Synthesis and Dielectric Properties of Polyimide-Chain-End Tethered Polyhedral Oligomeric Silsesquioxane Nanocomposites

Chyi-Ming Leu,[†] G. Mahesh Reddy,[†] Kung-Hwa Wei,*,[†] and Ching-Fong Shu[‡]

Department of Materials Science and Engineering and Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan 30049, R. O. C.

Received August 27, 2002. Revised Manuscript Received February 26, 2003

Nanoporous polyhedral oligomeric silsesquioxanes (POSS) containing amine groups (NH_2−POSS) were reacted with poly(amic acid) having anhydride end groups to form porous POSS/polyimide nanocomposites. The van der Waals interaction between tethered POSS molecules is incompatible with the polar−polar interaction of imide segments, resulting in a self-assembled system of zigzag shaped cylinders or lamellas about 60 nm long and 5 nm wide, as determined by transmission electron microscopy. The incorporation of 2.5 mol % nanoporous POSS results in a reduction of the dielectric constant of the polyimide nanocomposite from 3.40 for the pure polyimide to 3.09 without any degradation in mechanical strength.

Introduction

Organic−inorganic nanocomposites with well-defined architectures have attracted a great deal of attention as they not only have synergistic properties, but can also be tailored to specific technical applications.[1−3] One class of inorganic component − polyhedral oligomeric silsesquioxanes (POSS) − has nanometer-sized structures with high surface area and controlled porosity, and has been demonstrated to be an efficient method in the design of hybrid materials.[4−18] POSS consists of a rigid, cubic silica core with a 0.53-nm side length and can have

organic functional groups connected to the vertexes of the cubic core for further reaction. Because of their capacity for attaching different functional groups and high solubility in several solvents, POSS molecules can form covalent bonds with themselves or organic monomers. POSS molecules are typically stable up to 400 °C, higher than the thermal degradation temperatures of most polymers. Their incorporation into some polymers has led to enhancements in thermal stability and mechanical properties.[5,6,9] For instance, POSS molecules have been successfully incorporated into acrylics,[4] styryls,[6] epoxy,[7,11,15] and polyethylene.[18]

Polyimides are well-known for their high-temperature durability (service temperatures can exceed 300 °C) and strength. Polyimides are used as interlayer dielectrics in microelectronics applications.[19] The need for lower dielectric constant materials becomes more stringent as the size of electronic devices is reduced in order to avoid cross talk between conducting wires. A variety of approaches to alter the structure of polyimides physically or chemically to obtain lower dielectric constants have been attempted. The synthesis of fluorinated polyimides is one of the most common approaches.[20−22] Although the dielectric constant of fluorinated polyimide is low (less than 3.0), poor mechanical properties and high monomer costs compromise its use. Another way to reduce the dielectric constant[23−27] is to form polyimide foams by introducing nanopores through thermal deg-

* To whom correspondence should be addressed. Tel: 886-35-731871. Fax: 886-35-724727. E-mail: khwei@cc.nctu.edu.tw.
    † Department of Materials Science and Engineering.
    ‡ Department of Applied Chemistry.
    (1) Klok, H. A.; Lecommandoux, S. *Adv. Mater.* **2001**, *13*, 1217.
    (2) Tsukruk, V. V. *Prog. Polym. Sci.* **1997**, *22*, 247.
    (3) Sanchez, C.; Soler-Illia, G. J. de A. A.; Ribot, F.; Lalot, T.; Mayer, C. R.; Cabuil, V. *Chem. Mater.* **2001**, *13*, 3061.
    (4) Lichtenhan, J. D.; Vu, N. Q.; Carter, J. A.; Gilman, J. W.; Feher, F. J. *Macromolecules* **1993**, *26*, 2141.
    (5) Lichtenhan, J. D.; Otonari, Y. A.; Carr, M. J. *Macromlecules* **1995**, *28*, 8435.
    (6) Haddad, T. S.; Lichtenhan, J. D. *Macromolecules* **1996**, *29*, 7302.
    (7) Lee, A.; Lichtenhan, J. D. *Macromolecules* **1970**, *31*, 4970.
    (8) Feher, F. J.; Soulivong, D.; Eklud, A. G.; Wyndham, K. D. *Chem. Commun.* **1997**, 1185.
    (9) Fu, B. X.; Zhang, W. H.; Hsiao, B. S.; Rafailovich, M.; Sokolov, J.; Sauer, B. B.; Phillips, S.; Balnski, R. *High Perform. Polym.* **2000**, *12*, 565.
    (10) Jeon, H. G.; Mather, P. T.; Haddad, T. S. *Polym. Int.* **2000**, *49*, 453.
    (11) Haddad, T. S.; Mather, P. T.; Jeon, H. G.; Romo-Uribe, A.; Farris, R.; Lichtenhan, J. D. In *Organic/Inorganic Hybrid Materials*; Laine, R. M., et al., Eds.; MRS Symp. Ser. 519; Materials Research Society: Warrendale, PA, 1998; pp 381−386.
    (12) Gilman, J. W.; Schlitzere, D. S.; Lichtenhan, J. D. *J. Appl. Polym. Sci.* **1996**, *60*, 591.
    (13) Gonzalez, R. I.; Phillips, S. H.; Hoflund, G. B. *J. Spacecr. Rockets* **2000**B, *37*, 463.
    (14) 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.
    (15) Laine, R. M.; Choi, J.; Lee, I. *Adv. Mater.* **2001**, *13*, 800.
    (16) Zhang, C.; Laine, R. M. *J. Am. Chem. Soc.* **2000**, *122*, 6979.
    (17) Tamaki, R.; Tanaka, Y.; Asuncion, M. Z.; Choi, J.; Laine, R. M. *J. Am. Chem. Soc.* **2001**, *123*, 12416.

    (18) Zheng, L.; Waddon, A. J.; Farris, R. J.; Coughlin, E. B. *Macromolecules* **2002**, *35*, 2375.
   (19) Feger, C.; Franke, H. In *Polyimides Fundamentals and Applications*; Ghosh, M. K., Mittal, K. L., Eds.; Marcel Decker: New York, 1996; pp 759−814.
    (20) Haider, M.; Chenevey, E.; Vora, R. H.; Cooper, W.; Glick, M.; Jaffe, M. *Mater. Res. Soc. Symp. Proc.* **1991**, *227*, 379.
    (21) Auman, B. C.; Trofimenko, S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *34* (2), 244.
    (22) Auman, B. C. In *Advances in Polyimide Science and Technology*; Proceedings of the 4th International Conference on Polyimides, 1991.

Scheme 1

Cy- cyclohexyl   Cl-POSS   NO$_2$-POSS

NH$_2$-POSS   phthalimide-POSS (model compound)
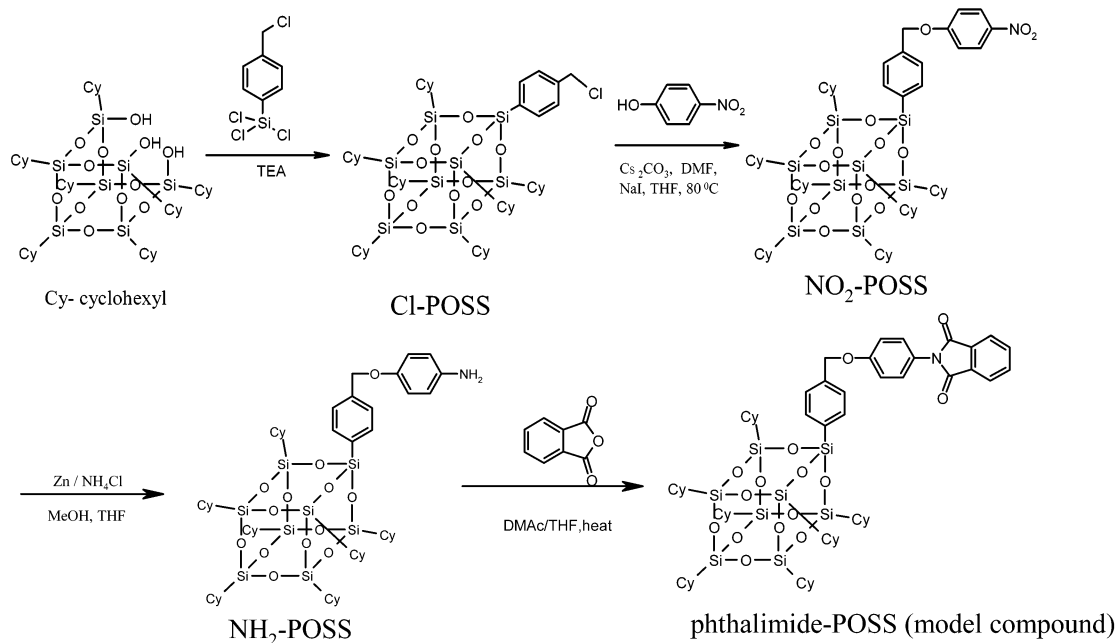
radation of polymethyl methacrylate block at 250 °C of a phase-separated polyimide–polymethyl methacrylate block copolymer (PI-*b*-PMMA). In this approach, it is difficult to completely remove residual PMMA and to produce uniform and controllable closed nanopores.

Recently, covalently bonded layered silicate/polyimide nanocomposites have been synthesized in our laboratory and were found to possess improved thermal, mechanical, and barrier properties as compared to those of the neat polyimide.[28-31] Pure nanoporous POSS macromolecules have been shown to have a very low dielectric constant (2.1–2.7) as reported in one study, due to the nanoporosity of POSS molecules.[32] Covalently combining nanoporous POSS molecules with polyimide to form nanocomposites may be an effective way to reduce the dielectric constant of polyimides without degrading their mechanical properties.

We report here a third approach involving the covalent tethering of nanoporous POSS to the chain ends of polyimides to produce POSS/polyimide nanocomposites with reduced dielectric constants. First, the modified POSS compound (NH$_2$–POSS) was synthesized in three steps, as shown in Scheme 1. A model compound for the covalently bonded POSS/polyimide nanocomposite was produced by reacting NH$_2$–POSS with phthalic anhydride to form phthalimide–POSS. Subsequently, the NH$_2$–POSS was grafted to the poly(amic acid) chain end

by reacting the amino end group with the anhydride end group of poly(amic acid) in an *N,N*-dimethylacetamide/ tetrahydrofuran (DMAc/THF) cosolvent system. After imidization at 300 °C, a POSS/polyimide (PMDA–ODA) nanocomposite formed. The detailed process for preparing the POSS/polyimide nanocomposite is given in Scheme 2.

The polar–polar interaction between imide segments is quite different from the van der Waals interaction between POSS molecules; the grafting of POSS molecules to the ends of the polyimides is expected to lead to a phase-separated system, as demonstrated in other studies,[1-3] because POSS molecules are uniformly porous in nanometer-range size, and these nanopores contain air (with dielectric constant close to 1). Hence, the polyimide-tethered-POSS structure can exhibit lower dielectric constant without degrading the effective mechanical properties of polyimide.

Experiment

Materials. Cyclohexyltrisilanol–POSS was obtained from Hybrid Plastics Company and all solvents used were obtained from Aldrich (Milwaukee, WI). Pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA) were purchased from TCI in Tokyo, Japan.

Cyclohexyltrisilanol–POSS. ^{29}Si NMR (THF, δ ppm): −60.0, −68.1, −69.6.

Cl–POSS. The Cl–POSS was prepared by reacting trichloro [4-(chloromethyl)-phenyl] silane (1.0 mL, 5.61 mmol) with cyclohexyltrisilano–POSS (5.00 g, 5.11 mmol) in the presence of triethylamine (2.2 mL, 15.41 mmol) in 30.0 mL of dry THF. The reaction flask was stirred under nitrogen for 2 h, followed by filtration to remove the HNEt$_3$Cl byproduct. The clear THF solution was dropped into a beaker of rapidly stirred acetonitrile. The resultant product was collected by filtration and dried in a vacuum. (4.61 g, 80%).

^{1}H NMR (CDCl$_3$, δ ppm): 7.59 (d, J = 7.5 Hz, Si–Ar–H, 2H), 7.33 (d, J = 7.5 Hz, Si–Ar–H, 2H), 4.52 (s, Ar–CH$_2$–Cl, 2H), 1.66–1.63 (m, Cy–CH$_2$, 35H), 1.17–1.16 (m, Cy–CH$_2$, 35H), 0.74–0.67 (m, Cy–CH, 7H). ^{13}C NMR (CDCl$_3$, δ ppm): 139.2, 134.5, 132.9, 127.7, 46.1, 27.4, 26.8, 26.6, 26,5, 23.1, 20.0. ^{29}Si NMR (THF, δ ppm): −67.8, −68.2, −79.6. GPC data: M_w 836.1, M_n 757.8, polydispersity 1.10.

(23) Feger, C., Khojasteh, M. M., Htoo, M. S., Eds.; Technomic: Lancaster, PA, 1993; pp 15–32.

(24) Meyers, R. A. *J. Polym. Sci., Part A-1* **1969**, *7*, 2757.

(25) Carleton, P. S.; Farrisey, W. J.; Rose, J. S. *J. Appl. Polym. Sci.* **1972**, *16*, 2983.

(26) Carter, K. R.; DiPietro, R. A.; Sanchez, M. I.; Russell, T. P.; Lakshmanan, P.; McGrath, J. E. *Chem. Mater.* **1997**, *9*, 105.

(27) Hedrick, J. L.; Carter, K. R.; Richter, R.; Miller, R. D.; Russell, T. P.; Flores, V. *Chem. Mater.* **1998**, *10* (1), 39.

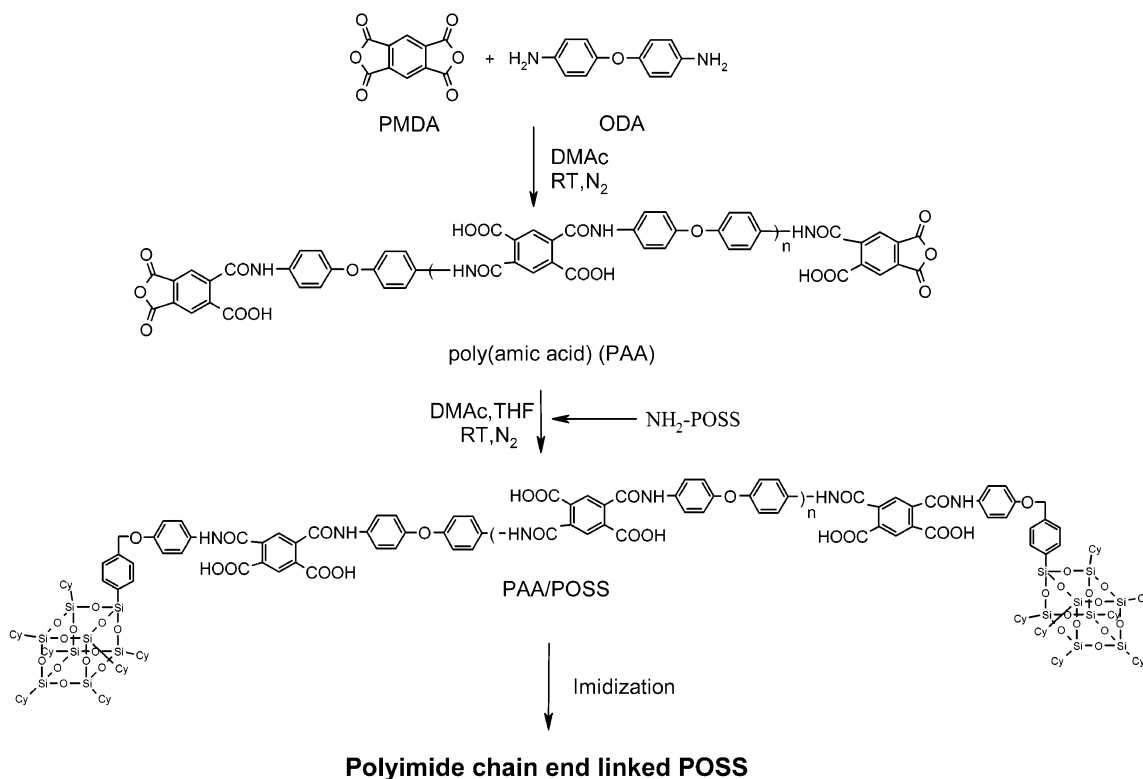(28) Leu, C. M.; Wu, Z. W.; Wei, K. H. *Chem. Mater.* **2002**, *14*, 3016.

(29) Jiang, L. Y.; Leu, C. M.; Wei, K. H. *Adv. Mater.* **2002**, *14*, 426.

(30) Tyan, H. L.; Liu, Y. C.; Wei, K. H. *Chem. Mater.* **1999**, *11*, 1942.

(31) Tyan, H. L.; Leu, C. M.; Wei, K. H. *Chem. Mater.* **2001**, *13*, 222.

(32) Su, R. Q.; Muller, T. E.; Prochazka, J.; Lercher J. A. *Adv. Mater.* **2002**, *14*, 1369.

Scheme 2

PMDA   ODA

DMAc
RT, N$_2$

poly(amic acid) (PAA)

DMAc, THF
RT, N$_2$ NH$_2$-POSS

PAA/POSS

Imidization

Polyimide chain end linked POSS

NO$_2$−POSS. *p*-Nitro phenol (0.14 g, 1.06 mmol) and Cs$_2$-CO$_3$ (0.32 g, 0.98 mmol) were taken in DMF (10.0 mL) and the reaction mixture was heated at 80 °C under nitrogen atmosphere for 1 h. The Cl−POSS (1.00 g, 0.80 mmol) was dissolved in dry THF (10.0 mL) and added dropwise to the above solution for 0.5 h. NaI (0.14 g, 0.98 mmol) was added to the reaction mixture and heating was continued for 4 h. The solution was diluted with water and extracted with dichloromethane (3 × 15.0 mL). The organic layer was washed with water (2 × 50.0 mL) and concentrated in a vacuum to furnish NO$_2$−POSS as a light yellow powder (1.01 g, 97%).

^{1}H NMR (CDCl$_3$, δ ppm): 8.19 (d, J = 9.0 Hz, NO$_2$−Ar−H, 2H), 7.70 (d, J = 8.2 Hz, Si−Ar−H, 2H), 7.42 (d, J = 8.2 Hz, Si−Ar−H, 2H), 7.02 (d, J = 9.0 Hz, NO$_2$−Ar−H, 2H), 5.16 (s, Ar−CH$_2$−O, 2H), 1.68−1.71 (m, Cy−CH$_2$, 35H), 1.19−1.23 (m, Cy−CH$_2$, 35H), 0.76−0.79 (m, Cy−CH, 7H). ^{13}C NMR (CDCl$_3$, δ ppm): 163.6, 141.7, 137.3, 134.5, 132.5, 126.5, 125.9, 114.8, 70.5, 27.4, 26.8, 26.6, 26,5, 23.1, 20.0. ^{29}Si NMR (THF, δ ppm): −67.9, −68.2, −79.6. GPC data: M_w 988.4, M_n 902.3, polydispersity 1.09.

NH$_2$−POSS. NH$_4$Cl (0.20 g, 3.72 mmol) and Zn powder (1.07 g, 14.88 mmol) were added to a solution of NO$_2$−POSS (0.90 g, 0.71 mmol) in MeOH/THF (30.0 mL, 1:1) at 80 °C. After the mixture was gently refluxed for 1 h, the insoluble materials were removed by filtration and washed with THF. The filtrate was concentrated in a vacuum. The residue was purified by column chromatography (Al$_2$O$_3$, eluent AcOEt/hexane 1:3) to give NH$_2$−POSS (0.55 g, 63%) as a light brown powder.

^{1}H NMR (CDCl$_3$, δ ppm): 7.66 (d, J = 7.8 Hz, Si−Ar−H, 2H), 7.42 (d, J = 7.8 Hz, Si−Ar−H, 2H), 6.80 (d, J = 8.6 Hz, N−Ar−H, 2H), 6.64 (d, J = 8.6 Hz N−Ar−H, 2H), 4.99 (s, Ar−CH$_2$−O, 2H), 1.70−1.72 (m, Cy−CH$_2$, 35H), 1.21−1.23 (m, Cy−CH$_2$, 35H), 0.76−0.79 (m, Cy−CH, 7H). ^{13}C NMR (CDCl$_3$, δ ppm): 152.3, 139.4, 134.3, 131.5, 126.5, 116.6, 116.0, 70.7, 27.4, 26.8, 26.6, 26,5, 23.1, 20.0. ^{29}Si NMR (THF, δ ppm): −67.9, −68.2, −79.3. GPC data: M_w 1021.7, M_n 917.5, polydispersity 1.11.

Phthalimide−POSS. Phthalic anhydride (0.03 g, 0.03 mmol) was added to a premixed solution of DMAc and THF (30.0/3.0 mL) containing NH$_2$−POSS (0.30 g, 0.03 mmol) at room temperature. After the mixture was stirred for 3 h, acetic

anhydride and pyridine were added, and then the mixture was heated to 80 °C for 2 h. The resulting mixture was slowly added to excess MeOH. The resulting white solid was filtered, washed with MeOH, and dried.

^{1}H NMR (CDCl$_3$, δ ppm): 7.92−7.95 (m, Ar−H of phthalimide, 2H), 7.76−7.78 (m, Ar−H of phthalimide, 2H), 7.72 (d, J = 7.5 Hz, N−Ar−H, 2H), 7.46 (d, J = 7.5 Hz, Si−Ar−H, 2H), 7.36 (d, J = 8.7 Hz, Si−Ar−H, 2H), 7.09 (d, J = 8.7 Hz, N−Ar−H, 2H), 5.12 (s, Ar−CH$_2$−O, 2H), 1.72−1.75 (m, Cy−CH$_2$, 35H), 1.22−1.25 (m, Cy−CH$_2$, 35H), 0.77−0.80 (m, Cy−CH, 7H). ^{13}C NMR (CDCl$_3$, δ ppm): 167.5, 158.5, 138.6, 134.4, 134.2, 131.9, 131.8, 127.9, 127.3, 126.5, 124.6, 123.7, 115.4, 70.2, 27.4, 26.8, 26.6, 26,5, 23.1, 23.0. ^{29}Si NMR (THF, δ ppm): −67.9, −68.2, −79.5. GPC data: M_w 1057.5, M_n 938.8, polydispersity 1.10.

POSS/Polyimide Nanocomposite. Poly(amic acid) (PAA) was synthesized by first putting 14.70 mmol of ODA into a three-necked flask containing 32.92 g of DMAc under nitrogen purge at 25 °C. Then, after the ODA dissolved completely, 15.00 mmol of PMDA, divided into three batches, was added to the flask batch-by-batch with a time interval of 0.5 h between batches. When the PMDA was completely dissolved in DMAc, the solutions were stirred for 1 h, and a viscous PAA solution was obtained. NH$_2$−POSS (0.60 mmol) in DMAc/THF (16.81/1.00 g) was added to the mixture and mixed for 12 h using a mechanical stirrer. The final content of PAA in DMAc was 11 wt %. The POSS/PAA mixture was cast on glass slides using a doctor blade, and subsequently put in a vacuum oven at 30 °C for 48 h before the imidization step. Imidization of POSS/PAA was carried out by putting the samples in an air-circulation oven at 100, 150, 200, and 250 °C for 1 h, and then at 300 °C for 0.5 h. The heat treatment at 300 °C for 0.5 h is to ensure complete imidization.

Characterization. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity-300 NMR spectrometer. ^{29}Si NMR spectra were obtained from a DMX-600 NMR spectrometer. The molecular weights of POSS compounds and POSS/PAA were measured with gel permeation chromatography (GPC) by using THF and DMF as solvents, respectively. Polystyrene standards were used for calibration of the GPC. Element analyses of the nanocomposites were carried out with Heraeus CHN−OS

Table 1. Intrinsic Viscosities, Molecular Weights, Element Analysis, and Dielectric Constants of PMDA−ODA and PMDA−ODA/POSS

	intrinsic viscosity (dL/g)	$M_w{}^a$	$M_n{}^a$	weight percentage by element analysis			dielectric constant (measured at 1 Hz)
				C (%)	H (%)	N (%)	
PMDA−ODA	1.29	101 899	40 759	65.79	4.40	7.67	3.40 ± 0.02
PMDA−ODA containing 2.5 mol % POSS[b]	1.35	121 459	59 947	65.09	4.07	7.20	3.09 ± 0.03

[a] Obtained from GPC using DMF as solvent and calibrated with polystyrene standards. [b] The weight percentages of POSS were found by comparing the element analysis data of PMDA−ODA and PMDA/POSS.

Rapid instrument. An X-ray diffraction study of the sample was carried out using a MAC Science MXP18 X-ray diffractometer (30 kV, 20 mA) with a copper target (λ = 1.54 Å) at a scanning rate of 4°/min. Thermal gravimetric analyses of the polyimide films were carried out with a Du Pont TGA 2950 at a heating rate of 20 °C/min with a nitrogen purge. Measurements of glass transition temperatures and coefficients of thermal expansion (CTE) for the films were carried out using a Du Pont TMA 2940 (film probe) at a heating rate of 10 °C/min in a nitrogen atmosphere. Samples for the transmission electron microscopy (TEM) study were first prepared by putting PMDA−ODA/POSS films into epoxy capsules and curing the epoxy at 70 °C for 48 h in a vacuum oven. Then, the cured epoxy samples were microtomed with a Leica Ultracut Uct into about 90-nm-thick slices. Subsequently, a layer of carbon about 3 nm thick was deposited onto these slices and they were placed on 200-mesh copper nets for TEM observation. The TEM instrument used was a JEOL-2000 FX, with an acceleration voltage of 200 kV. The dielectric constant measurements for PMDA−ODA and POSS/PMDA−ODA were carried out in a sandwich structure (aluminum (Al)/polyimide/platinum (Pt) on Si wafer. The top Al electrode, with a diameter of 1.5 mm, was deposited by thermal evaporation in a vacuum at 4×10^{-6} Pa on polyimide films, which was spun and imidized on a Si wafer plated with platinum. Then, these films were dried at 130 °C under vacuum for 2 days. The thicknesses of PMDA−ODA and POSS/PMDA−ODA films are 1.90 and 2.30 μm, respectively. The capacitance of the samples was determined with a HP4280A at a frequency of 1 MHz. The dielectric constant of the samples can be calculated from their capacitances. The tensile properties of polyimide films were measured according to ASTM D882-88 at a crosshead speed of 2 mm/min.

Results and Discussion

Table 1 gives the intrinsic viscosities and molecular weights of poly(amic acid)(PAA) and POSS/PAA. The intrinsic viscosities of PAA and PAA/POSS in DMAc at 30 °C are 1.29 and 1.35 dl/g, respectively. Separately, the molecular weights of PAA and PAA/POSS are determined to be 102 000 and 121 000 g/mol, respectively, as measured by GPC with polystyrene standards. The polyimide tethered POSS was resulted from the reaction of NH$_2$−POSS with the anhydride end groups of poly(amic acid). If all the NH$_2$−POSS reacted, the maximum POSS tethered to polyimide would be 4 mol %. The actual amount of POSS tethered to polyimide was 2.5 mol % as determined from the element analysis result in Table 1. The volume ratio of POSS to polyimide is about 10% as calculated from the approximate densities of POSS and polyimide (1.1 and 1.4 g/cm³).

Figure 1 shows the X-ray diffraction curves for POSS, polyimide, and their derivatives. Sharp diffraction peaks appear at 2θ = 7.5° (1.18 nm) and 1 ° (0.49 nm) for NH$_2$−POSS, indicative of a structure with high crystallinity. On the other hand, much smaller peaks for phthalimide−POSS were observed, implying the phthalimide group sterically hinders the crystallization of
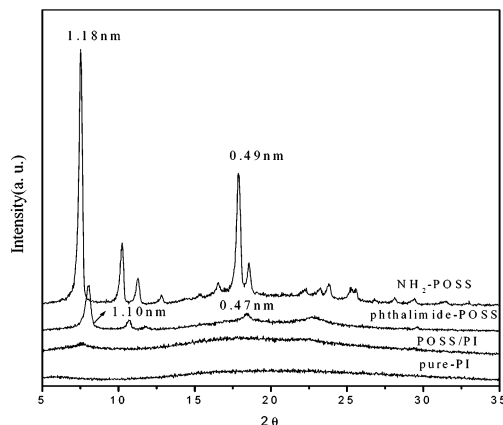
Figure 1. X-ray diffraction profiles of (a) NH$_2$−POSS, (b) phthalimide−POSS, (c) PMDA−ODA/POSS, and (d) PMDA−ODA.
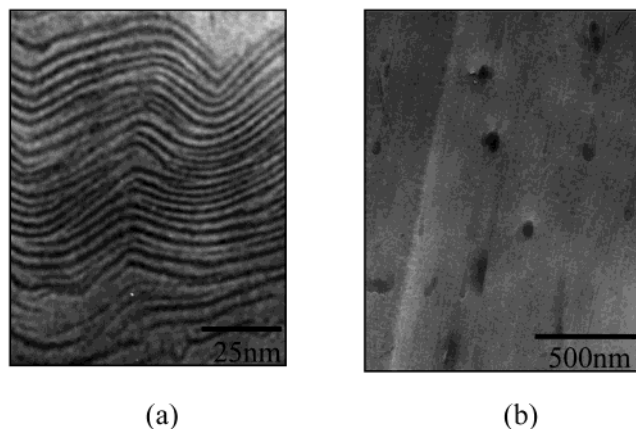
Figure 2. TEM morphology of a cross section of a POSS/polyimide nanocomposite film in the direction (a) normal to the film plane and to the casting direction, and (b) normal to the film plane but parallel to the casting direction.

POSS. A small but broad peak at 2θ = 8° is also observed in the diffraction curve of POSS/polyimide, indicating that the POSS molecules still retain their dimensions of approximately 1 nm in polyimide.

Figure 2(a) and (b) represent normal and parallel cross-section views, respectively, with respect to the casting direction of the POSS/polyimide nanocomposite films, by transmission electron microscopy. In Figure 2(a), the POSS molecules are apparently seen to self-assemble into zigzag dark rods or lamellae parallel to each other but normal to the casting direction in the polyimide matrix. This indicates that the orientations of the polyimide molecular chains are most likely parallel to the casting direction due to the shear, as the average length of a polyimide molecule chain is more than 50 nm. In the parallel cross-section view, dark and sphere-shaped POSS aggregated domains about

Table 2. Thermal and Tensile Mechanical Properties of PMDA−ODA and PMDA−ODA/POSS

	T_d^a (°C)	T_g^b (°C)	CTE (ppm/°C) $_{50-250\ °C}$	Young's modulus (GPa)	max. stress (MPa)	max. elongation (%)
PMDA−ODA	574	362.0	67.2	1.60 ± 0.06	44.1 ± 3.1	6 ± 2
PMDA−ODA containing 2.5 mol % POSS	536	360.2	67.1	1.71 ± 0.05	47.2 ± 4.2	3 ± 1

^{a} T_d, degradation temperature at 5 wt % loss. ^{b} T_g values were found from CTE curves.
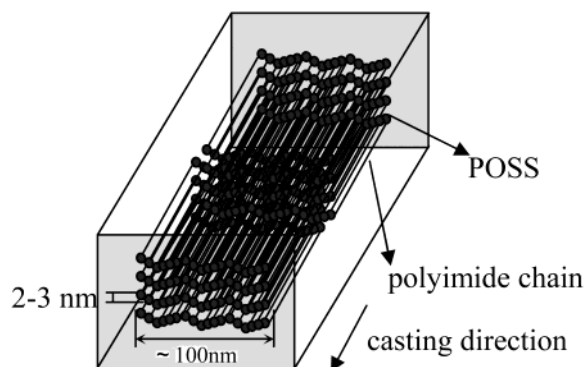

Figure 3. Illustration of self-assembly in polyimide covalently bonded polyhedral oligomeric silsesquioxane nanocomposites.

60−70 nm in size appear, as shown in Figure 2(b) (about 20 rods). The size of the domains is almost equivalent to the total thickness of the dark rods in one domain in Figure 2(a). Hence, the morphology of the self-assembled POSS in a polyimide matrix is possibly zigzag-shaped cylinders or lamellas with particular orientations. A schematic of the formation of a polyimide-tethered POSS cylinder is presented in Figure 3.

The measured dielectric constants of PMDA−ODA and PMDA−ODA/POSS are also shown in Table 1. The measured dielectric constant of PMDA−ODA/POSS is smaller than that of pure PMDA−ODA (3.09 vs 3.40). The reduction in the dielectric constant of the POSS/polyimide nanocomposite may be caused by the nanoporous POSS in the polyimide or the change in free volume of polyimide. These nanostructured and phase-separated POSS/polyimide composites have advantages over nanoporous polyimides synthesized by block co-

polymer approaches. Degradation in mechanical properties is less likely to occur than ,in nanoporous polyimides made by block copolymer approaches. This is provided by the tensile mechanical properties of PMDA−ODA/POSS and PMDA−ODA in Table 2. The Young's modulus and maximum stress of PMDA−ODA/POSS are slightly higher than those of the pure PMDA−ODA. The maximum elongation of the polyimide, however, is lower than that of pure polyimide, probably owing to the aggregated domain of POSS molecules.

Table 2 also presents the thermal properties of PMDA−ODA/POSS and PMDA−ODA. The 5 wt % loss temperature of PMDA−ODA/POSS is lower than that of pure PMDA−ODA, caused by the degradation of POSS molecules. The glass transition temperature (T_g) of PMDA−ODA/POSS is the same as that of pure PMDA−ODA, and the CTE values of PMDA−ODA/POSS are about the same as that of pure PMDA−ODA.

Conclusion

Polyimide chain-end tethered POSS can self-assemble into zigzag shaped cylinders or lamellae, 60−70 nm long and 5 nm wide. The resultant dielectric constant of the polyimide nanocomposite was reduced from 3.40 for the pure polyimide to 3.09 by incorporating only 2.5 mol % of POSS molecules. The tensile properties were retained with a reduction in thermal degradation temperatures.

CM0208408