Formation of Silver Nanoparticles in Poly(methyl methacrylate) by UV Irradiation

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Silver nanoclusters in poly(methyl methacrylate) (Ag/PMMA) were prepared by bulk polymerization of MMA with radical initiators (AIBN or BPO) in the presence of silver(I) trifluoroacetate, followed by a period of UV irradiation. It was revealed that any of Ag/PMMA samples prepared by both the initiators shows a plasmon absorption peak at ca. 420 nm, whereas an additional peak at ca. 340 nm was found exclusively for those samples prepared in the presence of BPO.

Nanoscale materials have currently attracted a great deal of attention due to their interesting chemical and physical properties.[1–3] In the meantime, it is known that small metallic clusters have a size-dependent atomic structure and electronic configuration. Their characteristic surface plasmon modes can be exited optically. Drastic changes of the plasmon band, which due to discrete electronic states, have been found in Na, K, Au and Ag particles of less than about 10^5 atoms/particle.[4] For example, in the early studies on the growth of Ag particles, it has been established[5–7] that the primary reduction products are Ag^0, Ag_2^+, Ag_4^{2+}, and Ag_2^0. These embryonic clusters undergo further aggregation steps which lead to the formation of colloidal silver having an intense optical absorption at 380–400 nm, although the absorption peak depends also on matrices applied.[8] In general, it seems that a pulse radiolytic method[9–11] is the only technique for the study of such short-lived species, since the embryonic particles are extremely labile species and have a spontaneity towards more advanced aggregation.

In our previous studies, solid sols of Ag/PMMA were prepared by a series of polymerization and post-heating, and the effect of radical initiators on the size and formation of Ag nanoparticles was investigated.[12,13] Furthermore, it was revealed that the growing polymer radical is responsible for the Ag ions reduction, and thus prepared small metallic Ag particles can act as nuclei for the formation of larger metallic Ag particles.[14]

During the course of our investigations, we have noticed that our preparative method is also advantageous to a study on aggregation process of small particles. Based on our method, since embryonic Ag particles are formed in an early stage of the polymerization, it might be true that once such particles in the PMMA are prepared, they are not able to easily diffuse to aggregate themselves until an external driving force (e.g., heating) is applied. It is expected, therefore, that a time dependent growth of intermediate Ag species is easily controlled to keep the aggregation growing or freezing, just by heating.

Since UV irradiation is generally more powerful and controllable than heat-treatment, in this paper, applying our method and choosing UV irradiation as an external driving force instead of post-heating, aggregation of Ag particle in PMMA was investigated.

A source of Ag(I) was silver(I) trifluoroacetate (AgTfa), and 2,2'-azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO) were used as radical initiators. Hereafter, each of those initial concentrations is denoted as $[AgTfa]_0$, $[AIBN]_0$ and $[BPO]_0$. A typical preparation was as follows. A mixture of AgTfa and a radical initiator in MMA (20 mL) was transferred into a mold, and then heated at 60 °C for 20 h. Upon removing the sample from the mold, a clear Ag/PMMA plate (3 × 5 cm, 1 mm thickness) was obtained. The plates thus obtained were then UV irradiated with a high-pressure Hg UV lamp (400 W, $\lambda = 310$ nm) at 25 °C, and the UV spectra of the irradiated samples at adequate time intervals were measured by a Shimadzu UV-3100 spectrometer.

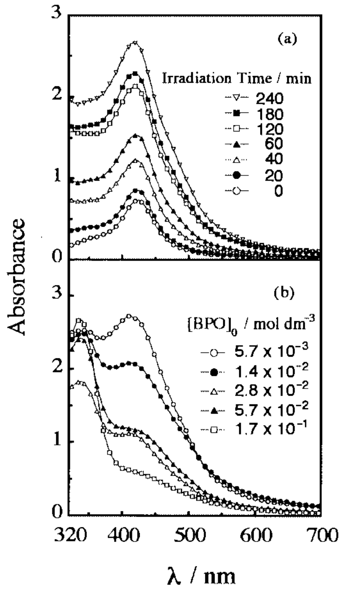

Figure 1. Absorption spectra of Ag/PMMA. (a) Effect of the irradiation time; $[AgTfa]_0 = 2.8 \times 10^{-2}$ mol dm^{-3}, $[AIBN]_0 = 2.8 \times 10^{-2}$ mol dm^{-3}. (b) Effect of the initiator BPO concentration; $[AgTfa]_0 = 2.8 \times 10^{-2}$ mol dm^{-3} and irradiated for 240 min.

After irradiation, the initially faintly colored Ag/PMMA sample became a yellowish brown color. Shown in Figure 1(a) are the absorption spectra of such colored samples that were prepared by $[AIBN]_0 = 2.85 \times 10^{-2}$ mol dm^{-3} with constant $[AgTfa]_0$ (2.85×10^{-2} mol dm^{-3}) and irradiated at 25 °C for various times. As shown in the figure, an absorption peak at ca. 420 nm grows depending on the UV irradiation time and shifts slightly to the shorter-wavelength. On the basis of the literature,[11] the peaks observed at ca. 420 nm in Figure 1(a) can be reasonably assigned to a surface plasmon absorption due to the metallic silver cluster dispersed in the PMMA.

Even though the $[AIBN]_0$ and $[AgTfa]_0$ were changed, the tendencies of the absorption peak bands of various Ag/PMMA samples prepared by AIBN were almost the same: i.e., (1) only one peak at ca. 420 nm was observed, (2) in all the cases the peak intensity depends on the time of irradiation, and (3) when the irradiation time is the same, the higher are the $[AIBN]_0$ and $[AgTfa]_0$, the stronger is the peak intensity.

On the other hand, when BPO was chosen as an initiator, the absorption spectra of the irradiated Ag/PMMA samples were quite different. A new peak at ca. 340 nm was found, in addition to the 420 nm peak observed in those samples prepared by AIBN. The peak intensities, both at the 420 nm and at the 340 nm, are strongly affected by $[BPO]_0$, $[AgTfa]_0$ and the irradiation time. Among those experimental factors, however, the effect of $[BPO]_0$ on the change of the absorption bands was the most effective. One can see in Figure 1(b) that as the $[BPO]_0$ increases, the peak intensity at 420 nm gradually disappears, whereas that of 340 nm drastically increases.

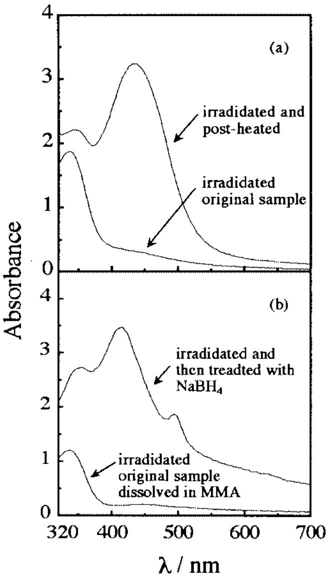

Figure 2. Absorption spectra of Ag/PMMA. (a) Effect of the post-heating; $[AgTfa]_0 = 2.8 \times 10^{-2}$ mol dm^{-3}, $[BPO]_0 = 1.7 \times 10^{-1}$ mol dm^{-3}, irradiation time of 240 min, and then post-heated for 180 min. (b) Effect of addition of $NaBH_4$; the same sample used for (a) was dissolved in 25 mL of MMA, and then a portion of 1.0×10^{-4} mol dm^{-3} of $NaBH_4$ was added.

In order to reveal which chemical species are responsible for the occurrence of the 340 nm band, the Ag/PMMA sample, which has already been UV-irradiated, was subjected to the thermal or chemical treatments. As shown in Figure 2(a), the heat-treatment caused a new appearance of the 420 nm band. On the other hand, a piece of the irradiated sample was dissolved into MMA, and then, the UV spectra were taken before and after the addition of a few drops of MMA solution containing $NaBH_4$ (ca. 1.0×10^{-4} mol dm^{-3}). Again, the 420 nm band was only observed for the sample after being treated by $NaBH_4$, as seen in Figure 2(b). However, when a MMA solution containing the Ag/PMMA sample prepared by AIBN was treated similarly by the heating or the addition of $NaBH_4$, the intensity of the 420 nm band increased.

On the γ-irradiation study of aqueous solution containing $AgNO_3$, Mostafavi et al.[10,15] reported that Ag clusters of a few atoms such as Ag_n ($1 \le n \le 3$), Ag_n ($4 \le n \le 7$) and Ag_n ($8 \le n \le 12$) are characterized by UV bands of 292, 325 and 370–380 nm, respectively. Applying a pulse radiolysis technique to aqueous Ag^+ solution, Henglein[11] revealed that so-called none-metallic dimeric (Ag_2^+) and tetrameric (Ag_4^{2+}) species, and quasimetallic Ag^0 nanocluster were assigned peaks at 310, 275 and 360 nm, respectively. Furthermore, analogs of small Ag particles were found by Ershov et al.[8,16]; Ag_2^+ (265 and 310 nm), Ag_4^{2+} (265 nm), Ag_1^0 (360 nm), Ag_2^0 (270 nm), Ag_4^0 (340 nm).

In the present study, it is explained that Ag^+ ions still remain in the Ag/PMMA samples prepared not only by the AIBN but also by the BPO initiator, even after the UV irradiation. Moreover, it might be true that the amount of Ag^+ ions remaining in the BPO sample is larger than that of AIBN, and that the average Ag^0 particle size of BPO sample is much smaller than that prepared by AIBN. It can be thought that such differences in the amount and the size of the Ag^0 particle are attributable to the substantial chemical reactivity of the primary radical generated form AIBN or BPO at the early stage of the polymerization.[14,17]

Thus, the evidence that the 340 nm peak slightly increases and the dramatic appearance of the 420 nm, as shown in Figure 2, arises from a series of successive processes that proceed the combination of the reduction of Ag^+ ions and the subsequent aggregation between the small newly formed Ag^0 particles and the Ag^0 particles which already existed. Consequently, considering the literature cited assignments to the absorption bands for the very small Ag particles, it is reasonably concluded that the 340-nm peak observed in the present study is attributable to an oligomeric species with a general formula Ag_m^0, in which $m < 7$, whereas that at 420 nm is caused by a colloidal particle of Ag_n^0 with $n >> 10$.

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