Self-Catalyzed Silicon-Containing Phthalonitrile Resins with Low Melting Point, Excellent Solubility and Thermal Stability

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ABSTRACT: A series of silicon-containing self-catalyzed phthalonitrile derivatives (SiPNs) have been successfully synthesized from reaction of 4-(4-aminophenoxy)phthalonitrile (APN) with corresponding chlorosilanes. The chemical structures of the SiPNs were confirmed by spectroscopic techniques. The introduction of silicon-containing unit into the phthalonitrile structure has dramatically decreased the melting point from 143°C for APN to 40–60°C for the new SiPNs, which also exhibit improved solubility and are soluble in many common solvents. Differential scanning calorimetry analysis showed that they possess the self-catalyzed behavior with the temperature of exothermic peak due to the self-catalyzed reaction between 255 and 281°C. The cured SiPNs exhibit excellent thermal stability with glass transition temperature above 450°C, the temperature of 5% weight loss in range of 535–570°C under nitrogen, and 543–562°C under air. Their char yields at 1000°C are in the range of 80.2–82.6% in nitrogen, and 10.1–12.5% in air, respectively. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40919.

INTRODUCTION

As one of high-temperature materials, phthalonitrile resins were originally developed by the U.S. Naval Research Laboratory more than 30 years ago. The phthalonitrile resins possess a number of exceptional properties such as high glass transition temperature, outstanding thermal and thermo-oxidative stability, excellent mechanical properties, good moisture, and fire resistant performance.[1–5] Combination of these properties and good processability has made the phthalonitrile resins become attractive materials in many advanced technological applications, such as composites, adhesives, electronic conductors, and carbon precursors.[6–10]

With the first development of aromatic ether structure-containing phthalonitrile resins,[11–13] imide,[14–17] sulfoxide,[5,18] fluorine,[19,20] and benzoxazines[21,22] structures were introduced into the phthalonitrile resins, to improve the thermal stability or solvent resistance of the cured phthalonitrile resins. Unfortunately, these resins could not polymerize in the absence of catalysts even at high temperature. Therefore, small molecules such as amine or phenol compound as catalysts were added into the resin to shorten the curing time and lower the curing temperature. Besides, phenolic and epoxy resins could also efficiently catalyzed the curing of phthalonitrile.[23–25] However, it has been found that the addition of easy-volatile small molecules catalysts

and low-temperature stable phenolic and epoxy resins has adverse effect on the high-temperature performance of the cured polymer.

Recently, phthalonitrile resins, which contain different proportions of amino or hydroxy in the molecular structure, were found to exhibit self-promoted cure behaviors.[26–29] The self-catalyzed phthalonirile resins avoid the usage of addition catalysts, and, therefore, have been paid more and more attentions. For the past few years, a variety of self-catalyzed phthalonitrile resins with different main chain structures, such as aromatic ether, aromatic ether ketone, and aromatic ether imide have been developed.

Nevertheless, because of their chain rigidity and strong inter-chain interaction, the solubility of phthalonitrile resins in common solvents still remain a problem, which limits the application of the resins. Although, efforts, such as the introduction of flexible segments into the main chain of the phthalonitrile resins, have been made to improve the solubility and processibility, the thermal stability would be degraded. Conversely, the introduction of silicon-containing units into aromatic polymers, such as poly(esters) and poly(amide-imide)s has shown remarkable effect on simultaneously improving the solubility and thermal stability of the resins.[30,31] However, little attention has been paid on the modification of phthalonitrile resins with silicon-containing structures.

In this work, a series of silicon-containing phthalonitrile (SiPN) resins have been synthsized by a convenient aminolysis reaction of 4-(4-aminophenoxy)phthalonitrile (APN) with corresponding chlorosilanes under mild reaction condition. Best to our knowledge, this is the first report about silicon-containing phthalonitrile derivatives. Compared to the self-catalyzed APN, these new SiPN monomers still can polymerize in absence of any catalyst and exhibit better solubility in the common solvents such as acetone and tetrahydrofuran (THF). The introduction of silicon-containing units also dramatically decreases the melting point of the monomer and enhances thermal properties of the polymer, which will further expand the application of phthalonitrile resins. The detailed synthesis, characterization, and curing of the new compounds as well as thermal analysis of the new phthalonitrile resins have been described.

EXPERIMENTAL

Material

All manipulations in the experiments were performed under nitrogen atmosphere. APN was synthesized in our laboratory.[32] Due to the superior thermal property and processability, APN monomer with amino group in para position was selected in this study. Dimethyldichlorosilane, methylvinyldichlorosilane, and methyldichlorosilane were purchased from ACROS and used as received. All solvents were purchased from Beijing Chemical Co. Triethylamine (Et_3N) was distilled from calcium hydride and THF was dried by 4A molecular sieve prior to use.

Measurements

Fourier Transform Infrared Spectroscopy (FTIR) spectra were recorded on a Bruker Tensor-27 FTIR spectrometer in the wavenumber range of 400–4000 cm^{-1} with KBr pellets. Differential scanning calorimetry (DSC) was performed on a SII EXTRA 6200 instrument in flowing nitrogen (50 mL min^{-1}) at a heating rate of 10°C min^{-1}. Thermogravimetric analysis (TGA) was carried out on a SII EXSTAR TG/DTA6300 instrument in flowing nitrogen or air atmosphere (200 mL min^{-1}) at a heating rate 10°C min^{-1}. Proton Nuclear Magnetic Resonance (^{1}H-NMR) spectra were recorded in $CDCl_3$ solution with a Bruker AVANCE 400 spectrometer at 400 MHz. ^{29}Si-NMR spectra were recorded in $CDCl_3$ solution with Bruker DMX 300 spectrometer at 300 MHz. Dynamic mechanical analysis (DMA) was performed on a NETZSCH DMA 242c in flowing nitrogen (50 mL min^{-1}) with a heating rate of 5°C min^{-1} and a frequency of 1.0 Hz. A three-point bending mode was used with specimen size of 20.0 mm × 5.0 mm × 1.5 mm.

Synthesis of Silazane-Containing Phthalonitrile Monomer

Silicon-containing self-catalyzed phthalonitrile derivatives (SiPNs) with silicon-containing units in the backbone of phthalontirle monomers were prepared by aminolysis reaction of chlorosilanes with APN (Scheme 1). This is an exthomeric reaction, which can smoothly proceed at low temperature of 35°C. To avoid the hydrolysis of chlorisilanes, inert atmosphere is necessary.

Synthesis of MeSiPN Monomer.

All reactions were carried out under nitrogen atmosphere. APN (4.704 g, 20 mmol) was dissolved in THF/ Et_3N (90/30 mL) mixed solvent at room temperature. First, a solution of 1.2 mL (10 mmol)
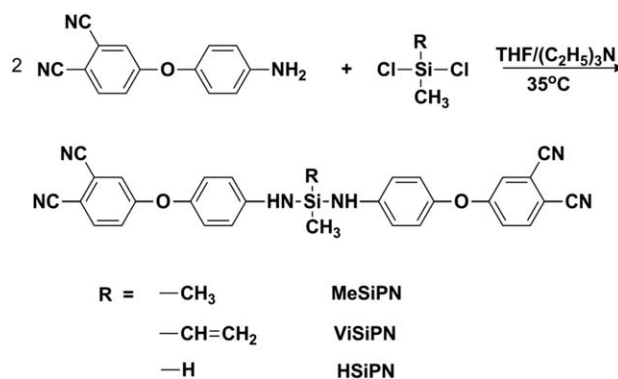
Scheme 1. Synthesis of MeSiPN, ViSiPN, and HSiPN.

dimethyldichlorosilane in 30 mL THF was added dropwise into the APN solution. After the completion of the addition, the mixture was stirred at 35°C for 12 h. Then, the reaction mixture was filtered and concentrated under reduced pressure. To remove the THF completely, the obtained sample was further dried at 110°C for 1 h. Finally, a brown solid product was obtained in 72% Yield. mp: 59°C; ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.68 (d, J = 9.1 Hz, 2H), 7.29–7.17 (m, 4H), 6.91–6.79 (m, 8H), 3.83 (s, 2H), 0.48 (s, 6H); ^{29}Si-NMR (300 MHz, $CDCl_3$, δ): −11.92; IR (KBr, v cm^{-1}): 3375 (N—H), 2232 (C≡N), 1608, 1504 (C=C), 1314 (C—N), 1278 (Si—C), 1250 (C—O—C), 1087 (Si—N).

Synthesis of ViSiPN Monomer.

ViSiPN was synthesized essentially in the similar manner as described for MeSiPN by the reaction of methlvinyldichlorosilane (10 mmol) and APN (20 mmol) in 74% yield as a brown solid. mp: 40°C; ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.68 (d, J = 8.3 Hz, 2H), 7.28–7.17 (m, 4H), 6.86(d, J = 8.8Hz, 8H), 6.37–6.19(m, 3H), 3.88(s, 2H), 0.54 (s, 3H); ^{29}Si-NMR (300 MHz, $CDCl_3$, δ): −21.45; IR (KBr, v cm^{-1}): 3375 (N—H), 2232 (C≡N), 1608,1505 (C=C), 1314 (C—N), 1279 (Si—C), 1250 (C—O—C), 1087 (Si—N).

Synthesis of HSiPN Monomer.

HSiPN was synthesized in the similar manner as described for MeSiPN by the reaction of methyldichlorosilane (10 mmol) and APN (20 mmol) in 73% yield as a brown solid. mp: 43°C; ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.69 (d, J = 8.3 Hz, 2H), 7.28–7.17 (m, 4H), 6.96–6.81 (m, 8H), 5.11 (s, J = 22 Hz, 1H), 3.90 (s, 2H), 0.55 (d, J = 2.2 Hz, 3H); ^{29}Si-NMR (300 MHz, $CDCl_3$, δ): −28.14; IR (KBr, v cm^{-1}): 3377 (N—H), 2233 (C≡N), 2168 (Si—H), 1608,1508 (C=C), 1314 (C—N), 1280 (Si—C), 1250 (C—O—C), 1088 (Si—N).

Curing of the Monomers

To compare the thermal property of SiPNs and APN, the SiPNs were cured with the reported heating profile of APN: 170°C for 1 h, 200°C for 1 h, 250°C for 5 h, 315°C for 5 h, and 375°C for 5 h in an argon-circulation oven.[32] The weight loss during the curing process of MeSiPN, ViSiPN, HSiPN, and APN were 3.6, 4.3, 7.4, and 7.0%, respectively.

To determine the glass transition temperature of the cured polymers, the quartz fiber reinforced SiPNs and APN composites were prepared using the following procedures: the resins were spread evenly over 10 quartz fiber cloths of 40.0 mm × 20.0
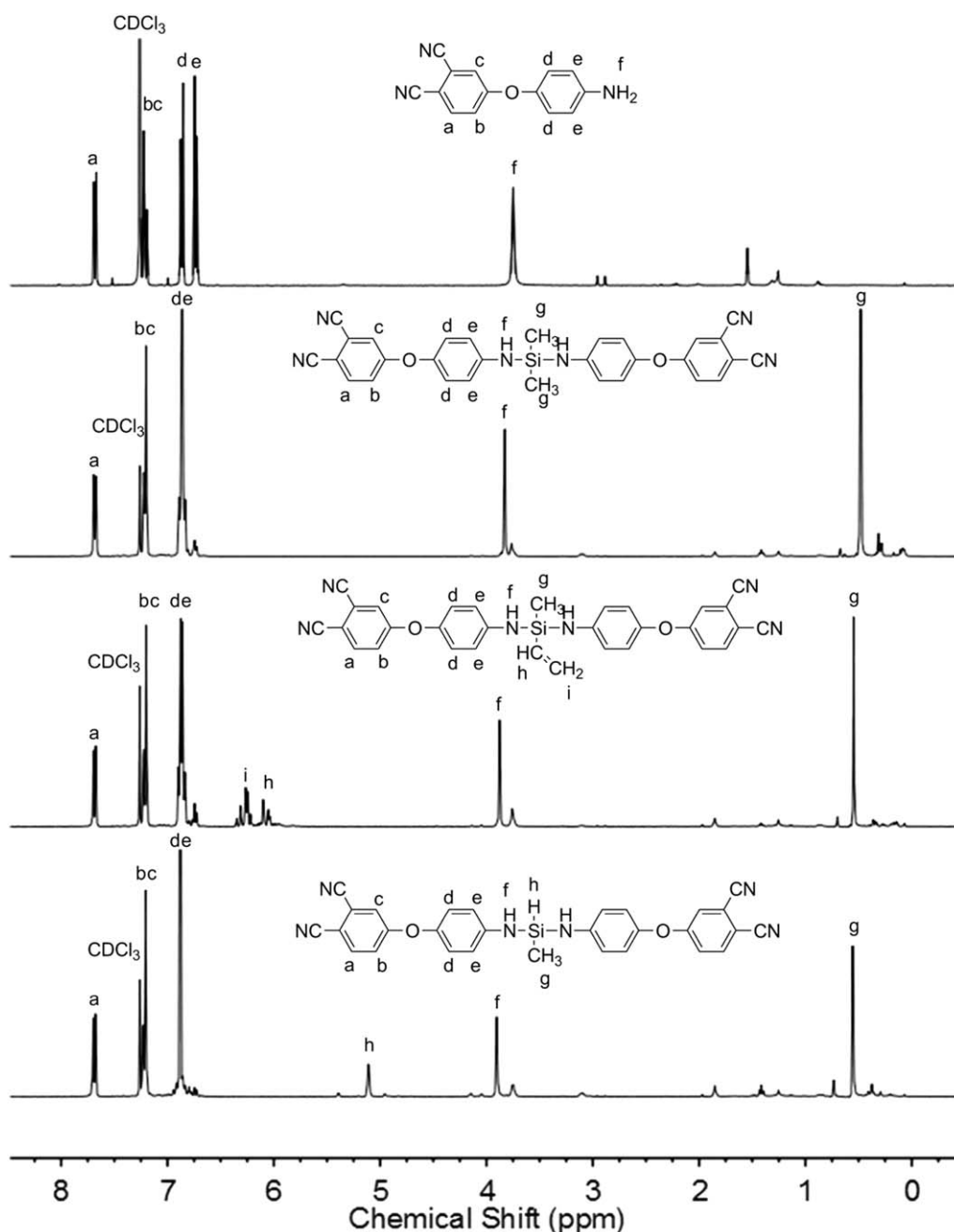
Figure 1. ^{1}H-NMR spectra of SiPNs and APN.

mm × 1.8 mm. A stack of the resin coated fabrics was then cured in a closed steel mold at a pressure of 0.7 MPa by the follow heating profile: 170°C for 1 h, 200°C for 1 h, 250°C for 5 h, 315°C for 5 h, and 375°C for 5 h in an argon-circulation oven. The cut composite sample with size of 20.0 mm × 5.0 mm × 1.5 mm was used for DMA test. The weight percentage of the resin in the final composites was about 40%.

RESULTS AND DISCUSSION

Characterization of Monomers

The structure of all the synthesized monomers was confirmed by ^{1}H-NMR and ^{29}Si-NMR spectra (Figures 1 and 2). In the

^{1}H-NMR spectra, the characteristic peak at 4.10 ppm is corresponding to primary amine (—NH$_2$) protons of APN, and other peaks at 3.82, 3.88, and 3.91 ppm are assigned to secondary amine (=NH) of MeSiPN, ViSiPN, and HSiPN. The characteristic peak at 0.54 ppm for MeSiPN is attributed to the Si—CH$_3$, peaks ranged from 6.04 to 6.34 ppm are assigned to Si—CH=CH$_2$ of ViSiPN, and the characteristic peak at 5.11 ppm for HSiPN is attributed to the Si—H. In the ^{29}Si NMR spectra, the characteristic peaks appear at −11.92, −21.45, and −28.14 ppm for MeSiPN, ViSiPN, and HSiPN, respectively. These results prove that the silicon-containing units have been successfully introduced into the phthalontirle structure.
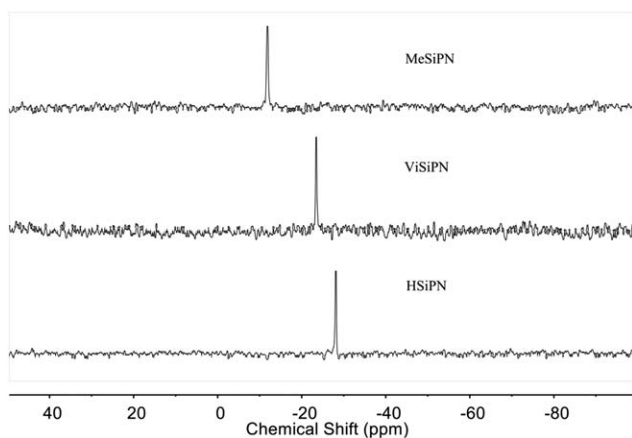
Figure 2. ^{29}Si-NMR spectra of SiPNs.

Figure 3. DSC thermograms of APN, MeSiPN, ViSiPN, and HSiPN.

The solubility of the SiPNs and APN were tested in different solvents, and the results were summarized in Table I. All the compounds show excellent solubility in strong polar solvent such as acetone (Acet.) and dimethylformamide (DMF). While, the SiPNs exhibit better solubility than APN in the weak polar solvents, such as chloroform (THMS), diethylamine (DEA), and ethyl acetate (EA). It is shown by the results that the solubility of the phthalonitrile monomers is improved evidently after the introduction of silicon-containing units into APN.

Curing Behavior

Polymerization studies of SiPNs and APN were carried out by DSC analysis from 20 to 400°C at a heating rate of 10°C min^{-1} in nitrogen atmosphere (Figure 3). From the DSC curves, we can find that all the monomers exhibit obvious endothermic peaks, which is attributed to the characteristic melting transition. It is also apparent that the melting point of SiPNs, which is below 60°C, is lower than that of APN, 135°C. Due to the effect of silicon-containing units, this is the lowest melting point of the reported phthalonitrile derivatives. Meanwhile, the exothermic peaks between 249 and 282°C of the monomers are attributed to the self-catalyzed reaction, which involves the triazine ring formation from the cyclotrimerization of phthalonitrile via its cyano groups. It can be observed from the DSC thermograms that the exothermic peak temperature of SiPNs is slightly higher than that of APN by 6–33°C. This is because that the basicity of —NH— in the new monomers is lower than that of —NH$_2$ in APN, which is owing to the electron withdrawing (d-p)π conjugated effect derived from the occupation of the empty 3d orbit of Si atom by the lone electron pair of N atom.

For the three silicon-containing monomers, the temperature of exothermic peak owing to the formation of triazine is different with HSiPN at 255°C, ViSiPN at 271°C, and MeSiPN at 282°C. Due to the smallest steric hindrance of organic group attached to the Si atom, HSiPN shows lower curing temperature than MeSiPN and ViSiPN. As the electron donating (d-p)π conjugated effect derived from vinyl structure and Si atom, the ViSiPN possesses stronger basic property than MeSiPN. Therefore, the exothermic peak temperature of ViSiPN is lower than that of MeSiPN. Besides, due to the overlap of addition reaction of the vinyl groups and curing reaction of cynao groups, a shoulder peak is found in the DSC curve of ViSiPN and the exothermic enthalpy of ViSiPN during curing is evidently higher than that of MeSiPN and HSiPN (Table II).[33] Considering the contribution of vinyl addition reaction to the exothermic enthalpy of ViSiPN, the heat enthalpy due to the self-catalyzed reaction of all the SiPNs is smaller than that of APN. This phenomenon implies the SiPNs have lower self-catalyzed activity than APN, which is coincided with our discussion about the basicity change from —NH$_2$ in APN to —NH— in SiPNs.

It should be noted here that the DSC thermograms of HSiPN shows another broaden exothermic peak at 373°C aside from the peak at 255°C attributed to the reaction of cyano groups. We speculated that the broadened exothermic process is owing to the dehydrogenation reaction between the Si—H and N—H bonds in the molecular structure (Scheme 2), which is confirmed by the FTIR spectra for HSiPN monomer, cured HSiPN heated at 315°C and cured HSiPN heated at 375°C in nitrogen atmosphere. As shown in Figure 4, the intensity of Si—H

Table I. The Solubility of the New Phthalonitrile Monomers and APN

Sample	DMF	Acet.	CH$_2$Cl$_2$	THMS	DEA	EA
MeSiPN	++	++	++	++	++	++
ViSiPN	++	++	++	++	++	++
HSiPN	++	++	++	++	++	++
APN	++	++	+	+−	+−	+

Solubility (20°C) ++: soluble; +: partly soluble; +−: slightly soluble

Table II. Characteristic Data of APN, MeSiPN, ViSiPN, and HSiPN Obtained from DSC Curves

Monomer	Exothermic peak (°C)	Heat enthalpy (mJ/mg)
MeSiPN	282	98.9
ViSiPN	271	158.0
HSiPN	255,373	97.0, 71.9
APN	249	107.5
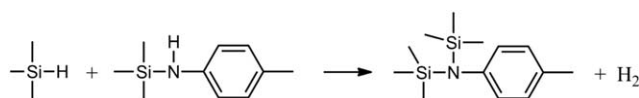
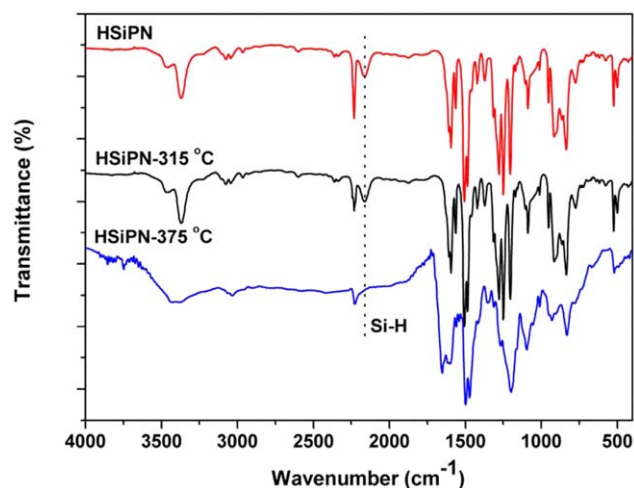**Scheme 2.** The dehydrogenation reaction of HSiPN.

Figure 4. FTIR spectra of HSiPN, HSiPN cured at 315°C and HSiPN cured at 375°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

characteristic absorption peak remains almost unchanged after heating treatment at 315°C for the monomer, while the intensity of cyano groups decreases. But after the curing process at 375°C, the peak belonging to Si—H groups is negligible. Besides, the weight loss during curing process of the three SiPNs provides further evidence for this speculation. Because of the dehydrogenation reaction, the HSiPN exhibits the highest weight loss, 7.4%, while for MeSiPN and ViSiPN, the weight loss is only 3.6 and 4.3%, respectively.

Characterization of Polymers

Figure 5 shows the FTIR spectra of the as-synthesized and cured SiPNs. The cynao characteristic absorption peak is observed in the FTIR spectra of as-synthesized SiPNs at about 2232 cm^{-1}. After cured, the intensity of nitrile peaks decrease, while two new peaks appear at 1354 and 1048 cm^{-1}, which is the characteristic adsorption peak of the triazine and phthalocyanine units formed during the reaction of cynao, respectively.[8] Therefore, although the curing reaction temperature of the silicon-containing monomers is higher than that of APN, the as-synthesized new phthalonitrile resins still possess self-promoted curing property.

Additionally, the vinyl characteristic absorption bands of ViSiPN are all overlapped with that of phenyl groups. Therefore, we cannot find the characteristic absorption bands only assigned to Si—CH=CH$_2$. However, it can be observed from the FTIR spectra that ViSiPN has a stronger absorption peak than MeSiPN and HSiPN at 1010 cm^{-1} due to rocking vibration of =C—H bonds. After cured, the intensity of peaks at 1010 cm^{-1} of the three different silicon-containing monomers are similar, indicating that the vinyl groups goes through thermal crosslinking reaction when heated.
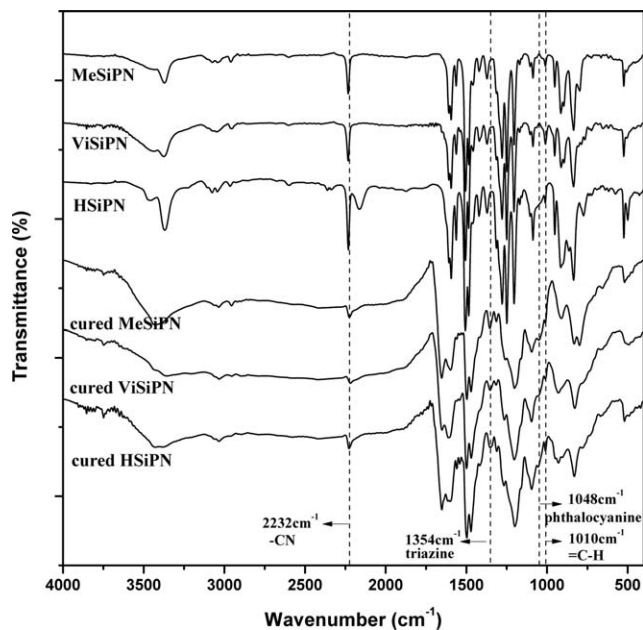

Figure 5. FTIR spectra of the uncured and cured SiPNs.

Thermal Properties of the Polymers

The thermal and thermo-oxidative stabilities of the cured SiPNs and cured APN were studied by TGA in nitrogen or air atmosphere as shown in Figures 6 and 7. The characteristic data of thermal analysis for all investigated resins are summarized in Table III.

The results show that all the new polymers exhibit excellent thermal and thermo-oxidative stability. All the parameters, T_5, T_{10}, and Y_c of the cured SiPNs are higher than that of cured APN both in nitrogen and in air. Particularly, cured HSiPN has the highest T_5 and T_{10}, which are higher than those of APN by 51 and 116°C in nitrogen, 55 and 64°C in air, respectively. We believe that the inorganic Si—N crosslink structure in cured HSiPN formed by the dehydrogenation reaction is responsible for its excellent thermal stability. For ViSiPN, as the addition reaction of vinyl groups induced by heat will increase the crosslinking density of cured ViSiPN, it shows higher T_5 and T_{10}
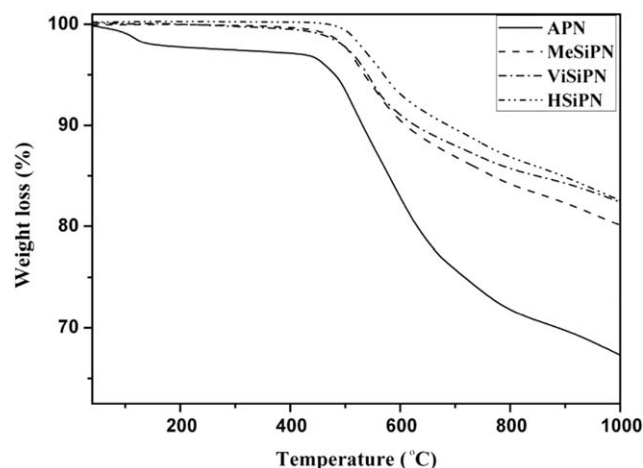

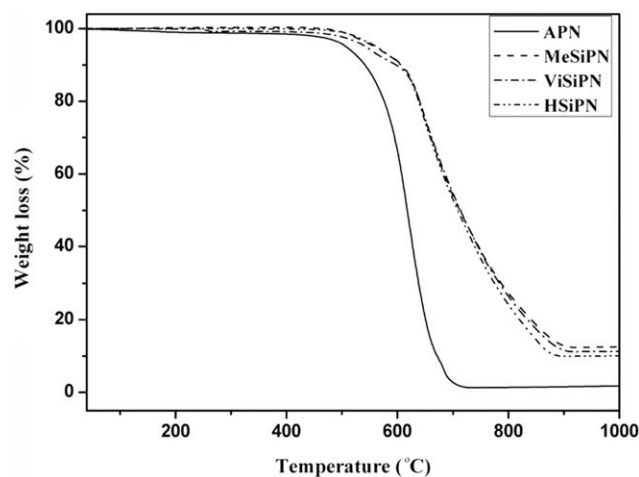**Figure 6.** TGA curves of cured SiPNs and APN in nitrogen.

Figure 7. TGA curves of cured SiPNs and APN in air.

Figure 8. Storage modulus (E') as a function of temperature for cured samples.

than MeSiPN. However, the —C—C— chain derived from vinyl groups is less stable than the Si—C and Si—N bonds in the air. Therefore, cured ViSiPN exhibits the lowest thermal oxidation stability among the three new silicon-containing polymers. Besides, introduction of silicon-containing units to APN has also increased the char yield in the air of the cured phthalonitrile polymers, which may be due to the formation of silica by oxidation of silicon-containing structure.

DMA Results

DMA is conducted to evaluate the samples' modulus as a function of temperature and determinate the glass transition temperature (T_g) of the composite. As shown in Figure 8, the initial storage modulus (E') of cured SiPNs are in the range of 3050–4000 MPa and, whereas the cured APN composites shows a lower storage modulus of about 3000 MPa. Besides, the E' of cured APN, MeSiPN, and ViSiPN do not show obvious decrease up to 448, 424, and 428°C, respectively. While, the E' of cured HSiPN exhibits distinct changing trend with the increase of temperature, which first goes down at 100°C, then reaches the lowest value of 3125 MPa at 250°C, and finally slowly rises up to the highest value of 4124 MPa at 458°C. As indicated from the DSC curve of HSiPN (Figure 3), a broad exothermic peak attributed to the dehydrogenation reaction exists between 300 and 425°C, which has been verified by the FTIR results of cured HSiPN at different temperature (Figure 4). Therefore, we speculated that the remaining dehydrogenation reaction of HSiPN

accounts for the change trend of the storage modulus of cured HSiPN. Meanwhile, T_g is a very important parameters and estimated on the basis of the peak temperatures tan δ curves. Since there is no peak found in the tan δ curves of all the samples in the measured temperature range (Figure 9), it can be concluded that all the cured SiPNs possess T_g above 450°C.[32,34,35]

CONCLUSIONS

A series of SiPNs were prepared and characterized. The monomers can be thermally polymerized in the absence of any catalysts. The introduction of the silicon-containing units makes the new compounds possess low melting temperature and excellent solubility. After the curing, the resulting polymers exhibit exceptional thermal and thermo-oxidative stability in both nitrogen and air atmosphere. This convenient synthesis method for preparing silicon-containing phthalonitrile shows potentials for modification of other self-catalyzed phthalonitrile resins with amino and hydroxy groups in their structure, especially, those with higher melting point and worse solubility. Additionally, synthesis of chloride-terminated siloxanes and silazanes has well

Table III. Thermal Properties of the Cured Silicon-Containing Monomers and APN

Polymers	In nitrogen			In air		
	T_5 (°C)	T_{10} (°C)	Y_c (%)	T_5 (°C)	T_{10} (°C)	Y_c (%)
APN	519	572	75.1	507	542	1.8
MeSiPN	535	610	80.2	558	607	12.5
ViSiPN	541	627	82.4	543	597	11.3
HSiPN	570	687	82.6	562	606	10.1

T_5: Decomposition temperature at 5% weight loss; T_{10}: Decomposition temperature at 10% weight loss; Y_c: Char yield at 1000°C
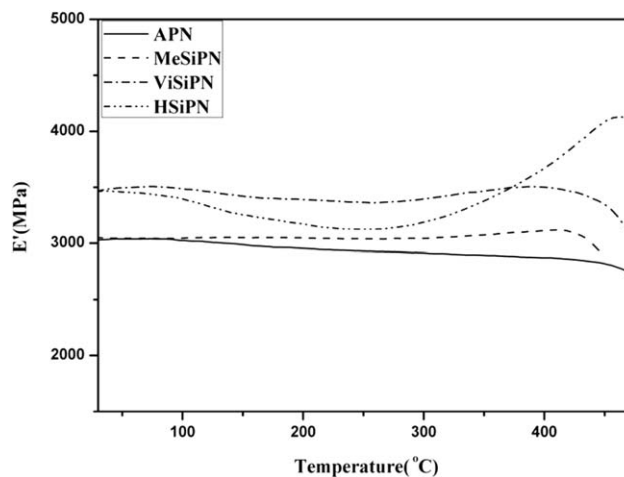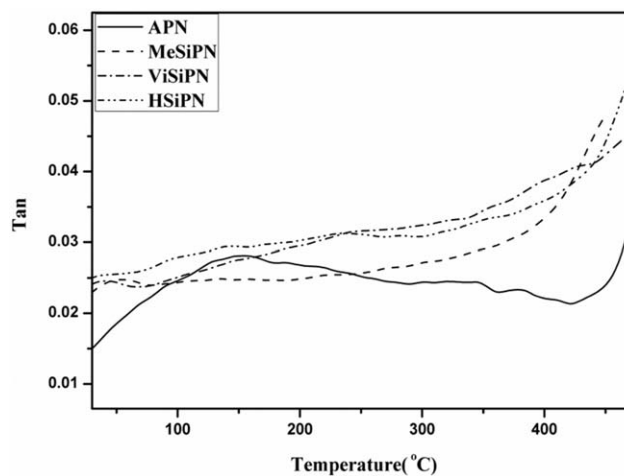

Figure 9. Damping factor (tan δ) as a function of temperature for cured samples.

reported, which provides more possibilities to modify the self-catalyzed phthalonitrile resins.

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