

Organic-Inorganic Polymer Hybrids of Polystyrene with Ladderlike Polyphenylsilsesquioxanes

By Young-Chul AN,¹ Nae-Youn JANG,¹ Seung Woo LEE,² Jung-Hyurk LIM,¹ and Kyung-Min KIM^{1,*}

The synthesis of homogeneous polymer hybrids from ladderlike polyphenylsilsesquioxanes (PPSQ) with polystyrene (PS) *via* aromatic (π - π) interactions was investigated. Polymer hybrids from ladderlike PPSQ with PS showed that the homogeneity gradually increased as the weight ratio of PS to PPSQ increased. Thus, physical bonding, namely aromatic (π - π) interactions between phenyl groups of PS and ladderlike PPSQ played a critical role for the homogeneity and transparency of polymer hybrids. The obtained homogeneous and transparent hybrid materials could be dissolved in solvents and cast again without any separation because of physical bonding between PS and ladderlike PPSQ. The thermal stability of polymer hybrids with ladderlike PPSQ was checked by TGA measurement. The homogeneity of polymer hybrids based on ladderlike PPSQ was confirmed by the results of DSC, SEM, and AFM, which demonstrated a nano-meter level integration of PS and ladderlike PPSQ.

KEY WORDS: Polymer Hybrids / Aromatic (π - π) Interactions / Ladderlike PPSQ / PS /

Organic-inorganic hybrid nanocomposites are materials whose components are mixed at a molecular scale. Due to their quantum-scale sizes, they exhibit different and unique properties from conventional microcomposites.^{1,2} The growing interest in hybrid nanocomposites stems from immense potential for many fields such as optics, coatings, electronics, mechanics, sensors, membranes, and biologies. Organic-inorganic hybrid materials have been elaborated with various inorganic hosts such as inorganic clay compounds,³ metal oxo clusters,⁴ mesoporous silica (zeolite),⁵ calcium carbonate⁶ and metal or inorganic nanoparticles.^{7,8} Among them, sol-gel process with metal alkoxides is most widely used for the preparation of organic-inorganic hybrid materials at nano meter scale because sol-gel chemistry offers a versatile approach to design new hybrid materials.^{9,10} Chujo's group has elaborated and developed polymer hybrids utilizing physical interaction between organic polymer and inorganic phases through the sol-gel process.¹¹⁻¹³ Physical interactions such as hydrogen bonding, ionic, and aromatic interactions are mainly used. The obtained polymer hybrids show high transparency, good gas barrier property, excellent thermal, mechanical, and solvent-resistant properties.

In recent years, silsesquioxanes-based hybrid polymers or nanocomposites have emerged as unique materials for hybrids with well-ordered structures and excellent properties.^{14,15} Silsesquioxanes exist as ladder- or cage-type nanostructures.¹⁶ Silsesquioxanes-based hybrids, in contrast to silica matrix obtained from sol-gel hybrid systems, can be easily soluble in organic solvents and cast again without any separation because of various organic functionalities attached to the silsesquioxanes. In addition, silsesquioxanes-based hybrids are good candidates for addressing the problem caused by sol-gel

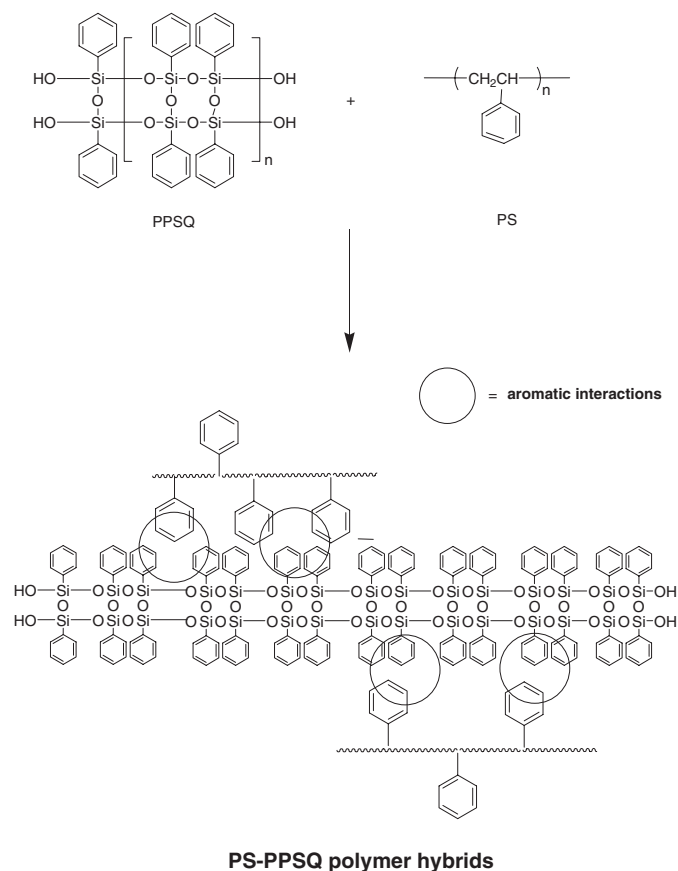
process, which is the extraordinary shrinkage from the loss of alcohol or water during the condensation reaction.¹⁷ Cage-type, polyhedral oligomeric silsesquioxanes (POSS), molecules are generally incorporated into a polymer chain by covalent bond, or they can be blended with a polymer matrix.^{18,19} Also, silsesquioxanes consisting of a siloxane ladder structure (ladder-type) have excellent thermal stability, oxidative resistance, and mechanical strength.^{20,21} The application fields of ladder-type silsesquioxanes have ranged to coatings for electronics, optical devices, interlayer dielectrics, and gas separation membranes.²²

We have recently explored a wide variety of hybrid materials based on silsesquioxanes. Such examples are hybrid nanocomposites (self-assembly of metal nanoparticles and hydrophobic CaCO₃ composite particles),^{23,24} organic-inorganic hybrid polymers (hybrid gels, hybrid LC polymers, and hybrid micelles),²⁵⁻²⁸ and transparent organic-inorganic polymer hybrids.^{29,30} They showed interesting and valuable properties derived from a unique structure of POSS for the promising applications in the field of materials chemistry. Here, we report, the first synthesis and characterization of the transparent hybrid materials from ladder-type silsesquioxanes and polystyrene (PS) *via* aromatic (π - π) interactions. We describe the homogeneous dispersion of ladderlike polyphenylsilsesquioxanes (PPSQ) in polystyrene matrix. A key concept is using both structure property (high rigidity and regularity) of PPSQ as a template and physical bonding (π - π) interactions between PPSQ and PS for soluble polymer hybrids. To the best of our knowledge, ladder-type silsesquioxanes as the inorganic hosts for organic-inorganic hybrid materials using aromatic (π - π) interactions have not been used previously.

¹Department of Polymer Science and Engineering/RIC-ReSEM, Chungju National University, Chungju, Chungbuk 380-702, Korea

²School of Display and Chemical Engineering, Yeungnam University, Dae-Dong, Gyeongsan 712-749, Korea

*To whom correspondence should be addressed (Tel: +82-43-841-5429, Fax: +82-43-841-5420, E-mail: kmkim@chungju.ac.kr).



Scheme 1.

EXPERIMENTAL

General Procedure

^1H NMR spectra were obtained on a Bruker AVANCE400 400 MHz FT NMR spectrometer. Differential scanning calorimetry (DSC) thermograms were obtained with a DSC2010, TA Instruments, Inc., at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. The thermal behavior was examined by thermogravimetric analysis (TGA) (TGA S-1000, Scinco) under nitrogen atmosphere. The morphologies of polymer hybrids were observed by scanning electron microscopy (SEM) (JEOL JSM-5310/LV). The crystallinities of PPSQ and polymer hybrids were determined by X-ray diffraction (XRD) (Rigaku Rint2000). The surface images and nanostructure of polymer hybrids were measured using a tapping mode atomic force microscopy (TM-AFM) (XE-100, PSIA) operating at room temperature. Height and phase images were recorded simultaneously.

Materials

All solvents and reagents were used as supplied except for the following materials. Phenyltrimethoxysilane (PTMOS) was used after distillation under nitrogen. 1,2-dichloroethane was distilled from magnesium sulfate under nitrogen. Toluene and methanol were distilled from sodium metal and magnesium

methoxide, respectively. 2,2-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol below 40°C . Polystyrene (PS) ($M_n = 17,000$, $M_w = 25,000$, $M_w/M_n = 1.47$) was synthesized by carrying out AIBN-initiated free radical polymerization in benzene.

Synthesis of LadderLike Polyphenylsilsesquioxanes (PPSQ)

PPSQ was prepared by the detailed experimental procedures described in a previous article.³²

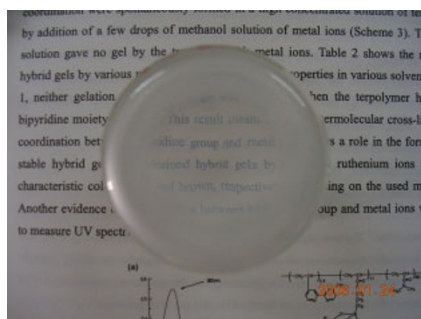
Preparation of Polymer Hybrids with PS and PPSQ

Polystyrene and PPSQ ($M_n = 3000$, $M_w/M_n = 2.26$) were dissolved in THF with various weight ratios (20/1-1/1). After being stirred in a vial for 1 h at room temperature, the mixture was placed in a sealed container, and heated in an oven at 40°C . After removal of the solvent completely, polymer hybrids were obtained as a glassy material.

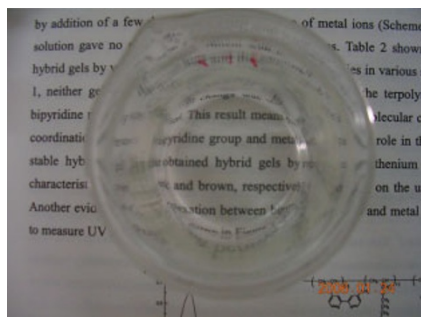
RESULTS AND DISCUSSION

Polymer Hybrids with Ladderlike PPSQ and PS

PPSQ was prepared from phenyltrimethoxysilane under basic conditions and polymer hybrids were obtained by mixing both PPSQ and PS in a THF solution (Scheme 1). In the ^{29}Si NMR spectra of PPSQ, two groups of peaks (-70 , -78 ppm) indicated the Si atom connected to the hydroxyphen-



(a)



(b)

Figure 1. Optical images of PS-PPSQ polymer hybrids. (a) PS/PPSQ = 5/1 and (b) PS/PPSQ = 20/1.

Table I. Preparation of PS-PPSQ polymer hybrids^a

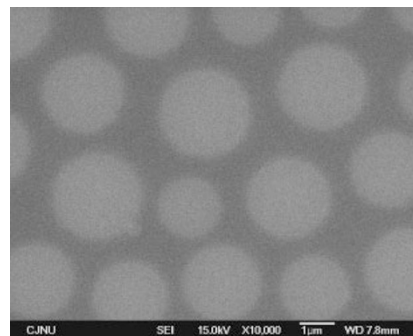
Run	PPSQ (g)	PS (g)	PPSQ/PS (wt)	Appearance ^b
1	0.01	0.2	1/20	transparent
2	0.02	0.2	1/10	transparent
3	0.03	0.2	1/7	translucent
4	0.04	0.2	1/5	turbid
5	0.1	0.2	1/2	turbid
6	0.2	0.2	1/1	turbid

^aPS and PPSQ were dissolved in THF. The mixture was stirred for 1 h and heated at 40 °C in an oven for 24 h until the solvent was evaporated completely. ^bHomogeneity was observed optically.

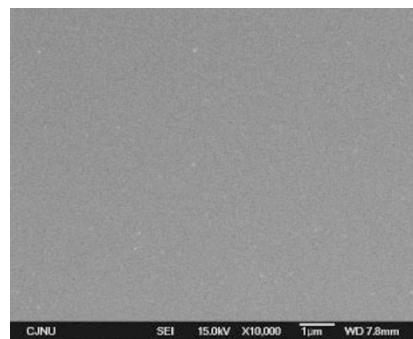
ylsiloxo unit and the fully condensed Si atom in the ladderlike double-chain structure, respectively. The 10% decomposition temperature for PPSQ was more than 550 °C, which meant PPSQ had no defects and branching. The characterization results of PPSQ from TGA and ²⁹Si NMR indicated that PPSQ obtained had a linear, rigid, soluble, and ladderlike structure.

The results of polymer hybrids prepared over a wide range of mass ratios (20/1–1/1) were turbid as the mass ratio (PS/PPSQ) was 1/1, 2/1, and 5/1 (run 4–6, Figure 1a). However, the transparency of the sample with mass ratio (7/1) of PS to PPSQ clearly increased and the appearance was translucent (run 3). In the sample with mass ratios (PS/PPSQ) over more than 10/1, PS and PPSQ were homogeneously mixed at a nanometer level (run 1–2, Figure 1b) *via* aromatic (π - π) interactions (Table I).

The transparency of the obtained polymer hybrids was gradually increased according to the increase of amount of PS



(a)



(b)

Figure 2. SEM images of PS-PPSQ polymer hybrids. (a) PS/PPSQ = 1/1 and (b) PS/PPSQ = 20/1.

used. It is obvious that the movement of PPSQ with highly rigid skeleton is limited with increasing the weight of PPSQ in the PS/PPSQ hybrid system, in which means that PS and PPSQ are not homogeneously mixed and aggregated each other. The SEM images of the obtained polymer hybrids are shown in Figure 2. In case of run 6, phase separation between PS and PPSQ was clearly observed at 10,000 magnifications (Figure 2a). On the other hand, in case of run 1, there is no phase separation as shown in Figure 2b. The homogeneity and nanostructure of polymer hybrids were also examined by TM-AFM (Figure 3). The turbid polymer hybrid (run 6, using high PPSQ ratio) showed large particles, whose size could be around 2–3 μ m, indicated the aggregation of PPSQ (Figure 3a).

On the other hand, PPSQ with 40–80 nm sizes were homogeneously dispersed in PS matrix in case of the transparent polymer hybrid (Figure 3b, run 1, using low PPSQ ratio). These SEM and AFM observations suggest that low content of PPSQ with highly rigid skeleton can be easily dispersed in PS matrix at the nanometer level.

Another attempt for homogeneity was made to estimate the crystallinity of PS/PPSQ hybrids by the powder X-ray diffraction measurements. In pure PPSQ, PPSQ itself is amorphous (Figure 4a). There are some aggregations in hybrids (rich PPSQ) that are formed by the molecules of PPSQ due to the rigid and hard structure property of PPSQ. In other words, in case of hybrids with small content of PPSQ, PPSQ are well mixed and entangled with PS at the nano-meter

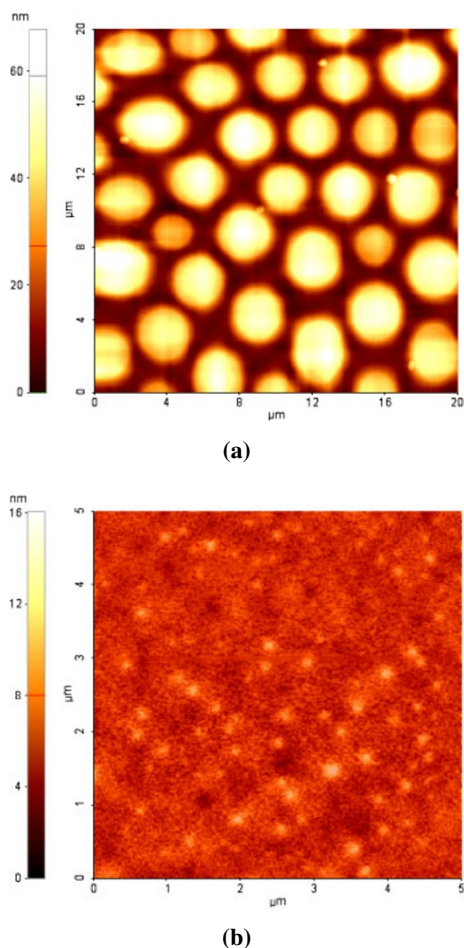


Figure 3. TM-AFM images of PS-PPSQ polymer hybrids. (a) PS/PPSQ = 1/1 and (b) PS/PPSQ = 20/1.

level *via* π - π interactions. This aggregation of PPSQ causes the weak interactions between PS and PPSQ, which result in the phase separation of two phases. For PS/PPSQ hybrids (Figure 4b, run 1), the diffraction patterns are featureless, showing only broad amorphous halos. This result indicates that the homogeneous mixing of PS and PPSQ caused by aromatic (π - π) interactions results in the transparent PS/PPSQ hybrids. These results mean that aromatic (π - π) interactions between the phenyl rings of PPSQ and PS are driving force for the homogeneous dispersion in the hybrid system.

Figure 5 shows the DSC thermograms of PS and PS/PPSQ hybrid. The glass transition temperature (T_g) of PS was observed around 99 °C. In the case of PS/PPSQ hybrids (20/1), T_g became higher to above 105 °C. This result is similar to that of the polymer hybrids prepared from sol-gel reaction, which suggests that ladderlike PPSQ prevents the mobility of PS due to the aromatic (π - π) interactions between PS and PPSQ. The thermal stability of PS/PPSQ hybrids was measured by TGA measurement (Figure 6).

The decomposition temperature of PS/PPSQ hybrids was higher than that of PS and became higher with the increase of the content of PPSQ in PS/PPSQ hybrids. It means that the rigid and hard inorganic PPSQ improve thermal stability of PS/

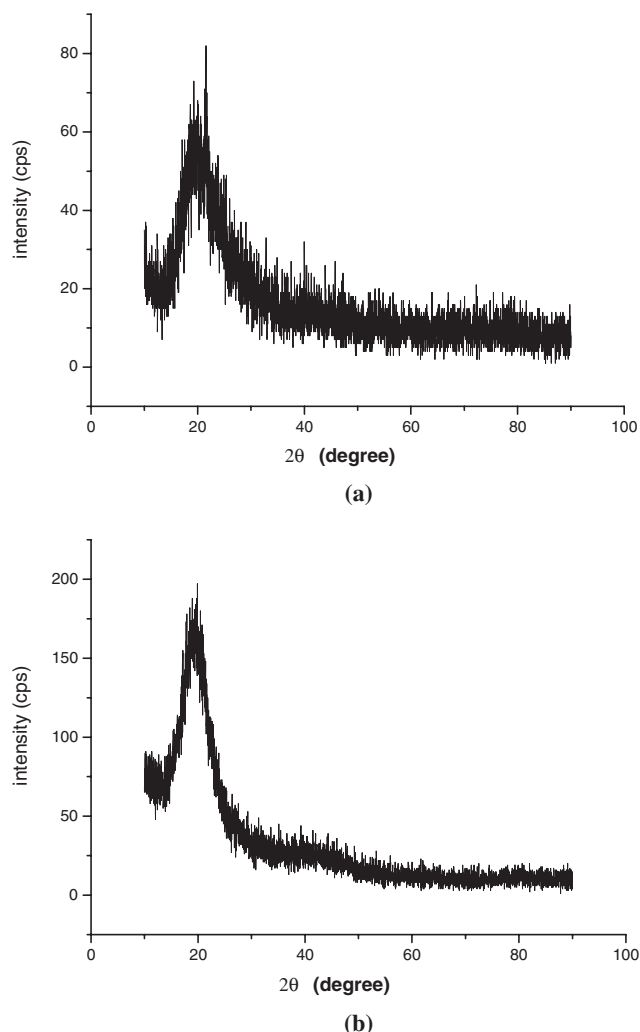


Figure 4. X-Ray diffraction (XRD) patterns of (a) PPQS and (b) PS-PPSQ polymer hybrids (PS/PPSQ = 20/1).

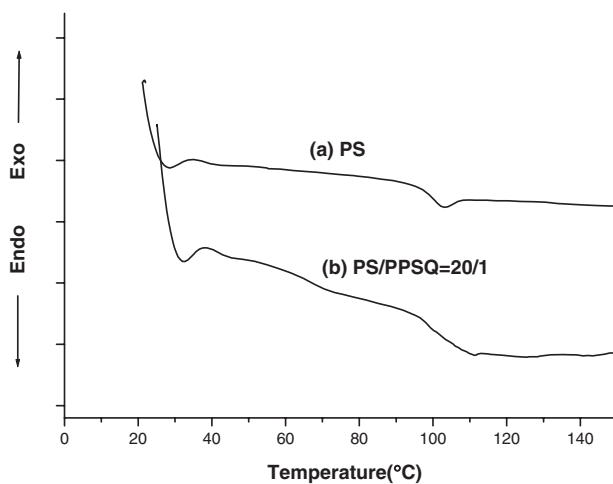


Figure 5. DSC thermograms of (a) PS and (b) PS-PPSQ polymer hybrids (PS/PPSQ = 20/1).

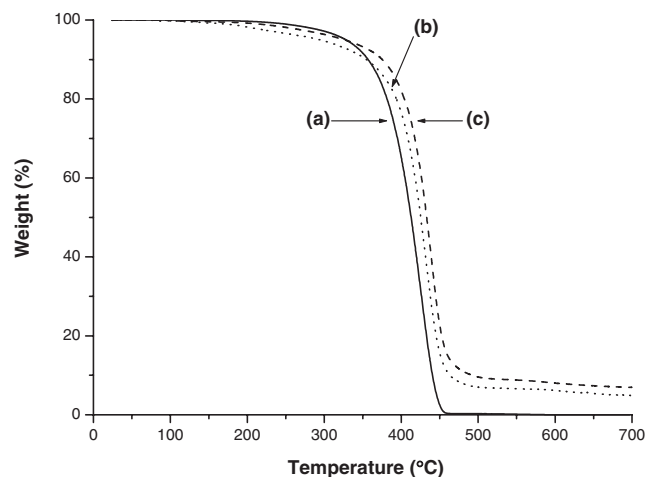


Figure 6. TGA thermograms of PS-PPSQ polymer hybrids. (a) PS, (b) PS/PPSQ = 20/1, and (c) PS/PPSQ = 10/1.

PPSQ hybrids. The effectiveness of aromatic (π - π) interactions are also supported by the previous results observed in the synthesis of poly(diallyl phthalate) hybrids prepared by utilizing sol-gel reaction of phenyltrimethoxysilane,³³ the synthesis of polystyrene and silica gel polymer hybrids *via* π - π interactions,³⁴ and the synthesis of polymer hybrids with ladderlike polyphenylsilsesquioxane as a template *via* the sol-gel reaction of phenyltrimethoxysilane.³⁵

CONCLUSIONS

We have first synthesized organic-inorganic polymer hybrids with PS and PPSQ *via* aromatic (π - π) interactions. In case of polymer hybrids with ladderlike PPSQ, the transparent and homogeneous polymer hybrids could be obtained with higher PS ratio to PPSQ (20/1, 10/1) and lower PS ratio (1/1–5/1) brought about the phase separation. This result might be attributed to PPSQ with highly rigid structure, which can be easily aggregated at the higher PPSQ. In this hybrid systems, aromatic (π - π) interactions between the phenyl rings of PS and PPSQ play a critical role for homogeneous polymer hybrids. The thermal stability of PS/PPSQ hybrids was dependent on the increase of the PPSQ content in polymer hybrids. The obtained homogeneous and transparent hybrid materials could be dissolved in solvents and cast again without any separation.

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