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Reverse Atom Transfer Radical Polymerization of MMA in the Presence of $CaCO_3/SiO_2$ Two-Component Composite Particles

*Long Jiang, Kai Pan, Juan Zhang, Yi Dan**

Summary: We previously discovered that structurally well-defined polymer/inorganic composite particles, i.e., poly(methyl methacrylate) (PMMA)/$CaCO_3/SiO_2$ three-component composite particles, can be achieved via reverse atom transfer radical polymerization (ATRP), using 2,2′-azo-bis-isobutyronitrile as initiator and Cu^{II} bromide as catalyst. In the present study, the influence of the mass ratio of $CaCO_3/SiO_2$ two-component composite particles to methyl methacrylate (MMA) on the rate and behavior of the polymerization was studied in detail. The results illustrate that increasing the mass ratio of $CaCO_3/SiO_2$ two-component composite particles will decrease the overall rate of polymerization of MMA under standard reverse ATRP conditions. Thermal properties of the obtained well-defined particles were characterized and determined by thermogravimetric analysis (TGA). The results indicate that well-defined PMMA chains grafted on the surface of $CaCO_3/SiO_2$ particles were only degraded by random chain scission of C–C linkages within the PMMA chain, which is different from the degradation of PMMA chains prepared via traditional radical polymerization. This difference is reasonably ascribed to the difference between the end groups of PMMA prepared via reverse ATRP and that via traditional radical polymerization, which has been confirmed by end group analysis measured by ^1H–NMR spectroscopy.

Keywords: $CaCO_3/SiO_2$ two-component composite particles; poly(methyl methacrylate); reverse ATRP; thermal property

Introduction

Polymer/inorganic composite materials have attracted much interest in both theoretical and applied research fields because of the combination of both the properties of the inorganic particles (optical, electronic, and magnetic) and those of the polymer (easy processing and good solubility).[1–3] The use of classic free radical polymerization to prepare polymer/inorganic composite materials is one of the most convenient and effective methods because of its advantages,[4] such as tolerance of impurities and functional groups, a large variety of vinyl monomers for polymerization and copolymerization, and mild reaction conditions, but there is poor control over chain length, chain structure, and terminal chain functionality of the resultant polymer.

A controlled/‘living’ radical polymerization such as atom transfer radical polymerization (ATRP) is, therefore, a possible method to synthesize polymers with well-defined structure and controlled molecular weight distribution. With regards to the formation of well-defined polymer/inorganic materials, ATRP is preferred to other controlled/‘living’ radical polymerizations, because the initiator of ATRP can be attached to a surface of inorganic materials to make the polymer chains grow from the surface. Such is a case with a study by von

State Key Laboratory of Polymer Materials Engineering (Sichuan University), Polymer Research Institute of Sichuan University, Chengdu 610065, P. R. China
E-mail: ph9nix@163.com

Werne and Patten.[5] In this study, well-defined poly(methyl methacrylate) (PMMA) and polystyrene (PSt) were grafted from the surface of spherical SiO_2 particles where initiator molecules of ATRP (2-(4-chloromethylphenyl)ethyldimethylethoxysilane) were previously immobilized. The influence of particle size of SiO_2 on the polymerization kinetics and molecular weight control was carefully studied by von Werne and Patten, and the results showed that polymerization of MMA and St via ATRP is controlled with smaller silica particles (75 –nm diameter) but not in the case of larger silica particles (300 –nm diameter). Using the work of von Werne and Patten as a base, ATRP was successfully used to prepare poly(*n*-butyl acrylate)/SiO_2 composite particles by Carrot et al.[6] Carrot et al. investigated the effect of solvent polarity on polymerization rate and behavior in detail. Subsequently, numerous works using ATRP to graft well-defined polymer chains from the surface of inorganic materials were documented.[7–9]

From the above investigations, we can see that using ATRP to prepare well-defined polymer/inorganic composite materials has been well studied. Nevertheless, the reported works focused almost solely on the conventional ATRP method using organic halides as initiators and transition metals in the lower oxidation state, such as Cu^{I}, as catalyst. In this case, before copolymerization with monomers, inorganic particles need to be modified by specific ATRP initiator molecules which are not commercial or very expensive. Besides the cost of the initiator, the conventional ATRP method has other problems: the organic halides are toxic, and the catalysts Mt^n/Lx are easily oxidized by air. To overcome these drawbacks, reverse ATRP would be optimal. In our laboratory a series of systematical studies on the preparation of well-defined polymer/inorganic composite particles via reverse ATRP are proceeding. Some works, i.e., the method to graft polymer onto the surface of inorganic particles via reverse ATRP, have been reported.[10] We previously disclosed that well-defined PMMA can covalently graft from the surface of $CaCO_3/SiO_2$ two-component composite particles which were only modified by a commercial vinyl silane coupling agent prior to polymerization. As disclosed in the article, modified $CaCO_3/SiO_2$ two-component composite particles copolymerized with MMA though the C=C groups provided by the silane coupling agent. Thus, it is expected that the $CaCO_3/SiO_2$ two-component composite particles may affect the behavior of the reverse ATRP of MMA, which was not clearly explored in the paper and needed further research.

In the present work, we are particularly interested in the polymerization kinetics of MMA in the presence of $CaCO_3/SiO_2$ two-component composite particles. The thermal properties of PMMA prepared by reverse ATRP are also studied in this paper. The reverse ATRP of MMA in the presence of $CaCO_3/SiO_2$ two-component composite particles were conducted using Cu^{II} bromide as catalyst and 2,2′-azo-bis-isobutytonitrile (AIBN) as initiator.

Experimental Part

Materials

Methyl methacrylate (MMA) was purchased from Chengdu Kelong Chemical Reagent Factory (Chengdu, China) and distilled at a reduced pressure prior to use. 2,2′-Azo-bis-isobutyronitrile (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 (A.R.) from Chengdu Kelong Chemical Reagent Factory (Chengdu, China), was used directly. The modifying agent from Ha'erbin Chemical Research Institute (Ha'erbin, China), was used without further purification. The *p*-xylene, tetrahydrofuran (THF), and methanol used in this work were used as received from Chengdu Kelong Chemical Reagent Factory (Chengdu, China). $CaCO_3/SiO_2$ inorganic composite particles, with an average diameter of about 70 nm, were prepared in our laboratory.[10–13] All other reagents employed in the work were purchased commercially and used without further purification.

Modification of the $CaCO_3/SiO_2$ Two-Component Composite Particles

Before polymerization, the $CaCO_3/SiO_2$ composite particles were modified by a silane coupling agent. A general procedure for the surface modification reaction was as follows: to a three necked flask was added a $CaCO_3/SiO_2$ composite particle suspension in ethanol, and the suspension was heated to 40 °C. To this suspension the 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 hours. It was then heated at 80 °C for 8 hours. 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.

Reverse ATRP of MMA in the Presence of $CaCO_3/SiO_2$ Two-Component Composite Particles

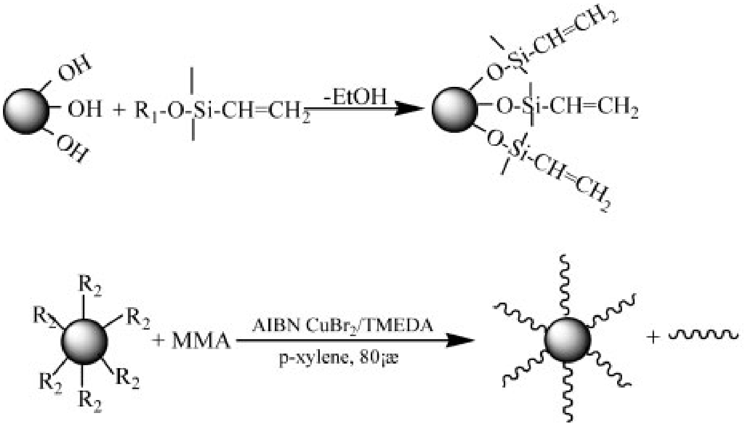
Typically, the experiments described in this work were conducted with the following ratios: $[MMA]/[AIBN]/[CuBr_2]/[TMEDA] = 600/1.6/1/2$ and MMA/*p*-xylene = 3/7 (v/v). The mass ratio of modified $CaCO_3/SiO_2$ two-component composite particles to MMA was in the range of 1:40 to 1:5. To a 150 mL Schlenk flask that contained a stirrer bar was added modified $CaCO_3/SiO_2$ composite particles, $CuBr_2$, and AIBN. MMA, p-xylene, and TMEDA 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 via a syringe to monitor the conversion and molecular weight. The monomer conversion was determined gravimetrically, and the samples were redissolved in THF and precipitated into methanol to obtain the PMMA/$CaCO_3/SiO_2$ three-component composite particles.

Characterization

The conversion of MMA was determined gravimetrically. The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n, where M_w is the weight-average molecular weight) of the resultant polymer samples were measured at 35 °C by gel permeation chromatography (GPC) on a Waters 2410 instrument using THF as the solvent (1 mL/min). Calibration was made using monodispersed polystyrene as the standards. The thermogravimetric analysis (TGA) of PMMA/$CaCO_3/SiO_2$ three-component composite particles was performed with a Dupond 2100 thermal analysis instrument. The samples were heated over a temperature range of 25–600 °C with a rate of 10 °C per min in a nitrogen atmosphere, and the nitrogen flow rate was 50 mL per min. ^1H NMR spectra of all the samples were determined using a Bruker ARX400 (400 MHz) spectrometer at 25 °C, using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal reference.

Results and Discussion

In this present work, $CaCO_3/SiO_2$ two-composite particles with $CaCO_3$ as core and SiO_2 as shell were employed. To graft polymer from its surface, the $CaCO_3/SiO_2$ two-component composite particles were modified with a silane coupling agent. The couping agent consists of siloxane groups, which provide a site for covalent attachment to the surface of the SiO_2 shell, and vinyl groups that can react with MMA in the copolymerization (see Scheme 1). Although our previous work has proven that well-defined PMMA/$CaCO_3/SiO_2$ composite particles can be prepared by this method, there has been no systematic investigation of the affecting factors, such as initiator concentration, catalyst concentration, and the mass ratio of MMA to



Scheme 1.
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.

$CaCO_3/SiO_2$, etc., on the polymerization rate and behavior of the reverse ATRP of MMA in the presence of $CaCO_3/SiO_2$ composite particles. In this research, the influence of the mass ratio of MMA to $CaCO_3/SiO_2$ two-component composite particles on the kinetics of the reverse ATRP of MMA was studied in detail.

To study the influence of the mass ratio of the $CaCO_3/SiO_2$ two-component composite particles to MMA (abbreviated as CS-CPs*:MMA in this paper), reverse ATRP of MMA with a series of CS-CPs*:MMA ratios in range of 1:40 to 1:5 were carried out. The other reaction conditions were the same as described in experimental section, and samples were taken periodically to monitor the conversion. Shown in Figure 1 is the influence of CS-CPs*:MMA on the kinetics of the reverse ATRP of MMA. From this figure, it can be seen that the overall rate of polymerization decreased upon increasing the amount of modified $CaCO_3/SiO_2$ two-component composite particles, which means that the $CaCO_3/SiO_2$ can affect the rate and behavior of the reverse ATRP. From the plots of lograrithmic conversion data $\ln([M]_0/[M])$ versus polymerization time shown in Figure 1, it can be seen that while CS-CPs*:MMA is smaller than 1:10, $\ln([M]_0/[M])$ increases linearly with time within the error of the experiment, which illustrates that the polymerization appears to follow first-order kinetics up to high conversion. This first-order relationship shows that the concentrations of the propagating active species remains nearly constant throughout the course of the polymerization, and that no termination occurs, which is one of the characteristics of a controlled/'living' radical polymerization. These results indicate that the $CaCO_3/SiO_2$ two-component composite particles did not affect the control of the polymerization, but only slowed down the overall rate of polymerization when the CS-CPs*:MMA ratio is suitable. However, from this figure, it can still be seen that the plot of $\ln([M]_0/[M])$ versus polymerization time shows a deviation from linear correspondence when the CS-CPs*:MMA ratio is increased to 1:5. The upward curvature of the plot implies that the rate of polymerization is slower during the early stages of polymerization.

The influence of the $CaCO_3/SiO_2$ two-component composite particles on the rate and behavior of the reverse ATRP of MMA most likely can be ascribed to differences between the activity of immobilized active polymer chain grafted on the surface of inorganic particles and that of free active polymer chain in solvent. Scheme 2 illustrates the possible propagation modes for the reverse ATRP of MMA in the presence of modified $CaCO_3/SiO_2$ two-component

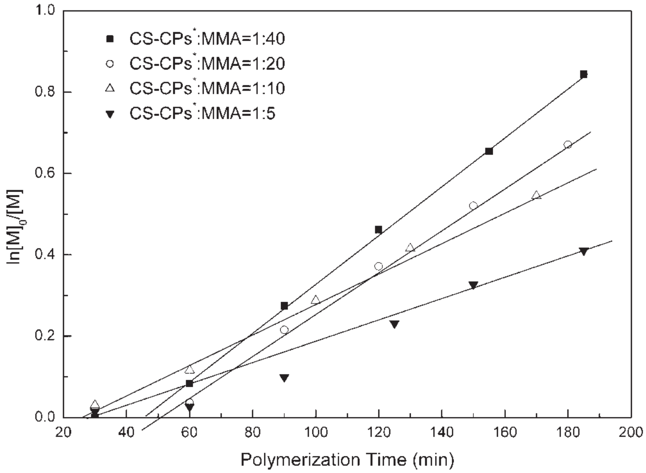
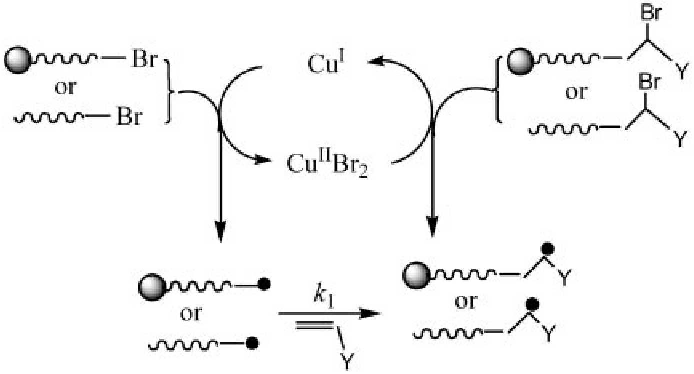


Figure 1.
Kinetics plot of the polymerization of MMA in the presence of modified $CaCO_3/SiO_2$ composite particles (Reaction condition: $V_{MMA}:V_{p\text{-xylene}} = 3:7$, $[MMA]_0:[AIBN]:[CuBr_2]:[TMEDA] = 600:1.6:1:2$, $T = 80\,^{\circ}C$).

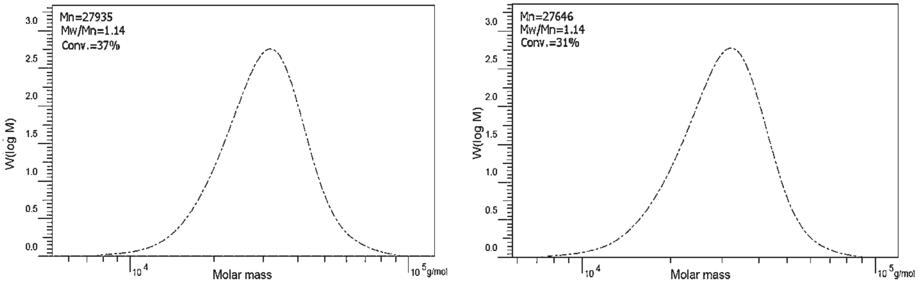
composite particles. From this scheme, it can be seen that 1) the propagation of the polymer chain occurred not only on the surface of the inorganic particles, but in solvent; 2) the active polymer chain immobilized on the surface of the inorganic particle had less freedom to diffuse than that in solvent, which indicates the difference of activity between them. Typically, no more than 1% of the total polymer chains are activated in reverse ATRP at the same time,[14] which is different from the traditional radical polymerization. Thus, the activity of the active polymer chains controls the total rate of the polymerization. The greater the number of low-activity polymer chains (the active polymer chains are immobilized on the surface of the inorganic particles) in the reaction system, the slower the total rate of polymerization. In this system, upon increasing the amount of $CaCO_3/SiO_2$ two-component composite particles, the possibility and numbers of active polymer chains immobilized on the surface of the inorganic particles increases, which results in a reduction of the total rate of the polymerization, as shown in Figure 1. From these results, it can be expected that



Scheme 2.
Schematic diagram of the possible propagation modes for the reverse ATRP of MMA in the presence of modified $CaCO_3/SiO_2$ composite particles.

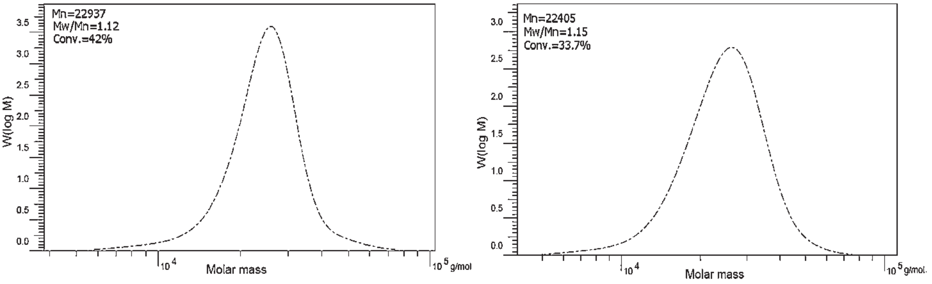
the rate of the polymerization would be apparently affected by the change of activity of the active polymer chains attached to inorganic particles when the amount of $CaCO_3/SiO_2$ two-component composite particles is high enough. At the early polymerization stage, the polymer chains grown from the surface of the inorganic particles were short and closely attached to the inorganic particles surface, so the rate of polymerization was very slow. As the polymer chains grow and the active chain end becomes less closely associated with the inorganic particles surface and have more freedom to diffuse, so the total rate of the polymerization is faster, which leads to the upward curvature of the plot of $\ln([M]_0/[M])$ versus polymerization time, as shown in Figure 1 when the CS-CPs*:MMA ratio increases to 1:5.

Another impotant characteristic of controlled/'living' polymerization is that the molecular weight distribution of the obtained polymer should be narrow. To obtain information about the molecular weight and molecular weight distribution of the grafted PMMA, the $CaCO_3/SiO_2$ two-component composite particle core was etched by HCl and HF. A 5% HF aqueous solution and a phase transfer catalyst were added to a *p*-xylene suspension of the PMMA/$CaCO_3/SiO_2$ composite particles and stirred vigorously for 2 h to remove the silica. The aqueous layer was then 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 Figure 2 are the GPC results of PMMA prepared via reverse ATRP in the presence of various amounts of $CaCO_3/SiO_2$ two-component composite particles. From the figure, it can be seen that each polymer sample had a narrow molecular weight distribution (M_w/M_n <1.2), and all the GPC



CS-CPs*:MMA=1:40

CS-CPs*:MMA=1:20



CS-CPs*:MMA=1:10

CS-CPs*:MMA=1:5

Figure 2.

Effect of the mass ratios of the modified $CaCO_3/SiO_2$ two components composite particles to MMA (CS-CPs*:MMA) on the molecular weight of PMMA prepared via reverse ATRP.

curves show Gaussian distributions, which illustrates that the polymer chains all grow at the same rate. These results confirm the conclusion mentioned above that the $CaCO_3/SiO_2$ two-component composite particles did not affect the control of the polymerization, but only slowed down the overall rate of polymerization.

In order to understand the thermal properties of the $PMMA/CaCO_3/SiO_2$ composite particles prepared via reverse ATRP, the decomposition of the obtained particles was determined by TGA. Before the measurement, $PMMA/CaCO_3/SiO_2$ composite particles were purified by extracting with THF for 72 hours to remove the ATRP catalyst and any possible ungrafted chains. Although numerous studies have been performed on the thermal properties of PMMA and PMMA/inorganic composite particles prepared by traditional radical polymerization,[15–17] there has been no study of the thermal properties of PMMA/inorganic composite particles prepared via reverse ATRP. It has been shown that the end groups of the polymer chain might have significant effects on the thermal stability of the polymers.[15,16] Thus, it is expected that the $PMMA/CaCO_3/SiO_2$ composite particles will display a novel thermal degradation behavior due to the different end groups of the PMMA prepared via ATRP and that via traditional radical polymerization. A comparison of the TGA results between the $PMMA/CaCO_3/SiO_2$ composite particles prepared via reverse ATRP and those prepared via traditional radical polymerization is shown in Figure 3. The traditional radical polymerized $PMMA/CaCO_3/SiO_2$ composite particles were prepared as described in ref.[18], and both of the samples were purified by extracting with THF for 72 hours to remove catalyst, initiator, and un-grafted polymer chains. From this figure, it can be seen that the TGA curve of sample A (the traditional radical-polymerized $PMMA/CaCO_3/SiO_2$ composite particles) shows a two-step weight loss, around 250 and 360 °C, at a heating rate of 10 °C per min in a nitrogen atmosphere; but for sample B (well-defined $PMMA/CaCO_3/SiO_2$ composite particles prepared via reverse ATRP), only a one-step weight loss was observed under the same measurement conditions. The differences might result from the difference of the polymerization methods. As described the ref. [15,16], if MMA is polymerized by a free-radical initiator, a termination reaction

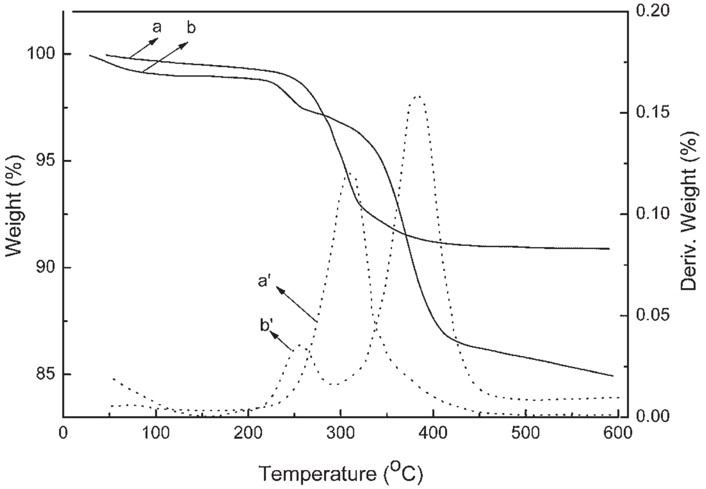
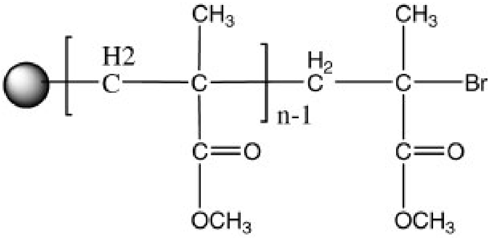


Figure 3.
TGA curves of (a) $PMMA/CaCO_3/SiO_2$ composite particles prepared via reverse ATRP (sample a), (b) $PMMA/CaCO_3/SiO_2$ composite particles prepared via traditional radical polymerization (sample b).



Scheme 3.
Schematic diagrams of the structure of the PMMA/$CaCO_3$/SiO_2 three components composite particles.

will occur mainly through disproportionation reactions of two radical chains, which will yield an equal number of polymer chains that have an unsaturated end group and saturated end group. A polymer chain that has an unsaturated end group is less thermally stable than that with saturated end groups. Thus, when the temperature is raised to about 250 °C, the unsaturated end groups began to degrade, resulting in the first-step weight loss in the TGA curve. When the temperature increased to about 340 °C, random chain scission at the C–C linkages within the PMMA chain starts to occur, which results in the second-step weigh loss. With regards to the well-defined PMMA/$CaCO_3$/SiO_2 composite particles (sample B), there was no chain termination during the polymerization, and the theoretical end group is shown in Scheme 3. From the scheme, it can be observed that there is no thermally unstable unsaturated group. Thus, the weight loss of the well-defined PMMA was not observed in the range of 160–280 °C, which is the degradation temperature range of unsaturated groups.[16] The degration of PMMA around 300 °C was reasonably ascribed to be the random chain scission of C–C linkages. Additional analysis of the end group of the PMMA grafted onto the $CaCO_3$/SiO_2 composite particles surface was carried out by ^{1}H NMR measurement. Prior to measurement, the core of the $CaCO_3$/SiO_2 compo-

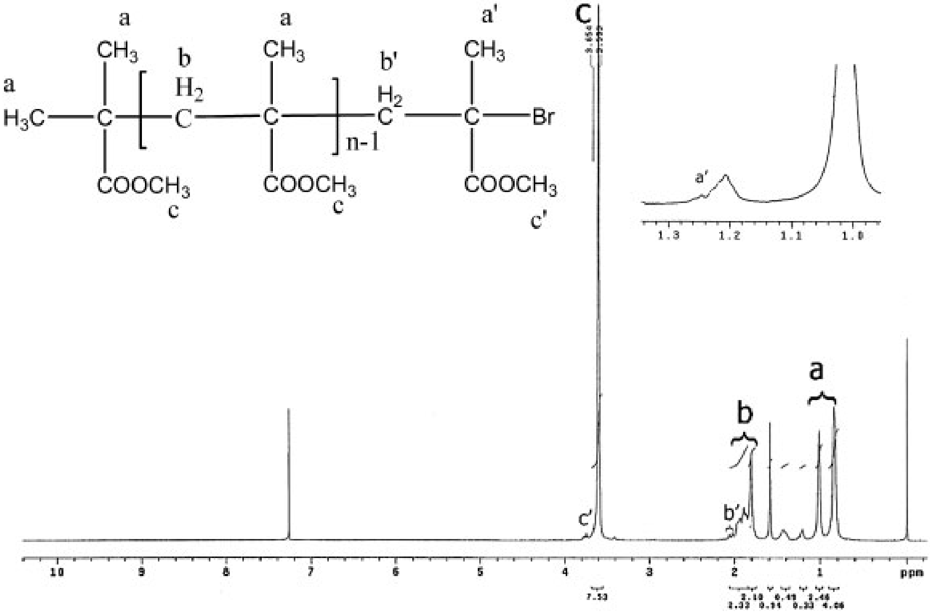


Figure 4.
^{1}H NMR spectrum of PMMA.

site particles was etched and the obtained PMMA was dissolved in THF, and then passed through a neutral aluminum oxide column to remove the catalyst. The polymer was purified by precipitation into methanol. Figure 4 shows a representative ^{1}H NMR spectrum of the well-defined PMMA from the surface of $CaCO_3/SiO_2$ composite particles. From this figure, the characteristic signals of the protons of the methyl groups (peak a) of $–C(CH_3)(COOCH_3)$, methylene groups (peak b) of $–CH_2–$, and methoxy groups (peak c) of $–C(CH_3)(COOCH_3)$ were observed at 0.84–1.02, 1.80–1.97, and 3.6 ppm, respectively. The results illustrate that the chains of the PMMA only have methyl groups and methylene groups. Meanwhile, the signals at 1.25 (peak a'), 2.02–2.06 (peak b'), and 3.7 ppm (peak c') can be found in this spectrum, which indicates that one end group of the PMMA chain is a bromine atom.[19,20] Because of the electron withdrawal from bromine atom, the resonances shifted from 0.84–1.02 ppm to 1.25 ppm for the methyl protons, from 1.80–1.97 ppm to 2.02–2.06 ppm for the methylene protons, and from 3.6 ppm to 3.7 ppm for the methoxy protons. On the other hand, no characteristic signals of vinyl protons can be found in this ^{1}H NMR spectrum. Thus, the ^{1}H NMR results indicate that the PMMA prepared via reverse ATRP in the presence of $CaCO_3/SiO_2$ composite particles have bromide ends, corresponding to the results of TGA.

Conclusion

The influence of $CaCO_3/SiO_2$ two-component composite particles on the rate and behavior of the reverse ATRP of MMA was studied in detail. Increasing the proportion of $CaCO_3/SiO_2$ two-component composite particles in the reaction system would decrease the overall polymerization rate of MMA. Meanwhile, it was also observed that there is no significant influence of $CaCO_3/SiO_2$ two-component composite particles on the molecular weight distribution of PMMA chains prepared via reverse ATRP. This factor is important for the preparation of structurally well-defined polymer/inorganic composite particles via reverse ATRP. Further research on the thermal properties of the obtained PMMA/$CaCO_3/SiO_2$ composite particles indicate that well-defined PMMA chains grafted on the inorganic particle surface are only degraded by random scission of C–C linkages within the PMMA chain. This finding may help to improve the thermal stability of the resultant composite particles.

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[1] R. Gvishi, U. Narang, G. Ruland, D. N. Kumar, *Appl. Organomet. Chem.* **1997**, *11*, 107.

[2] S. P. Armes, *Polym. News* **1995**, *20*, 233.

[3] D. Y. Godovsky, *Adv. Polym. Sci.* **1995**, *119*, 79.

[4] P. J. Flory, "*Principlesof. Polymer. Chemistry*". Cornell University Press, ITHACA and LONDON p. 51.

[5] T. von Werne, T. E. Patten, *J. Am. Chem. Soc.* **2001**, *123*, 7497.

[6] G. Carrot, S. Diamanti, M. Manuszak, B. Charleux, J.-P. Vairon, *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 4294.

[7] G. Kickelbick, D. Holzinger, C. Brick, G. Trimmel, E. Moons, *Chem. Mater.* **2002**, *14*, 4382.

[8] G. F. Li, J. Fan, R. Jiang, Y. Gao, *Chem. Mater.* **2004**, *16*, 1835.

[9] S. M. Gravaimo, R. Dumas, K. Liu, T. E. Patten, *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 3675.

[10] L. Jiang, K. Pan, Y. Dan, *Colloid Polym. Sci.* **2006**, *285*, 65.

[11] W. Stober, A. Fink, E. Bohn, *J. Colloid Interf. Sci.* **1968**, *26*, 62.

[12] M. Ohmori, E. Matijevic, *J. Colloid Interf. Sci.* **1992**, *150*, 594.

[13] M. Ohmori, E. Matijevic, *J. Colloid Interf. Sci.* **1993**, *160*, 288.

[14] T. von Werne, T. E. Patten, *J. Am. Chem. Soc.* **1999**, *121*, 7409.

[15] T. Hirata, T. Kashiwagi, J. E. Brown, *Macromolecules* **1985**, *18*, 1410.

[16] T. Kashiwagi, A. Inaba, J. E. Brown, *Macromolecules* **1986**, *19*, 2160.

[17] Y. H. Yang, Y. Dan, *Colloid Polym. Sci.* **2003**, *281*, 794.

[18] L. Jiang, Y. Dan, *Colloid Polym. Sci.* **2004**, *282*, 1374.

[19] T. Ando, M. Kamigaito, M. Sawamoto, *Macromolecules* **1998**, *31*, 6708.

[20] X. P. Chen, K.-Y. Qiu, *Macromolecules* **1999**, *32*, 8711.