

Syntheses of an Azo-Group-Bound Silica Initiator and Silica–Polystyrene Composites

Libang Feng, Jiaofeng Ye, Xiaohu Qiang, Hongxia Zhang

School of Mechatronic Engineering, Lanzhou Jiaotong University, Lanzhou 730070, China

Received 12 August 2010; accepted 17 October 2010

DOI 10.1002/app.33639

Published online 22 February 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: In this article, we present a facile method for the synthesis of an azo-group-bound silica (SiO_2 -azo) initiator. The azo groups were introduced onto the surface of silica (SiO_2) nanoparticles via facile condensation between 4,4'-azobis-4-cyanopentanoic acid and the alkyl-hydroxyl groups - immobilized on the SiO_2 nanoparticle surface under ambient conditions. The polystyrene (PS) chains were grafted onto the SiO_2 nanoparticle surface by *in situ* polymerization with the resulting SiO_2 -azo as an initiator, and then, the SiO_2 -PS composite was prepared. The syntheses and properties of the SiO_2 -azo initiator and the composite were characterized by Fourier transform

infrared spectroscopy, X-ray photoelectron spectroscopy, thermogravimetric analysis, gel permeation chromatography, and differential scanning calorimetry techniques. The results confirm that the SiO_2 -azo initiator and the composite were synthesized successfully. Styrene was polymerized with the initiation of SiO_2 -azo, and the resulting PS domain accounted for 48.6% of the total amount of composite. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 454–461, 2011

Key words: composites; initiators; nanoparticle; polystyrene; silicas

INTRODUCTION

Recently, organic–inorganic hybrid materials have been considered a kind of innovative advanced material in the fields of ceramics, polymer chemistry, organic and inorganic chemistry, mechanics, and electrochemistry.^{1–3} Polymer-encapsulated inorganic nanoparticles are important hybrid materials, and the design and synthesis of polymer/inorganic composites is a fascinating area with numerous scientific and technological applications in the fields of optics, mechanics, ionoelectronics, and biology.^{4,5} Polymer/inorganic composites can be divided into two distinct classes with respect to the chemical nature of their polymer–inorganic interface. In class I composites, polymer and inorganic components are mixed together, and only ionic or weak bonds (hydrogen, Van der Waals, etc) govern the cohesion of the whole structure. In class II composites, the polymer–inorganic phases are linked together through strong chemical bonds (covalent or ionocovalent bonds).^{6,7}

Chemically bound polymer–inorganic composites can be synthesized by chemical grafting techniques. Generally, chemical grafting techniques include the grafting-to and grafting-from methods. The method of grafting to involves the reaction of appropriate end-capped functional groups or side pendant groups in polymers with the inorganic particles. This method is simple, but the graft density is fairly low because the diffusion of polymer chains to the surface of the particles is hindered sterically.^{8–10} This limitation can be circumvented by the grafting-from method, in which initiating groups are anchored onto the surface of the particles followed by *in situ* polymerization. Because the chain radicals are consistently on the surface of the grafted polymers, and the diffusion of smaller monomers is relatively easier. Consequently, the graft density is determined by the density of the initiating groups, and generally, a higher graft density can be achieved.^{11,12} A variety of polymerization techniques can be used in the grafting-from method, including conventional free-radical polymerization,^{13,14} cationic polymerization,¹⁵ anionic polymerization,¹⁶ ring-opening polymerization,¹⁷ atom transfer radical polymerization,^{18–20} nitroxide-mediated polymerization,²¹ and reversible addition fragmentation chain-transfer polymerization.²² In a previous study, poly(methyl methacrylate) chains were successfully grafted onto the surface of silica (SiO_2) nanoparticles by direct facile esterification condensation between carboxyl-terminated poly(methyl methacrylate) and alkyl-

Correspondence to: L. Feng (lepond@hotmail.com).

Contract grant sponsor: "Qing Lan" Talent Engineering Funds by Lanzhou Jiaotong University; contract grant number: QL-08-03A.

Contract grant sponsor: Natural Science Foundation of Gansu Province, China; contract grant number: 1010RJZA062.

Journal of Applied Polymer Science, Vol. 121, 454–461 (2011)
© 2011 Wiley Periodicals, Inc.

hydroxyl-terminated SiO₂ nanoparticles under mild conditions, such as ambient temperature and moisture and atmospheric pressure.²³ In this research, azo-group-bound SiO₂ (SiO₂-azo) initiator was synthesized via esterification condensation between 4,4'-azobis-4-cyanopentanoic acid (ACPA) and alkyl-hydroxyl groups of SiO₂ nanoparticles under similar mild conditions. Then, the resulting SiO₂-azo nanoparticle was used as an initiator, and SiO₂-polystyrene (PS) composites were prepared.

EXPERIMENTAL

Materials

SiO₂ nanoparticles, with a mean size of 80 nm, were synthesized according to the well-known Stöber et al.²⁴ method and dried *in vacuo* at 110°C for 24 h before use. 3-Glycidoxypropyl trimethoxysilane (GPS) and 4,4'-azobis-4-cyanopentanoic acid (ACPA) were received from Aldrich and were used as received. 4-(Dimethylamino) pyridine, *p*-toluenesulfonic acid, and *N,N'*-dicyclohexylcarbodiimide (DCC) were purchased from Sinopharm Group Chemical Reagent Co., Ltd. (Shanghai, China) and were used as received. Toluene and 1,2-dichloroethane, analytical grade, were dried with 3A molecular sieves before use. Tetrahydrofuran (THF), *N,N'*-dimethylformamide, ethanol, acetone, toluene, and 1,4-dioxane were from BASF Chemical Engineering Co., Ltd. (Shanghai, China). Styrene (St; Sinopharm Group Chemical Reagent Co., Shanghai, China) was treated with 5 wt % aqueous NaOH to remove the inhibitor, dried over anhydrous calcium chloride, and then stored at low temperature before use.

Synthesis of 4-(dimethylamino) pyridinium-*p*-toluenesulfonate (DPTS)

The DPTS catalyst was prepared by the reaction between equimolar *p*-toluenesulfonic acid and 4-(dimethylamino) pyridine in a warm benzene solution. The resulting suspension was filtered and purified by recrystallization from dry 1,2-dichloroethane. The detailed procedure was described in a previous article.²⁵ Finally, white needles with a melting point of 165°C were obtained.

Introduction of epoxy and alkyl-hydroxyl groups onto the SiO₂ nanoparticle surface

The epoxy-group-grafted SiO₂ nanoparticles, SiO₂-GPS, was prepared by the modification of the SiO₂ nanoparticles with epoxy-group-containing silane (GPS). The detailed procedure was described in a previous article.²³ The typical procedure was as follows: SiO₂ nanoparticles and GPS were refluxed in dry toluene for 8 h under an N₂ atmosphere, and

the resulting suspension was centrifuged and redispersed in dry toluene and anhydrous ethanol, respectively. The obtained precipitate, SiO₂-GPS, was dried *in vacuo*.

The introduction of alkyl-hydroxyl groups onto the surface of the SiO₂ nanoparticles was achieved by the refluxing of SiO₂-GPS in an ethanol solution of hydrochloric acid (1.6M). In this case, the epoxy groups on the surface of the SiO₂ nanoparticles were converted into alkyl-hydroxyl units.²⁶ The resulting suspension was centrifuged and rinsed with distilled water thoroughly until the pH was 7. Finally, the precipitate was redispersed in ethanol and then centrifuged again. The treated SiO₂ nanoparticles are abbreviated as SiO₂-ROH.

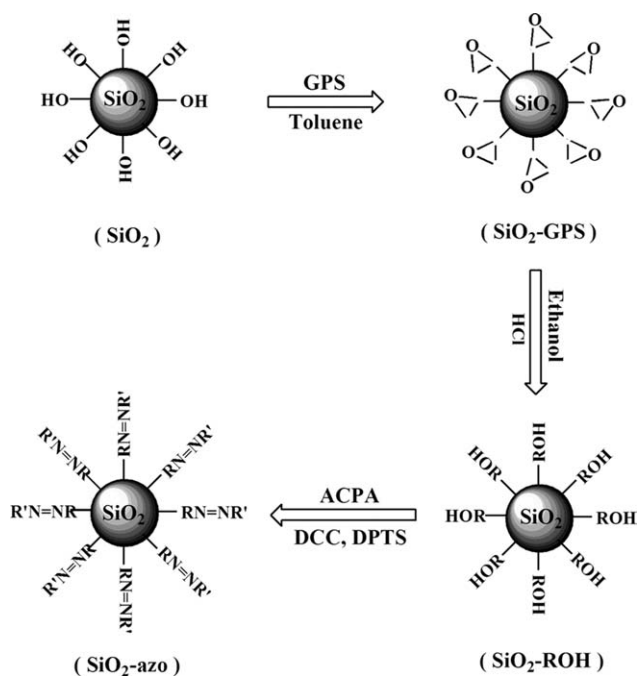
Synthesis of the SiO₂-azo initiator

The SiO₂ initiator, SiO₂-azo, was prepared by the grafting of carboxyl-terminated ACPA, which contained azo groups and could be used as an initiator, onto the nanosized SiO₂ surface. This reaction was accomplished via a direct one-step esterification reaction by the use of DCC as an activating agent and DPTS as a catalyst under extremely mild conditions, that is, ambient temperature and atmospheric pressure, just as in the synthesis of macrozooinitiators.^{27,28} A typical synthesis procedure was as follows: SiO₂-ROH (3.0 g), ACPA (1.5 g), and DPTS (0.045 g) were charged into a 250-mL, round-bottom flask containing mixed solvents (60 mL of THF and 18 mL of *N,N'*-dimethylformamide) and ultrasonicated for 10 min. Then, a solution containing 0.09 g of DCC and 30 mL of THF was added drop by drop under magnetic stirring. After this addition was finished, the reaction was carried out at room temperature for 24 h. The resulting suspension was centrifuged, and the collected precipitate was redispersed with ultrasonication and extracted extensively with THF and toluene, respectively, to remove the unreacted ACPA and other substances. Finally, the product was dried at room temperature *in vacuo* to a constant weight, and a white powder with a yield of over 80% was obtained. The resulting SiO₂ initiator, abbreviated as SiO₂-azo, was stored in the dark below 0°C.

The schematic procedure for synthesis of SiO₂-azo is shown in Scheme 1.

Synthesis of the SiO₂-PS composites

In a further step, SiO₂-azo was used to initiate St to polymerize, and the polymerization was carried out in a three-necked flask under an N₂ atmosphere. The typical process was as follows: first, 5.0 g of St was dissolved into 5 g of 1,4-dioxane in a flask, and then, the temperature was increased to 50°C. Second, 1.0 g of SiO₂-azo was charged into the flask, and



Scheme 1 Procedure of the synthesis of $\text{SiO}_2\text{-azo}$.

then, the mixture was kept at 70°C for 12 h under stirring. After the graft polymerization process, the resulting suspension was isolated by slow precipitation with methanol. Next, the collected precipitate was redispersed in 1,4-dioxane with ultrasonication, and then, the suspension was precipitated again. Finally, the white powder composite, which was denoted as $\text{SiO}_2\text{-PS}$, was dried *in vacuo* at 40°C to a constant weight.

Cleavage of the grafted PS from the SiO_2 nanoparticles

PS chains fixed at the SiO_2 nanoparticles were cleaved as described in a reference procedure.²⁹ The $\text{SiO}_2\text{-PS}$ composite (0.5 g) was vigorously stirred in a polyethylene flask containing 15 mL of toluene and 10 mL of 20 wt % aqueous hydrofluoric acid, along with Aliquat 336 as a phase-transfer catalyst. The aqueous layer was removed after 2 h, and 10 mL of 20 wt % hydrofluoric acid containing Aliquat 336 was added and stirred for another 2 h. This procedure was repeated until no impurities could be detected by gel permeation chromatography (GPC). The PS contained in the organic layer was recovered by precipitation in methanol and vacuum filtration through a fine-grain glass frit. Finally, the white powder PS was obtained.

Characterization

Fourier transform infrared (FTIR) spectroscopy analysis

The chemical structure of the samples was measured by FTIR spectroscopy with a VERTEX 70 FTIR

spectrometer (Bruker, Karlsruhe, Germany) in the range $400\text{--}4000\text{ cm}^{-1}$, and the KBr pellet technique was used.

Differential scanning calorimetry (DSC) measurement

DSC measurements were conducted on a Shimadzu DSC-60 instrument (Kyoto, Japan) calibrated with indium and *n*-octane. The sample, with a weight of about 10 mg, was heated from 25 to 160°C at a heating rate of $10^\circ\text{C}/\text{min}$. The glass-transition temperature (T_g) was determined from the midpoint of the change in the heat capacity.

Gel permeation chromatography (GPC) measurement

The molecular weight and its distribution were measured by GPC (PL-50, Polymer Lab, Church Stretton, UK). THF was used as the eluent, and narrow PS was used as the calibration standard.

X-ray photoelectron spectroscopy (XPS) measurement

The surface composition of the resulting samples was investigated by XPS with a PHI-5702 multifunctional spectrometer (Perkin-Elmer Physical Electronics, Foster City, USA) with an Al $K\alpha$ X-ray source under 14.0 kV, 2500 W, and a less than 10^{-6} Pa analyzer chamber pressure. Narrow-scan spectra of C1s, O1s, and Si2p were collected at a pass energy of 29.35 eV, and peak analyses were performed with Multipak software (Multipak 6.0, Perkin-Elmer Physical Electronics, Foster City, USA). A binding energy (BE) of C1s of 285.0 eV was used as a reference.

Thermogravimetric analysis (TGA)

TGA was performed on a Netzsch STA 449C thermogravimetric instrument (Selb, Germany). The temperature ranged from 30 to 1000°C , with a heating rate of $20^\circ\text{C}/\text{min}$ under an argon atmosphere.

RESULTS AND DISCUSSION

Introduction of epoxy and then alkyl-hydroxyl groups onto the SiO_2 nanoparticle surface

It is well known that silanol groups on the SiO_2 surface can react with a silane coupling agent to readily form surface-functional groups. In our experiment, epoxy-group-modified SiO_2 was achieved by the treatment of SiO_2 with GPS, and it was possible to approach a reproducible preparation of a covalently bound thin layer of GPS on the SiO_2 particle surface. The successful preparation of epoxy-group-modified

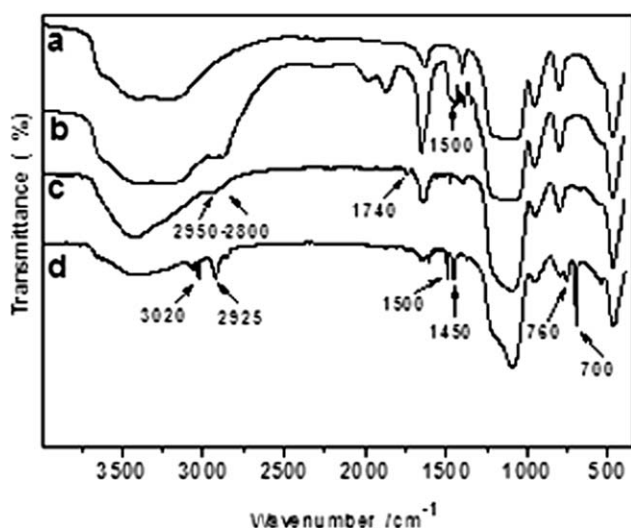


Figure 1 FTIR spectra of (a) the untreated SiO_2 , (b) SiO_2 -GPS, (c) SiO_2 -azo, and (d) SiO_2 -PS.

SiO_2 nanoparticles was confirmed by FTIR and XPS measurements.

FTIR was used to confirm the successful grafting of azo groups, as shown in Figure 1. Figure 1(a) shows the FTIR spectrum of the untreated SiO_2 . The absorption peak at $1020\text{--}1110\text{ cm}^{-1}$ was assigned to Si—O—Si asymmetric stretching vibrations, and the peaks at 960 and 800 cm^{-1} were ascribed to the asymmetric bending and stretching vibration of Si—OH, respectively. By contrast, the new absorption of the —CH stretching vibration at $2800\text{--}2950\text{ cm}^{-1}$ was present in the FTIR spectrum of SiO_2 -GPS [Fig. 1(b)]. Meanwhile, Figure 1(b) shows the asymmetrical deformation vibration of the epoxy groups at 1500 cm^{-1} ; this indicates that the epoxy groups were successfully fixed onto the SiO_2 nanoparticle surface. In addition, there were also absorption peaks around 1640 and $3000\text{--}3600\text{ cm}^{-1}$ for both spectra; these were assigned to the bending mode of physically absorbed water molecules.

The resulting SiO_2 -GPS was also characterized with XPS, as shown in Figure 2. Figure 2(a) shows the survey scan spectrum of SiO_2 -GPS. The major peak component at a BE of 532.8 eV was attributable to O1s, and the minor peak component at a BE of 285.0 eV was assigned to C1s. Meanwhile, peaks at BEs of 154.4 and 103.2 eV corresponded to Si2s and Si2p, respectively. The peak of Si2p could be curve-fitted with two peak components with BEs of 103.6 and 101.7 eV , and these two peaks were attributable to O—Si—O and O—Si—C species, respectively, as shown in Figure 2(b). In addition, the full widths at half-maximum of the curve-fitted peaks were 1.71 and 1.69 , respectively; this showed the rationality of the curve fit. Thereupon, it was proven that GPS was covalently bound to the SiO_2 nanoparticle surface.

The epoxy groups at the surface of the SiO_2 nanoparticles could be converted into alkyl-hydroxyl groups through the refluxing of SiO_2 -GPS in an ethanol solution of hydrochloric acid, and then, SiO_2 -ROH resulted. The successful synthesis of SiO_2 -ROH was also characterized with the FTIR and XPS techniques, and results similar to those of SiO_2 -GPS were obtained.

Synthesis of the SiO_2 -azo initiator

The azo compound is a commonly used radical initiator, and it can initiate the vinyl monomer to polymerize. In our research, carboxyl-terminated ACPA was adopted to react with the alkyl-hydroxyl groups on the SiO_2 surface to introduce azo groups at the SiO_2 surface, and then, the SiO_2 initiator, SiO_2 -azo, was prepared. The successful preparation of SiO_2 -azo was confirmed by techniques such as FTIR spectroscopy, XPS, and DSC.

Figure 1(c) shows the FTIR spectrum of the resulting SiO_2 -azo. Similarly, the —CH absorption peak was present at $2800\text{--}2950\text{ cm}^{-1}$. More importantly,

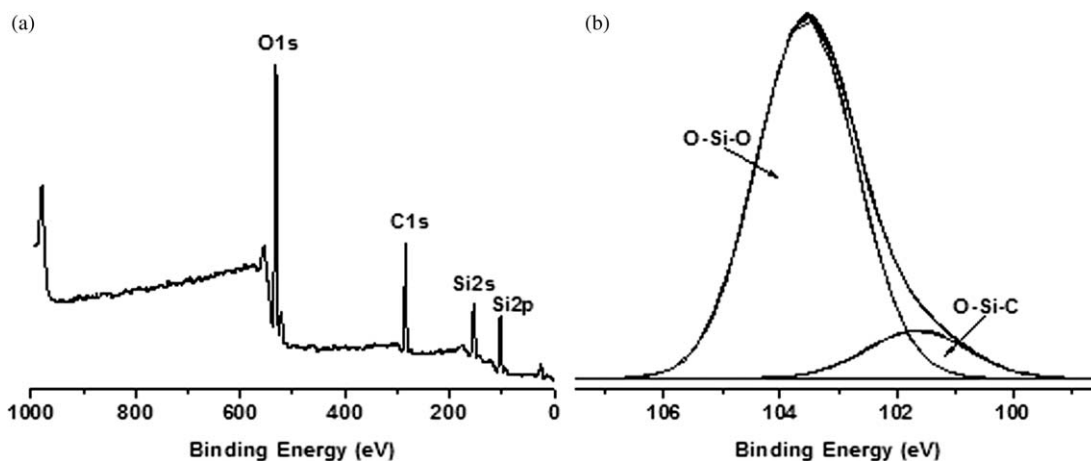


Figure 2 XPS spectra of SiO_2 -GPS: (a) the survey scan spectrum and (b) the Si2p core-level spectrum.

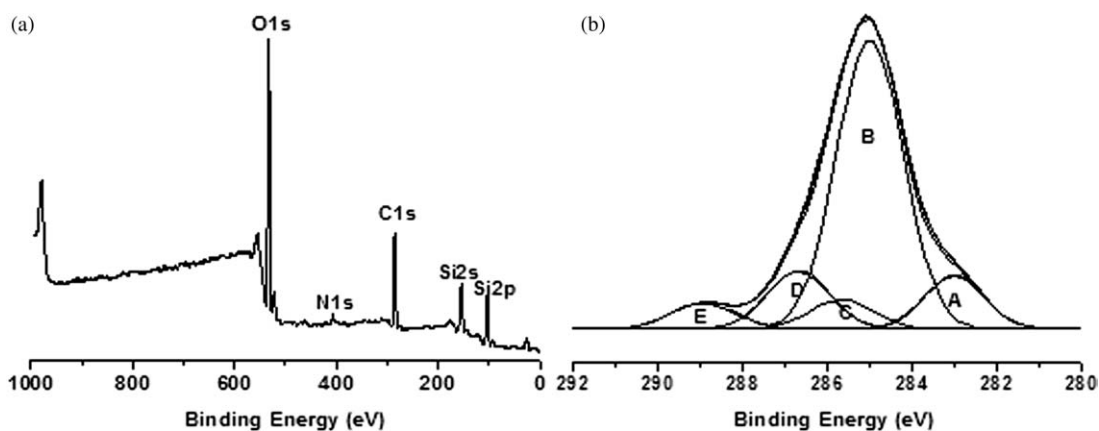


Figure 3 XPS spectra of the SiO₂-azo: (a) the survey scan spectrum and the (b) the C1s core-level spectrum.

the characteristic absorption band of the carbonyl group at 1740 cm⁻¹ was present; this manifested that the esterification reaction between ACPA and alkyl-hydroxyl-modified SiO₂ took place effectively under the selected mild conditions. As a result, the SiO₂-azo initiator was synthesized.

Figure 3(a) shows the XPS survey scan spectrum of the resulting SiO₂-azo. Compared with the scan spectrum of SiO₂-GPS [Fig. 2(a)], an N1s peak at 405.4 eV was observed on the wide XPS spectrum; this indicated that the azo groups were successfully grafted onto the SiO₂ surfaces. As further proof for this conclusion, the typical high-resolution C1s spectrum of SiO₂-azo was consistent with five different carbon environments because of their BEs at 282.9, 285.0, 285.7, 286.7, and 288.9 eV, as shown in Figure 3(b) and Table I, which were attributable to peaks A (C–Si), B (C–C/C–H), C (C–N), D (C–O), and E (C=O), respectively. The appearance of the component peak C–N showed that the reaction between the alkyl-hydroxyl groups on the SiO₂ surface and the carboxyl-terminated ACPA indeed occurred, and the azo groups were undoubtedly immobilized on the SiO₂ surfaces. As a result, a kind of SiO₂-azo initiator was prepared.

DSC was used to determine the content of azo groups introduced onto the SiO₂ nanoparticle surface by comparison with the exothermic peak area of SiO₂-azo and ACPA. Figure 4(a–c) shows the DSC

curves of the untreated SiO₂, ACPA, and SiO₂-azo, respectively. There was no exothermic peak on the DSC trace of the untreated SiO₂ [Fig. 4(a)]. By contrast, the DSC traces of both ACPA [Fig. 4(b)] and SiO₂-azo [Fig. 4(c)] showed a distinct exothermic peak at the temperature 120–140°C, respectively, due to the decomposition of azo groups. This also confirmed the successful introduction of azo groups onto the SiO₂. Finally, the content of the azo groups introduced onto the SiO₂ was determined to be 0.25 mmol/g.

Synthesis of the SiO₂-PS composite

The SiO₂-azo was used as an initiator to initiate the polymerization of St. In the polymerization process, azo groups bound to the SiO₂ surface produced both surface radicals and primary (fragment) radicals. The surface radicals initiated the graft polymerization and brought on the grafted PS, whereas the

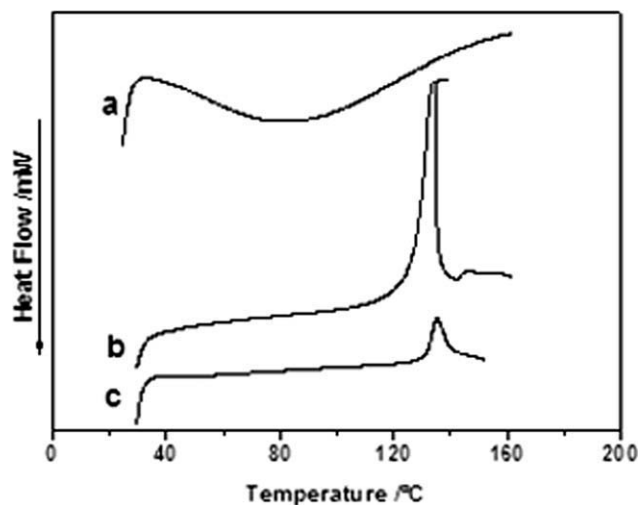
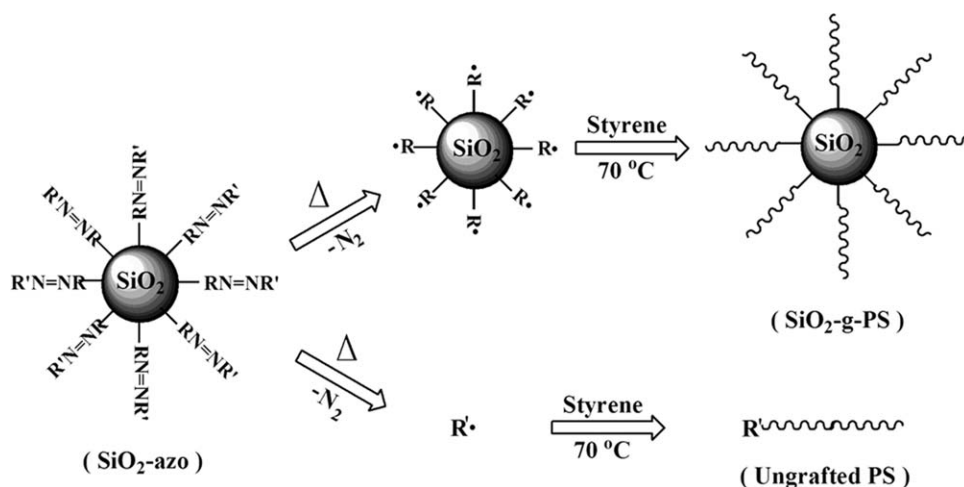


Figure 4 DSC curves of (a) the untreated SiO₂, (b) ACPA, and (c) SiO₂-azo.

TABLE I
C1s Core-Level Spectrum Parameters for SiO₂-Azo

Peak	BE (eV)	Full width at half-maximum	Peak area
A (C–Si)	282.9	1.42	6915
B [C–C(H)]	285.0	1.52	41907
C (C–N)	285.7	1.47	3971
D (C–O)	286.7	1.45	7811
E (C=O)	288.9	1.50	3600



Scheme 2 Schematic diagram of the two-mode polymerization initiated with $\text{SiO}_2\text{-azo}$.

fragment radicals produced free linear PS (ungrafted PS), just as shown in the schematic diagram of the polymerization initiated with $\text{SiO}_2\text{-azo}$ in Scheme 2. Because the ungrafted PS was not removed in the experiment, the $\text{SiO}_2\text{-PS}$ composite resulted.

Figure 1(d) also shows the FTIR spectrum of the $\text{SiO}_2\text{-PS}$ composite. The characteristic peaks of the stretching vibration for $-\text{CH}$ groups at 3020 and 2925 cm^{-1} were very obvious. Also, several characteristic absorption peaks of the aromatic ring were present in the spectrum. For instance, the peak at 2000–1700 cm^{-1} was ascribed to the overtone absorption, the peaks at 1500 and 1450 cm^{-1} were assigned to the stretching vibration of the $\text{C}=\text{C}$ framework, and the peaks at 760 and 700 cm^{-1} were characteristic absorptions of the single-replaced phenyl ring. Meanwhile, the characteristic peaks at 1020–1110, 960, and 800 cm^{-1} for SiO_2 adsorption were also present in the spectrum; this indicated that the resulting product was composed of PS chains and SiO_2 .

Content of PS in the resulting composite

The relative amount of PS in the resulting composite was estimated by TGA, and TGA traces of the original SiO_2 and the $\text{SiO}_2\text{-PS}$ composite are shown in Figure 5. Figure 5(a) shows the thermogravimetric loss process of the original SiO_2 . The weight loss before 300 °C was due to the loss of the adsorbed water molecules and the release of structural water, whereas the weight loss between the temperatures of 300 and 600 °C were due to the decomposition of the organic groups and the rupture of $\text{Si}-\text{OH}$, which came from the precursor when SiO_2 was synthesized. The total weight loss of the original SiO_2 was around 5.5%. Figure 5(b) shows the thermogravimetric loss process of the $\text{SiO}_2\text{-PS}$ composite. Two main

ranges of weight loss were located around 300–400 and 520–580 °C, respectively. The first step corresponded to the decomposition of PS domains, whereas the second one resulted from the thermal cracking of $\text{Si}-\text{OR}$ and $\text{Si}-\text{OH}$. The total weight loss of the composite was about 54.1%. By comparison of the weight losses of the original SiO_2 and the composite, we determined that the PS segment accounted for about 48.6% of the total amount of the composite.

Molecular weight of the resulting PS

To further demonstrate the efficiency of the initiation and polymerization, the grafted PS chains were cleaved from the SiO_2 . The recovered PS was then subjected to GPC analysis, and the investigated GPC trace is illustrated in Figure 6. The GPC trace of the cloven PS was symmetrically unimodal. The weight-average molecular weight and the molecular weight

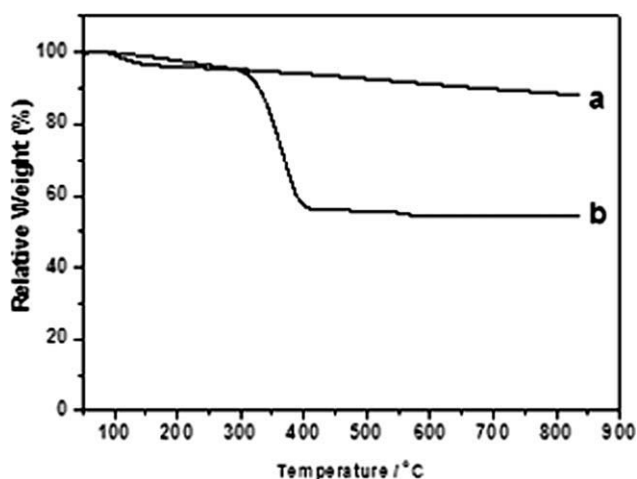


Figure 5 TGA traces of the (a) original SiO_2 and (b) $\text{SiO}_2\text{-PS}$ composite.

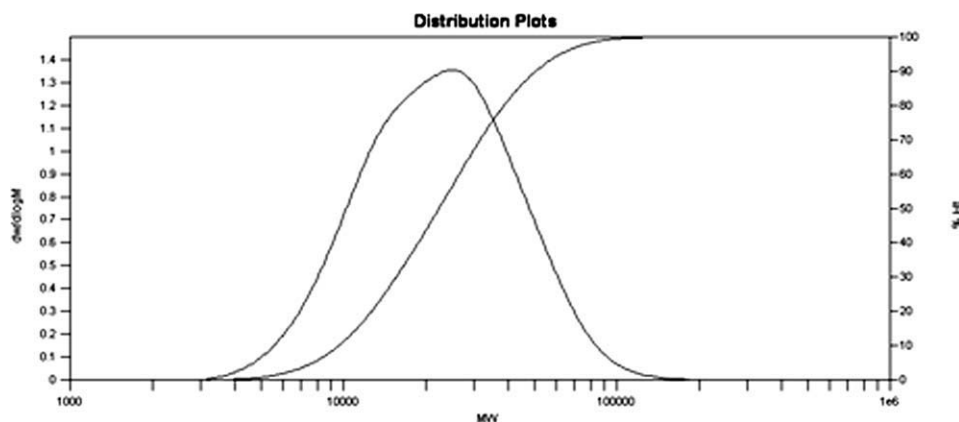


Figure 6 GPC trace of the cloven polystyrene (PS).

distribution (weight-average molecular weight/number-average molecular weight) of the cloven PS were 28,100 and 1.63, respectively. This indicated that the SiO₂-azo had a high initiating efficiency. Consequently, the PS chains were grafted onto the SiO₂ nanoparticle surface effectively, with a very high molecular weight.

Thermal transition temperature of the PS

The thermal transition temperatures of the obtained composite together with the cloven PS were investigated with DSC, and the measurement traces are shown in Figure 7. The results show that the PS domain in the SiO₂-PS composite had a T_g of about 106.5°C; this was higher than that of the cloven PS, which was 97.3°C. This showed that the mobility of the PS chains grafted at the particle surface was hindered. Therefore, T_g of the grafted PS domain at the surface of the SiO₂ nanoparticles increased.

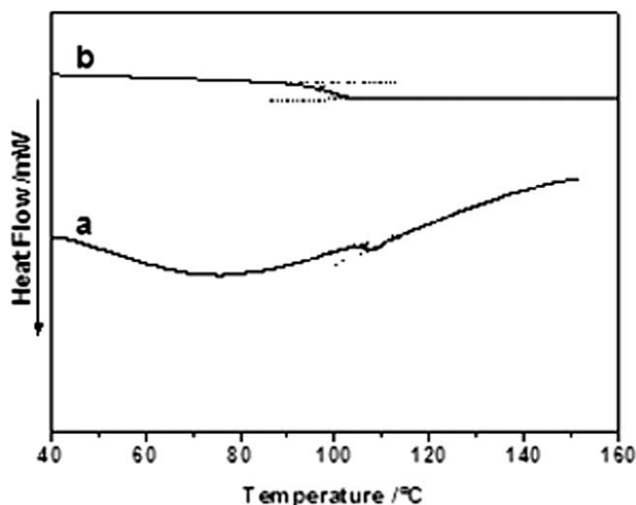


Figure 7 DSC traces of the (a) SiO₂-PS composite and (b) cloven PS.

CONCLUSIONS

In this article, we presented the syntheses of an SiO₂-azo nanoparticle initiator along with that of the SiO₂-PS composite. The SiO₂-azo nanoparticle initiator was prepared by the modification of the SiO₂ nanoparticle surface, first with GPS and then with the grafting of the azo group onto the nanoparticles via an esterification reaction under mild conditions. The SiO₂-PS composite was synthesized by the radical polymerization of St initiated by the resulting SiO₂-azo initiator. The results show that the PS domain accounted for 48.6% of the total amount of the composite. T_g of the grafted PS was about 9°C higher than that of the cloven PS domain. Additionally, this facile esterification method could be extended to the preparation of other inorganic initiators, and the resulting inorganic initiators could also be used to synthesize various inorganic polymer composites.

References

- Chang, M. H.; Hsieh, T. E.; Huang, B. R.; Hsieh, H. E.; Juang, F. S.; Tsai, Y. S.; Liu, M. O.; Lin, J. L. *Mater Chem Phys* 2009, 115, 541.
- Huang, G. C.; Lee, J. K. *Compos A* 2010, 41, 473.
- Chen, D. L.; Wen, H. J.; Chen, H. M.; Wang, H. L.; Zhang, R.; Xu, H. L.; Yang, D. Y.; Lu, H. X. *Mater Chem Phys* 2009, 116, 507.
- Ji, Q.; Wang, X.; Zhang, Y. H.; Kong, Q. S.; Xia, Y. Z. *Compos A* 2009, 40, 878.
- Tsubokawa, N. *Polym J* 2005, 37, 637.
- Lesot, P.; Chapuis, S.; Bayle, J. P.; Rault, J.; Lafontaine, E.; Campero, A.; Judeinstein, P. *J Mater Chem* 1998, 8, 147.
- Yoon, T. J.; Kim, J. S.; Kim, B. G.; Yu, K. N.; Cho, M. H.; Lee, J. K. *Angew Chem Int Ed* 2005, 44, 1068.
- Lyatskaya, Y.; Balazs, A. C. *Macromolecules* 1998, 31, 6676.
- Mansky, P.; Liu, Y.; Huang, E.; Russel, T. P.; Hawker, C. *Science* 1997, 275, 1458.
- Taniguchi, Y.; Ogawa, M.; Gang, W.; Saitoh, H.; Fujiki, K.; Yamauchi, T.; Tsubokawa, N. *Mater Chem Phys* 2008, 108, 397.
- Radhakrishnan, B.; Ranjan, R.; Brittain, W. J. *Soft Matter* 2006, 2, 386.

12. Edmondson, S.; Osborne, V. L.; Huck, W. T. S. *Chem Soc Rev* 2004, 33, 14.
13. Bachmann, S.; Wang, H. Y.; Albert, K.; Partch, R. J. *Colloid Interface Sci* 2007, 309, 169.
14. Yokoyama, R.; Suzuki, S.; Shirai, K.; Yamauchi, T.; Tsubokawa, N.; Tsuchimochi, M. *Eur Polym J* 2006, 42, 3221.
15. Ueda, J.; Gang, W.; Shirai, K.; Yamauchi, T.; Tsubokawa, N. *Polym Bull* 2007, 60, 617.
16. Zhou, Q. Y.; Wang, S. X.; Fan, X. W.; Advincula, R. *Langmuir* 2002, 18, 3324.
17. Jordi, M. A.; Seery, T. A. P. *J Am Chem Soc* 2005, 127, 4416.
18. Airaud, C.; Ibarboure, E.; Gaillard, C.; Héroguez, V. *J Polym Sci Part A: Polym Chem* 2009, 47, 4014.
19. Zhang, H.; Lei, X. P.; Su, Z. X.; Liu, P. *J Polym Res* 2007, 14, 253.
20. Harrak, A.; Carrot, G.; Oberdisse, J.; Jestin, J.; Boue, F. *Polymer* 2005, 46, 1095.
21. Stenzel, M. H.; Zhang, L.; Huck, W. T. S. *Macromol Rapid Commun* 2006, 27, 1121.
22. Liu, C. H.; Pan, C. Y. *Polymer* 2007, 48, 3679.
23. Feng, L. B.; He, L.; Ma, Y. X.; Wang, Y. L. *Mater Chem Phys* 2009, 116, 158.
24. Stöber, W.; Fink, A.; Bohn, E. *J Colloid Interface Sci* 1968, 26, 62.
25. Feng, L. B.; Fang, H. X.; Zhou, S. X.; Wu, L. M. *Macromol Chem Phys* 2006, 207, 1575.
26. Hong, C. Y.; Li, X.; Pan, C. Y. *Eur Polym J* 2007, 43, 4114.
27. Feng, L. B.; Fang, H. X.; Zhou, S. X.; Wu, L. M.; You, B. *J Appl Polym Sci* 2007, 104, 3356.
28. Feng, L. B.; Fang, H. X.; Zhou, S. X.; Gu, G. X.; Wu, L. M. *Acta Polym Sin* 2007, 5, 472.
29. Pyun, J.; Jia, S.; Kowalewski, T.; Patterson, G. D.; Matyjaszewski, K. *Macromolecules* 2003, 36, 5094.