Colloid Polym Sci (2006) 285: 65–74
DOI 10.1007/s00396-006-1535-2

ORIGINAL CONTRIBUTION

Long Jiang
Kai Pan
Yi Dan

Synthesis and characterization of well-defined poly(methyl methacrylate)/$CaCO_3$/SiO_2 three-component composite particles via reverse atom transfer radical polymerization

Received: 28 October 2005
Accepted: 9 April 2006
Published online: 16 August 2006

L. Jiang · K. Pan · Y. Dan (✉)
State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute, Sichuan University, Chengdu 610065
Sichuan, People's Republic of China
e-mail: ph9nix@163.com
Tel.: +86-28-85407286
Fax: +86-28-85402465

Abstract The attempt to prepare structurally well-defined polymer/inorganic composite particles, i.e., poly(methyl methacrylate) (PMMA)/$CaCO_3$/SiO_2 three-component composite particles, via reverse atom transfer radical polymerization (ATRP), using 2-2′-azo-*bis*-isobutyronitrile as initiator and Cu(II) bromide as catalyst was reported. $CaCO_3$/SiO_2 two-component composite particles were first obtained through sol–gel method, and their morphology and surface element information were determined by transmission electron microscopy and X-ray photoelectron spectroscopy, respectively. The results indicate that the $CaCO_3$ was encapsulated by the obtained SiO_2. After being modified by silane coupling agent, the $CaCO_3$/SiO_2 composite particles copolymerized with methyl methacrylate (MMA) under standard reverse ATRP conditions to produce PMMA/$CaCO_3$/SiO_2 three-component composite particles. In the case concerned, first-order kinetic plots and linear increase of molecular weight (Mn) vs conversion and narrow molecular weight distribution for the graft polymer samples were observed. Furthermore, the gel permeation chromatography results illustrated that both the free PMMA chains from the solvent and the graft PMMA chains from the surface of $CaCO_3$/SiO_2 two-component composite particles were growing at the same rate. Characterizations of the PMMA-grafted $CaCO_3$/SiO_2 composite particles were done by Fourier transform infrared and thermogravimetric analysis. The results showed that the surface of the modified inorganic particles was grafted by the MMA and that the grafting percentage was about 8.7%.

Keywords Reverse atom transfer radical polymerization · Well-defined · Multicomponent composite particles · $CaCO_3$/SiO_2 composite particle · Poly(methyl methacrylate)

Introduction

Owing to their extraordinary properties derived from the synergism between the properties of inorganic particles (optical, electronic, and magnetic) and those of the polymer (easy processing and good solubility), polymer/inorganic composite materials attract strong interest [1–3]. Many methods for preparing polymer/inorganic composite materials have been reported, but most of them are based on the weak interaction, such as van der Waals forces or hydrogen bonding, between the polymer and the surface of inorganic materials [4]. A disadvantage of these systems is thermal and solvolytic instability. To circumvent this shortcoming, grafting polymer chain from the surface of inorganic particles, which establishes a chemical bond between the two parts of the composite particles, may be the most prominent method [5, 6]. In the case of the grafting process, polymerizations are mostly carried out through radical polymerization because of its advantages, such as a large variety of vinyl monomers for polymerization or copolymerization, tolerance of impurities and functional groups, and no requirement of stringent reaction condition [7].

However, the conventional radical polymerization does not control over the molecule weight, molecule weight distribution, and the structure of the resulting polymer. These features may lead to unpredictable physical and mechanical properties of the produced composite particles.

A relatively new method to synthesize well-defined polymer/inorganic composite particles is controlled/"living" radical polymerization. Several controlled/"living" radical polymerizations, such as iniferters [8], stable nitroxide-mediated radical polymerization [9, 10], reversible addition–fragmentation chain transfer polymerization [11, 12], and atom transfer radical polymerization (ATRP) [13–16], have been well documented. Furthermore, ATRP is the most effective method because it allows for the polymerization of a wide range of monomers such as styrenes, acrylates, and methacrylates [17–19].

The application of ATRP to polymer/inorganic composite material synthesis has attracted many attentions. Bin and William [20] grafted polystyrene onto the surface of a planar silica by carbocationic polymerization, then used the obtained polystyrene/silica composite as macroinitiator, CuBr as catalyst, and *N*,*N*,*N*,*N*,*N*-pentamethyldiethylenetriamine as ligand, entailed poly(methyl methacrylate) (PMMA) to the end of polystyrene chain. The first attempt to graft polymer from the surface of SiO_2 spherical particles via ATRP was reported by Werne and Patten [21, 22]. They tethered 2-(4-chloromethylphenyl)ethyldimethylethoxysilane (CDES) on the surface of silica particles, then used the modified silica particles as macroinitiator, Cu(I) (X=Br, Cl) as catalyst, and bpy or dNbpy as ligand to prepare well-defined polymer/inorganic composite particles. The application of ATRP to prepare well-defined polymer/inorganic composite particles was reported by several other groups too [23–30].

According to the literatures, ATRP has been successfully used to prepare well-defined polymer/inorganic composite materials, and systematic studies on this have been carried out. However, some fields are relatively unexplored, which can be summarized as follows:

(1) The reported works focused only on the conventional ATRP method, using organic halides as initiators and transition metals in their lower oxidation state, such as Cu(I) as catalyst. Although this method is effective for preparing well-defined polymer/inorganic composite materials, it has two major problems: the organic halides are toxic, and the catalysts Mt^n/Lx are easily oxidized by air [31]. To overcome these drawbacks, reverse ATRP would be optimal [31–33]. However, the application of the reverse ATRP method to prepare well-defined polymer/inorganic materials has not been reported.
(2) The research focused mostly on entailing well-defined polymer chains to single-material inorganic particles. As shown in the reported works [34, 35], the functions of multicomponent inorganic particles promise to be far more interesting and diverse than that of single material. However, there is no attempt to graft well-defined polymer chains onto multicomponent inorganic particle via controlled/"living" polymerization.

Using our previous works as the base [36–38], we attempt to explore the technique for preparation of well-defined multicomponent polymer/inorganic composite particles via reverse ATRP.

The PMMA/$CaCO_3$/SiO_2 system was chosen as a model to investigate the technique of preparing well-defined polymer/inorganic part I/inorganic part II three-component composite particles. The reactions were conducted using Cu(II) bromide as catalyst and 2-2′-azo-*bis*-isobutyronitrile (AIBN) as initiator. The kinetics of the polymerization, the structure information about the graft PMMA, and the grafting percentage and efficiency of grafting were studied.

Experimental

Materials

MMA was distilled at a reduced pressure before use. AIBN (A.R.) was obtained from Beijing Chemical Reagent Factory (Beijing, China) and recrystallized from methanol. *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (99%) (Aldrich) was used as received. Copper(II) bromide from Chengdu Kelong Chemical Reagent Factory (Chengdu, China) was an analytical reagent grade and was used without further purification. The modifying agent from Ha'erbin Chemical Research Institute (Ha'erbin, China) was used as received. *p*-xylene, tetrahydrofuran (THF), methanol, and ethanol used in this work were available commercially. $CaCO_3$/SiO_2 inorganic composite particles, with an average diameter of about 70 nm, were prepared in our laboratory [39–41]. All other reagents employed in this work were purchased commercially and used without further purification.

Preparation of $CaCO_3$/SiO_2 two-component composite particles

The $CaCO_3$/SiO_2 two-component composite particles with $CaCO_3$ as core and SiO_2 as shell were prepared via Stober method [39–41]. A typical preparation procedure was as follows: to a solution of 0.5 mol/l triethyl amine, 7 mol/l H_2O in ethanol, a 0.125-mol/l calcium carbonate was added under vigorous stirring in a 500-ml reaction vessel. The mixture was then dispersed through ultrasonic irradiation by a 20-kHz ultrasonic generator at 200 kV of power for 10 min. After this, the vessel was placed into a constant-temperature water bath of 40 °C. To this dispersion was added 0.0105 mol/l tetraethylorthosilicate (TEOS) continuously with controlled rate (e.g., 0.1 mg/s). After TEOS

was fully charged into the vessel, the mixture was sealed and stirred for 30 h at 40 °C. The particles were isolated from the solution by centrifugation at a rate of 5,000 rpm for 8 min, washed with ethanol to remove unreacted substances, and spray dried.

Modification of the $CaCO_3/SiO_2$ two-component composite particles

Before polymerization, the $CaCO_3/SiO_2$ composite particles were modified by silane coupling agent. A general procedure for the surface modification reaction was as follows: to a three-necked flask was added $CaCO_3/SiO_2$ composite particle suspension in ethanol, and the suspension was heated at 40 °C. To this suspension silane coupling agent (5% of the amount of $CaCO_3/SiO_2$ composite particles by weight) was added, and the mixture was heated at 40 °C for 3 h. Then, it was heated at 80 °C for 8 h. The particles were isolated by centrifugation. To remove any adsorbed coupling agent, the particles were washed with three cycles of centrifugation and resuspension in ethanol and dried at 60 °C.

Polymerization of MMA from $CaCO_3/SiO_2$ two-component composite particles via reverse ATRP

Modified $CaCO_3/SiO_2$ composite particles (1.2 g), $CuBr_2$ (62.5 mg), and AIBN (78 mg) were weighted into a Schleck flask containing a stir bar. MMA (18 ml), *p*-xylene (42 ml), and TMEDA (65.3 mg) were added using syringes, and the flask was deoxygenated by three pump/argon cycles. The mixture was stirred vigorously to get a uniform suspension, and the flask was placed in a water bath with magnetic stirring at 80 °C. Samples were taken periodically using an argon-flushed syringe to monitor the conversion and molecular weight. The monomer conversion was determined gravimetrically, and the samples were redissolved in THF and precipitated in methanol to obtain the PMMA/$CaCO_3/SiO_2$ three-component composite particles.

Characterization

X-ray photoelectron spectroscopy measurement

X-ray photoelectron spectroscopy (XPS) analysis was performed on an XPS spectrometer with CuKα radiation (40 kV, 25 mA) at a scanning speed 0.03 °/s. Before the XPS measurement, the $CaCO_3/SiO_2$ composite particles were washed by ethanol to remove impurity and dried at 100 °C for 24 h.

Transmission electron microscopy (TEM) measurement

Before observation, the $CaCO_3/SiO_2$ composite particles were dispersed in ethanol through ultrasonic irradiation, then the dispersion was dropped on copper grids to observe the morphology of the $CaCO_3/SiO_2$ composite particles on a Hitachi H-600 TEM.

Fourier transform infrared (FTIR) measurement

The chemical structures of all the samples were determined using a Nicolet Magna 560 FTIR spectrometer. Before the FTIR measurement, all samples were extracted with THF at reflux for 72 h in a Soxhlet extractor and dried at 60 °C to remove the solvent. Then, the samples for characterization were pretreated in the form of KBr pellets.

Thermogravimetric analysis (TGA) measurement

The TGA of PMMA/$CaCO_3/SiO_2$ three-component composite particles was performed with a Dupond 2100 thermal analysis instrument. The samples were heated at a temperature range of 25–600 °C with a rate of 10 °C min^{-1} in a nitrogen atmosphere, and the nitrogen flow rate was 50 ml per min.

Gel permeation chromatography (GPC) measurement

Molecular weight and molecular weight distribution of polymer samples were measured at 35 °C by GPC on a Waters 2410 instrument using THF as the solvent (1 ml/min).

Determination of the conversion of MMA

The conversion of MMA (C%) was determined gravimetrically and was calculated using the following equation:

$$C\% = \frac{M_2 - M_1 Y}{M_1 X} \times 100\% \quad (1)$$

where M_1 is the mass of the polymerized sample, M_2 is the mass of the solid after drying, X is the mass percentage of MMA based on total input materials, and Y is the mass percentage of $CuBr_2$, AIBN, and $CaCO_3/SiO_2$ composite particles based on total input materials.

Determination of the grafting percentage

The grafting percentage was defined as the mass percentage of polymer grafted onto inorganic particles based on the total inorganic particles used and was determined by the following equation [42]:

$$\text{Percentage of grafting (G\%)} = \frac{\text{Polymer grafted (g)}}{\text{CaCO}_3/\text{SiO}_2\text{ used (g)}} \times 100\% \quad (2)$$

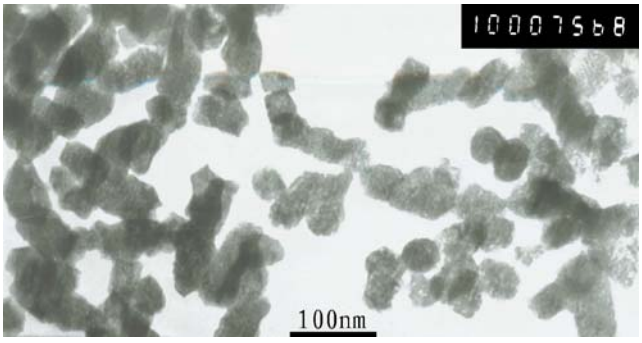


Fig. 1 TEM micrograph of $CaCO_3/SiO_2$ two-component composite particles

Determination of the grafting efficiency

The grafting efficiency was defined as the mass percentage of PMMA grafted on $CaCO_3/SiO_2$ composite particles, based on the total PMMA, and was determined by the following equation:

$$\text{Grafting efficiency } (E\%) = \frac{\text{CaCO}_3/\text{SiO}_2\text{ used} \times \text{percentage of grafting}}{\text{MMA used} \times \text{conversion of MMA}} \times 100\% \quad (3)$$

Results and discussion

For this research, $CaCO_3/SiO_2$ two-component composite particles (Scheme 1) were employed because the silica coated on the surface was easy to react with silane coupling agent, providing a means for copolymerization with other vinyl monomer, and systematic studies on this field have been done in our group [36–38].

$CaCO_3/SiO_2$ two-component composite particles were obtained through coating $CaCO_3$ particles with SiO_2 via Stober method, and the process was described in Scheme 1.

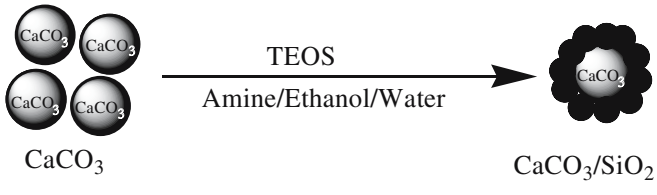
The morphology of $CaCO_3/SiO_2$ two-component composite particles was examined with TEM, and the result was shown in Fig. 1. From this figure, we can see that the particle's diameter is at the range from 50 to 100 nm. Furthermore, no free small silica particles can be observed in the figure, which inferred that all the obtained silica was coated on the surface of $CaCO_3$ particles. This conclusion was supported by the results of XPS measurements. X-ray photoelectron spectroscopy is widely used to monitor the relative ratio of elements in the material surface. Figures 2 and 3 illustrate the XPS spectra of Si 1s and Ca $2p_{3/2}$ and Ca $2p_{1/2}$ in $CaCO_3/SiO_2$ composite particles, respectively. The molecular ratio of Si/Ca on the surface of the $CaCO_3/SiO_2$ composite particles can be calculated through the following formula [43]:

$$\frac{Si}{Ca} = \frac{I_{Si}}{I_{Ca}} \times \frac{S_{Ca}}{S_{Si}} \quad (4)$$

where I_{Si} and I_{Ca} means the areas of Si 1s peak and Ca 2p peak, respectively, while S_{Ca} and S_{Si} means the sensitivity factors of Ca and Si, respectively. The areas of Si 1s peak and Ca 2p peak, obtained from Figs. 2 and 3, and the sensitivity factors are given in Table 1.

According to Table 1 and Eq. 4, we can calculate the molecular ratio of Si/Ca on the surface, which is 1.02. From the recipe for preparing $CaCO_3/SiO_2$, as shown in the "Experimental" section, the molecular ratio of Si/Ca in this composite system can be calculated, and the result is 0.084. Comparing the molecular ratio of Si/Ca on the surface and that in the system, conclusion can be drawn that the obtained SiO_2 particles are mainly encapsulated onto the surface of $CaCO_3$ particles, and the obtained $CaCO_3/SiO_2$ composite particles have a $CaCO_3$ core and a SiO_2 shell.

Before copolymerization with MMA, the $CaCO_3/SiO_2$ composite particles were modified in modifying agent



Scheme 1 Schematic diagram of the preparation of $CaCO_3/SiO_2$ composite particles

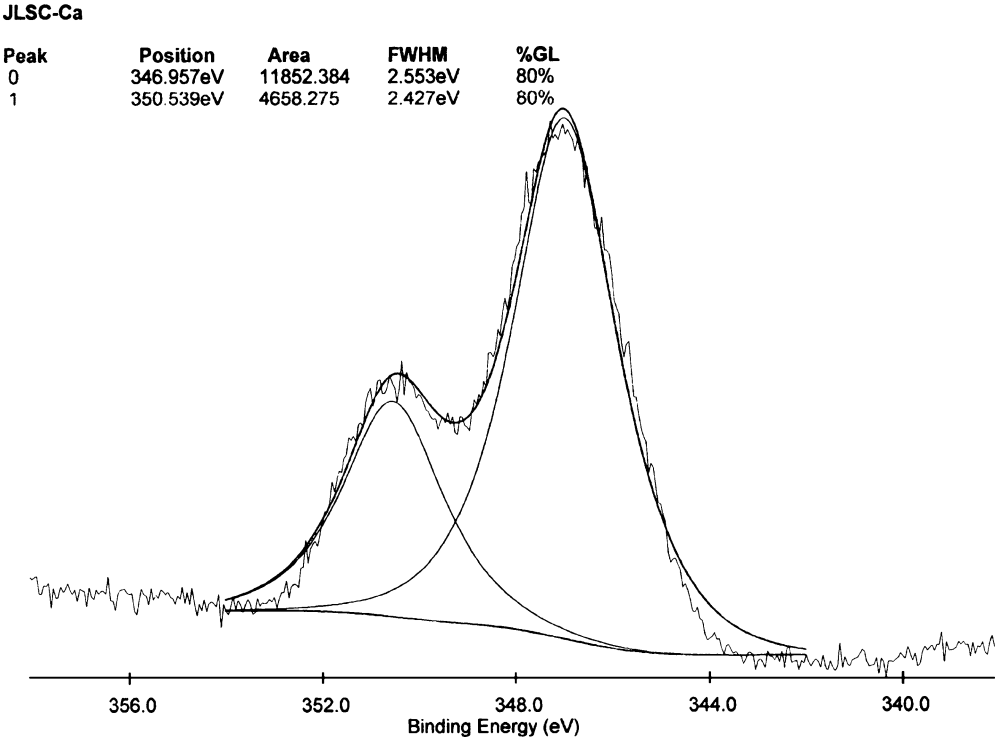


Fig. 2 X-ray photoelectron spectrum of $CaCO_3/SiO_2$ composite particles, showing Ca $2p_{3/2}$ and $2p_{1/2}$ peak

ethanol solution. The modifying agent had siloxane groups, providing a site for covalent attachment to the composite particle surface via reaction with hydroxyl groups on the surface of $CaCO_3/SiO_2$ composite particle, and vinyl groups which can react with MMA in the copolymerization (Scheme 2).

The modified $CaCO_3/SiO_2$ composite particles were washed with three cycles of centrifugation and resuspen-

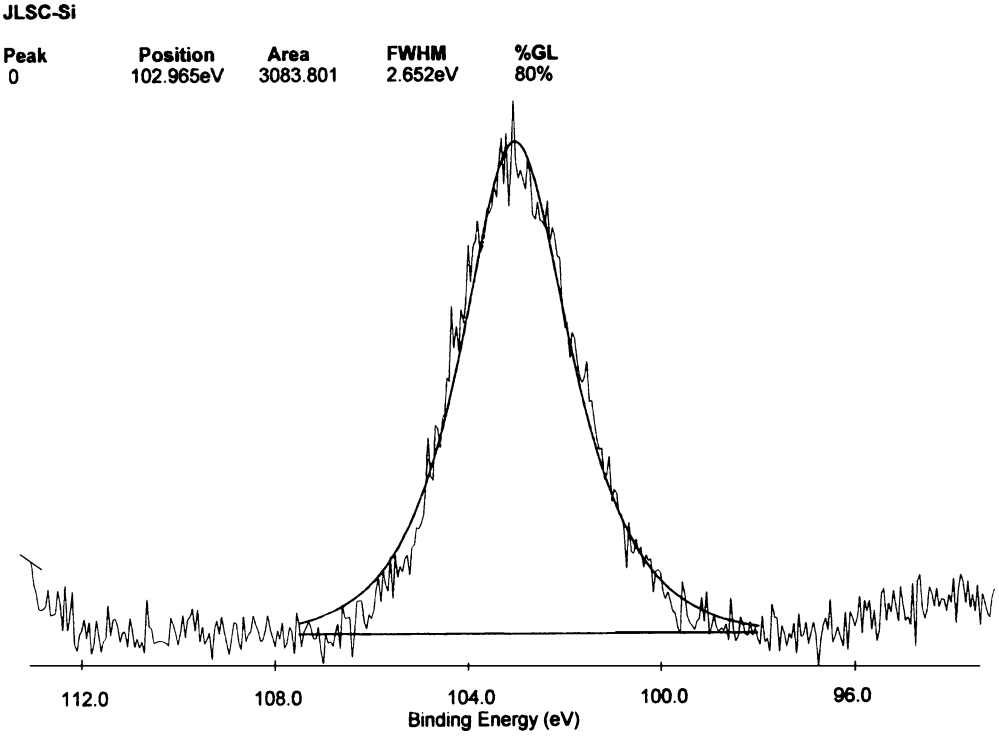


Fig. 3 X-ray photoelectron spectrum of $CaCO_3/SiO_2$ composite particles, showing Si 2p peak

Table 1 The peak areas (*I*) and sensitivity factors (*S*) of Ca and Si in $CaCO_3/SiO_2$ composite particles from XPS analysis

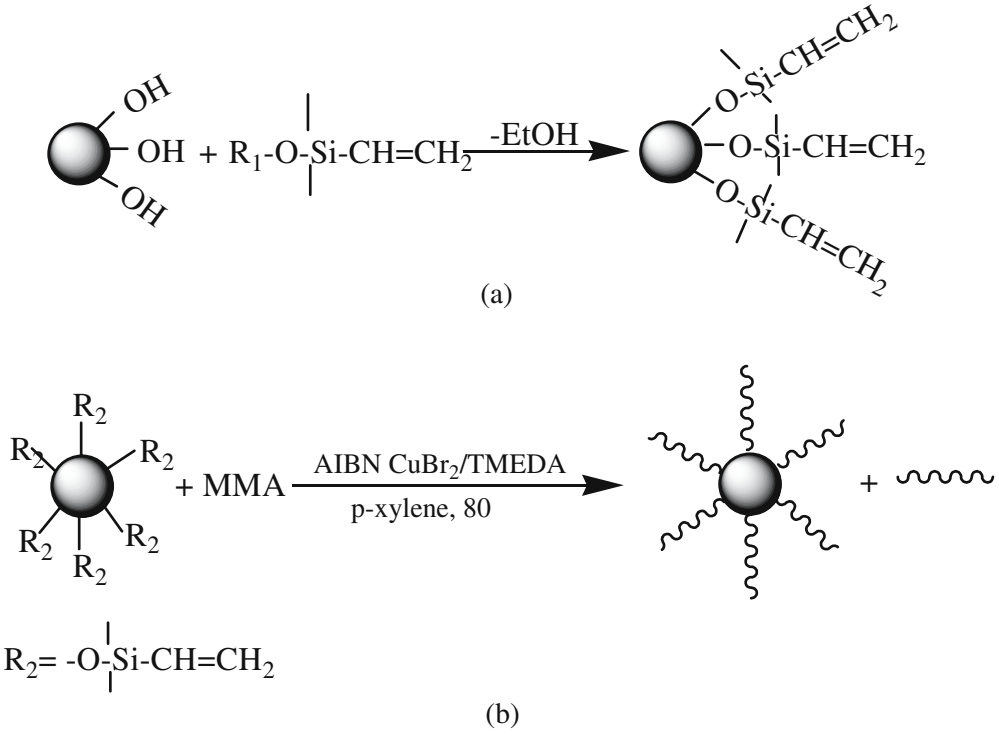
Element	*I*	*S*
Si	3,083.8	0.29
Ca	16,510.7	1.58

sion in ethanol to remove adsorbed modifying agent, and the volatile materials were removed by drying at 60 °C. Then, the modified $CaCO_3/SiO_2$ composite particles were heated with monomer, copper(II) bromide, ligand, initiator, and solvent to carry out a standard reverse ATRP. Samples were taken periodically to monitor the conversion and molecular weight. Conversions of MMA were measured gravimetrically.

To get information about the molecular weight and molecular weight distribution of the grafting polymer, the $CaCO_3/SiO_2$ composite particle core was etched by HCl and HF. A 5% HF aqueous solution and a phase transfer catalyst were added to *p*-xylene suspension of the PMMA/$CaCO_3/SiO_2$ three-component composite particles and stirred vigorously for 2 h to remove the silica. Then, the aqueous layer was removed. To the *p*-xylene suspension, a 5% HCl aqueous solution was added, and the mixture was stirred for 2 h. The organic layer was collected, the polymer was isolated by precipitation from methanol, and filtration and drying were performed to remove the volatiles. To measure its molecular weight and molecular weight distribution, GPC was employed.

Shown in Figs. 4 and 5 are the kinetic results and molecular weight vs conversion curve for the reverse ATRP of MMA in the presence of modified $CaCO_3/SiO_2$ particles. From Fig. 4, it can be seen that the logarithmic conversion data $\ln([M]_0/[M])$ increases linearly with time within the error of the experiment, which illustrates that the polymerization is quite accurately of the first-order up to higher conversion. This result indicates that the propagating active species are constant during the polymerization. The straight line, however, is not through the origin, indicating that the polymerization has an induction period. The plots of number-average molecular weight and molecular weight distribution vs conversion are shown in Fig. 5. From this figure, two important features of controlled/"living" radical polymerization are gained. One feature is that the number-average molecular weight increases linearly with monomer conversion within the error of experiment, which means that the amount of growing chains is constant and there are essentially no chain termination and chain transfer. Another feature is the narrow molecular weight distribution (Mw/Mn<1.25), indicating that all chains grow simultaneously.

As the polymerization principle of the system, described in Scheme 2, it showed that polymerization was occurring both from the surface and in solution. Do the chains grow at the same rate? The GPC results can answer this question. The molecular weight distribution of every polymer sample is narrow (shown in Fig. 5), and the GPC curve appears to be a monomodal distribution of molecular weight (shown in Fig. 6). These results indicate that all the chains, no



Scheme 2 Schematic diagrams of **a** modification of $CaCO_3/SiO_2$ composite particles and **b** grafting of methyl methacrylate onto the surface of $CaCO_3/SiO_2$ composite particles via reverse ATRP

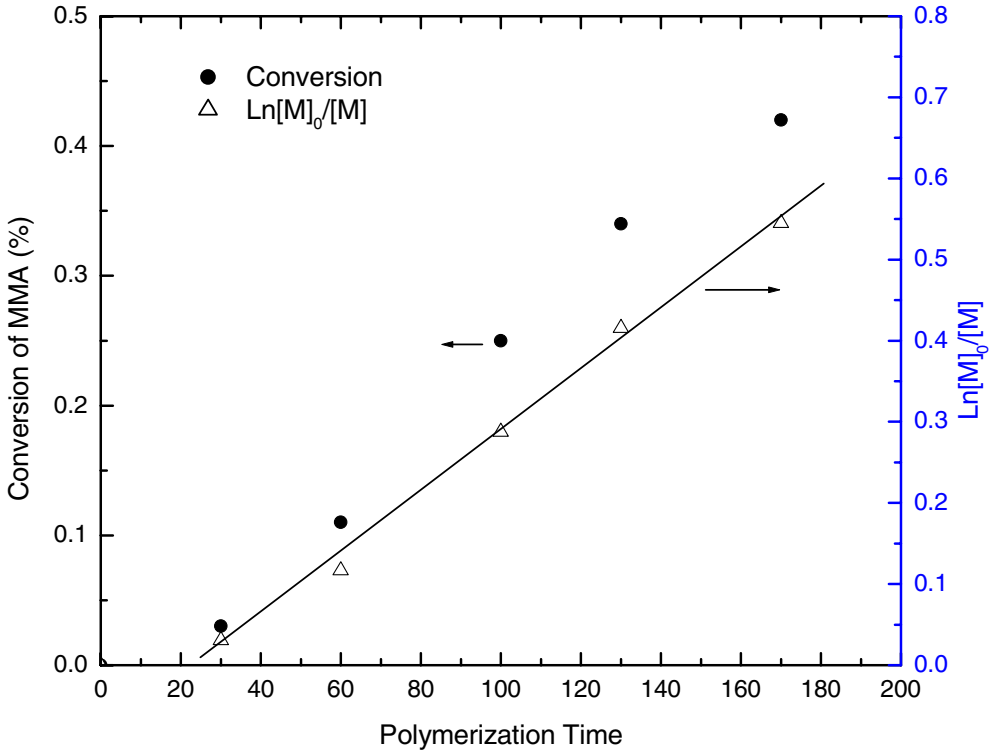


Fig. 4 First-order kinetic plot for the reverse ATRP of MMA in the presence of modified $CaCO_3/SiO_2$ composite particles

matter where they were from, were growing at the same rate. If they grew at different rate, the molecular weight distribution would be wide and the GPC curve would show a dimodal distribution of molecular weight. Additional analyst of this system was carried out by separating the polymer chains grafted from the surface of $CaCO_3/SiO_2$ particles from the polymer chain grown in the solvent. A large quantity of the obtained mixture in this polymerization was suspended in *p*-xylene and then centrifuged. The supernatant was decanted and precipitated in methanol to isolate the free polymer. Fresh *p*-xylene was added to the mixture, and the process was repeated several times until

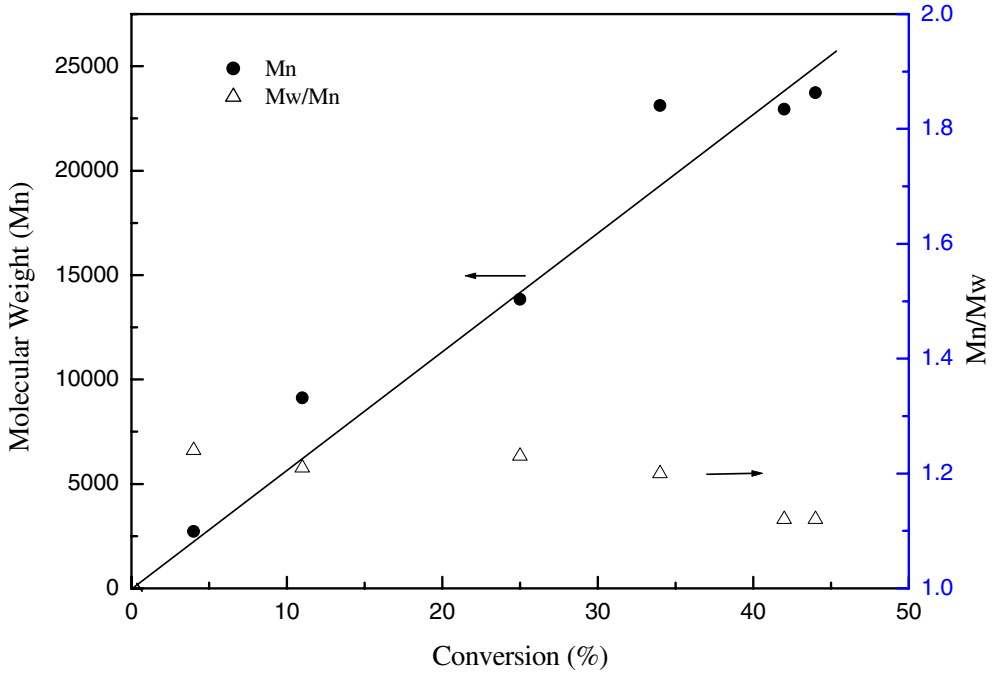


Fig. 5 Molecular weight (Mn) and molecular weight distribution (Mw/Mn) vs conversion in the reverse ATRP of MMA in the presence of modified $CaCO_3/SiO_2$ composite particles

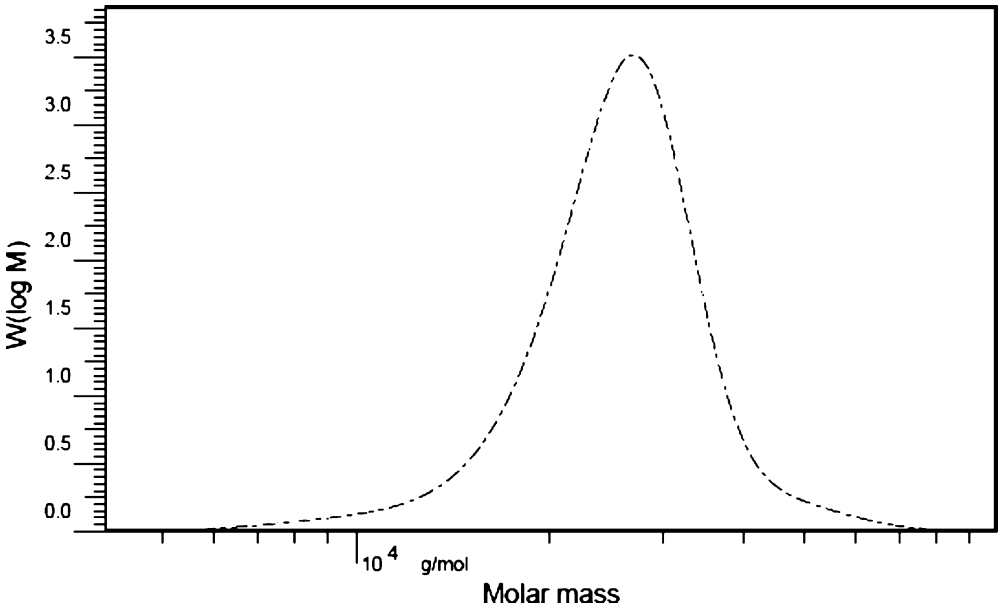


Fig. 6 GPC chromatograms for the reverse ATRP of MMA in the presence of modified $CaCO_3/SiO_2$ composite particles

no free polymer could be precipitated when the supernatant was added to methanol. The graft polymer was obtained by etching $CaCO_3/SiO_2$ core with HCl and HF followed by precipitation. Both of the samples were measured by GPC, and the results were shown in Table 2. From the table, it can be seen that both the number-average molecular weight and the molecular distribution of the free polymer and the graft polymer are approximately equal. This result confirms the conclusion that either the polymer chain grafting from the surface or the polymer chain occurring in solvent is growing at the same rate.

To account for the polymerization of MMA from the surface of $CaCO_3/SiO_2$ particles, FTIR and TGA measurements were carried out. Before measurement, the sample was extracted by THF for 72 h. The free PMMA would be extracted, and the remaining PMMA was supposed to be grafted onto the surface of $CaCO_3/SiO_2$ particles. To make sure that all the free PMMA had been extracted, the purified PMMA/$CaCO_3/SiO_2$ three-component composite

Table 2 GPC data for the free and surface-bound polymer chains from the reverse ATRP of MMA in the presence of modified $CaCO_3/SiO_2$ composite particles

	Molecular weight (Mn)	Mw/Mn
Free polymer in solution	2.61×10^4	1.20
Surface-grafted polymer	2.68×10^4	1.21

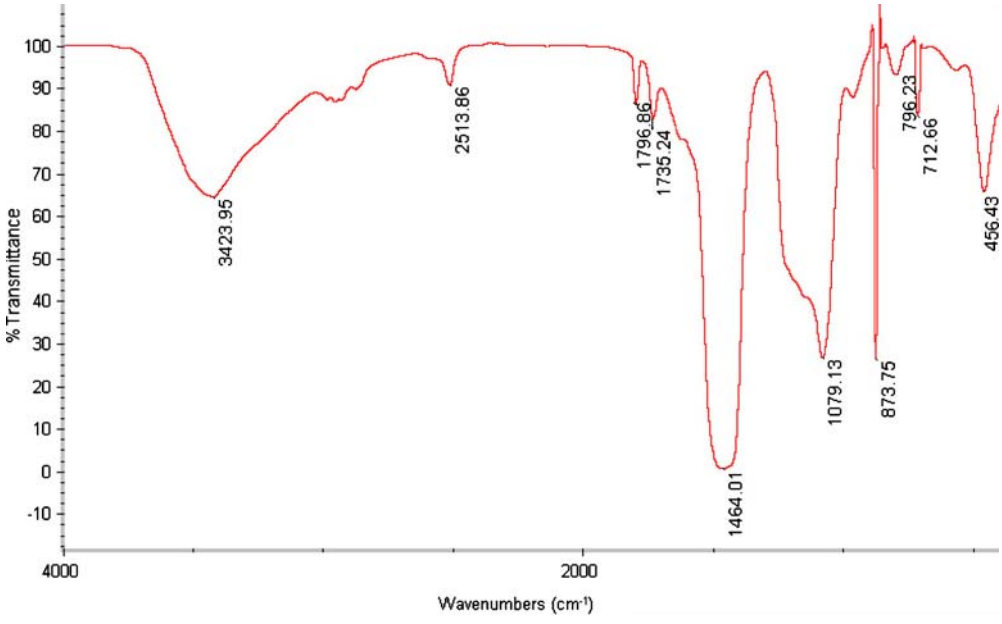


Fig. 7 FTIR spectrum of the PMMA/$CaCO_3/SiO_2$ three-component composite particles

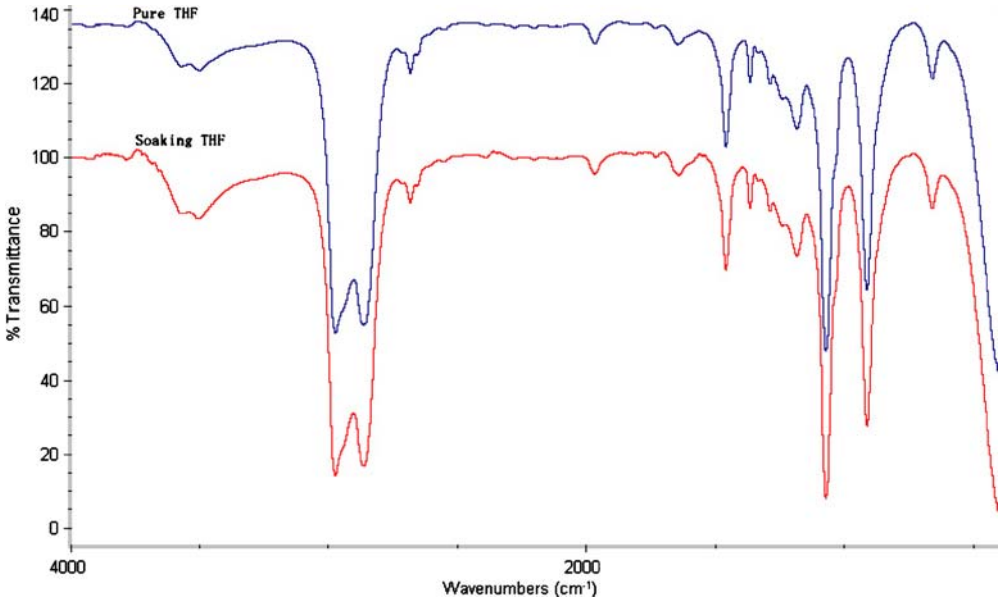


Fig. 8 FTIR spectra of the pure THF and the THF in which the $CaCO_3/SiO_2$ was soaked

particles were soaked in fresh THF for another 4 h, the particles were separated by filtration, and the THF solvent was collected. Shown in Figs. 7 and 8 are the FTIR spectra of PMMA/$CaCO_3/SiO_2$ and that of THF, respectively. From Fig. 8, it can be seen that there was no difference between the spectra of the soaking THF and the pure THF within the error of experiment, indicating that all the free PMMA had been extracted. Figure 7 shows the IR spectrum of PMMA/$CaCO_3/SiO_2$ three-component composite particles. From the figure, the characteristic absorption band of carbonyl (>C=O) in PMMA at 1,735 cm^{-1} is observed. The result showing that the PMMA molecules were grafted onto the surface of $CaCO_3/SiO_2$ composite particles was measured using TGA. As the free PMMA was extracted before TGA measurement, the lost mass and the remains of the sample during TGA measurement can substitute the mass of PMMA grafted and that of $CaCO_3/SiO_2$ composite particles in Eq. 2. The TGA result of the extracted PMMA/$CaCO_3/SiO_2$ particles was shown in Fig. 9. In the figure, the lost mass is 8%, which represents the mount of PMMA grafting onto the surface of $CaCO_3/SiO_2$ particles, and the percentage of the remains of the

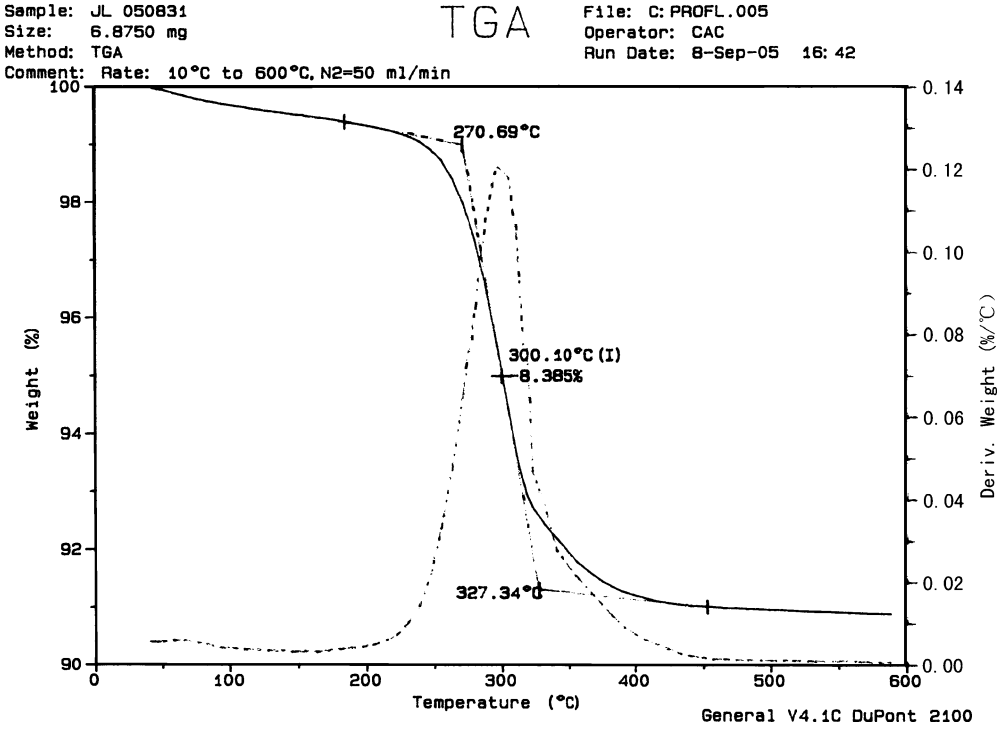


Fig. 9 Thermogravimetric analysis curve of the PMMA/$CaCO_3/SiO_2$ three-component composite particles

sample is 92%. Thus, the grafting percentage is 8.7%, according to Eq. 2, while the conversion of MMA is 42% as measured gravimetrically; the grafting efficiency can be calculated as 2.2% according to Eq. 3. In-depth research on increasing the grafting percentage and the grafting efficiency is ongoing in our laboratory, and the results will be reported as soon as possible.

Conclusion

Polymerization of MMA in the presence of modified $CaCO_3/SiO_2$ exhibits the features of controlled/"living" radical polymerization. First-order kinetic plots and linear increase of molecular weight (Mn) vs conversion were observed. Moreover, the molecular weight distribution of every polymer sample is narrow (Mw/Mn<1.25). Further researches on the polymerization indicate that both the free PMMA chains from the solvent and the graft PMMA chains from the surface of $CaCO_3/SiO_2$ inorganic particles were growing simultaneously. Even though the grafting percentage and the grafting efficiency are low and need to increase, which is the focus of our following work, this research provides a novel method for preparing well-defined multicomponent polymer/inorganic composite via reverse ATRP under relatively tolerant and innoxious reaction conditions comparing with that of traditional ATRP.

Acknowledgement The authors are grateful to the National Natural Science Foundation of China (20374036) for the support of this research.

References

1. Gvishi R, Narang U, Ruland G, Kumar DN (1997) Appl Organomet Chem 11:107–127
2. Armes SP (1995) Polym News 20:233–237
3. Godovsky DY (1995) Adv Polym Sci 119:79–122
4. Cosgrove T, Fleer GJ, Cohen Stuart MA, Scheutjens JM, Vincent B (1993) Polymers at interfaces. Chapman & Hall, London, UK
5. Prucker O, Ruehe J (1998) Macromolecules 31:592–601
6. Prucker O, Ruehe J (1998) Macromolecules 31:602–613
7. Flory PJ (1953) Principles of polymer chemistry. Cornell University Press, Ithaca, New York, pp 51–57
8. Otsu T, Kuriyama A (1983) J Macromol Sci Chem A21:961–977
9. Fukuda T, Terauchi T, Goto A, Ohno K, Tsujii Y, Miyamoto T, Kobatake S, Yamada B (1996) Macromolecules 29:6393–6398
10. Fukuda T, Terauchi T, Goto A, Ohno K, Tsujii Y, Miyamoto T, Shimizu Y (1996) Macromolecules 29:3050–3052
11. Chiefari J, Chong YK, Ercole F, Krstina J, Jeffery J, Le TPT, Mayadunne RTA, Meijs GF, Moad CL, Moad G, Rizzardo E, Thang SH (1998) Macromolecules 31:5559–5562
12. Mayadunne RTA, Rizzardo E, Chiefari J, Chong YK, Moad G, Thang SH (1999) Macromolecules 32:6977–6980
13. Wayland BB, Poszmik G, Mukerjee SL, Fryd M (1994) J Am Chem Soc 116:7943–7944
14. Kato M, Kamigaito M, Sawamoto M, Higashimura T (1995) Macromolecules 28:1721–1723
15. Granel C, Dubois P, Jerome R, Teyssie P (1996) Macromolecules 29:8576–8582
16. Wang JS, Matyjaszewski K (1995) Macromolecules 28:7572
17. Matyjaszewski K, Patten TE, Xia J (1997) J Am Chem Soc 119:674–680
18. Davis KA, Paik H-J, Matyjaszewski K (1999) Macromolecules 32:1767–1776
19. Wang J-L, Grimaud T, Matyjaszewski K (1997) Macromolecules 30:6507–6512
20. Bin Z, William JB (1999) J Am Chem Soc 121:3557–3558
21. von Werne T, Patten TE (1999) J Am Chem Soc 121:7409–7410
22. von Werne T, Patten TE (2001) J Am Chem Soc 123:7497–7505
23. Matyjaszewski K, Miller PJ, Shukla N, Immaraporn B, Gelman A, Luokala BB, Siclovan TM, Kickelbick G, Vallant T, Hoffmann H, Pakula T (1999) Macromolecules 32:8716
24. Bei J, Pang JB, Qiu KY, Wei Y (2002) Chin J Polym Sci 20:261–267
25. Nakagawa P, Miller PJ, Matyjaszewski K (1998) Polymer 39:5163–5170
26. Patten TE, Matyjaszewsk K (1998) Adv Mater 10:1–15
27. Guifeng Li, Jinda Fan, Rong Jiang, Yong Gao (2004) Chem Mater 16:1835–1837
28. Peng Liu, Jun Tian, Weimin Liu, Qunji Xue (2004) Polym Int 53:127–130
29. Kickelbick G, Holzinger D, Brick C, Trimmel G, Moons E (2002) Chem Mater 14:4382–4389
30. Gravaimo, Stefanie M, Dumas R, Liu K, Patten TE (2005) J Polym Sci A Polym Chem 43:3675–3688
31. Moineau G, Dubois P, Jerome R, Senningger T, Teyssie P (1998) Macromolecules 31:545
32. Wang, JS, Matyjaszewski K (1995) Macromolecules 32:5199
33. Xia JH, Matyjaszewski K (1997) Macromolecules 30:7692
34. Kortan AR, Hull R, Opila RL, Bawendi MG, Steigerwald ML, Carroll PJ, Brus LE (1990) J Am Chem Soc 112:1317–1332
35. Peng X, Schlamp MC, Kadavanich AV, Alivisatos AP (1997) J Am Chem Soc 119:7019–7029
36. Jiang L, Dan Y (2004) Colloid Polym Sci 282:1374–1380
37. Pan K, Dan Y (2006) J Appl Polym Sci (Accepted for publication)
38. Yuanhua Y, Dan Y (2003) Colloid Polym Sci 281:794–799
39. Stober W, Fink A, Bohn E (1968) J Colloid Interface Sci 26:62–69
40. Ohmori M, Matijevic E (1992) J Colloid Interface Sci 150:594
41. Ohmori M, Matijevic E (1993) J Colloid Interface Sci 160:288–292
42. Tsubokawa N, Fujiki K, Sone Y (1988) Polym J 20:213–220
43. Plyuto IV, Shpak AP, Babich IV, Plyuto YV, Sharanda LF, Stoch J, Moulijn JA (1999) Surf Interface Anal 27: 911–914