Synthesis and thermal stability of star polymer with eight arms using polyhedral oligomeric silsesquioxane as a core

Lei Liu, Wenping Wang,* Xianran Guo

*School of Chemical and Engineering, Hefei University of Technology, Hefei, 230009, Anhui, P. R. China; tel.:+86-551-2904027; fax: +86-551-2901450; e-mail: wap@hfut.edu.cn.

(Received: 20 October, 2008; published: 11 December, 2010)

Abstract: A Polyhedral oligomeric silsesquioxane (POSS) containing eight 3-chloropropyl groups was synthesized and incorporated into poly(methyl methacrylates) to form star polymer. First, octa(3-chloropropyl) POSS \[\text{[(ClCH}_2\text{CH}_2\text{CH}_2\text{)}_8\text{Si}_8\text{O}_{12}]\] was prepared by hydrolysis and condensation of 3-chloropropyltriethoxysilane, and then two star-shaped POSS/PMMA composites with different POSS content was synthesized at 110 °C, using octa(3-chloropropyl) POSS as an multifunctional initiator, CuCl and 2,2'-bipyridine (Bpy) as catalyst system. The structures of octa(3-chloropropyl) POSS and star-shaped POSS/PMMA composite were characterized by analytical methods including FTIR, NMR, GPC and XRD, with results showing that POSS molecule was successfully formed which accorded well with the reported work and was dispersed into PMMA matrix evenly by atom transfer radical polymerization method. The TGA results indicated that synthetic POSS molecule possessed good thermal stability, and the thermal stability of POSS/PMMA composite enhanced with the increase of POSS content, which is due to the incorporation of inorganic POSS molecule.

Introduction

Recently, the synthesis of organic/inorganic hybrid polymers containing polyhedral oligomeric silsesquioxane (POSS) group has attracted much attention [1-5]. The advantage of the POSS-containing nanocomposites is that the POSS groups can dramatically improve thermal and mechanical properties of the polymers [6-9]. Numerous strategies have been reported in the synthesis of POSS-containing nanocomposites such as condensation polymerization [10, 11], free radical polymerization techniques [12, 13], and ring-open polymerization [14-16]. Schiraldi [17] produced a series of composite materials of POSS-derivatives containing polycarbonate (PC) by melt blending, and the improvement of mechanical properties including tensile and dynamic mechanical modulus was reported. Pittman [18] prepared cyanate ester composite containing trisilanophenyl-POSS with different POSS content, with results showing that the incorporation of small amounts (≤5 wt %) of trisilanophenyl-POSS into cyanate ester could improve the storage modulus and high-temperature properties. However, at a high POSS content, POSS molecules cannot be evenly dispersed in polymer matrix by merely physical blend, which would inevitably result in the aggregation of POSS molecule and reduce the expected improvement in thermal and mechanical properties [19, 20]. Whereas, to the best of our knowledge, if POSS molecules are chemically bonded with polymers, the above disadvantages could be properly overcome. Kuo and Chang [21] prepared polybenzoxazine/POSS nanocomposite with network structure using multifunctional
MBZ-POSS as a curing agent, and the chemically-boned POSS unit greatly enhanced the thermal properties (\(T_g\) and \(T_d\)) of pristine polymer.

In the pursuit to understand the effect of POSS inclusions in polymeric hybrids precisely, it is necessary to synthesize well-defined model polymers with precise molar mass, composition and architecture [22, 23]. Living/controlled free radical polymerization methods were usually used to produce tailor-made macromolecules (star-shaped, block and grafted polymers) with controlled backbone length and branch length and can meet the above requirement, such as atom transfer radical polymerization (ATRP), and reversible addition-fragmentation chain transfer (RAFT) polymerization [24-27]. Matyjaszewski and Mather [28] reported the synthesis of well-defined ABA triblock containing POSS via atom transfer radical polymerization. Thermal study revealed the existence of two clear glass transitions in the product, with the \(T_g\) of the p(MA-POSS) phase from triblock copolymer nearly 25 °C higher than that of p(MA-POSS) homopolymer with comparable molar mass. Wei [29] synthesized polyimide-tethered POSS nanocomposite with well-defined structure by copolymerization of POSS-diamine, 4,4’-oxydianiline (ODA) and pyromellitic dianhydride (PMDA) and found that when the content of POSS exceeded 10 mol%, this kind of nanocomposite presented self-assembly characteristics. Meanwhile, the flexural strength and flexural modulus were also raised by POSS incorporation. However, no articles have reported the synthesis of star polymer with eight arms using polyhedral oligomeric silsesquioxane as a core.

Herein, we reported the synthesis and characterization of star-shaped poly(methyl methacrylates) with eight arms via ATRP using polyhedral oligomeric silsesquioxane as a core. The mono-dispersion of POSS in PMMA matrix was obtained, meaning that there is only one POSS cage in a PMMA chain. And then, the stability of star-shaped POSS/PMMA composite was studied by TGA.

**Results and discussion**

*Synthesis of octa(3-chloropropyl) POSS*

The synthesis route of star-shaped POSS/PMMA composite is shown in Scheme 1.

**Scheme 1.** The synthesis route of star-shaped POSS/PMMA composite.
Firstly, octa(3-chloropropyl) POSS was prepared from 3-chloropropyltriethoxysilane according to references. This step of reaction consisted of complex processes of hydrolysis, dehydration, condensation and structure reforming, and often took a rather long time.

![FTIR spectra](image)

**Fig. 1.** FTIR spectra of POSS (a) and star-shaped POSS/PMMA composite [sample 1] (b).

![NMR spectra](image)

**Fig. 2.** $^1$H-NMR spectra of POSS (a) and star-shaped POSS/PMMA composite [sample1] (b).

The FTIR spectrum of octa(3-chloropropyl) POSS (white powder) is shown in Figure 1a, in which the absorption peak at 1108 cm$^{-1}$ is ascribed to the characteristic peak of POSS cage, i.e. Si-O-Si stretching vibration. The absorption band around 2955 cm$^{-1}$ attributed to the C-H stretching vibration, and the peak at 698 cm$^{-1}$ referred to C-Cl stretching vibration. To further confirm the structure of POSS, NMR
measurement is employed and the results are exhibited in Figure 2a and Figure 3. In the $^1$H-NMR spectrum (Figure 2a) of POSS, the signals at 3.52, 1.87 and 0.80 ppm are assigned to the three kinds of protons in the structure of 3-chloropropyl, respectively. And in the $^{29}$Si-NMR spectrum of POSS, the only signal of resonance at -67.0 ppm indicates that all Si nuclei in POSS molecule have the same chemical conditions, which accords well with the reference [32].

![Fig. 3. $^{29}$Si-NMR spectrum of POSS.](image)

Figure 4 shows the X-ray diffraction of POSS, and there are five distinct diffraction peaks at $2\theta=7.34^\circ$, 9.14 $^\circ$, 12.02 $^\circ$, 21.94 $^\circ$ and 23.02 $^\circ$, which correspond to the d-spacing of 12.03 Å, 9.67 Å, 7.36 Å, 4.05 Å and 3.86 Å, respectively, according to literature [30,31]. All the diffraction peaks indicate that the rhombohedral crystal structure of POSS molecules is formed, proving the formation of octa(3-chloropropyl) POSS.

**Synthesis of star-shaped POSS/PMMA**

The octa(3-chloropropyl) POSS as-synthesized is used as a core to produce star-shaped POSS/PMMA composite with eight arms via atom transfer radical polymerization. The conditions and results of POSS/PMMA composite via ATRP are shown in Table 1.

**Tab. 1.** The conditions a and results of POSS/PMMA composite via ATRP.

<table>
<thead>
<tr>
<th>Sample</th>
<th>t (h)</th>
<th>$M_n$ b</th>
<th>$M_w$ b</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>79600</td>
<td>95400</td>
<td>1.19</td>
</tr>
<tr>
<td>2</td>
<td>11</td>
<td>120700</td>
<td>138400</td>
<td>1.14</td>
</tr>
</tbody>
</table>

a:[MMA]₀/[POSS]₀/[CuCl]₀/[Bpy]₀=2000:1:8:24 (molar ratio), and V(MMA)/V(toluene)=1
b: $M_n$ and $M_w$ were obtained through GPC
FTIR spectrum of star-shaped POSS/PMMA is shown in Figure 1b. Compared to the FTIR spectrum of POSS (Figure 1a), the typical absorptions at 1730 and 1147 cm⁻¹ are assigned to the carbonyl stretching vibration and C-O-C stretching vibration, respectively. The characteristic stretching vibration peak of Si-O-Si of POSS cage at 1110 cm⁻¹ is overlapped with the characteristic stretching vibration peak of C-O-C in PMMA matrix [32].

¹H-NMR of star-shaped POSS/PMMA is exhibited in Figure 2b. The peak 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, while the proton on POSS cage is around 1.50 ppm. By comparing the ¹H-NMR spectra of POSS with star-shaped POSS/PMMA composite, it can be inferred that POSS cage have been chemically incorporated into PMMA matrix.

Fig. 4. XRD patterns of POSS (a) and star-shaped POSS/PMMA composite [Sample 1] (b).

Fig. 5. GPC traces of star-shaped POSS/PMMA composite [sample 1].
X-ray diffraction is employed to investigate the structure of star-shaped POSS/PMMA with scanning range between 5° and 50° (sample 1). Figure 4b shows a broad peak resulting from the diffuse amorphous PMMA chains [33]. Compared with Figure 4a, there are a great number of diversities of microstructure between two curves, indicating that POSS molecule has been evenly dispersed in polymer matrix. After that, we investigated the structure of the star-shaped POSS/PMMA composite in details by GPC.

GPC curves of star-shaped POSS/PMMA with different polymerization times are given in Figure 5, and the curves are symmetrical and monomodal. And with the increasing polymerization times, the molecular weight is augmented, which accords with the principle of polymerization. Moreover, the PDI of star-shaped POSS/PMMA is rather narrow which indicates the successful formation of MMA using multifunctional POSS as an initiator via ATRP.

**Thermal stability of POSS and star-shaped POSS/PMMA**

Figure 6 shows the TGA thermograms of pure PMMA, POSS and star-shaped POSS/PMMA composites. T_d and char yield at 450 °C are summarized in Table 2. Pure POSS exhibits good thermal stability, and its T_d is much higher than POSS/PMMA composites and PMMA. When the temperature reaches 450 °C, pure PMMA is evaporated completely, but there is 0.4% and 2.0% char yield of sample 1 and 2 respectively which are refer to the inorganic POSS core. In addition, with the increase of POSS content from 0.4% to 2.0%, the T_d of star-shaped POSS/PMMA composites is enhanced from 281 °C to 303 °C.

**Tab. 2.** Thermal stability of POSS and POSS/PMMA composites.

<table>
<thead>
<tr>
<th></th>
<th>Pure PMMA</th>
<th>POSS</th>
<th>Sample 1</th>
<th>Sample 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>T_d (°C)</td>
<td>286</td>
<td>319</td>
<td>303</td>
<td>281</td>
</tr>
<tr>
<td>Char Yield (%) at 450 °C</td>
<td>0</td>
<td>45.1</td>
<td>2.0</td>
<td>0.4</td>
</tr>
</tbody>
</table>

**Fig. 6.** TGA curves of pure POSS (a), sample 1 (b), sample 2 (c) and pure PMMA (d).
Conclusions

In this work, octa(3-chloropropyl) POSS was prepared by the hydrolysis and condensation of 3-chloropropyltriethoxysilane, and then star-shaped POSS/PMMA composite with eight arms was synthesized via atom transfer radical polymerization at 110 °C, with octa(3-chloropropyl) POSS as a core and CuCl/Bpy as catalysis system. The structures of POSS and star-shaped POSS/PMMA composite were investigated by many instruments, including FTIR, NMR and XRD, with result showing that the mono-dispersion of POSS in PMMA matrix was achieved by ATRP, meaning that there is only one POSS cage in a PMMA chain. Moreover, the POSS/PMMA composites have better thermal stability, and the $T_d$ increases with the increase of POSS content in the composite.

Experimental part

Materials

3-Chloropropyltriethoxysilane [ClCH$_2$CH$_2$CH$_2$Si(OCH$_2$CH$_3$)$_3$,] (98%) was purchased from Jingzhou jianghang fine chemical Co. (china). Methyl methacrylates came from Sinopharm Chemical Regent Co. (China), which was passed through a column with activated Al$_2$O$_3$ (neutral) in order to remove the inhibitor, vacuum distilled and kept in refrigerator prior to use. Toluene was distilled from calcium hydride (CaH$_2$) before using. 2,2’-Bipyridine (Bpy) was purified and prepared according to previously reported procedures [34].

Synthesis of octa(3-chloropropyl) POSS

Octa(3-chloropropyl) POSS was synthesized in our laboratory according to the reported method [35, 36]. First, 50 mL ethanol, 20 mL 3-chloropropyltriethoxysilane and 8 mL deionized water was mixed, and then concentrated hydrochloric was added to adjust the acidity of the mixture. Finally, reaction was carried out at least 2 weeks at 60 °C. After the mixture was cooled down and filtered, a colorless crystal was obtained. The colorless crystal was washed with ethanol three times and then dried in vacuum at 40 °C for 48 h. (Yield: 25 %.)

Synthesis of star-shaped POSS/PMMA

The ATRP reaction was carried out employing octa(3-chloropropyl) POSS as an octafunctional initiator. POSS (10 mg, 0.0097 mmol), Bpy (36 mg, 0.233 mmol), CuCl (7.6 mg, 0.077 mmol), MMA (2.0 mL, 19.4mmol) and toluene (2.0 mL) were added into a flask equipped with magnetic stirrer. After the system was vacuumed and back-filled with dry nitrogen 3 times, the flask was airproofed and placed in an oil bath at 110 °C under magnetic churn for a prescribed time. The mixture was diluted with THF, filtered over alumina column to remove the catalyst and poured into methanol to obtain the product. The POSS/PMMA composite was dried in vacuum for 24 h at 40 °C.

Characterization

$^1$H-NMR and $^{29}$Si-NMR spectra were carried out on a Bruker AVAN300 CE from Switzerland at 297.7 K with the solvent CDCl$_3$ and tetramethylsilane (TMS) as a standard. Gel permeation chromatography (GPC) was recorded at room temperature using Waters 515 GPC and THF was used as the eluent at 1.0 mL/min. Molecular
weights were calculated using polystyrene standards. FT-IR was determined on a Bruker VECTOR-22 IR spectrometer using spectroscopic grade KBr powder at room temperature. XRD spectra were collected on an M18XHF-SPA X-ray diffraction instrument from Mac Science Co. (Japan) with Cu Kα radiation (λ=1.5406 Å) at the scanning rate of 0.1 °C/s between 2θ=5°~50°. Thermogravimetric analysis (TGA) was recorded on a Diamond TG PerkinElmer with the heating rate of 10 °C/min from room temperature to 600 °C under air. The thermal degradation temperature (Td) is defined as the temperature at 5% weight loss of the sample.

Acknowledgements
This work was financially supported by National Natural Science Foundation of China [NO: 50673023].

References