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Thermosensitive Gold Nanoclusters Stabilized by Well-Defined Vinyl Ether Star Polymers: Reusable and Durable Catalysts for Aerobic Alcohol Oxidation

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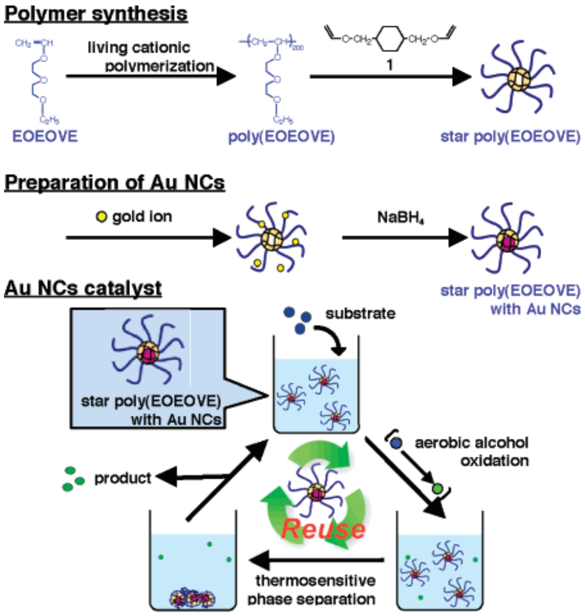
Since Haruta's pioneering work in the area of gold cluster catalysts,[1] the chemical properties of these clusters in various environments, including on a metal oxide support,[2,3] isolated in the gas phase,[4,5] and soft-landed on a clean surface,[6] have been the subject of extensive study. The preparation of finely dispersed gold clusters in solution is of key importance in the study of catalytic mechanisms and the size dependence of catalytic activity in real-world catalytic reactions.[7−14] However, a persistent problem in their practical use is aggregation of Au nanoclusters (NCs), especially during reactions and/or workup procedures.

A stable micelle structure would be used as a scaffold to prevent aggregation of these species. A star polymer[15,16] consisting of many hydrophilic arms and a hydrophobic core, prepared via polymer-linking reaction (Scheme 1), can be regarded as a unimolecular micelle. Recently, Aoshima et al. achieved a significant advance in star polymer synthesis, demonstrating quantitative formation of vinyl ether star polymers with low polydispersity ($M_w/M_n = 1.1-1.2$).[17] In addition, it has been found that poly(vinyl ethers) with oxyethylene side chains exhibit LCST (lower critical solution temperature)-type phase-separation behavior in water.[17−19] In this study, therefore, we examined the preparation of Au NCs in water using star polymers consisting of 2-(2-ethoxy)ethoxyethyl vinyl ether (EOEOVE), as illustrated in Scheme 1. The resulting clusters were shown to catalyze aerobic oxidation under mild conditions without deterioration. Furthermore, the catalyst could be recovered for reuse via simple procedures using thermosensitivity of the arm chains.

Star poly(EOEOVE) was prepared by the reaction of living EOEOVE polymers with divinyl ether **1** via base-stabilized living cationic polymerization as follows. In the first step of the reaction, EOEOVE was converted to a living polymer in the presence of $Et_{1.5}AlCl_{1.5}$ and 1,4-dioxane in toluene at 0 °C. Under these conditions, EOEOVE was consumed almost quantitatively in 23 min to yield a living polymer with low polydispersity ($DP_n = 200$, $M_w/M_n = 1.16$). To the living polymer mixture was added a small amount of **1** ($[\mathbf{1}]_0$/[living ends] = 10). Within 8 h, the starting living polymers and **1** were consumed quantitatively, and a star polymer was obtained in quantitative yield (M_w(GPC-MALLS) $= 9.4 \times 10^5$, $M_w/M_n = 1.36$, 28 arms). The resulting star polymer was soluble not only in toluene (the reaction medium) and chloroform but also in water at room temperature.

Scheme 1. Preparation and Catalytic Use of Au NCs



Au NCs were prepared as previously reported (see the Supporting Information).[7,8] In the UV-vis spectrum (Figure 1) of a resulting transparent and brownish solution, a very small absorbance at 520 nm, attributed to the surface plasmon resonance characteristic of the metallic gold clusters, was observed, indicating the formation of very small NCs.[7,8] A TEM image, shown in Figure 1, also demonstrated the presence of small Au NCs throughout a whole cross-section. Inspection of the TEM image revealed that the solution contained Au NCs of less than 4 nm with a relatively narrow size distribution. Moreover, small Au NCs were successfully prepared using star poly(EOEOVE) of different arm lengths (DP_n = 100, 50) (see the Supporting Information).

In view of the fact that poly(EOEOVE) undergoes LCST-type phase separation in water at around 40 °C, as described above, we

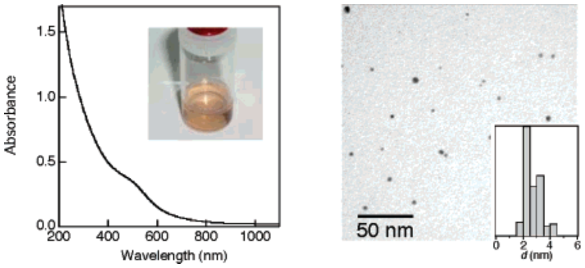


Figure 1. Absorption spectrum and TEM image of Au NCs in water supported by star poly(EOEOVE).

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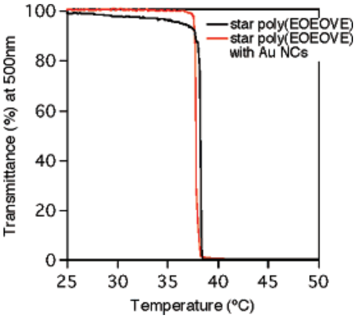
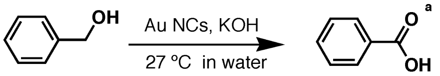
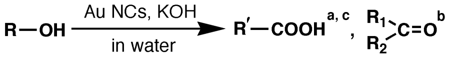


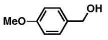
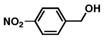
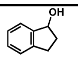
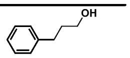
Figure 2. Temperature dependence of transmittance for aqueous solutions (1.0 wt %) of star poly(EOEOVE) and Au NCs supported by star poly(EOEOVE), monitored with a UV−vis spectrometer at 500 nm.

Table 1. Reusability and Versatility of Au NCs



	run 1	run 2	run 3	run 4	run 5	run 6
Yield (%)	> 99	> 99	> 99	> 99	> 99	> 99



Substrate				
Yield (%)	93[a]	89[a]	91[b]	71[c]

[a,b] [Substrate]$_0$ = 16.7 mM, [Au] = 0.33 mM, [KOH] = 50 mM, at 27 °C in water. [c] [Au] = 0.66 mM, at 32 °C in water.

examined the thermosensitive behavior of the star-polymer-stabilized Au NCs. Figure 2 shows the temperature dependence of UV transmittance for a solution of Au NCs. The cloud point and sensitivity of the polymer-stabilizing cluster were found to be very similar to those of the original star polymer. An important feature of the Au NCs is that the phase-separated solution reverted to a clear solution with decreasing temperature. In addition, no aggregation of the clusters was detected in UV−vis and TEM measurements (see the Supporting Information).

The resulting Au NCs were shown to catalyze the oxidation of benzyl alcohol in water under aerobic and mild conditions ([benzyl alcohol]$_0$ = 16.7 mM, [Au] = 0.33 mM, [KOH] = 50 mM, at 27 °C, in water). Benzyl alcohol was completely consumed in 4.5 h to yield the corresponding acid (benzoic acid) in almost quantitative yield as shown in Table 1. In addition, the Au NCs induced several aerobic oxidation reactions of benzyl alcohol derivatives into the corresponding carboxylic acids (*p*-nitrobenzyl alcohol, 89% in 24 h; *p*-methoxybenzyl alcohol, 93% in 4 h) and secondary alcohol into the corresponding ketone (1-hydroxyindane, 91% in 1 h) under similar conditions. Moreover, the Au NCs were able to catalyze oxidation from an primary alcohol to the corresponding carboxylic acid (3-phenyl-1-propanol, 71% in 24 h; [3-phenyl-1-propanol]$_0$ = 16.7 mM, [Au] = 0.66 mM, [KOH] = 50 mM, at 32 °C, in water). In all cases, oxidation reactions proceeded under milder conditions, compared to previous studies.[11,12] It should be noted that the Au NCs did not undergo negative aggregation at any point during the reaction or even during workup procedures, which was confirmed using the TEM method (see the Supporting Information). This is in contrast to the reaction using linear diblock copolymers of EOEOVE and isobutyl vinyl ether or PVP,[7] which did undergo aggregation during the reaction. In these star-polymer-stabilized Au NCs, gold clusters are likely to exist in hydrophobic layers (the core region of a star polymer). Such isolation of Au NCs would prevent their spontaneous aggregation and/or surface poisoning by the resulting carboxylates. This high level of stability has never yet been reported for any type of polymer-stabilized Au NCs.

After the reaction, the clusters were successfully separated by decantation at a temperature higher than the clouding point such as 60 °C. This simple procedure allows almost quantitative recovery of the cluster. When reused, they showed catalytic activity that was very similar to that of the virgin counterpart. Furthermore, the catalytic activity was maintained at least until the sixth use, with the oxidation of benzyl alcohol occurring almost quantitatively (>99%) in each run (Table 1). In contrast, Au NCs using PVP could not be reused because of their negative aggregation during the catalytic reaction.[7,8]

In conclusion, we have developed a simple preparation for stable and durable Au nanoclusters of less than 4 nm using thermosensitive vinyl ether star polymers obtained by living cationic polymerization. The resulting clusters effectively catalyzed the aerobic oxidation of alcohols such as benzyl alcohol. The clusters were easily separated from the reaction mixture by utilizing their thermosensitive nature, allowing for repeated reuse.

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Supporting Information Available: Experimental procedures, UV diagrams, and TEM images after the oxidation reaction. This material is available free of charge via the Internet at http://pubs.acs.org.

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