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Preparation of polystyrene/silica nanocomposites by radical copolymerization of styrene with silica macromonomer

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A two-stage process has been developed to generate the silica-based macromonomer through surface-modification of silica with polymerizable vinyl groups. The silica surfaces were treated with excess 2,4-toluene diisocynate (TDI), after which the residual isocyanate groups were converted into polymerizable vinyl groups by reaction with hydroxypropylacrylate (HPA). Thus, polystyrene/silica nanocomposites were prepared by conventional radical copolymerization of styrene with silica macromonomer. The main effecting factors, such as ratios of styrene to the macromonomer, together with polymerization time on the copolymerization were studied in detail. FTIR, DSC and TGA were utilized to characterize the nanocomposites. Experimental results revealed that the silica nanoparticles act as cross-linking points in the polystytene/silica nanocomposites, and the glass transition temperatures of the nanocomposites are higher than that of the corresponding pure polystyrene. The glass transition temperatures of nanocomposites increased with the increasing of silica contents, which were further ascertained by DSC.

silica nanoparticles, surface modification, styrene, radical copolymerization, nanocomposites

1 Introduction

In recent years, an increased interest has been devoted to the preparation and application of polymer/inorganic nanocomposites, which has been pursued as a route to combine the advantageous properties of the nanometer materials, inorganic compounds and polymer into one material. The particular surface effect and quantum size effect of nanometer materials, the rigidness, dimension stability and thermal stability of inorganic materials, and the toughness, easy processability, and dielectric properties of polymer were combined in the polymer/inorganic nanocomposites. Further, the polymer/inorganic nanocomposites may possess some particular properties or functions, which are not provided by the original components[1−3], and have a high potential for applications in many fields, including optics, electronics, ionics, mechanics, membranes, protective coatings, catalysis, sensors, and biology[4−6]. Recently, much attention has centered on the synthesis of polymer/inorganic nanocomposites by sol-gel process[7−11]. However, the nanocomposites prepared by sol-gel technology embrittle easily because of the internal stress, which is brought out by the volatilization of solvent, little molecule and water during the sol-gel process, and this method also requires the polymer can be dissolved and stability maintained after gel[12,13]. In addition, the precursors are toxic and expensive. Due to all these disadvantages the process of generalization and application of this method has been seriously restricted. Compared with the sol-gel process employed to synthesize organic/inorganic nanocomposites, blend of inorganic nanoparticles with polymer directly to prepare polymer/inorganic nanocomposites has

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several advantages. Firstly, the morphology and dimension of the nanoparticles can be controlled because the nanoparticles and nanocomposites are prepared through a different step. Further, the operating procedure is simple and can be carried out easily.

In this study, we describe a different strategy to immobilize carbon-carbon double bonds at the surface of silica particles, i.e., by treating the silica particles surface with excess 2,4-toluene diisocynate (TDI) first and consecutively with the hydroxypropylacrylate (HPA). The thus immobilized vinyl groups (macromonomer) have been used to copolymerize with styrene to prepare polystyrene/silica nanocomposites. Nanocomposites with different silica content can be prepared by copolymerization of styrene with the thus prepared macromonomer, and the chains architecture can also be modified easily by a choice of the comonomer ratio in the feed. Polymer/silica nanocomposites prepared by this approach may be used as materials directly without separation of the homopolymer formed in this procedure. Furthermore, a much stronger adhesion between the polymer chains and the substrate can be achieved because the macromolecules are covalently bound to the surface of silica nanoparticles, which act as cross-linking points in the polystyrene matrix. The aggregation of the silica particles can be hindered in the polymer/silica nanocomposites. This modification method opens up a new avenue to design and prepare polymer/silica nanocomposites.

2 Experimental

2.1 Materials

Silica nanoparticles, with an average diameter of 10 nm and surface hydroxyl groups of 1.0 mmol/g, were obtained from Zhoushan Mingri Nanomaterials Co., Ltd., China, and were dried for 24 h at 110℃ under vacuum before use. 2,4-toluene disiocynate (TDI) (99%, Shanghai Chemical Industrial Co., Ltd., China) were distilled in vacuum before use. Toluene was distilled under a nitrogen atmosphere from sodium/potassium using benzophenone as an indicator. Hydroxypropylacrylate (HPA) (99%, Laporte performance Chemicals UK Limited) and Styrene (99%, Shanghai Chemical Industrial Co., Ltd., China) were all dried over CaH_2 for 24 h and then distilled in vacuum. 2,2′-Azobis(isobutyronitrile) (AIBN, 99.8%) was purchased from Aldrich and purified by recrystallization from methanol.

2.2 Characterization

FTIR spectroscope (KBr film) was carried out on a PE Spectrum One B. Differential scanning calorimetric (DSC) traces were recorded on a TA DSC Q10 at a scan rate of 20 K/min under nitrogen. Thermogravimetric measurements were performed using Shimadza TG-40 analyzer by heating the sample in a flow of nitrogen at 10℃/min.

2.3 Preparation of silica macromonomer

The surface modification procedure was carried out as follows: in a typical experiment, a mixture with 3.0 g silica particles (3.0 mmol based on hydroxyl groups) and 3.13 g TDI (18.0 mmol) dispersing in 90 mL dried toluene was placed in an ultrasonic bath for 10 min, then the mixture was degassed by three freeze-pump-thaw cycles under the atmosphere of nitrogen. The reaction mixture was magnetic stirred at the temperature of 90℃ maintained by a thermostat for 6 h. The powder product was separated by centrifugation and then carefully washed with dry toluene to remove the unreacted and physical-absorbed TDI. The product, TDI modified silica (SiO_2-TDI), was dried in vacuum at 80℃ for 24 h.

The silica macromonomer was synthesized by reacting as-synthesized SiO_2-TDI with HPA. A suspension of 2.0 g SiO_2-TDI (1.42 mmol based on —NCO groups) and 60 mL dry toluene in a round-bottom flask was placed in an ultrasonic bath for 10 min, and then 0.55 g HPA (4.26 mmol) was added. Then after, the suspension was placed in an oil bath at 90℃ for 48 h with stirring. This solution was centrifuged at 3000 r/min for a certain time, which led to sedimentation of the macromonomer (SiO_2-HPA). The supernatant, which contained unreacted HPA and toluene, was discarded and replaced with dry toluene, and this procedure was repeated 3—4 times. The samples for further characterization were extracted with toluene for 48 h to remove any physically absorbed species and were dried at 80℃ for 24 h.

2.4 Synthesis of polystyrene/silica nanocomposites

A series of copolymerization experiments have been conducted with various styrene-to-macromonomer mass ratios. In a typical bulk copolymerization experiment, 1.0 g SiO_2-HPA and 71.0 mg AIBN were dispersed in 9.0 g styrene. The solution was carefully degassed through at least three freeze–thaw-cycles to remove all oxygen traces. Then, the suspension was placed in an ultrasonic bath to prepolymerize at the temperature of 75℃ for 12 h, and after that, the copolymerization mixture was placed in an oil bath at 110℃ for 36 h. After copolymerization, the product was extracted using tetrahydrofuran (THF) in a Soxhlet apparatus for at least 48 h. This procedure was found to be mandatory to remove the entire homopolymer (*homo*-PS) that is formed in the polymerization. The sample obtained after extracting is the product of the copolymer of SiO_2-HPA and styrene, denoted as SiO_2-HPA/St. The copolymer and *homo*-PS were both collected and dried at 80℃ for 24 h before further characterization.

3 Results and discussion

3.1 Preparation of silica macromonomer

As is illustrated in Figure 1, a two-stage process has been developed to bind polymerizable vinyl groups on a silica particle surfaces and using the inorganic particles as macromonomers. Thus, silica particle surface was firstly treated with excess TDI, and in the presence of excess TDI in the reaction system, accessible surface silanol preferentially reacted with a *para*-isocyanate group and left an *ortho*-isocyanate group unreacted due to the difference in reactivity of the two isocyanate groups together with steric hindrance in the TDI molecule. Therefore, a hydroxyl group on the silica surface reacts with a TDI molecule and leaves an unreacted isocyanate group for further reaction, which provides a means for covalent attachment of polymerizable monomers to the silica particle surface. An abundance of polymer/silica nanocomposites can be prepared by conventional radical copolymerization of different monomers with the thus prepared macromonomer, which has a wide range of potential applications.

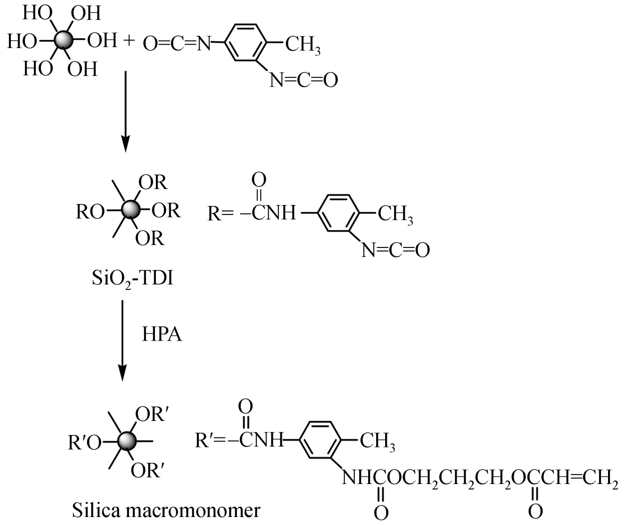

Figure 1 Synthetic procedures for silica macromonomer.

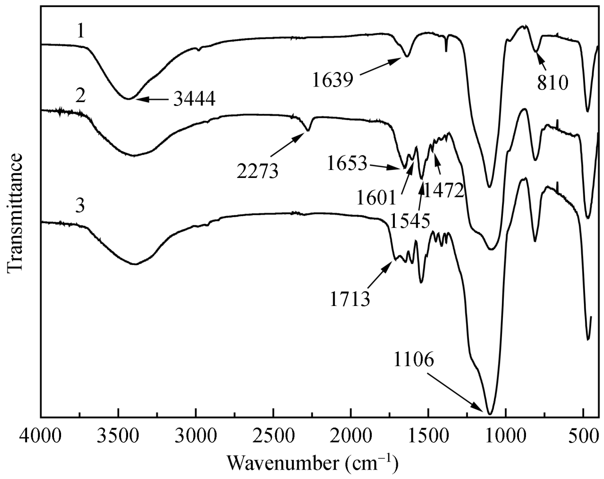

Figure 2 FTIR spectra of SiO_2 (1), SiO_2-TDI (2) and SiO_2-HPA (3).

Figure 2 shows the FTIR spectra of unmodified silica and TDI-modified silica, as well as the silica-based macromonomer. The FTIR spectrum of unmodified silica (Figure 2, curve 1) is relatively simple and well assigned[20]. The strong absorbance at 1106 cm^{-1} is reasonably attributed to the Si—O—Si stretch of silica, and the absorbance at 1639 and 3444 cm^{-1} are assigned to the surface hydroxyl groups of silica. Curve 2 in Figure 3 shows the FTIR spectrum of TDI modified silica (SiO_2-TDI), and compared with the spectrum of the unmodified silica, the TDI modified silica exhibited peaks at 2273, 1653, 1605, 1545 and 1472 cm^{-1} in addition to the peaks of original silica. The peak at 2273 cm^{-1} can be attributed to the *ortho*-isocyanate groups of TDI attached to the silica surface, while the bands at 1653 and 1545 cm^{-1} can be reasonably assigned to the group of —CONH— formed in the reaction[21], and the peaks at 1605 and 1472 cm^{-1} are reasonably attributed to the phenyl ring of TDI. The results clearly confirmed that the TDI molecule was covalently linked to silica particles, suggesting successful surface modification of the silica particles with TDI. Curve 3 in Figure 2 shows the spectrum of the silica macromonomer. Compared with the FTIR spectrum of SiO_2-TDI, it can be obviously observed that the absorbance of —NCO group has disappeared completely, which gives clear evidence that the —NCO groups on the TDI-modified silica surface have reacted with hydroxyl groups of HPA, and a new peak at 1713 cm^{-1} is observed which can be attrib-

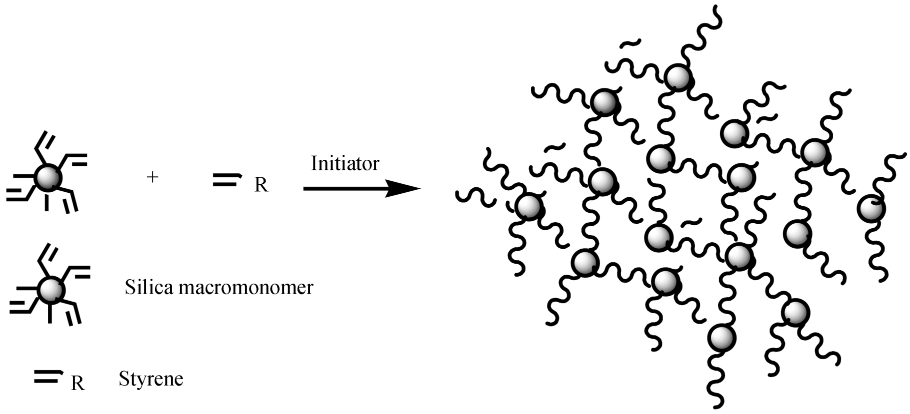

Figure 3 Schematic diagram illustrating the copolymerization of silica macromonomer with styrene.

uted to carbonyl (C═O) of covalent linked HPA[22]. In addition, the peaks at 1650 cm^{-1}, 1546 cm^{-1} became stronger due to the formation of another —NHCO— group. These results clearly demonstrate double bonds were successfully covalently bonded at the silica particles surface.

3.2 Synthesis of polystyrene/silica nanocomposites

Polystyrene/silica nanocomposites were synthesized by radical copolymerization of as-synthesized silica macromonomer with styrene, which was carried out by suspending the macromonomer in styrene in the presence of azobisisobutyronitrile (AIBN), which is shown schematically in Figure 3. The silica macromonomers may act as a cross-linking agent in the copolymerization system, provided that all or part of the immobilized double bonds can be copolymerized. Nanocomposites prepared by this method are composed of a portion of homopolymer and cross-linking copolymer that the cross-linking density can be controlled by the ratio of comonomer in the feed. The silica nanoparticles have been immobilized in the as-synthesized polymer/silica nanocomposites, which contributed to improve the compatibility between inorganic particles and polymer, avoiding the nanoparticles aggregation. In addition, the chemical acting force can also be conducive to make the silica nanoparticles disperse in matrix uniformly, which was in line with the findings of GAO Qibiao et al. [23]. Furthermore, the silica dispersion in such composites can be improved by the formation of polymer between particles, which may result in silica exfoliation.

3.2.1 Copolymerization of silica macromonomer with styrene. To gain a deeper insight into the copolymerization of silica macromonomer with styrene, a series of polymerization experiments have been conducted in bulk with a fixed mole ratio of styrene to AIBN ([St]/[AIBN]=200:1). The results of the copolymerization of SiO_2-HPA with styrene are showed in Table 1.

It can be obviously observed in Table 1 that a high amount of copolymerized styrene can be achieved by increasing the ratio of [St]/[SiO_2-HPA]. For example, when experiments are carried out under the experimental conditions with a variable [St]/[SiO_2-HPA] ratio, the amount of copolymerized styrene increases from 1.2 g for [St]/[SiO_2-HPA] = 9∶1 to 2.1 g for [St]∶[SiO_2-HPA] = 24:1. However, further increasing the [St]/[SiO_2-HPA] ratio showed no improvement in the amount of copolymerized styrene. For instance, when the ratio reaches 49:1, the amount of copolymerized styrene was still 2.2 g, and a large amount of styrene homopolymerized to form *homo*-PS. All these indicated that the macromonomer can be homogenized in styrene by increasing the ratio of [St]/[SiO_2-HPA], which can drive the styrene to coplymerize with the silica macromonomer. Additionally, as can be seen from Table 1, a relatively low amount of styrene can copolymerize with silica macromonomer; however, a large amount of styrene homopolymerize to form *homo*-PS despite of the almost 100% conversion of styrene. This result is in agreement with the grafting poly(methyl methacrylate) onto microparticulate silica reported by Boven G et al.[20]. This phenomenon can be explained as follows: Firstly, the free radical might not be readily accessible to the double bonds immobilized at the large silica particles surface to initiate polymerization, whereas the free radical can readily initiate styrene polymerization. Secondly, a portion of the *homo*-PS might be formed by thermal polymerization. Thirdly, the chain transfer reaction from a

Table 1 Radical copolymerization of silica macromonomer with styrene[a)]

Run	m (SiO_2-HPA) (g)	m (St) (g)	m (Copolymer) (g)	m (C-St)[b)] (g)	m (H-St)[b)] (g)	Conversion of St (%)	Silica content[c)] (%)
1	0.5	24.5	1.6	1.1	22.91	98	1.64
2	1.0	24.0	3.1	2.1	21.18	97	3.32
3	1.0	15.7	2.8	1.8	13.56	98	4.92
4	1.0	11.5	2.7	1.7	9.23	95	6.76
5	1.0	9.0	2.2	1.2	7.35	95	8.44
6	1.0	6.0	1.5	0.5	5.08	93	12.25

a) Copolymerization was performed at 75℃ for 12 h, 110℃ for 36 h, mole ratio of [St]/[AIBN] is fixed at 200:1; b) m (C-St) and m (H-St) is the amount of styrene copolymerized with macromonomer and homopolymerized, respectively; c) silica content of bulk materials (including *homo*-PS) is determined by TGA.

copolymer chain to a (free) monomer molecule may contribute to another portion of homopolymer. The plots of monomer conversion versus time for copolymerization of styrene with macromonomer are illuminated in Figure 4, which were conducted in solution ([St]:[Toluene] =1∶1(V/V)) at 75℃ under a fixed mole ratio of [St]∶[AIBN]=200∶1. Figure 4 revealed that the conversion of styrene increased with prolonging reaction time, which is conforming to the rule of radical copolymerization.

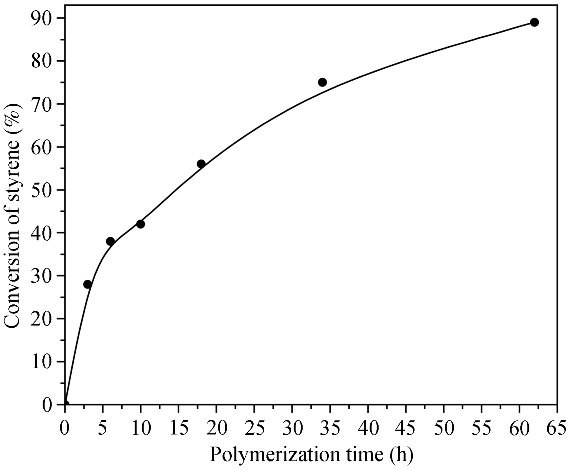

Figure 4 Plots of styrene conversion vs time.

3.2.2 Characterization of polystyrene/silica nanocomposites. FTIR spectroscopy was employed to characterize the formation of copolymer of SiO_2-HPA and styrene. After copolymerization, the homopolymer of styrene (*homo*-PS) was carefully separated by extensive extraction with THF until no *homo*-PS can be found in the cleaning solutions. Figure 5 shows the FTIR spectrum of the recovered copolymer. In comparison with the silica macromonomer (Figure 2, curve 3), the FTIR spectrum of SiO_2-HPA/St shows several additional absorbance bands. The new bands at 3059, 3025, 2920, 1600, 1451, 756 and 696 cm^{-1} were all characteristic absorbance bands of polystyrene, which are well in accord with that reported by Bartholome C et al.[24]. This supports the successful preparation of the copolymer of styrene with SiO_2-HPA, i.e., polymer/silica nanocomposites can be prepared by this method.

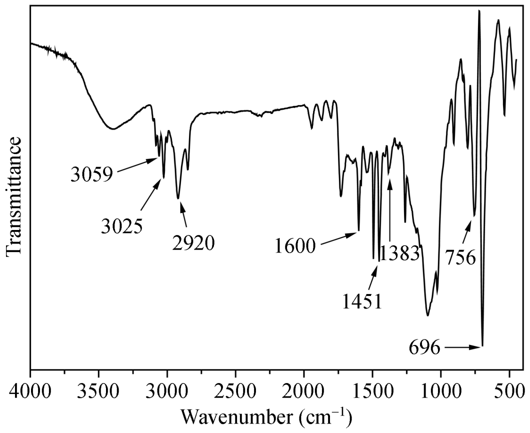

Figure 5 FTIR spectrum of copolymer SiO_2-HPA/St.

Figure 6 shows the DSC cooling traces of the copolymer SiO_2-HPA/St with different silica contents, as well as *homo*-PS (pure PS) samples. Curve 1 in Figure 6 shows the DSC cooling trace of the *homo*-PS. It can be observed in Figure 6 that the SiO_2-HPA/St exhibits higher glass transition temperatures (T_gs) than their counterpart *homo*-PS. The T_g of the copolymer increases slightly with the increasing of the content of silica. For example, the T_g of *homo*-PS is around 90℃, whereas the T_g is shifted to around 110℃ for the SiO_2-HPA/St with silica content of 38.05 wt% (referring to the content of SiO_2-HPA). These observations are well in agreement with the results reported by other research groups[11,25]. The T_gs of SiO_2-HPA/St samples shift to higher temperatures may be well attributed to the silica particles serving as cross-linking points in the polystyrene/silica nanocomposites. Furthermore, the cross-linking density increases with the increasing content of silica, which may contribute to the slightly increased T_gs with increasing silica content. In addition, the interaction be-

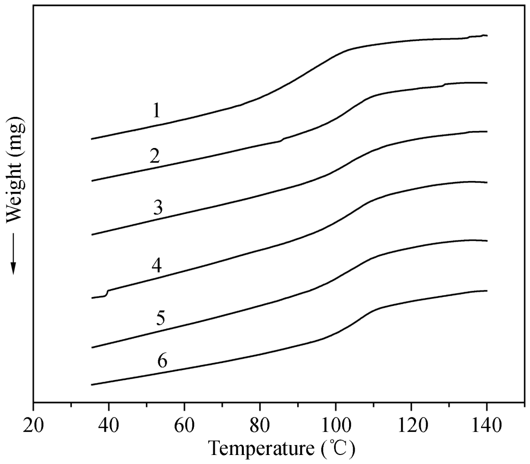

Figure 6 DSC cooling traces of *homo*-PS (1) and SiO_2-HPA/St, silica content (%, referring SiO_2-HPA content) of 31.25 (2), 32.26 (3), 35.71 (4), 37.04 (5), 38.05 (6).

tween the nanoparticles may also lead to a higher T_g. These higher glass transition temperatures, in turn, provide further evidences for the copolymerization of styrene with SiO_2-HPA.

The TGA thermogram of the copolymer SiO_2-HPA/St at a heating rate of 10℃/min in nitrogen is shown in Figure 7. It can be found in Figure 7 that at the temperature range of 190—750℃ the weight loss amounted to 74%, which can be reasonably attributed to the weight loss of macromonomer and the copolymerized styrene. The weight loss under the temperature 300℃ is attributed to SiO_2-HPA, indicating the greater part of the weight loss is the copolymerized styrene. These results obviously further revealed that the as-synthesized macromonomer can copolymerize with styrene to generate polystyrene/silica nanocomposites.

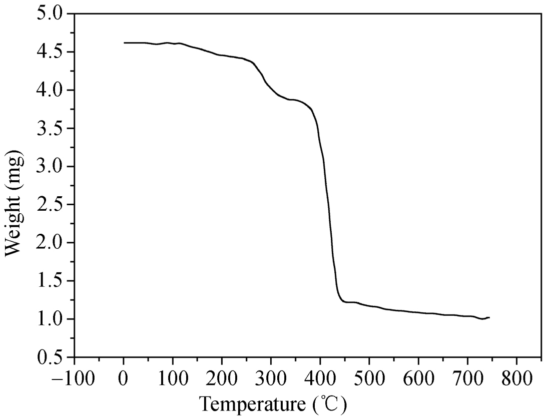

Figure 7 TGA curves of copolymer SiO_2-HPA/St (sample of Run 2 in Table 1).

Furthermore, the copolymer SiO_2-HPA/St cannot be dissolved in toluene, THF or other organic solvents, but it can swell due to the silica acting as cross-linking point; however, the cross-linking density can be controlled by a choice ratio of comonomer in the feed.

4 Conclusions

We have demonstrated a novel highly efficient approach to the preparation of polymer/silica nanocomposites by conventional radical copolymerization of styrene with silica-based macromonomer. A two-stage process has been successfully developed to synthesize the macromonomer through surface-modification of silica with TDI and polymerizable vinyl group consecutively. The silica nanoparticles have been immobilized in the as-synthesized materials hindering silica aggregation and the compatibility has been significantly improved. DSC and dissolution experiments indicated that the silica particles have acted as chemical and physical cross-linking points, which lead to the finding that the T_g of the nanocomposites (copolymer) is higher than that of corresponding *homo*-PS. The quantity of the copolymerized styrene will increase by increasing the ratio of [St]/[SiO_2-HPA]. The conversion of styrene increased with prolonging reaction time, which is well in accord with the rule of radical copolymerization. A relatively low amount of styrene can copolymerize with silica macromonomer; however, a large amount of styrene homopolymerize to form *homo*-PS despite the almost 100% conversion of styrene. Nanocomposites prepared by this approach may be used as materials directly without separation of the homopolymer formed in this procedure.

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