Synthesis of a New Siloxane-Containing Alicyclic Dianhydride and the Derived Polyimides with Improved Solubility and Hydrophobicity

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ABSTRACT: The structural transformation strategy of *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride (NA) was performed by esterification. The double bond on the diester of NA showed adequate hydrosilylation reactivity with Si—H bonds of phenyl-containing disiloxane. Thereby, a new siloxane-containing alicyclic dianhydride, 5,5′-*exo*-(1,3-dimethyl-1,3-diphenyl-disiloxane-1,5-diyl)bisbicyclo[2,2,1]heptane-2,3-*endo*-dicarboxylic anhydride **6** was successfully synthesized starting from NA, 1,3-dimethyl-1,3-diphenyldisiloxane and platinum complex catalyst. The whole synthetic route of dianhydride **6** consisted of esterification, hydrosilylation, saponification, acidification, and dehydration. A series of polyimides (PIs) were prepared from dianhydride comonomers of **6** and 4,4′-biphenyltetracarboxylic dianhydride (BPDA) in different molar ratio together with the diamine 4,4′-oxydianiline (ODA). The thermal and mechanical properties of PIs showed somewhat decrease with increasing content of dianhydride 6. The solubility of PIs increased with the increasing content of dianhydride 6, and further calculation from Bragg's equation indicated that average interchain distance (*d*-spacing value) increased with increasing content of siloxane and alicyclic segments in the backbone of PIs. It was revealed that the hydrophobicity of PIs increased with the increasing content of dianhydride **6**. Polyimide **7g**, which was prepared from 100% **6** and ODA, showed water adsorption of less than 0.7% and contact angle against water of 101.1°. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: siloxane-containing alicyclic dianhydride; hydrosilylation; structural transformation; solubility; hydrophobicity
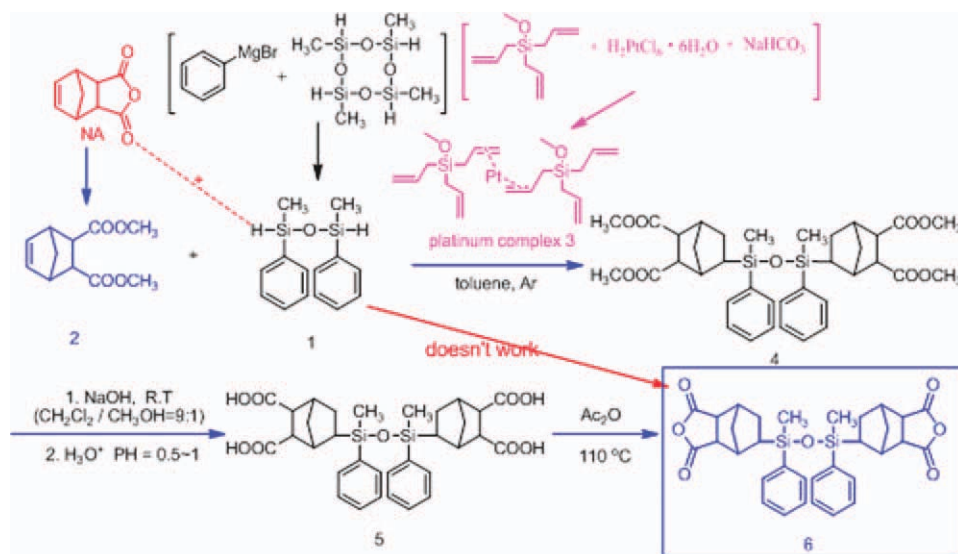
INTRODUCTION

Polyimides (PIs), a well-known class of the high performance polymers, have found various applications in aerospace, automobile, microelectronics, optoelectronics, and many other high-tech fields for their excellent temperature resistance, adhesive, physicomechanical, and dielectric properties.[1,2] Nevertheless, the modest moisture resistance of PIs[3] adversely influences their application in flexible printing circuit, semiconductor coatings, and other microelectronics fields.[4–6] The incorporation of hydrophobic siloxane segments has been proved to be effective to increase the water ingression resistance of PIs in the past years.[6–8] Considerable amount of works have researched the preparation of the siloxane-containing PI from a siloxane-containing dianhydride with an aromatic diamine,[9] from a siloxane-containing diamine with an aromatic dianhydride,[10] or from the allyl-terminated PI with a siloxane via hydrosilylation.[11] Alternatively, introducing alicyclic segments to the main chain of PI could significantly increase the moisture resistance of PIs.[12] Alicyclic PIs were usually prepared by an alicyclic dia-

nhydride or an alicyclic diamine.[13–15] Meanwhile, introduction of siloxane segment (flexible linkage) or alicyclic segment (bulky group) to polymer backbone would enhance the solubility of PIs.[16,17]

Therefore, it could be expected that the incorporation of both flexible siloxane units and alicyclic segments into polymer backbone would bring about synergistic effect on improving the hydrophobicity and solubility of PIs. Siloxane-containing alicyclic PIs have been prepared from the traditional diamines with the siloxane-containing alicyclic dianhydrides. Methods to synthesize the siloxane-containing alicyclic dianhydrides include (1) direct hydrosilylation of an alicyclic anhydride with double bond and a disiloxane with two reactive Si—H bonds[18]; (2) hydrosilylation of an alicyclic anhydride with a chrolosilane, followed by bimolecular hydrolysis condensation to generate the dianhydride[19]; and (3) organometallic approaches involving the use of *n*-BuLi or Grignard reagent.[20,21] Among these methods, direct hydrosilylation is characterized with synthetic convenience and high yield. Nevertheless, the steric requirements of the

Scheme 1. General synthetic route of siloxane-containing alicyclic dianhydride 5,5′-exo-(1,3-dimethyl-1,3-diphenyl-disiloxane-1,5-diyl)bisbicyclo[2,2,1]-heptane-2,3-endo-dicarboxylic anhydride **6**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reactants (alkene with double bond and siloxane with Si—H bond) need to be finely balanced for a successful hydrosilylation reaction.[22] From few published works dealing with direct hydrosilylation, 1,1,3,3,5,5-hexamethyltrisiloxane was the only reported Si—H group-containing siloxane to synthesize the siloxane-containing alicyclic dianhydride. Using this trisiloxane, Kakimoto et al. synthesized a new siloxane-containing alicyclic dianhydride via direct hydrosilylation approach and thereby prepared a series of organosoluble PIs with enhanced UV-vis transparency.[16]

In this work, the synthesis of a new siloxane-containing alicyclic dianhydride was initially attempted by direct hydrosilylation of cis-5-norbornene-endo-2,3-dicarboxylic anhydride (NA) with Si—H group-containing 1,3-dimethyl-1,3-diphenyl disiloxane. However, such attempts all ended up in failures even when equal weight of the platinum complex catalyst was used. Indicatively, steric hindrance of phenyl group of disiloxane prevented the hydrosilylation reaction from taking place. Fortunately, by learning from the strategy of structural transformation of maleopimaric acid for hydrogenation of double bond adjacent to dicarboxylic anhydride ring, a similar method was developed to satisfy the steric requirement of the hydrosilylation between the Si—H group of 1,3-dimethyl-1,3-diphenyl disiloxane and double bond of NA.[23] Experimentally, the structural transformation of esterifying NA was performed to open the dicarboxylic anhydride ring, and the obtained diester with decreased steric hindrance showed the adequate reactivity for direct hydrosilylation with 1,3-dimethyl-1,3-diphenyl disiloxane to give the siloxane-containing alicyclic tetraester. Then saponification, acidification, and dehydration were sequentially performed to generate the desired siloxane-containing alicyclic dianhydride, 5,5′-exo-(1,3-dimethyl-1,3-diphenyl-disiloxane-1,5-diyl)bisbicyclo[2,2,1]heptane-2,3-endo-dicarboxylic anhydride **6**. The whole synthetic route of dianhydride **6** is shown in Scheme 1. In view of comparison, 4,4′-biphenyltetracarboxylic dianhydride (BPDA), one dianhydride which endows lowest water adsorption with PIs among the commercially available dianhydrides,[24] was

selected as dianhydride comonomer with **6** to prepare PIs with varied content of siloxane and alicyclic segments in the polymer backbone. The synthesis of PI films prepared from varied content of dianhydride **6** is shown in Scheme 2. The properties of each PI film with varied content of **6** and BPDA such as thermal properties, inherent viscosity, mechanical properties, solubility, wide angle X-ray diffraction, water adsorption, and contact angle were investigated and compared.
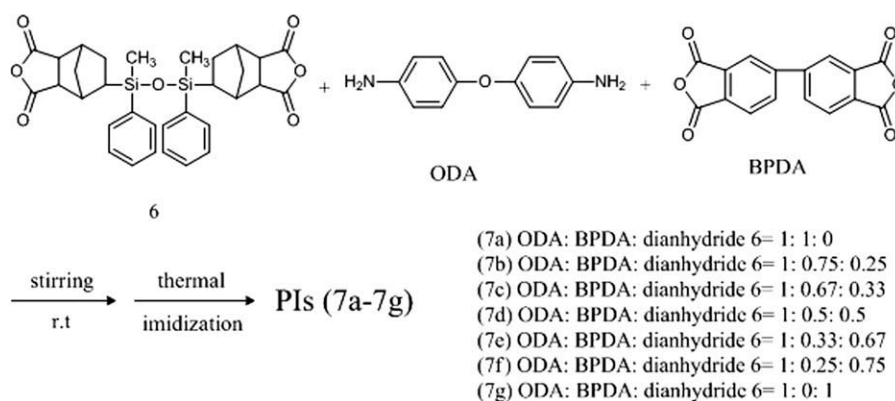
EXPERIMENTAL

Materials

NA, 2,4,6,8-tetramethylcyclotetrasiloxane (TMCTS), and chloroplatinic acid were purchased from Puyang Huicheng Chemicals Co., (China), Jiangxi Jiayi New Material Co., (China), and Shenyang Jinke Chemical Reagent Factory (China), respectively, and used as received. 4,4′-oxydianiline (ODA) and BPDA were purchased from Shanghai Jiachen Chemical Reagent Co. (China) and used as received. Methoxytriallylsilane was self-made in our laboratory. N,N′-dimethylacetylamide (DMAc) was distilled under vacuum over phosphorus pentoxide and stored over 4 Å molecular sieves. Ether and toluene were distilled over sodium. Ethanol was distilled over magnesium and iodine. All the other reagents were commercially available and used as received.

Measurements

^{1}H-NMR and ^{13}C-NMR measurements were performed by a Bruker DRX 500 MHz spectrometer in CDCl$_3$ or DMSO-d_6 using TMS as an internal standard. Infrared spectra were obtained using a Bruker FTIR 460 plus Fourier-transform infrared spectrophotometer. Melting points were measured in open capillary tubes on a SGW-X4 melting point apparatus and the temperatures were uncorrected. The inherent viscosities of the poly(amic acid)s (PAIs) were determined at 0.5 g/dL concentration in DMAc using a ubbelohde viscometer at 30°C. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed with a Perkin-Elmer TGA 8000 and a Perkin-Elmer DSC 8000 with a heating rate of 20°C/min under

Scheme 2. The synthesis of PI films (**7a-7g**) with varied content of siloxane-containing alicyclic dianhydride **6**.

nitrogen. Mechanical properties were measured on a TOYO BALDWIN Corp. TENSILON/UTM-1120 with a load cell of 5 kg at a drawing speed of 5 mm/min. WAXD spectra were recorded using Philips model XPERT-PRO X-ray diffraction spectrometer with a scan range (2θ) from 5 to 50° in transmission mode. The X-rays (wavelength = 1.54 Å) were produced by Cu-Kα source. The voltage and the current settings used to generate the X-rays were 40 kV and 30 mA, respectively. Contact angle measurements were performed by using Drop Master 300 Contact A M system (Kyowa Interface Science Co., Saitama, Japan).

Synthesis of 1,3-dimethyl-1,3-diphenyldisiloxane 1

The synthesis of 1,3-dimethyl-1,3-diphenyldisiloxane **1** was performed referring to the reported process.[25,26] Metallic magnesium powder (24.00 g, 1.00 mol) and bromobenzene (150.72 g, 0.96 mol) in 300 mL of diethyl ether were added to a 1 L three-necked flask equipped with mechanical stirrer, thermometer, and reflux condenser. The mixture was stirred for ~ 2 h at 45°C, then at 7°C, the TMCTS (115.98 g, 0.48 mol) was added drop wise into the mixture. The reactants were stirred for another 2 h and quenched by 400 mL of 17.5% hydrochloric acid. The collected organic layer was distilled in vacuum to give 31.78 g colorless liquid. Yield: 26%, b.p. 154°C at 7 mmHg (lit. b.p.: 120°C at 2 mmHg).[26]

Synthesis of bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid-2,3-dimethyl ester 2

The synthesis of bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid-2,3-dimethyl ester **2** was performed based on the reported method.[27] NA (108.43 g, 0.66 mol) and 5.00 g of toluene-4-sulfonic acid as the catalyst were dissolved in 150 mL of methanol in a 250 mL flask. The mixture was kept refluxing for approximately 12 hours. After methanol was removed by evaporation, the mixture was then distilled in vacuum to offer 130.23 g of colorless liquid. Yield: 94%, b.p.: 135°C at 7 mmHg (lit. b.p.: 119-120°C at 4 mmHg).[27]

Synthesis of the Platinum Complex of Unsaturated Siloxane 3

The synthesis of platinum complex **3** was performed based on the reported method with some modification.[28] Methoxytriallyl-silane (1.53 g) and sodium bicarbonate (1.82 g) were placed in a 100 mL three-necked flask under protective atmosphere of argon. Thirty milliliters of the solution of chloroplatinic acid in

ethanol (10 mg·mL^{-1}) was added, and the reaction was stirred for approximately 1 hour at 70°C until the solution turned as light yellow. The reaction mixture was filtered off inorganic solids, extracted six times with cyclohexane, and concentrated in vacuum to give the platinum complex of unsaturated siloxane **3** as yellow liquid.

Synthesis of Siloxane-Containing Alicyclic Dianhydride 6

Diester **2** (22.96 g, 0.11 mol), platinum complex catalyst **3** (0.71 g), and 100 mL of toluene were placed in a 500 mL three-necked flask under protective atmosphere of argon and the mixture was stirred for 30 min at 85°C. The disiloxane **1** (13.39 g, 0.052 mol) was added drop wise into and the hydrosilylation reaction was stirred until the depletion of the disiloxane was monitored by TLC. The obtained siloxane-containing alicyclic tetraester of 5,5'-(1,3-dimethyl-1,3-diphenyl-1,1,3,3-disiloxane-diyl)-bis-norborane-2,2',3,3'-tetramethyl ester **4** was not separated out and the yellow mixture was directly saponified by pouring into the mixture of 10 g sodium hydroxide, 900 mL dichloromethane, and 100 mL methanol and stirred for 24 h at room temperature. After addition of 500 mL water into the mixture and phase separation, the tetracarboxylate-containing aqueous phase was acidified by 98% sulfuric acid till pH value reaching 0.5–1. The precipitate was washed with water and dried in vacuum at 55°C overnight to offer 18.74 g of siloxane-containing alicyclic tetracarboxylic acid of 5,5'-(1,3-di-methyl-1,3-diphenyl-1,1,3,3-disiloxanediallyl)-bis-norborane-2,2',3,3'-tetracarboxylic acid **5** as white crystalline solid. Yield: 58%, mp: 120–124°C.

Tetracarboxylic acid **5** (18.01 g) and acetic anhydride (30.02 g) were placed in a 100 mL flask and stirred for 24 h at 110°C to perform the dehydration reaction, and then the solution was poured into ether. After most of acetic acid and acetic anhydride were removed by distillation in vacuum, an off-white precipitate was obtained. The crude product was washed three times with petroleum ether and dried in vacuum at 150°C overnight to give 10.51 g white powder of target anhydride siloxane-containing alicyclic dianhydride of 5,5'-*exo*-(1,3-dimethyl-1,3-di-phenyl-disiloxane-1,5-diyl)bisbicyclo[2,2,1]heptane-2,3-*endo*-dicarboxylic anhydride **6**. Yield: 62%, mp: 248–250°C.
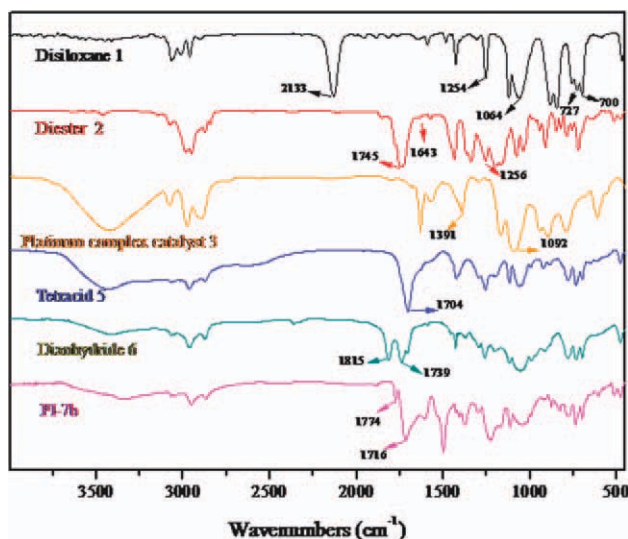
Figure 1. FTIR spectra of the disiloxane **1**, the diester **2,** the platinum complex **3**, the tetracarboxylic acid **5**, the dianhydride **6** and PI-**7b**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

General Preparation Procedure of Siloxane-Containing Alicyclic PIs 7a-7g

Polycondensation was performed by reacting **6**, BPDA and ODA with different molar ratio in DMAc with total solids concentration of 15 wt % for 12 h at room temperature. The obtained polyamic acid solution was cast onto a glass plate, and the imidization was performed via heating successively at 70, 100, 140, 180, and 220°C for 6, 1, 1/2, 1, and 2 h, respectively.
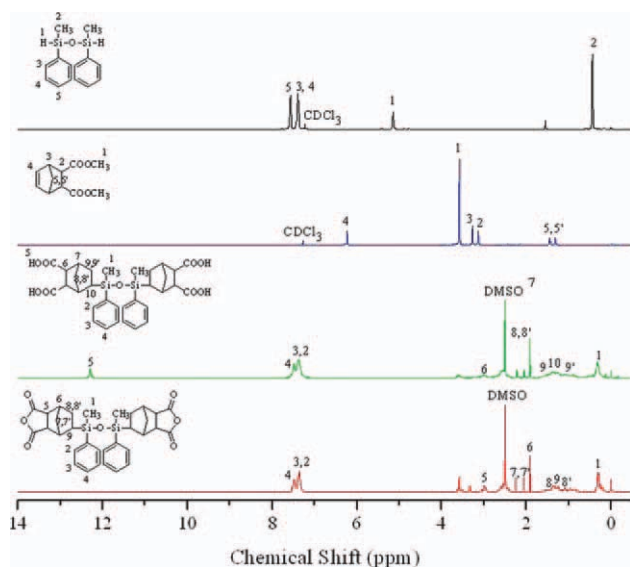
RESULTS AND DISCUSSION

Dianhydride Monomer Synthesis

For the synthesis of 1,3-dimethyl-1,3-diphenyldisiloxane, selection of the molar ratio of phenyl Grignard reagent to TMCTS and reaction temperature control are very important. The preferable molar ratio of phenyl Grignard reagent to TMCTS should be selected between 1 and 2, and the reaction temperature should be about 40°C. Otherwise, an undesired side reaction would take place, in which the Si—H groups of the target disiloxane were converted into Si—CH_3 groups, or the reaction would become impractically slow.[25]

Hydrosilylation is key to the synthesis of dianhydride **6**. The activity of the platinum complex catalyst **3** plays an important role for the hydrosilylation. It was reported that the inorganic chlorine in platinum catalyst would seriously influence the catalyst activity.[28] Therefore, during the preparation of the platinum complex catalyst in this research, the mixture was kept at a standstill for ~ 15 h before filtration to equilibrate precipitation. The adequate separation of the inorganic precipitates could effectively improve the activity of the catalyst.

Typical saponification processes involve the use of aqueous solutions, combining water and other water miscible organic solvents, which necessitates high temperature and long time for the complete conversion.[29] In this work, the mixture of dichloromethane and methanol with volume ratio of 9 : 1 was selected as the solvent for the saponification of siloxane-containing alicyclic tetraester **4,** as referred to the reported process.[30] By adopting the organic system, the saponification process took place very rapidly at room temperature, and it also helped to readily separate the saponification product tetracarboxylate by aqueous extraction. The obtained siloxane-containing tetracarboxylate was mixed with bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate which was transformed from unreacted diester
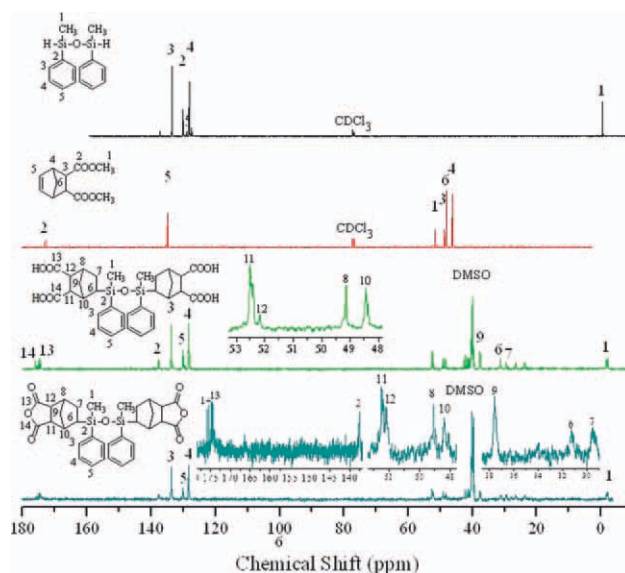

Figure 2. ^{1}H-NMR spectra of the disiloxane **1**, the diester **2,** the tetracarboxylic acid **5** and the dianhydride **6**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 3. ^{13}C-NMR spectra of the disiloxane **1**, the diester **2,** the tetracarboxylic acid **5** and the dianhydride **6**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Summary of the Thermal and Mechanical Properties, Inherent Viscosities, and WAXD of PIs

PIs	Thermal properties			Inherent viscosities and mechanical properties				WAXD properties	
	$T_g{}^a$ (°C)	$T_{d5}{}^b$ (°C)	$T_{d10}{}^b$ (°C)	Inherent viscosities^c (dL/g)	Tensile strength (MPa)	Elongation (%)	Tensile modulus (MPa)	$2\theta^d$ (°)	d spacing^e (Å)
7a	285	564	589	0.65	135	14.1	3630	14.82	5.97
7b	258	308	474	0.48	65.8	7.2	1930	14.29	6.19
7c	241	302	422	0.42	45.7	4.7	1790	14.13	6.26
7d	234	295	420	0.35	23.1	3.1	1650	13.89	6.37
7e	222	290	418	0.36	$-^f$	$-^f$	$-^f$	13.87	6.38
7f	213	285	415	0.28	$-^f$	$-^f$	$-^f$	13.65	6.48
7g	196	283	412	0.24	$-^f$	$-^f$	$-^f$	13.48	6.56

^{a}From DSC on the second heating at a heating rate of 20°C/min in nitrogen, ^{b}From TGA at a heating rate of 20°C/min in nitrogen, ^{c}Measured at a concentration of 0.5 g/dL poly(amic acid)s in DMAc at 30°C, $^d2\theta$ values were measured corresponding to the maximum intensity in the amorphous scattering region, $^e d$-spacing values were calculated using the Bragg's equation, ^{f}The data were unavailable because the films are too fragile.

2. The purification could be readily attained during acidification process by aqueous filtration separation. After acidification, the desired siloxane-containing tetracarboxylic acid would precipitate from aqueous solution, whereas bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid showed an excellent solubility in water.

The Structure Characterization

The disiloxane 1, the diester 2, the platinum complex of unsaturated siloxane 3, siloxane-containing alicyclic tetracarboxylic acid 5, and the target dianhydride 6 were identified by FTIR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy, as shown in Figures 1–3, respectively.

In the FTIR spectra, the structure of the disiloxane 1 was identified by the presence of the Si[—]O—Si asymmetric stretching absorptions at 1064 cm^{-1}, the Si—Me absorptions at 1254 cm^{-1}, the Si—Ph absorptions at 727 and 700 cm^{-1}, and the Si—H absorptions at 2133 cm^{-1}. For the diester 2, the appearance of characteristic C=O and C—O—C absorptions at 1745 and 1256 cm^{-1}, the disappearance of the absorptions at 1739 and 1815 cm^{-1} characteristic of the carboxylic anhydride C=O absorption, and the presence of the C=C absorptions at 1643 cm^{-1} indicated that the esterification was complete and that the double bond for ensuing hydrosilylation was maintained. For the platinum complex catalyst 3, the appearance of absorptions at 1391 and 1092 cm^{-1} indicated that the platinum complex of unsaturated siloxane was formed, which was consistent with Karstdet's results.[28] For the siloxane-containing alicyclic tetracarboxylic acid 5, the disappearance of 2133 cm^{-1} characteristic of the Si—H absorption, the presence of the Si—O—Si asymmetric stretching absorptions at 1066 cm^{-1}, the Si—Me absorptions at 1258 cm^{-1}, and the Si—Ph absorptions at 734 and 699 cm^{-1} indicated that the incorporation of siloxane segment via hydrosilylation was successfully performed. The appearance of characteristic carboxylic C=O absorptions at 1704 cm^{-1} and the disappearance of the absorptions at 1643, 1745 cm^{-1} characteristic of the carboxylate C=O absorption indicated that the acidification of siloxane-containing alicyclic tetraester were complete. For the target dianhydride 6, the appearance of the characteristic anhydride C=O absorptions at 1739 and

1815 cm^{-1} and the disappearance at 1704 cm^{-1} characteristic of the carboxylic C=O absorption indicated the complete dehydration of tetracarboxylic acid and the synthesis of the target dianhydride 6. For PI films, as represented by 7b, the appearance of characteristic imide C=O absorptions at 1716 and 1760 cm^{-1} indicated that the imidization was fully performed. The presence of the Si—O—Si asymmetric stretching absorptions at 1040 cm^{-1} and the Si—Me absorptions at 1230 cm^{-1} further indicated the presence of siloxane segment in the PI backbone.

In the ^{1}H-NMR spectra, for the disiloxane 1, the proton signals of the phenyl groups were separated into peaks at 7.40, 7.38, and 7.57 ppm. The signal of the Si—H was observed at 5.15 ppm, and the signal of Si—CH$_3$ was observed at 0.44 ppm. For the diester 2, the proton signals of the C=C—CH and C=C—C—CH were observed at 3.27 and 3.14 ppm, respectively. The proton signal of the —CH=CH— was observed at 6.23 ppm, and the appearance of the proton signal of the —COOCH$_3$ was detected at 3.58 ppm. For the tetracarboxylic acid 5, the appearance of the alicyclic proton signal of the
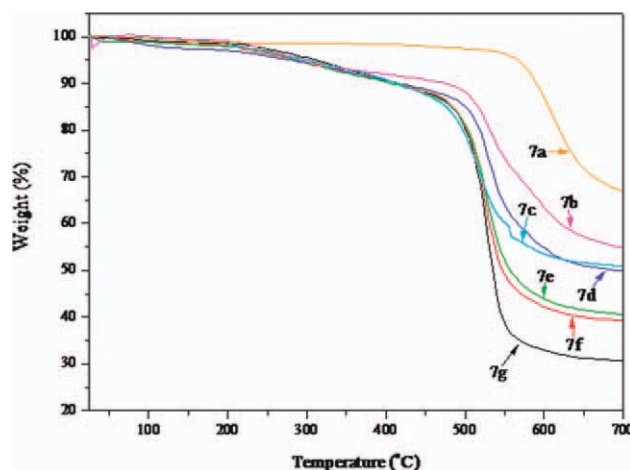

Figure 4. TGA curves (in N$_2$) of the PIs prepared from the varied content of dianhydride comonomers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. The Solubility of the Tetracarboxylic Acid 5, the Dianhydride 6, and PIs

Substances	Solubility						
	m cresol	THF	NMP	DMSO	DMF	DMAc	Acetone
5	+	+	+	+	±	+h	+
6	+	-	+	+	±	±	-
7a	±	-	-	-	-	-	-
7b	+h	-	±	-	-	-	-
7c	+h	-	+h	±	±	±	-
7d	+h	±	+h	±	±	±	-
7e	+h	±	+h	+h	±	±	-
7f	+h	+h	+	+h	+	+	±
7g	+	+h	+	+	+	+	±

+, soluble at room temperature; +h, soluble on heating; -, insoluble even on heating; ±, partially soluble or swelling on heating.

Si—CH as multiplet at 1.52–1.26 ppm and the disappearance of the proton signal at 6.23 ppm characteristic of the double bond indicated that the hydrosilylation reaction took place completely. The appearance of the carboxylic proton signal at 12.29 ppm and the disappearance of the proton signal at 3.58 ppm characteristic of the C—O—CH$_3$ indicated the successful acidification. Compared with the spectrum of the tetracarboxylic acid 5, the disappearance of the carboxylic proton signal on the spectrum of dianhydride 6 indicated that the dehydration of tetracarboxylic acid 5 was complete, and hence the synthesis of the target dianhydride 6 was successfully performed.

In the ^{13}C-NMR spectra, for the disiloxane 1, the peaks of the phenyl groups were observed at 130.06, 133.54, 128.06, and 128.89 ppm. The peak of the Si—CH$_3$ was observed at -0.47 ppm. For the diester 2, the peak of the —C≡C— was observed at 134.88 ppm. The appearance of the peak at 51.47 ppm characteristic of the carboxylate indicated that esterification was complete. For the tetracarboxylic acid 5, the characteristic carboxylic peaks were observed at 174.51 and 175.95 ppm. The appearance of the peak at 31.25 ppm characteristic of the alicyclic Si—CH indicated that the incorporation of siloxane segment via hydrosilylation reaction was effectively performed. For the target dianhydride 6, the peaks of the carboxylic anhydride were observed at 174.78 and 175.50 ppm.

The Thermal and Mechanical Properties and Solubility

The thermal properties of the PIs (7a-7g) evaluated by DSC and TGA are summarized in Table I. The synthesized PIs showed glass transition temperature (T_g) between 196 and 285°C in N$_2$. The 5% weight loss temperature (T_{d5}) of the PIs with varied dianhydride comonomers content ranged from 283 to 308°C in N$_2$. The 10% weight loss temperature (T_{d10}) in N$_2$ ranged from 412 to 474°C. It is explicitly revealed in Figure 4 that the thermal decomposition stability of the PIs decreased when the content of the dianhydride 6 was increased. As also revealed elsewhere,[31] the incorporation of the siloxane and alicyclic segments lead to some decrease of the thermal properties of the PI copolymer. Still, the results showed that the thermal stabilities of these synthesized PIs are similar to other semiaromatic PIs used in microelectronic applications.[17,32]

The inherent viscosities of the PAIs ranged from 0.65 to 0.24 dL/g in Table I, presenting an obvious decreasing trend with increased content of dianhydride 6 in dianhydride comonomers. Meanwhile, as shown in Table I, the membranes had measured tensile strengths in the range of 135 to 23.1 MPa, measured tensile moduli in the range of 3.6–1.65 GPa and measured elongations at break from 14.1 to 3.1%. It is revealed that the mechanical properties of PIs sharply decreased when the content of the dianhydride 6 was increased. The PIs (7e-7g) derived from more than 67% dianhydride 6 in dianhydride comonomers were all very fragile and so the mechanical properties were not obtained, which can be explained as the increase of backbone rigidity attributed to the two sterically congesting phenyl groups in dianhydride 6.

The solubility of the tetracarboxylic acid 5, the dianhydride 6, and the PIs are studied and summarized in Table II. It can be seen that the tetracarboxylic acid 5 and the dianhydride 6 were soluble in various solvents such as *m*-cresol and DMSO at room temperature. Moreover, the solubility of the PIs increased with the increasing content of the dianhydride 6.
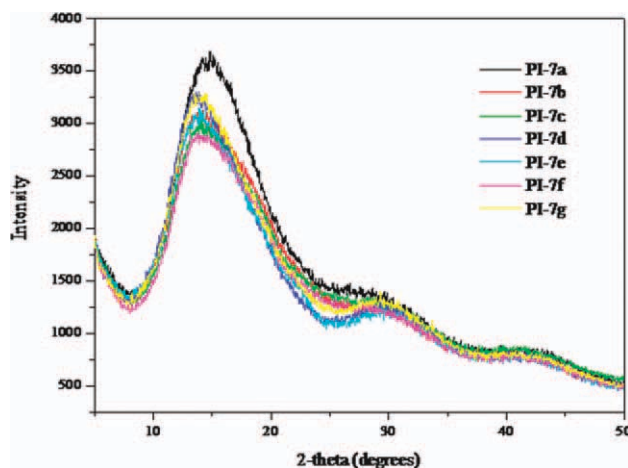

Figure 5. WAXD spectra of the PI films with varied content of the dianhydride comonomer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
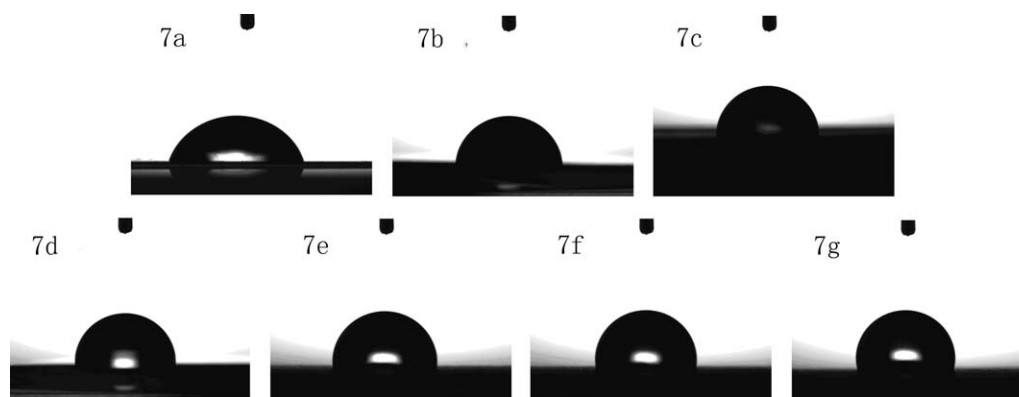
Figure 6. Representative images of contact angles of the PI films with varied content of the siloxane-containing alicyclic dianhydride **6**.

Especially, **7g** is readily soluble in various solvents such as DMAc and DMF at room temperature. Obviously, the incorporation of both alicyclic and siloxane segments greatly improved the solubility of PIs.

Figure 5 shows the wide angle X-ray diffraction pattern of the synthesized PI films. The broad and structureless diffraction patterns indicated that all the PIs were amorphous in nature. It was also found that the crystallinity of different PI films was very similar, which scarcely changed with the content of the dianhydride **6**.

In the WAXD spectra, the broad band amorphous halo implied a d-spacing distribution. The most prominent peak in the spectrum of an amorphous polymer is often used to estimate the average interchain spacing distance (d-spacing). The d-spacing value from the diffraction pattern was calculated using the Bragg's equation:

$$2d\sin\theta = n\lambda \qquad (1)$$

The θ value was measured corresponding to the maximum intensity in the amorphous scattering region. By inspecting interchain distance, one can estimate the degree of entanglement in a polymer.[33] When the d-spacing value increases, the entanglement will decrease, and so the solubility of polymer increase. The d-spacing values of PIs (**7a-7g**), calculated using the Eq. (1), are summarized in Table I. As can be seen in the Table, the d-spacing values of PIs exhibited an increasing tendency with the increasing dianhydride **6** content in comonomers. The **7a** showed the lowest d-spacing value, whereas, **7g** showed the highest d-spacing value. It indicated that the increasing content of siloxane and alicyclic segments in the

polymer backbone can lead to the increased solubility of the PI films. The enhanced solubility brought about by alicyclic and siloxane segments may be a result of reduced intermolecular charge transfer interaction and consequently the increased flexibility of the PIs chains.

The Contact Angle and Water Adsorption of PIs

The contact angles of PIs with varied content of the dianhydride comonomers were measured at ambient temperature and double distilled water was used as solvent for the studies. Equilibrium contact angle was measured for a time period of 120 s depending on the stability of the drop. Average of the results obtained from three experiments was taken for contact angle measurements. As explicitly shown in Figure 6, PIs prepared from higher dianhydride 6 content exhibited bigger contact angle against water. Table III also shows that the value of contact angle of the PIs increased with increasing content of siloxane-containing alicyclic dianhydride **6**. The hydrophobic nature of siloxane segments and the further enrichment of siloxane fraction on the film surface resulting from its low free energy, greatly contributed to improve the water repellence of PIs.[34,35]

However, compared with aromatic structure, alicyclic segments in polymer backbone would endow PIs with better water resistance. Asano et al. studied the effect of aliphatic diamine to the hydrolytic stability of PIs.[36,37] By semiempirical MO calculations of model compounds, they found that the imide nitrogen atom attached to aliphatic group possessed higher electron density than that attached to aromatic group. The higher electron density of aliphatic imide nitrogen atom reduced the susceptibility of PIs to nucleophilic attack by water molecules. The effect of alicyclic segment of the dianhydride **6** to the water resistance of PIs was analyzed by using model compounds, as shown in

Table III. The Water Adsorption and Contact Angles Values of the PIs

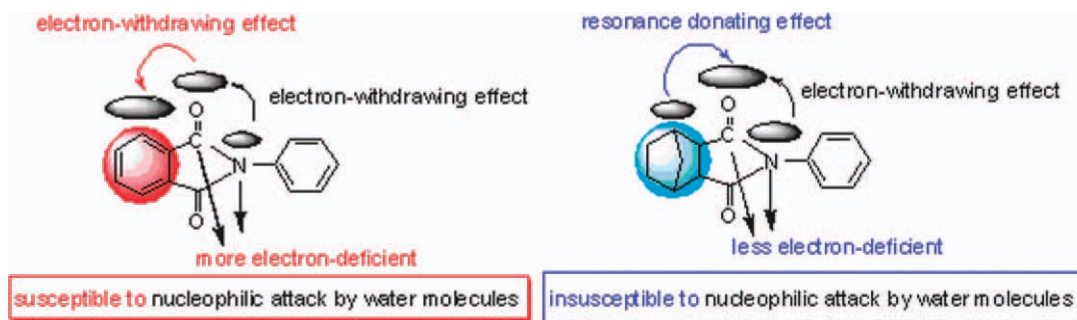| Measurements	PIs						
	7a	**7b**	**7c**	**7d**	**7e**	**7f**	**7g**
Contact angle (°)	79.6	82.4	83.7	87.1	92.4	95.3	101.1
M_d (g)	0.1499	0.1496	0.1453	0.1417	0.1432	0.1437	0.1407
$M_{w(eq)}$ (g)	0.1516	0.1512	0.1468	0.1431	0.1445	0.1449	0.1417
M (%)	1.1341	1.0700	1.0323	0.9880	0.9078	0.8351	0.7107

Figure 7. The hydrolytic stability analysis of model compounds of both aromatic and alicyclic PIs under nucleophilic attack by the water molecules. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 7. Contrasting with the electron-withdrawing effect of the aromatic group to imide carbonyl, the electron of alicyclic segment would transfer to imide carbonyl. Consequently, the carbonyl carbons attached to alicyclic segment would be less electron-deficient than those attached to aromatic segment. Meanwhile, the electron-withdrawing effect of the alicyclic segment neighboring carbonyl to the imide nitrogen atom would be reduced, resulting in a higher electron density of the imide carbonyl attached to alicyclic segment than that attached to aromatic group. Combined, PIs synthesized by alicyclic dianhydride and aromatic diamines were more insusceptible to nucleophilic attack by water molecules, showing better water resistance.

As a matter of fact, the introduction of both hydrophobic siloxane and alicyclic segments remarkably modified the surface property of the PI films. The appreciable contact angle value difference between **7a** (79.6°) and **7g** (101°) further demonstrated the surface modification efficiency of PI films by incorporating the hydrophobic dianhydride **6** moiety.

The water adsorption property of PI bulk films was determined by swelling films in water at room temperature until equilib-
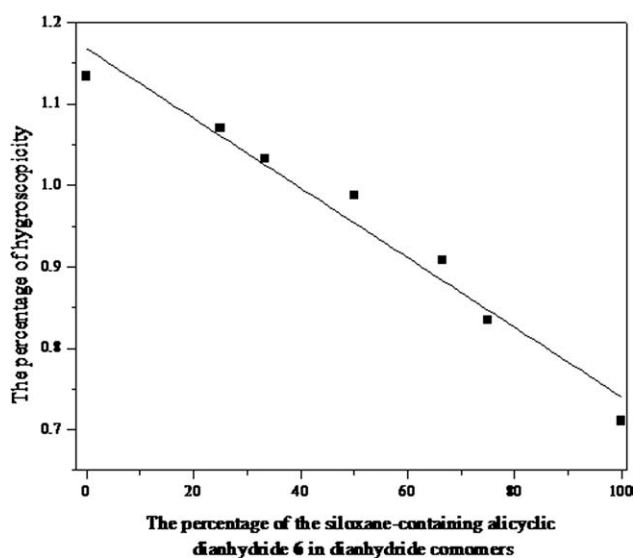
rium of swelling was reached. Dried and preweighed PI films with varied dianhydride **6** content were immersed in the water, and periodically taken out to remove the excess water at the surface by blotting with tissue paper. The rate of hygroscopicity (M) of the material was expressed using the well-known equation:

$$M = \frac{M_{W(eq)} - M_d}{M_d} \tag{2}$$

where $M_{w(eq)}$ was the mass of the wet sample at equilibrium state and M_d, the dry mass. The water adsorption of PIs with varied dianhydride comonomers content, as shown in Table III, exhibited the same hydrophobicity changing tendency as those of contact angle. It was shown that the water resistance of the PI bulk films increased with the increasing content of siloxane and alicyclic segments in the polymer backbone. The hygroscopicity vs. the concentration of the dianhydride **6** was plotted and a roughly linear relationship with the slope of -4.28×10^{-3} was fitted, as shown in Figure 8. It explicitly revealed that the increasing siloxane and alicyclic segments led to the enhanced water repellence of PIs. Interestingly, it was also found in experiments that the PI films curled up slowly with the increasing content of the dianhydride BPDA when taking out of the water. The reason for it could be the hydrophilic orientation of the less hydrophobic BPDA moiety at the surface of the PI films.[38]

CONCLUSIONS

The structural transformation of esterifying NA was proved to be an effective strategy to decrease the steric hindrance, and therefore, to increase the reactivity for the double bond on NA to react with Si—H bonds of 1,3-dimethyl-1,3-diphenyldisiloxane via hydrosilylation under the catalysis of the platinum complex of unsaturated siloxane. Thereby, starting from NA and the phenyl-containing disiloxane, successfully synthesized was a new siloxane-containing alicyclic dianhydride 5,5′-exo-(1,3-dimethyl-1,3-diphenyl-disiloxane-1,5-diyl)bisbicyclo[2,2,1]heptane-2,3-endo-dicarboxylic anhydride **6**. The synthesis of the target dianhydride **6** consisted of esterification, hydrosilylation, acidification, and dehydration. The thermal and mechanical properties of the PIs showed somewhat decrease with the increasing content of dianhydride **6**. The siloxane and alicyclic segments of

Figure 8. The correlation between the hygroscopicity of the PIs and the content of the dianhydride 6 in the dianhydride comonomers.

dianhydride **6** endowed the PI films with improved solubility. Preliminary average interchain spacing distance (*d*-spacing) analysis from WXAD spectra led to the inference that the increasing content of the siloxane and alicyclic segments in the polymer backbone contributed to increased solubility of PIs. Meanwhile, the incorporation of the siloxane and alicyclic segments would enhance the hydrophobicity of the PIs. Experimental results revealed that the PIs with increasing content of the dianhydride **6** exhibited decreased water adsorption and increased contact angle against water.

ACKNOWLEDGMENTS

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