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Synthesis of organic-inorganic star-shaped polyoxazolines using octafunctional silsesquioxane as an initiator

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Summary

Hybrid star-shaped polyoxazolines having POSS core were prepared by ring-opening polymerization of 2-methyl-2-oxazoline using various octafunctional POSS as an initiator with changing the feed ratio of POSS to 2-methyl-2-oxazoline. The core-first method, which uses an active multifunctional core to initiate growth of polymer chains, was applicable to make hybrid POSS-core star-shaped polyoxazolines. The kinetic rate of the polymerization and the structures of hybrid star-shaped polyoxazolines were characterized by gas chromatography (GC) and ^{1}H NMR, respectively. Their thermal properties were investigated in detail by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

Introduction

Polyhedral oligomeric silsesquioxanes (POSS) have been widely regarded as one of the promising and rapidly emerging nanoparticles in the field of organic-inorganic nanocomposite materials [1-4]. A typical POSS nanoparticle has an inorganic Si_8O_{12} core surrounded by eight organic groups on the corner, which promote solubility in organic solvents. The various methodologies for preparing copolymers or blends containing POSS, which show property enhancements via POSS such as reduced heat evolution and flammability, altered mechanicals, improved thermal property, and reduced viscosity, have been explored by Lichtenhan and coworkers as the examples including copolymers of polysiloxane [5], epoxy [6-7], polynorbornene [8], and polyurethane [9].

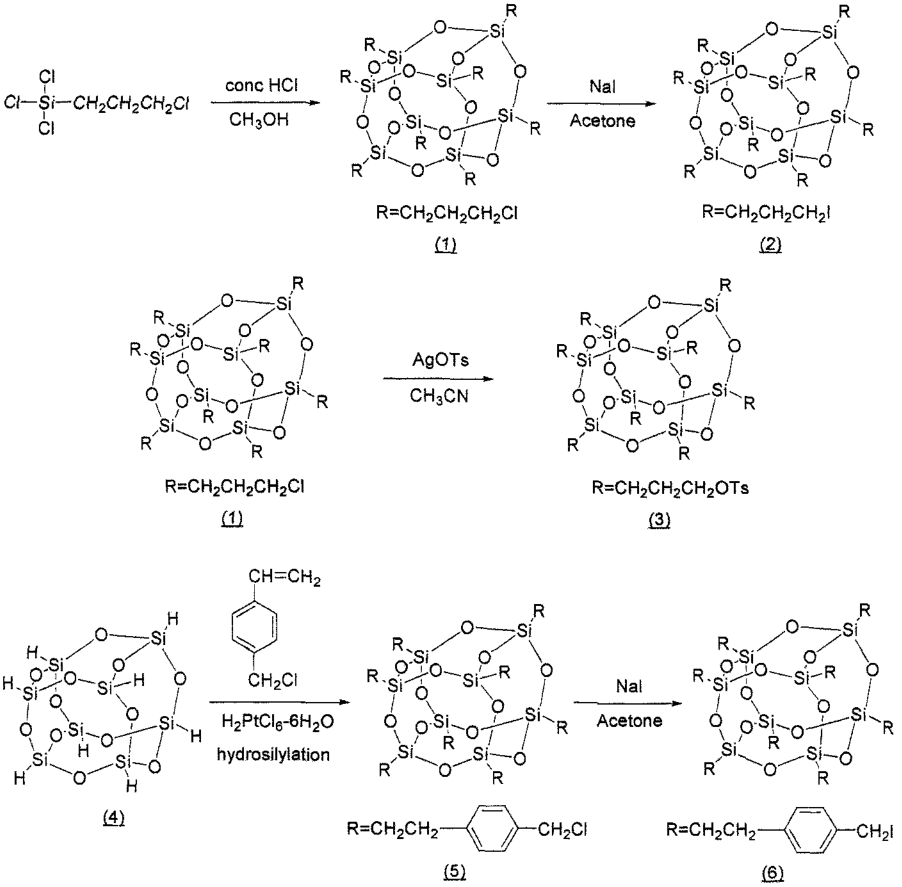
Star polymers constitute unique three-dimensional structures where a large number of arm chains radiating from the central core among the branched polymers since each molecule has only one branching point [10-11]. Well-defined star polymers offer lower melt and solution viscosities compared to those of linear polymers. Living polymerization is one of the best methods to synthesize a variety of star polymers of well defined architectures. We have steadily studied a wide variety of functional materials based on ring-opening polymerization of 2-methyl-2-oxazoline, which is a good candidate for living polymerization because the obtained polyoxazoline has unique properties such as hydrophilicity and good compatibility with common organic polymers [12-13].

We have recently explored various organic-inorganic nanocomposites consisting of POSS. Such examples include hybrid micelles [14], hybrid gels [15], hybrid LC polymers [16-17], self-assembly of metal nanoparticles [18], hydrophobic $CaCO_3$ composite particles [19], transparent polymer hybrids materials [20-21]. They showed interesting and valuable properties derived from a unique structure of POSS for the promising applications in the field of materials chemistry. In this paper, we describe the hybrid POSS-core star-shaped polyoxazolines using various octafunctional POSS as an initiator, and we also examine the kinetic rate of the polymerization and the properties of the hybrid star-shaped polyoxazolines

Experimental Section

General Procedure

^1H NMR spectra were recorded using a 270MHz JEOL-JNM-GX270 NMR spectrometer. The thermal behavior was examined by DSC and TGA (Seiko Instruments Inc., Shimadzu DT-30) under a nitrogen and air atmosphere, respectively.



Scheme 1

Gel permeation chromatography (GPC) analysis was carried out on TSK gel α-3000 by using DMF as an eluent at 40 □ after calibration with the standard polystyrene samples.

Materials

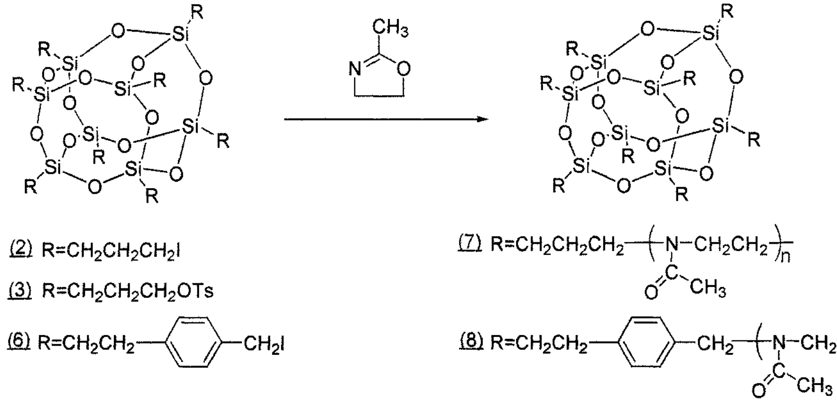
1,2-Dichloroethane and acetonitrile were distilled from calcium hydride under nitrogen. Chloroform and acetone were distilled from sodium sulfate and potassium carbonate, respectively. 2-Methyl-2-oxazoline was distilled from KOH and stored under nitrogen. Sodium iodide or silver *p*-toluenesulfonate was dried in vacuum for a few hours before use. Trichlorosilane and 3-chloropropyltrichloro-silane were purchased from TCI (Tokyo Chemical Industry Co., Ltd). All other reagents and solvents were used as received.

Synthesis of POSS as an initiator

Octa(3-iodopropyl)-octasilsesquioxane (Cube-I) **(2)** and octa(hydridosilsesquioxane) **(4)** were prepared according to the procedure reported before [22-23].

Synthesis of octa(3-tosylpropyl)-octasilsesquioxane (Cube-OTs) **(3)**. Under nitrogen, Cube-Cl **(1)** (1.02 g, 0.99 mmol) was dissolved in 50 mL of distilled acetonitrile. To this solution was added silver *p*-toluenesulfonate (5.33 g, 19.1 mmol) under nitrogen atmosphere. The suspension was refluxed for 24 h in dark under nitrogen. After evaporation of acetonitrile, the white mixture was extracted with methylene chloride and the insoluble parts were removed by filtration. After methylene chloride was removed under reduced pressure, the raw product was again reacted with silver *p*-toluenesulfonate in anhydrous acetonitrile. The work-up procedure was repeated three times and then the product was gained as a yellow solid. ^{1}H NMR ($CDCl_3$): δ7.8 (m, 16H), 7.4 (m, 16H), 4.0 (t, 16H), 2.4 (s, 24H), 1.7 (m, 16H), 0.64 (m, 16H).

Synthesis of octa(2-(p-iodobenzyl)ethyl)-octasilsesquioxane (Cube-benzylI) **(6)**. Octa(hydridosilsesquioxane) **(4)** (1.19 g, 2.82 mmol) was dissolved in distilled 1,2-dichloroethane (60 ml). The mixture was stirred, and vinylbenzyl chloride (4.80 g, 34.1 mmol) and 1.65 mL of a 3.17 mM 1,2-dimethoxyethane solution of $H_2PtCl_6 \cdot 6H_2O$ were added. The reaction mixture was refluxed for 4 days under nitrogen. After evaporation of 1,2-dichloroethane, the crude product was subjected to



Scheme 2

chromatography through a silica gel column using hexane as an eluent. Octa(2-(*p*-chlorobenzyl)ethyl)-octasilsesquioxane **(5)** was obtained as a solid residue (3.94 g, 85%). **(6)** was prepared by the same method as the above procedures of making Cube-OTs (0.10 g, 12.4%). According to the results of ^{1}H NMR, the reaction generated 58% of the β-adduct and 42% of the the α-adduct. ^{1}H NMR ($CDCl_3$): δ7.3 (m, 32H), 4.6 (s, 16H), 2.7 (m, 9.28H, β), 2.3 (m, 3.36H, α), 1.3 (m, 10.08H, α), 0.9 (m, 9.28H, β).

Synthesis of star-shaped polyoxazoline using POSS as an initiator

A typical procedure is as follows. To a solution of 2-methyl-2-oxazoline (0.50 g, 5.89 mmol) in chloroform (5 mL) was added Cube-I **(2)** (0.13 g, 0.07 mmol) at room temperature under nitrogen. The reaction mixture was heated at 70 □ for 3 days. The resulting yellow solution was diluted with 15 mL of chloroform. This polymer solution was poured into ca. 200 mL of diethyl ether to precipitate the polymeric product. The white precipitate was collected by filtration and dried in vacuum (0. 90 g, 79%).

Results and Discussion

To obtain POSS initiators for hybrid star-shaped polymers, two synthetic routes were used (Scheme 1). One is that the hydrolytic condensation of 3-chloropropyltrichlorosilane affords Cube-Cl, which upon reaction with sodium iodide or *p*-toluenesulfonate affords Cube-I or Cube-OTs, respectively. The other is that the hydrosilylation of vinylbenzyl chloride with octa(hydridosilsesquioxane) followed by reaction with sodium iodide leads to the formation of Cube-benzylI. In the ^{1}H NMR spectra of Cube-I and Cube-OTs, the iodomethylene and the toluenesulfonylmethylene protons of POSS were clearly shifted to 3.2 ppm and 4.0 ppm, respectively compared to the chloromethylene protons of Cube-Cl (3.5 ppm). The synthetic procedure of Cube-benzylI resulted in a mixture of α- (42%) and β-silylated (58%) isomers according to the results of ^{1}H NMR. The characteristic peaks and relative integral ratio matched well with their structures as we expected.

The polymerization of 2-methyl-2-oxazoline using three kinds of POSS as an initiator was carried out at 70 □ in chloroform or acetonitrile (Scheme 2). The hybrid POSS-core star-shaped polyoxazolines were characterized by ^{1}H NMR, in which the ring protons of oxazolinium living end, the methylene protons of POSS, and the methyl protons of the monomer were recognized atδ4.0-4.5, 0.7, 1.9, and 2.1 ppm, respectively. From the results of ^{1}H NMR and GPC, we concluded that star-shaped polyoxazolines having at most four or five with different lengths out of eight possible arms were obtained. This inefficient initiation and the different lengths of four or five arms 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. Table 1 shows the results of the preparation of star-shaped polyoxazolines initiated by Cube-I, which indicates the quantitative consumption of the monomer by the progress of the polymerization. Figure 1 shows the comparsion of the kinetic rate of polymerization initiated by methyl *p*-toluenesulfonate (MeOTs) with that of polymerization initiated by Cube-OTs. The kinetic rate of using MeOTs is faster than that of using Cube-OTs, which is another evidence to confirm the steric hindrance by POSS structure.

Table 1. Preparation of star-shaped polyoxazolines initiated by Cube-I

run	initiator / monomer	number of monomer to one initiator calcd.[a]	calcd.[b]
1	1/20	16	23
2	1/40	42	50
3	1/80	84	93
4	1/100	93	160
5	1/160	-[c]	160
6	1/200	-[c]	170
7	1/400	-[c]	390

[a]Determined by ^1H NMR. [b]Determined by TGA. [c]The peaks derived from Cube-I in polymer were too small to calculate the number of monomer to one initiator by ^1H NMR.

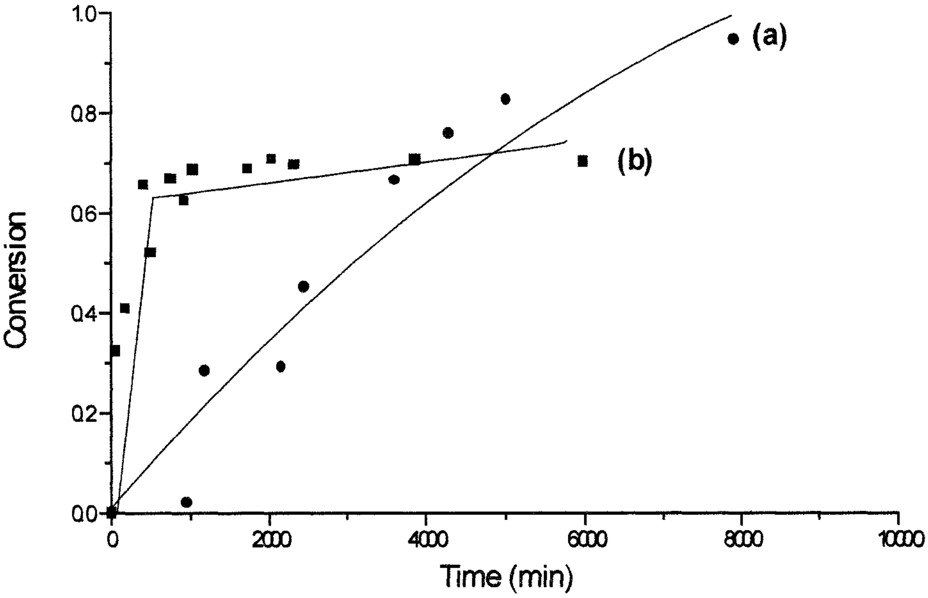


Figure 1. The kinetic rate of polymerization using Cube-OTs (a) and MeOTs (b).

Hybrid star-shaped polyoxazolines having POSS core show an increase in glass transition temperature (T_g), compared to that of polyoxazoline initiated by MeOTs (POZO) as shown in Figure 2. Other hybrid star-shaped polyoxazolines initiated by Cube-OTs or Cube-benzylI revealed the same phenomenon. This can be attributed to the reduction of segmental mobility of POZO in star-shaped polyoxazolines, which was caused by the incorporation of hard, compact POSS moiety to the core of star polymer with the"core-first"technique.

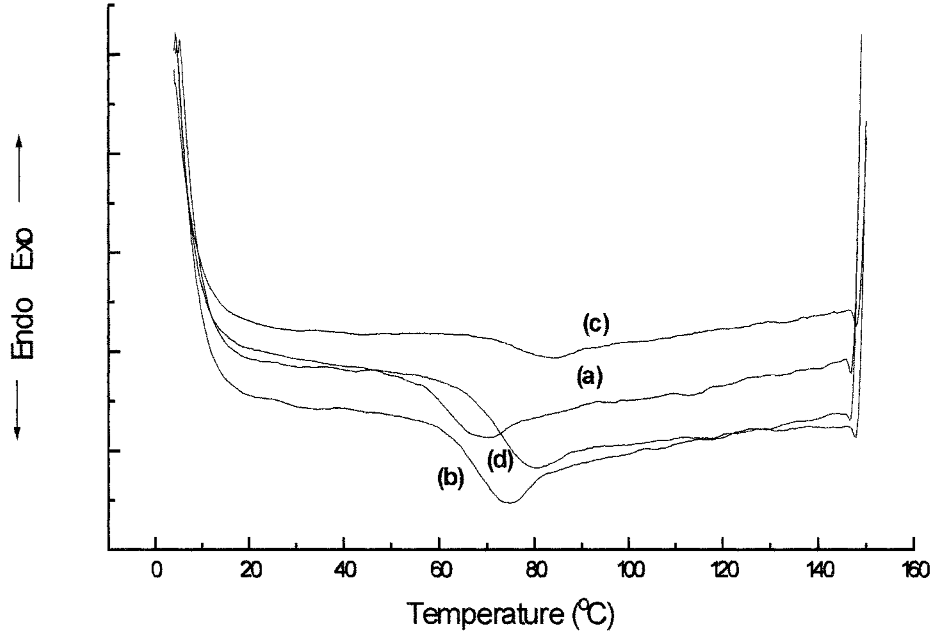


Figure 2. DSC thermograms of star-shaped polymers initiated by Cube-I with a heating rate of 10 □ min^{-1}: (a) POZO, (b) 1/40, (c) 1/200, (d) 1/400 (feed ratio).

Figure 3 is representative TGA thermograms of star-shaped polymers initiated by Cube-OTs. The thermal stabilities of star-shaped polymers increased as the weight % of POSS was increased. This is a measure of the effect of the inorganic POSS unit on polymer thermal properties. The sudden increase of thermal stability around 500 □ can be explained by the transformation from the cube structure of POSS to the amorphous silica matrix (Si_8O_{16}).

Conclusions

Hybrid POSS-core star-shaped polyoxazolines having average four or five arms were synthesized from POSS as an initiator via living polymerization of 2-methyl-2-oxazoline using the"core-first"method. The slow kinetic rate of the polymerization by POSS having multi-initiation sites leaded to the inefficient initiation and the different lengths of four or five arms because of the unique structure of POSS. The thermal stability of the star-shaped polymers from POSS was increased compared to that of linear polyoxazoline from MeOTs.

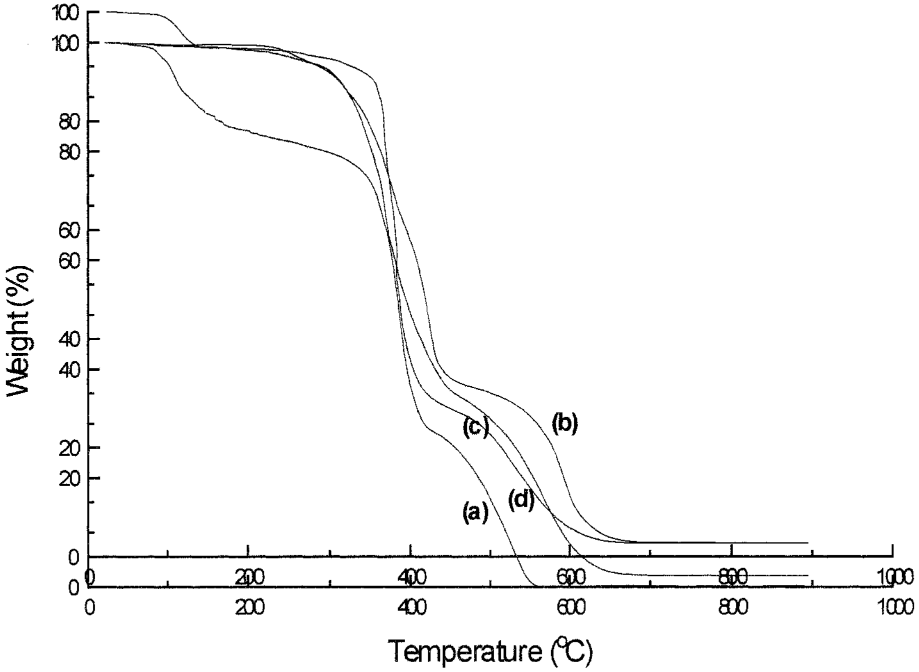


Figure 3. TGA thermograms of star-shaped polymers initiated by Cube-OTs with a heating rate of 10 □ min^{-1}: (a) POZO, (b) 1/40, (c) 1/80, (d) 1/400 (feed ratio).

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