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Organic-inorganic Polyimides with Double Decker Silsesquioxane in the Main Chains

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ABSTRACT

In this contribution, we reported a facile synthesis of a well-defined POSS diamine *via* Heck reaction. First, 3,13-divinyloctaphenyl double decker silsesquioxane (3,13-divinyl DDSQ) was synthesized *via* the silylation reaction of octaphenyldicycloocatasiloxane tetrasodium silanolate with methylvinyldichlorosilane. Thereafter, the 3,13-divinyl DDSQ was reacted with 4-bromoaniline with palladium catalyst. This POSS diamine (*viz.* 3,13-dianilino DDSQ) has been employed to synthesize the organic-inorganic polyimides with DDSQ in the main chains. C Compared to plain polyimide, the organic-inorganic hybrids displayed the improved thermal stability and surface hydrophobicity. The dielectric analysis indicates the dielectric constants of the organic-inorganic polyimides were significantly decreased with the inclusion of the DDSQ in the main chains whereas the dielectric loss of the polyimides remained almost unchanged.

(Keywords: POSS; polyimides; organic-inorganic hybrids; dielectric properties)

INTRODUCTION

Polyhedral oligomeric silsesquioxanes (POSS) are a family of nanosized, cage-like molecules, each of which consists of an inorganic Si-O framework and organic ligands bonded to the corner silicon atoms. Owing to low density, high thermal stability and well-defined functionalities, POSS have been used as the nanobuilding blocks to prepare organic-inorganic nanocomposites [1-7]. The POSS-containing polymer nanocomposites can display excellent comprehensive properties through the synergistic interactions between the inorganic POSS microdomains and the organic matrix [8-11]. Generally, POSS can be incorporated into organic polymers *via* physical or chemical approaches [3-6]. Chemical approach is efficient to suppress the occurrence of macroscopic phase separation in the composite systems *via* the formation of chemical links between POSS cages and polymer matrices. In the past years, there has been ample literature on the preparation of the POSS-polymer hybrids by using mono- or octafunctional POSS macromers [12-23]. In these composite systems, POSS macromers act as pendent [12,13,15] (or/and terminal) groups or crosslinking sites [14,16-23] whereas the main chains of polymers remain unchanged. If POSS cages can be introduced into the main chains of polymers to form the so-called “bead-like” chain structures, the organic-inorganic hybrids could display new properties since the motions of the main chains of polymers were affected by the bulky POSS cages. Recently, there have been a few reports on the synthesis of this class of organic-inorganic hybrids [24-26]. In general, the organic-inorganic hybrids with POSS in the main chains of polymers can be synthesized *via* step-growth polymerization by the use of well-defined difunctional POSS macromers. However, such an investigation remains largely unexplored. The main reason is that the efficient preparation of well-defined difunctional POSS macromers is still a challenging task.

Polyimides are a class of high performance materials. Their excellent mechanical strength and good resistance to high temperature endow polyimides with the wide-spread application in microelectronics, aerospace industry and other fields [27-31]. Recently, considerable interest has been attracted to improve the properties of polyimides by the use of POSS [31-40]. Most of these previous works deal with the preparation of the POSS-containing polyimides with mono- or octafunctional POSS macromers. Under the circumstances, POSS cages were grafted onto the main chains or acted as the crosslinking site of polyimide chains. In the preparation of POSS-containing polyimides, the POSS macromers bearing amino groups can be directly used to react with dianhydrides to afford the poly(amic acid)s [41-44]. If the POSS macromer is a well-defined diamine, a new organic-inorganic poly(amic acid) can be obtained and its imidization would afford the organic-inorganic polyimides with POSS in the main chains.

In 2003, Wright and Feher *et al.* [45] first reported the synthesis of a POSS framework bearing two aniline groups. This well-defined POSS diamine was then used as one of copolymerization monomers for polyimide. It was found that the glass transition temperatures (T_g's) and the curing kinetics of phenyl-ethynyl-terminated imide resins (PETI) remained unaffected with the inclusion of POSS units in the main chains of polyimides. Recently, Kakimoto *et al*. [46] reported that synthesis and characterization of semiaromatic polyimides containing POSS in the main chain by using a double-decker silsesquioxane (DDSQ). It is worth noting that the POSS-polyimides possessed good thermal stability and mechanical properties, low water absorption, alkali resistance as well as low dielectric constant. More recently, Kakimoto *et al.* [47] synthesized organosoluble aromatic polyimides with POSS in the main chain by the use of a DDSQ-diamine. The polyimides were synthesized from DDSQ-type aromatic tetracarboxylic dianhydride (DDSQDA) and several aromatic diamines *via* one-step high temperature solution method. The inclusion of DDSQ unit endowed the polyimides with some improved thermomechanical properties and with decreased dielectric constant. In the preparation of this article, we noted that a report on the synthesis of a novel DDSQ diamine and the organic-inorganic polyimides with DDSQ in the main chains by Wu *et al* [48]. A multi-step reaction methodology was used. It was found that the DDSQ in the main chains of the sulfonated polyimides facilitated the dispersion of the POSS cages and thus enhanced the proton conductivity *via* the formation of continuous proton transformation channels.

In this work, we reported a facile synthesis of a well-defined POSS diamine *via* the Heck reaction. First, 3,13-divinyloctaphenyl double decker silsesquioxane (3,13-divinyl DDSQ) was synthesized *via* the silylation reaction of octaphenyldicycloocatasiloxane tetrasodium silanolate with methylvinyldichlorosilane. Thereafter, the 3,13-divinyl DDSQ was allowed to react with 4-bromoaniline with palladium catalyst. This POSS diamine was further employed to synthesize the organic-inorganic polyimides with DDSQ in the main chains. The formation of POSS microdomains in the organic-inorganic polyimides was investigated by means of transmission electron microscopy (TEM); the thermomechanical properties of the organic-inorganic polyimides were examined by means of thermogravimetric analysis (TGA) and surface contact angle measurements. The dielectric properties of the organic-inorganic polyimides were measured by means of a broad-band dielectric spectroscopy (BDS).

EXPERIMENTAL

Materials

Phenyltrimethoxysilane (98%) was purchased from Zhejiang Chemical Technology Co., Ltd, China; methylvinyldichlorosilane was obtained from Alfa Aesar Co., Ltd, China; both of the organosilanes were used as received. Sodium hydroxide, triphenylphosphine and 4,4'-diaminodiphenyl ether (ODA) were supplied by Shanghai Reagent Co., Ltd, China. 3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA) and 4-bromoanilines were obtained from Adamas Reagent Co., China. Palladium (II) acetate was purchased from J & K Scientific Co., China. Organic solvents such as toluene, tetrahydrofuran (THF), triethylamine, methanol, isopropanol and N,N'-dimethylacetamide (DMAc) were of chemically pure grade, obtained from Shanghai Regent Co., China. Before use, toluene and THF were refluxed above sodium and then distilled; triethylamine was refluxed over CaH_2 and distilled; DMAc was distilled over calcium hydride (CaH_2) under decreased pressure and then stored in the presence of 4Å molecular sieve.

Synthesis of 3,13-Divinyl DDSQ

First, occtaphenyldicycloocatasiloxane tetrasodium silanolate [denoted $Na_4O_{14}Si_8(C_6H_5)_8$] was synthesized by following the method of literature reported by Kakimoto *et al.* [49] with slight modification. Typically, to a flask equipped with a condenser and a magnetic stirrer, phenyltrimethoxysiloxane (71.380 g, 0.36 mol), isopropanol (360 mL), deionized water (7.450 g, 0.414 mol) and sodium hydroxide (9.500 g, 0.238 mol) were charged. The system was refluxed for 4 hours and then was cooled down to room temperature, at which the system was maintained with vigorous stirring for additional 15 hours. All the solvents and other volatile compounds were removed *via* rotary evaporation and the white solids were obtained. After drying *in vacuo* at 60 ^{o}C for 12 hours, $Na_4O_{14}Si_8(C_6H_5)_8$ (50.65 g) was obtained with the yield of 97%.

Second, the silylation reaction between $Na_4O_{14}Si_8(C_6H_5)_8$ and methylvinyl dichlorosilane was carried out. Typically, to a flask equipped with a magnetic stirrer, $Na_4O_{14}Si_8(C_6H_5)_8$ (57.20 g, 49.4 mmol), triethylamine (21 mL) and anhydrous THF (300 mL) were charged with vigorous stirring. The flask was immersed into an ice-water bath and then purged with highly pure argon for one hour. Thereafter, methylvinyldichlorosilane (20.86 g, 147.9 mmol) dissolved in 30 mL of anhydrous THF was dropwise added within 30 min. The reaction was performed at 0 ^{o}C for 2 hours and at room temperature for 20 hours. The insoluble solids (*i.e.*, sodium chloride and unreacted tetrasodium silanolate) were removed by filtration and the solvents together with other volatile compounds were eliminated *via* rotary evaporation to afford the white solids. The solids were washed with methanol three times and dried *in vacuo* at 40 ^{o}C for 24 hours; the product (23.90 g) was obtained with the yield of 42%. ^{1}H NMR (ppm, CDCl3): 0.38 (*d*, 6.0H, C$\boldsymbol{H_3}$-Si), 5.89 ~ 6.22 (*d*, 6.0H, Si-C$\boldsymbol{H}$=C$\boldsymbol{H_2}$), 7.14 ~ 7.60 (*m*, 40H, protons of aromatic rings); ^{29}Si NMR (ppm, CDCl3): -31.33, -78.27 and -79.47. MALDI-TOF-MS (product + Na^{+}): 1227.1 Da (calculated: 1227.1 Da).

Synthesis of 3,13-Dianilino DDSQ

3,13-Dianilino DDSQ was synthesized *via* the Heck reaction of 3,13-divinyl DDSQ with 4-bromoaniline. To a flask, 3,13-divinyl DDSQ (12.05 g, 10 mmol), 4-bromoaniline (17.20 g, 100 mmol), palladium (II) acetate (250 mg, 1.11 mmol), triphenylphosphine (550 mg, 2.10 mmol) dissolved in 100 mL of anhydrous toluene and triethylamine (20 mL) were charged with vigorous stirring; this flask was purged with highly pure argon for 30 minutes. The reaction was performed at 100 ^{o}C for 48 hours. The insoluble solids [*i.e.*, the complex of triphenylphosphine and palladium (II) acetate] were removed by filtration and the reacted mixture was concentrated *via* rotary evaporation and then dropped into 300 mL of methanol to afford the precipitates. After drying *in vacuo* at 30 °C for 24 hours, the product (12.65 g) was obtained with the yield of 91%. ^{1}H NMR (ppm, $CDCl_3$): 0.35 (*d*, 6.0H, C***H*₃**-Si), 3.69 (*s*, 4.0H, -N***H*₂**), 6.53 ~ 6.64 (*m*, 2.0H, Si-C***H***=CH-), 7.16 ~ 7.28 (*m*, 2.0H, Si-CH=C***H***-), 7.28 ~ 7.30 (*m*, 4.0H, protons of aminophenyl groups), 7.30 ~ 7.68 (*m*, 40H, protons of DDSQ phenyl groups), 7.72 ~ 7.85 (*m*, 4.0H, protons of aminophenyl groups); ^{29}Si NMR (ppm, $CDCl_3$): -17.30, -78.03 and -79.27. MALDI-TOF-MS (product + Na^+): 1409.2 Da (calculated: 1409.2 Da).

Synthesis of Organic-inorganic Polyimide with DDSQ in the Main Chains

Typically, 3,13-dianilino DDSQ (0.200 g, 0.144 mmol), 4,4'-diaminodiphenyl ether (ODA) (0.800 g, 3.99 mmol) and anhydrous DMAc (10 mL) were added to a flask with vigorous stirring and then 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) (1.340 g, 4.16 mmol) dissolved in 10 mL of anhydrous DMAc was added with vigorous stirring. The flask was purged with highly pure argon for additional 15 minutes and the reaction was carried out at room temperature for 20 hours to obtain the poly(amic acid). The solution of the poly(amic acid) was cast onto a glass plate and then the solvent was evaporated at 120 °C for 24 hours to obtain the poly(amic acid) film. In a tube furnace, the film was heated up to 200 °C in a nitrogen atmosphere and at the heating rate of 1 °C/min and held at this temperature for 2 hours and thereafter, the temperature was raised to 300 °C within 2 hours. At 300 °C, the imidization reaction was performed for 2 hours and then cooled to room temperature; the organic-inorganic polyimide film was obtained. The complete imidization was evidenced by the observation that the bands at 1806 and 1860 cm^{-1} assignable to the stretching vibration of carboxyl groups of poly(amic acid)s disappeared by means of Fourier transform infrared (FTIR) spectroscopy. In this work, the molar ratios of ODA to 3,13-dianilino DDSQ was systematically changed and the equimolar BTDA (with respect of the total amino groups from ODA and 3,13-dianilino DDSQ) was used to obtain the organic-inorganic polyimides with DDSQ and the compositions of the organic-inorganic hybrids are shown in Table 1.

Measurements and Techniques

Nuclear Magnetic Resonance (NMR) Spectroscopy

The ^{1}H NMR measurements were carried out on a Varian Mercury Plus 400 MHz NMR spectrometer at 25 ^{o}C and the ^{29}Si NMR spectra were obtained on a Bruker Avance III 400 MHz NMR spectrometer. All the samples were dissolved with deuterium chloroform ($CDCl_3$) and the spectra were recorded with tetramethylsilane (TMS) as a reference.

Matrix-Assisted Ultraviolet Laser Desorption/Ionization Time-of-Flight Mass (MALDI-TOF-MS) Spectroscopy

The MALDI-TOF-MS experiments were carried out on an IonSpec HiResMALDI mass spectrometer equipped with a pulsed nitrogen laser (λ=337 nm; pulse with = 3 ns). This instrument operated at an accelerating potential of 20 kV in reflector mode. Sodium is used as the cationizing agent and all the data shown are for positive ions. In the measurements, gentisic acid (2,5-dihydroxybenzoic acid, DHB) was used as the matrix and dichloromethane was used as the solvent.

Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR measurements were conducted on a Perkin-Elmer Paragon 1000 spectrometer at room temperature. The samples were ground and the powder was mixed with KBr pellets to press into the small flakes for measurements. All the specimens were sufficiently thin to be within a range where the Beer-Lambert law is obeyed. In all cases 32 scans at a resolution of 2 cm^{-1} were used to record the spectra.

Thermal Gravimetric Analysis (TGA)

A TA Instruments Q5000 thermal gravimetric analyzer was used to investigate the thermal stability of the polymers. The measurements were conducted in nitrogen atmosphere from ambient temperature to 800 ^{o}C at the heating rate of 20 ^{o}C min^{-1}. The temperature of initial degradation (T_d) was taken as the onset temperature of initial degradation (T_d) at which 5 wt% of weight loss occurs.

Surface Contact Angle Analysis

The films of the polyimide samples were subjected to the measurements of static contact angles. The static contact angle measurements were carried out at room temperature on a DSA30 contact angle measurement apparatus (Krüss GmbH, Germany) with ultrapure water and ethylene glycol as the probe liquids, respectively.

Dielectric Analysis

The dielectric analysis was carried out on a GmbH Concept 40 dielectric analyzer. All the measurements were carried out in the frequency range 10^3 to 10^6 Hz at room temperature, applying 1.0 AC voltage across two opposite sides of a film specimen and a layer of gold sputtered on each of two surfaces of a film served as electrode.

Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) was performed on a JEOL JEM-2010 high-resolution transmission electron microscope at an acceleration voltage of 120 kV. The polyimide samples were first embedded into epoxy thermosets and the thermosets were then sliced with a microtome machine equipped with a diamond blade. The sections containing the polyimide (*c.a.,* 70 nm in thickness) were placed in 200 mesh copper grids for the morphological observations.

RESULTS AND DISCUSSION

Synthesis of 3,13-Dianilino DDSQ

The route of synthesis for 3,13-dianilinooctphenyl double decker silsesquioxane (denoted 3,13-dianilino DDSQ) was shown in Scheme 1. First, octaphenyldicycloocatasiloxane tetrasodium silanolate [denoted $Na_4O_{14}Si_8(C_6H_5)_8$] was synthesized by following the method of the literature reported by Kakimoto *et al.* [49] and then the silylation reaction of $Na_4O_{14}Si_8(C_6H_5)_8$ with methylvinyldichlorosilane [$Si(CH_3)(CH{=}CH_2)Cl_2$] was performed to obtain 3,13-divinyl DDSQ. Second, the Heck reaction between 3,13-divinyl DDSQ and 4-bromoaniline was carried out to afford 3,13-dianilino DDSQ.

The ^{1}H NMR spectra of 3,13-divinyl DDSQ and 3,13-dianilino DDSQ are shown in Figure 1. For the 3,13-divinyl DDSQ, the signals of resonance assignable to protons of phenyl, vinyl and methyl groups were detected at 7.14 ~ 7.60, 5.89 ~ 6.22 and 0.38 ppm, respectively. The ratio of integral intensity for these signals of resonance was measured to be 20 : 3 : 3, which was exactly identical with the value calculated according to the structural formula of 3,13-divinyl DDSQ. For 3,13-dianilino DDSQ, the signals of resonance assignable to the protons of vinyl groups at 5.89 ~ 6.22 ppm completely disappeared, indicating that the Heck reaction was performed to completion. Concurrently, there appeared several new peaks at 3.69, 6.59, 7.29 and 7.75 ppm, respectively. The broad peak of resonance at 3.69 ppm is attributable to the protons of amino groups. The signals of proton resonance at 6.59 and 7.29 ppm are characteristic of the double bonds between DDSQ and aniline groups. The multiple peaks in the range of 7.0 ~ 7.8 ppm resulted from the resonance of phenyl protons of DDSQ cages. Shown in Figure 2 are the ^{29}Si NMR spectra of 3,13-divinyl and 3,13-dianilino DDSQ. For 3,13-divinyl DDSQ, three peaks were clearly displayed at -31.33, -78.27, and -79.47 ppm, respectively. The peak at -31.33 ppm is assignable to the silicon nucleus connected to both hydro and methyl group whereas those at -78.27 and -79.47 ppm to the silicon nuclei in the DDSQ cage. For 3,13-dianilino DDSQ, three peaks were also exhibited. Nonetheless, the positions of the resonance were changed with the occurrence of the Heck reaction. Notably, the resonance at -31.33 ppm, assignable to the vortex silicon atoms in 3,13-divinyl DDSQ shifted to the high field at -17.1 ppm whereas the resonance of backbone silicon nuclei of DDSQ slightly shifted to -78.03, and -79.27 ppm, respectively. Both 3,13-divinyl and 3,13-dianilino DDSQ were subjected to MALDI-TOF mass spectroscopy and their mass spectra were presented in Figures 3 and 4, respectively. For 3,13-divinyl DDSQ, the molecular weight was measured to be M = 1204.1 (*viz*. 1227.1-23) whereas that of 3,13-dianilino DDSQ to be M = 1386.2 (*viz*. 1409.2-23). It should be pointed out that there were two minor peaks at 150 m/z and 1265 m/z, respectively. They could be attributed to the oligomeric silsesquioxanes with the number of silicon atoms smaller and higher than ten. Both of the molecular weights were exactly identical with those calculated according to their structural formulas. The results of ^{1}H and ^{29}Si NMR and MALDI-TOF mass spectroscopy indicate that POSS diamine (*viz.*, 3,13-dianilino DDSQ) was successfully obtained.

Synthesis of Organic-Inorganic Polyimides

The mixture of 3,13-dianilino DDSQ and 4,4'-diaminodiphenyl ether (ODA) was allowed to react with the equimolar 3,3',4,4'-benzophenonetetracarboxylic anhydride (BTDA) (with respect of amino groups from 1,13-dianilino DDSQ and ODA) to obtain the poly(amic acid)s. The poly(amic acid)s were used as the precursor to obtain an organic-inorganic polyimide *via* the imidization reaction at elevated temperature. In all the polymerizations, the molar ratios of amino groups from 3,13-dianilino DDSQ and ODA to anhydride groups from BTDA were controlled to be 1:1. By changing the mass ratios of 3,13-dianilino DDSQ to ODA, a series of organic-inorganic polyimides were obtained with the content of 3,13-dianilino DDSQ up to 19.4 wt% as summarized in Table 1.

The organic-inorganic polyimides with DDSQ in the main chains were subjected to Fourier transform infrared (FTIR) spectroscopy and the FTIR spectra were shown in Figure 5. In all the samples, the bands at 1720 and 1780 cm^{-1} were exhibited, which are characteristic of the stretching vibration of imide groups. The fact that no bands at 1806 and 1860 cm^{-1}, which are assignable to the stretching vibration of carboxyl groups in poly(amic acid)s, were displayed indicates that the imidization reactions have been undergone to completion. For the organic-inorganic polyimides, there appeared the new bands at 1122 cm^{-1}, the intensity of which increased with the content of 3,13-dianilino DDSQ. The new bands are assignable to the stretching vibration of Si-O-Si linkages of DDSQ. The FTIR spectroscopy indicates that: i) the imidization reactions have been performed to completion and ii) the resulting products combined the structural features from polyimide and 3,13-dianilino DDSQ. Therefore, the organic-inorganic polyimides were successfully obtained. In the range of the compositions investigated, the flexible organic-inorganic polyimide films were transparent, indicating that no macroscopic phase separation occurred (See Figure 6). Nonetheless, the clarity does not exclude the possibility that the organic-inorganic hybrids were microphase-separated at the nanometer scale.

Therefore, the organic-inorganic polyimides were subjected to the morphological observation by means of transmission electronic microscopy (TEM). The TEM images were shown in Figure 7. It is seen that the organic-inorganic polyimides displayed the microphase-separated morphologies, in which the microdomains with the size of 5 ~ 20 nm were dispersed in the continuous matrix. In terms of electron density contrast, it is judged that the dark microdomains are attributable to the aggregates of DDSQ whereas the continuous matrices to polyimides. Notably, the size of the POSS microdomains decreased with increasing the content of 3,13-dianilino DDSQ. For PI-DDSQ4, the spherical microdomains had the size of 20 nm in diameter. With the increment of the content of 3,13-dianilino DDSQ, the quantity of the microdomains increased but their sizes decreased. While the content of 3,13-dianilino DDSQ was 19.4 wt%, the microdomains were observed to have the size of about 5 nm in diameter.

Properties of Organic-Inorganic Polyimides

Shown in Figure 8 are the TGA curves of the organic-inorganic polyimides. It is seen that all the organic-inorganic polyimides displayed the TGA profiles similar to the plain polyimide, suggesting that the incorporation of DDSQ into the main chains did not significantly alter the degradation mechanism. The organic-inorganic polyimides exhibited the temperatures of initial degradation (T_d) at 550 ^{o}C or higher. It is noted that the T_d's of the organic-inorganic polyimides are significantly higher than plain polyimide, irrespective of the content of 3,13-dianilino DDSQ. In addition, the yields of the degradation residues were significantly higher than the plain polyimide, increasing with the content of 3,13-dianilino DDSQ. The TGA results showed that the thermal stability of the polyimide was significantly enhanced with inclusion of DDSQ in the main chains. It is proposed that DDSQ cages in place of ODA in the main chains of polyimides could significantly retard the chain scission, which resulted in the enhanced T_d's. On the other hand, the nanoscaled dispersion of DDSQ in the form of the microdomains was important to suppress the release of gaseous products from segmental decomposition. In addition, the increased residue yields of degradation are responsible for the formation of the silica from the thermal oxidation of silsesquioxane in the process of degradation and decomposition.

Compared to the plain polyimide, the organic-inorganic polyimides displayed enhanced surface hydrophobicity owing to the inclusion of the organosilicon component (*viz.* DDSQ) in the main chains. Figure 9 shows the plot of the water contact angle as a function of the content of 3,13-dianilino DDSQ. For the plain polyimide, the water contact angle was measured to be 87^o, suggesting that this polymer was quite hydrophilic. Upon introducing DDSQ into the main chains, the water contact angles were significantly enhanced; the water contact angles increased with the content of 3,13-dianilino DDSQ. The water contact angle was measured to be 107^o while the content of 3,13-dianilino DDSQ was 19.4 wt%. According to the values of contact angles with water and ethylene glycol as the probe liquids, the surface free energies of the polyimides were calculated with the geometric mean model [50-52]; it was found that the surface free energy was decreased from 28.8 to 18.3 ($mN \times m^{-1}$) while the content of the of 3,13-dianilino DDSQ increased from 0 to 19.4 % (See Table 2). The increased water contact angles (or decreased surface free energy) indicate that the surface hydrophobicity of polyimide was significantly enhanced with the formation of the DDSQ microdomains, which is important for the application of the polyimides as the electric encapsulation materials.

The organic-inorganic polyimides were subjected to the dielectric measurement. The plots of dielectric constant and loss as functions of the content of 3,13-dianilino DDSQ are shown Figure 10. For the plain polyimide, the constants were measured to be 6.1 and 5.9 at the frequencies of alternate electric field to be 10^2 and 10^6 Hz, respectively. With the inclusion of DDSQ in the main chains, the dielectric constants were significantly depressed and they decreased with the content of 3,13-dianilino DDSQ. While the content of 3,13-dianilino DDSQ was 19.4 %, the dielectric constants have been decreased to 4.2 and 4.1 at the frequencies of alternate electric field to be 10^2 and 10^6 Hz, respectively. The decreased dielectric constants could be accounted for the following two aspects: i) the inclusion of low dielectric constant component (*viz.*, DDSQ) and ii) the restriction of DDSQ microdomains on the motion of the dipoles in the materials. The low dielectric constant of the POSS component is responsible for the low polarity of silsesquioxane and ii) the hollow structure of POSS cages. In the organic-inorganic polyimides, DDSQ cages were self-assembled into the microdomains with the size of 5 ~ 20 nm and they behaved as the nanoreinforcement agent to restrict the motion of the dipoles in the materials.

Notably, the dielectric loss remained almost unchanged, irrespective of the content of 3,13-dianilino DDSQ. The overall dielectric loss of the organic-inorganic polyimides was still smaller than 0.01, being at the quite low level.

CONCLUSIONS

In summary, a well-defined difunctional POSS diamine (*viz.* 3,13-dianilino DDSQ) was synthesized *via* the Heck reaction of 4-bromoaniline with 3,13-divinyl DDSQ. The successful synthesis has been evidenced by ^{1}H, ^{29}Si NMR and MALDI-TOF-mass spectroscopy. This POSS diamine was employed to synthesize the organic-inorganic polyimides with DDSQ in the main chains. The results of TEM showed that the organic-inorganic polyimides were microphase-separated and the POSS cages were self-organized into the spherical microdomains with the size of 5 ~ 20 nm in diameter and were dispersed into the continuous polyimide matrix. The thermogravimetric analysis (TGA) and surface contact angle measurements showed that the organic-inorganic polyimides displayed the improved thermal stability and surface hydrophobicity. The dielectric analysis indicates the dielectric constants of the organic-inorganic polyimides were significantly depressed with the inclusion of the DDSQ in the main chains whereas the dielectric loss of the polyimides remained almost unchanged and at the quite low level.

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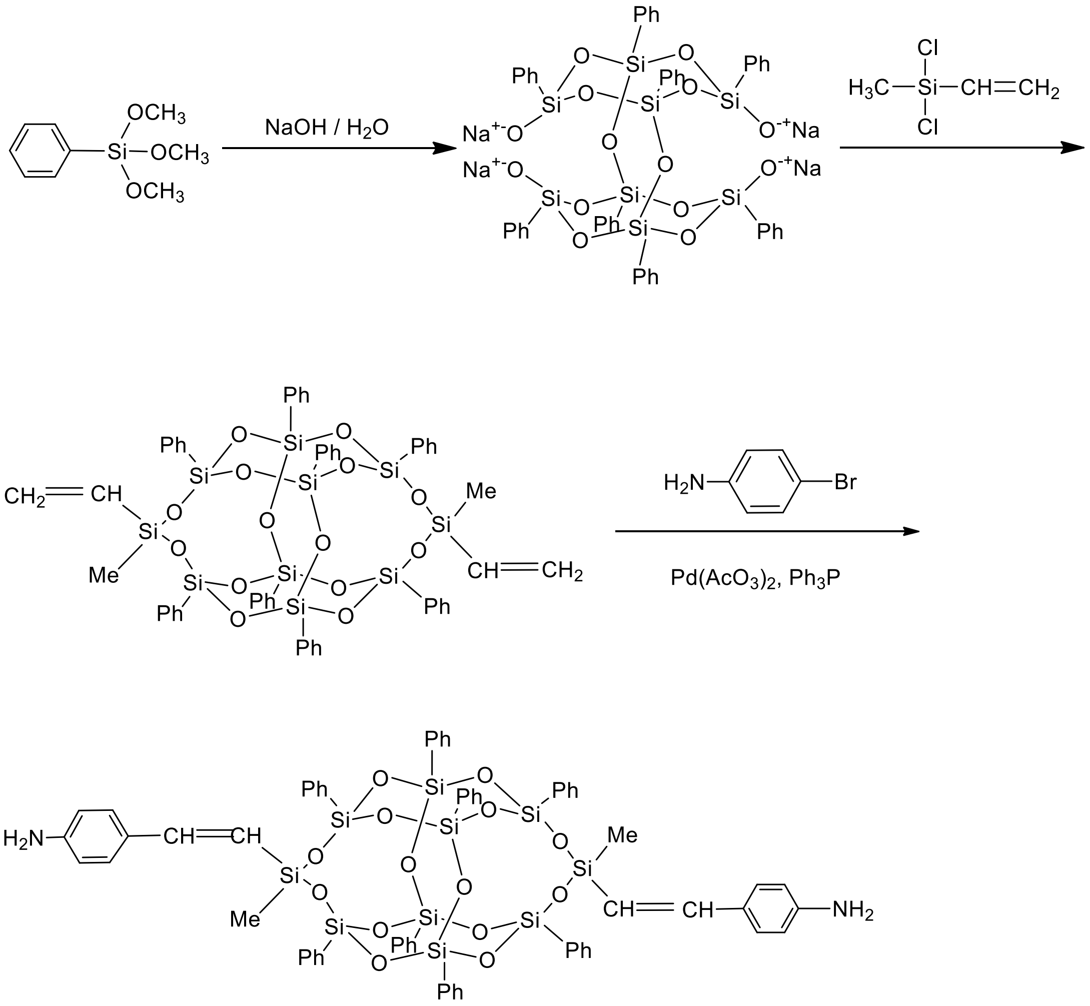
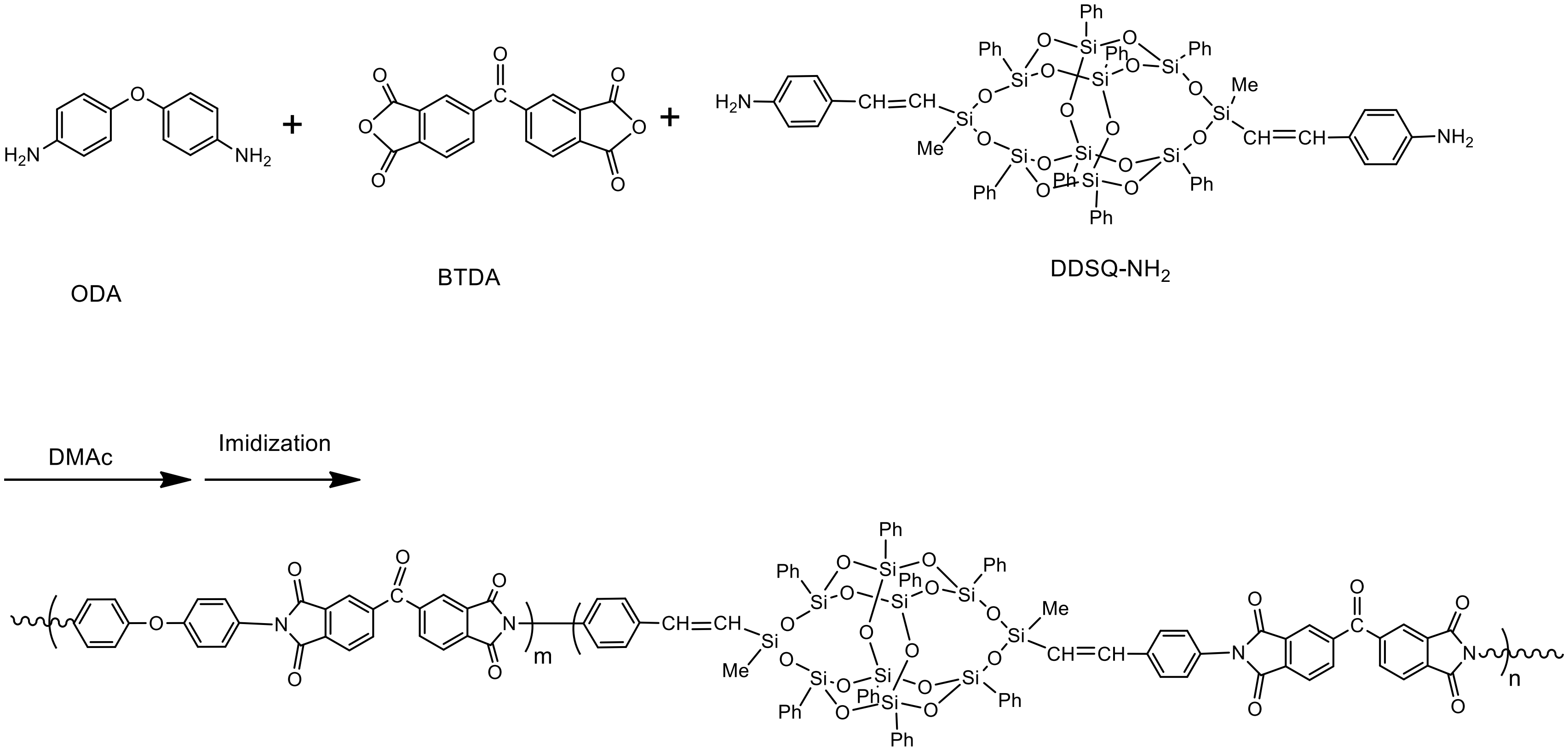
SCHEMES



Scheme 1 Synthesis of 3,13-dianilino DDSQ



Scheme 2 Synthesis of organic-inorganic polyimide with DDSQ in the main chain

Table 1 Composition and thermal stability of the organic-inorganic polyimides with DDSQ in the main chains

Samples	**DDSQ : ODA (wt)**	**DDSQ (wt %)**	**T_d (^oC)**	**Residue (wt%)**
PI	0 : 100	0	528.6	55.5
PI-DDSQ4	10 : 90	4.0	546.9	61.4
PI-DDSQ9	20 : 80	8.6	547.9	62.7
PI-DDSQ14	30 : 70	13.7	549.2	63.2
PI-DDSQ19	40 : 60	19.4	550.0	64.7

Table 2 Static contact angles and surface free energy of polyimide containing DDSQ

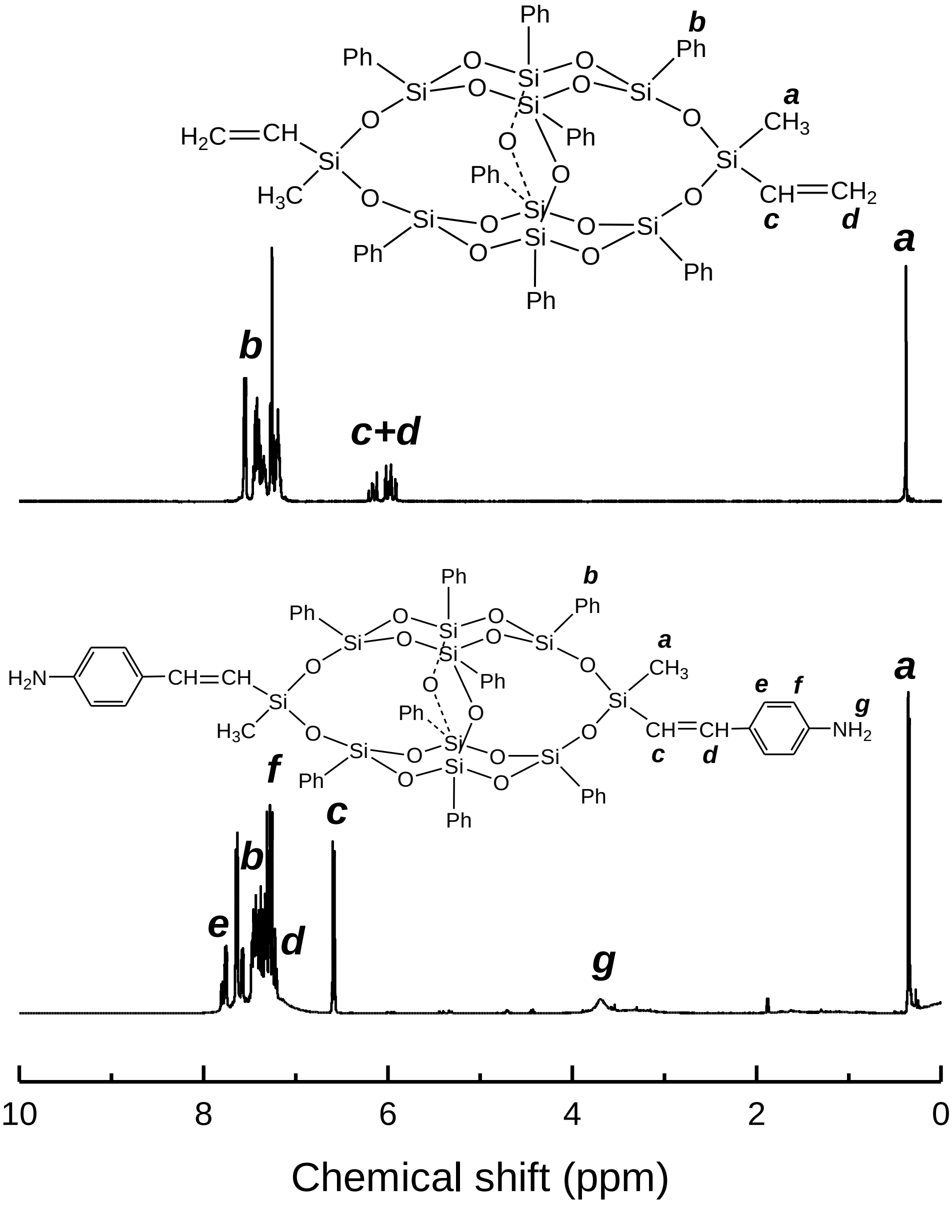
Samples	**Static contact angle (degree)**		**Surface free energy ($mN \times m^{-1}$)**		
	θ_{H2O} (deg)	$\theta_{\text{ethylene glycol}}$ (deg)	γ_s^d	γ_s^p	γ_s
PI	87.6 ±0.6	61.1 ±0.4	24.47	4.31	28.78
PI-DDSQ4	90.7 ±0.4	65.4 ±0.5	22.89	3.64	26.52
PI-DDSQ9	94.6 ±0.3	69.7 ±0.3	22.28	2.57	24.85
PI-DDSQ14	100.2 ±0.4	75.9 ±0.7	21.03	1.43	22.46
PI-DDSQ19	107.1 ±0.5	84.6 ±0.4	17.57	0.74	18.30

Water: γ_L = 72.8mN/m, γ_L^d = 21.8 mN/m, γ_L^p = 51.0 mN/m.

Ethylene glycol: γ_L = 48.3 mN/m, γ_L^d = 29.3 mN/m, γ_L^p = 19.0mN/m.

FIGURE CAPTIONS

Figure 1.	^{1}H NMR spectra of 3,13-divinyl DDSQ and 3,13-dianilino DDSQ.
Figure 2.	^{29}Si NMR spectra of 3,13-divinyl DDSQ and 3,13-dianilino DDSQ.
Figure 3.	MALDI-TOF mass spectrum of 3,13-divinyl DDSQ.
Figure 4.	MALDI-TOF mass spectrum of 3,13-dianilino DDSQ.
Figure 5.	FTIR spectra of plain polyimide and polyimide containing 4, 9, 14, and 19 wt % of 3,13-dianilino DDSQ.
Figure 6.	Photos of PI-DDSQ14. Up: transparency; down: flexibility.
Figure 7.	TEM micrographs of the organic-inorganic nanocomposites containing: A) 4, B) 9, C) 14, and D) 19 wt % of 3,13-dianilino DDSQ.
Figure 8.	TGA curves of pure polyimide and polyimide containing 4, 9, 14, and 19 wt % of 3,13-dianilino DDSQ.
Figure 9.	Plots of dielectric constants and loss as functions of AC frequency for the plain and organic-inorganic polyimides
Figure 10.	Plots of surface water contact angles as a function of the content of 3,13-dianilino DDSQ.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b
Ph
Ph
O
Si
O
Si
O
O
Si
a
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Si
O
H3C
Si
Ph
O
O
CH=CH2
c
d
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O
Si
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b
c+d
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Si
e
f
g
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CH=CH
NH2
c
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Ph
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d
g
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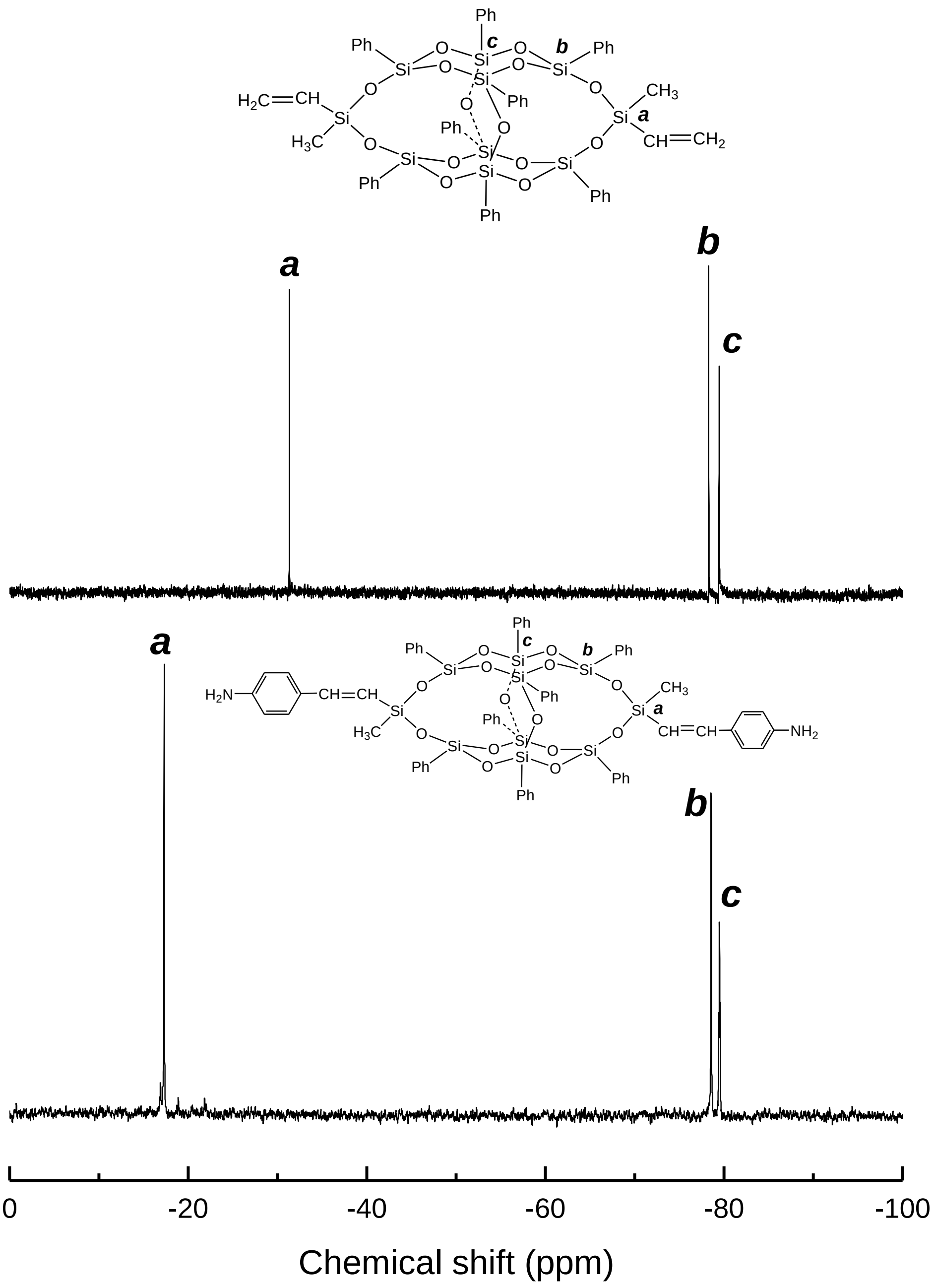
6
4
2
0
Chemical shift (ppm)

Figure 1



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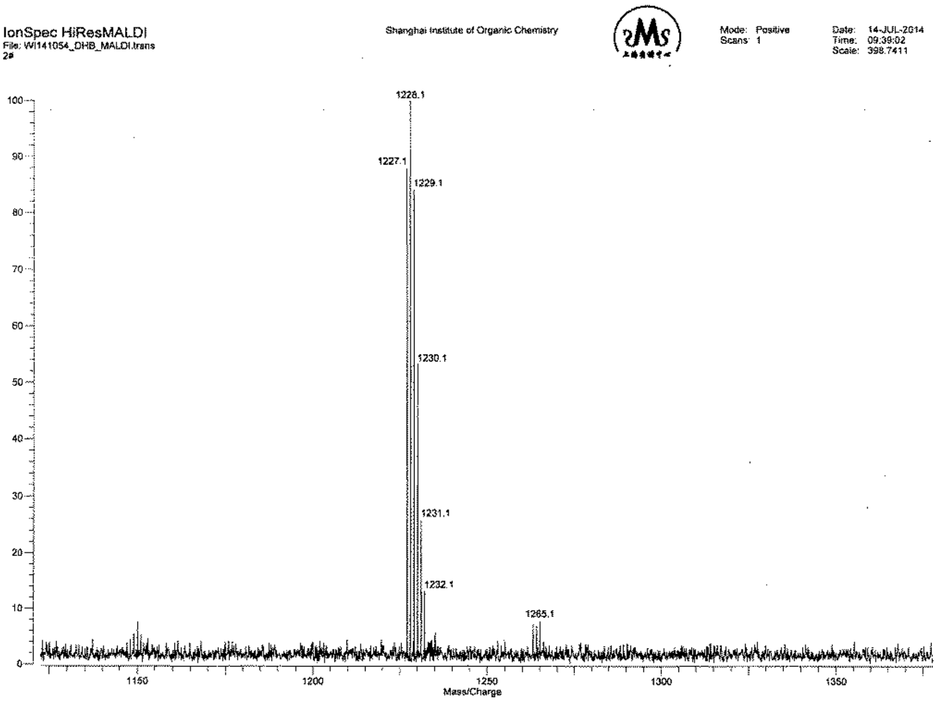
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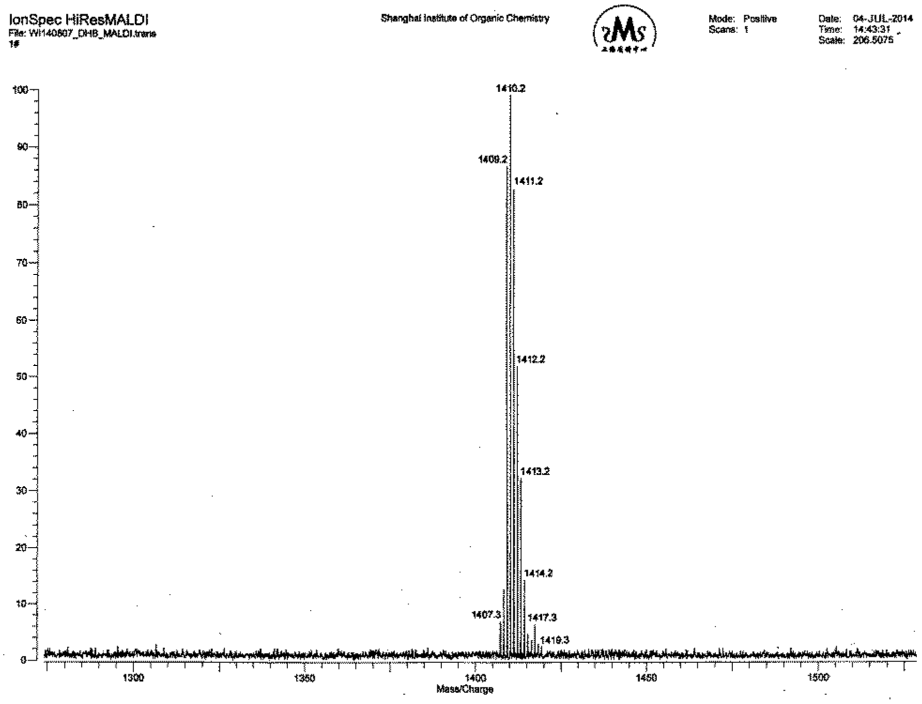
1300
1350
Mass/Charge

Figure 3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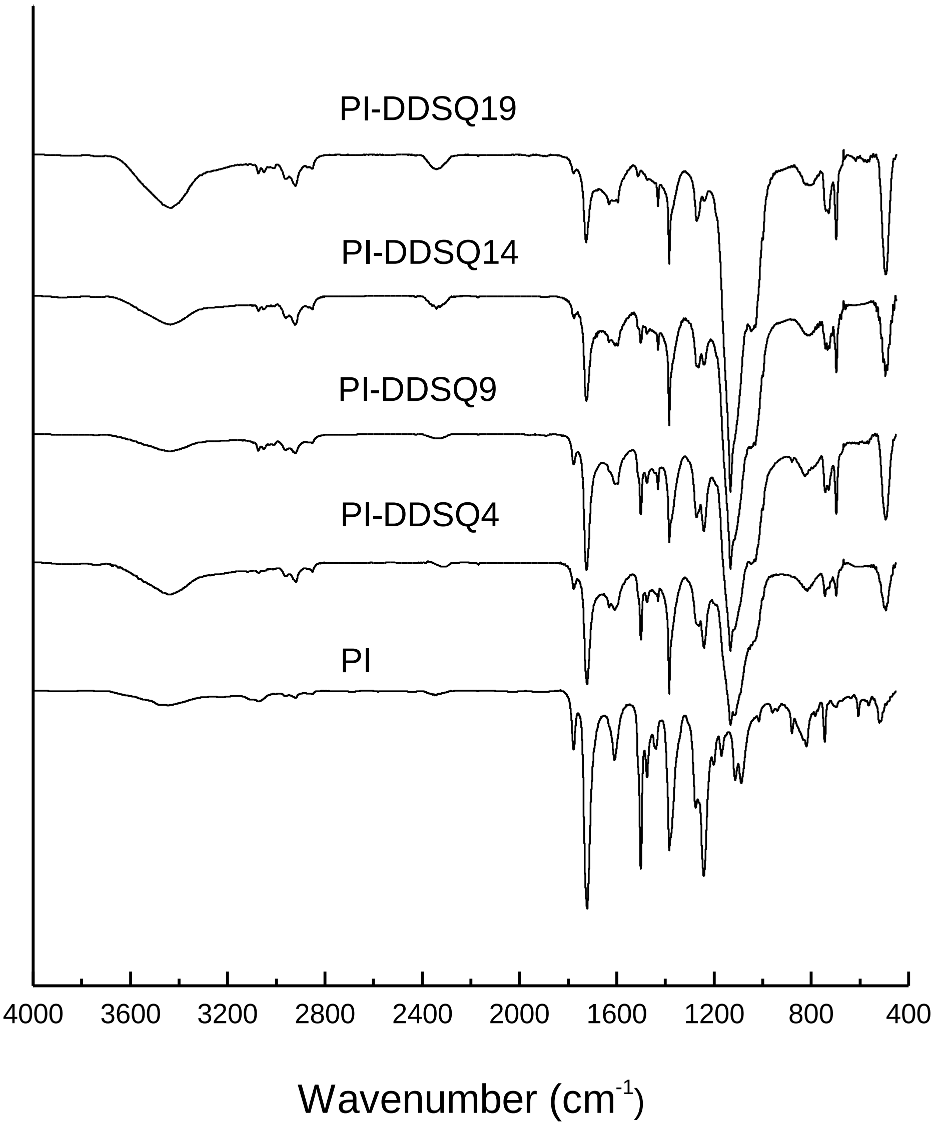
1400
1450
1500
Mass/Charge

Figure 4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PI-DDSQ14
PI-DDSQ9
PI-DDSQ4
PI
4000
3600
3200
2800
2400
2000
1600
1200
800
400
Wavenumber (cm^{-1})

Figure 5

Figure 6

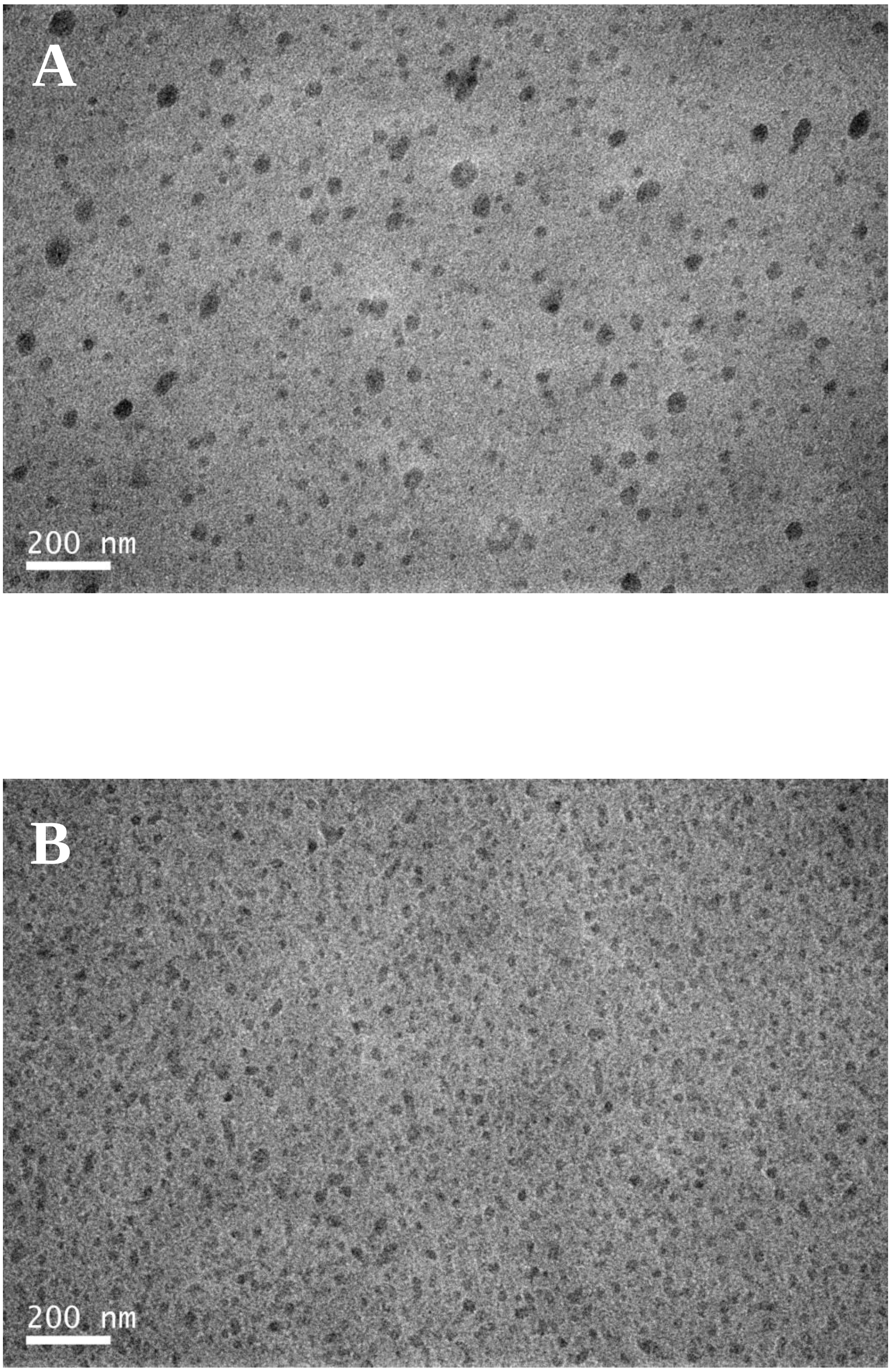


Figure 7

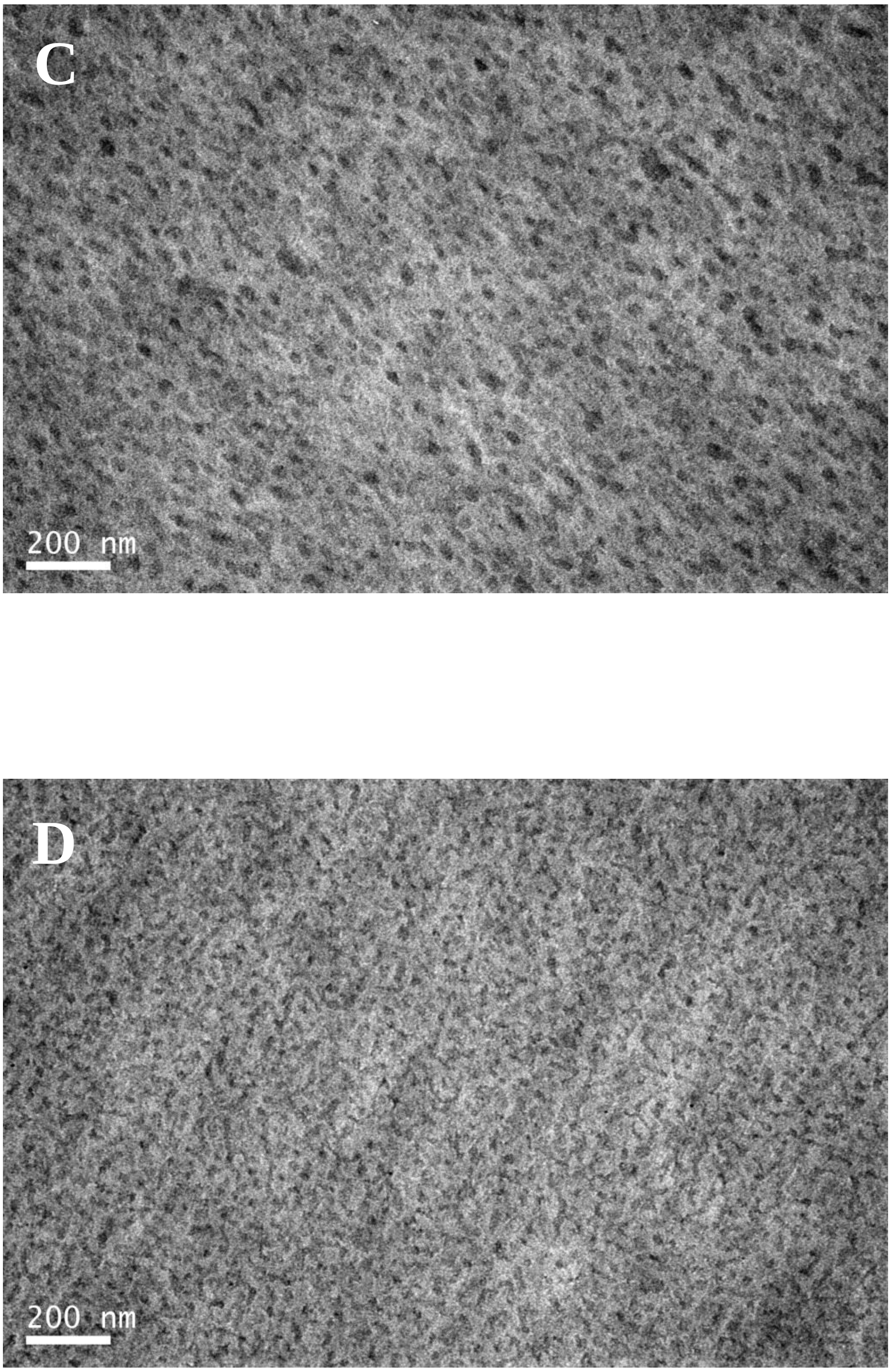
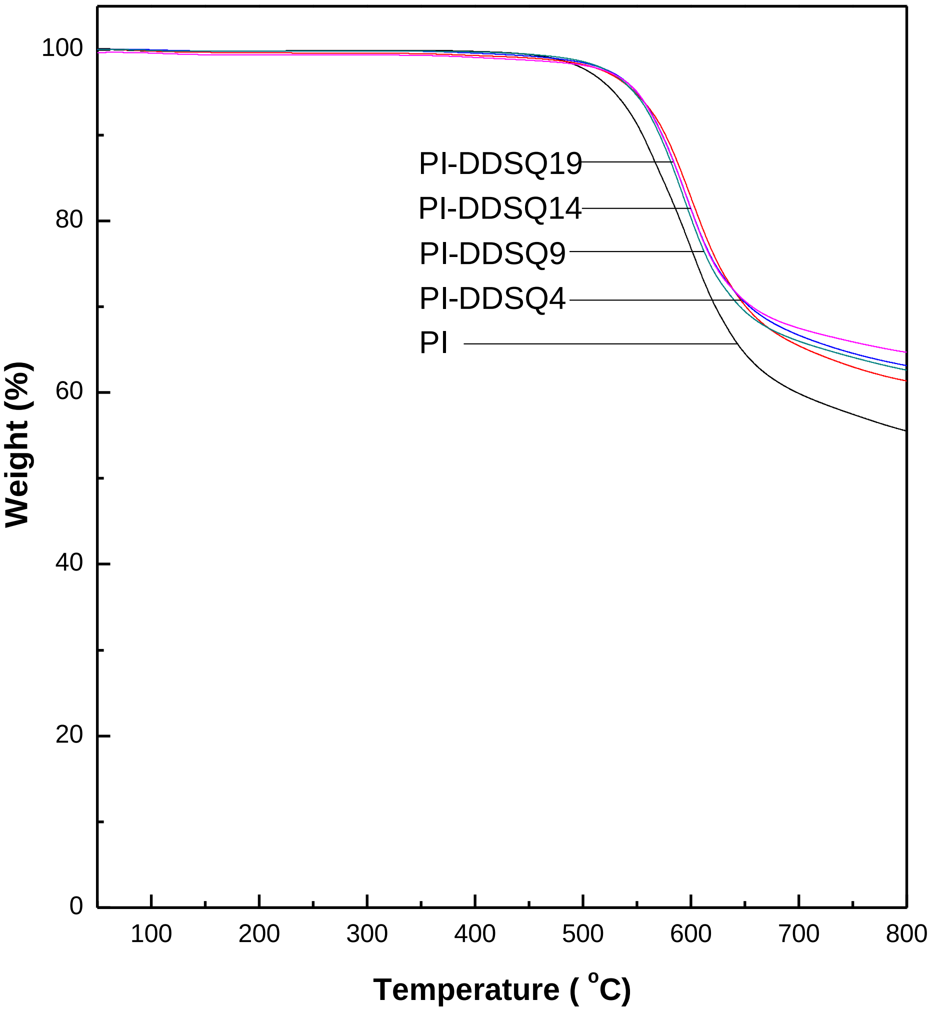


Figure 7 (*Continued*)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PI-DDSQ14
PI-DDSQ9
PI-DDSQ4
PI
Weight (%)
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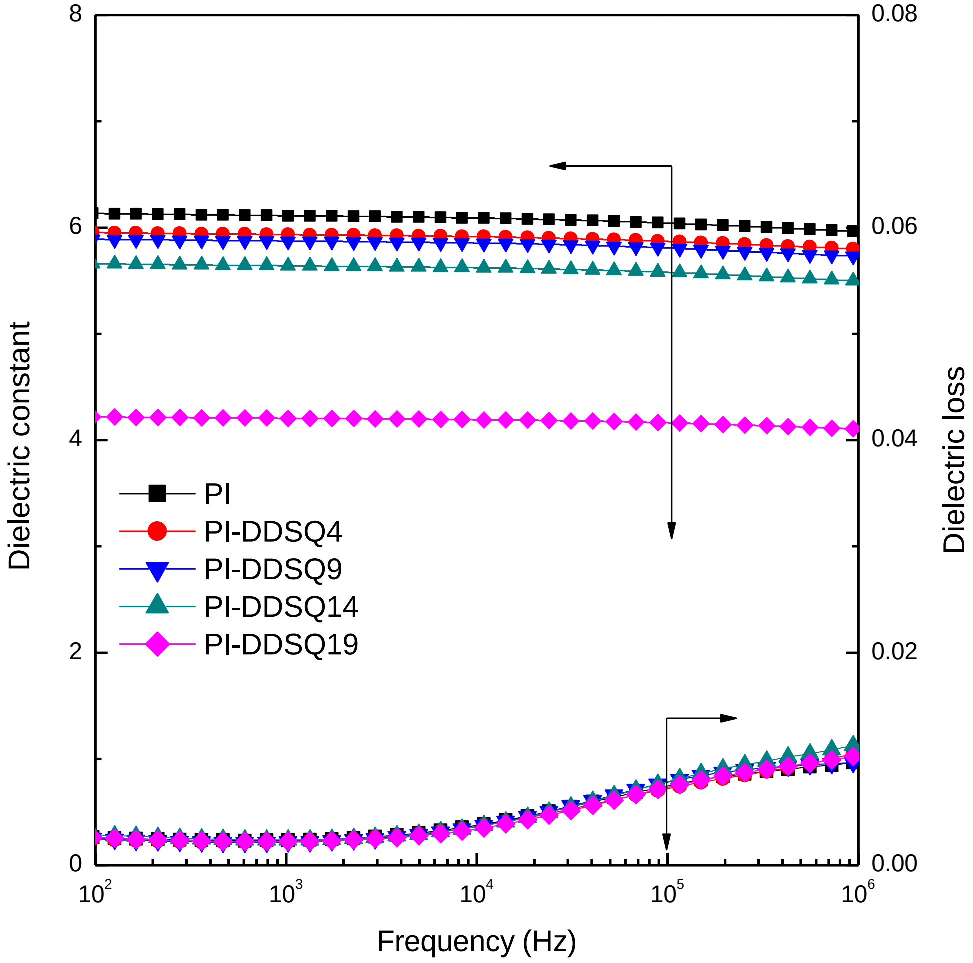
20
40
60
80
100
100
200
300
400
500
600
700
800
Temperature (°C)

Figure 8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6
4
2
0
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0.06
0.04
0.02
0.00
Dielectric constant
Dielectric loss
10^2
10^3
10^4
10^5
10^6
Frequency (Hz)
PI
PI-DDSQ4
PI-DDSQ9
PI-DDSQ14
PI-DDSQ19

Figure 9

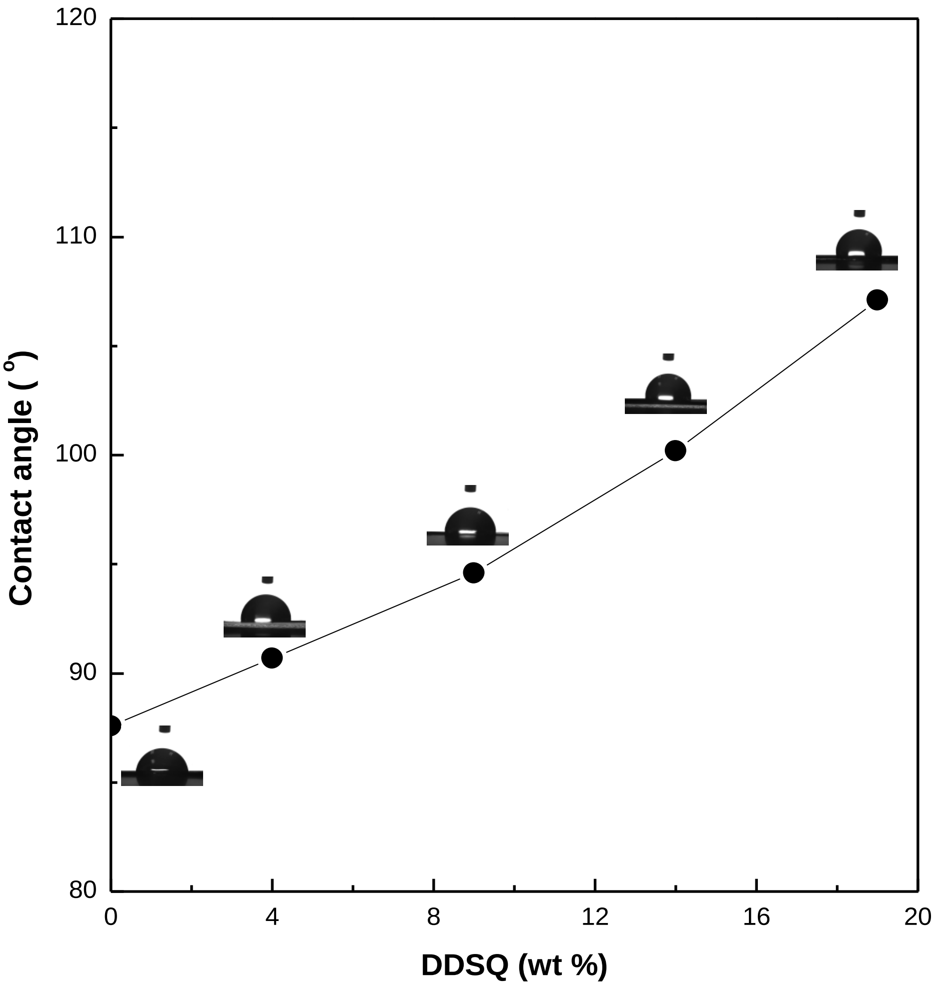
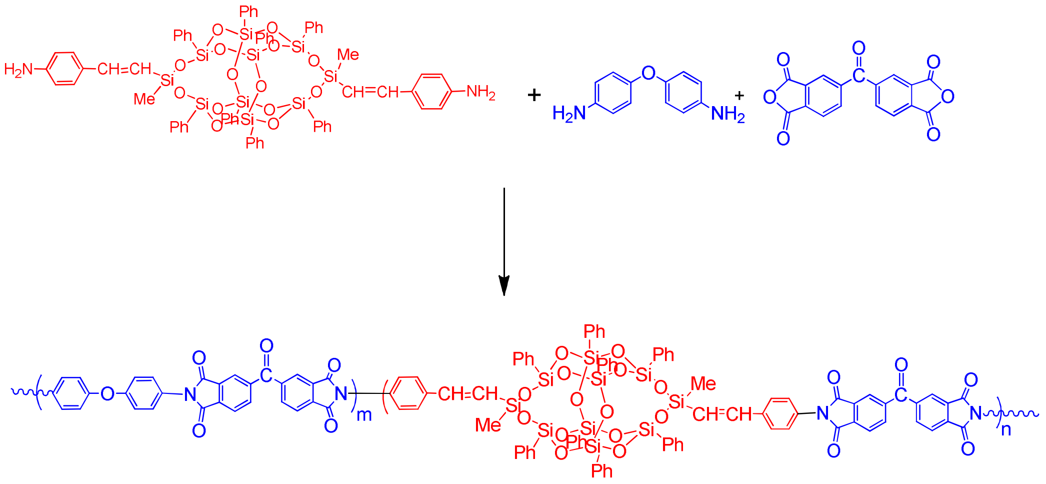


Figure 10

Organic-inorganic Polyimides with Double Decker Silsesquioxane in the Main Chains

Ning Liu, Kun Wei, Lei Wang and Sixun Zheng*



In this contribution, we reported the synthesis of organic-inorganic polyimides with double decker silsesquioxane in the main chains with a novel and well-defined POSS diamine.