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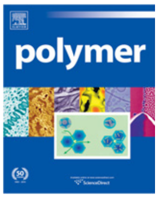

Photo-initiated miniemulsion polymerization as a route to the synthesis of gold nanoparticle encapsulated latexes

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ABSTRACT

We report the first use of photo-initiated miniemulsion polymerization for the synthesis of well defined poly(methyl methacrylate) (PMMA) latexes. Furthermore, the application of photo-initiation is employed to the incorporation of decanethiol-capped gold nanoparticles (AuNPs). The procedure provides a low temperature polymerization for an oil-in-water miniemulsion with temperatures not exceeding 40 °C and polymerization times of only one hour. Using these mild reaction conditions allows the use of miniemulsion polymerization for the encapsulation of temperature sensitive species within the latex. Furthermore, we demonstrate the applicability of this method for the incorporation of decanethiol-capped AuNPs. Particle size distribution and morphology was studied using dynamic light scattering (DLS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). PMMA latexes ranged between 100 and 200 nm in diameter showing good particle size distribution and tendencies to form semi-ordered domains. We show that variations in surfactant, hydrophobe and initiator concentrations behave in the same manner as miniemulsions initiated through conventional thermal methods. TEM observations revealed that the latexes with encapsulated AuNPs displayed even distributions of AuNPs throughout the PMMA latex with no aggregation witnessed.

1. Introduction

The application of miniemulsion techniques for the production of polymer latexes provides an exciting synthetic route for the incorporation of a range of species including: inorganic materials, dyes, nanoparticles (NPs), antiseptics and carbohydrates [1–8]. The incorporation into a polymer matrix also provides the ability to act as drug delivery and templating agents [9,10].

Latex production via miniemulsion polymerization is a well established technique though is conventionally initiated using thermal initiators. This restricts the potential additives for incorporation into a latex to those which are not thermally sensitive. In a variety of cases this eliminates the potential for many biomolecules and drugs from being incorporated. Our previous investigations into encapsulation of decanethiol-capped AuNPs has shown that elevated temperatures (~70 °C) used in thermal initiation tended to destabilize the AuNPs causing them to precipitate from the miniemulsion without being encapsulated within the latex. Studies that have been performed on the desorption of alkanethiols on gold surfaces [11,12] may be the possible reason for this behavior. From this, it was shown that the gold-thiol bond begins to degrade at temperatures above 60 °C.

Described in this article is an alternative to thermal initiation whereby photo-initiation has been used as a low temperature method of polymerization that may be utilised to produce latexes via the miniemulsion technique. Moreover, the encapsulation of AuNPs using this technique is also briefly described. Kuo et al. [13] reported photo-initiation of styrene in a *macro*emulsion using dibenzyl ketone and studied the polymerization rates as a function of initiator concentration and light intensity. The work by Liu and co-workers [14] use a photo-initiated miniemulsion for the production of latex spheres though required the use of a nitroxide radical mediator (HTEMPO). Our work provides a simpler low temperature, non-mediated photo-initiated miniemulsion polymerization method of which, to the author's knowledge, is the first such reported case of this and which may have applicability in the incorporation and delivery of biologically active molecular species. It should also be mentioned that redox initiation may also be used as a low temperature initiation method for miniemulsion polymerization particularly for use in interfacial miniemulsion polymerization [15–17].

Emulsion polymerization is widely accepted to follow the Smith–Ewart Theory [18] of which homogenous nucleation is the dominant mechanism [19]. Alternatively, miniemulsion

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polymerization, particularly with the use of an oil-soluble initiator, primarily follows droplet nucleation [20] and is required for the encapsulation of an additive.

The process of encapsulating an inorganic material within a miniemulsion system requires the control of two primary interfaces. Firstly, as the inorganic material must be dispersed in the monomer phase, and since conventionally, the monomer is hydrophobic, the inorganic material/dye/pigment must also be hydrophobic. Secondly, the interface between the monomer droplet and the aqueous phase must prevent the diffusion of monomer out of the droplet, or the loss of the additive. The monomer droplet/aqueous phase interface can be stabilised by the use of a surfactant and hydrophobe to prevent Ostwald ripening whereas the target additive, if hydrophilic in nature, must be made soluble in the monomer/polymer phase.

It was shown that $CaCO_3$ could be encapsulated within a polystyrene (PS) latex by first coating with a layer of stearic acid [21]. Similarly, TiO_2 was incorporated into PS latexes at 3 wt% by capping in poly-butene-succinimide pentamine (OLOA 370) [22]. CdSe quantum dots (QDs) coated in ZnS were encapsulated into PS latexes using trioctylphosphine oxide (TOPO) or 4-mercaptovinylbenzene [2]. CdSe QDs have also been encapsulated without the use of a passivating agent [23]. Recently, van Berkel et al. created ‘multimodal’ latexes containing Au and $MnFe_2O_4$ nanoparticles [24]. Van Berkel et al.’s polymerizations were performed over 4 hours at 50 °C using a thermal initiator and the latex produced was unstable and had poor re-dispersion in a solvent. In all cases, the encapsulated species was prone to aggregation within the latex. This may be a result of the elevated temperatures needed for the thermal initiation of the miniemulsions acting to destabilize the alkanethiol protected AuNPs. The general composition of a miniemulsion, before and after polymerization, for the encapsulation of gold nanoparticles (AuNPs), is shown in Fig. 1.

This paper aims to firstly investigate an alternative to thermal initiation for the synthesis of well-defined PMMA latexes and secondly to explore the possibility for encapsulation of AuNPs with the intention to better distribute the additive throughout the latex. To achieve this, the use of Tween80 as a biologically compatible surfactant and an organically soluble initiator, benzoyl peroxide (BPO) is described. Tween80 has advantageous properties in that it has the potential for use in drug delivery applications while BPO forms radicals under ultraviolet (UV) irradiation [25] and allows polymerization to occur inside the monomer droplet (droplet nucleation). In this way, the final latex is a one-to-one copy of the initial miniemulsion conditions [26] and provides an excellent mechanism for the incorporation of additives into a latex to create “multimodal” materials. In this work we highlight the ease with which semi-ordered latexes may be produced by the non-mediated photoinitiated miniemulsion of methyl methacrylate (MMA). Furthermore, described herein is the incorporation of AuNPs into such a system.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA) was used only after the removal of the stabilizer performed by distillation over CaH_2 under reduced pressure. BPO was recrystallized before use from a chloroform/methanol solvent/non-solvent pair. Decanethiol, $HAuCl_4 \cdot 3H_2O$, $NaBH_4$, tetradecane (TD) and Tween80 were used as received from Sigma–Aldrich.

2.2. Instrumentation

A 200 Watt high pressure (HP) mercury vapor lamp was used for photo-initiation. All samples were placed at the focal length of 15 cm from the opening; corresponding to a power of 0.83 W/cm^2. The lamp was allowed 15 minutes to heat up before samples were placed in front of the beam. All photo-initiated polymerizations were performed in quick-fit quartz tubes with an internal diameter of 20 mm.

All sonication was performed in a Soniclean 750HT Ultrasonic cleaner with ‘low’, ‘medium’ and ‘high’ power settings.

Dynamic light scattering (DLS) measurements were recorded using a Malvern Zetasizer Nano ZS set with a backscatter optical configuration of 173 degrees. Samples were placed in 0.75 mL

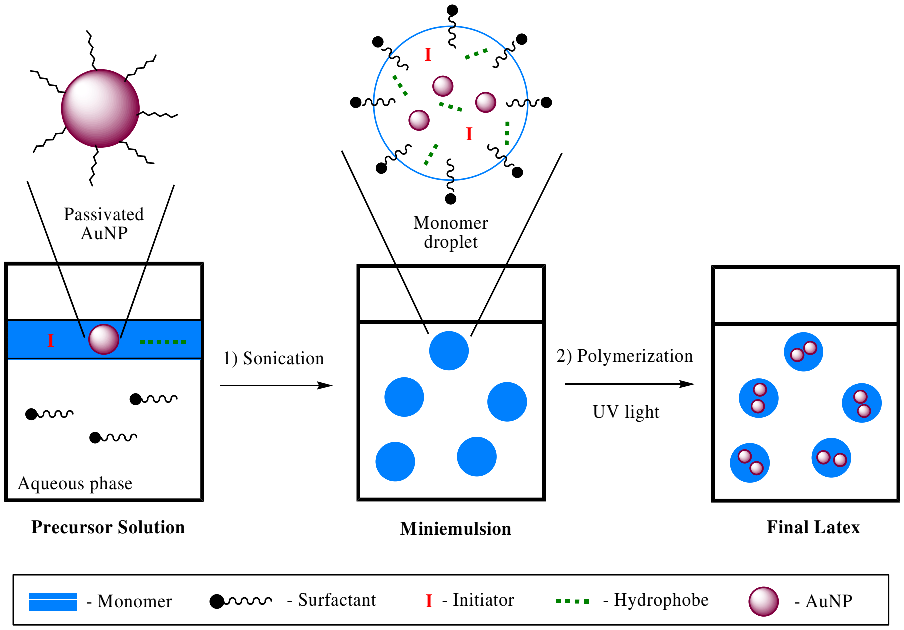

Fig. 1. The preparation of AuNP encapsulated PMMA latexes via photo-initiated miniemulsion polymerization.

disposable polycarbonate capillary cells and measurements were performed in triplicate.

Scanning electron microscope (SEM) images were obtained using a FEI Quanta 200 Environmental SEM equipped with an Everhart–Thornley detector (ETD) and all samples were deposited onto glass slides, allowed to dry and coated in sputtered gold films. SEM latex bead size analysis was conducted by measurement of in excess of 200 spheres.

Transmission electron microscopy (TEM) images were acquired on a PHILIPS CM200 Analytical TEM operating at 200 kV. All samples were deposited on carbon coated 400 mesh copper grids and allowed to dry. TEM latex bead size analysis was conducted by measurement of in excess of 200 spheres.

2.3. *Preparation of decanethiol-capped AuNPs*

The Brust method was used to produce decanethiol-capped AuNPs [27]. Briefly, an aqueous solution of $AuCl_4^-$ (1×10^{-2} M, 0.08 mmol) was transferred into toluene using tetraoctylammonium bromide (5×10^{-2} M, 0.40 mmol) as the transfer agent. After approximately 20 minutes the organic layer turned orange-red in color. 1-decanethiol (0.087 mmol) was quickly added to the mixture followed by the dropwise addition of an aqueous solution of $NaBH_4$ (1.0 M, 1.0 mmol). The resultant solution was stirred for 3 hours where the organic layer turned purple-black. The aqueous layer was removed and the organic layer was washed twice with water to remove any excess transfer agent and salts. The decanethiol-capped AuNPs were then precipitated overnight in an ice bath with the addition of excess ethanol. The NPs were filtered and washed further with ethanol and collected by dissolution in an organic solvent of choice. NPs could be dried and resuspended readily yielding approximately 18–20 mg of decanethiol-capped AuNPs. Solutions prepared were stable in excess of 3 months. For use in the various emulsions, the AuNPs were dried by solvent evaporation and were easily re-dispersed within the monomer phase.

2.4. *Photo-initiated miniemulsion polymerization*

The general procedure for the polymerization of an oil-in-water miniemulsion was performed by the initial addition of the aqueous and monomer phases under constant stirring. The aqueous phase contained a predetermined amount of surfactant (Tween80) and to this the monomer phase mixture was added in a quickfit quartz tube. The monomer phase contained the hydrophobe (TD) and initiator (BPO), as outlined in Table 1.

This mixture was stirred well for 30 minutes in an ice bath during which the solution was degassed by bubbling with argon. Once the crude emulsion had formed, the entire sealed reaction mixture was subjected to an ultrasonic bath for 5 minutes on ‘low’ intensity to produce the miniemulsion mixture. Miniemulsions were then placed at a distance of 15 cm perpendicular to the opening of the UV lamp. The beam was focused onto the vessel so that the incident light (approximately 3 cm in diameter) covered the entire reaction mixture. The photo-initiated miniemulsions were irradiated for 60 minutes where the temperature of the reaction was measured at 40 °C. The polymerization was quenched by the addition of 0.5 mL of a 1 w/v % hydroquinone solution. It should be noted that polymerization did not occur when a UV filter was employed thus ruling out infrared and visible radiation as initiation sources. Conversion percentages were measured gravimetrically calculated using total solids content. It should be noted that conversion percentages reached 65 ± 4% for all samples independent on whether AuNPs were added.

Table 1
The preparation of photo-initiated miniemulsion polymerizations.

Sample	Monomer[a]	BPO[b]	TD[b]	Tween 80[b]
1	MMA	1.0	1.3	1.4
2	MMA	1.0	1.3	4.1
3	MMA	1.0	2.8	1.4
4	MMA	2.1	1.4	1.4

[a] MMA concentration was kept at 20% w/w vs. H_2O for all reactions and was set at 1 g.
[b] Reagent amounts are % w/w vs. monomer.

Table 2
Reagent concentrations for the incorporation of AuNPs within a photo-initiated miniemulsion.

Sample	MMA	Water	Tween80	BPO	TD	AuNPs
5	1.0105 g	5.0 mL	0.0198 g	0.0108 g	0.0150 g	6.5 mg

2.5. *Preparation of AuNP containing PMMA latex*

The miniemulsion containing decanethiol-capped AuNPs was prepared as above with the incorporation of the dried decanethiol-capped AuNPs into the monomer mixture. Reagent concentrations are given in Table 2.

3. Results and discussion

3.1. *Photoinitiated miniemulsion polymerization*

The UV initiated polymerization of a stable MMA miniemulsion in water (Sample **1**) produced a latex with an average particle diameter of 183 nm as measured using SEM (Table 3). The SEM image shows a semi-ordered packing of the latex suggesting a narrow particle size distribution (Fig. 2a). The TEM (Fig 2b) does not show this since the amount of sample placed on the TEM grid must be kept to a minimum so as to obtain a good transmission image. DLS analysis provides an average particle diameter of 232 nm which suggested a hydrodynamic radius of 25 nm (obtained by the difference between the SEM and DLS data). Sample **1**, however, includes the presence of some irregularly shaped beads and thus may not be a true representation of the hydrodynamic radius. Though droplet nucleation is accepted as the dominant mechanism in miniemulsion polymerization, other forms of nucleation cannot be completely ruled out as at least partial contributors to latex formation. The irregular and slightly larger latexes may have been produced through either homogenous or micellar nucleation. It should also be noted that viewing of the latexes under SEM conditions can cause deterioration and slight melting of the latex, which can contribute to the appearance of an irregular morphology.

Sample **2** employs the use of a 3-fold increase in surfactant (Tween 80) to that used in Sample **1**. This was seen to decrease the latex diameter to 121 nm as measured using SEM (Fig. 3a). Studies

Table 3
Latex size analysis of photo-initiated miniemulsions.

Sample	Particle Diameter (nm)		
	SEM	DLS	TEM
1	183 ± 16%	232 ± 10%	177 ± 18%
2	121 ± 20%	232 ± 23%	
3	184 ± 14%	261 ± 13%	
4	135 ± 19%	270 ± 15%	

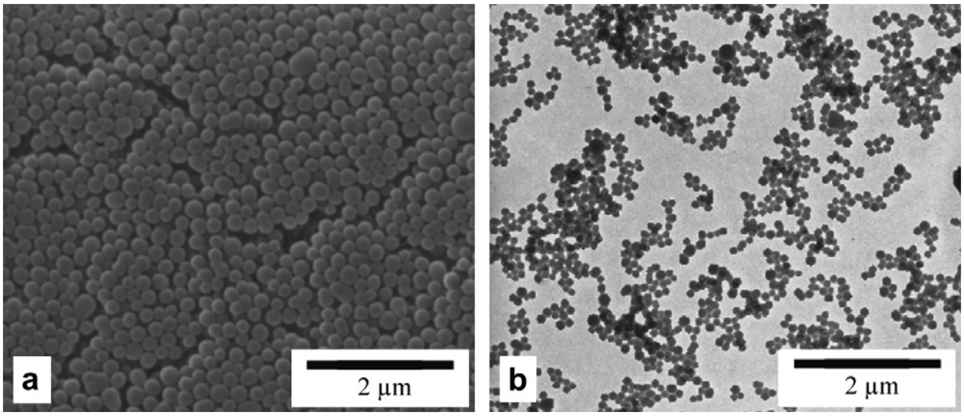

Fig. 2. SEM (a) and TEM (b) images of Sample **1**.

have shown that when concentrations of surfactants such as sodium dodecyl sulfate, cetyl trimethylammonium bromide or Tween 80 are increased, the latex size decreased [28–30]. A greater concentration of surfactant allows the stabilization of a greater surface area of monomer droplets within the miniemulsion, hence decreasing final latex size. The DLS data contradicted this belief as it showed no decrease in size when compared to the DLS of Sample **1**. As DLS measures the volume of a solvated sphere, any excess surfactant not present in providing direct latex stabilization is thought to have contributed to the measured volume of the solvated sphere (Fig. 3a).

There was no apparent change of latex size when the hydrophobe content was increased 2.8 times (Sample **3**) to that of Sample **1**. SEM showed an average diameter of 184 nm (Fig. 3b) of which appears highly similar to that of the SEM of Sample **1** (Fig 2a). This result agrees with work by Antonietti and Landfester [31] that describes the hydrophobe content (when already at minimum molar ratio of hydrophobe to monomer) does not change the final latex size. Analysis by DLS provides a latex size of 261 nm and is within the relative error of the size measured for Sample **1**.

Sample **4** investigated the addition of a 2-fold increase in BPO. Typically, this acts to increase the average number of radicals formed within each monomer droplet causing increases in the polymerization rate, decreased miniemulsion stability and produces varied molecular weight distributions [32]. It should, however, have no effect on the latex diameter as each monomer droplet, once formed, is considered stable with negligible transport across the phase boundary. Nevertheless, latex sizes showed a smaller than expected average diameter of 135 nm as seen in Fig. 3c. The discrepancy is thought to arise from the fact that many

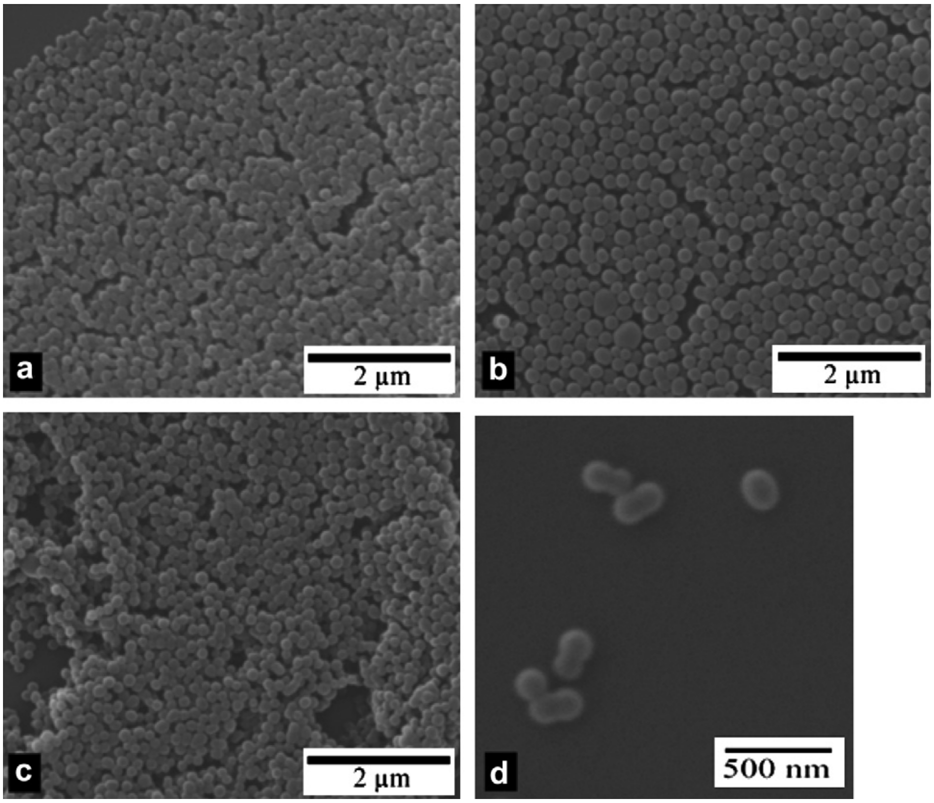

Fig. 3. SEM images of (a) Sample **2**; (b) Sample **3**; (c) Sample **4** and (d) highlighting the 'twinned' nature of Sample **4**.

of the latex spheres appeared to have formed 'twinned' beads (Fig. 3d). The DLS data, which does not recognize twinned morphologies, showed a latex size of 270 nm which corresponds to approximately double the size recorded using SEM measurements. It could be suggested that, with an excess of BPO, the monomer droplets may develop microdomains in which there is more than one growing polymer competing for monomer within the same droplet [33]. Another theory suggests droplet 'budding' is occurring and is caused by the primary latex splitting throughout the polymerization [34]. Budding is known to occur for vesicles when extreme surface bending effects take place though has not yet been observed for latexes [35]. Work to further explain this result is currently in progress.

3.2. AuNP incorporated photoinitiated miniemulsion polymerization

The photo-initiated miniemulsion polymerization of a MMA miniemulsion containing decanethiol-capped AuNPs produced a stable PMMA latex suspension. The TEM image (Fig. 4a) of Sample **5** shows an abundance of a PMMA latex with a varied size distribution (taking into account the degradation under the electron beam). On closer inspection with TEM (Fig. 4c) and in comparison to decanethiol-capped AuNPs (Fig. 4b) which had a measured diameter of 5.6 ± 2.4 nm, the presence of incorporated AuNPs is clearly visible (highlighted in Fig. 4c). Also of note was how the AuNPs did not tend to aggregate within the latex and the ease with which they were incorporated into the miniemulsion system requiring no pre- or post-treatment.

The AuNPs used in the present study were capped with decylthiol and no aggregation was witnessed. This is contrary to van Berkel et al.'s results where pre-treatment of the AuNPs by grafting with thiolated polystyrene was required and whom found that with dodecylthiol- or oleylamine-capped AuNPs, significant aggregation resulted [24]. It is proposed that the results obtained by van Berkel et al. arose due to the instability of the gold-thiol bond at the temperatures that were used i.e. approximately 50 °C. This destabilization would reduce the solubility of the AuNPs within the monomer through a loss of capping agent, thus forming aggregates within the miniemulsion. The concentrations of AuNPs used in the current study are small (~0.6 w/w %) and it is expected that at higher concentrations a swelling of the monomer droplet would occur resulting in a larger than expected size with the possibility of some aggregation. Many studies have investigated the addition of up

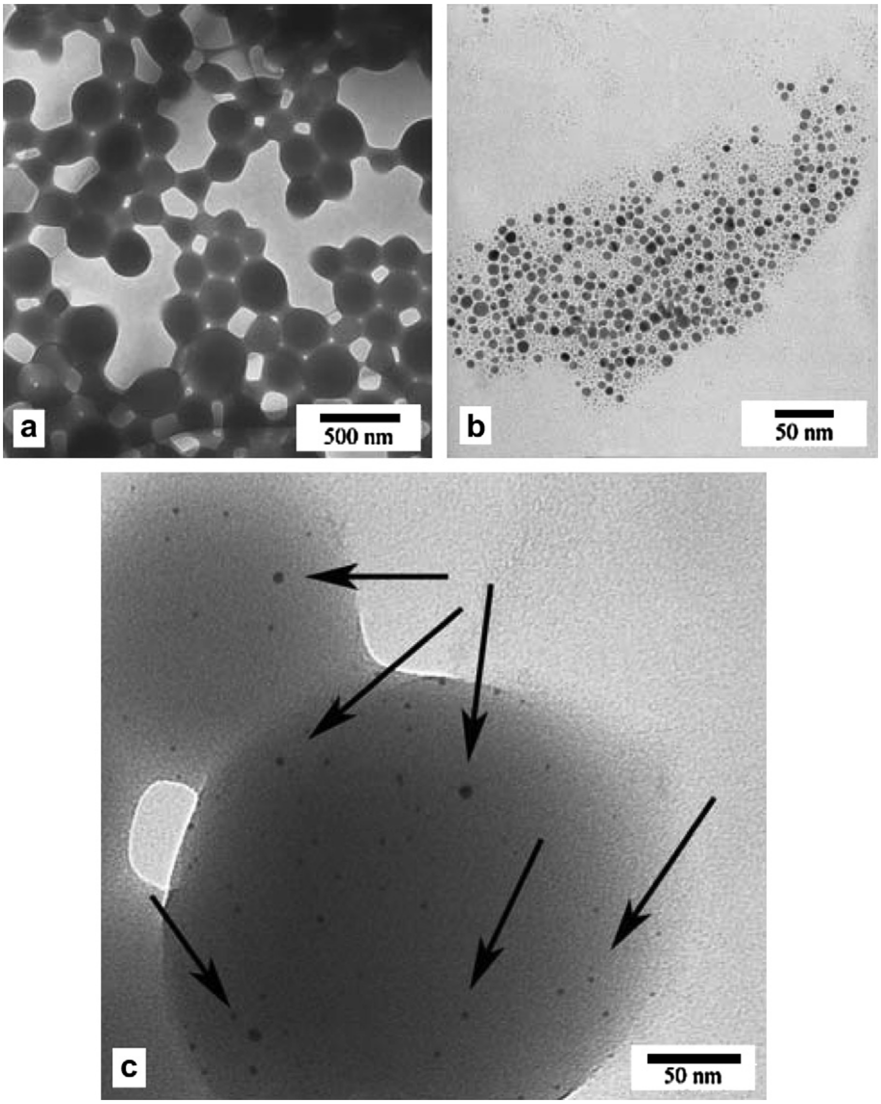

Fig. 4. TEM images of (a) Sample **5**; (b) decanethiol-capped AuNPs and (c) AuNPs incorporated within PMMA latexes.

to 10% content of inorganic material, though mostly result in inhomogeneous dispersions caused by strong interactions and therefore clustering of the materials [36]. Also, it is realized that AuNP loadings are an important aspect in the synthesis of latexes incorporated with inorganic materials. The small loading percentages used in this study make it hard to quantify. Work is continuing into the loading of higher amounts of AuNPs with the idea of quantification.

4. Summary

In summary, the photoinitiation of an oil-in-water miniemulsion produced PMMA latexes of narrow particle size distribution showing tendencies to form semi-ordered arrays. The miniemulsions were polymerized by an organically soluble UV initiator (BPO) by a non-mediated free radical mechanism using Tween80 as surfactant. Mild conditions were used in these polymerizations (40 °C and one hour polymerization time). It was demonstrated that variation of surfactant, hydrophobe and initiator behaved as expected with respect to latex size and morphology compared to conventional thermal initiation. To the best of our knowledge, this is the first example of such a photo-initiated miniemulsion.

AuNPs were successfully incorporated into a PMMA latex produced via photo-initiated miniemulsion polymerization. AuNPs were easily dissolved in the monomer phase and latexes produced contained an excellent dispersion of AuNPs throughout the latex spheres with no evidence of aggregation.

Since this technique used mild reaction conditions, it is envisaged that this work may provide a successful method for the encapsulation of thermally sensitive materials into a latex. Further work is being conducted to investigate an increase in AuNP content and the efficiency of encapsulation of AuNPs and of other inorganic NPs within the latex.

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