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Surface modification of silica nanoparticles by UV-induced graft polymerization of methyl methacrylate

Sooyeon Kim, Eunhye Kim, Sungsoo Kim [*], Woosik Kim

Department of Chemical Engineering, College of Environmental and Applied Chemistry, Kyung Hee University, Yongin, Gyeonggi-Do 447-701, Republic of Korea

Abstract

In this study we modified the surface of silica nanoparticles with methyl methacrylate by UV-induced graft polymerization. It is a surface-initiated polymerization reaction induced by ultraviolet irradiation. The resulting organic–inorganic nanocomposites were near-monodisperse and fabricated without homopolymerization of the monomer. Substantial increase in mean particle size was observed by SEM image analysis after UV-induced grafting of methyl methacrylate onto pure silica particles. FT-Raman spectroscopy and X-ray photoelectron spectroscopy studies of these materials revealed the successful grafting of methyl methacrylate onto the silica surface. The formation of a covalent bond between the grafted PMMA chains and silica surface was indicated by FT-Raman spectra. Thermogravimetric analysis of the PMMA-grafted silica particles indicated the polymer contents in good agreement with SEM photographs.
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Keywords: Silica nanoparticles; Surface modification; UV-induced graft polymerization; PMMA

1. Introduction

The surface modification of inorganic nanoparticles with polymers is an area of increasing research activity because the resulting organic–inorganic composite particles offer many potential applications in areas as diverse as photocatalysis [1], lithography [2], optics [3], biotechnology [4] and electronic devices [5]. The chemical treatment and functionalization of the nanoparticle surface can be used to enhance and/or control the nanoparticles' overall properties for targeted applications. The grafting of polymers onto silica nanoparticles is one of the most effective and versatile methods for this modification purpose. It has been proven to significantly enhance the stability of silica dispersions in polymer solvents by increasing the affinity of the surface for organic substances [6].

The surface of silica particles can be grafted with polymers via surface-initiated polymerization (SIP). A wide variety of polymerization methods of SIP have been reported in recent years. Notably, von Werne and Patten grafted methyl methacrylate (MMA) and styrene onto the surface of colloidal silica particles using atom transfer radical polymerization [7,8]. Likewise, a number of surface-modified silica particles with well-defined polymer chains had also been prepared by premodification of silica particles with organosiloxane coupling agents [9,10]. However, it is usually very difficult in these experiments to graft-polymerize as individual particles. Instead, they tend to form clusters due to agglomeration of particles during the modification process. Also, there is the formation of ungrafted polymer, i.e., homopolymerization of the monomer. To overcome these problems, we employed surface grafting reaction initiated by ultraviolet irradiation [11]. These reactions are of special interest because they are efficient and fast. They are limited to the surface without affecting the bulk properties [12]. Reactive hydroxyl groups on the surface of the silica nanoparticles are of great importance because they provide sites for UV-induced radical graft polymerization, thus imparting the desired characteristics to silica-based nanoparticles for applications such as in [13].

In this paper, we present an improved and more effective preparation method for monodisperse PMMA–silica composites without agglomeration of the particles and homopolymerization of the monomer. We also propose a mechanism of UV-

* Corresponding author.
E-mail address: sungkim@khu.ac.kr (S.S. Kim).

induced graft polymerization of MMA onto silica nanoparticles. By grafting of reactive monomers like MMA, the silica surface is made reactive to other polymers, which gives functional properties of interest. The mean size increase of silica particles due to the graft polymerization of the monomer is observed by scanning electron microscopy (SEM) and discussed in relation to polymer contents obtained by TGA. X-ray photoelectron spectroscopy analysis is performed to correlate the carbon content of the polymer-grafted silica particles with the mean size increase observed by SEM. The formation of the covalent bonding between the polymer and silica nanoparticles is confirmed by the chemical structural analysis of the polymer-grafted silica particles.

2. Experimental

2.1. Materials and reagents

Methyl methacrylate was purchased from Aldrich Chemical Co., and used after removing the inhibitor, monomethyl ether hydroquinone using inhibitor-remover column also purchased from Aldrich. Methanol, ethanol and benzophenone were also purchased from Aldrich and used as received.

The spherical silica nanoparticles were prepared by sol-precipitation method using tetraethyl orthosilicate (TEOS) as the main reactant. The details of the silica nanoparticle synthesis are described elsewhere [14]. To precipitate the particles, the colloidal suspension was centrifuged at 5000 rpm for 5 min. The silica precipitate was dispersed in methanol and centrifuged repeatedly. The final precipitate was dried in vacuum at 100 °C for 24 h before use.

2.2. UV-induced graft polymerization

Into a shallow glass Petri dish of 150 mm diameter, 2.5 g of silica, 25 g of ethanol and 0.05 g of benzophenone (BP) were charged. The Petri dish was placed under a UV lamp and irradiated for 20 min at room temperature. A 1000 W high-pressure mercury lamp from Oriel Co. (London, UK) was used for UV-induced graft polymerization. Its wavelength ranged from 200 to 500 nm. The distance between the reaction mixture and the light source was 25 cm. Benzophenone (BP) having optimum absorption wavelength about a range of 240–350 nm was used as an initiator of UV-induced reaction.

The reaction mixture was stirred with a magnetic stirrer under dry nitrogen at room temperature during the irradiation. After irradiation, 2.5 g of monomer, MMA was charged into the reaction mixture and again irradiated for a set of different times. A small amount of the reaction mixture was taken out at each specified time for analyses. The reaction mixture was centrifuged at 5000 rpm for 5 min in methanol, which led to sedimentation of the polymer-grafted silica particles. The supernatant, which contained unreacted monomer and residual initiator, was discarded. The particulate sediment was re-dispersed in methanol and centrifuged two more times. To remove the ungrafted polymer, the precipitate was dispersed

in tetrahydrofuran (THF) and centrifuged repeatedly. The off-white polymer-grafted silica was collected and dried in vacuum at 100 °C for 24 h before characterization.

3. Results and discussion

3.1. Particle size analysis

Particle size analysis of the silica particles and the PMMA-grafted silica particles was performed with scanning electron microscopy (SEM, Leica Stereoscan 440, England). Average particle sizes were obtained using image analysis software (Image-Pro Plus). As can be seen in Fig. 1, both pure silica particles and PMMA-grafted composites are spherical and the polydispersity is low. Also, the surface modification occurred in the form of single particles not clusters. A substantial increase in the mean diameter of the particles was observed after irradiation due to the graft polymerization of MMA onto the surface of the silica. Fig. 2 shows the maximum diameter increase around 25 min of irradiation. The mean diameter increased from 376 to 456 nm after 25 min of irradiation, resulting in a 78% increase in volume of the particles. Tsubokawa and coworkers have reported that the percentage of thermal grafting of vinyl monomers initiated by azo group becomes constant at the middle and last stage of the polymerization, because the surface initiating sites are blocked by grafted polymer chains [15]. In this case of UV-induced graft polymerization, the size growth of the grafted particles decreased after reaching a maximum at 25 min. This suggested that a fraction of the polymer chains become detached from the silica surface after 25 min. This may be due to the degradation of the grafted PMMA on silica particles with prolonged exposure to UV irradiation. Kaczmarek et al. have proved that the polymer chains become shorter as a consequence of breaking C–C bonds during UV degradation [16].

3.2. Polymer content by thermogravimetry

The amount of grafted polymer on the silica particle surface was also assessed by thermogravimetry. Fig. 3 shows the weight loss of the PMMA-grafted silica particles when heated to 700 °C at 20 °C/min in air (Perkin–Elmer TGA-7). Pure PMMA has a degradation temperature of 360 °C as expected. 15 min particles showed a weight lost of 25% and 25 min particles showed the largest weight loss of 31% as expected. 35 min particles show a weight loss close to 15 min particles, thus indicating UV degradation of PMMA polymer chains after the optimum time of 25 min. From these results, we conclude that grafted polymer contents of the composites are in good agreement with mean diameter increase estimated from SEM photographs.

3.3. Calcination of PMMA-grafted silica nanoparticles

To confirm the mean diameter increase of pure silica nanoparticles upon UV-irradiation is due to the graft polymerization of the monomer, MMA, calcination of the PMMA-grafted silica nanoparticles was performed. PMMA-grafted silica nanoparticles were heated at the rate of 5 °C/min from 35
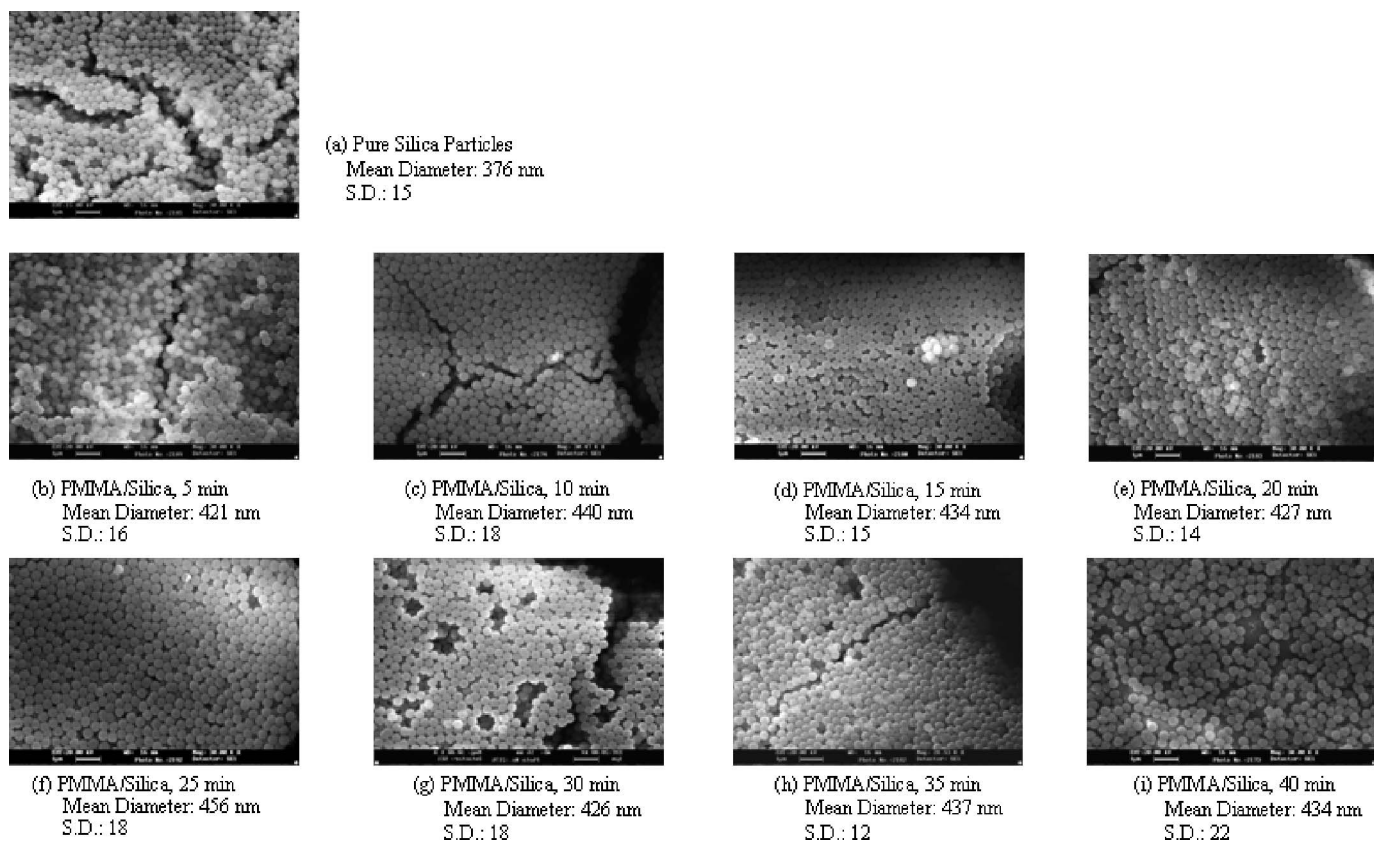
Fig. 1. SEM photographs of (a) pure silica particles; (b) to (i) PMMA-grafted silica particles after 5–40 min of irradiation (PMMA/Silica, 5–40 min).
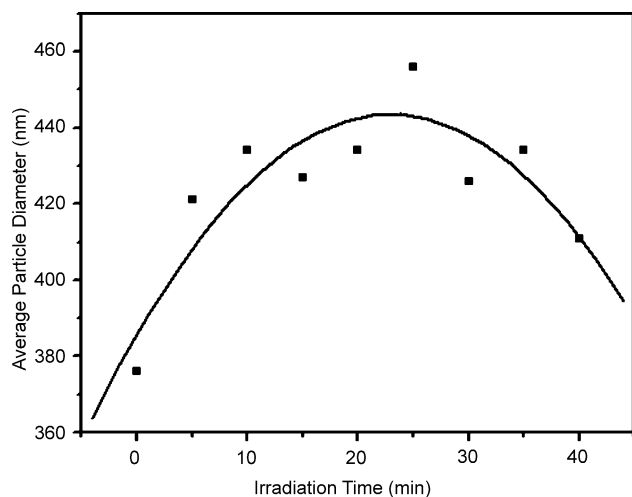

Fig. 2. Effect of irradiation time on mean particle diameter of PMMA-grafted silica particles.

Fig. 3. Weight loss curve of the pure silica and PMMA-grafted silica particles when heated to 700 °C at 20 °C/min.

to 700 °C, and held at the final temperature for 2 h. The calcined composite particles were dispersed in ethanol and dried at 100 °C for 24 h before analysis. Fig. 4 shows the SEM photographs of calcined particles compared with pure silica particles and particles before calcination. It was observed that after calcination, the mean diameter of PMMA-grafted silica particles decreased due to the degradation of grafted polymer chains. The mean diameter of calcined particles was 495 nm, a value very close to the mean diameter of the pure silica particles
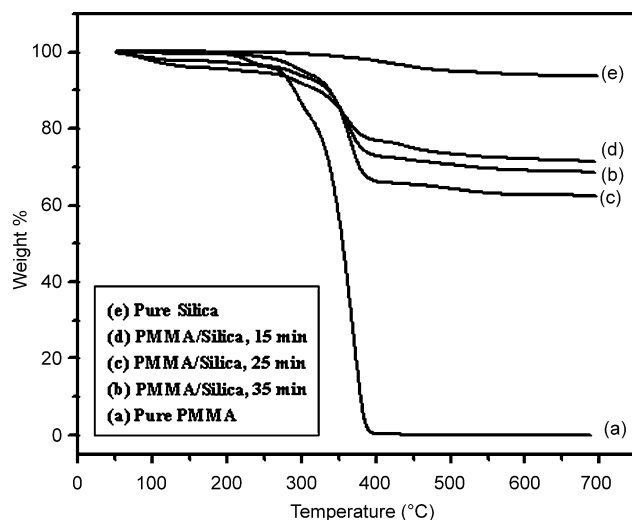
(497 nm) thus confirming the UV-induced graft polymerization of MMA.

3.4. Mechanism of grafting

The mechanism of UV-induced grafting of MMA on silica nanoparticles is shown in Scheme 1. Benzophenone as photoinitiator absorbs in the far UV spectrum near 250 nm and forms free radicals that abstract hydrogen from the silica surface. The
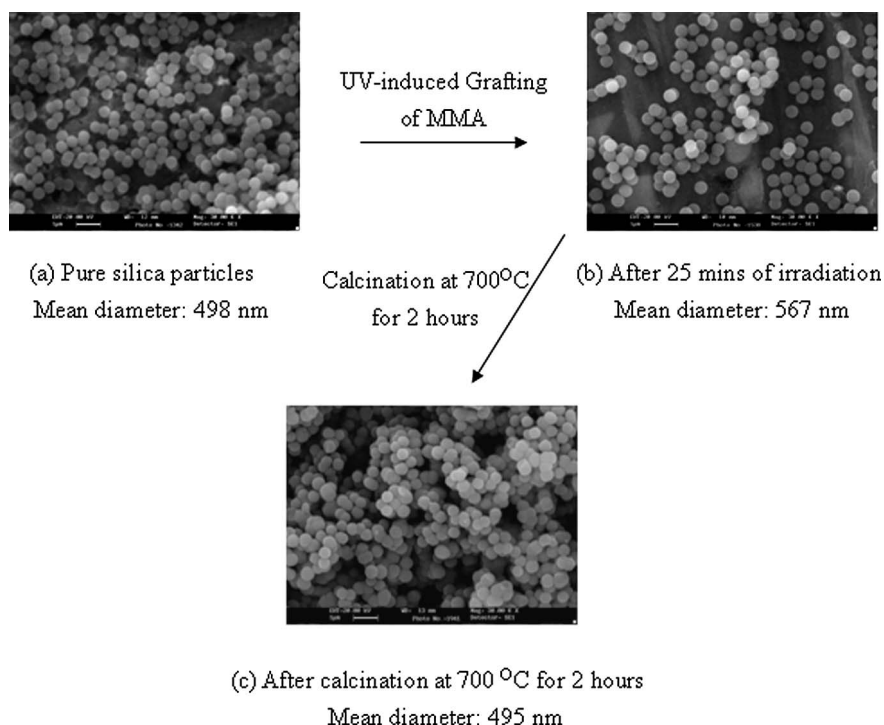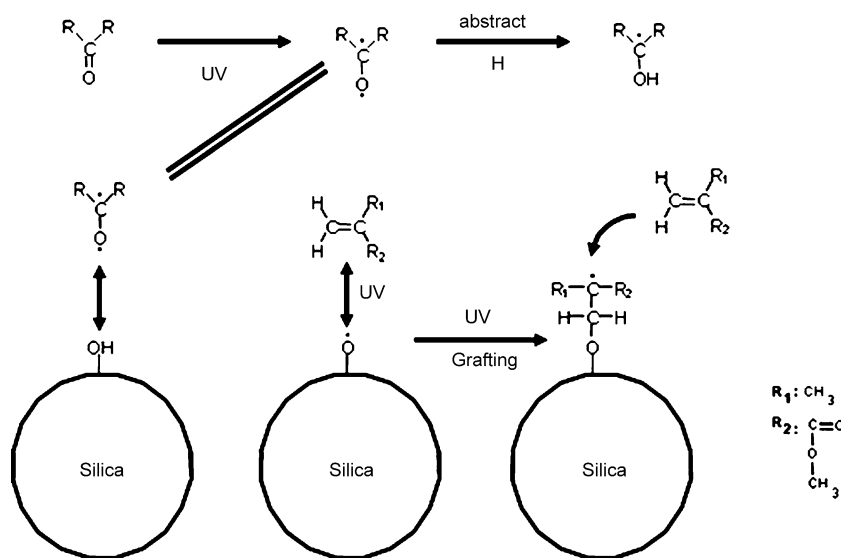
Fig. 4. SEM photographs of (a) pure silica particles, (b) PMMA-grafted particles, (c) PMMA-grafted silica particles after calcination at 700 °C for 2 h.

Scheme 1. Grafting of PMMA onto silica nanoparticles by UV-induced polymerization.

radical formed on the silica surface reacts with MMA, which initiates the growth of a grafted chain. Thus a new covalent bond, Si–O–C, is formed on the surface of silica. This unprecedented finding of Si–O–C bond is confirmed by the following FT-Raman analysis.

3.5. Chemical structure analysis of PMMA-grafted particles

Fourier-Transform Raman Spectroscopy (RFS-100/S, Bruker, Germany) analysis was performed to study the chemical structure of PMMA-grafted composites. Fig. 5 shows the FT-Raman spectra, recorded in the 400–3700 cm^{-1} range, for pure silica particles, PMMA homopolymer and PMMA-grafted silica particles with irradiation times of 15, 25, and 35 min. The pure silica particles show vibration peaks at 452 and 975 cm^{-1} due to rocking and stretching of Si–O–Si, respectively. PMMA-grafted silica particles show additional peaks than pure silica particles as expected. These peaks will be discussed in detail later. PMMA homopolymer particles show characteristic peaks at 1730 and 1454 cm^{-1} for C=O stretching and C–H bending, respectively. Since these new peaks must come from the grafted PMMA chains, these peaks are compared with peaks from the PMMA homopolymer in the range of 900–1900 cm^{-1} in Fig. 6. The characteristic C–H bending at 1454 cm^{-1} due to

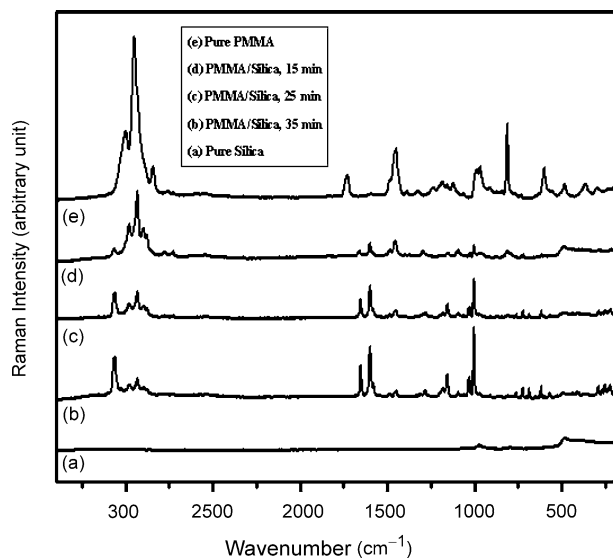Fig. 5. The FT-Raman spectra of pure silica, PMMA homopolymer and PMMA-grafted silica particles.

Fig. 6. The FT-Raman spectra of PMMA homopolymer with PMMA-grafted silica particles showing new peaks.

the PMMA chain is clearly detected in PMMA-grafted silica particles. However, the characteristic peak for C=O stretching at 1740 cm^{-1} was not detected for PMMA-grafted silica particles. Instead, the PMMA-grafted silica particles show new peaks at 1650 and 1600 cm^{-1}, possibly associated with formation of carboxylic acid groups and carboxylate anions, respectively [17,18]. Authors speculate that formations of these new groups are due to the degradation of PMMA chains, particularly C=O groups during UV-irradiation. Furthermore, the strong peaks at 1003 and 1030 cm^{-1} for PMMA-grafted particles are also shown in Fig. 6. These peaks are due to new Si–O–C bond formed on the silica surface [18]. Thus spectral analysis supports the proposed mechanism of UV-induced graft polymerization of MMA onto the surface of silica particles by a covalent bond.

3.6. Surface composition analysis

X-ray photoelectron spectroscopy (ESCA 2000, VG MicroTech) analysis was carried out in order to determine the surface compositions of the pure and PMMA-grafted silica particles. In these experiments the Si$_{2p}$ signal accounts for the silica
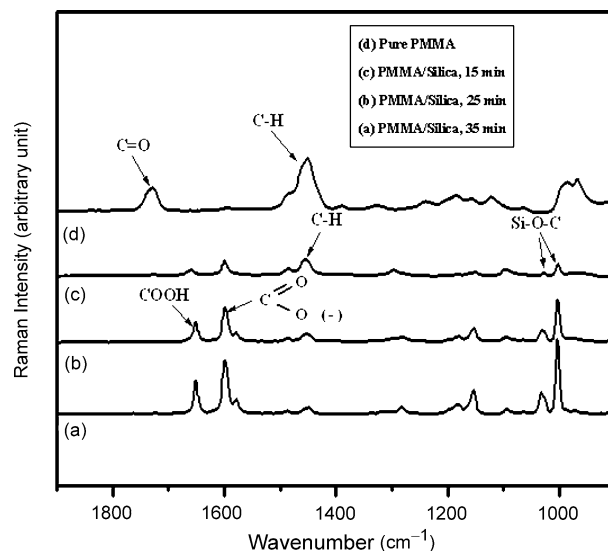
particles and almost all of the C$_{1s}$ signal is due to the surface-grafted PMMA chains. Besides the expected peaks, a weak C$_{1s}$ peak was also observed in pure silica particle sample. This C$_{1s}$ signal might be due to the incomplete hydrolysis of the alkoxide precursor used for the synthesis of the pure silica particles. The C/Si atomic ratios are summarized in Table 1 along with the mean diameter and polymer content of the particles by TGA. As the mean diameter increased the C/Si atomic ratio increased. 25 min composite particles showed the highest carbon content of 2.5 as expected. It was found that highest carbon element content of the surface layer of the modified silica nanoparticles was 40% (25 min particles) and the Si element content of pure silica particles decreased from 31 to 16% (25 min particles) after the graft polymerization of MMA. These XPS results confirm the successful grafting of MMA on the silica surface.

4. Conclusion

UV-induced graft polymerization of MMA onto the surface of silica nanoparticles is an improved and more effective method to fabricate monodisperse PMMA–silica composite particles. From SEM images, we observed a 78% increase in

Table 1
Summary of the mean diameter, polymer content, surface compositions of PMMA-grafted silica particles prepared by UV-induced graft polymerization

Sample description	Mean diameter by SEM (nm)	Volume increase by SEM (%)	Polymer content by TGA (wt%)	Atomic concentration by XPS Si/C/O (%)	C/Si atomic ratio by XPS
Pure silica	376			30.91/6.80/62.29	0.22
PMMA/silica, 5 min	421	40	14	21.60/34.49/43.91	1.60
PMMA/silica, 10 min	440	60	15	21.63/36.02/41.14	1.67
PMMA/silica, 15 min	434	54	25	21.33/39.25/39.42	1.84
PMMA/silica, 20 min	427	46	26	20.50/38.75/40.74	1.89
PMMA/silica, 25 min	456	78	31	16.08/40.20/43.72	2.50
PMMA/silica, 30 min	426	45	24	18.86/41.05/40.11	2.17
PMMA/silica, 35 min	437	57	23	19.03/40.41/40.28	2.12
PMMA/silica, 40 min	434	54	23	21.60/37.63/40.77	1.74

volume of the particles after UV-induced graft polymerization of MMA onto silica nanoparticles. Thermogravimetric analysis indicated a polymer content of 31% (wt%) for the composite particles after 25 min of UV irradiation. In XPS analysis of the composites, carbon element content increased from 6 to 40% after graft polymerization indicating successful grafting of MMA. Based on FT-Raman spectra of pure silica and PMMA-grafted silica particles, we can conclude the formation of a new covalent bond, the Si–O–C bond, during graft polymerization of MMA onto the surface of silica nanoparticles.

Acknowledgments

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