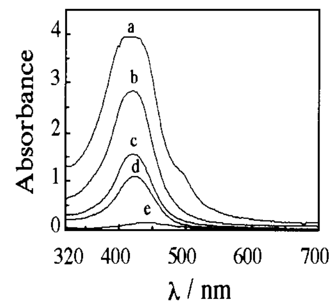

Figure 1. Absorption Spectra of Ag/PMMA prepared by various AIBN concentration; $[AgTfa]_0 = 2.8 \times 10^{-2}$ M, 10 min post-heating at 120 °C, [AIBN]0 : (a) 0.17; (b) 5.7×10^{-2}; (c) 2.85×10^{-2}; (d) 1.43×10^{-2}; (d) 5.7×10^{-2} M.

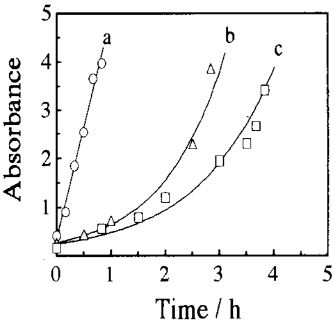

Figure 2. Effect of the post-heating duration on the absorption of Ag/PMMA; $[AIBN]_0 = 2.85 \times 10^{-2}$ M, post-heating at 120 °C, $[AgTfa]_0$: (a) 4.7×10^{-2}; (b) 2.8×10^{-2}; (c) 5.7×10^{-3} M.

a function of the concentration of AIBN, and shifts slightly to the shorter-wavelength. The same tendency was observed for the Ag plasmon peak when the concentration of AgTfa was changed; the higher the concentration of AIBN, the more intense the peak. Furthermore, as shown in Figure 2, the absorbance increases and the duration of the post-heating decreases with increasing initial concentrations of AgTfa. In our preliminary measurements by TEM,[10] it was estimated that the average diameter of a typical Ag/PMMA sample varies from 3 to 10 nm, depending on the aforementioned experimental conditions. The observed size of the Ag particles is in good agreement with previously reported values.[8,11] In general, it has been understood that absorbance increases with increasing diameter of Ag particles.[12,13] Therefore, the general trend observed in this study suggests that higher concentrations of AgTfa and AIBN and longer duration of post-heating cause the growth of the silver particles.

In order to verify whether the polymerization process and the post-heating process make the same effect on the growth of the silver particle or not, two cast films (A and B) of Ag/PMMA were prepared by a different procedure. Film A was made from toluene solution containing a sample of Ag/PMMA which was once prepared by the aforementioned method but not heat-treated. Film B was made as follows; PMMA was obtained at first and then PMMA and AgTfa was dissolved together in toluene solution. The concentrations of AgTfa and AIBN were the same in both the samples, and they were heat-treated at 120 °C for 10 h. It is noteworthy that almost no absorption peak corresponding to the plasmon resonance of Ag cluster was observed for the film B. Thus, it is reasonably safe to assume that at least no reduction of Ag ion occurs in the course of the post-heating process.

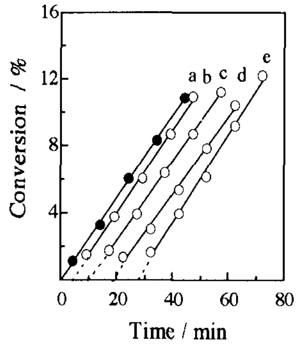

Figure 3. Effect of AgTfa on the polymerization of MMA initiated with AIBN at 60 °C; $[AIBN]_0$ =2.85 x 10^{-2} M, $[AgTfa]_0$: (a) 0; (b) 1.5 x 10^{-3}; (c) 8.0 x 10^{-3}; (d) 1.4 x 10^{-2}; (e) 2.0 x 10^{-2} M.

Then, we examined the kinetics of the polymerization of MMA in the presence of AgTfa. The rates of the polymerization were estimated by precipitation and weighing of the polymer after various reaction times. The percentages of polymerization against time curves are shown in Figure 3 for various concentrations of AgTfa at a constant concentration of AIBN. It is unequivocally demonstrated that an induction period, which was obtained by extrapolating the linear portion of the percentage polymerization against time, is observed. Furthermore, it is obvious that the induction period increases with increase in concentration of AgTfa, whereas the final rate of the polymerization in the steady state seems not to be affected by the addition of the Ag complex, as shown in Figure 3. A plot of the rate of polymerization against the square root of the AIBN concentration was linear (but, not passed exactly through the origin), showing that once the inhibitor had been removed the termination process again became second-order with respect to the growing polymer radicals. Thus, it admits no doubt that the growing polymer radical is the main chemical species which governs the reduction of silver ion. This result is consistent with early studies on the effects of such metal compounds as $FeCl_3$[14] and $CuCl_2$[15] on vinyl polymerization.

On the basis of the above observations, we conclude that the formation of Ag cluster is completed by the successive reaction steps of: (1) the reduction of Ag ion, (2) the nucleation of Ag particle, and (3) the agglomeration of Ag particles. Ag ions are first reduced to metallic silver by growing polymer chain radicals in the course of polymerization, with the formation of small particles that can act as a nucleus to form larger Ag particles. These particles subsequently diffuse toward each other in the polymer matrix to form successively larger clusters during the post-heating.

The ease of the diffusion of Ag particles as well as the polymer segment may depend on the molecular weight of polymer. It is understood that the higher the initiator concentration, the lower the molecular weight (i.e., the average polymer length is short). This concept definitely supports our observation that the higher concentration of AIBN, the easier the growth of the Ag particles, as shown in Figure 1. Thus, in this study it was also revealed that the initiator[16] plays a very important role both in the reduction and agglomeration of silver in the formation of silver nanocluster in PMMA.

The author is grateful to the Shinsei Shigen Kyokai Foundation of Fujikura Co. for financial support of this research.

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16 A referee pointed out the specificity of the use of AIBN. It might be possible that the same effect is expected when other radical initiator (e.g., BPO) is used instead of the AIBN. Since we do not have any experimental data, we can not deny this possibility and need further studies.