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Synthesis of Hybrid Polyacetylene Gels Using Octafunctional POSS Initiator

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Summary: Hybrid polyacetylene gels having polyhedral oligomeric silsesquioxanes (POSS) moieties were prepared by polymerization of 2-ethynylpyridine using octafunctional POSS as an initiator with changing the feed ratio of POSS to 2-ethynylpyridine. The resulting black polyacetylene gels were not soluble in any organic solvents such as THF, chloroform, methanol, DMF, and acetone. The polyacetylene gels with higher mole ratio of 2-ethynylpyridine to POSS show higher thermal stability because of the tight polymer network caused by high degree of polymerization. It is proposed that the tether structure between polyacetylene matrix and POSS cages was crucial to the great improvement in thermal stabilities of hybrid polyacetylene gels with POSS.

Keywords: 2-ethynylpyridine; hybrid polyacetylene gels; initiator; polyhedral oligomeric silsesquioxanes (POSS)

Introduction

A lot of attentions have been recently paid to POSS combining unique hybrid chemical compositions (organic-inorganic) with nano-sized cage structures.[1,2] POSS, intermediate $(RSiO_{1.5})_n$ between silica (SiO_2) and silicone (R_2SiO), are an interesting inorganic particles which can replace of sol-gel derived materials. POSS are easily incorporated into common plastics by means of copolymerization or blending, requiring little or no alteration to existing synthetic processes because POSS have an inorganic SiO_2 core surrounded by eight organic groups, which make it soluble in various organic solvents. POSS containing copolymers or blends have increased oxygen permeability, are thermoplastic or curable, have oxidation resistance, and higher thermal properties than those without the POSS moieties. One efficient technique for achieving hybrid materials based on POSS is using the formation of covalent bonds or physical interactions between POSS and polymer matrix.[3–5] The other approach using POSS is incorporation of POSS moieties into polymer chain.[6,7] POSS moieties mdified various polymers were reported and showed high thermal, mechanical properties due to the reinforcement of polymer chain by siliceous POSS moieties at the molecular scale.[8–10] Nonetheless, the preparation of hybrid gels polymerized by octafunctional POSS as an initiator has not been reported. The hybrid polyacetylene gels have three-dimensional netrwork structures with POSS as a crosslinker.

In this study, we describes the hybrid polyacetylene gels using octafunctional POSS as an initaitor together with the morphologies and the properties of the hybrid polyacetylene gels.

Experimental Part

General Procedure

^{1}H NMR spectra were obtained on a Bruker AVANCE400 400 MHz FT-NMR spectrometer. Fourier transform infrared

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(FT-IR) spectra were recorded on a Bio-Rad FTS-6000 infrared spectrometer. Differential scanning calorimetry (DSC) thermograms were obtained with a DSC2010, TA Instruments, Inc., at a heating rate of 10 °C/min under a nitrogen atmosphere. The thermal behavior was examined by thermogravimetric analysis (TGA) (TGA S-1000, Scinco) under nitrogen atmosphere. The morphologies of hybrid polyacetylene gels were observed by scanning electron microscopy (SEM) (JEOL JSM-6700/LV). The crystallinities of POSS-8I and hybrid polyacetylene gels were determined by X-ray diffraction (XRD) (Rigaku Rint2000).

Materials

Toluene and acetone were distilled from sodium and potassium carbonate under nitrogen, respectively. Methanol was distilled from magnesium methoxide under nitrogen. 3-Chloropropyltrimethoxysilane, 2-ethynylpyridine, and sodium iodide were purchased form Aldrich Chemical Co. and used as received. All other reagents and solvents were used as received.

Synthesis of Hybrid Polyacetylene Gels with POSS

To obtain POSS initiator, the hydrolytic condensation of 3-chloropropyltrichlorosilane is done to make Cube-8Cl, which upon reaction with sodium iodide affords Cube-8I.[11] Hybrid polyacetylene gels having POSS moiety were prepared by polymerization of 2-ethynylpyridine using octafunctional POSS as an initiator with changing the feed ratio of POSS to 2-ethynylpyridine (Figure 1). The more detailed procedures for hybrid polyacetylene gels are as follows. Under nitrogen atmosphere POSS-8I and 2-ethynylpyridine were dissolved in toluene. The mixture was heated at 80 °C for 96 h. The color of the solution was changed from colorless to black during the heating. The resulting solution was reprecipitated into methanol several times. The black powder was obtained in a quantitative yield. The structure and thermal properties of the hybrid polyacetylene gels were confirmed by FT-IR, EDX, SEM, XRD, DSC, and TGA.

Results and Discussion

The polymerization of 2-ethynylpyridine using POSS as an initiator was carried out at 80 °C for 96 h in toluene with changing the feed ratio of POSS to 2-ethynylpyridine (Table 1). The resulting black polyacetylene gels were not soluble in any organic solvents such as THF, chloroform, methanol, DMF, and acetone. As control experiments, the polymerization of 2-ethynylpyridine by POSS-1I with one iodopropyl group and seven cyclopentyl groups was conducted to obtain the hybrid polymer which was highly soluble in organic solvents. The hybrid polyacetylene gels have three-dimensional netrwork structures with POSS as a cross-linker. The formation of three-dimensional network structures in the hybrid polyacetylene gels might be due to the steric hindrance and the individually different initiation rate in eight initiation sites, which are derived from the unique structure of POSS.

FT-IR spectrum of hybrid polyacetylene gel shows that the strong new absorption peaks at 1620 and 1510 cm^{-1} are indicative of the conjugated double-bond structure, and new peak at 1100 cm^{-1} is due to Si–O–Si absorption peak for POSS (Figure 2).

Figure 3a and 3b present scanning electron microscopy (SEM) images of hybrid polyacetylene gels. These images revealed that continuous network structures were formed without any discontinuity. The existence of the uninterrupted matrix was a consequence of the gelation of polyacetylene initiated by octafunctional POSS. The structure of hybrid polyacetylene gel with POSS was also confirmed by analyzing hybrid polyacetylene gel sample's energy dispersive spectrum (EDS; Figure 3c). The appearance of Si and I atom's spectra in EDS image showed that

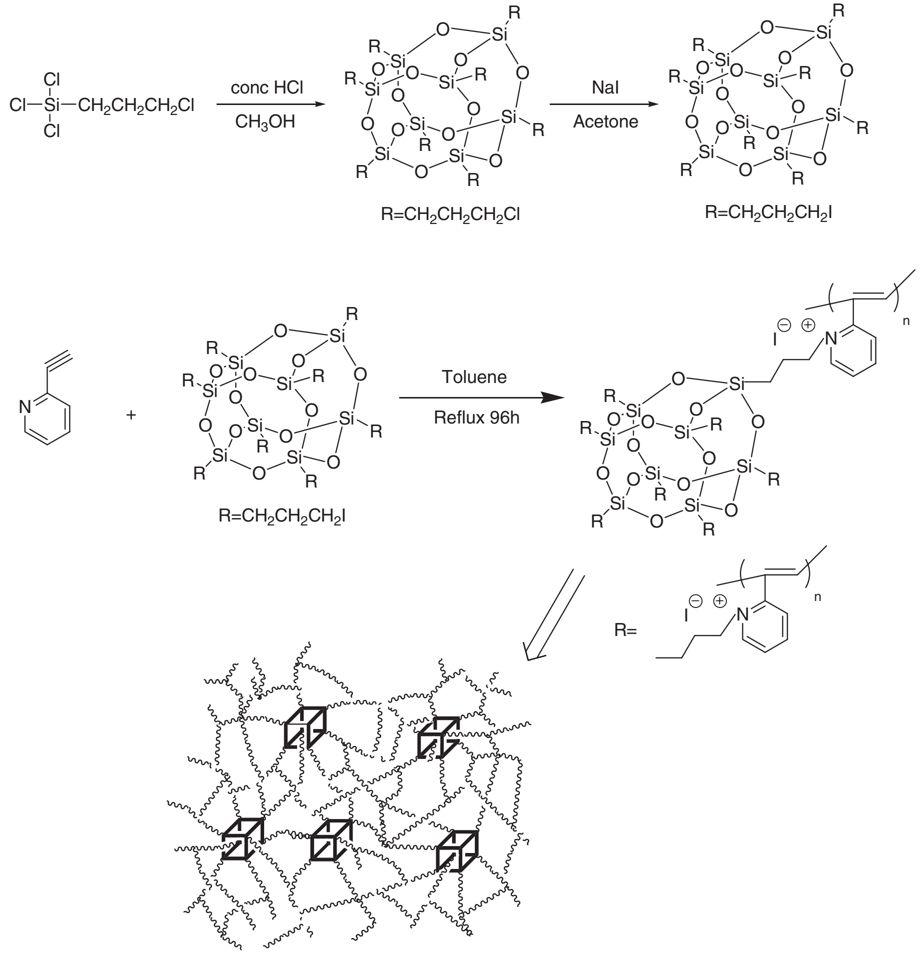

Figure 1.
Preparation of POSS initiator and the hybrid polyacetylene gels.

polyacetylene was hybrized with three-dimensional network formation by inorganic mutifunctional POSS.

The crystallinity of the hybrid polyacetylene gel with POSS was examined by powder X-ray diffraction (XRD) pattern measurement (Figure 4). POSS-8I showed sharp diffraction patterns around 20–30°. Sharp diffraction patterns were observed at the same position in the hybrid polyacetylene gel with POSS. This result means that hybrid polyacetylene gel has crystallinity derived from the high crystalline POSS segments.

Table 1.
Preparation of hybrid gels initiated by POSS.

Ratio (mol)	POSS-8I (g)	2-Ethynylpyridine (g)	Solvent (Toluene) (ml)
1:20	0.1	0.15	4
1:80	0.1	0.60	4
1:100	0.1	0.75	4
1:160	0.1	1.20	4
1:200	0.1	1.50	4

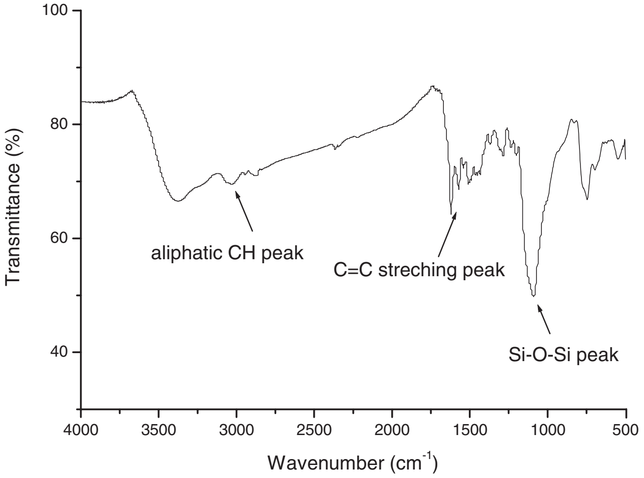

Figure 2.
FT-IR spectrum of hybrid polyacetylene gel with POSS.

Figure 5 represents DSC thermograms for hybrid polyacetylene gels. The endotherm peak gradually shifted to a high temperature as the POSS component of hybrid polyacetylene gels (Figure 5b, 5c). However, the endotherm peak shifted to a low temperature compared to polyacetylene initiated by propyliodide (poly

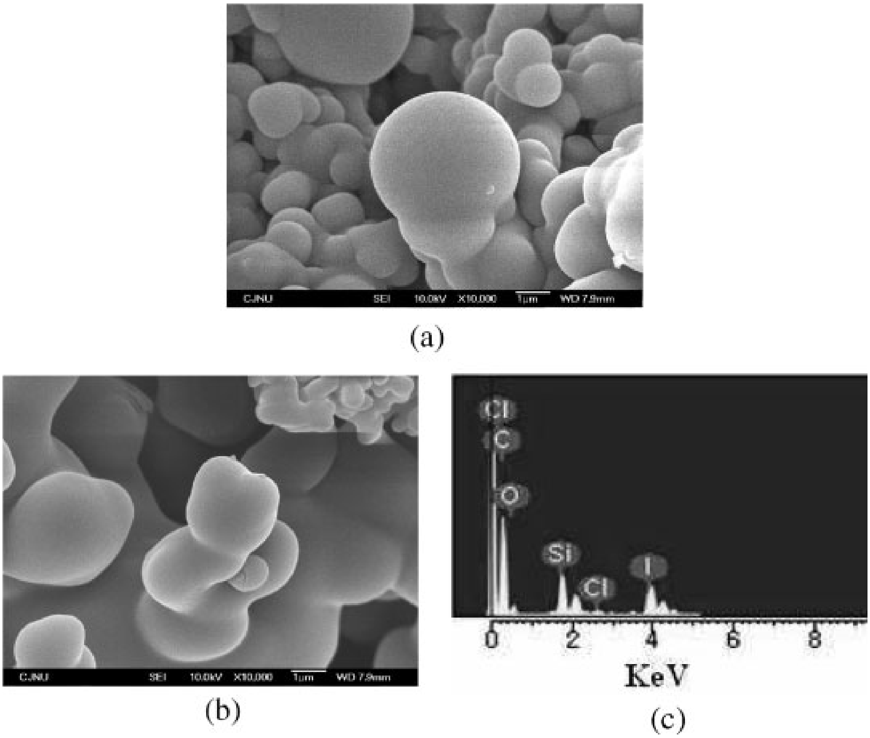

Figure 3.
SEM images of hybrid polyacetylene gels. (a) 2-ethynylpyridine/ POSS-8I = 100/1; (b) 2-ethynylpyridine/ POSS-8I = 200/1; (c) EDS image of hybrid polyacetylene gel (2-ethynylpyridine/ POSS-8I = 200/1).

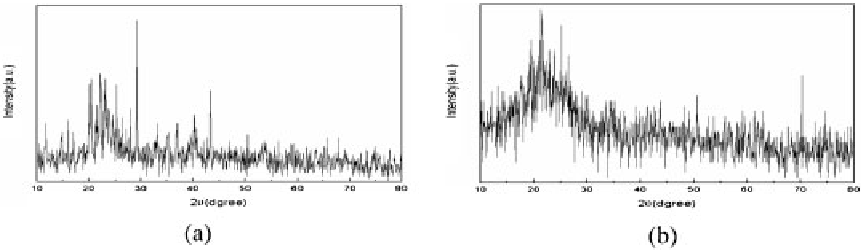

Figure 4.
X-ray diffraction (XRD) patterns of (a) POSS-8I and (b) hybrid polyacetylene gel (2-ethynylpyridine/ POSS-8I = 20/1).

(*N*-propyl-2-ethynylpyridinium iodide)) in Figure 5d. This result indicates that the effect of the inorganic POSS moieties in hybrid gels is little because of the polymer network with few POSS moieties caused by high degree of polymerization. TGA was applied to evaluate the thermal stability of the hybrid polyacetylene gels with POSS. Shown in Figure 6 are the TGA curves of (a) polyacetylene initiated by propyliodide (poly(*N*-propyl-2-ethynylpyridinium iodide)) and (b)-(f) hybrid polyacetylene gels with POSS, recorded in air atmosphere at 20 °C/min. As expected, no ceramic and char yields were obtained in air for the poly(*N*-propyl-2-ethynylpyridinium iodide) with no POSS. For the polyacetylene gels with POSS, the ceramic yield increased with increasing the POSS concentration. In terms of the decomposition temperatures and ceramic yields, the thermal stability of the polyacetylene gels with POSS was significantly enchanced as compared to poly(*N*-propyl-2-ethynylpyridinium iodide) with no POSS because of the hybrid gels consisting of three-demensional network structures and inorganic POSS cages. The decomposition temperature of polyacetylene gels was increased with increasing the mole ratio of 2-ethynylpyridine to POSS because of the tight polymer network caused by high degree of polymerization. This result indicates that the thermal stability of polyacetylene gels is more

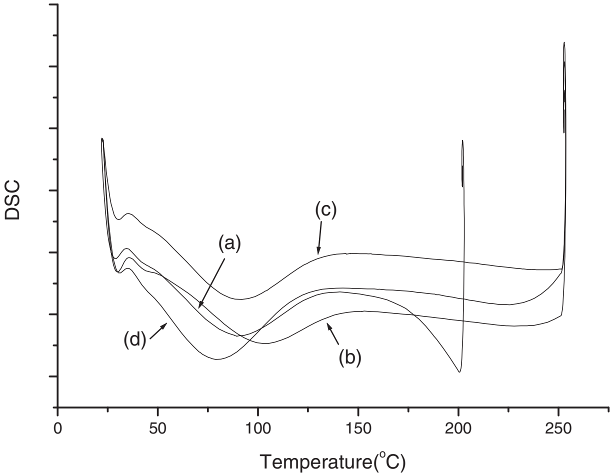

Figure 5.
DSC thermograms of hybrid polyacetylene gels with a heating rate of 10 °C min^{-1} under nitrogen: (a) poly(*N*-propyl-2-ethynylpyridinium iodide), (b) 2-ethynylpyridine/ POSS-8I = 20/1, (c) 2-ethynylpyridine/POSS-8I = 100/1, (d) 2-ethynylpyridine/ POSS-8I = 200/1.

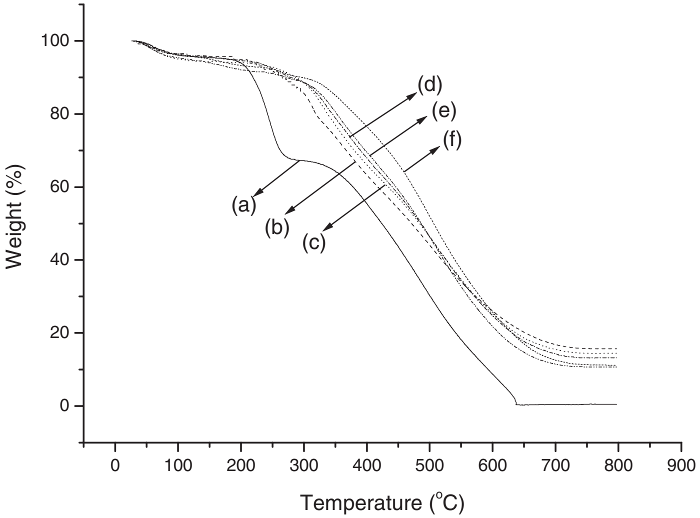

Figure 6.
TGA thermograms of (a) poly(*N*-propyl-2-ethynylpyridinium iodide), (b) 2-ethynylpyridine/ POSS-8I = 20/1, (c) 2-ethynylpyridine/ POSS-8I = 80/1, (d) 2-ethynylpyridine/ POSS-8I = 100/1, (e) 2-ethynylpyridine/POSS-8I = 160/1, (f) 2-ethynylpyridine/ POSS-8I = 200/1.

influenced by the tight polymer network matrix than POSS moieties.

Conclusion

We have synthesized novel hybrid polyacetylene gels using octafunctional POSS as an initiator with changing the feed ratio of POSS to 2-ethynylpyridine. In terms of the results of FT-IR, SEM, EDS, and XRD, it is noted that hybrid polyacetylene gels were successfully formed with three-dimensionl network structure by incorporating the POSS moieties as an initiator into polymer matrix. TGA showed that all the hybrid polyacetylene gels containing POSS displayed the improved thermal stability. It is proposed that the tether structure between polyacetylene matrix and POSS cages was crucial to improvement in thermal stabilities of hybrid polyacetylene gels with POSS.

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