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Synthesis of silver nanoparticles in surfactant-free light-cured methacrylate resins

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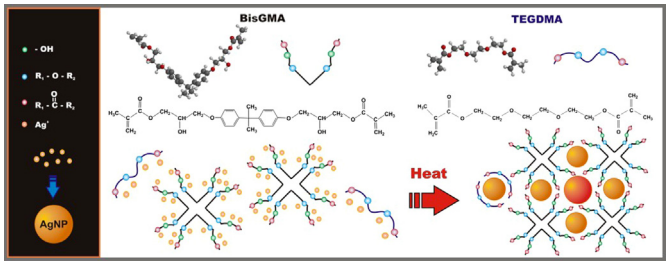
HIGHLIGHTS

- Silver nanoparticles were synthesized in surfactant-free methacrylate resins.
- Methacrylate resins act as efficient particle stabilizers.
- Dispersions stored for nine months showed no drastic change in particle size.

GRAPHICAL ABSTRACT



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ABSTRACT

The present study describes a simple method for preparing stable, highly dispersed spherical silver nanoparticles (Ag NPs) in surfactant-free methacrylate resins. Colloidal dispersions of silver in methacrylate resins were obtained by *in situ* reduction of silver nitrate. The reducing agents were hydroquinone (HQ), hydroquinone methyl ether (MEHQ) and 2,6-di-tert-butyl-para-cresol (BHT), which are added to the resins to prevent premature polymerization. The obtained finely dispersed Ag NPs, that were 5–10 nm in diameter, were maintained in a stable colloidal state for more than nine months at ambient temperature. UV–vis and TEM analysis revealed that the particle size did not change with the reaction time. Moreover, UV–vis spectra and TEM micrographs of samples stored for 9 months, showed no drastic change in average particle size. From these studies, it is concluded that the methacrylate resins used as reactive solvent act as efficient particle stabilizers preventing particle coalescence and thereby enabling long term stability. The dispersions Ag NPs/methacrylate resins were photoactivated with 0.5 wt% of 2,2-dimethoxy-2-phenylacetophenone and were photo polymerized with a UV light source of irradiance centred at 365 nm. The effective utilization of the surfaces of the formed metal nanoparticles is an advantage associated with nanoparticles formed *via* a surfactant-free synthesis method. The proposed process offers the possibility to use these synthesized materials for the production of colour filters for optical devices and biomaterials with improved antimicrobial properties.

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1. Introduction

Over the past 20 years, the development of solution based techniques for synthesizing metal nanoparticles, such as the chemical reduction of precursor ions in solution by a reducing agent, has allowed the size and the shape of the nanoparticles to be controlled [1,2]. The solution based synthesis of metal nanoparticles usually makes use of a soluble metal salt, a reducing agent, and a stabilizing agent. Stabilizing agents bind to the surface of the nanoparticle and prevent further growth or aggregation. It is well known that polymers are very effective to inhibit the agglomeration of nanosized particles [1–4]. However, the effect of small molecules, such as

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monomers, on stability of colloidal metal particles is less known [4]. The size and shape of the metal nanoparticles can be controlled by selecting the type of stabilizer and the molar ratio of the stabilizer to the precursor ions during the synthesis [1–3]. In some cases, however, the active sites on the surfaces of the nanoparticles might be blocked by the stabilizing agent, resulting in the less-than-effective utilization of the nanoparticle surfaces. For example, the blocking of the active sites may result in a loss in catalytic activity [5]. Because of the effective utilization of their surfaces, metal nanoparticles prepared without surfactants or polymers, are expected to exhibit better performance than those that must be stabilized in the presence of stabilizing agents [5].

The present study describes a simple method for preparing stable, highly dispersed spherical metallic silver nanoparticles (Ag NPs) in surfactant-free methacrylate monomers. To the best of our knowledge, this is the first report describing the *in situ* synthesis of Ag NPs using methacrylate monomers as both reactive solvent and stabilizing agent. The materials synthesized in this study can be used for the production of colour filters for optical devices [6] or biomaterials with improved antimicrobial properties [7].

2. Experimental

2.1. Materials

Silver nitrate ($AgNO_3$, ≥99%, Aldrich) and absolute ethanol (Merck) were employed as received. 2,2-Dimethoxy-2-phenylacetophenone (DMPA, 99%) and 2,6-di-tert-butyl-p-cresol (BHT, ≥99%) were from Sigma Aldrich, USA.

The methacrylate resins used for this study were 2,2-bis[4-(2-hydroxy-3-methacryloxyprop-1-oxy)phenyl]-propane (BisGMA, 90%, from Esstech, Essington, PA), 2,2-bis[4-(2-methacryloxyethoxy)phenyl]propane (BisEMA, 98%, from Esstech, Essington, PA), and triethylene glycol dimethacrylate (TEGDMA, 95%, from Aldrich, USA). BisTEG stands for a blend 70:30 BisGMA/TEGDMA. The resins were used without further purification. The methacrylate resins contain hydroquinone (HQ), hydroquinone methyl ether (MEHQ) and 2,6-di-tert-butyl-p-cresol (BHT) as inhibitors to prevent premature polymerization during storage. BisEMA contains 300 ppm MEQH and 200 ppm BHT. BisTEG contains 400 ppm MEQH, 5 ppm HQ, and 200 ppm BHT. Different amounts of each inhibitor are added to the methacrylate resins by the manufacturer to prevent polymerization during storage and to minimize the increase in colour produced by the inhibitors (yellowing). The structures of the resins are shown in Fig. 1.

The resins were activated for UV light polymerization by the addition of 0.5 wt% DMPA. The light source was assembled from a light emitting diode (LED) with its irradiance centred at 365 nm (OTLH-0480-UV, Optotech). The intensity of the LED was 175 mW.

2.2. Preparation of dispersions of Ag NPs

Colloidal dispersions of silver particles were obtained by reduction of silver nitrate in methacrylate (BisEMA and BisTEG) resins in the absence of protective agents. $AgNO_3$ (0.126 g) was dissolved in 10 ml of absolute ethanol (solution A). The solution was stirred at room temperature until complete dissolution of the silver nitrate was achieved. Solution A was diluted with ethanol to volume ratios 1:5 (solution B) or 1:20 (solution C). Dispersions having different silver content were prepared by mixing 1 ml of the corresponding solution of $AgNO_3$ (A, B or C) with the appropriate amount of methacrylate resin. The silver proportion in the resins was varied in the ranges: 3000–5000 ppm using solution A, 400–2000 ppm using solution B, and 50–300 ppm using solution C. In all cases, the required amount of ethanol was added in order to have a resin/ethanol mass ratio equal to 2. The reaction was carried out in glass tubes placed in a thermostat held at 70 °C allowing continuous evaporation of volatiles. The reaction was allowed to proceed for ~24 h in order to ensure complete evaporation of the ethanol. Silver cations were reduced by HQ, MEHQ and BHT present in the methacrylate resins. Fig. 2 is a schematic diagram of the synthesis of Ag NPs.

2.3. Characterization

The absorption spectra of dispersions of silver nanoparticles in methacrylate monomers were measured with an UV–vis spectrophotometer 1601 PC Shimadzu at room temperature (20 ± 2 °C). The resin was contained in thin cells (~0.5 mm) constructed from two quartz microscope slides separated by a PTFE gasket. An identical cell containing the BisEMA or BisTEG monomer was used as the reference.

The size distribution of Ag NPs was determined using a Philips CM-12 transmission electron microscope (TEM) operated at an accelerating voltage of 100 kV. In order to obtain good quality images, the dispersions of Ag NPs in methacrylate resins were diluted with ethanol (1 drop of the methacrylate resin in 600 μl de ethanol). Samples for TEM images were prepared by dropping 6 μl of the diluted dispersion of the particles on a copper grid coated with Formvar and a carbon film.

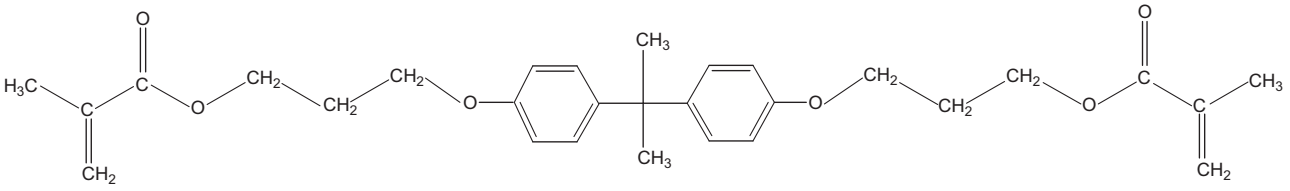
2.4. Photopolymerization

Measurements of monomer conversion *versus* irradiation time were carried out at room temperature (20 °C) using near infrared spectroscopy (NIR) with a Nicolet 6700 Thermo Scientific. The NIR spectra were acquired over the range 4500–7000 cm^{-1} from 16 co-added scans at 2 cm^{-1} resolution. The resins were contained in a 10 mm diameter well constructed from a rubber gasket material sandwiched between two glass plates. The thickness of the samples was 2 mm. With the assembly positioned in a vertical position, the light source was placed in contact with the glass surface. The samples were irradiated at regular time intervals and the spectra were collected immediately after each exposure interval. These spectra were corrected with the background spectrum collected through an empty mould assembly fitted with only one glass slide to avoid internal reflectance patterns. The conversion profiles were calculated from the decay of the absorption band located at 6165 cm^{-1} [8]. Two replicates were used in the measurement of conversion.

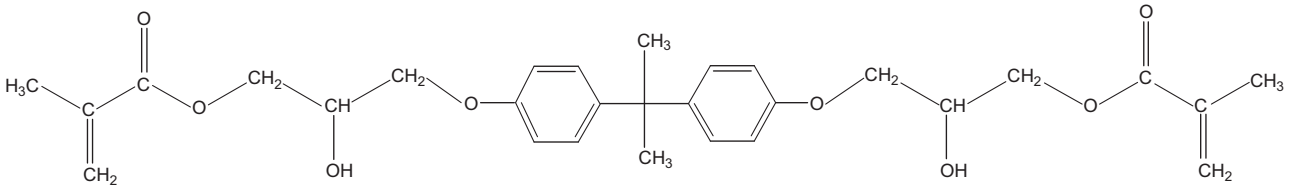
3. Results and discussion

3.1. Synthesis of silver nanoparticles in methacrylate monomers

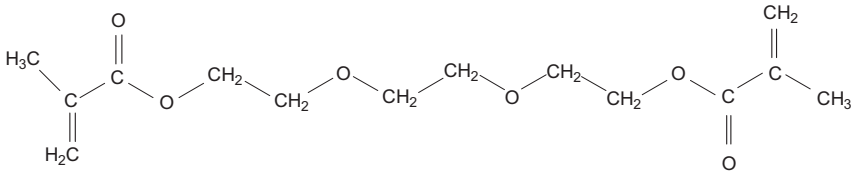
Highly stable colloidal dispersions of Ag NPs in methacrylate resins were synthesized using a one-step synthesis method. Ag NPs were *in situ* synthesized in methacrylate resins through reduction of $AgNO_3$ with HQ, MEHQ, and BHT, in the absence of surfactant. Generally, for the preparation of Ag/polymer nanocomposites the silver ions are dispersed in the polymer matrix and reduced to zero valent state by a reducing agent [8,9]. Reagents commonly used to reduce silver ions include N,N-dimethylformamide, hydrazine, ferric ions, and sodium borohydride. Unfortunately, those reducing agents exhibit undesired toxicity, which limit their application in medical and packaging products. In this study, low toxicity agents for reducing silver ions were employed in the preparation of Ag/methacrylate nanocomposites. HQ and MEHQ are both used in topical drug preparations as depigmenting agents for the skin. Similarly, BHT is an antioxidant phenolic acid that is often added



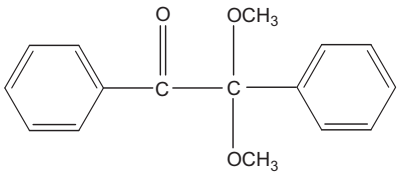
BisEMA



BisGMA



TEGDMA



DMPA

Fig. 1. Structure of the methacrylate monomers and photoinitiator used in this study.

to foods to preserve fats and is also used as an antioxidant additive in polymers.

It is well known that HQ is unable to reduce isolated silver ions but is able to sustain particle growth when added onto pre-existing silver metallic clusters of at least four atoms in size [10]. In practice, very low levels of sodium borohydride are used to form seed particles [10]. Alternatively, controlled growth can be initiated by exposing the samples to UV radiation, relying on the photo reactivity of hydroquinone to start the process [10], and then the radiation can be removed to allow HQ to finish the Ag NPs growth on its own in dark. The reason for this selectivity is that the redox potential for reducing isolated silver ions is markedly different than when adding to metallic clusters. The redox potential for hydroquinone ($E^0 = -0.7$ V) is unable to overcome the highly negative redox potential of isolated silver (−1.8 V), but is sufficient to reduce silver onto stable clusters or onto solid Ag electrodes (+0.8 V) [10].

In trying to elucidate the source of the initial metal seeds, which made possible the growth of silver particles in our system, several studies were carried out. At first, the generation of the initial clusters was attributed to the heating of the solution of $AgNO_3$ in the mixture ethanol/methacrylate resin. The oxidation of primary alcohols (R-CH_2OH) by Ag^+ is well established:

$$2Ag^+ + \text{R-CH}_2\text{OH} \rightarrow 2Ag^0 + 2H^+ + \text{R-CHO} \quad (1)$$

In addition, Ag^+ easily reacts with produced R-CHO:

$$2Ag^+ + 2\text{R-CHO} \rightarrow 2Ag^0 + 2H^+ + \text{R-COCO-R} \quad (2)$$

In order to test the proposed mechanism for the generation of initial silver clusters, a solution of $AgNO_3$ in ethanol containing (500 ppm) HQ was heated at 70 °C. The absence of Ag NPs after 36 h heating revealed that, under the experimental conditions used, the reduction of silver ions by ethanol is a very slow

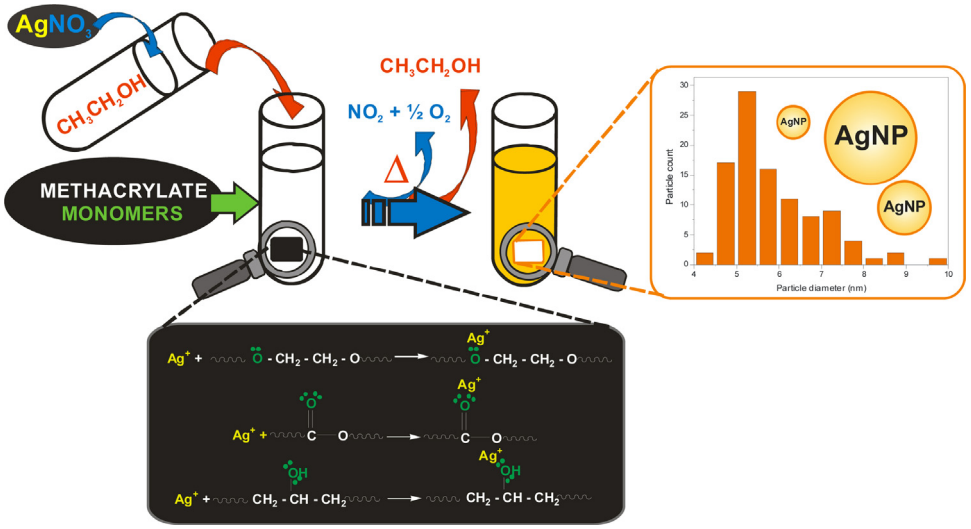


Fig. 2. Colloidal dispersions of silver particles were obtained by reduction of silver nitrate in methacrylate resins in the absence of protective agents. The reaction was allowed to proceed for ~24 h at 70 °C allowing continuous evaporation of volatiles. Silver cations were reduced by HQ, MEHQ and BHT present in the methacrylate resins.

process. Results reported in the literature show that preparation of Ag NPs by reduction with alcohols requires heating of the reacting medium at higher temperature than that used in the present study. For example, Huang et al. [11] prepared Ag NPs by reduction of $AgNO_3$ with ethylene glycol. Ag NPs were obtained after 4 h heating at 160 °C [11]. Alternatively, the formation of initial metal seeds in the present study may be attributed to the presence of a reducer impurity in the methacrylate resins. In order to test that hypothesis, $AgNO_3$ was dissolved in absolute ethanol at room temperature. To this solution, an alternative methacrylate monomer (bisphenol A ethoxylate dimethacrylate, EBisEMA from Sigma–Aldrich, containing 200 ppm MEHQ) was added. Then, the solution was heated at 70 °C. No silver nanoparticles were produced after 40 h heating even after the addition of 200 ppm BHT. This is attributed to the absence of reducer impurities in the EBisEMA monomer. From the analysis of these results, it emerges that the initial clusters of silver might be generated through the reduction of silver ion by bisphenol A which is an impurity of BisEMA and BisTEG monomers [12].

Alternatively, Kassaee et al. [8] proposed that silver ions can be reduced by BHT. Application of heat or light dissociates the O—H bond of BHT rendering very stable oxygen radicals. The authors found that hydrogen radicals (H•) generated from thermolysis of BHT could reduce silver ions leading to formation of Ag NPs. Once the seeds are formed HQ, MEHQ and BHT add additional silver atoms directly to the growing seeds. After ~1 h the solutions became yellow indicating the formation of Ag NPs. The absence of Ag NPs in the solution of $AgNO_3$/EBisEMA indicates that, under the experimental conditions used in this study, reducer radicals from BHT were not formed. Dispersion of methacrylate monomers containing different mass fractions of Ag were prepared in order to study the effect of the Ag concentration on the formation of nanoparticles. At silver mass fraction lower than 0.03 wt% in BisEMA or 0.5 wt% in BisTEG the dispersions were stable against coalescence and oxidation even after 9 months, whereas at silver concentration above those values, precipitation on the walls of the container occurred within days after the preparation of the

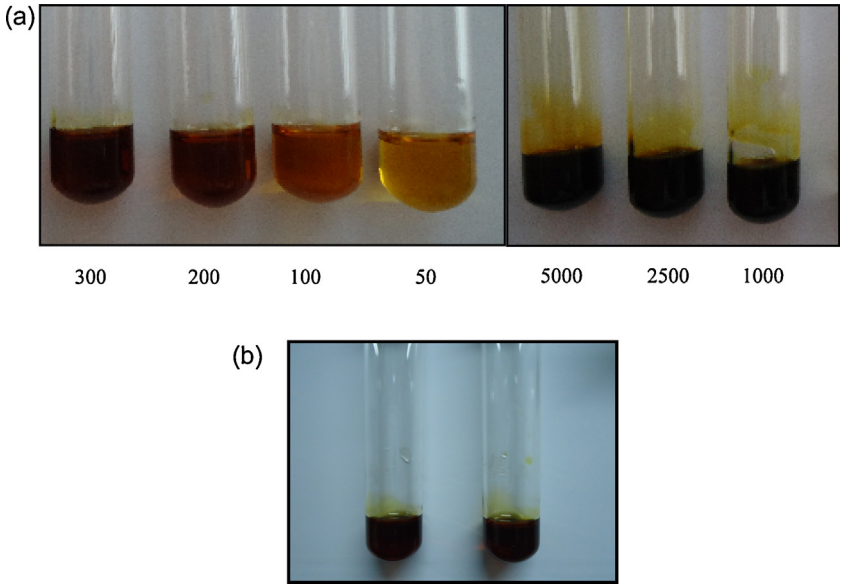


Fig. 3. (a) Ag NPs in BisEMA (50, 100, 200 and 300 ppm) and BisTEG (1000, 2500 and 5000 ppm), (b) pictures of BisEMA containing 300 ppm Ag NPs taken 24 h after the synthesis and after 9 months storage in air at room temperature.

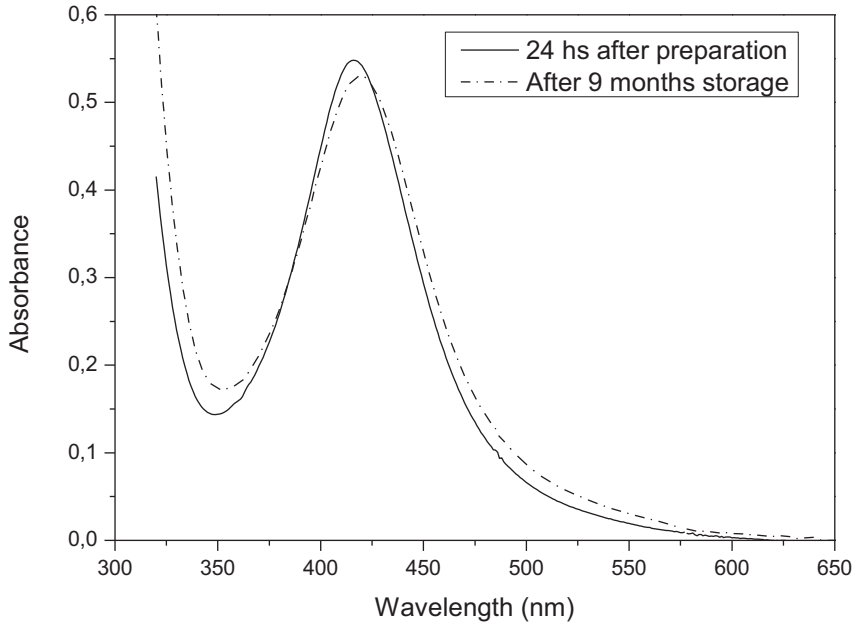


Fig. 4. UV–vis spectra of dispersions of Ag NPs in BisEMA containing 0.02 wt% silver. Spectra were taken after 24 h reaction (solid line) and after storage for 9 months. It is seen that the UV–vis spectra obtained after a prolonged storage period changed only a little.

solutions. Fig. 3 is a picture of stable dispersions of Ag NPs in methacrylate resins. The dispersions showed a very intense colour, which became darker with increasing concentration of Ag NPs. Fig. 3 shows that no appreciable change in colour occurred after 9 months of storage in air at room temperature.

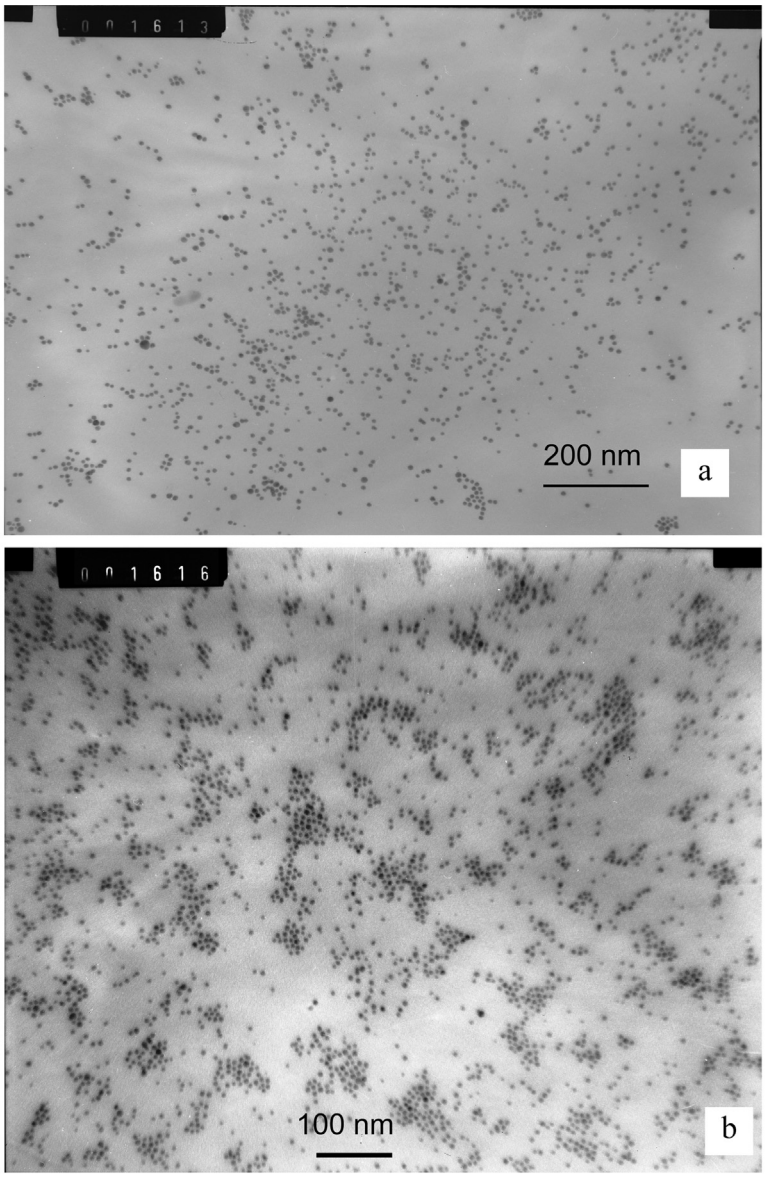
The use of organic capping agents is usually required in the synthesis of silver nanoparticles to control the agglomeration, particle size, and morphology [4,13–15]. The capping agents carry specific functional groups to anchor them onto the surface of the nanoparticles, thereby preventing particle agglomeration and growth. It is well known that polymers are very effective to inhibit the agglomeration of nanosized particles [3,4]. However, the effect of small molecules, such as monomers, on stability of colloidal metal particles is less known. Pastoriza-Santos and Liz-Marzán have studied and explained the mechanism of the surfactant-free formation and stabilization of the Ag NPs in N,N-dimethylformamide (DMF) [16,17]. Ma et al. reported a systematic study of the interaction of silver ions with six different amides [18]. The authors suggested possible binding modes of Ag(I)-amide complexes by oxygen or nitrogen atoms as well as by the pairs nitrogen–oxygen, oxygen–carbon and nitrogen–carbon. Recently, Sigoli et al. described the spontaneous formation of highly dispersed spherical Ag NP in surfactant-free N,N-dimethylacetamide solution [19]. The resins investigated here, BisEMA and BisTEG, have oxygen-containing groups capable of forming complexes with metal species [20]. Ag NPs interact with ester [21,22], ether [23,24], and hydroxyl groups [25] through no covalent bonding. Thus, it is conceivable that in a first stage Ag^+ ions disperse and coordinate to the oxygen atoms of those functional groups. Then, the reduction of the dispersed Ag^+ ions gives atomic silver which aggregate to form Ag NPs. Again, the oxygen-containing groups present in the monomer structure prevent precipitation and further aggregation of Ag NPs while stabilizes them. Thus, the ligand molecules bound to the nanoparticle surface not only control the growth of the particles during synthesis, but also prevent their aggregation during storage.

As it was mentioned previously, at silver mass fraction higher than 0.03 wt% in BisEMA or 0.5 wt% in BisTEG precipitation occurred. The difference in stabilization ability between BisTEG and BisEMA is attributed to structural differences between these molecules. The BisEMA and BisTEG monomers contain the same mol% of carbonyl and ether groups. However, in BisTEG the ratio phenyl alkyl ether (from BisGMA)/alkyl ether (from TEGDMA) is ~50/50 mol%. Although the mol of ether groups in BisEMA and BisTEG on weight basis is the same, we speculate that due to its greater flexibility, TEGDMA could probably arrange itself to provide better coverage on the surface of silver colloids compared with BisGMA and BisEMA. In addition, BisTEG contains hydroxyl groups in its structure. This could explain the better protection from agglomeration of BisTEG compared with BisEMA. An additional factor affecting the capacity of the monomers to stabilize the particles is its viscosity. The viscosity of BisEMA at room temperature (3 Pa s) is lower than that of BisTEG (12 Pa s), consequently, as a result of increased mobility in BisEMA, the probability of particle collision, adhesion and subsequent coalescence is enhanced. This will result in a reduced capacity of stabilization of Ag NPs of BisEMA compared with BisTEG.

Silver and silver ions have long been known to exhibit powerful antimicrobial activity [7,26]. Moreover, nanoparticulate silver release Ag ions more effectively and therefore have better bactericidal activity due to its high surface area-to-volume ratio [7,27]. This makes the light-cured nanocomposites prepared very attractive for the preparation of dental materials and coating with improved biocompatibility.

3.2. Characterization of de dispersions of AgNPs

The dispersions of Ag NPs in methacrylate resins were examined by UV–vis spectroscopy. Fig. 4 shows the absorption spectra of BisEMA containing 0.02 wt% silver. The Ag NPs show well-defined surface plasmon resonance absorption in the visible region (418 nm). This band arises from the collective oscillations of the free conduction band electrons that are induced by the incident electromagnetic radiation. According to Mie's theory, the resonance position and shape are closely related to the particle size and shape [28]. The peaks in Fig. 4 are well defined and symmetric, which suggests the formation of spherical silver NPs with uniform particle size [29]. After storage in air and in the dark for 9 months the



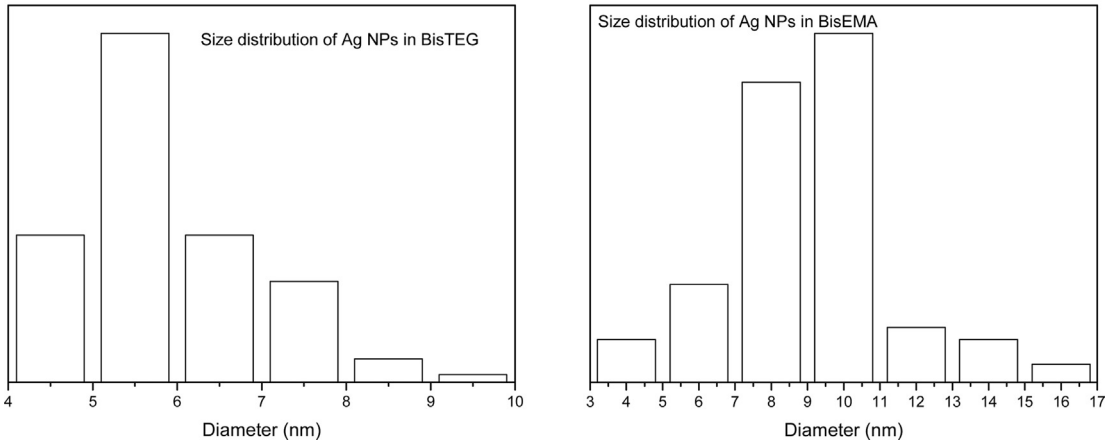


Fig. 5. TEM images of (a) dispersion of 300 ppm Ag NPs in BisEMA, (b) 2500 ppm Ag NPs in BisTEG. The corresponding histograms of size distribution in BisEMA and BisTEG are also shown (100 particles counted).

silver sols were still clear, and the UV–vis spectra obtained after this storage period shown in Fig. 4 changed only a little. Since the reduction was performed in air it has to be expected that the silver nanoparticles are partially oxidized, due to the sensitivity of the colloidal silver nanoparticles towards oxidation [29]. Henglein has shown that such oxidation processes are associated with a strong decrease and broadening of the absorption bands [29]. The slight changes of the absorption bands after storage observed here, however, indicate that such oxidation processes either do not have a large influence with these protective monomers, or are completed after a short initial period.

Morphological information on Ag NPs in methacrylate monomers was obtained from TEM images. Fig. 5a and b show the photographs of BisEMA and BisTEG monomers containing 0.03 and 0.25 wt% dispersed Ag NPs respectively. Histograms of size distribution, calculated from the TEM images by measuring the diameters of at least 100 particles, are also shown. In agreement with UV–vis studies, the morphology of NPs in Fig. 5 are defined spheres, TEM images reveal that silver nanoparticles distribute homogeneously in the wide area of the photograph and the formation of aggregated silver nanoparticles was also recognized. The presence of aggregates may arise from the preparation of the samples for TEM studies. In order to obtain good quality TEM images, the dispersions of Ag NPs in BisTEG or BisEMA were diluted with absolute ethanol. A colour change from pale yellow to dark grey after the addition of ethanol (~5 min) was observed, indicating either oxidation of Ag NPs or formation of precipitate. This is attributed to a reduction in the monomer/Ag NPs mass ratio. When the amount of monomer is not enough, a complete protection layer cannot be formed and, therefore, the particles form the aggregates (Fig. 6). From the histograms of size distribution, it is seen that the Ag NPs synthesized in BisTEG had a smaller average size than those prepared in BisEMA. This difference in size can be attributed to a stronger interaction of BisTEG with the Ag^+ ions compared with BisEMA. This trend is in agreement with results reported by Sigoli et al. on the preparation of Ag NPs in N,N-dimethylformamide and N,N-dimethylacetamide [19]. The comparatively smaller average size of nanoparticles obtained using N,N-dimethylacetamide was correlated to a stronger interaction of silver ions/N,N-dimethylacetamide compared to that of silver ions/N,N-dimethylformamide. Fig. 7 is a conceptual diagram showing the proposed stabilization of Ag NPs in (a) BisEMA and (b) BisTEG. TEM micrographs of samples stored for 9 months, showed no drastic change in average particle diameter and particle shape. From UV–vis and TEM studies, it is concluded that, at the silver concentrations used, the BisEMA and BisTEG monomers act as efficient particle stabilizers preventing particle coalescence thereby enabling long term stability.

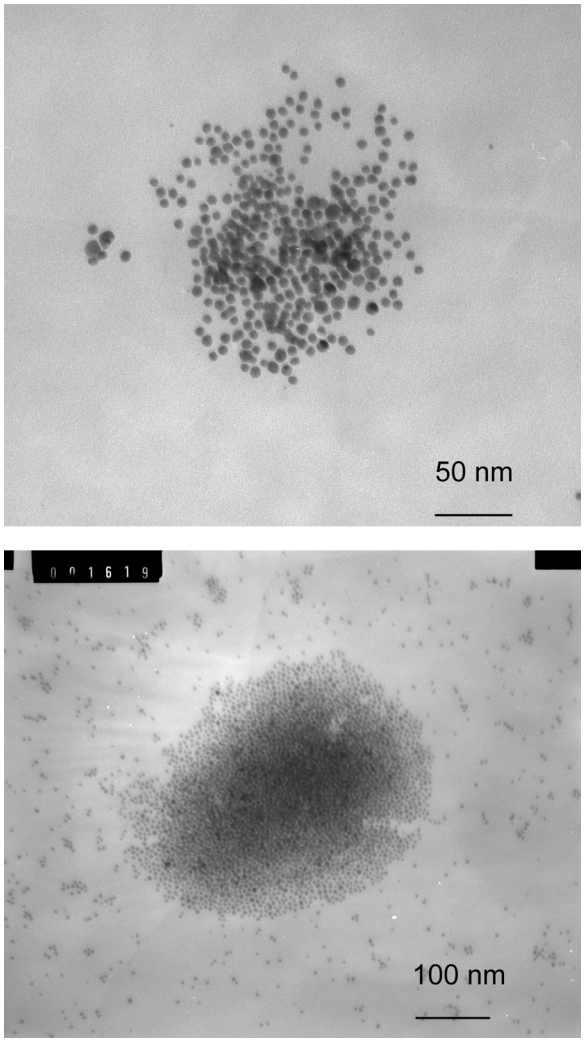


Fig. 6. TEM images showing agglomerations seen in dispersions Fig. 5a and b when diluting with ethanol during the preparation of the samples.

3.3. Photopolymerization

BisEMA and BisTEG monomers containing Ag NPs were photo activated with 0.5 wt% DMPA photo sensitizer that absorbs in the range 305–390 nm and were photo polymerized with a LED of irradiance centred at 365 nm. The conversion profiles were calculated by NIR spectroscopy from the decay of the absorption band located at 6165 cm^{-1}. Typical NIR spectra are shown in Fig. 8. Fig. 9 shows the conversion profiles of resins containing different amounts of Ag NPs. It is seen that as the Ag NPs concentration increased it became more difficult to cure the specimens. Although the final conversions in resins containing 0 or 300 ppm Ag NPs were similar, the polymerization rate decreased appreciably on increasing the Ag NPs concentration.

When an assembly of nanoparticles is irradiated by a plane wave, the incident light is scattered and absorbed by each particle to a certain extent [30]. As a result of these absorption and scattering processes the transmitted light decreases along the propagation direction of the incident light. The LED source emits in a narrow wavelength centred at 365 nm while the Ag NPs absorb light in the range 350–550 nm (Fig. 4). Thus, a fraction of the incident light is absorbed by the Ag NPs. The presence of light absorbing species in a photo curing resin inevitably results in attenuation of the light intensity along the radiation path [31]. In addition, the intensity of the transmitted light in dispersions of metal nanoparticles is affected by optical losses according to the following relationship [30]:

$$I_{trans}(\lambda) = [1 - R_1(\lambda)]^2 [1 - R_2(\lambda)^2]^2 A(\lambda) I_{inc}(\lambda) \quad (3)$$

where I_{inc} and I_{trans} are the incident and transmitted light respectively, for each wavelength λ, the factor $A(\lambda)$ contains all absorption and scattering losses in the measuring volume. $R_1(\lambda)$ and $R_2(\lambda)$ are the reflection losses at the front side and at the rear side respectively. The reduced polymerization rate with increasing Ag NPs content is attributed to the related losses in Eq. (3), which increase with the Ag NPs content. Although unfilled BisTEG and BisEMA methacrylate monomers display similar reactivity [31], photopolymerization of BisTEG resin containing Ag NPs (not shown in Fig. 9) was markedly slower than that of BisEMA resin presented in Fig. 9. This is attributed to a higher content of Ag NPs

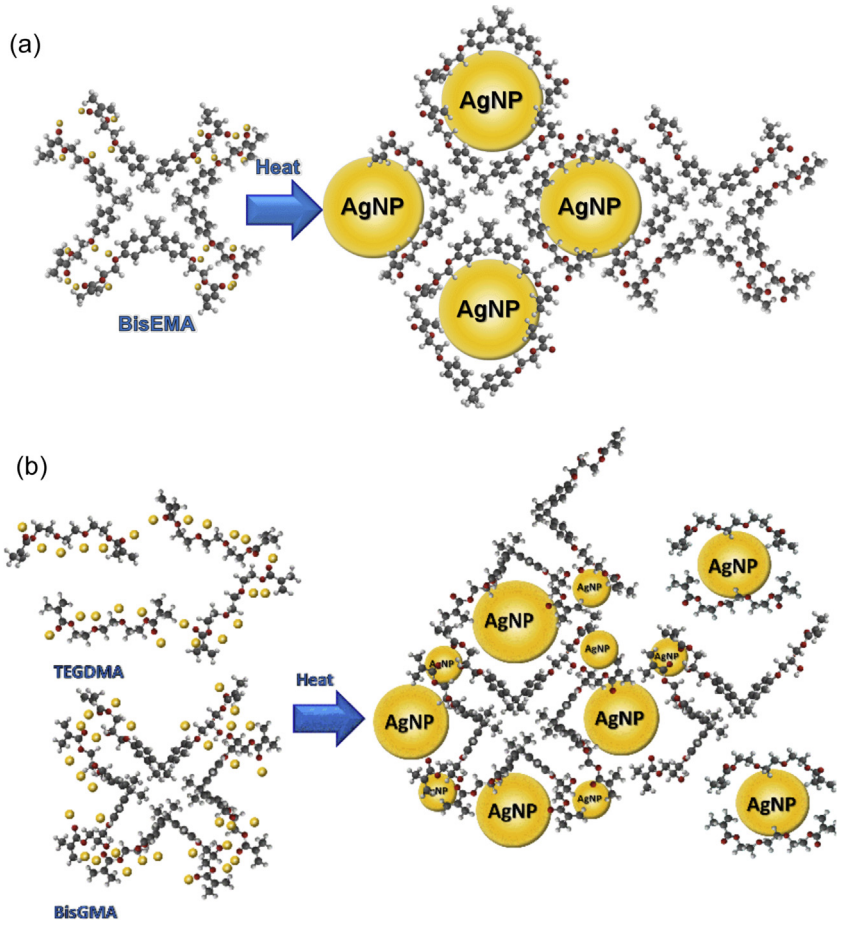


Fig. 7. Conceptual diagram of the stabilization of Ag NPs in (a) BisEMA and (b) BisTEG.

in BisTEG; which results in light attenuation along the irradiation path according to Eq. (3). It is worth mentioning that irradiation of 2 mm thick specimen of BisTEG containing 0.1 wt% Ag NPs for 5 min on both sides resulted in incompletely cured resins. From these observations, it is clear that in order to cure thick layers of resins containing high proportions of Ag NPs, high intensity LED sources must be used or, alternatively, the resins must be thermally cured.

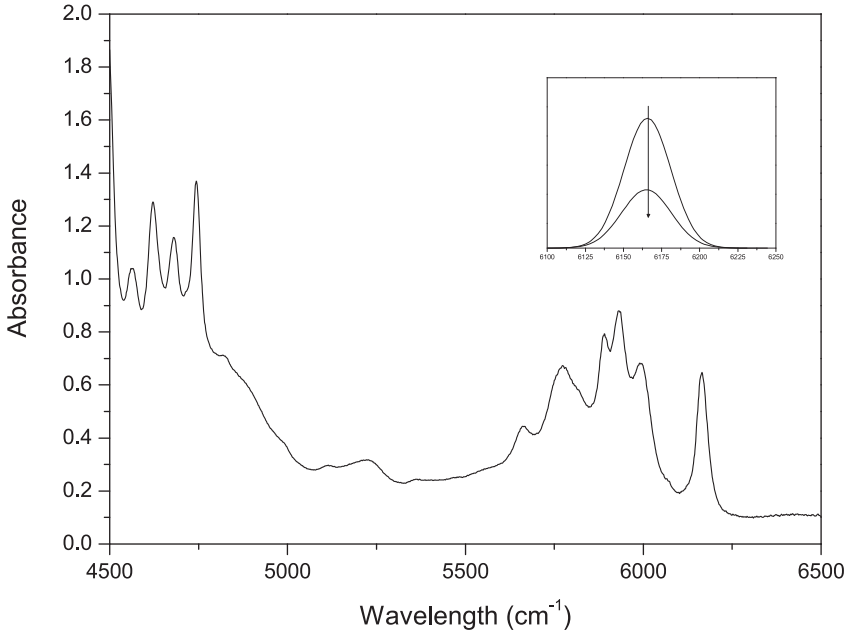


Fig. 8. Typical NIR spectra of the BisTEG resin. The decrease of the absorption of the band at 6165 cm^{-1}, corresponding to the methacrylate double bond, at different collection times is also shown.

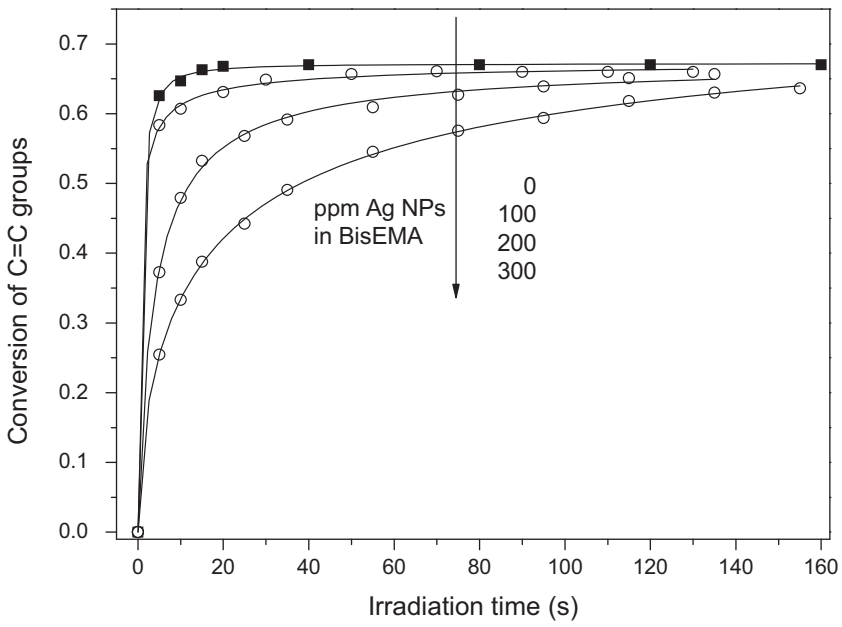


Fig. 9. Conversion of methacrylate groups *versus* irradiation time in BisEMA monomer containing different amounts of Ag NPs (ppm). Samples containing 0.5 wt% DMPA were irradiated at 365 nm. The specimens were 10-mm diameter and 1-mm thick.

4. Conclusions

Highly dispersed spherical Ag NPs were prepared *in situ* in methacrylate monomers in the absence of surfactant.

Finely dispersed Ag NPs, between 5 and 10 nm in diameter, were maintained in a stable colloidal state for more than nine months at ambient temperature. UV–vis and TEM studies revealed that the dispersions stored for nine months, showed no drastic change in particle size.

From these studies, it is concluded that the methacrylate monomers used as reactive solvent act as efficient particle stabilizers preventing particle coalescence and thereby enabling long term stability.

The effective utilization of the surfaces of the formed metal nanoparticles is an advantage associated with nanoparticles formed *via* a surfactant-free synthesis method. The proposed process offers the possibility to use these synthesized materials for the production of colour filters for optical devices and biomaterials with improved antimicrobial properties.

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