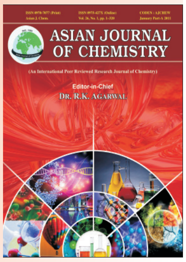
Asian Journal of Chemistry; Vol. 26, No. 10 (2014), 2987-2991

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.16245



Synthesis and Characterization of Poly(methyl methacrylate) Brushes on Silica Particles by Surface-Initiated Atom Transfer Radical Polymerization

HUI LIU[1,2,3,*], HUANQING CUI[1], RUIMENG WANG[1], SI CHEN[1] and WANZHU ZHOU[4]

[1]College of Chemistry and Chemical Engineering, Central South University, Lushan South Road, Changsha 410083, P.R. China
[2]Key Laboratory of Resource Chemistry of Nonferrous Metals, Ministry of Education, Central South University, Lushan South Road, Changsha 410083, P.R. China
[3]State Key Laboratory for Powder Metallurgy, Central South University, Lushan South Road, Changsha 410083, P.R. China
[4]Guangzhou Research Institute of Non-ferrous Metals, Guangzhou 510651, P.R. China

*Corresponding author: Fax: +86 731 8887 9616; Tel: +86 731 8887 6605; E-mail: liuhui@csu.edu.cn

Received: 26 August 2013; *Accepted*: 17 November 2013; *Published online*: 10 May 2014; AJC-15164

We synthesized herein poly(methyl methacrylate) (PMMA) brushes from silica particles *via* surface-initiated atom transfer radical polymerization. The resulting polymer brushes were characterized by means of Fourier transform infrared spectra, thermal gravimetric analysis, X-ray photoelectron spectrometer and transmission electron microscope. The molecular weight and distribution of free polymer were analyzed by gel permeation chromatography and it was found that molecular weight (M_n) decreased from 40600 to 14200 with the increasing free initiator concentration and polydispersities index ranged from 1.26 to 1.49.

Keywords: Poly(methyl methacrylate), Surface-initiated atom transfer radical polymerization, Silica particles, Polymer brushes.

INTRODUCTION

In recent years, silica particles have attracted increasing attention since they have been widely used as filler in the manufacture of paints, rubbers, plastics, binders, functional fibers, anti-virus materials, *etc*.[1-3]. However, their agglomeration and incompatibility with the organic matrix are impending problems, which seriously limits their further efficient application. Surface modification of silica particles is one of useful methods to meet the requirement, leading to a great deal of research as reported elsewhere[4,5]. The synthesis of polymer brushes on the surface of silica particles is an effective approach to improve the agglomeration and incompatibility in polymeric matrix. Freris *et al*.[6] reported the polymer encapsulation of submicrometer-sized silica particles by synthesis of poly(methyl methacrylate) under static conditions in a reaction medium free of surfactants and stabilizing agents. 3-(Trimethoxysilyl)propyl methacrylate, a kind of the silane coupling agents, was used to reinforce the mutual bonding between the polymeric layer and the particles. Feng *et al*.[7] synthesized poly(ethylene glycol) grafted silica nanoparticles using a facile esterification condensation method and the resulting silica nanoparticles have core-shell structure with poly(ethylene glycol) on the outside and silica in the core.

The principle means to prepare polymer brushes usually include "grafting to" and "grafting from"[8,9] and the latter is considered as the better method to achieve high density grafting brushes. The grafting can not only improve the compatibility between the substrate and polymer but also expand the application of the inorganic/organic matrix materials. As a kind of "grafting from" technique, surface-initiated atom transfer radical polymerization (SI-ATRP) is a very useful method in the synthesis of polymer brushes which has been attracting considerable research interest since it was first put forward in 1995[10-12]. At present, SI-ATRP is still widely used in the preparation of well controlled polymers with narrow molecular weight distribution due to its relatively moderate condition[13,14]. Based on this situation, SI-ATRP is the priority method in the synthesis of well controlled polymer brushes[15].

To get a better understanding, we herein report the synthesis and characterization of PMMA brushes on the surface of silica particles by SI-ATRP. We first immobilize the ATRP initiator on the surface of silica particles and then construct PMMA brushes on the activated particles. The aim is to avoid the incompatibility of inorganic substrates with hydrophobic methyl methacrylate polymer and choose a suitable manner to synthesize the organic/inorganic complex materials.

EXPERIMENTAL

Silica particles (SiO_2) with an average size of 5 μm were supplied by Weifang Haihua Co. Ltd., China. Methyl methacrylate (MMA, 99 %, TCI) as the monomer was distilled over calcium hydride under reduced pressure before use. Copper(I) chloride (CuCl, 99.99 %, TCI) was stirred in glacial acetic acid overnight, filtered and washed with anhydrous ethanol under argon atmosphere. 3-Aminopropyltriethoxysilane (APTES, 99 %, TCI), 2-bromoisobutyryl bromide (BiBB, 97 %), 1,1,4,7,10,10-hexamethyl triethylenetetramine (HMTETA, 99 %, TCI), ethyl 2-bromoisobutyrate (EBiB, 99 %, TCI) and copper(II) chloride ($CuCl_2$, 98 %, TCI) were all used as received.

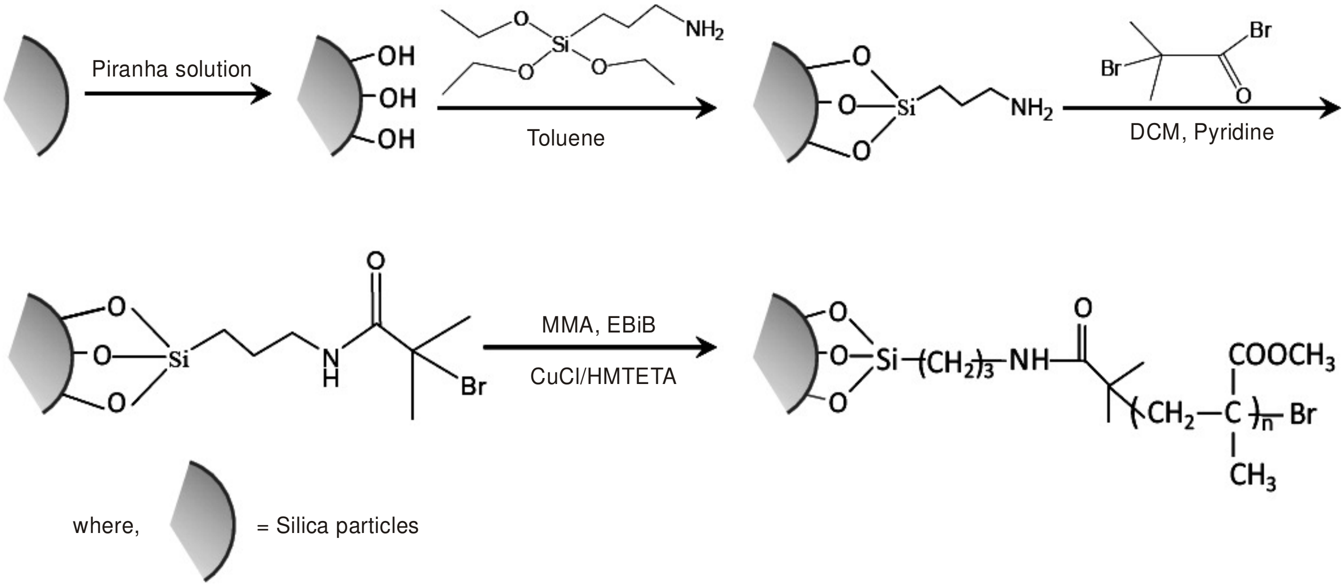
Immobilization of atom transfer radical polymerization initiator on the substrate: 10 g of silica particles (SiO_2) were immersed with 200 mL freshly prepared "Piranha solution" (7/3, v/v, 98 % H_2SO_4/30 % H_2O_2) at ambient temperature for 3 h and rinsed with deionized water, then dried under vacuum. 5 g of the resulting particles (SiO_2-OH) were stirred with 15 mL APTES in 100 mL toluene for 9 h and rinsed with toluene. In 100 mL dichloromethane (DCM), 3 g of the amino group modified silica particles (SiO_2-NH_2) were reacted with 20 mL BiBB in the presence of pyridine (20 mL). After immersion over 12 h, the ATRP initiator immobilized silica particles (SiO_2-Br) were rinsed with water-ethanol mixture (1:1 v/v) and dried under vacuum before SI-ATRP (**Scheme-I**).

Surface initiated-atom transfer radical polymerization of methyl methacrylate from the substrate: A typical procedure for the SI-ATRP from silica particles was as follows: 500 mg of SiO_2-Br was added into a Schlenk tube containing CuCl (7.425 mg, 0.06 mmol), EBiB (11 μL, 0.075 mmol) and MMA (1.5 mL, 14 mmol) in the molar ratio of 1.0:1.0:188. The nitrogen was carefully introduced into the tube to remove oxygen and HMTETA (21.03 μL, 0.075 mmol) as the ligand was injected into the mixture. The Schlenk tube was then placed into an oil bath at 90 °C for 12 h. The solidified reaction mixture was diluted with tetrahydrofuran (THF) and separated by filtration. The cake was extracted with THF for 24 h in a Soxhlet apparatus and the resulting PMMA grafted silica particles (PMMA-g-SiO_2) were dried under vacuum. The filtrate was passed through a column of alumina to remove copper catalyst. In order to get the free polymer which was formed in the solution due to the addition of EBiB as the sacrificial initiator, the resulting transparent liquid was precipitated into excess methanol, filtered and dried under vacuum.

Characterization: Fourier transform infrared (FTIR) spectra were recorded from KBr performed at room temperature on a Dig lab FTS 3000 instrument. Thermal gravimetric analysis (TGA) was performed from room temperature to 800 °C at a scanning rate of 10 °C/min under a nitrogen atmosphere on a Perkin Elmer instrument TGA/SDTA 851e, METLER Company. The surface characterization of silica particles was accomplished by using an ESCALAB MK II Multi-functional X-ray photoelectron spectrometer (XPS) with pass energy of 29.35 eV and an Mg Kα line excitation source. The binding energy of C1s (284.6 eV) was used as a reference. The morphology of the resulting PMMA-g-silica brush was investigated by transmission electron microscopy (TEM, Tecnai G^2 20 ST). Nuclear magnetic resonance (NMR) spectrum of the free polymer was recorded on a JEOL spectrometer for ^1H at 300 MHz using chloroform ($CDCl_3$) as the solvent. Gel permeation chromatography (GPC) analysis of free polymers was performed in THF at a flow rate of 1 mL/min and using standard polystyrene as the calibration curve by a Waters GPCV2000 equipment.

RESULTS AND DISCUSSION

Analysis of FTIR: Fig. 1 demonstrates the FTIR spectra of (a) silica particles, (b) SiO_2-NH_2, (c) SiO_2-Br and (d) PMMA-g-SiO_2. In Fig. 1 (a), the characteristic adsorption peak at 1106 cm^{-1} can be attributed to the Si-O-Si stretching vibration. The broad band centered around 3442 cm^{-1} is associated with O-H stretching vibrations of hydroxyl group which is attributed to residual water on the surface of SiO_2 particles. Peak at 1643 cm^{-1} comes from H-O-H bending vibration and peak at 973 cm^{-1} is attributable to Si-OH vibration. The peaks between 2930 and 2851 cm^{-1} belonging to the C-H stretching vibrations are not observed, which indicates that no organic groups exist on the particles. In Fig. 1(b), the peak for the symmetric bending



Scheme-I: Synthetic route for SI-ATRP of MMA from silica particles vibration of CH_2 connecting with NH_2 is observed at 1384 cm^{-1} and no peaks at 1450 cm^{-1} is found in the curve of SiO_2-NH_2. It verifies that the CH_2 group is connected with the nitrogen atom and APTES has been chemically grafted to the particles. While in Fig. 1 (c), the N-H bending vibration is observed around 1538 cm^{-1}, showing that the ATRP initiator group has been immobilized on the surface of the substrates. As shown in Fig. 1 (d), the strong absorbance peak of the C=O at 1734 cm^{-1} is found in the spectrum of PMMA-g-SiO_2 and the peak at 1454 cm^{-1} can be attributed to the bending vibration of alkyl group in PMMA. Also, we observe the bands of -CH_2 and α-CH_3 at 3000-2900 cm^{-1} and the peak of wave vibrations belonging to the alkyl group of polymers at 750 cm^{-1}. All these evidences demonstrate that PMMA brushes have been successfully synthesized on the surface of silica particles *via* SI-ATRP as shown in **Scheme-I**.

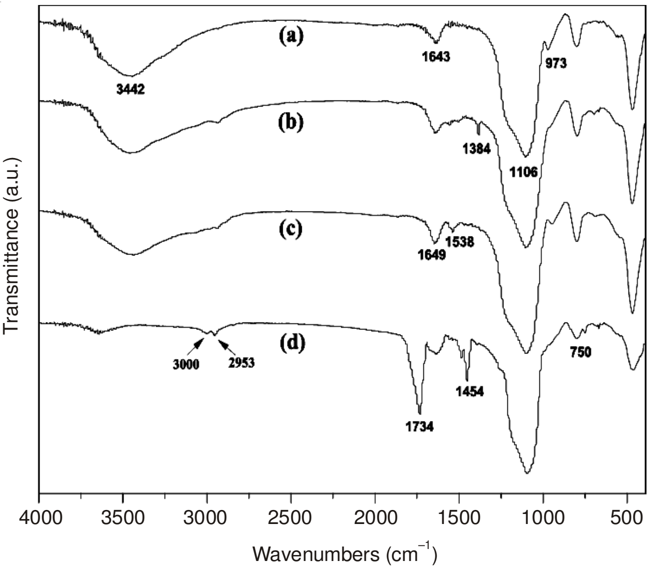


Fig. 1. FTIR spectra of (a) silica particles, (b) SiO_2-NH_2, (c) SiO_2-Br and (d) PMMA-g-SiO_2

Analysis of TGA: Fig. 2 shows the TGA curves of (a) silica particles, (b) SiO_2-Br, (c) PMMA-g-SiO_2 and (d) pure PMMA. As can be seen, there is a slight weight loss due to the physisorbed water in the curve of silica particles (Fig. 2a) and the residual mass percentage is 90 % at 450 °C. In Fig. 2(b), the total residual mass percentage is about 75 %. Except for the weight loss of physisorbed water, the following loss beginning at 250 °C can be thought as the decomposition of ATRP initiator in the curve of SiO_2-Br, indicating the grafting percentage of initiator is about 15 %.

In Fig. 2 (d), pure PMMA breaks down when temperature is up to 300 °C and decomposes completely at 400 °C. For the curve of PMMA-g-SiO_2 (Fig. 2 c), the weight loss can be divided into three stages. The first weight loss from room temperature to 250 °C is due to the desorption of physically adsorbed water and the second stage in the temperature ranging from 250 to 370 °C is attributed to the decomposition of initiators. The last stage from 370 to 450 °C is ascribed to the decomposition of grafted PMMA and the residual mass percentage is 45 %. It is concluded that the weight percentage of polymer grafted on silica is close to 30 %. Moreover, the initial decomposition temperature of PMMA-g-SiO_2 is higher than that of pure PMMA, implying that the grafted PMMA has better thermal stability than pure polymer. It can be explained by the strong chemical covalent bond between the polymer and particles.

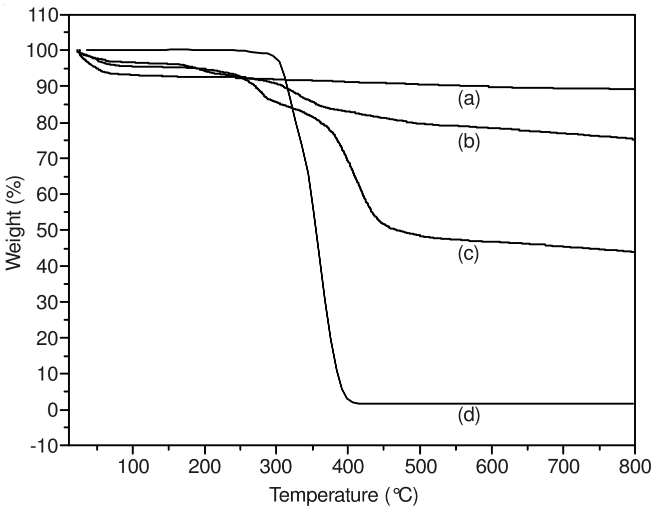


Fig. 2. TGA curves of (a) silica particles, (b) SiO_2-Br, (c) PMMA-g-SiO_2 and (d) pure PMMA

Analysis of XPS: XPS is usually employed to analyze the relative elemental content and chemical bond on the surface of samples. The XPS full-survey spectra of SiO_2 and PMMA-g-SiO_2 are illustrated in Fig. 3 and the surface elemental composition is listed in Table-1. In the full-survey spectrum of PMMA-g-SiO_2 composite particle, the appearance of Br 3d peak at around 68 eV verifies the formation of the polymer layer *via* SI-ATRP. Compared to SiO_2, the contents of Si, C and O for PMMA-g-SiO_2 change from 29.11, 16.66 and 54.23 % to 18.22, 43.38 and 37.61 %, respectively and the content of Br emerging in PMMA-g-SiO_2 is 0.8 %, manifesting that PMMA has been grafted on the surface of SiO_2. In order to clarify the status of surface chemical bond, the high resolution XPS spectra of O1s has been scanned and they are fitted through the software 'XPSPEAKFIT' in the light of Lorentzian-Gaussian principle[16,17].

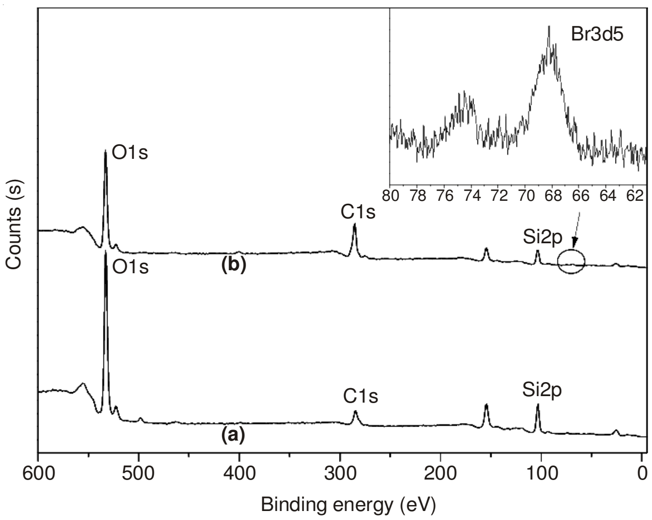


Fig. 3. XPS full-survey spectra of (a) SiO_2 and (b) PMMA-g-SiO_2 composite particles

TABLE-1
SURFACE ELEMENTAL COMPOSITION OF SiO_2 AND PMMA-g-SiO_2 COMPOSITE PARTICLES

Samples	Si (%)	C (%)	O (%)	Br (%)
SiO_2	29.11	16.66	54.23	–
PMMA-g-SiO_2	18.22	43.38	37.61	0.8

Fig. 4(a) and (b) present the high-resolution O1s XPS spectra and curve-fitting of SiO_2 and PMMA-g-SiO_2, respectively and Table-2 illustrates the binding energies and the attributions of O1s peaks. We can see that the decrease of Si-O, the increase of C-O and the emergence of C=O (531.5 eV) are essentially caused by the PMMA grafted onto the surface of SiO_2. Different from the O1s curve-fitting peaks of SiO_2, the negative chemical shifts of binding energies are found in the curve-fitting peaks of PMMA-g-SiO_2, which is possibly relevant to the uncrystallized polymeric layer and special core-shell structure of PMMA-g-SiO_2.

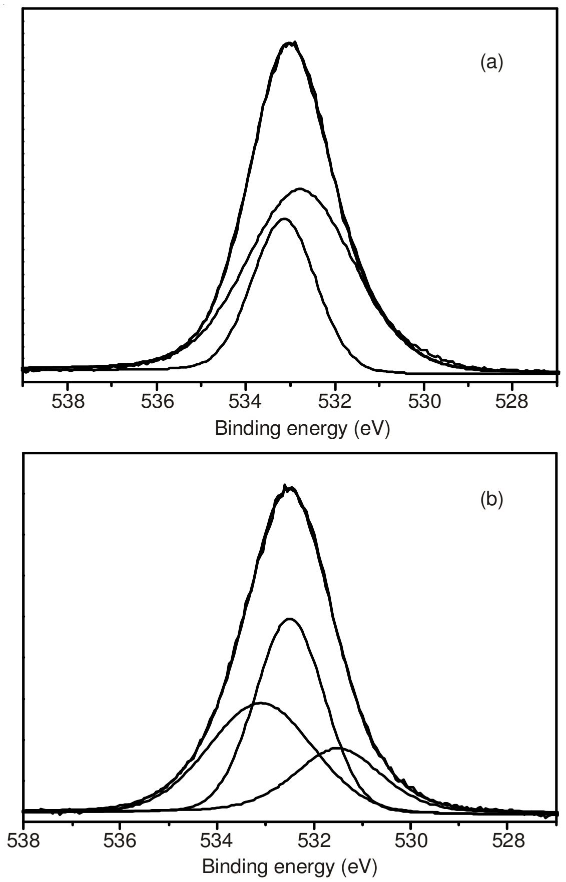


Fig. 4. High resolution XPS spectra and curve-fitting of O1s of (a) SiO_2 and (b) PMMA-g-SiO_2

TABLE-2
XPS ANALYSIS OF O1s OF SiO_2 AND PMMA-g-SiO_2 COMPOSITE PARTICLES

Samples	Standard position (eV)	Actual position (eV)	Chemical shift (eV)	Content (%)	Attribution
SiO_2	532.50	532.76	+0.22	67.93	Si-O
	533.10	533.13	+0.03	32.07	C-O
PMMA-g-SiO_2	532.00	531.50	-0.50	20.89	C=O
	532.10	533.03	-0.01	36.35	C-O
	533.10	533.09	-0.01	36.35	C-O

Finally, XPS analysis indicates that PMMA-g-SiO_2 composite particle has been successfully prepared by SI-ATRP and PMMA has been grafted on the surface of SiO_2 through chemical bond, rather than the simple physical adsorption.

Analysis of TEM: TEM is used to observe the morphology of the resulting PMMA-g-silica and the result is shown is Fig. 5. As can be clearly seen, silica particle is encapsulated with a layer of polymer with the thickness of about 10 nm. The uniform polymeric layer indicates that good control on SI-ATRP of MMA has been successfully achieved on the surface of silica particles, which is in good agreement with the FTIR, TGA and XPS analysis.

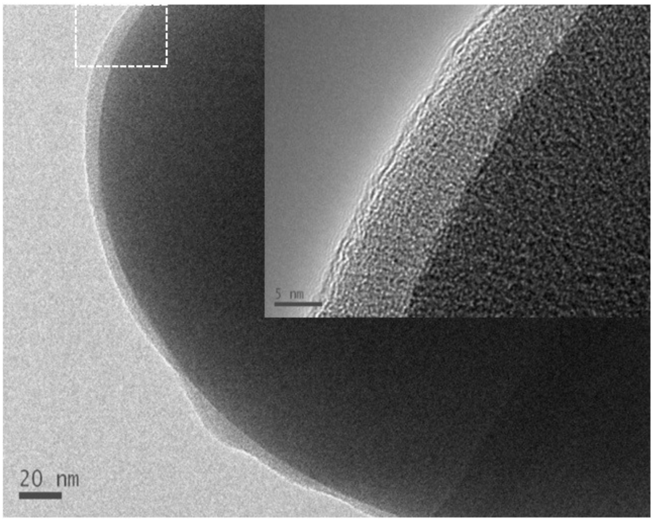


Fig. 5. TEM image of the resulting PMMA-g-SiO_2

Analysis of ^1H NMR: The ^1H NMR spectrum also gives support to the free polymer of PMMA produced in the solvent (Fig. 6). The spectrum displays the expected methyl protons (a; 0.68-1.12 ppm), alkyl protons (b; 1.8-1.9 ppm) and methoxyl protons (c; 3.60 ppm) of PMMA grafted chains. The peaks of protons in C=C double bond around 5.8-6.5 ppm are not found, which indicates that all the monomers have reacted completely during the polymerization process.

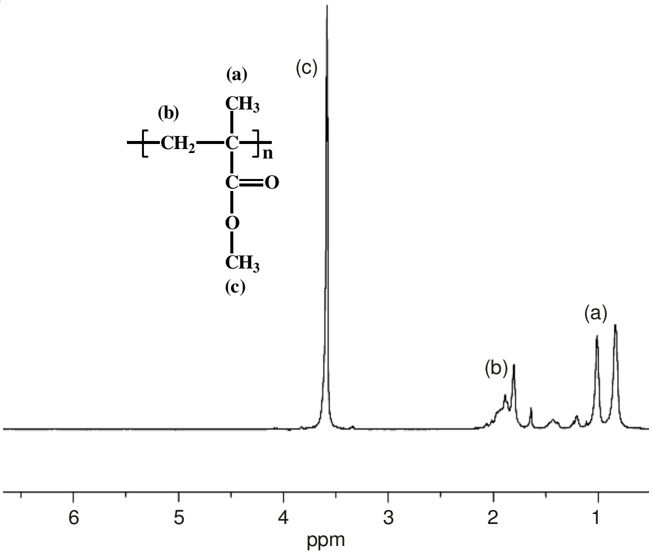


Fig. 6. ^1H NMR spectrum of free PMMA in $CDCl_3$

Analysis of gel permeation chromatography: Gel permeation chromatography is employed to analyze the free polymers and the results are shown in Fig. 7. The normal distribution shape is almost observed in all the elution curves of the free polymers implying the well-controlled polymerization. The initial elution time delays with the increasing EBiB concentration, indicating the decrease of molecular weight.

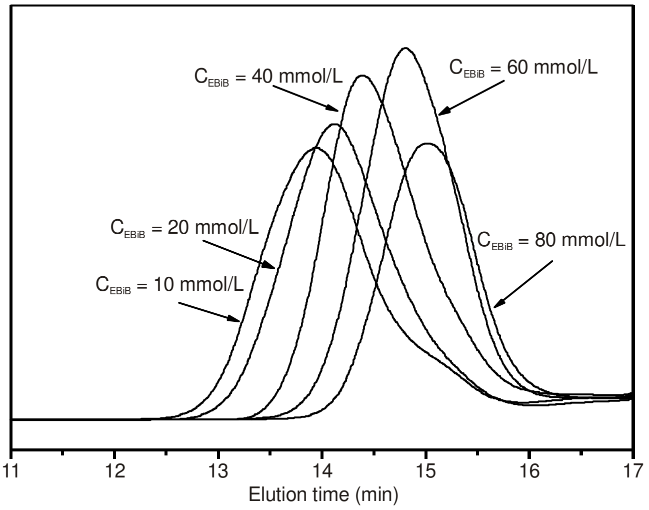


Fig. 7. GPC curves of free PMMA separated from the grafting particles at different free initiator concentration (T = 90 °C, t = 12 h, [CuCl]:[HMTETA]:[MMA] = 1.0:1.0:188, the solvent is toluene, molecular weight (Mn) is determined by GPC using standard polystyrene as the calibration curve, and C_{EBiB} is the concentration of EBiB in toluene)

To get a better understanding, we calculate the molecular weight using standard polystyrene as the calibration curve. Fig. 8 shows that the number average molecular weight (M_n) decreases from 40600 to 14200 with the increasing free initiator (EBiB) concentration and polydispersities index ranges from 1.26 to 1.49 showing the even molecular weight distribution. When EBiB concentration is 80 mmol/L, the polydispersities index is 1.26, which means narrow molecular weight distribution and controllable polymerization. For SI-ATRP, the initiator concentration on the surface is usually low compared to that used for bulk or solution ATRP. To quickly establish equilibrium between dormant and active chains during SI-ATRP, an excess amount of deactivating Cu(II) complex may be added[11,18].

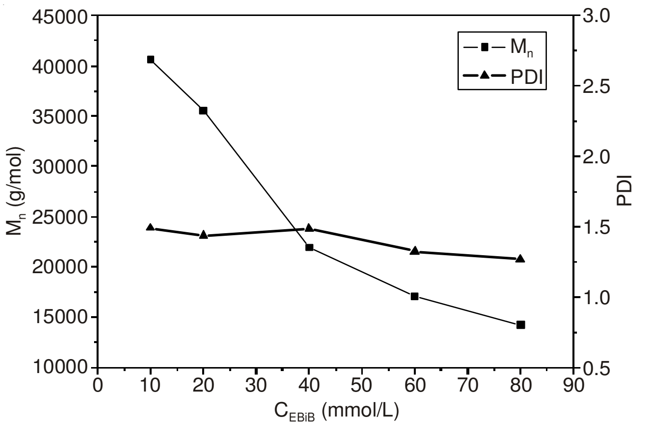


Fig. 8. Influence of EBiB concentration on the molecular weight and distribution of the free PMMA

Conclusion

We report herein PMMA brush is grafted from silica particles *via* surface-initiated atom transfer radical polymerization (SI-ATRP). The process contains immobilization of ATRP initiator and polymerization of monomer on the inorganic surfaces. FTIR, TGA, XPS and TEM verify that PMMA-g-SiO_2 has been successfully synthesized by SI-ATRP and has higher thermal stability than the pure PMMA. For the free PMMA produced in the solution, molecular weight (M_n) decreases from 40600 to 14200 with the increasing free initiator concentration and polydispersities index (PDI) ranges from 1.26 to 1.49, which means narrow molecular weight distribution and controllable polymerization. This work can expand the application domain of silica particles to a large extent. Furthermore, the synthetic route may also be used to modify other particles and offer new opportunities for comprehensive potential applications in many interrelated fields.

ACKNOWLEDGEMENTS

This work was financially supported by the National Natural Science Foundation of China (Grant No. 21376271), the Scientific Research Foundation for the Returned Overseas Chinese Scholars of State Education Ministry, Opening Foundation of State Key Laboratory of Powder Metallurgy (Grant No. 20110825), Undergraduates Innovative Training Project (Grant No. CL12129, 201310533008), the Fundamental Research Funds for the Central Universities of Central South University (Grant No. Z12060) and the Open-End Fund for the Valuable and Precision Instruments of Central South University (Grant No. CSUZC2013008).

REFERENCES

1. N.Y. Hebalkar, S. Acharya and T.N. Rao, *J. Colloid Interf. Sci.*, **364**, 24 (2011).
2. S. Affandi, H. Setyawan, S. Winardi, A. Purwanto and R. Balgis, *Adv. Powder Technol.*, **20**, 468 (2009).
3. P. Liu, W.M. Liu and Q.J. Xue, *Mater. Chem. Phys.*, **87**, 109 (2004).
4. M.A. Rahman, M.A.J. Miah, H. Minami and H. Ahmad, *Polym. Adv. Technol.*, **24**, 174 (2013).
5. T. Fontecave, C. Sanchez, T. Azais and C. Boissiere, *Chem. Mater.*, **24**, 4326 (2012).
6. T. Freris, D. Cristofori, P. Riello and A. Benedetti, *J. Colloid Interf. Sci.*, **331**, 351 (2009).
7. L.B. Feng, Y.L. Wang, N. Wang and Y.X. Ma, *Polym. Bull.*, **63**, 313 (2009).
8. J.H. Yang and S.H. Choi, *J. Appl. Polym. Sci.*, **127**, 4122 (2013).
9. S. Hansson, V. Trouillet, T. Tischer, A.S. Goldmann, A. Carlmark, C. Barner-Kowollik and E. Malmstrom, *Biomacromolecules*, **14**, 64 (2013).
10. J.S. Wang and K. Matyjaszewski, *J. Am. Chem. Soc.*, **117**, 5614 (1995).
11. J.S. Wang and K. Matyjaszewski, *Macromolecules*, **28**, 7901 (1995).
12. M. Kato, M. Kamigaito, M. Sawamoto and T. Higashimura, *Macromolecules*, **28**, 1721 (1995).
13. O.Y.F. Henry, A.D. Mehdi, S. Kirwan, J.L.A. Sanchez and C.K. O'Sullivan, *Macromol. Rapid Commun.*, **32**, 1405 (2011).
14. D.J. Haloi, S. Ata and N.K. Singha, *Ind. Eng. Chem. Res.*, **51**, 9760 (2012).
15. P. Liu, *Curr. Org. Chem.*, **17**, 39 (2013).
16. R. Rajagopalan and J.O. Iroh, *Appl. Surf. Sci.*, **218**, 58 (2003).
17. C. Perruchot, M.A. Khan, A. Kamitsi, S.P. Armes, J.F. Watts, T. von Werne and T.E. Patten, *Eur. Polym. J.*, **40**, 2129 (2004).
18. A. Kajiwara, K. Matyjaszewski and M. Kamachi, *Macromolecules*, **31**, 5695 (1998).