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In Situ Synthesis of Silver−Epoxy Nanocomposites by Photoinduced Electron Transfer and Cationic Polymerization Processes

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Metallic nanoparticles have special properties that may allow their use in a number of advanced functional applications. As a result, the fabrication of polymer−metal nanocomposites has attracted a great deal of attention in recent years.[1−5] Nanocomposite materials consisting of dispersed metal nanoclusters in a polymeric matrix show extraordinary physical properties and they have been proposed for optical,[6] electrical,[7] and medical[8] applications as well as for data storage.[9]

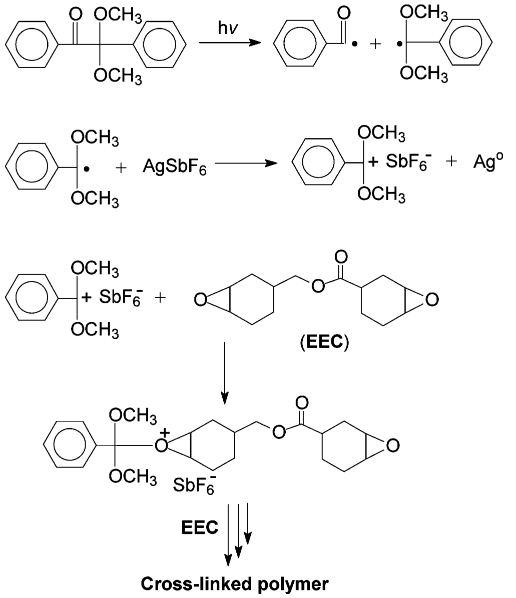
In particular silver nanoparticles are very important for their excellent electrical conductivity,[10] antimicrobial effect,[11] and optical properties.[12] Nevertheless, the homogeneous dispersion of these metal nanoparticles is a key challenge due to their easy agglomeration arising from their high surface free energy. Silver nanoparticles can be readily produced by reductive processes in homogeneous or micellar solution or in preformed polymer films. However, until recently in situ formation of well dispersed metallic nanoparticle polymer composites have been scarcely investigated. Kim et al.[13] reported simultaneous synthesis of silver nanoparticles and the polymer film constituting the nanocomposite film through an in situ electron-transfer reaction and the copolymerization of styrene and amphiphilic urethane acrylate nonionomer, which contains hydrophobic poly(propylene oxide) segments and hydrophilic poly(ethylene oxide) segments along the same backbone.

Many photolytically formed radicals can be oxidized[14] by suitable oxidants such as onium salts. The cations thus generated are used as initiating species for cationic polymerizations.[15]

Being photolyzed with fairly high quantum yields (0.41 for benzoin),[16] benzoin derivatives are so far the most effective photoinitiators. The photolysis of a typical benzoin derivative, 2,2-dimethoxy-2-phenyl acetophenone (DMPA), results in the generation of strong electron donor radicals. The efficiency of oxidizing agents is related to their electron affinity. The higher the oxidation power of the oxidant, the higher (more positive) is the reduction potential $E_{1/2}^{\mathrm{red}}$.[17,18] Diphenyliodonium and *N*-alkoxy pyridinium salts have a relatively high reduction potential. Being very suitable for the oxidation of free radicals, these salts have been most frequently used for the oxidation of photogenerated free radicals.[19−21]

In contrast, triphenylsulphonium salts have only limited potential for radical-induced cationic polymerizations due to their low reduction potential. Besides onium salts, silver salts with non-nucleophilic counter anions such as $\mathrm{SbF6}^-$, $\mathrm{PF_6}^-$, $\mathrm{AsF_6}^-$, and $\mathrm{BF_4}^-$ are very suitable oxidants in radical promoted cationic polymerization.[22] As part of our ongoing research efforts in the design and development of photoinitiating systems for the preparation of complex macromolecular architectures, we report herein an efficient synthetic methodology for in situ generation of silver nanoparticles during photoinduced cationic curing of bisepoxides. Our approach toward the preparation of silver nanocomposites is unique in the way that silver nanoparticles and initiating cations are formed in a single redox process. In the design of nanocomposites, one must consider both the properties of the polymer matrix as well as the stability of the nanoparticle and, importantly, prevention of particle aggregation. Depending on the radical concentration rather stable silver nanoparticles are formed through the oxidation of radicals in the polymerizing medium.[13]

Scheme 1. Photoinduced Synthesis of Silver−Epoxy Nanocomposites



For our studies, we chose 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexanecarboxylate (EEC) to serve as the cationically polymerizable monomer; it can ultimately form cross-linked networks due to the two epoxy groups present in the structure.

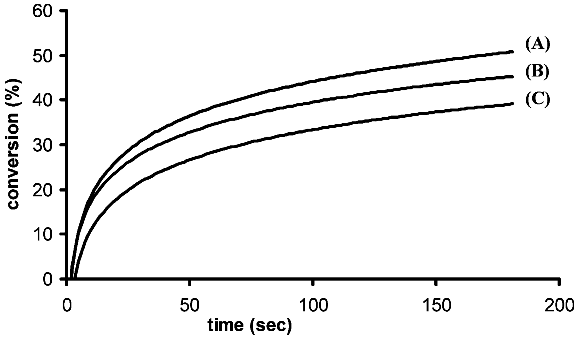


Figure 1. Real-time FTIR kinetic conversion curves for the UV curing of 3,4-epoxy cyclohexylmethyl-3′,4′-epoxycyclohexanecarboxylate resin containing different concentrations of $\mathrm{AgSbF_6}$ and 2,2-dimethoxy-2-phenyl acetophenone (2 wt %). 1 wt % $\mathrm{AgSbF_6}$ (curve A), 3 wt % $\mathrm{AgSbF_6}$ (curve B), 5 wt % $\mathrm{AgSbF_6}$ (curve C).

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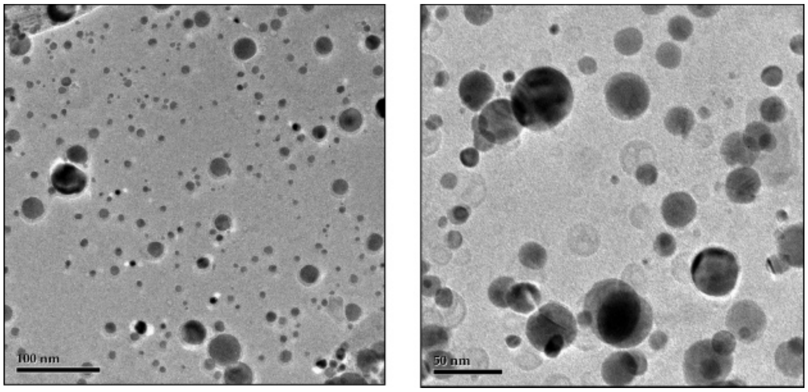

Figure 2. Bright field TEM micrograph the UV cured films obtained by irradiation of 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexanecarboxylate resin containing 5 wt % $AgSbF_6$ and 2 wt % 2,2-dimethoxy-2-phenyl acetophenone (DMPA).

Table 1. Properties of the UV Cured Films Obtained by Irradiation of 3,4-Epoxycyclohexylmethyl-3′,4′-epoxycyclohexanecarboxylate (EEC) Resin Containing $AgSbF_6$ and 2,2-Dimethoxy-2-phenyl Acetophenone (DMPA, 2 wt %)

sample	$AgSbF_6$ (wt %)	gel content[a] (%)	T_g[b] (°C)
EEC-1	1	98	235
EEC-2	3	99	242
EEC-3	5	98	250

[a] Determined by solvent extraction [b] Determined by dynamic−mechanical thermal analysis.

Photoinduced cleavage of DMPA is a good source of electron donor radicals, namely alkoxy benzyl radicals.[23] In this connection, it should be pointed out that other kinds of oxidizable radicals, i.e., ketyl radicals, can also be generated from the photolysis of benzophenone.[19] However, these systems require additional hydrogen donors such as amines. Depending on the basicity, such hydrogen donors readily react with the propagating cations and consequently terminate the polymerization.[24] Moreover, hydrogen abstraction may compete with Ag^+ quenching.[25] Thus, irradiation of DMPA in our system in the presence of AgSbF6 leads to its reduction with rapid generation of both metallic silver and initiating cations without any undesirable side reactions. The overall process is represented in Scheme 1.

Experimentally, the silver salt was added in EEC resin, in the range between 1 and 5 wt %, together with the radical photoinitiator, DMPA. The samples were irradiated by UV light (light intensity on the surface of the samples of about 30 mW/cm^2) and the extent of polymerization was detected by a real-time FT-IR technique. The two components of the initiating system are indispensable for the polymerization to occur; no polymer is formed in the absence of either compound under our reaction conditions. 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 silver hexafluoroantimonate is quite efficient at converting UV-generated free-radicals into propagating carbocations, which start cationic epoxy ring-opening polymerization with high reactivity. Relatively lower rate of conversions observed at increased concentrations may be due to the competing tail absorption of silver salt. Thus, a lower amount of electron donor radicals, and in turn, initiating cations are formed. Nevertheless, high gel content values (above 98%) are obtained in all cases (Table 1), indicating the formation of a highly cross-linked polymer network.

All of the cured samples were transparent, indicating the formation of metallic particles in nanometer range size, which was also confirmed by TEM analysis. In Figure 2, bright field TEM micrographs for the cured films containing 5 wt % of silver salt in the epoxy resin is reported. Metallic particles are well dispersed with no significant macroscopic agglomerations. The observed features have a size distribution ranging between 10 and 50 nm.

Dynamic−mechanical thermal analysis (DMTA) was also carried out on cured films. DMTA measurements give information on the microstructure of a polymeric materials; it allows the evaluation of the thermal and viscoelastic properties of the material in a large temperature interval. The storage modulus (E') and tan δ curves, as a function of temperature, were measured for all UV-cured networks. The glass transition temperature, T_g, is defined as the peak of tan δ curves, and the values are collected in Table 1. From the DMTA curves, it was possible to observe that by increasing silver salt concentration, a shift toward higher temperature of tan δ peak resulted and a higher storage modulus was evident in the rubbery region. This behavior can be attributed to the impediment of the segmental motion of the polymeric chains induced by the silver nanoparticles in the polymer network. The increase of constrains of the segmental motions of polymeric chains is mainly due to a uniform distribution of the metallic nanoparticles which was also evidenced by TEM analysis.

In conclusion, the in situ synthesis of silver−epoxy nanocomposite was achieved by simultaneous photoinduced electron transfer and cationic polymerization processes. These results establish a novel approach for the preparation of nanocomposites by which nanoparticle formation and cross-linking processes can be accomplished in one-pot by simply irradiating appropriate formulations and demonstrate the nanoparticles are homogenously distributed in the network without macroscopic agglomeration. Not only is this method applicable to silver nanoparticles but also it is presumably applicable to any other metal salts, such as gold salts, which undergo similar redox reactions with photochemically generated electron donor radicals. Further studies in this line are now in progress.

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Supporting Information Available: Text giving materials, experimental procedures, and characterizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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