

SYNTHESIS AND CHARACTERIZATION OF STRUCTURALLY WELL-DEFINED POLYMER-INORGANIC HYBRID NANOPARTICLES VIA ATRP*

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Abstract Atom transfer radical polymerization (ATRP) using cuprous chloride/2,2'-bipyridine (bipy) was applied to graft polymerization of styrene on the surface of silica nanoparticles to synthesize polymer-inorganic hybrid nanoparticles. 2-(4-Chloromethylphenyl) ethyltriethoxysilane (CTES) was immobilized on the surface of silica nanoparticles through condensation reaction of the silanol groups on silica with triethoxysilane group of CTES. Then ATRP of St was initiated by this surface-modified silica nanoparticles bearing benzyl chloride groups, and formed PSt graft chains on the surface of silica nanoparticles. The thickness of the graft chains increased with reaction time. End group analysis confirmed the occurrence of ATRP. Thermal analysis indicated that thermal stabilization of these resulting hybrid nanoparticles also increases with polymerization conversion. The results above show that this “grafting from” reaction could be used for the preparation of polymer-inorganic hybrid nanoparticles with controlled structure of the polymer's end groups.

Keywords Atom transfer radical polymerization, Polymer-inorganic hybrid nanoparticles, 2-(4-Chloromethylphenyl)-ethyltriethoxysilane, Surface-modification

INTRODUCTION

In order to modify the surface of inorganic substrates (e.g., silica gels, silicon wafers), recently much attention has been directed toward the “grafting from” method. Initiating species is immobilized on the surface of inorganic substrate, and graft polymerization can start with these initiating sites. Atom transfer radical polymerization (ATRP) was applied to the surface-initiated graft polymerization in order to have control over molecular weight, molecular weight distribution, and the structure of resulting polymer. It was often used to conduct a controlled/living polymerization^[1–4] from the surface of inorganic substrate. Werne and Patten^[5, 6] reported the synthesis of structurally well-defined polymer-nanoparticle hybrids with ATRP reaction. They fixed 2-(4-chloromethylphenyl) ethyldimethylethoxysilane (CDES) on the surface of silica nanoparticles, which were then used to initiate ATRP of St, yielding a nanoparticle with an inorganic core and an outer layer of covalently attached well-defined polymer chains. They also investigated the influence of the size of silica nanoparticles on the surface-initiated ATRP of St. Several other studies have been published in which graft polymerization from flat and porous silica surfaces using controlled/living radical polymerization were described^[7–9].

This paper describes the synthesis of well-defined polymer-inorganic hybrid nanoparticles via two-step reaction: ATRP initiator was first fixed on the surface of silica nanoparticles with which the ATRP of St was then initiated. Silica nanoparticles with about 110 nm diameter were prepared and treated with an organic silicon compound 2-(4-chloromethylphenyl) ethyltriethoxysilane (CTES) bearing a benzyl chloride group, to form

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ATRP initiator-modified silica nanoparticles. Since CTES has three ethoxy groups, it could easily be immobilized on the surface of silica nanoparticles. Then ATRP of St was initiated by these CTES surface-modified silica nanoparticles to form structurally well-defined polymer-inorganic hybrid nanoparticles composed of an inorganic core and a polymer shell.

EXPERIMENTS

Materials

Dicyclopentadiene (Acros Organics, 95%), 4-vinylbenzyl chloride (Aldrich, 90%), triethoxysilane (Aldrich, 99%), tetraethoxysilane (TEOS, Acros Organics, 98%) and tricaprylmethylammonium chloride (Aliquot® 336, Aldrich) were used as received. Analytical grade St (Beijing Chemical Company) was washed with 5% aqueous NaOH solution for three times and with distilled water to pH = 7, then dried with MgSO₄ for 7 h and distilled under vacuum before use. CuCl was washed with glacial acetic acid until colorless and the volatile materials were removed under vacuum. Tetrahydrofuran (THF) was dried over CaH₂ and distilled before use. Toluene was washed three times with concentrated H₂SO₄ and with distilled water to pH = 7 and then dried and distilled before use. *Para*-xylene was dried over CaCl₂ and distilled before use. CTES was prepared by the catalytic hydrosilylation of 4-vinylbenzyl chloride with triethoxysilane. Other solvents were used as received.

Preparation of the Catalyst for Hydrosilylation: Dicyclopentadienyl Platinum (II) Chloride (DPPC)

DPPC was prepared according to the literature^[10]. 0.5 g Hexachloroplatinic acid hexahydrate (H₂PtCl₆ · 6H₂O) was dissolved in 1.0 mL glacial acetic acid at ambient temperature, and diluted with 2.5 mL water. Then 0.5 mL dicyclopentadiene was added dropwise at 70°C. The mixture was stirred vigorously at 60°C for 24 h and then allowed to cool. Appropriate volume of THF was added to dilute the solution and to dissolve DPPC. After filtration, the filtrate was concentrated by distillation and crystallized. The resulting DPPC was recrystallized with THF to give a thin needlelike crystal, m.p. 218–219°C.

Preparation of CTES

CTES was prepared by catalytic hydrosilylation according to the literature^[11, 12]. Under the protection of argon, 2.5 mL 4-vinylbenzyl chloride and 3.28 mL triethoxysilane was added dropwise to a solution of 0.0157 g DPPC in 10 mL THF under stirring at 50°C. After complete addition, the mixture was heated to reflux for 12 h and then allowed to cool. The reaction product was distilled under vacuum and CTES was collected at 144–146°C/260 Pa, yield: 43%.

Immobilization of CTES on Silica Surfaces

At first silica nanoparticles were prepared according to the literature^[5]. A 0.22 wt% aqueous Na₂SiO₃ solution was prepared by diluting of 40 wt% Na₂SiO₃ solution. To 1000 mL of absolute ethanol, 20 mL of the Na₂SiO₃ solution was added, and the mixture was agitated ultrasonically to ensure the formation of separate particles. To this suspension, 70 mL of NH₄OH (28% NH₃) and 100 mL of absolute ethanol were added, and the solution was stirred evenly. Then, 4 mL of TEOS was added, and the particles were allowed to grow for some time to reach a suitable average diameter.

The above silica/ethanol/ammonia suspension was treated in a rotatory evaporator to reduce the volume to approximately 10 mL. Then 10 mL toluene was added while agitating ultrasonically, and 1.0 g CTES dissolved in 5 mL toluene was added dropwise. The solution was vigorously stirred at room temperature for 15 h, then heated to reflux at 80°C for 6 h. After cooling, the solution was stirred at room temperature again for 15 h and then 10 mL pentane was added, particles were isolated by centrifugation. 10 mL of pentane was added to these particles again while agitating ultrasonically. Any unreacted or absorbed CTES was removed by centrifugation. The surface-modified particles were collected, and volatile materials were removed by heating under an infrared lamp. The product was a white powder and denoted as PI-1.

Polymerization

In a typical run, St (0.5 mL) was added to a dry glass tube together with 0.1544 g surface-modified SiO₂

nanoparticles, 0.0014 g CuCl, 0.0068g 2,2'-bipyridine (bipy), and 0.24 mL *para*-xylene. The mixture was immediately degassed by three freeze-thaw cycles and sealed under vacuum. The tube was immersed in an oil bath thermostated at 120°C. After 21 h, the tube was quenched with ice water to stop the reaction and the resulting polymer was dissolved in 10 mL THF, then precipitated with 150 mL methanol and dried. The conversion (0.047 g PSt, 10.4%) of polymerization was determined gravimetrically.

Cleavage of Polymer from Silica Particles

The polymer/silica hybrid nanoparticles (0.25 g) were dissolved in 5 mL toluene and 75 mg Aliquot® 336 was added as a phase transfer catalyst. A 5% aqueous HF solution (5 mL) was added and the mixture was stirred for 4 h. The upper organic layer was removed, and the polymer was precipitated from methanol and filtered off. The resulting polymer was dried under an infrared lamp.

Characterization

Scanning electron micrographs (SEM) were recorded on a Hitachi H-9000NAR HREM SEM. The samples were prepared by evaporation of solvent from its dilute suspension on the silicon sheet. Fourier transform infrared (FT-IR) spectra were measured using a Nicolet Magna-IR 750 spectrometer with KBr pellets. ¹H-NMR spectra were recorded using a Bruker ARX400 (400 MHz) spectrometer in CDCl₃ at 25°C, using tetramethylsilane as internal reference. Thermal analysis was performed on a TG-DTA Thermal Analysis SDT2960 instrument with a heating rate of 10 K/min and 100 mL/min nitrogen flow. Molecular weight and molecular weight distribution of the polymer samples were measured at 35°C by gel permeation chromatography (GPC) on a Waters 2410 instrument using THF as the eluent (1.0 mL/min); calibration was conducted with polystyrene standards.

RESULTS AND DISCUSSION

Preparation of CTES Surface-Modified Silica Nanoparticles

CTES was prepared by the catalytic hydrosilylation of 4-vinylbenzyl chloride with triethoxysilane. The structure of CTES was characterized by ¹H-NMR spectrum analysis as shown in Fig. 1, the chemical shifts δ and assignments were as follows: 1.23 (9H, -OCH₂CH₃), 3.81 (6H, -OCH₂CH₃), 0.99 (2H, -Si-CH₂-CH₂-), 2.75 (2H, -Si-CH₂-CH₂-), 7.26 (4H, -C₆H₄-) and 4.57 (2H, -CH₂Cl). Elemental analysis shows that the found values agree with the values calculated from the formula (found: C 55.06%, H 7.83%; calculated: C 56.82%, H 7.89%).

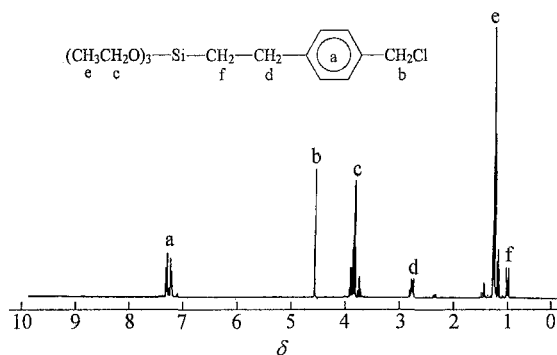


Fig. 1 The ¹H-NMR spectrum of CTES

CTES surface-modified silica nanoparticles PI-1 were obtained via the condensation reaction of silanol groups on the surface of silica nanoparticles with triethoxysilane group of CTES. Elemental analysis reveals that the content of Cl element was 0.335% per gram silica particles. The data could be translated into an average content of CTES of 0.0904 mmol in every gram of silica particles and a grafting density of 2.6 CTES per nm². The latter value can be compared to the generally accepted silica surface hydroxyl group density, 5 hydroxyl groups per nm^{2[13]}. Such a grafting density would be expected, because the CTES group is much larger than

hydroxyl group and, consequently, would occupy more surface area per unit^[14]. Figure 2 is a diffuse reflectance infrared Fourier transform (DRIFT) spectrum of CTES surface-modified silica nanoparticles. The sharp vibration bands at 2800–2990 and 1400–1500 cm^{-1} are characteristic for the C–H stretching vibration of methylene groups and phenyl groups respectively. A broad band between 3700 and 3000 cm^{-1} is caused by water that was absorbed during the measurement.

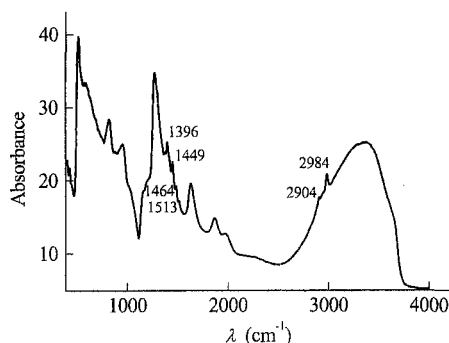


Fig. 2 The DRIFT spectrum of silica with immobilized ATRP initiator CTES

ATRP of St

As CTES was bound to the surface by one end, the other end bearing benzyl chloride group could diffuse into solution and started the ATRP of St there in conjunction with CuCl/bipy (Table 1). PI-1 was used as initiator and the solution polymerization occurred with a molar ratio of $[\text{St}]_0:[\text{CTES}]_0:[\text{CuCl}]_0:[\text{bipy}]_0 = 300:1:1:3$ at 120°C. The correlation of conversion and $\ln([\text{M}]_0/[\text{M}])$ versus time is shown in Fig. 3. A straight line can be drawn passing through the origin, which indicates that the kinetics is first order in monomer. This result reveals that the living radical polymerization of St was successfully conducted. The hybrid nanoparticles are a white powder. They disperse easily in good solvents for PSt such as THF to form a limpid solution. But, after 69 h the conversion increases dramatically and reaches 81.0%. This is ascribed to the occurrence of thermal polymerization of St itself. Because the whole system is so heterogeneous and the polymerization temperature is high and because the reaction time is so long, thermal polymerization of St happens inevitably.

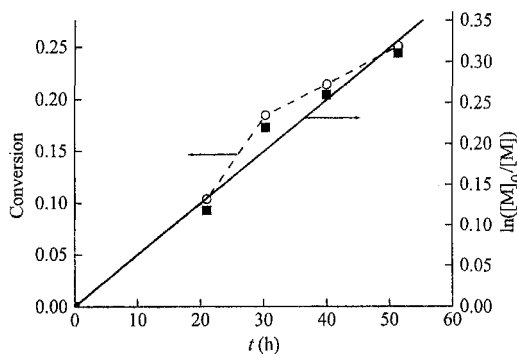


Fig. 3 The correlation of conversion and $\ln([\text{M}]_0/[\text{M}])$ versus time

After the silica cores were etched, the molecular weight (M_n) of the grafted polymer was determined by GPC. The shoulder in the chromatogram only implied that small particle aggregates were formed in the particle synthesis^[15]. So the value of M_w/M_n should be calculated by excluding this shoulder part. M_n increases with polymerization conversion (Table 1), and the molecular weight distribution (M_w/M_n) remains narrow during this polymerization (Table 1). The efficiency of initiator PI-1, that is the value of f in this polymerization system was calculated from equation $f = M_{n, \text{cal}}/M_{n, \text{GPC}}$, such as 0.243 for sample 4. It was so low due to the heterogeneity of

this ATRP system.

Table 1. The results of ATRP of St initiated by PI-1

	Sample			
	1	2	3	4
Conversion (%)	10.4	18.5	21.4	25.0
$M_{n, cal}^a$	3245	5800	6711	7800
Measured M_n	13500	28600	29800	32200
M_w/M_n	1.19	1.17	1.14	1.14

^a $M_{n, cal}$ is evaluated by the equation $M_{n, cal} = ([M]/[I])_0 \times M_{w, St} \times \text{Conv.}$

Thermal Analysis

Through thermal analysis of hybrid nanoparticles the relation between thermal stabilization of polymer and its composition and structure can be obtained. Corresponding to the TG (Thermogravimetry) signals, the DTA (Differential Thermal Analysis) curve is also obtained. The thermal analysis of hybrid nanoparticles initiated by PI-1 is shown in Fig. 4 (from curve a to curve d, the increasing peak area shows the increasing monomer conversion).

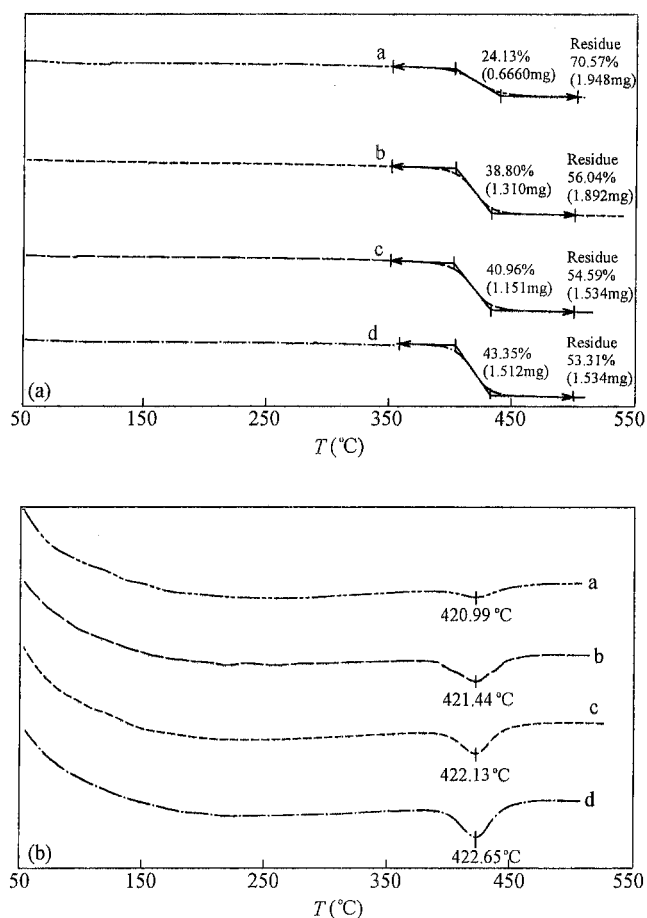


Fig. 4 Thermal analysis of hybrid nanoparticles
(a) TG curves; (b) DTA curves

In Fig. 4(a), monomer conversions can be obtained through TG curves and their values are in good agreement with those obtained from the methanol precipitation method. The peak temperatures in Fig. 4(b) are

the decomposing temperatures (T_d) of hybrid nanoparticles. They increase from curve a (420.99 °C), b (421.44 °C), c (422.13 °C) to d (422.65 °C). This indicates that the thermal stabilization of these hybrid nanoparticles increases with polymerization conversion.

SEM Characterization

SEM was used to confirm the formation and to estimate the average diameter of spherical particles as shown in Figs. 5 and 6. Figure 5 shows the silica nanoparticles after growing for 24 h, they are mostly spherical particles with a size of about 110 nm and not seriously aggregated.



Fig. 5 The SEM microphotograph of SiO₂ nanoparticles

After polymerization, an increase in diameter of the particles as a function of conversion was monitored by SEM. Figure 6 is the SEM micrograph of hybrid nanoparticles of 25.0% conversion. The grafted PSt chains form a white polymer shell around the silica core. And these hybrid nanoparticles are so closely packed that they look like a bunch of grapes. The average diameter of these four polymerization samples increases from 116 nm, 123 nm, 125 nm, to 128 nm, so the thickness of the grafted PSt chains of hybrid nanoparticles can be manipulated through the control of monomer conversion of ATRP reaction.

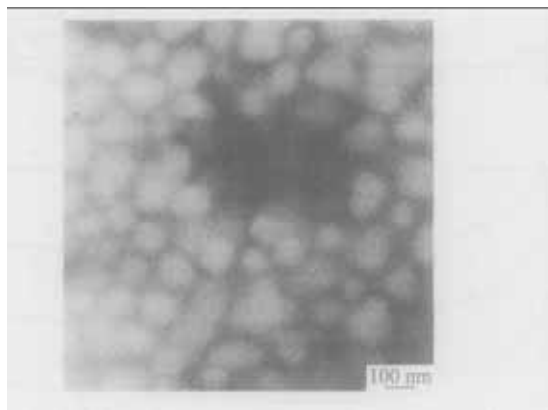


Fig. 6 The SEM microphotograph of hybrid nanoparticles with 25.0% monomer conversion

The FT-IR spectra of the PSt-modified silica nanoparticles initiated by PI-1 are presented in Fig. 7, and the monomer conversion increases from a to d. Figure 7 shows the vibration bands corresponding to both PSt and silica, and the intensity of characteristic peaks of PSt at 3050, 2800–2990, 1450 and 700 cm⁻¹ increases with monomer conversion.

After etching the silica cores, end group analysis of the resulting PSt is carried out using ¹H-NMR spectroscopy as shown in Fig. 8. The signal at $\delta = 4.3$ is ascribed to the proton of $-\text{CH}_2\text{C}(\text{Ph})\text{H}-\text{Cl}$. As evidenced by ¹H-NMR analysis, the obtained PSt is functionalized with an ω -Cl group. It reveals that the polymerization proceeds according to the ATRP mechanism.

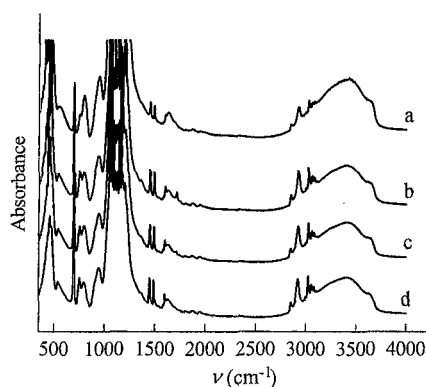


Fig. 7 The FT-IR spectra of hybrid nanoparticles at different monomer conversions

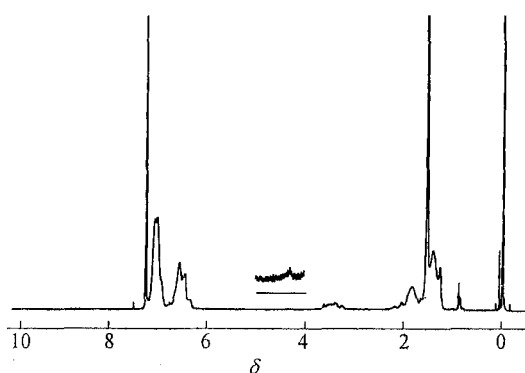


Fig. 8 The ^1H -NMR spectrum of PSt etched silica nanoparticles with 10.4% conversion

CONCLUSIONS

Polymer-inorganic hybrid nanoparticles with well-defined structure were synthesized by modifying the surface of silica nanoparticles with ATRP initiator CTES, which was then used to initiate ATRP of St. Polymerization displayed the diagnostic criteria of a controlled/living radical polymerization. Typical ATRP reaction occurred in a solution system from the surface of silica nanoparticles. The thickness of grafted PSt chains of hybrid nanoparticles can be manipulated through the control of monomer conversion of ATRP reaction.

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