Synthesis and Characterization of Gold/Polymer Nanocomposites by Thermal Cationic and Radical Polymerization Processes: Initiating Systems Based on Amine and/or Silane Reducing Agents

Mohamad-Ali Tehfe, Saïd Elkoun and Mathieu Robert
Carrefour of Innovative Technology and Ecodesign (CITE), Faculty of Engineering, University of Sherbrooke; 2500 blvd Université, Sherbrooke, Québec J1K 2R1, Canada

New initiating systems based on silane (diphenylsilane (DPSi)) and/or amine (triethylamine (TEA)) and gold salt (Gold(III) chloride trihydrate (HAuCl₄)) are proposed for an easy thermal cationic and/or radical polymerization of ε-caprolactone (ε-CL) and trimethylolpropane triacrylate (TMPTA) at room temperature and under air. They ensure good to excellent polymerizations. Moreover, a direct incorporation of the gold nanoparticles (Au(0) NPs) through this one pot synthetic procedure is observed. We report on the use of TEA and/or DPSi as reducing agents in the formation of gold nanoparticles. We can predict whether the amine and silane will function as reducing agents in this reaction based on their redox properties. The kinetics of Au(0) NPs formation by amine can be understood in terms of Marcus electron transfer theory and by silane by an attack of the electrophile on a Si-H bond. Interestingly, using TMPTA/ε-CL blends are also easily polymerized at RT and under air and lead to the formation of interpenetrating polymer networks IPN exhibiting no phase separation. The as-synthesized nanocomposite materials contained nanoparticles homogeneously dispersed in the polymer matrices. The nanoparticles were characterized by X-ray diffraction (XRD), X-ray spectrometry (EDS), transmission electron microscopy (TEM), and UV-vis spectroscopy. A coherent picture of the involved chemical mechanisms is presented.

**Keywords:** Amine; Silane; Gold Salt; Gold nanoparticles; Thermal Cationic and/or radical Polymerization; Interpenetrating polymer networks IPN; ε-caprolactone; Trimethylolpropane triacrylate

1. Introduction

Gold nanoparticles (Au(0) NPs) are rapidly growing area of materials chemistry because of the chemical versatility of the Au(0) NP surface and the relationship between their size and optical properties. Gold nanoparticles (Au(0) NPs) feature a wide range of potential applications in fields such as medicine [1], biotechnology [2], catalysis [3] and are thus among the most intensely studied nanoscale materials. Au(0) NPs can be prepared via various synthesis routes including chemical, sonochemical, or photochemical paths [4]. The most common chemical route is precipitation of the Au(0) NPs in aqueous solution from a dissolved gold precursor, for example HAuCl₄, by a reducing agent such as sodium citrate, ascorbic acid, sodium boron hydride or blockcopolymers.

Amines have been used in AuNP synthesis as both reducing agents and as stabilizers after Au(0) NP formation [5–10]. A variety of amines have been explored, including simple primary amines [9,10], amino acids [5–7] and multifunctional amines including polymers [8]. Amines are a particularly attractive class of reducing agents because of their nearly universal presence in biological and environmental systems. We report here on our examination of an amine (TEA) and silane (DPSi) with the goal of determining whether they function as reducing agents in the formation of Au(0) NPs by thermal radical and/or cationic polymerization processes under air and at room temperature.

Thermally and photochemically induced free radical polymerizations (FRPs) have been the subject of numerous studies [11a]. In thermal FRPs, redox initiated processes are very attractive due, for example, to the absence of solvents and the use of quite low reaction temperatures. However, such FRPs suffer from a strong drawback concerned with the well-known oxygen inhibition [11,12]. Indeed, both the initiating and propagating radicals are scavenged by O₂ and converted into stable peroxy radicals which cannot participate in any further polymerization initiation reactions and lead to a decrease of both polymerization rates and final conversions [13,14].

In cationic polymerization, such an inhibition does not exist and, interestingly, the use of less toxic monomers than the acrylates can be highly worthwhile. Redox systems being able to initiate a cationic polymerization have been already proposed [15–18]. Very recently, new bi-component combinations based on onium salt (diaryliodonium or triarylsulfonium salt) and organosilane (R₃SiH) as the reducing agent were elegantly proposed: the redox reaction is catalyzed by noble metal complexes (platinum, palladium, rhodium) and leads to a silylium cation which directly attacks the epoxide or/and reacts with water to form a Brønsted acid [19]. Other systems combining a diaryliodonium hexafluorophosphate and a dialkylborane were also proposed: in that case, the redox process generates a fluorinated borane and phosphorus pentfluoride that further acts a Lewis acid for the ring-opening polymerization [20].

In the present paper, we propose here totally different and new redox two component systems based on an amine or silane/gold salt combination (Scheme 1) in order to initiate a thermal radical and/or cationic polymerization of trimethylolpropane triacrylate and ε-caprolactone monomers, that should result in the formation of a Au(0) NPs containing film. On the other hand, our system should open up a new way for i) the cationic ROP of ε-CL and free
radical polymerization (FRP) of TMPTA initiated by a true redox process at RT and under air and ii) the in-situ incorporation of nanoparticles into PCL or PTMPTA. Finally, the overall polymerization process has been investigated and the cured films characterized.

2. Experimental part

2.1 Compounds

The compounds with the best purity available used are presented in Scheme 1. Gold(III) chloride trihydrate (Au), Triethylamine (TEA), Diphenylsilane (DPSi), ɛ-caprolactone (ɛ-CL) and Trimethylolpropane triacrylate (TMPTA) were all purchased from Sigma-Aldrich and used as received.

2.2 Radical and Cationic Polymerization

Gold salt (0.3% w/w) was dissolved in the selected monomer (ɛ-CL or TMPTA) and diphenylsilane (DPSi) or triethylamine (TEA) were introduced into the formulation by a syringe at RT. The polymerization of ɛ-CL or TMPTA was carried out in pill-box for a simple of 1g. The progress of the exothermic polymerization is followed by monitoring the sample temperature using a thermocouple connected to a DaqPro-5300 (resolution 0.1 °C). A magnetic stirrer in contact with the pill-box was used to ensure a good homogeneity. The addition of the DPSi or TEA into the formulation corresponds to time t = 0 s.

Since most of radical or cationic polymerizations rapidly take place with the release of a large amount of heat, it has been shown [19,20] that the increase of the temperature is directly proportional to the monomer conversion. However, as the set-up used here is not adiabatic, the relationship between the conversion and the temperature is only valid for the first steps of the polymerization process.

2.3 Interpenetrated Polymer Network Synthesis

For the polymerization of TMPTA/ɛ-CL (50%/50% w/w) blends, gold salt (0.3% w/w) was dissolved into the mixture of monomers and DPSi was introduced into the formulation by a syringe at RT. The polymerization of TMPTA/ɛ-CL was carried out in pill-box for a simple of 1g. The progress of the exothermic polymerization is followed by monitoring the sample temperature using a thermocouple connected to a DaqPro-5300 (resolution 0.1 °C). A magnetic stirrer in contact with the pill-box was used to ensure a good homogeneity. The addition of the DPSi into the formulation corresponds to time t = 0 s.

2.4 Characterization

UV measurements were carried out with a Spectra max plus 384 spectrometer, whereas Fourier-transform infrared spectra (FTIR) were performed on a ABB Bomen Spectrometer.

X-ray diffraction (XRD) of powder was performed using a Philips X’Pert diffractometer equipped with a general area detector diffraction system with Cu Kα radiation (k = 0.1542 nm) operating at 50 kV and 40 mA. The experiments were performed in the diffraction angle range 20 = 30–90°.

Elemental analysis was obtained by energy-dispersive X-ray spectrometry (EDS) using an EDS spectrometer.

Transmission electron microscopy (TEM) analyses of composite materials were carried out at an accelerated voltage of 80 kV using a Hitachi H-7500 TEM.
3. Results and discussion

3.1 Cationic Polymerization (CP)

The polymerization of ε-CL smoothly proceeds at room temperature using DPSi and gold(III) chloride trihydrate (Fig. 1A); the polymerization is observed within some hours (the gel time is about 5-7 hours). The polymerization does not occur using DPSi or gold(III) chloride trihydrate independently thereby demonstrating that this combination is necessary to initiate the process. Almost no inhibition is noted as a short period is already requested for the solubilization of the silane into the formulation. The polymerization is noticeably same under air than under argon (Fig. 1A). This result shows that (i) no strong oxygen inhibition obviously occurs and (ii) oxygen should positively participate in the initiation process (see below). This can open new opportunities for mass production and applications of PCL. The formation of PCL is well evidenced by IR spectra of the obtained polymer which are fully consistent with the spectra reported which show polyester bands at 1065 and 1108 cm$^{-1}$ (Fig. 1B) [15,20].

3.2 Free Radical Polymerization (FRP)

Using DPSi/gold salt initiating system, the polymerization of Trimethylolpropane triacrylate (TMPTA) is quite slow under air and at RT (tack free about 10 min) (Fig. 2A). The polymerization does not occur using DPSi or gold salt independently. As a result, a combination of both compounds is necessary to initiate the process. Remarkably, the polymerization is noticeably faster under argon than under air (e.g. tack free time ~2 min vs ~10 min for FRP under argon and under air, respectively) (Fig. 2A). This result shows that a strong oxygen inhibition obviously occurs using TMPTA as monomer for FRP. Indeed, in FRP the oxygen/radical interaction is a nearly diffusion controlled reaction (e.g. in very low viscosity monomer as TMPTA (~ 70-100 cP), the re-oxygenation remains efficient leading to strongly reduced monomer conversions) [21]. The polymerization only starts when oxygen is consumed. In another way it can explain that silyl radicals formed react with oxygen rather than with the acrylate double band (C=C). This is not the case of cationic polymerization which presents the great advantage not to be inhibited by oxygen [13c,22]. The formation of polyacrylate (PTMPTA) is well evidenced by IR spectra by the observation of the disappearance of the characteristic band of the acrylate double bonds at 1620 cm$^{-1}$ (Fig. 2B) [23].
Fig. 2  (A) Role of the atmosphere in the free radical polymerization of TMPTA in the presence of DPSi/gold salt (2%/0.3% w/w): (1) under air and (2) under argon. (B) Real-time FT-IR spectra in the 1500 – 1700 cm\(^{-1}\) wavenumber range of sample containing 0.3% (wt) of gold salt and 2% (wt) of DPSi in TMPTA under argon (1- before and 2- after polymerization).

Using triethylamine (TEA) instead DPSi with gold salt as initiating system, a similar process occurs but more slowly (e.g. tack free time ~6 min for TEA vs ~2 min for DPSi at RT and under argon) (Fig. 3). This is explained by two different types of reactions, when the kinetics of Au(0) NPs formation by amine can be understood in terms of Marcus electron transfer theory and by silane by an attack of the electrophile on a Si-H bond.

Fig. 3  Role of the atmosphere in the free radical polymerization of TMPTA in the presence of TEA/gold salt (2%/0.3% w/w).

3.3 Interpenetrated Polymer Networks Synthesis (IPN)

Because of the formation of both radical and ionic initiating structures in the same reaction, the new DPSi/gold salt two-component initiating system is highly efficient for the synthesis of interpenetrated polymer networks by thermal polymerization (Fig. 4A). This ability to polymerize TMPTA/ɛ-CL blend (TMPTA/ɛ-CL 50%/50% w/w) in a one-step hybrid cure process at room temperature and under air leads to interesting materials. The addition of the DPSi into the formulation corresponds to time t = 0 s. They ensure good to excellent polymerizations are always obtained leading to tack free surface coatings after only 4 minutes. Moreover, a direct incorporation of the gold nanoparticles (Au(0) NPs) through this one pot synthetic procedure is observed (see below). In the TMPTA/ɛ-CL matrix, the TMPTA thermal polymerization becomes feasible under air (in contrast to the results shown in part 2 of Results and Discussion) because the progressive formation of the polyether network renders the medium more and more viscous and thereby reduces the oxygen inhibition effect. The formation of PCL and polyacrylate (PTMPTA) is well evidenced by IR spectra of the obtained polymer which are fully consistent with the spectra reported which show bands at 1108 cm\(^{-1}\) for polyester and at 1620 cm\(^{-1}\) for polyacrylate (Fig. 4B).
3.4 In-situ Incorporation of gold

The in-situ formation of gold nanoparticles (Au(0) NPs) during the polymerization process is demonstrated by UV-visible spectroscopy (Fig. 5). The addition of DPSi or TEA to gold salt in ε-CL and/or TMPTA leads to the formation of Au(0) NPs clearly evidenced by UV-visible spectroscopy [i.e. surface plasmon resonance (SPR) band typical of gold nanoparticles observed at about 540 nm as it has been reported in [24]] (Figure 5).

Fig. 5 (A) UV-visible absorption spectra of HAuCl₄ in TMPTA under argon just before (1) and after addition of DPSi (2); Insert : Evolution of Au(0) NPs colors during the synthesis in TMPTA at RT and under argon. (B) UV-visible absorption spectra of HAuCl₄ in ε-CL under air just before (1) and after addition of DPSi (2). (C) UV-visible absorption spectra of HAuCl₄ in the interpenetrated polymer networks synthesis of TMPTA/ε-CL (50%/50% w/w) under air and at RT just before (1) and after addition of DPSi (2).
3.5 Reaction Mechanisms

The reduction of HAuCl₄ occurs due to transfer of electrons from the amine to the metal ion [24] or by an attack of the electrophile on a Si-H bond from the silane [25–27] resulting in the formation of Au(0) NPs, with the reaction being generically described according to Scheme 2.

Recently, it has been found that amines act as reducing agents for Au(III) in organic solvent [24]. In the present work, it is found that compounds being Si-H bond or an amine as TEA in combination with gold salt acts as a very powerful initiating system. The role of reactions (Scheme 2) is clearly outlined: DPSi or TEA/gold salt (2%/0.3% w/w) leads to an efficient polymerization process at RT. The good polymerization ability of DPSi or TEA/gold salt systems appears here in full agreement with the formation of R₃Si⁺ and H⁺ for cationic polymerization and with the formation of R₃Si⁺ and TEA⁺ for free radical polymerization. These species (R₃Si⁺, H⁺, R₃Si⁺ and TEA⁺) are largely known as efficient initiating species for both thermal and photochemical cationic and radical polymerization of ε-CL and TMPTA [28,29].

\[
\text{HAuCl₄} + 3 \text{TEA} \rightarrow 3[\text{TEA}]^{\bullet} + \text{Au}(0) + H⁺ + 4\text{Cl}⁻
\]

\[
\text{H⁺} + \text{TEA}⁺ \xrightarrow{\text{TMPTA}} \text{Polymer}
\]

\[
\text{HAuCl₄} + R₃\text{Si-H} \rightarrow R₃\text{Si⁺} + \text{Au}(0) + H⁺ + 4\text{Cl}⁻
\]

\[
\text{Polymer} \xrightarrow{\text{TMPTA}} R₃\text{Si⁺} \rightarrow \text{ε-CL} \rightarrow \text{Polymer}
\]

Scheme 2.

3.6 Characterization of gold nanoparticles (Au(0) NPs)

Functionalized Au(0) NPs were characterized by XRD, EDS, TEM and XPS. The XRD analysis confirms the presence of gold nanoparticles synthesized in situ in the polymer matrix by thermal polymerization process at RT with a high degree of crystallinity as shown in Fig. 6A, where the presence of diffraction peaks corresponding to (111), (200), (220), (311) and (420) planes, located at 2θ = 38.43°, 44.41°, 64.77°, 77.63° and 81.95° respectively, indicates the presence of the face-centered cubic (fcc) crystalline structure of gold nanoparticles (JCPDS 00-004-0784). This result consistent as reported in the literature and depicted in ref [30].

The formation of Au(0) NPs created in situ in this hybrid polymer matrix during thermal radical and/or cationic polymerization at room temperature were monitored using energy dispersive X-ray (EDS) spectroscopy analysis, as shown in Fig. 6B. Indeed, in the resulting EDS pattern, C, O, Si and Au peaks are clearly shown, demonstrating that gold/polymer composites were successfully prepared by this one-step process.

Fig. 6 (A) XRD patterns of as-synthesized Au(0) nanoparticles using DPSi/gold salt (2%/0.3% w/w) in (1) ε-CL; (2) TMPTA; (3) ε-CL/TMPTA (50%/50% W/W). (B) EDS analysis recorded from Au(0) nanoparticles in (3).

A bright field transmission electron microscopy image (TEM) is shown in Fig. 7. The formation of gold nanoparticles is clear from the TEM image. The TEM micrograph (Fig. 7) of gold nanoparticles obtained after thermal
polymerization at RT shows that the Au(0) NPs (0.3%, w/w) remain well-dispersed in the polymer matrix. The mean diameter of the gold core as observed from the TEM images is between 20-30 nm. Near spherical geometry was noticed for most of the particles. The TEM image suggests the possibility of a nearly homogeneous polymeric coating on the nanoparticle surface. These morphological results are in agreement with ref [24, 30a].

Fig. 7 TEM micrograph of gold nanoparticles (Au(0) NPs) dispersed into the polymer matrix obtained after thermal polymerization at RT and under air using DPSi/gold salt (2%/0.3% w/w) in \( \varepsilon \)-CL.

4. Conclusion

In the present paper, new redox systems were proposed to initiate in two-component systems (DPSi or TEA/gold salt) the ring-opening polymerization (ROP) of \( \varepsilon \)-caprolactone (\( \varepsilon \)-CL) and the free radical polymerization (FRP) of trimethylolpropane triacrylate (TMPTA). Interestingly, at room temperature and under air, this two-component system generates free radicals (TEA* and \( R_3Si^* \)) or ions (\( R_3Si^+ \) and \( H^+ \)). Remarkably, fast ROP and FRP are observed. Interestingly, these initiators can also be used for the synthesis of interpenetrated polymer networks (IPN), e.g., for the polymerization of TMPTA/ \( \varepsilon \)-CL blends. Highly crosslinked network were achieved and the nanocomposite obtained, contains near spherical geometry for most of the nanoparticles, homogeneously dispersed in the polymer network without significant agglomeration as a result of a surrounding effect of polymer chains formed by the rapid cationic and/or radical chain growth. The mechanical and optical properties of the obtained new organic polymer/gold nanoparticles will be investigated in near future.

References

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