

Synthesis and Properties of Semiaromatic Polyimides Containing POSS in Main Chain Derived from DDSQ

Shouming Wu, Teruaki Hayakawa, Ryohei Kikuchi, Jiro Hamaya, Masa-aki Kakimoto, and ²Hisao Oikawa
Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama 2-12-1,
Meguro-ku, Tokyo 152-8552, Japan

²Goi Research Center, Chisso Petrochemical Corporation, 5-1 Goi-Kaigan, Ichihara, Chiba 290-8551,
Japan

Introduction

Polyhedral oligomeric silsesquioxane (POSS), an inner cage with an inorganic silicon and oxygen framework which is externally covered by organic substituents, are cube-octameric molecules of nanoscale dimensions that may be functionalized with reactive groups suitable for the synthesis of new organic-inorganic hybrids, thus providing the opportunity to design and build materials with extremely well-defined dimensions possessing nanophase behavior.¹⁻⁵ It has a nanometer-sized cage structure and can be functionalized with various organic groups.^{6,7} The incorporation of POSS into some polymers has offered the opportunity to develop high-performance materials that combine many desirable properties of conventional organic and inorganic components such as good thermal and mechanical properties, solubility, nonflammability, and excellent dielectric properties.⁸⁻¹² In addition, the polymers based on POSS were reported to show 10 times higher durability than the aromatic polyimide Kapton[®], which has the highest resistance among the conventional polymers against active oxygen.¹³⁻¹⁷ Because the surface of the polymer is converted into an SiO₂ layer further decomposition of the bulk polymer material is prevented when these polymers are exposed to active (atomic) oxygen.¹³⁻¹⁷

Polyimides (PIs) have outstanding thermal resistance, good mechanical properties and excellent dielectric properties necessary for use in microelectronics as the interlayer dielectrics in integrated circuit fabrication.¹¹ The introduction of POSS into polyimides can improve these properties further. Recently, some POSS-containing polyimides have been reported by Leu et al.^{8,12} who prepared polyimide-side-chain tethered POSS nanocomposites for low dielectric films. While side-chain incorporation of POSS did reduce the dielectric constant, no significant effect on the mechanical properties was observed. In most reported cases, the POSS-based materials were prepared with POSS as a side chains or as an end group in hybrid polymers.⁶⁻¹² There are few examples for the synthesis of main chain POSS in the literature.

We previously reported the synthesis of a POSS, double-decker-shaped silsesquioxane (DDSQ).⁷ In this paper we reported the synthesis of double-decker-shaped silsesquioxane dianhydride (DDSQDA) (**3**) via hydrosilylation of *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride (**2**) with double-decker-shaped silsesquioxane (DDSQ), and its subsequent reaction with 4,4'-oxydianiline (ODA) to produce a double-decker-shaped silsesquioxane diamine (DDSQ-diamine) (**4**). A series of linear semiaromatic polyimides containing POSS in

main chain (POSS-PIs) from the DDSQ-diamine with various aromatic tetracarboxylic dianhydrides were synthesized and characterized.

Experimental Section

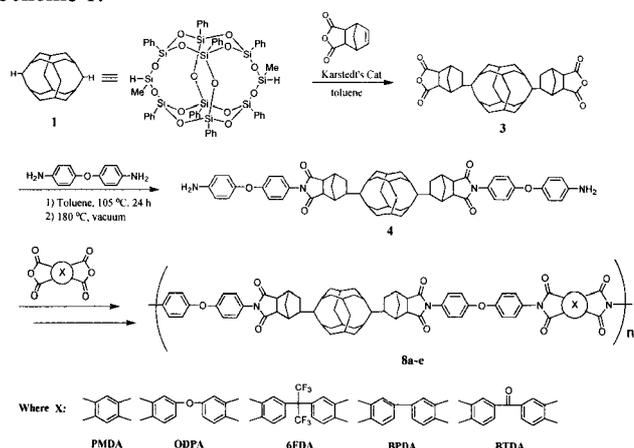
Synthesis of DDSQDA (3). In a 20 mL two-necked round-bottomed flask equipped with a magnetic stirrer were placed the DDSQ (0.50 g, 0.43 mmol), **2** (0.56 g, 3.4 mmol), and toluene (4 mL) under an argon stream. The reaction was carried out catalyzed by 0.2 mol % of Karstedt's catalyst (Pt(dvs)) in toluene at 75 °C for 24 h to afford **3** (0.61 g, 96% yield): mp > 350 °C; IR (KBr): $\nu = 1860, 1782$ (anhydride C=O), 1265 (Si-CH₃), 1220 (Si-Ph), 1132, 1090 (Si-O-Si) cm⁻¹. ¹H NMR (300 MHz, CDCl₃): 7.48–7.19 (40H, m), 3.25–3.20 (4H, m), 2.89 (2H, s), 2.67 (2H, s), 1.80–1.57 (6H, m), 1.28 (2H, m), 0.83 (2H, t, *J* = 7.8 Hz), 0.28 (6H, s) ppm. ¹³C NMR (75 MHz, CDCl₃): 172.1, 171.6, 133.9, 131.1, 127.8, 52.3, 49.6, 41.7, 40.9, 40.2, 26.3, 24.6, –1.9 ppm. ²⁹Si NMR (60 MHz, CDCl₃): –22.1, –77.9, –78.9 ppm. Anal. Calcd for C₆₈H₆₄O₂₀Si₁₀ (%): C, 55.11; H, 4.35. Found: C, 54.96; H, 4.38.

Synthesis of DDSQ-diamine (4). A mixture of **3** (0.50 g, 0.34 mmol), and ODA (0.41 g, 2.04 mmol) were added into a 100 mL two-necked round-bottomed flask, which was then stirred in toluene at 105 °C for 24 h, and dried under vacuum at 180 °C to give a yellow solid (**4**) in a 98%: mp > 350 °C; IR (KBr): $\nu = 3406$ (–NH₂), 1770, 1707 (amide C=O), 1384 (C–N), 1265 (Si-CH₃), 1236 (Si-Ph), 1133, 1051 (Si-O-Si) cm⁻¹. ¹H NMR (300 MHz, acetone-*d*₆): 7.72–7.65 (8H, dd, *J* = 7.2, 6.9 Hz), 7.60–7.53 (8H, dd, *J* = 7.8, 7.2 Hz), 7.47–7.24 (24H, m), 7.10 (4H, d, *J* = 8.7 Hz), 6.93–6.88 (8H, m), 6.78 (4H, d, *J* = 8.7 Hz), 4.67 (4H, s), 3.28 (4H, s), 3.02 (2H, s), 2.72 (2H, s), 1.92 (4H, d, *J* = 8.4 Hz), 1.74–1.57 (4H, m), 1.05 (2H, t, *J* = 8.4 Hz), 0.42 (6H, s) ppm. ¹³C NMR (75 MHz): 177.8, 177.7, 160.0, 147.1, 146.5, 134.6, 131.6, 129.0, 127.1, 122.2, 119.9, 117.2, 116.1, 51.7, 49.3, 41.8, 41.1, 40.3, 26.9, 25.4, –1.8 ppm. ²⁹Si NMR (60 MHz): –21.8, –78.3, –78.9 ppm. Anal. Calcd for C₉₂H₈₄N₄O₂₀Si₁₀ (%): C, 59.84; H, 4.59; N, 3.03. Found: C, 59.86; H, 4.48; N, 2.81.

Synthesis of POSS-PAAs 7. In a typical experiment, **4** (0.50 g, 0.27 mol) was dissolved in 10 mL DMAc in a 25 mL three-necked, to which, BPDA (**d**, 0.08 g, 0.27 mol) was added while stirring. The suspension was stirred for 24 h at room temperature to yield a viscous solution, which was then poured into methanol. The precipitate was filtered off, washed with

water, and dried under vacuum at 40 °C. The inherent viscosity of the resulting POSS–PAA **7d** is 0.38 dL/g, measured at a concentration of 0.5 g/dL in DMAc at 30 °C. IR (KBr): $\nu = 3445$ (N–H), 1767, 1709 (amide C=O), 1634 (C=O, carboxylic acid), 1264 (Si–Me), 1234 (Si–Ph), 1132, 1083 (Si–O–Si) cm^{-1} . ^1H NMR (300 MHz, DMSO- d_6): 10.55 (2H, br), 8.12–7.95 (8H, m), 7.79 (2H, br), 7.46 (2H, br), 3.40(4H, br), 3.25(2H, br), 2.86(2H, br), 1.74 (4H, br), 1.51 (4H, br), 0.83 (2H, br), 0.32 (6H, br) ppm. ^{13}C NMR (75 MHz, DMSO- d_6): 177.6, 177.5, 167.7, 167.2, 157.8, 156.4, 151.6, 136.4, 133.7, 131.5, 130.9, 130.1, 128.6, 127.1, 121.7, 120.5, 119.5, 118.1, 50.9, 48.6, 40.7, 40.1, 39.3, 26.3, 24.6, –1.7 ppm. ^{29}Si NMR (60 MHz, DMSO- d_6): –21.6, –77.7, 78.3, –79.2 ppm.

Scheme 1.



Other POSS–PAAs, **7a**, **7b**, **7c**, and **7e**, were prepared in a similar procedure by the polymerization of 1 equiv. of **4** to 1 equiv. of dianhydride PMDA(**a**), ODPA(**b**), 6FDA(**c**) and BTDA(**e**) as shown in Scheme 1. The prepared polymers have inherent viscosities in the range 0.25–0.53 dL/g (Table 2).

Polyimide films were prepared by casting the polyamic acid solution from DMAc onto a silicon wafer then cured by a stepped thermal sequence (80 °C/2 h, 120 °C/1 h, 180 °C/1 h, 250 °C/2 h, 300 °C/1 h) under nitrogen atmosphere to produce the imidized POSS–PIs **8a–e**.

IR of **8a** (KBr): $\nu = 1781$, 1714 (amide C=O), 1376 (C–N), 1261 (Si–CH₃), 1242 (Si–Ph), 1136, 1078 (Si–O–Si) cm^{-1} .

IR of **8b** (KBr): $\nu = 1776$, 1718 (amide C=O), 1380 (C–N), 1268 (Si–CH₃), 1241 (Si–Ph), 1143–1087 (Si–O–Si) cm^{-1} .

IR of **8c** (KBr): $\nu = 1783$, 1716 (amide C=O), 1375 (C–N), 1264 (Si–CH₃), 1243 (Si–Ph), 1142–1090 (Si–O–Si) cm^{-1} .

IR of **8d** (KBr): $\nu = 1780$, 1716 (amide C=O), 1378 (C–N), 1266 (Si–CH₃), 1234 (Si–Ph), 1114, 1071 (Si–O–Si) cm^{-1} .

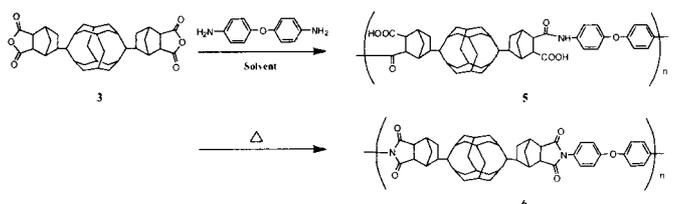
IR of **8e** (KBr): $\nu = 1781$, 1717 (amide C=O), 1378 (C–N), 1265 (Si–CH₃), 1242 (Si–Ph), 1115, 1088 (Si–O–Si) cm^{-1} .

Results and Discussion

Synthesis of POSS–PAA 5. The polymerization of **3** with ODA was carried out in DMAc at room temperature to give POSS–PAA **5**. The inherent viscosity is low (0.14–0.20 dL/g) implying that POSS–PAA **5** has a relatively low

molecular weight. The inherent viscosity remained unchanged even when the reaction temperature was increased to 180 °C by one-step high temperature solution polymerization procedure and reaction time prolonged to 30 h as shown in Table 1. The POSS–PI **6** prepared from POSS–PAA **5** by thermal imidization was also fragile. The low molecular weights are likely due to a deactivation of the anhydride ring by the norbornane moiety.¹⁰

Table 1. Synthesis of Polyamic Acid (**5**)



Run ^a	temp (°C)	Solvent /Catalyst	Time (h)	Inherent Viscosity ^b (dL/g)	Film quality of 6
1	25	<i>m</i> -cresol	24	0.15	–
2	25	NMP	24	0.14	–
3	25	DMAc	24	0.18	brittle
4 ^c	180	<i>m</i> -cresol/isoquinoline	24	0.19	brittle
5 ^c	180	<i>m</i> -cresol/isoquinoline	30	0.20	brittle

^aPolymerization was carried out with 0.5mmol of each monomer in the solvent under nitrogen. ^bMeasured at a concentration 0.5 g / dL in each solvent at 30 °C. ^cOne-step high temperature solution polymerization procedure.

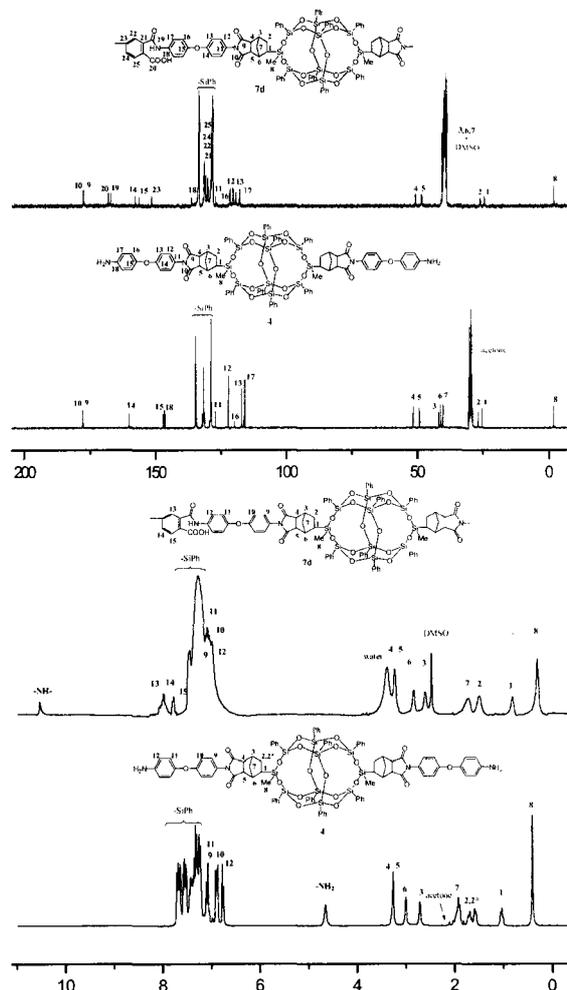


Figure 1. ^1H , ^{13}C NMR spectra of POSS-PAA **7d** in DMSO- d_6 and **4** in acetone- d_6 .

Polymer Characterization. POSS – PAAs **7** containing POSS in the main chain have high molecular weights were synthesized by functional group conversion method. Figure 1 show the ^1H and ^{13}C NMR spectra of POSS – PAA **7d** and monomer **4**, respectively. The ^1H NMR peaks for POSS – PAA **7d** are less resolved than those of monomer **4**, typical of polymeric materials. The peak due to the amine proton (4.67 ppm) of monomer **4** is absent in **7d**, and a new peak typical of an amide proton is observed at 10.55 ppm. The comparison of the ^1H NMR spectra of **4** and **7d** indicates that peak 2 which split into two broad groups 2 and 2* in the monomer **4** became a single broad signal in the polymer **7d**. This might be attributed to the rotation hindrance of polymer chain. The data are consistent with the formation of a polyamic acid. In the ^{13}C NMR spectra, the singlet peak 8 due to the proton of the methyl group signal, seven peaks (1 – 7) due to the carbons of methylene groups in the norbornane moiety. These are relatively unshifted from monomer **4** to POSS – PAA **7d**.

It indicates that the methyl group and norbornane moiety remain intact following the reaction. The ^{29}Si NMR spectra of polymer **7d** (DMSO- d_6) and **4** (acetone- d_6) are shown in Figure 2, in which the signal SiMeO₂ (peak 1) of **7d** was barely shifted compared with **4**. It provides direct evidence that the silsesquioxane cages remain intact following the reaction. The broad peak 2 centered at -78.3 ppm in **4** split into a doublet at -77.7 and -78.3 ppm in **7d**. A chiral center can cause the splitting of ^{29}Si NMR signal, which means that different stereo-configurations cause this splitting.

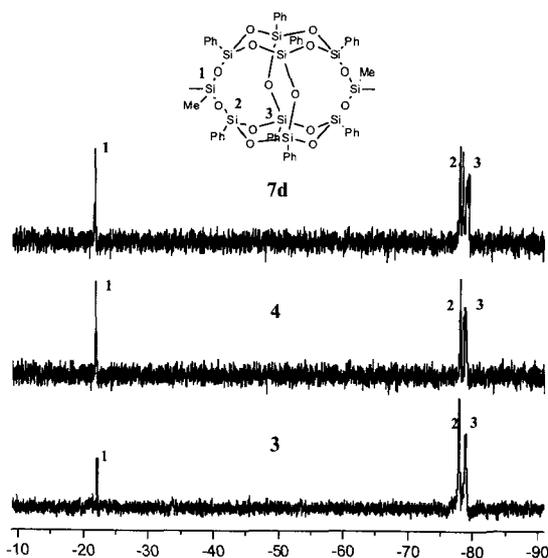


Figure 2. ^{29}Si NMR spectra of monomer **3**, monomer **4** and POSS-PAA **7d**.

Thermal Properties of POSS – PIs **8.** The thermal properties of the POSS – PIs were evaluated by DSC and TGA (Table 2). The T_g values of POSS – PIs in nitrogen ranged from 255 °C to 267 °C. The T_g is very typical compared to those of polyimides.¹¹ The T_g of POSS – PI **8e** (267 °C) is highest and not that for **8a** (264 °C), which is basically the same as for the other polyimides. It can be explained that the flexible ODA unit of monomer **4** due to the T_g of the polyimides. The POSS unit has no noticeable effect on T_g . However, while the T_g is

unchanged the 5% weight loss temperatures (T_{d5}) and 10% weight loss temperatures (T_{d10}) in air are improved up to 514 °C and 551 °C (**8e**), respectively. The results indicate that the POSS moiety improves the thermal stability over current semiaromatic polyimides used in the microelectronic applications.

Table 2. Summary of the Properties of the POSS – PIs and PMDA/ODA

PI	T_g^a (°C)	T_{d5}^b (°C)	T_{d10}^c (°C)	density (g/cm ³)	contact Angle (°)	inherent viscosity ^d (dL/g)
8a	264	504	541	1.41	84	0.25
8b	261	501	538	1.42	86	0.27
8c	255	495	521	1.43	79	0.53
8d	262	503	537	1.42	83	0.45
8e	267	514	551	1.44	84	0.38
6	248	498	537	1.40	85	0.39
PMDA/ODA	362	470	530	1.44	54	2.04

^aFrom DSC on the second heating at a heating rate of 30 °C/min in nitrogen. ^bTemperature at which 5% weight loss was recorded by thermogravimetry at a heating rate of 10 °C/min in air. ^cTemperature at which 10% weight loss was recorded by thermogravimetry at a heating rate of 10 °C/min in air. ^dPolyamic Acid (**7**) measured at a concentration 0.5 g / dL in each solvent at 30 °C.

Mechanical Properties of POSS – PIs **8.** Table 4 summarizes the mechanical properties of POSS – PIs **8** series. The polyimide films (**8**) have tensile strengths of 42.1 – 74.1 MPa, initial modulus of 1.51 – 2.32 GPa, and elongation at breakage of 2.9 – 6.0%. The elongation of **8a** is unusually low (2.9%). This is likely due to the lower molecular weight of **8a** as compared with the other polyimides. However, **8b** derived from ODA showed the highest elongation of 6.0%, which might be attributed to the higher molecular weight and the flexible ether linkage in the polymer backbone.

Alkali and Acid Resistance. In order to investigate the alkali and acid resistance of the present PIs, the mechanical properties of POSS – PI **8b** and the polyimide (PMDA/ODA) were measured before and after immersion in the 5 wt% NaOH solution and in 95 wt% sulfuric acid, respectively. As shown in Table 4, after immersion in 5% NaOH at 40 °C for 72 h the POSS – PI **8b** still remained flexible and its mechanical properties were only slightly degraded: tensile strength of 65.9 MPa, elongation of 3.8%, and initial modulus of 1.96 GPa. However, the reference PMDA/ODA film lost its flexibility and its mechanical properties could not be remeasured. Immersion of the PMDA/ODA film in 95% sulfuric acid dissolved within minutes. However, the sulfuric acid only swelled POSS – PIs **8**, and it was observed that 92 – 97% of the film mass was retained after 3 days. The film after acid treatment was too brittle to mechanically test, possibly indicating that the mass loss is due to extraction of low molecular weight species that were acting as a plasticizer. Overall, the POSS moiety added exceptional acid and base resistance to the PI.

The high resistance to acid and base is likely due to two main factors. First, the POSS – PI contact angle of water is significantly higher than that of the PMDA/ODA PI (Table 2). This correlates well with the low water absorption (Figure 7) of the POSS – PI **8b** (< 1%) to the PMDA/ODA film (4.8 – 6%). It is reasonable to conclude that the base solution cannot degrade

what it cannot interact with. Second, the unique molecular "silicone-oxygen" frame (silsesquioxane combination) of POSS (Si₂O₃) with the middle character of silicone (SiO) and silica (SiO₂), has the features of both an inorganic substance (silicone base) and organic matter (carbon base). It indicates POSS has a dramatic effect in chemical resistance etc. The combination of a hydrophobic polymer to minimize swelling and chemical stability of the POSS moiety imparts high resistance to acid and alkaline solutions.

Table 4. Mechanical properties and Dielectric Constant of POSS-PIs **8a-e**

POSS-PI	tensile strength (MPa)	elongation (%)	initial modulus (GPa)	Dielectric Constant ^b
8a	42.1	2.9	2.32	2.38
8b	74.1	6.0	2.15	2.63
8ba	65.9	3.8	1.96	-
8c	58.0	5.9	1.82	2.36
8d	52.3	5.0	1.51	2.55
8e	65.8	5.4	2.18	2.74

^aImmersed in the solution of 5% NaOH in water at 40 °C for 72 h. ^bDielectric Constant measured at 1 MHz.

Dielectric Constant of POSS-PIs 8. The POSS-PIs **8** possessed low dielectric constants of 2.36–2.74 at 1 MHz (Table 5). This can be attributed to the POSS of cubic silica core with the homogeneity nanopore increasing in the free volume. Second, the POSS molecules have a lower polarity, which also reduces the dielectric constant.¹⁷ The fluorinated semiaromatic polyimide **8c** and **8a** had similar dielectric constants. This indicates that the POSS unit is a effective, if not more effective, at decreasing the dielectric constant as fluorinated units. The values for POSS-PI **8a** and **8c** are similar to those for POSS-containing polyimides nanocomposites (2.32±0.05) without significantly affecting the mechanical properties.¹² They are slightly lower than the optically estimated dielectric constant of typical alicyclic polyimide (2.47)¹ and a fluorinated semiaromatic polyimide (2.6) and significantly lower than that of a typical semiaromatic polyimide (2.83).

Conclusions

The polymerization of double-decker-shaped silsesquioxane diamine **4** with aromatic tetracarboxylic dianhydrides in DMAc at room temperature afforded polyamic acids containing POSS in main chain with high molecular weights ($\eta_{inh} = 0.53$ dL/g). POSS-PI **8** had good thermal stability with the 5% weight loss temperature in air over 490 °C. The polyimide films have good mechanical properties with elongation at breakage of 2.9–6.0%, in which POSS-PI **8b** showed the highest elongation (6.0%). The water absorption of POSS-PI **8b** (<1%) was lower than that of the PMDA/ODA film. POSS-PIs **8** possessed excellent alkaline and acid resistance. POSS-PI **8b** kept its flexible mechanical properties after immersion in 5% NaOH solution at 40 °C for 72 h. POSS-PI **8a** and **8c** possessed low dielectric constants of 2.38 and 2.36, respectively.

References and Notes

- (1) Koh, K.; Sugiyama, S.; Morinaga, T.; Ohno, K.; Tsujii, Y.; Fukuda, T.; Yamahiro, M.; Iijima, T.; Oikawa, H.; Watanabe, K.; Miyashita, T. *Macromolecules* **2005**, *38*, 1264.
- (2) Provas, A.; Matisons, J. G. *Trends Polym. Sci.* **1997**, *5*, 327.
- (3) Baney, R. H.; Itoh, M.; Sakakibara, A.; Suzuki, T. *Chem. Rev.* **1995**, *95*, 1409.
- (4) Pescarmona, P. P.; Maschmeyer, T. *Aust. J. Chem.* **2001**, *54*, 583.
- (5) Laine, R. M.; Zhang, C.; Sellinger, A.; Viculis, L. *Appl. Organomet. Chem.* **1998**, *12*, 715.
- (6) Jones, R. G.; Ando, W.; Chojnowski, J., Eds.; *Silicon-Containing Polymers*; Springer-Verlag: New York, 2000.
- (7) (a) Wu, SM.; Hayakawa, T.; Kikuchi, R.; Stephen, J.; Kakimoto, M.; Oikawa, H. *Macromolecules* **2007**, *40*, 5698. (b) Seino, M.; Hayakawa, T.; Ishida, Y.; Kakimoto, M.; Watanabe, K.; Oikawa, H. *Macromolecules* **2006**, *39*, 3473.
- (8) Leu, C.; Chang, Y.; Wei, K. *Chem. Mater.* **2003**, *15*, 3721.
- (9) Zhang, C.; Babonneau, F.; Bonhomme, C.; Laine, R. M.; Soles, C. L.; Hristov, H. A.; Yee A. F. *J. Am. Chem. Soc.* **1998**, *120*, 8380.
- (10) Watanabe, Y.; Sakai, Y.; Shibasaki, Y.; Ando, S.; Ueda, M.; Oishi, Y.; Mori, K. *Macromolecules* **2002**, *35*, 2277.
- (11) Maier G. *Prog. Polym. Sci* **2001**, *26*, 3.
- (12) Leu, C.; Chang, Y.; Wei, K. *Macromolecules* **2003**, *36*, 9122.
- (13) Wright, M. E.; Petteys, B. J.; Guenther, A. J.; Faillis, S.; Yandek, G. R.; Tomczak, S. J.; Minton, T. K.; Brunsvold, A. *Macromolecules* **2006**, *39*, 4710.
- (14) Svejda, S.A.; Phillips, S. H.; Gonzalez, R.I.; Feher, F.J.; Lichtenhan, J. D.; Reinerth, W.A.; U. S. Patent 6,767,930, **2004**.
- (15) Lichtenhan, J.D. ; Vu, Gilman, J.W.; Feher, F.J.; United States Patent 5,412,053, **1995**.
- (16) Kawakami, Y. *React. Funct. Polym.* **2007**, *67*, 1137.
- (17) Ikeda, M. ; Saito, H. *React. Funct. Polym.* **2007**, *67*, 1148.