Synthesis and Characterization of Gold−Epoxy Nanocomposites by Visible Light Photoinduced Electron Transfer and Cationic Polymerization Processes

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Introduction. The preparation of nanostructured materials has become an important research field as these materials have specific optical and electronic properties, which differ significantly from the bulk. In particular, nanocomposite materials containing noble metal nanoparticles dispersed into polymer matrix are very interesting since they can exhibit novel physical and chemical properties that are of high scientific and technological relevance.[1] The combination of the physical properties of small size metal nanoparticles with those of the polymer matrix yields hybrid materials with unique and versatile properties.

In particular, the use of gold nanoparticles opens fascinating possibilities in various fields especially due to size-related electronic and optical features.[2] The gold nanoparticles dispersed into polymeric network were already used as various sensors,[3] for catalytic purposes,[4] in conductive inks,[5] and for electron or energy storage.[6] Because of their high surface reactivity, bare nanoparticles are unstable and tend to agglomerate.[7] For their applications it is mandatory to have particles with nanosize dimensions and a good distribution within the polymeric network; therefore, the homogeneous dispersion of these thermodynamically unstable nanoparticles is a key challenge. Their synthesis has been performed under a variety of conditions, including citrate reduction,[8] thiol stabilization,[9] and several thermal and photochemical techniques using thiols,[10] amines,[11] micelles,[12] dendrimers,[13] and polymers[14] as protective agents to aid in gold particles stabilization in aqueous or organic media.

In a recent publication from this group, the synthesis network polymer composites containing gold nanoparticles has been described.[15] The nanocomposites were obtained by simultaneous photoinduced electron transfer and free-radical polymerization of an acrylic formulation. Regarding the ultimate use of such nanocomposites in various technological applications, (meth)-acrylic based systems do not exhibit good thermal, mechanical, and chemical resistance, low shrinkage, and adhesion characteristics. It seemed, therefore, appropriate to expand the concept to epoxy based systems which give cross-linked materials with excellent thermal and chemical resistance. This paper reports on the in situ formation of gold nanoparticles within an epoxy matrix, by photoinduced electron transfer and cationic polymerization process, activated by visible light.

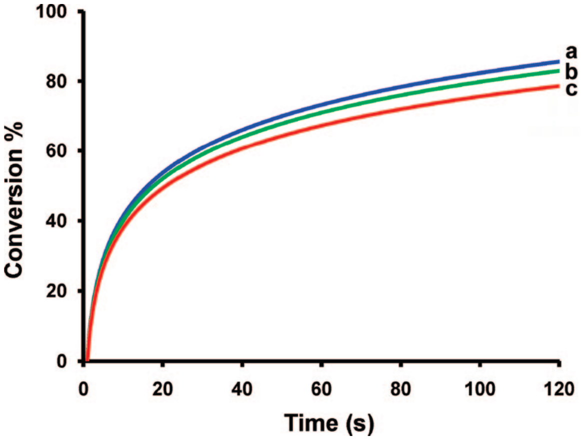

Figure 1. Real-time FTIR kinetic conversion curves for the UV curing of 1,3-bis(3,4-epoxycyclohexylethyl)tetramethyldisiloxane (EPOX) resin containing camphorquinone (2 wt %), Rhodorsil 2074 (2 wt %), and different concentrations of $HAuCl_4$ and 0 wt % $HAuCl_4$ (curve a), 0.5 wt % $HAuCl_4$ (curve b), and 1 wt % $HAuCl_4$ (curve c).

Results and Discussion. Recently, we showed that simultaneous photoinduced electron transfer and cationic polymerization processes exhibited high potential as a novel route to prepare silver epoxy nanocomposites.[15] The emergence of this approach led to develop gold−acrylic based polymer nanocomposites using the free radical mode in the process.[16] However, the corresponding gold−epoxy nanocomposites can not easily be prepared by a similar in situ method. The reducible gold precursor, $HAuCl_4$, is not soluble in a selected epoxy resin. Moreover, it does not contain non-nucleophilic counteranion to facilitate cationic chain propagation. The first step in this study was the design of appropriate oxidizing agents capable of generating both gold nanoparticles as well as initiating cations with non-nucleophilic counteranions. Thus, two different salts, namely iodonium salt and $HAuCl_4$, were used together in the formulation. Therefore, in the presence of a suitable photoinitiator, the visible light generated radicals reduce $HAuCl_4$ to form gold nanoparticles. In the meantime, a portion of the photochemically formed radicals are oxidized to the corresponding carbocations which could start cationic ring-opening polymerization reaction. Thus, formation of nanoparticles and cationic chain propagation occurs through different oxidants but proceeds concomitantly. The strategy implemented is outlined in Scheme 1 and involves the use of a radical photoinitiator.

The radical photoinitiator, camphorquinone (CQ), is active in the range of visible light and capable of generating radicals via Norrish type II reaction.[17] A silicone epoxy resin, 1,3-

Table 1. Properties of Cured Films Obtained by Irradiation of 1,3-Bis(3,4-epoxycyclohexylethyl)tetramethyldisiloxane (EPOX) Resin Containing Camphorquinone (2 wt %), Rhodorsil 2074 (2 wt %), and Different Concentrations of $HAuCl_4$

$HAuCl_4$ (wt %)	conversion[a] (%)	gel content[b] (%)	T_g[c] (°C)
0.0	98	100	46
0.5	95	98	50
1.0	90	100	58

[a] Determined by real-time FTIR at the end of 2 min irradiation. [b] Determined by solvent extraction. [c] Determined by dynamic-mechanical thermal analysis.

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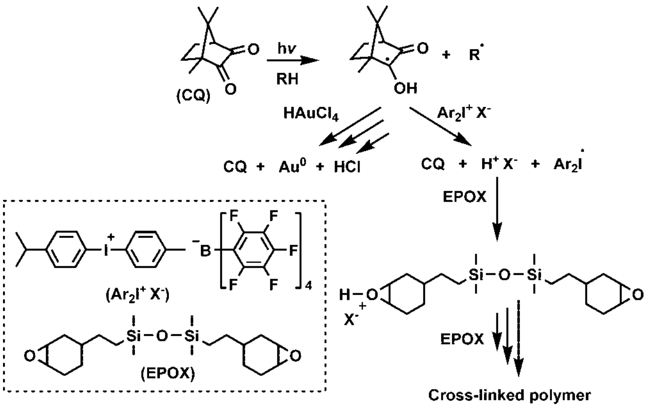
Scheme 1. Visible Light Induced Synthesis of Gold−Epoxy Nanocomposites



bis(3,4-epoxycyclohexylethyl)tetramethyldisiloxane (EPOX), was used as photocurable monomer which can ultimately form cross-linked networks due to the two epoxy groups present in the structure. Because of the poor solubility of $HAuCl_4$ in the selected epoxy resin, a small amount of poly(ethylene glycol) additive (between 1 and 2 wt %) was used. This way uniform solution of the formulation containing all components was achieved. Moreover, this additive has a promoting effect in the cationic polymerization since hydroxyl group containing compounds are known to participate in activated monomer polymerization.[18−20]

Epoxy group conversion as a function of irradiation time is reported in Figure 1. From the curves reported in Figure 1, it is evident that the redox process is quite efficient at converting light-generated free radicals into propagating carbocations, and polymerization is almost completed after 2 min of irradiation. A relatively lower rate of conversions is observed at increased gold precursor concentrations. This may be due to the increase of the stiffness of the polymeric network which limits the diffusion of the reactive species. All the cured films showed a gel content around 100% (Table 1), indicating high efficiency of the photopolymerization process and the absence of extractable monomers or oligomers.

The cured films obtained were transparent to visible light, indicating the absence of agglomeration forming particles above 400 nm. The formation of gold nanoparticles during polymerization was visually observed by the gradual change of the color from yellow to purple. UV−vis spectra (which is not reported) indicates a maximum absorbance at around 600 nm, which is close to the reported surface plasmon resonance of gold nanoparticles.[21] In Figure 2, the bright-field TEM micrographs for the cured films obtained by using various amount of the metal precursor are reported. As it can be seen, the nanoparticles

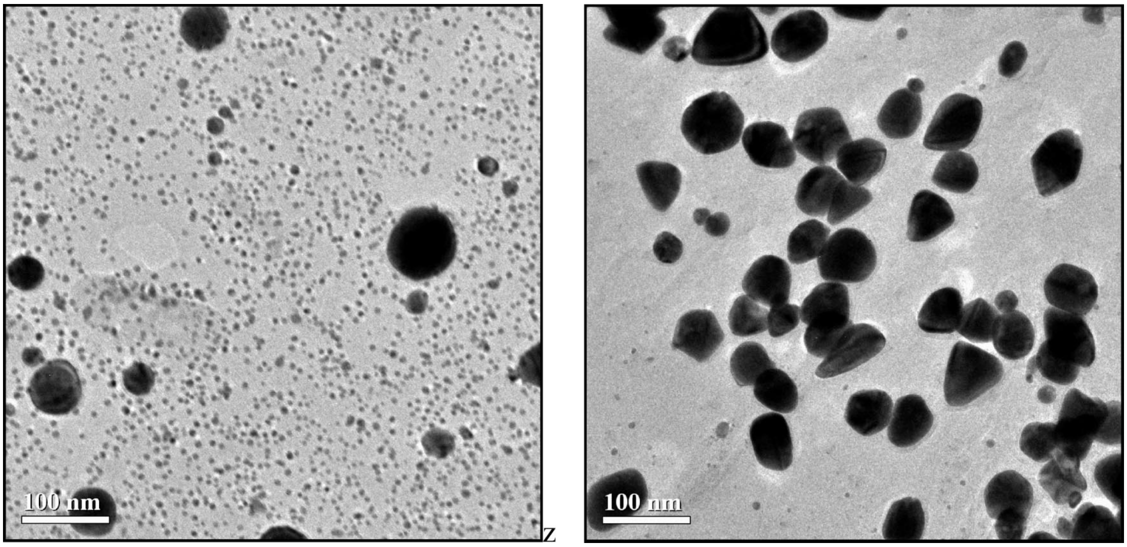


Figure 2. Bright-field TEM micrograph of the UV-cured films obtained by irradiation of 1,3-bis(3,4-epoxycyclohexylethyl)tetramethyldisiloxane (EPOX) resin containing 2 wt % camphorquinone, 2 wt % Rhodorsil 2074, and different concentrations of $HAuCl_4$. 0.5 wt % $HAuCl_4$ (left) and 1 wt % $HAuCl_4$ (right).

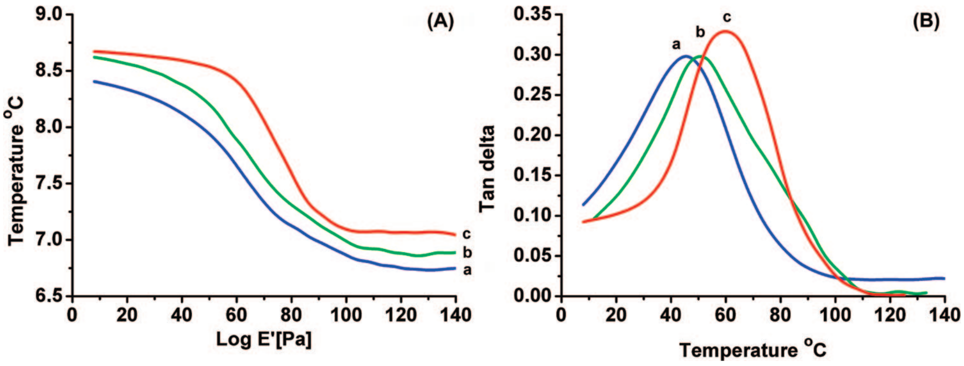


Figure 3. Storage modulus (A) and tan δ values (B) for the UV-cured films obtained by irradiation of 1,3-bis(3,4-epoxycyclohexylethyl)tetramethyldisiloxane (EPOX) resin containing 2 wt % camphorquinone, 2 wt % Rhodorsil 2074, and different concentrations of $HAuCl_4$. 0.0 wt % $HAuCl_4$ (curve a), 0.5 wt % $HAuCl_4$ (curve b), and 1 wt % $HAuCl_4$ (curve c).

were always well dispersed, and no macroscopic agglomeration occurred. It is also apparent that the nanoparticle dimension is strongly influenced by the gold precursor content in the photocurable formulations. When the $HAuCl_4$ content is 0.5 wt %, almost all the particles are 1−2 nm size and just a few nanoparticles are around 30−60 nm. By increasing the precursor content up to 1 wt % in the photocurable formulation, the particles size ranged from 50 to 60 nm, and some aggregates are noted.

Dynamic mechanical characterization of the UV-cured films were performed by means of DMTA analysis, which allows the evaluation for the elastic (E': storage modulus) and viscous (E'': loss modulus) components of the materials in a large temperature interval. In Figure 3, the DMTA thermograms are reported for the cured systems containing an increasing amount of gold nanoparticles precursor. In the T_g region a clear decrease of E' is evident (Figure 3A), while the tan δ curve (tan $\delta = E''/E'$: ratio loss modulus/storage modulus) shows a maximum which is assumed as the T_g of the cured films (Figure 3B). The T_g data are collected in Table 1 and show an increase of the glass transition temperature by increasing the amount of the gold nanoparticles in the photocurable formulation. This was evidenced by the shift of the maximum of tan δ peak toward higher temperature (see Figure 3B). At the same time an increase on E' modulus is evident in the rubbery region for the cured films containing nanoparticles (see Figure 3A). These results clearly indicate the good and homogeneous dispersion of nanoparticles within the polymeric network which could in turn hinder the polymer chain mobility and decrease the free volume of the network. Obviously, this behavior is the reason for the slight decrease on epoxy group conversion observed by RT-FTIR analysis (vide ante).

In order to demonstrate the general value of the method described here, polymerizability of two other commercially important epoxides was also tested. Experiments by using cycloaliphatic and aliphatic epoxy resins, namely 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate (CE) and 1,6-hexanediol diglycidyl ether (HDGE), respectively, under identical conditions exhibited similar polymerization behavior and yielded nanocomposites with comparable properties, i.e., conversion, gel content, storage modulus, and T_g (see Supporting Information).

In conclusion, gold−epoxy nanocomposites were in situ prepared by simultaneous visible light photoinduced electron transfer and cationic polymerization processes. The coaction of $HAuCl_4$ and iodonium salt in oxidizing photochemically generated free radicals accounts for the formation of gold nanoparticles and initiating cationic species, respectively. The nanoparticles were homogeneously distributed within the polymeric network without any macroscopic agglomeration. The particle size was increased by increasing the content of the gold precursor in the photocurable formulation.

Supporting Information Available: Details of experimental procedures, gel content, storage modulus, tan δ values, and T_gs of the UV-cured films obtained by commercially important epoxy resins, HDGE and CE. This material is available free of charge via the Internet at http://pubs.acs.org.

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