

Organic-inorganic polymer hybrids using octasilsesquioxanes with hydroxyl groups

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Received: 8 May 2001/Accepted: 24 May 2001

Summary

Polymer hybrids were prepared by three kinds of octasilsesquioxanes having hydroxyl groups and organic polymers such as poly(2-methyl-2-oxazoline) (POZO), poly(*N*-vinylpyrrolidone) (PVP), and poly(*N,N*-dimethylacrylamide) (PDMAAm) using hydrogen bonding interaction. The obtained homogeneous and transparent hybrid films could be dissolved in solvents and cast again without any separation. It was found that the high homogeneity of polymer hybrids was the result of hydrogen bonding interaction between octasilsesquioxanes and organic polymers from the carbonyl stretching shifts in IR measurement. Also, the influence of flexibility of eight arms bound to silica-like core on the homogeneity of polymer hybrids was examined.

Introduction

Composite materials by the combination of organic polymers and inorganic materials have long been studied for the purpose of applying to the industrial materials. The sol-gel reaction which is one of the most effective methods to prepare the hybrid materials has been widely used so far because of the condition of ambient temperature and high uniformity of organic parts in the silica matrix [1-3]. However, due to some problems caused by sol-gel reaction such as extraordinary shrinkage, difficulty of solvent choice, and hardship of precise design, various applications for material chemistry have been limited [4]. So, in order to solve the above mentioned problems, a lot of attentions have been recently paid to the new type of inorganic precursors which is polyhedral oligomeric silsesquioxanes (POSS) combining unique hybrid chemical compositions with nano-sized cage structures [5-7]. Many applications of POSS have been reported as precursors for hybrid nanocomposites [8, 9] and polymerizable reagents [10, 11] because they have unique, well-defined, and compact hybrid chemical structures involving several rings connected together with a finite three dimensional molecular skeleton.

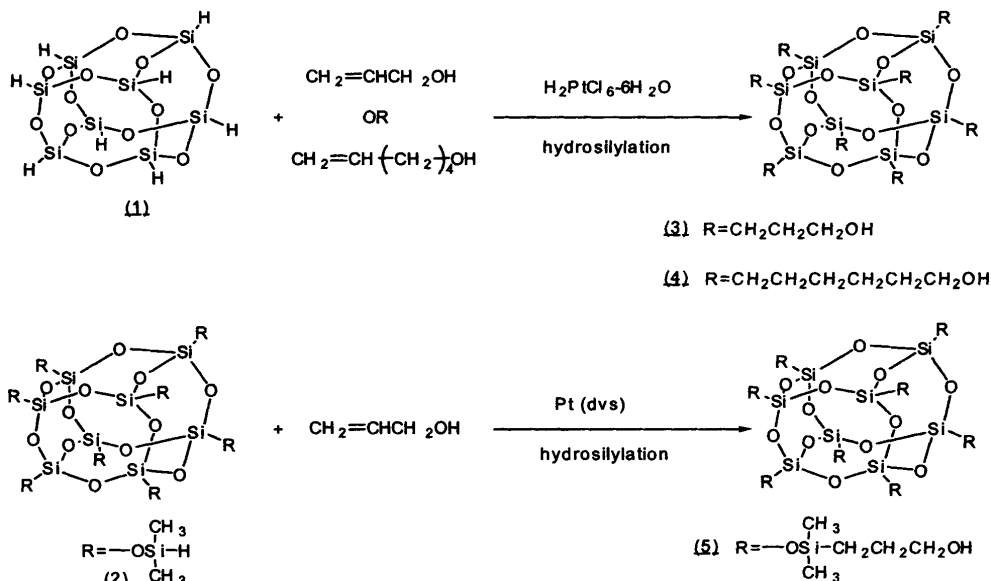
We have recently introduced a wide variety of LC hybrid materials based on POSS. Such examples are LC silsesquioxanes having various mesogenic moieties and LC organic-inorganic hybrid polymers using functionalized silsesquioxanes

[12,13]. The obtained LC hybrid materials using silsesquioxanes showed very wide temperature range of LC phase and high thermal stability. Also, homogeneous hybrid films were prepared from functionalized POSS and organic polymers utilizing physical interactions, i.e. hydrogen or aromatic interactions [14, 15]. Here, we present the preparation of polymer hybrids from POSS having hydroxyl groups and organic polymers using hydrogen bonding interaction and characterize them by IR, TGA, and SEM.

Experimental Section

General procedure

^1H NMR spectra were recorded using a 270MHz JEOL-JNM-GX270 NMR spectrometer. FT-IR spectra were recorded on a Hitachi 260-50 grating spectrophotometer. The thermal behavior was examined by TGA (Seiko Instruments Inc., Shimadzu DT-30) under nitrogen. The morphologies of polymer hybrids were observed by scanning electron microscopy (JEOL JSM-5310/LV).



Scheme 1

Materials

1,2-Dichloroethane was distilled from magnesium sulfate under nitrogen. Toluene and methanol were distilled from sodium metal and magnesium methoxide, respectively. 2-Methyl-2-oxazoline was distilled from KOH and stored under nitrogen. 2,2-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol below 40°C. N,N-Dimethylacrylamide and acetonitrile were distilled from calcium hydride under nitrogen. Other solvents and reagents were commercially supplied and used without further purification.

Synthesis of organic polymers (POZO, PVP, and PDMAAm)

Poly(2-methyl-2-oxazoline) (POZO) ($M_n=3000$, $M_w=6500$, $M_w/M_n=2.1$) was

prepared by the ring opening polymerization of 2-methyl-2-oxazoline initiated by methyl p-toluenesulfonate (MeOTs). Poly(N,N-dimethylacrylamide) (PDMAAm) ($M_n=19000$, $M_w=55000$, $M_w/M_n=2.9$) was synthesized by carrying out AIBN-initiated free radical polymerization. Poly(N-vinylpyrrolidone) (PVP) (average $M_w=630000$) was used as commercially available.

Synthesis of POSS having hydroxyl groups

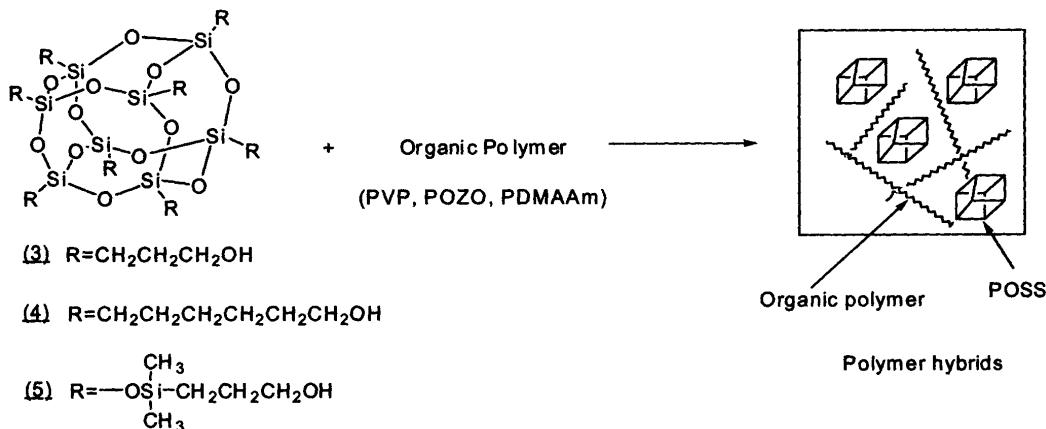
Octa(hydridosilsesquioxane) (**1**) and octa(3-hydroxypropyldimethylsiloxy)octasilsesquioxane (Cube-3DOH) (**4**) were prepared according to a literature procedure [16, 17].

Synthesis of Octa(3-hydroxypropyl)octasilsesquioxane (Cube-3OH) (2). Hydridosilsesquioxane (**1**) (0.3 g, 0.71 mmol) was dissolved in distilled 1,2-dichloroethane (20 ml). The mixture was stirred, and allyl alcohol (0.6 ml, 8.80 mmol) and 2.78 mM 1,2-dimethoxyethane solution of $H_2PtCl_6 \cdot 6H_2O$ were added. The reaction mixture was refluxed for 48h under nitrogen. The white precipitate appeared when the solution was cooled down to the room temperature. The white crude product was recrystallized from 1,2-dichloroethane (0.39 g, 60%). 1H NMR (DMSO- d_6): δ 4.5 (s, 8H), 3.4 (s, 16H), 1.5 (m, 16H), 0.6 (m, 16H), ^{29}Si NMR (DMSO- d_6): -65.7.

Synthesis of Octa(6-hydroxypropyl)octasilsesquioxane (Cube-6OH) (3). (**3**) was prepared by the same method as the above procedures. Yield was 49%. 1H NMR (DMSO- d_6): δ 4.4 (s, 8H), 3.4 (s, 32H), 1.3 (m, 48H), 0.6 (m, 16H), ^{29}Si NMR (DMSO- d_6): -65.8.

Preparation of polymer hybrids from POSS.

The organic polymer and silsesquioxane were dissolved in the solvent. The resulting mixture was stirred in a sealed bottle for 1h and then the solvent was evaporated. How to evaporate the solvent depended on the used solvent (DMSO, $CHCl_3$, and methanol was evaporated at 80-100°C, 60°C oven, and room temperature, respectively).



Scheme 2

Results and Discussion

The preparation of POSS having hydroxyl groups is shown in Scheme 1. Cube-3OH, 6OH, and Cube-3DOH were synthesized by direct hydrosilylation of allyl alcohol, 5-hexene-1-ol and allyl alcohol with octa(hydridosilsesquioxane) (**1**) and octa(dimethylsiloxy)octasilsesquioxane (**2**) using hexachloroplatinic acid and platinum divinyltetramethyldisiloxane as a catalyst, respectively. They showed a broad peak of methylene groups adjacent to Si atom (0.6 ppm) and the peak of hydroxyl groups (4.4 ppm) in the ^1H NMR. Also, the characteristic peaks and relative integral ratio matched well with their structures as we expected. Cube-3OH and Cube-6OH are only soluble in DMSO, while Cube-3DOH shows a good solubility in various organic solvents such as methanol, THF, CHCl_3 , etc. Good solubility of Cube-3DOH compared to that of Cube-3OH and Cube-6OH might be resulted from an increase of flexibility of eight arms bound to silicon caused by the introduction of dimethylsiloxy groups.

Polymer hybrids were prepared by the obtained POSS and organic polymers such as PVP, POZO or PDMAAm using hydrogen bonding interaction in various solvents. Table 1 describes the results of preparation of polymer hybrids from POSS. In case of polymer hybrids from Cube-3OH and Cube-6OH, the transparent and homogeneous polymer hybrids could be obtained only with higher polymer ratio (10/1), and lower polymer ratio (1/1) brought about the phase separation. Unfortunately, polymer hybrids using different polymers could not be prepared because of the poor solubility of Cube-3OH and Cube-6OH.

Table 1. Preparation of polymer hybrids from POSS

Run	POSS	Polymer	Polymer/POSS (wt/wt)	Solvent	Appearance
1	3	PVP	1/1	DMSO	Turbid
2	3	PVP	10/1	DMSO	Transparent
3	4	PVP	1/1	DMSO	Turbid
4	4	PVP	10/1	DMSO	Transparent
5	5	PVP	1/1	CHCl_3	Transparent
6	5	PVP	10/1	CHCl_3	Transparent
7	5	POZO	1/1	CHCl_3	Transparent
8	5	POZO	10/1	CHCl_3	Transparent
9	5	POZO	1/1	CHCl_3	Transparent
10	5	PDMAAm	1/1	CHCl_3	Transparent
11	5	PDMAAm	10/1	CHCl_3	Transparent
12	5	Polystyrene	1/1	CH_3OH	Turbid

Thus, polymer hybrids (from run 5 to run 12) from Cube-3DOH having a good solubility with various organic polymers were prepared. The high homogeneity was achieved in a wide range of polymer to POSS (10/1-1/1) with various organic polymers, whose result was different from that of polymer hybrids with Cube-3OH or Cube-6OH. This result might be explained that the flexibility of eight arms of POSS derived from dimethylsiloxo groups enhanced hydrogen bonding ability of POSS toward organic polymers for the homogeneity of the polymer hybrids. In addition, transparent polymer hybrids using Cube-3DOH could be prepared in various solvents. The polymer hybrids obtained from polystyrene and Cube-3DOH were turbid, which demonstrated the effectiveness of hydrogen bonding interaction between polymer and POSS.

FT-IR measurement of these polymer hybrids was conducted to confirm the shift of amide carbonyl peaks caused by hydrogen bonding interaction between polymer and POSS. Figure 1 is representative IR spectra of POZO and POZO-POSS hybrid. POZO has its original stretching vibration peak of carbonyl group

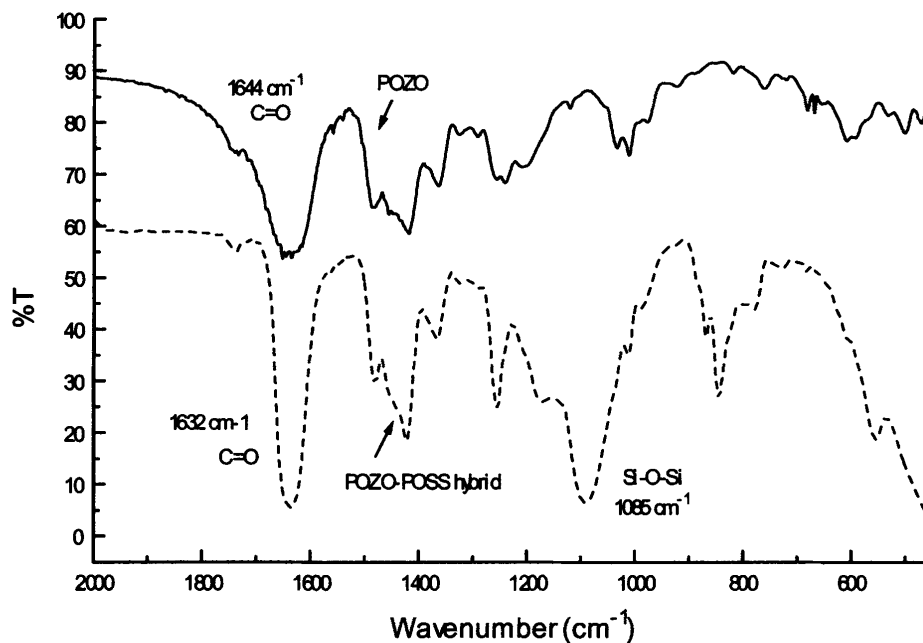


Figure 1. FT-IR spectra of POZO and POZO-POSS polymer hybrid.

at 1644 cm^{-1} and shifts to 1632 cm^{-1} with the formation of hydrogen bonding interaction. Also, it was shown that Si-O-Si peak of Cube-3DOH around 1085 cm^{-1} in polymer hybrid appeared strongly. The morphologies of homogeneous polymer hybrids were observed by SEM measurement. As shown in Figure 2, polymer hybrids from POSS with various organic polymers showed a homogeneous dispersion of the POSS and organic polymer at the molecular level (a, b, c). On the other hand, the phase separation could be observed in the polymer hybrid prepared from polystyrene and POSS (d). These results mean that driving force for a homogeneity of polymer hybrids from POSS is hydrogen bonding interaction.

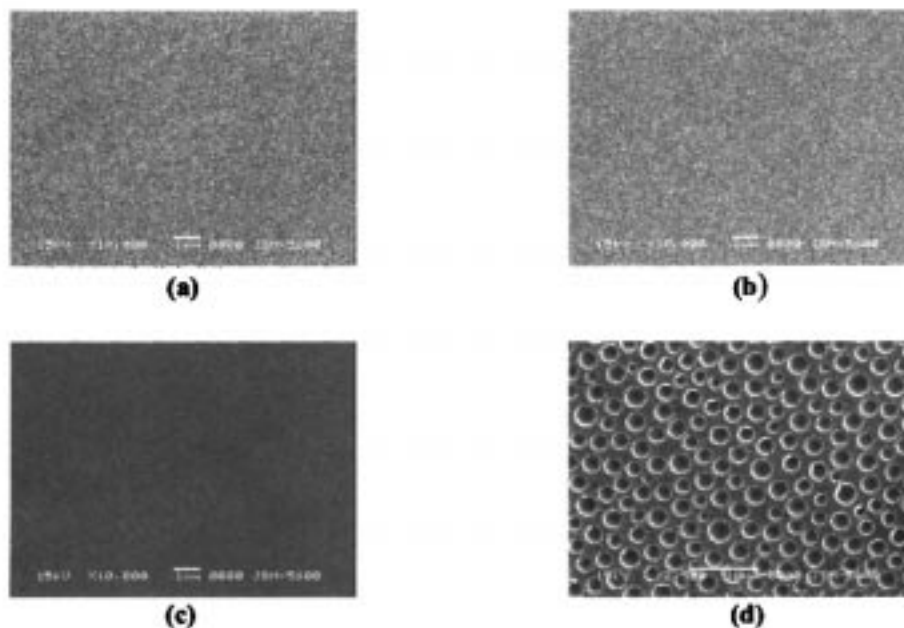


Figure 2. SEM images of polymer hybrids from POSS. (a) Cube-6OH/PVP=1/10 (b) Cube-3DOH/PVP=1/1 (c) Cube-3DOH/PDMAAm=1/1 (d) Cube-3DOH/PSt=1/20.

Conclusions

The polymer hybrids from POSS having hydroxyl groups were prepared with varying a range of weight ratios by utilizing hydrogen bonding interaction. The homogeneity of hybrid and evidence of hydrogen bonding interaction were examined by SEM and IR measurement, respectively. The solubility of POSS and transparency of polymer hybrids from POSS were closely dependent on the flexibility of eight arms having hydroxyl groups bound to silica-like core. It was also found that inorganic parts left of polymer hybrids in TGA were matched well with the calculated contents of inorganic parts.

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