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Synthesis, characterization, and properties of novel phenylene-silazane-acetylene polymers

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New phenylene-silazane-acetylene polymers, **P1** and **P2**, have been synthesized using Sonogashira cross-coupling reactions with a new designed ethynyl-ended silylenediamine, N,N′-bis(4-ethynylphenyl)-1,1-diphenylsilylenediamine (**1**), as the key monomer. This also represents the first example that construction of polymers containing silazane unit with Sonogashira coupling reaction. The structures of monomer and polymers were well characterized. Their thermal properties were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Both polymers had good thermal stability with their temperatures at 5% weight loss (T_{d5}) being higher than 394 °C under nitrogen and higher than 385 °C in air, respectively. Their char yields at 1000 °C under N_2 were above 70%. The fundamental photophysical properties in solution were also investigated. Both polymers showed fluorescence in ultraviolet region with moderate quantum yields. These polymers had potential to be used as high-temperature resistant resins and light-emitting materials with good thermal stability.

1. Introduction

Polymers based on the arylene, acetylene, and silicon-containing unit have been the subjects of intensive and varied interest in recent years. These polymers show high potential application in the microelectronic and aerospace industries, as processable light-weight, highly heat-resistant materials [1]. A vast of research related to such polymers has contributed to silylene-phenylene-acetylene polymers [2] (Scheme 1, a, b) and silarylene-siloxane-acetylene polymers (Scheme 1, c) [1a,3], which containing Si—C and Si—C/Si—O bonds in their main chains, respectively. Silylene-phenylene-acetylene polymers composed of an alternating arrangement of organosilicon, aromatic, and acetylene or diacetylene units display high potential as functional materials for optoelectronics [4] and high-temperature resistant thermosetting resins [5], while silarylene-siloxane-acetylene polymers containing flexible siloxane units in the main chain exhibit fascinating properties as high-temperature elastomers or resins [6]. The silicon-containing unit is generally monosilylene or multisilylene motif in silylene-phenylene-acetylene polymers [2,4a], and disiloxane motif in silarylene-siloxane-acetylene polymers [3,6]. That is, silicon-containing unit is directly connected with acetylene and/or arylene unit through Si—C bond in these polymers.

As an important class of chemical bonds to construct silicon-containing polymers, Si—N bond has been widely studied and various polymers based on the bond have been synthesized [7]. However, little attention has been paid on the polymers including Si—N bond and acetylene unit in backbone, the known examples were poly[(silylene)acetylene silazanes] (Scheme 1, d) and poly[(silylene)diacetylene silazanes] (Scheme 1, e) reported by Xie and co-workers [8]. As for polymer containing Si—N bond, arylene, and acetylene unit in main chain, to the best of our knowledge, there is no report.

On the other hand, Sonogashira cross-coupling reactions [9] have been widely used in the preparation of conjugated polymers containing acetylene and silylene units [4], we recently have also found the coupling reaction offer a convenient way of preparing silarylene-siloxane-acetylene polymers under mild conditions [10]. However, there is no report on construction of polymers containing Si—N bond using the reaction. On the basis of design and synthesis of a new ethynyl-terminated silylenediamine monomer, we have successfully achieved the first example of polymers containing Si—N bond, phenylene, and acetylene unit in main chain, namely, phenylene-silazane-acetylene polymers, by the cross-coupling reaction. This article is concerned with the synthesis, characterization, thermal analysis, and fundamental photophycical properties of the new polymers. Compared with the reported partly conjugated

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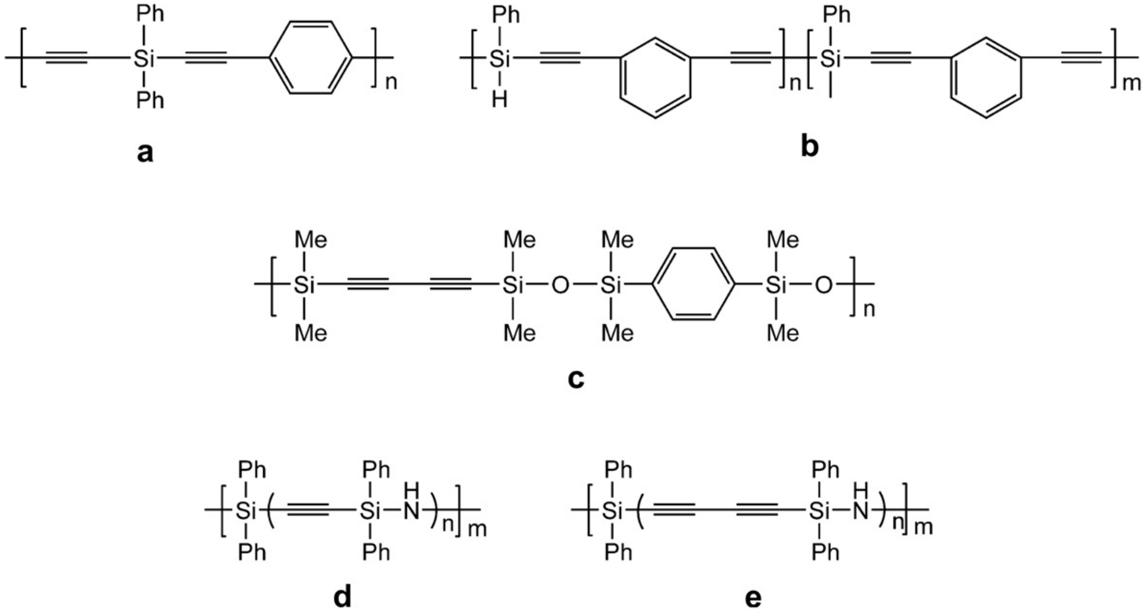


Scheme 1. Representative acetylene-containing organosilicon polymers.

polymers containing Si—N bond, the new polymers exhibit better environmental stability and thermal stability. They have potential to be used as high-temperature resistant resin, precursor for SiC/Si_3N_4 ceramic or light-emitting materials with good thermal stability.

2. Experimental

2.1. Materials

All manipulations in the experiments were performed under an inert atmosphere of nitrogen. Dichlorodiphenylsilane (Ph_2SiCl_2) was purchased from ACROS and used as received. 4-Ethynylaniline was prepared according to literature procedure [11]. All solvents were purchased from Beijing Chemical Co. Hexane, tetrahydrofuran (THF) and toluene were freshly distilled from sodium/benzophenone ketyl before use. Triethylamine (Et_3N) was distilled from calcium hydride prior to use. All other chemicals were purchased from Alfa Aesar and used as received.

2.2. Characterization methods

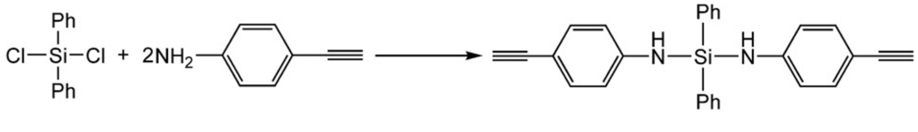
^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 spectrometer at frequency of 400 MHz in $CDCl_3$, DMSO-d_6 or acetone-d_6. ^{29}Si NMR spectra were recorded with a Bruker DMX 300 spectrometer at frequency of 300 MHz in acetone-d_6. Melting point (mp) determination was performed using a WRS-1A digital melting point apparatus. Elemental analysis was obtained with the FLASH EA1112 Microanalytical analyzer. Fourier transfer infrared spectra (FT-IR) were recorded with a Bruker TENSOR-27 IR spectrometer in the wave number range of 4000–400 cm^{-1} using standard procedures. Fourier transfer Raman spectra (FT-Raman) were recorded with a Bruker RFS100/s Raman spectrometer in the wave number range of 3600–400 cm^{-1}. Matrix-assisted laser desorption ionization time-of-flight (MALDI–TOF) mass spectra were obtained using a Bruker Biflex III MALDI–TOF mass spectrometer, equipped with delayed extraction, a multisampling probe, a TOF reflectron analyzer, a nitrogen laser with wave-length 337 nm and pulse width 3 ns, and a linear flight path length of 100 cm. The flight tube was evacuated to 10^{-7} Pa. All measurements were performed in linear mode and positive ion detection. The acceleration voltage was 19 KV and the delayed extraction voltage was 14.5–17 KV. Average Molecular weights were estimated by a gel permeation chromatography (GPC) analysis with polystyrene standard calibration using a WATERS 1515 Isocratic HPLC pump and WATERS 2414 refractive index detector equipped with HR_4 column at 35 °C in THF. Differential scanning calorimetry (DSC) measurements were performed on a SII EXTRA 6200 DSC in flowing nitrogen (50 mL/min) at a heating rate of 10 °C/min. Thermogravimetric analyses (TGA) were performed on a SII EXTRA 6300 TG/DTA at a heating rate of 10 °C/min under nitrogen or air atmosphere. UV–vis absorption and fluorescence spectra were measured at room temperature with a Shimadzu UV-1601PC spectrometer and a Hitachi F4500 spectrometer, respectively.

2.3. Synthesis of N,N′-bis (4-ethynylphenyl)-1, 1-diphenylsilylenediamine (***1***)

A solution of 9.10 g (0.036 mol) dichlorodiphenylsilane in 50 mL dry THF was added dropwise into a mixture of 8.42 g (0.072 mol) 4-ethynylaniline, 50 mL THF, and 100 mL Et_3N at 85 °C. After completion of dropping, the reaction mixture was further stirred for 18 h at the temperature. Then, the reaction mixture was filtered and concentrated. The obtained yellow powder was recrystallized from a mixed solvent of hexane and THF ($v/v = 60/40$) to give 13.70 g (0.033 mol) of compound **1** in 92% yield as a gray white powder. mp 168–170 °C, ^1H NMR (400 MHz, acetone–d_6): $\delta = 3.37$ (s, 2H), 5.94 (bs, 2H), 7.03 (d, $J = 11.4$Hz, 4H), 7.15 (d, $J = 11.4$Hz, 4H), 7.36–7.44 (m, 6H), 7.77 (m, 4H). ^{13}C NMR (400 MHz, acetone–d_6): $\delta = 147.83$, 134.73, 133.86, 133.17, 130.46, 128.26, 117.54, 111.96, 84.25, 76.12. ^{29}Si NMR (300 MHz, acetone–d_6): $\delta = -32.76$. Anal. Calcd. for $C_{28}H_{22}N_2Si$: C, 81.12; N, 6.76; H, 5.35. Found: C, 80.61; N, 6.84; H, 5.39.

2.4. A typical procedure for the synthesis of the polymers: polymer ***P1***

A mixture of 198.0 mg (0.48 mmol) **1**, 157.8 mg (0.48 mmol) 1,4-diiodobenzene, 6.7 mg (9.6 μmol) $Pd(PPh_3)_2Cl_2$, 3.6 mg (19 μmol) CuI in a 3/1 toluene/Et_3N mixed solvent (40 mL) was stirred at room temperature for 24 h. Then the reaction mixture



1 92%

Scheme 2. Synthesis of new silylenediamine containing terminal ethynyl. Condition and reagents: THF, Et_3N, 85 °C, 18 h.

was washed with brine, extracted with chloroform. The organic layer was dried over magnesium sulfate anhydrous, filtered, and concentrated under reduced pressure until about 3 mL of yellow solution was remained. Then, the concentrated solution was added dropwise into 90 mL of vigorously stirred *n*-hexane to form a yellow precipitation. After filtration, the solid was dried in vacuum to give 180 mg of polymer **P1** in 77% yield as a gray yellow powder. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 4.33$ (bs, 2H), 6.75–6.82 (m, 4H), 7.16–7.26 (m, 4H), 7.38–7.46 (m, 9H), 7.62–7.72 (m, 5H). ^{13}C NMR (400 MHz, DMSO-d_6): δ = 148.06, 137.46, 134.45, 133.60, 132.78, 132.27, 131.15, 130.26, 128.13, 122.52, 117.40, 110.91, 92.44, 87.20.

2.5. *Synthesis of polymer P2*

Polymer **P2** was synthesized essentially in the same manner as described for **P1** by the reaction of compound **1** and 1,3-diiodobenzene in 85% yield as an off-white solid. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ: 4.33(bs, 2H), 6.80–6.82 (m, 4H), 7.23–7.26 (m, 4H), 7.31–7.51 (m, 9H), 7.56–7.60 (m, 1H), 7.70–7.72 (m, 4H), ^{13}C NMR (400 MHz, DMSO-d_6, ppm) δ: 148.05, 138.93, 134.46, 133.60, 133.04, 132.32, 130.38, 130.25, 129.16, 128.13, 123.60, 117.40, 110.83, 91.23, 86.53.

3. Results and discussion

3.1. *Synthesis and characterizations*

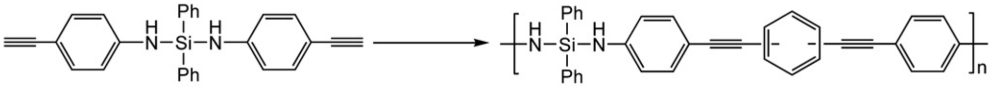
4-Ethynylaniline used in the present investigation was synthesized according to the reported method. The new silylenediamine **1** containing terminal ethynyl groups was synthesized by aminolysis reaction of dichlorodiphenylsilane with 4-ethynylaniline, as shown in Scheme 2. Triethylamine was used as catalyst and acid (HCl) scavenger in the reaction.

The aminolysis reaction was very sensitive to reaction conditions. The choice of appropriate reaction temperature was very crucial for obtaining **1** in high yield. The reaction was monitored by ^1H NMR spectra, no target compound **1** was detected when the reaction proceeded under 50 °C even for 36 h. This can be attributed to lower reactivity of dichlorodiphenylsilane toward 4-ethynylaniline at lower temperature, due to steric effect of bulky phenyl groups attached to silicon atom in dichlorodiphenylsilane, and nitrogen atom in the aniline. Besides steric effects, also the low basicity of aniline, because of incorporation of nitrogen's free electron pair into π-system, contributes strongly to the lower reactivity. Increase of temperature was effective for the reaction, a small amount of **1** was formed after reaction of 36 h at 65 °C, and 92% yield was achieved using the optimized conditions (85 °C, 18 h). Compound **1** has good solubility in common organic solvents, such as THF, acetone, chloroform, and toluene. In addition, compound **1** has certain stability in air and no variation in its ^1H NMR spectrum was observed after storing it for 3 months under ambient laboratory conditions.

Polymers **P1** and **P2** were synthesized by Sonogashira cross-coupling reactions between monomer **1** and the requisite diiodobenzenes using $Pd(PPh_3)_2Cl_2$ and CuI as co-catalysts (Scheme 3). The polymerization reactions proceeded well under the common conditions for Sonogashira cross-coupling reaction. Thus, the reaction of monomer **1** with 1,4-diiodobenzene and 1,3-diiodobenzene produced *para*-phenylene units containing polymer **P1** and *meta*-phenylene units containing polymer **P2** in good yields, respectively. Polymer **P2** is easily soluble in common organic solvents, including chloroform, toluene, DMSO, and THF. Polymer **P1** shows poorer solubility than that of **P2** because of its more rigid main chain structure, however, it still can be dissolved in THF, DMSO, hot toluene, and hot chloroform.

The structures of the monomer and polymers were characterized using FT-IR, FT-Raman, and NMR spectroscopies. Fig. 1 Shows the FT-IR and FT-Raman spectra of **1**, **P1**, and **P2**. Monomer **1** shows strong characteristic bands around 2099 cm^{-1} and 3280 cm^{-1}, which are attributed to the absorption of $-C\equiv C-$ and $C\equiv C-H$ groups, respectively. The absorption band of $=N-H$ groups appears at 3375 cm^{-1}. While, in the FT-IR spectra of polymers **P1** and **P2**, the characteristic band of internal ethynylene $-C\equiv C-$ groups appears around 2206 cm^{-1}, and both peaks are relatively weak because of their symmetrical molecular structure [12]. The existence of $-C\equiv C-$ groups in the polymers is further proved by the strong peaks at 2206 cm^{-1} in their corresponding FT-Raman spectra. The absorption band of $=N-H$ groups in the polymers also appears at 3375 cm^{-1}. The absence of absorption around 3280 cm^{-1} suggested that no detectable terminal acetylene group in both polymers, and the same result was also confirmed by their ^1H NMR spectra (Fig. 2).

Figs. 2 and 3 show ^1H and ^{13}C NMR spectra of **1**, **P1**, and **P2**. In the ^1H NMR spectra, the characteristic peak at 2.94 ppm for monomer **1** is attributed to the terminal $C\equiv C-H$ groups. Broad single peak attributed to N–H appears at 4.33 ppm for monomer and both polymers. Peaks ranged from 6.7 to 7.8 ppm are assigned to protons of phenyl groups. In the ^{13}C NMR spectra, the terminal $C\equiv C$ carbons in monomer **1** appear at 76 and 84 ppm, while the internal $C\equiv C$ carbons in polymers appear at 87 and 92 ppm. Peaks ranged from 110 to 150 ppm are assigned to the carbons of phenyl rings. The ^1H NMR and ^{13}C NMR spectra confirm the structure and purity of the



P1 *p*-phenylene, 77%

P2 *m*-phenylene, 85%

Scheme 3. Synthesis of new phenylene-silazane-acetylene polymers. Condition and reagents: diiodobenzene, toluene, Et_3N, $PdCl_2(PPh_3)_2$, CuI, r.t., 24 h.

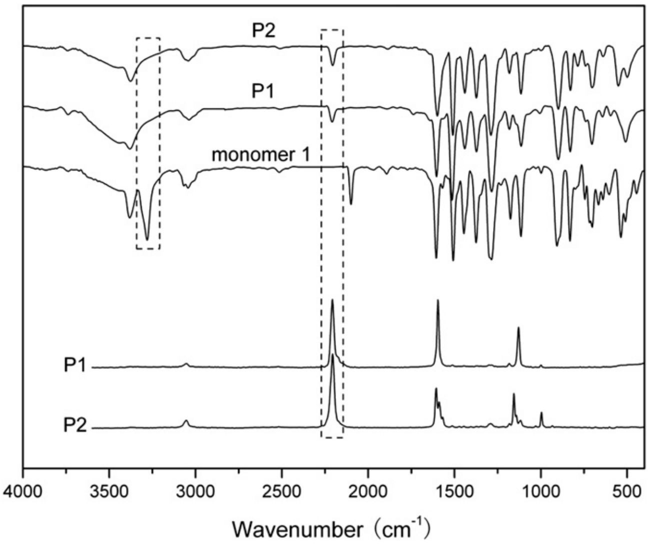


Fig. 1. FT-IR and FT-Raman spectra of monomer and polymers.

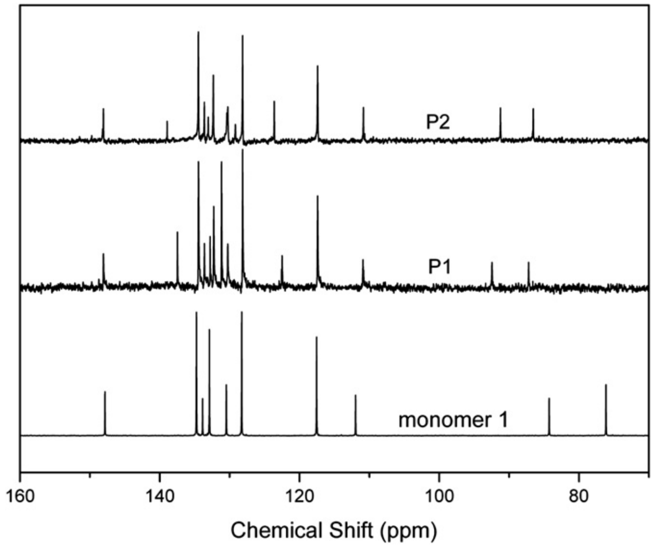


Fig. 3. ^{13}C NMR spectra of monomer and polymers.

monomer and polymers. Though they contain Si–N bonds, polymers **P1** and **P2** are very stable and no variation is observed in their ^{1}H NMR spectra (P1′ and P2′ in Fig. 2) after being washed many times with water or stored in air for four months at room temperature. This is due to the steric effects of three bulky phenyl groups surrounding each Si–N bond, which prevent the bond from being attack by water.

The average molecular weights of the polymers were estimated by GPC measurement using polystyrene standards. Fig. 4 shows the GPC traces of both polymers and the detailed data obtained from GPC analyses are listed in Table 1. The number average molecular weights (M_n) of **P1** and **P2** are 2.68×10^3 and 3.06×10^3, with their polydispersity distribution indexes (PDI) 1.28 and 1.32, respectively. Both polymers show relatively low M_n and narrow PDI.

MALDI–TOF mass spectra were utilized for further characterizing the molecular weight of polymers. Fig. 5 shows the molecular weight obtained from MALDI–TOF mass spectra, by which high molecular weight polymers also was not detected. This fact further confirmed that only polymers with low degree of polymerization ($n = 2–6$) were obtained under current conditions.

3.2. Thermal properties

3.2.1. DSC analysis

The thermal properties of the monomer and polymers were studied primarily by DSC analysis at a heating rate of 10 °C/min under nitrogen atmosphere. The DSC traces (in nitrogen) for **1** and both polymers are shown in Figs. 6 and 7, respectively. The DSC curve of **1** (Fig. 6) displays a sharp endothermic peak at 169 °C and a strong broad exothermic peak centered at 234 °C. The endothermic peak is due to melting of the compound, while the exothermic peak is attributed to thermal cross-linking reactions of ethynyl groups [13]. The shoulder of the exotherm begins immediately after melting. The high exothermic enthalpy (739 J/g) indicates high activity of terminal ethynyl groups in the monomer.

Fig. 7 shows the DSC traces of polymers **P1** and **P2**. Different from that of monomer, in the temperature range of 25–300 °C,

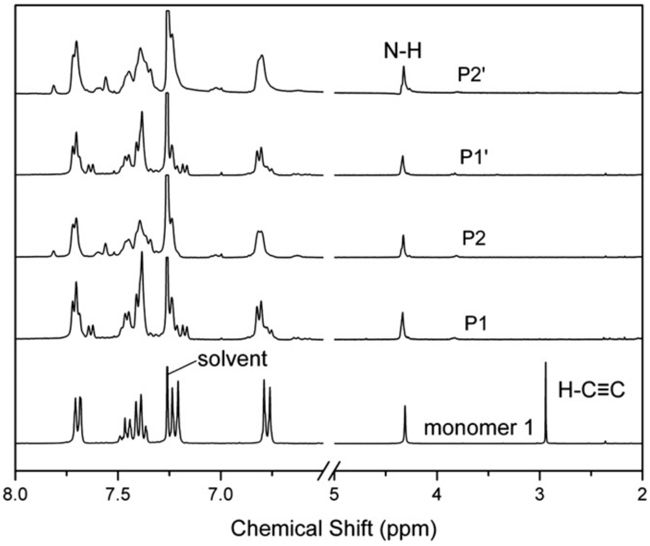


Fig. 2. ^{1}H NMR spectra of monomer and polymers.

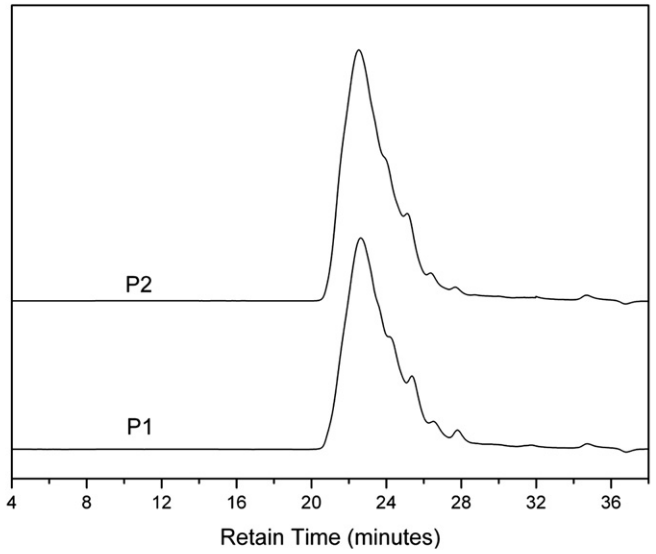


Fig. 4. GPC curves of polymers.

Table 1
Average molecular weights and polydispersity index of polymers.

Polymer	Yield[a] (%)	M_n[b]	M_w[b]	M_w/M_n
P1	77	2675	3431	1.28
P2	85	3064	4041	1.32

[a] After reprecipitation from *n*-hexane.
[b] Estimated by GPC in THF on the basis of a polystyrene calibration.

melting or glass transition (T_g) points were not observed for both polymers, and only broad exothermic peaks centered at 216 °C for **P1**, and 196 °C for **P2** were observed, respectively. In DSC traces, there might be a small step correspond to glass transition just before the broad exotherm for each polymer, however, it is difficult to be distinguished from the immediate exotherm. The exothermic transformation is related to a thermally induced cross-linking process involving internal ethynylene, which will irreversibly modify the backbone of the starting materials [14]. Significant broadening of the exothermic area indicates a slow cross-linking reaction [15].

Both polymers show lower exothermic peak temperature than that of monomer. This may be explained by the different micro-environment for cross-linking reactions of acetylene units between monomer and polymers. For both polymers, there is no melting points occurred before 160 °C, from which thermal cross-linking reaction started. Thus, the cross-linking reaction of polymers belongs to a solid-state type polymerization of acetylenes in an ordered crystalline-like phase [15,16]. However, the monomer **1** melts at 169 °C and thus undergoes thermal polymerization of acetylenes in a highly disordered amorphous state [15]. Considering reports that solid-state polymerization of acetylenes can occur even at room temperature and very easily at 80 °C [17], the lower exothermic temperature of the cross-linking reactions for both polymers than that of monomer is reasonable. The exothermic enthalpies of polymers (68, 75J/g for **P1** and **P2**, respectively) are rather lower than that of monomer, indicating that the polymers possess lower cross-linking activity. The peak temperature of **P1** corresponding to exothermic maximum is higher than that of **P2** by 20 °C, which is probably due to its more rigid backbone endued by *para*-phenylene units, meanwhile the *meta*-phenylene containing main chain of **P2** provides a favorable conformation for cross-linking reactions of acetylene units [18].

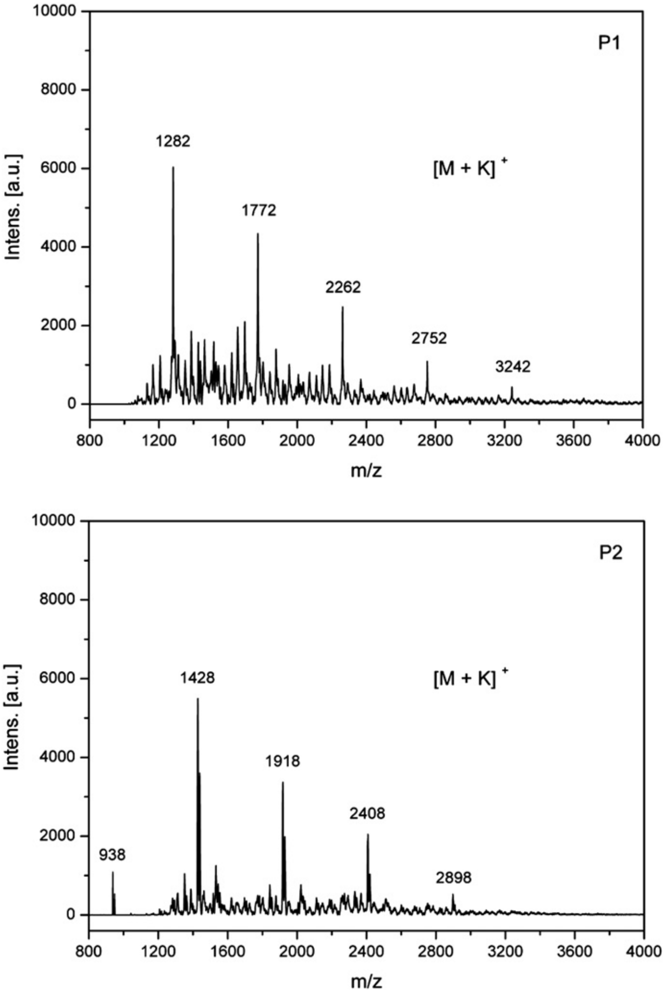


Fig. 5. MALDI-TOF mass spectra of polymers.

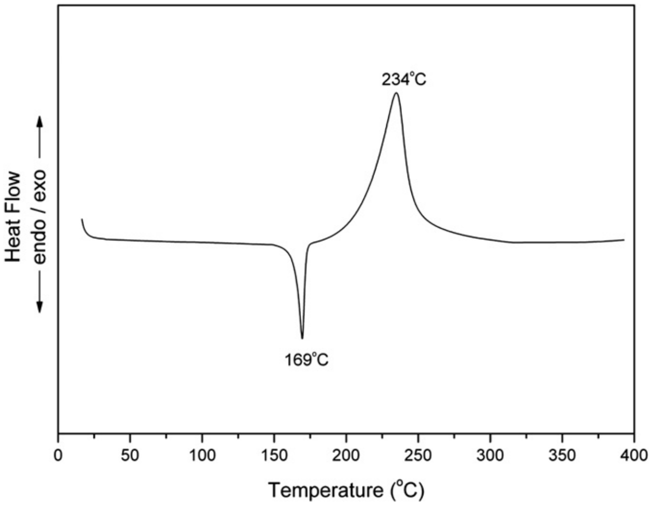


Fig. 6. DSC traces of monomer under nitrogen.

3.2.2. *TGA analysis*

Thermal degradation behavior of the monomer and polymers were investigated by TGA analyses under nitrogen or air atmosphere at a heating rate of 10 °C/min. The typical TGA thermograms

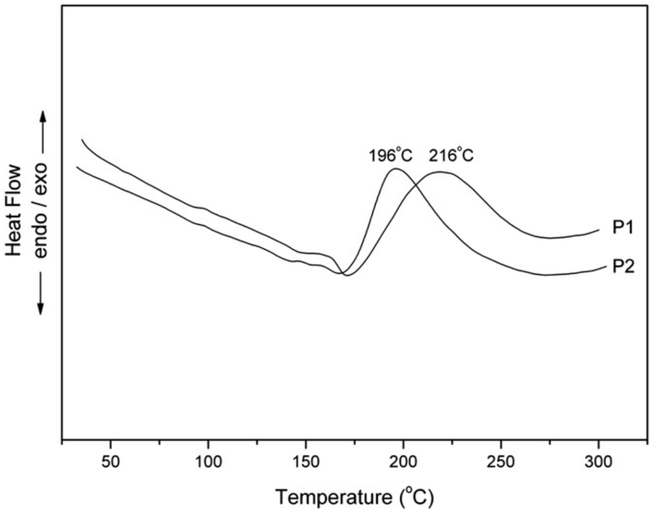


Fig. 7. DSC traces of polymers under nitrogen.

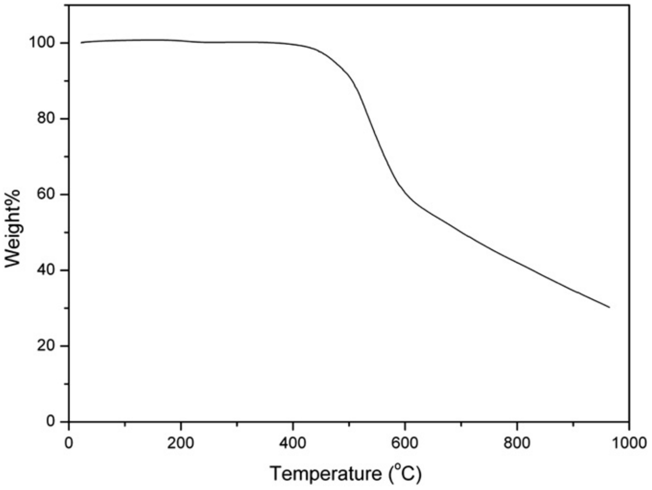


Fig. 8. TGA traces of monomer under nitrogen.

of **1** and polymers **P1**–**P2** are depicted in Figs. 8 and 9, respectively. The detailed thermal data obtained from the TGA analyses are summarized in Table 2.

The temperature of **1** at 5% weight loss (T_{d5}) in nitrogen is 474 °C (Fig. 8), which is higher than that of both polymers by more than 50 °C (Table 2). This may be attributed to higher reactivity of terminal acetylene groups in **1**, which resulted in a denser network by thermal cross-linking reactions in the temperature range of 180–280 °C, before decomposition. No weight loss was observed below 400 °C and the major weight loss occurred in the range of 450–800 °C. There was still obvious weight loss above 800 °C, and a relative low char yield of 30% at 1000 °C was obtained.

Under nitrogen and air atmosphere, polymers **P1** and **P2** exhibit the similar thermal stability. The T_{d5} of **P1** and **P2** under nitrogen are 394 °C and 420 °C, respectively (Fig. 9). Most of weight loss occurred between 400 and 700 °C was related to the extensive thermal degradation of crosslinked structure, which was formed during exothermic transformation of acetylene units [8b]. Both polymers have high char yields (>70%) at 1000 °C after pyrolysis in nitrogen, suggesting their potential use as precursors for Si/C/N based ceramics. It is interesting that the enormous difference in char yields upon pyrolysis in nitrogen between the monomer, which already includes all kinds of repeat units found in polymer, and the polymers. Although in both cases there are polymerizable acetylene groups, only in case of polymers, the polymerization of acetylenic groups leads to such a stabilized network that efficient carbonization is possible. This is closely related to the thermal polymerization of acetylenic groups and the crosslinked structure formed, which is being studied in our laboratory at present. Compared with the reported silazane-acetylene polymers [8], the T_{d5} of new phenylene-silazane-acetylene polymers are higher than that of the dimethyl or methyl and vinyl substituted polymers, but lower than that of the diphenyl substituted polymers. This is probably due to their different main chain structures and different thermal cross-linking mechanism, which significantly affects the structure and thermal stability of the crosslinked polymers.

Table 2
TGA data of monomer and polymers.

Compound/polymer	TGA in nitrogen		TGA in air	
	T_{d5} (°C)	weight% at 1000 °C	T_{d5} (°C)	weight% at 1000 °C
1	474	30.2	–	–
P1	394	72.4	386	13.9
P2	420	75.1	403	9.8

Under oxidative atmosphere (air), both polymers remained stable with no weight loss until 360 °C for **P1** and 380 °C for **P2**, respectively. The decomposition temperatures at 5% weight loss of **P1** and **P2** are 386 °C and 403 °C, respectively (Fig. 9). The abrupt weight loss started from about 500 °C and the weight had stabilized by 680 °C for **P1**, and 780 °C for **P2**, with their residue weight less than 20% at 1000 °C. More than 60% weight lost in the temperature range of 500–700 °C, which was mainly caused by the oxidation of the free carbon formed during pyrolysis of acetylene unit containing organosilicon polymers [14,15].

3.3. Photophysical properties

Fundamental photophysical properties of the new polymers were also investigated. UV–vis absorption and fluorescence emission spectra of the polymers in toluene are shown in Fig. 10 and their detailed photophysical data are summarized in Table 3. It is evidently observed that the introduction of *meta*-phenylene units into the polymer main chain results in significant shifts of the absorption and emission maxima to shorter wavelengths. As shown in Fig. 10, polymer **P1** containing *para*-phenylene units has its absorption maximum at 340 nm, while the absorption maximum of

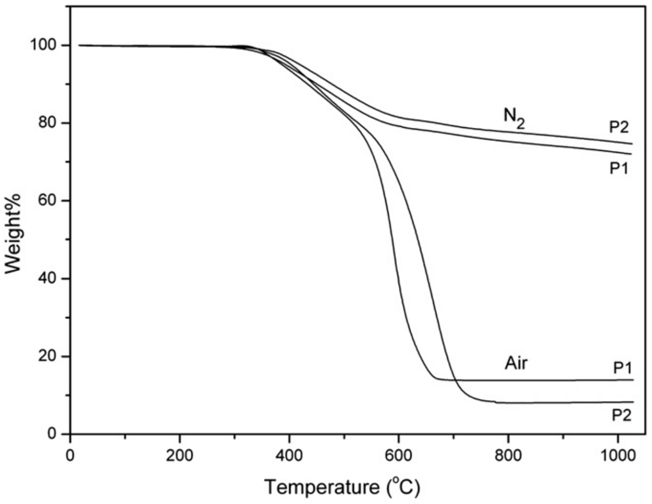


Fig. 9. TGA traces of polymers.

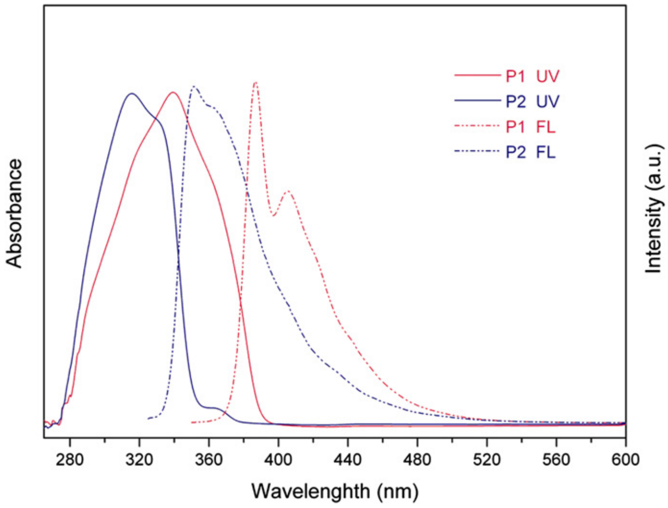


Fig. 10. UV absorption and fluorescence emission spectra of polymers.

Table 3
Photophysical properties of polymers.

Polymer	UV–Vis[a]		Fluorescence[a]	
	λ_{max} (nm)	log ε	λ_{max} (nm)[b]	Φ_F[d]
P1	340	4.42	386[c]	0.37
P2	315	4.50	351	0.10

[a] in toluene.

[b] Excited at 340 and 315 nm for **P1** and **P2**, respectively.

[c] P1 shown vibronic emission spectra, and only the longest emission is listed.

[d] Determined with anthracene as a standard. The Φ_F is the average values of repeated measurement within ±5% errors.

meta-phenylene unit linked polymer **P2** is blue-shifted to 315 nm. The similar blue shift is also observed in their fluorescence spectra. The emission maximum of **P1** appears at 386 nm, which is longer than that of **P2** by 35 nm. This finding is in accordance with the well known phenomenon that *meta*-phenylene units interrupt conjugation, which has been reported in many literatures [19]. The silazane unit effectively interrupts long distance conjugation and eventually there are only weak interactions between the oligomeric π-systems. In the case of all-*para* configured polymer **P1**, the conjugated segments Ph—C≡C—Ph—C≡C—Ph are efficiently conjugated, while in polymer **P2**, the conjugation is interrupted on the central *meta*-Ph ring, the segment then rather corresponds to two Ph—C≡C—Ph units sharing a Ph without efficient conjugation. Compared with the reported poly[(silylene)acetylene silazanes] with phenyl substituent on Si atom [8a], the emission maximum of **P1** is red-shifed by 16 nm. This is probably due to the incorporation of *p*-phenylene units into the main chains, which increased the conjugation of polymer **P1**.

4. Conclusion

On the basis of design and synthesis of new silylenediamine monomer, two new phenylene-silazane-acetylene polymers have been synthesized by Sonogashira cross-coupling reactions for the first time. Their thermal properties have been studied and both polymers showed similar thermal decomposition temperature and high ceramic yield at 1000 °C under nitrogen atmosphere. These polymers also show good thermal stability even in air with their temperature at 5% weight loss being higher than 386 °C. The thermal induced cross-linking polymerization of main chain acetylene groups partly accounts for their high char yield at high-temperature under nitrogen atmosphere. The photophysical properties of the new polymers have also been investigated. Both polymers showed fluorescence in ultraviolet region with their emission maxima at 386 nm for **P1** and 351 nm for **P2**, respectively. The new polymers have potential to be used as ceramic precursor and light-emitting materials with good thermal stability. Further studies involving the thermal cured behavior and mechanical properties of the new polymers, as well as the use of new monomer to synthesize other polymers containing silazane and acetylene units by coupling reactions are underway in our group.

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