Synthesis and characterization of poly(methyl methacrylate) using monofunctional polyhedral oligomeric silsesquioxane as an initiator

Lei Liu · Wenping Wang

Abstract POSS/PMMA composite was synthesized by atom transfer radical polymerization (ATRP) at 110 °C using commercial POSSCl as an initiator and CuCl/2,2′-bipyridine as catalyst system. The structures of POSS/PMMA and POSSCl were characterized by Fourier transfer infrared spectroscopy, Nuclear magnetic resonance spectroscopy, Ger permeation chromatography, X-ray diffraction and X-ray photoelectron spectroscopy, which confirmed that Si–Cl bond on POSS cage could successfully initiate the ATRP of methyl methacrylate, so there is only one POSS unit in a PMMA chain. The thermal properties of POSS/PMMA were investigated by Differential scanning calorimetry and Thermogravimetric analysis, the results show that the incorporation of POSS cage results in the enhancement of the glass transition temperature and the decomposition temperature of PMMA, which is mainly attributed to the mono-dispersion of POSS in PMMA matrix at molecular lever.

Keywords Polyhedral oligomeric silsesquioxane (POSS) ·
Atom transfer radical polymerization (ATRP) · Poly(methyl methacrylate) ·
Composites

Introduction

Recently, more and more interests are focused on the synthesis of inorganic-organic hybrid polymers, especially on the polymers containing polyhedral oligomeric silsequioxane (POSS) [1–5]. With the incorporation of POSS groups, thermal stability and mechanical properties of the polymers can be dramatically improved due to the silica and oxygen framework of POSS unit [6–10].

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Various processes have been employed to prepare polymers containing POSS, which can be classified into physical blend and chemical reaction. The organic groups attached on POSS cage enhance the compatibility with polymers. POSS has been blended with polycarbonate, poly(methyl methacrylate), cyanate ester and so on [11–13]. Whereas, at high POSS content (>10%), the aggregation of POSS molecule can be found and POSS molecule cannot be dispersed evenly, which may reduce the improvement in thermal and mechanical properties [14, 15]. To the best of our knowledge, the process of chemical reaction can overcome this disadvantage, such as radical polymerization and ring-open polymerization. Silverstein [16] reported the synthesis of POSS/PMMA nanocomposite via free radical solution polymerization, and pointed out that POSS enhanced the thermal properties of nanocomposite, that is the decomposition temperature was increased and the mass loss was reduced.

In the pursuit to understand the effect of POSS in polymeric hybrids, it is necessary to synthesize well-defined polymers containing POSS with predetermined molecular weight, controlled architectures and narrow polydispersity. Controlled/living radical polymerization (CRP) techniques can synthesize tail-made polymers and meet the above requirements [17–19]. Compared to other CRP techniques such as reversible addition-fragmentation termination (RAFT) and nitroxide mediated polymerizations (NMP), ATRP has been proved as the most robust and efficient tool for preparation of well-controlled macromolecules in terms of the choice of functional monomers, polymerization temperature (100 °C or less), either aqueous or organic solvents [20–24]. Matyjaszewski and Mather prepared well-defined ABA copolymers possessing a rubbery poly (n-butyl acrylate) (pBA) middle segment and glassy p(MA-POSS) outer segments by ATRP which was initiated by C–Br bond, and MA-POSS was used as a monomer which possessed C=C bond [25]. Recently, Hu found that Si–Cl bond, CuCl and N, N, N', N'', N''' pentamethyldiethyltriamine could act as a new initiating system for the ATRP of MMA and St [26]. However, the ATRP of MMA initiated by Si–Cl bond on POSS cage has not been reported, and study on this polymerization should be useful for the improvement of PMMA properties.

In this paper, we attempted to synthesize POSS/PMMA composite using Si–Cl bond on monofunctional POSS as ATRP initiator, and NMR, XPS, XRD and GPC were used to characterize the product, the result demonstrated that the degree of polymerization was well controlled and mono-dispersion of POSS in PMMA matrix was achieved. The thermal properties of POSS/PMMA composite were investigated through DSC and TGA, and the results showed that the T_d and T_g of POSS/PMMA composite were increased.

Experimental

Materials

1-Chlorine-3,5,7,9,11,13,15-cyclopentyl polyhendral oligomeric silsesquioxane (POSS, Hybrid Co.) was used as receive. Methyl methacrylate (MMA, Shanghai

Lingfeng Chemical Reagents Co Ltd, China) was passed through a column with activated Al_2O_3 (neutral) in order to remove the inhibitor, and then distilled under vacuum, stored in refrigerator. Cuprous chloride (CuCl) obtained from Shanghai First Chemical Work of reagents was purified in acetic acid, washed with ethanol and dried under vacuum. 2,2′-Bipyridine (Bpy) was purified and prepared according to previously reported procedures [27]. Toluene was distilled from calcium hydride (CaH_2) before using. Other reagents were used as received without further purification.

Synthesis of POSS/PMMA composite

The ATRP of methyl methacrylate was carried out using Si–Cl bond on POSS cage as an initiation group. POSSCl (0.10 g, 0.10 mmol), CuCl (0.010 g, 0.10 mmol), bpy (0.047 g, 0.30 mmol), MMA (10 mL, 100 mmol) and toluene (10 mL) were added into a flask equipped with magnetic stir bar. The system was evacuated twice, filled with dry nitrogen and placed in an oil bath warmed at 110 °C. After 20 h, the mixture was diluted with THF, filtered over alumina column to remove the catalyst and poured into tenfold methanol. The product was obtained after filtration and drying at 50 °C in a vacuum overnight.

Instruments

FTIR was carried out on a Bruker VECTOR-22 IR spectrometer using spectroscopic grade KBr powder at room temperature. The ^1H NMR spectra were recorded on a Bruker AVAN300 CE from Switzerland at 297.7 K with the solvent $CDCl_3$ and tetramethylsilane (TMS) as a standard.

The weight-average (M_w) and number-average (M_n) molecular weights were measured on a Waters 515 gel permeation chromatograph (GPC) using polystyrene as standards and THF (1.0 ml/min) as the elution. XRD spectra were collected on an M18XHF-SPA X-ray diffraction instrument from Mac Science Co. (Japan) with Cu Kα radiation ($\lambda = 1.5406$ Å) at the scanning rate of 0.1 °C/s between $2\theta = 5°$–40°. X-ray photoelectron spectrum was recorded on Thermo ESCALAB-250 system fitted with a micro-focused, monochromatic Al Kα X-ray source (500 μm spot size) and the pass energy was set at 70.0 eV. The energy step size and number of energy sizes are 1.0 and 1,101 eV, respectively.

DSC analyses were determined on a Diamond DSC PerkinElmer. The samples were heated from 35 to 150 °C at the heating rate of 60 °C/min and then held at 150 °C for 2 min. The samples were cooled from 150 to 35 °C at the rate of 60 °C/min. Finally the samples were heated from 35 to 150 °C at the heating rate of 10 °C/min. The glass transition temperature (T_g) was calculated at the second circle of heating. Thermogravimetric analysis (TGA) was recorded on a Diamond TG PerkinElmer with the heating rate of 10 °C/min from 25 to 600 °C. The thermal degradation temperature (T_d) is defined as the temperature at 5% weight loss of the sample.

Results and discussion

Synthesis and characterization of POSS/PMMA composite

When MMA was initiated by POSSCl with CuCl/Bpy as catalysts at 110 °C, a novel composite, POSS/PMMA was prepared and the mono-dispersion of POSS in PMMA matrix was achieved (Scheme 1).
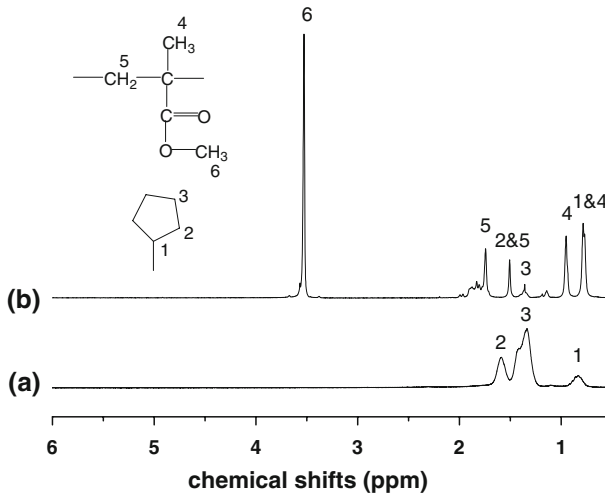
Figure 1 shows the FTIR spectra of pure POSS and POSS/PMMA composite. In Fig. 1a, there is a strong absorption band at 1,109 cm^{-1} which is attributed to the Si–O–Si stretching vibration band of POSS cage and Si–Cl stretching vibration peak is at 509 cm^{-1}. The peaks at 2,952 and 2,868 cm^{-1} refer to the non-activity cyclopentyl on POSS cage. The FTIR spectrum of POSS/PMMA (Fig. 1b) possesses characteristic absorption band of PMMA at 1,730 and 1,147 cm^{-1}, which are assigned to the carbonyl stretching vibration and C–O–C stretching vibration, respectively. The characteristic stretching vibration band of Si–O–Si of
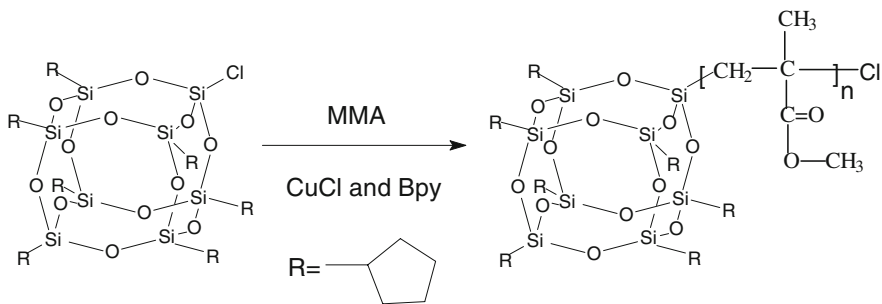
Scheme 1 The synthesis of POSS/PMMA composite by ATRP
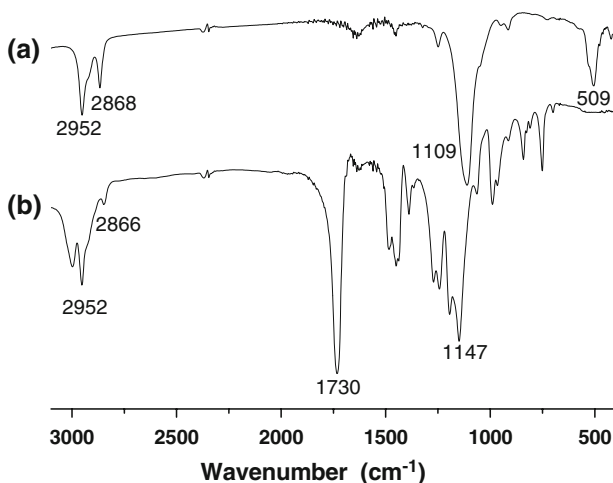
Fig. 1 FTIR spectra of pure POSS (a) and POSS/PMMA composite (b)

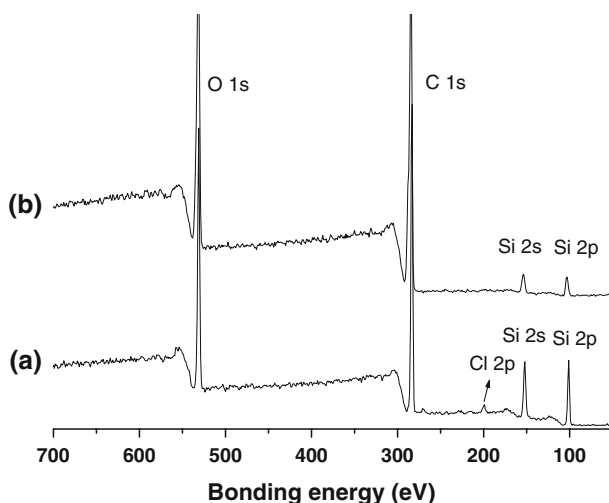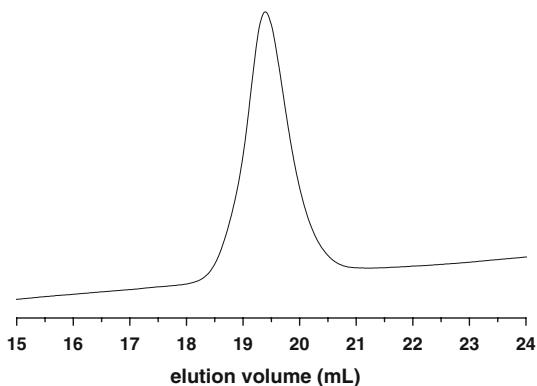**Fig. 2** The ^{1}H NMR spectra of pure POSS (**a**) and POSS/PMMA composite (**b**)

POSS cage at 1,109 cm^{-1} is partially overlapped with the peak of C–O–C in PMMA matrix [28]. Compared to the FTIR spectrum of pure POSS, the existence of the peak at 2,952 cm^{-1} and the disappearance of the peak at 509 cm^{-1} are the powerful evidence of polymerization. So we made the conclusion that POSS may be incorporated in PMMA chains.

To confirm that POSS is chemically bonded with PMMA chains in POSS/PMMA composite, ^{1}H NMR spectra of pure POSS (Fig. 2a) and POSS/PMMA composite (Fig. 2b) are introduced. For pure POSS, the signal at 0.83 ppm is assigned to the proton in the methine of cyclopentyl; the signals at 1.58 and 1.33 ppm are ascribed to the proton in the methylene of cyclopentyl. POSS/PMMA composite displays a different spectrum to that of pure POSS. The signal at 3.60 ppm is attributed to the methyl proton connected to ester group, and the proton resonance absorption of methylene is at 1.74 ppm and substituted methyl groups in PMMA matrix are at 0.77 and 0.95 ppm [28]. After comparison, the proton resonance absorptions of cyclopentyl are still existent, so it can be inferred that POSS cage have been chemically incorporated into PMMA matrix.

Figure 3 presents the GPC trace of POSS/PMMA composite, and the curve is symmetrical and monomodal. The weight-average molecular weight (M_w), number-average molecular weight (M_n) and PDI (M_w/M_n) are 1.50×10^5, 1.10×10^5 and 1.36, respectively. The results of GPC analysis explains that the structure and molecular weight of POSS/PMMA composite were well controlled.

The X-ray photoelectron spectra of pure POSS and POSS/PMMA composite are show in Fig. 4. The characteristic peaks of Si 2p and Si 2s centered at 103 and 154 eV manifest the presence of Si element on the surface of POSS/PMMA composite [29]. Moreover, the intensity of the peaks of Si element become weaker after PMMA is attached to POSS cage; that is to say, PMMA has been successfully grafted on to the POSS cage. In Fig. 4a, the peak at 200 eV is ascribed to the

Fig. 3 GPC trace of POSS/
PMMA composite

Fig. 4 XPS survey spectra of pure POSS (**a**) and POSS/PMMA composite (**b**)

presence of Cl element of POSS cage. However, the characteristic peak of Cl 2p in POSS/PMMA isn't detected, because of the low content of Cl element.

In order to prove the initiation of Si–Cl bond on POSS cage, Fig. 5 shows the XPS spectra of Si 2p of POSS and POSS/PMMA composite. In Fig. 5a, there are two different types of Si 2p curves centered at 104.7 and 102.5 eV. The former is attributed to the Si linked to the chlorine, whereas the latter is attributed to the Si linked to cyclopentyl, and the ratio of the two peaks is about 1:7. Figure 5b presents the symmetrical peak of Si 2p centered at 102.3 eV [30]. Form the XPS measurement, we found that the Si–Cl bond initiate the ATRP of MMA. So according to theory of ATRP, there is only one POSS cage in a PMMA chain.

The X-ray diffraction measurement between 5° and 40° is employed to investigate the dispersion of POSS in PMMA in Fig. 6. There are five strong reflections at $2\theta = 8.2°$, 11.0°, 11.8°, 18.5° and 24.5° in Fig. 6a, corresponding to d-spacing of 10.6, 7.4, 7.0, 4.7 and 3.5 Å, respectively, which accord well with the
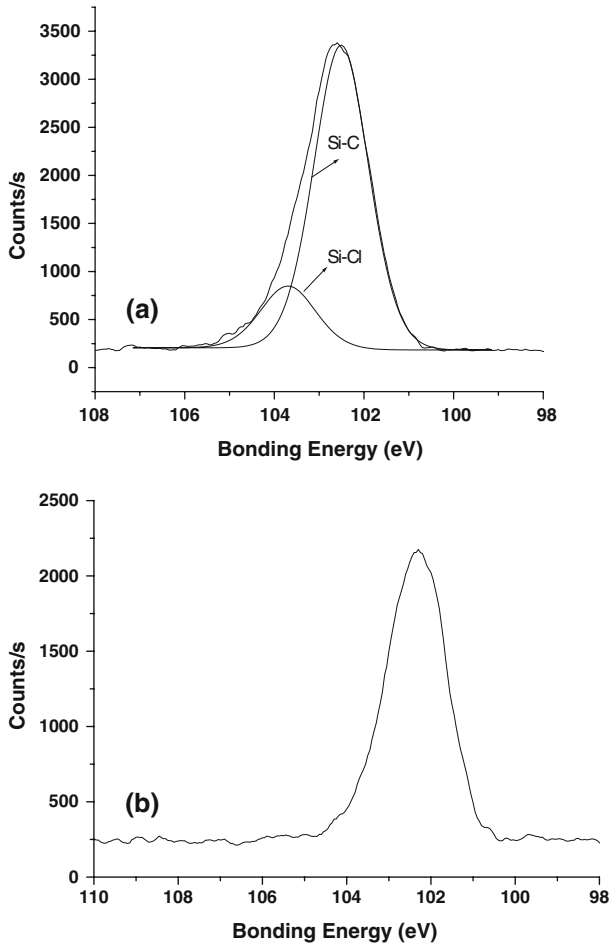
**Fig. 5** XPS spectra of Si 2p of pure POSS (**a**) and POSS/PMMA composite (**b**)

eference [31, 32]. And the reflection at $2\theta = 8.2°$ whose d-spacing is 10.6 Å is for the size of POSS molecules. All diffraction peaks indicate the rhombohedral crystal structure of POSS molecules. However, in Fig. 6b, there is a ruleless curve resulting from the diffuse amorphous PMMA chains, and no characteristic diffraction peaks of POSS cage is found, which shows that POSS molecule have been evenly dispersed in polymer matrix at molecular lever and no aggregation of POSS molecular is observed [33].

Thermal properties of POSS/PMMA composite

Previous studies on the thermal properties of POSS/polymer reveal the enhancement of the T_g and T_d after the incorporation of POSS into polymer matrix. In our work, PMMA was synthesized for comparison using 1-chlorobutane as initiator under the
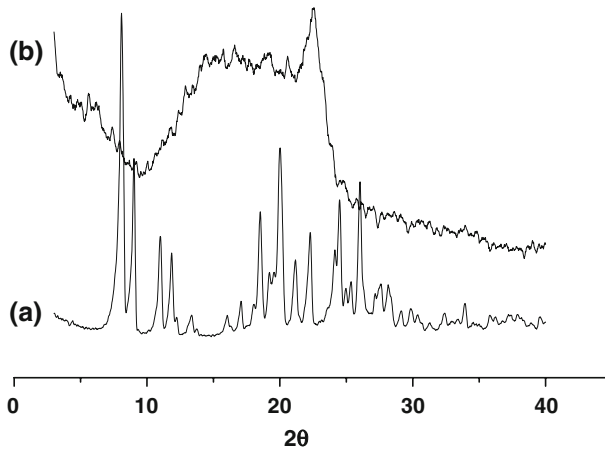
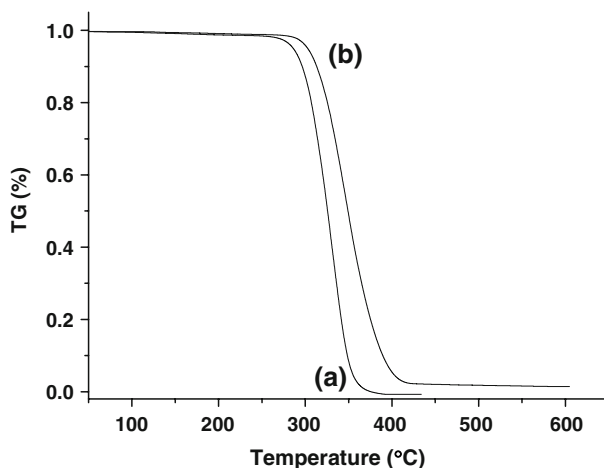**Fig. 6** XRD curves of pure POSS (**a**) and POSS/PMMA composite (**b**)
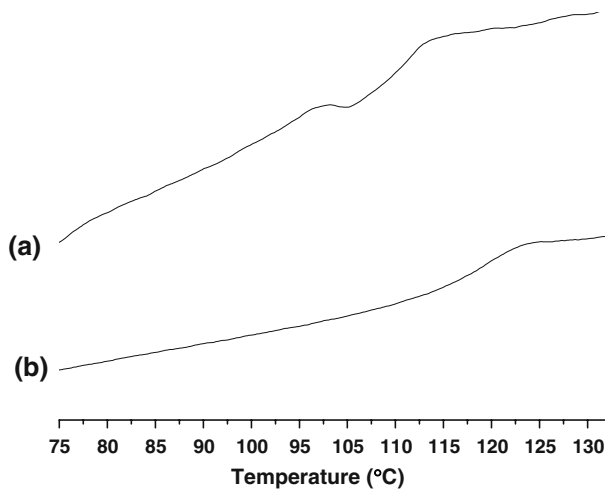
Fig. 7 DSC thermograms of PMMA (**a**) and POSS/PMMA composite (**b**)

identical reaction parameters as the synthesis of POSS/PMMA composite, and the M_n and M_w/M_n of pure PMMA is 1.20×10^5 and 1.30.

Figure 7 shows the DSC thermograms of pure PMMA and POSS/PMMA composite. Pure PMMA has a T_g at 106 °C, after the POSS is chemical bonded with PMMA, the T_g of POSS/PMMA composite increases to 120 °C that is much higher than the pure PMMA. The enhancement of T_g due to the rigid nature of POSS cage which has the Si–O–Si framework, and a typical polymer chain segment from vinyl type monomer is about 2–5 Å while the diameter of POSS moiety is about 5–25 Å, hence, it can imply that the POSS moiety may dominate the movement of the local chain of the polymer [34].

Fig. 8 TGA curves of PMMA (**a**) and POSS/PMMA composite (**b**)

Figure 8 gives the TGA curves of POSS/PMMA and pure PMMA under nitrogen atmosphere, and the T_d of POSS/PMMA composite is 302 °C which is 16 °C higher than that of the pure PMMA. When the temperature is increased to 430 °C, the pure PMMA is evaporated completely, but there is 2.0% of POSS/PMMA composite still remaining which refers to inorganic POSS core. So the POSS content of POSS/PMMA composite is 2.0 wt.%. The result further confirms that the incorporation of POSS enhances the thermal stability of PMMA which is consistent with the result of DSC analysis.

Conclusions

In this work, the mono-dispersed POSS/PMMA composite was successfully synthesized and characterized via ATRP using the Si–Cl bond on POSS cage as initiator agent. The structures of pure POSS and POSS/PMMA composite were investigated by means of FTIR and ^{1}H NMR. The surface properties of POSS/PMMA was investigated by XPS, and revealed the initiation from the chlorine attached on POSSS. GPC data showed the low PDI of POSS/PMMA which is consistent with the nature of ATRP. XRD experiment indicated that POSS was dispersed evenly in PMMA matrix at molecule level. The results of DSC and TGA shown that the T_g and T_d of PMMA are enhanced after the incorporation of POSS, which is mainly attributed to uniform dispersion of POSS cage that has the inorganic framework. In addition, the POSS content of the composite reached 2.0 wt.% obtained from the TGA curves.

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