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Facile synthesis of $\sigma - \pi$ conjugated organosilicon polymers via Click polymerization

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ABSTRACT

Poly[silylene-(1,2,3-triazol-4-yl)-1,4-phenylene]s have been prepared via Cu(I)-catalyzed Azides and Alkynes Cycloaddition (CuAAC) polymerization from diethynylsilanes and 1,4-diazidobenzene. The organosilicon units contribute to electronic transitions between the π -conjugated units, as well as improving the solubility and processability of the polymers. Fourier transform infrared spectroscopy (FT-IR) and nuclear magnetic resonance spectroscopy (NMR) have been utilized to confirm the structure of these polymers. The UV–visible spectra of polymers show almost identical absorption at around 270 nm. The fluorescence emission in CHCl₃ solutions were observed as similar broad band in visible blue region (ca. 430 nm). The quantum yields (Φ) were ranged from 0.19 to 0.37. The optical properties support the σ - π conjugation of the silylene and aromatic heterocycle groups, and the substituents on silicon atoms have negligible effect on the photoproperties.

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1. Introduction

The $\sigma-\pi$ conjugated polymers containing alternated organosilicon and π -conjugated units have been attracted much attention and thus many articles concerning silicon-containing conjugated polymers have been published to date [1–7]. In such polymers, the 3*d*-orbital of silicon atoms can change electron delocalization of the π -electron segments to suggest $\sigma-\pi$ interaction. So the siliconcontaining polymers will exhibit unique optical properties, and their processability and solubility can also be improved due to the flexible silicon linkers. Therefore, the silicon-containing polymers can be potentially applicable to organic light emitting devices (OLEDs), electroluminescent display, semiconductors, optical sensor and ceramic precursors.

Takagi et al. have obtained fluorene-based polymers incorporating organosilicon units from silylene-containing fluorene-based dibromo monomers and 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) by Suzuki coupling polymerization. Their UV–vis spectra reveal that the organosilicon units interrupt π -conjugation and contribute to an electronic communication between fluorenes. The polymers emitted visible green light in the spin-coated film [8]. Ohshita groups synthesize novel organosilicon polymers with different π -conjugation units (such as anthracene, pyrene, oligothiophenes and arylenenanthrylene) by Stille coupling reactions [9-12], and the polymers can be used as hole-transporting materials in OLEDs. In addition, many different linear, hyperbranched and star shaped poly(silylenephenylene)s are obtained by Hydrosilylation [13–15].

Most of $\sigma-\pi$ conjugated polymers are made by polycondensation of powerful coupling strategies, such as Suzuki reaction, Stille reaction, Heck reaction, Sonogashira reaction, Hydrosilylation and so on. But expensive metal catalysts (Palladium, Rhodium or Platinum complexes) and extreme conditions (isolation of humidity and oxygen) are always required in the above mentioned reactions, which limit the development of the $\sigma-\pi$ conjugated polymers. The low-cost and facile reaction conditions are also very important for business applications.

Since the Cu(I)-catalyzed azides and alkynes cycloaddition were reported by Sharpless [16] and Meldal [17] groups in 2002, the new synthesis methodology defined as "Click Chemistry" have been intensively applied in polymer chemistry for a variety of advantages, including benign reaction conditions, high reaction rate, solvent tolerance, good regioselectivity and excellent yield. We noticed the traits and attempted to introduce the "Click Chemistry" into the silicon-containing conjugated polymers.

In this paper, Poly[silylene-(1,2,3-triazol-4-yl)-1,4-phenylene]s (**P1**–**P3**) were prepared from diethynylsilanes and 1,4-diazidobenzene via CuAAC Click step-growth polymerization (Scheme 1). The Click coupling reaction was carried out in DMF/pyridine mixture using CuI as a catalyst. The fluorescence spectrum of the products in dilute CHCl₃

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Scheme 2. Preparation of M1.

solutions exhibited emission in visible blue region with moderate quantum yields, showing these polymers may be potentially applied as emission materials in OLEDs.

2. Results and discussion

2.1. Synthesis of model compound (M1) and polymers (P1-P3)

As we know, the Cu(I) catalyst plays a crucial role in CuAAC reaction, and usually can be obtained by two available methods, **A** and **B**. In method **A**, CuSO₄ and sodium ascorbate in water/alcohol mixture are used, and the Cu(II) is reduced to Cu(I) by sodium ascorbate. In method **B**, Cu-halide salts, such as CuI or CuBr, are used directly in polar solvents dimethyl sulfoxide (DMSO) or dimethylformamide (DMF), while an amine base is always required.

In order to understand the nature of polymers, we attempted to synthesize model compound (**M1**) as one repeating unit of the polymers. The products were insoluble when method A was used, because of low solubility of π -conjugated products in water/alcohol mixture. However, **M1** was synthesized successfully in the presence of Cul, pyridine and DMF at room temperature from trimethylsilylacetylene and 1,4-diazidobenzene (Scheme 2). Cul is partially soluble in DMF, and pyridine can protect Cu(I) from oxidation and enhance the catalysis of Cul. The FT-IR spectrum shows a new signal at 3143 cm⁻¹, which belongs to C–H stretching vibration of triazole group (Fig. 1). In ¹H NMR spectrum, the \equiv C–H signal of triazole is at 8.84 ppm, and the peak of phenylene attached to triazole shifts to 7.96 ppm, integral of all peaks well correspond with the structure (Fig. 2). The results of both FT-IR and ¹H NMR confirm that the Click reaction has occurred.



Fig. 1. FT-IR spectra of M1.



Fig. 2. ¹H NMR spectra of **M1**. ^aDMSO- d_6 as solvent, the solvent peaks are marked with asterisks.

Poly[silylene-(1,2,3-triazol-4-yl)-1,4-phenylene]s (**P1–P3**) were prepared from diethynylsilanes and 1,4-diazidobenzene at 60° C. Firstly we made products at room temperature, but the GPC results in Table 1 indicate only low to moderate molecular weight polymers could be obtained due to the rigid structure in main chains. The polydispersity (PDI) of **P2** and **P3** are high, and the results indicate that the reactivity is not enough because of the steric hindrance of Si–Ph groups, some imperfect oligomers were mixed with products. So we raised reaction temperature from room temperature to 60° C (reflux slightly) for conditions optimization, the PDI decreased while yields and M_n slightly increased, and the

Table 1The yields and GPC results of P1-P3.

	Yield (%) ^a	$M_n (g/mol)^{\rm b}$	$M_w(g/mol)^b$	PDI ^b	Conditions
P1	68	2720	3660	1.34	r.t.
	71	3200	4640	1.45	60° C
P2	60	4800	29,300	6.10	r.t.
	65	6110	12,100	1.98	60° C
P3	52	7640	41,900	5.48	r.t.
	62	9300	20,700	2.23	60° C

^a Isolated yield after reprecipitation into petroleum ether.

^b Estimated by GPC, THF as eluent, relative to PS standards.



Fig. 3. ¹H NMR spectra of P1. ^aDMSO- d_6 as solvent, the solvent peaks are marked with asterisks.

Iddic 2			
UV-vis a	and emission	data of P1-	P4 and M1.

	λ_{ab} (nm)	$\lambda_{em} (nm)^a$	Φ^{b}
P1	272	432	0.19
P2	273	429	0.28
P3	270	433	0.37
P4	283	_	_
M1	272	415, 435	0.09

^a All the polymers show broad band while **M1** is shoulder peak.

^b Quantum yields are based on quinine sulfate as standard.



Fig. 4. UV-vis absorption spectra of P1 \sim P4 and M1 in CHCl₃ (10⁻⁵ M).

yield of **M1** also increased. The results illuminate temperature elevation is an effective mean for the synthesis. The ¹H NMR of **P1** is shown in Fig. 3, the signals at about 8.88 and 8.00 are assigned to triazole and phenylene units, respectively. The spectra are similar with **M1**, and the peak ratio of the triazole, phenylene and methyl group resonances is about 1: 1.9: 3.3, which is close with the theoretical ratio (1: 2: 3). The results support the Click polymerization of diethynylsilanes and 1, 4-diazidobenzene.

2.2. Optical properties

Table 2 summarizes the UV–vis absorption and emission data of the polymers and **M1** in CHCl₃. In Fig. 4, the absorption maximum wavelengths of **P1, P2, P3** show similar absorptions at 272 nm, 273 nm and 270 nm, attributed to the $\pi \rightarrow \pi^*$ transitions involving the phenylene and triazole groups in the backbone.

In order to understand the nature of the polymers, we synthesized polymer **P4** (Scheme 3) and model compound **M1** (Scheme 2). The polymer **P4**, in which the methylene groups are introduced to interrupt the connection of silylene and triazole units, shows absorption at 283 nm. The absorption of **P4** is ca. 10 nm red-shift compared to that of **P1–P3**. The results indicate that the silylene group not only behaves as an electron insulator like methylene group, but also influences the UV–vis absorption by the electronic



Fig. 5. Emission spectra of P1–P3 and M1 excited at 350 nm in $CHCl_3$ (10⁻⁵ M).



Fig. 6. TGA profile of P1–P3 (10° C/min, N₂).

transitions between the silylene and π -conjugated units. On the other hand, the compound **M1**, whose structure is close to one repeating unit of the polymers, displays similar absorption with **P1–P3** at 272 nm. No evident wavelength shift illuminates that the electronic transitions are not strong enough to connect the whole backbones of the polymer and only weak σ - π conjugation occurred along the main chain.

The polymers and **M1** were further investigated by photoluminescence (PL) spectrum (Fig. 5). The fluorescence maxima of **P1–P3** in CHCl₃ solutions are observed as a broad band in visible blue region (ca. 430 nm) when excited at 350 nm, and the broad band is probably due to polymeric structure. **M1** emits shoulder peak at 415 and 435 nm, and no obvious wavelength shift is observed between the polymers and **M1**. However, **P1–P3** exhibit



Scheme 3. Preparation of P4.

stronger emission than **M1**, may be ascribed to the weak $\sigma-\pi$ conjugation. As shown in Table 2, the quantum yields (Φ) of **P1**, **P2** and **P3** are 0.19, 0.28 and 0.37, respectively. All the data is higher than that of **M1** (only 0.09), suggest that the $\sigma-\pi$ conjugation can effectively enhance the emission efficiency. Some published papers report the similar instances [18,19], silylene-functional conjugated polymers were synthesized via acyclic diene metathesis condensation. The authors find that the fluorescence quantum yields of the polymers (on a repeat unit basis) are 5-fold higher than the model compound and ascribe the phenomenon to the influence of $\sigma-\pi$ interaction. So we think that the results indicate the weak $\sigma-\pi$ conjugation in our obtained polymers.

In summary, the results of both UV–vis and PL measurements verify the weak σ – π conjugation of the obtained polymers. The similar spectra suggest that the side groups on the silicon atom had little effect on the photoproperties of the polymers.

2.3. Thermal properties

Fig. 6 shows thermal stability of **P1–P3** with heating rate of 10° C/min under N₂ atmosphere. The polymers only exhibit moderate heat-resistant properties. The temperature of 5% weight loss based on initial weight (T_{d5}) of **P1** is only 201° C, which may be related to the thermal decomposition of Si–CH₃ groups. Obviously, the Si–Ph groups have better thermal stability than Si–CH₃ groups, so the polymer **P3** with two phenyl groups attached on silicon atoms shows the best thermal stability among these polymers, and the T_{d5} and final weight residue at 800° C are 272° C and 79.5%, respectively. The polymers were also investigated by DSC measurement, but no obvious glass transition temperature (T_g) and melting points (T_m) were found for any polymer.

3. Conclusion

We have successfully prepared Poly[silylene-(1,2,3-triazol-4-yl)-1,4-phenylene]s from diethynylsilanes and diazidobenzene via CuAAC step-growth polymerization. The polymers showed unique UV-vis and PL properties, which indicated the weak σ - π conjugation between the silylene and aromatic heterocycle. The fluorescence emission spectrum was observed in visible blue region (ca. 430 nm), and the emission intensity and quantum yield were enhanced due to the σ - π interaction of the polymer main chains. The present results provided a facile and cheap method to obtain optical polymeric materials containing organosilicon groups. Other σ - π conjugated polymers with different organosilicon or aromatic units in backbone are currently in progress.

4. Experimental

4.1. General

Anhydrous tetrahydrofuran (THF) and diethyl ether (Et₂O) were freshly distilled over sodium and benzophenone before use. Compound 1,4-diazidobenzene was prepared by modifying the reported procedure [20,21]. Diethynyldimethylsilane, diethynylmethylphenylsilane and diethynyldiphenylsilane were prepared from reported papers elsewhere [22,23]. Dipropargyldiphenyl silane was obtained according to the published literature [24]. Trimethylsilylacetylene and other chemicals were purchased from Aldrich and used as received unless otherwise noted.

FT-IR spectra was recorded with a Bruker Tensor27 spectrophotometer. ¹H NMR and ¹³C NMR spectra were measured using CDCl₃ and DMSO- d_6 as solvent on Bruker AVANCE-300 NMR Spectrometer. UV–vis absorption and fluorescence spectra were analyzed with UV-7502PC and ISS K2-Digital spectrophotometer, respectively. Fluorescence quantum yields were measured using quinine sulfate in 0.1 N H₂SO₄ ($\Phi = 54.6\%$) as standard. TGA was carried out under nitrogen flow at a heating rate of 10° C/min on a MettlerToledo SDTA-854 TGA system. DSC measurements were performed with MettlerToledo DSC822 series. Elemental analysis was measured on a Vario EI III elemental analyzer. The average molecular weight of the polymers was determined in THF (1 ml/min) at 40° C by waters 515 liquid chromatograph equipped with the refractive-index detector and three Styragel columns, and using the standard polystyrene for calibration.

4.2. Preparation of 1,4-diazidobenzene

The mixture of 1,4-diiodobenzene (3.30 g, 10.0 mmol), NaN₃ (1.56 g, 24.0 mmol), CuSO₄ (0.16 g, 1.0 mmol), ascorbate acid (0.35 g, 2.0 mmol), Na₂CO₃ (0.21 g, 2.0 mmol), L-proline (0.23 g, 2.0 mmol), DMSO (9 ml) and H₂O (1 ml) was stirred in dark for 24 h at 65° C. Then the mixture was extracted with ethyl acetate (200 ml) and washed with H₂O (3 × 100 ml), dried over MgSO₄, filtered and distilled under reduced pressure. The crude product was purified by a silica gel column using petroleum ether as an eluent to give 1,4-diazidobenzene as a light yellow crystalline, which is light-sensitive (turn to brownish when exposed to light) and should be stored in the dark (Yield: 56%).

¹H NMR (δ in CDCl₃) 7.01 (s); ¹³C NMR (δ in CDCl₃) 120.4, 136.8 ppm; FT-IR (KBr plate) 2125 cm⁻¹($-N_3$).

4.3. Preparation of model compound (M1)

Trimethylsilylacetylene (0.10 g, 1 mmol), 1,4-diazidobenzene (0.16 g, 1 mmol), copper iodide (0.01 g, 5 mol %), pyridine (0.5 ml) and DMF (2 ml) was stirred for 24 h at 60° C under dark. Then the mixture was poured into ethyl acetate (100 ml) and washed with H₂O (3 × 50 ml), dried over MgSO₄, filtered and distilled under reduced pressure. The crude product was purified by a silica gel column using petroleum ether as an eluent to give **M1** as a pale yellow solid (Yield: 63%).

¹H NMR (δ in DMSO-*d*₆) 8.84 (s, 1H), 7.95 (d, 2H, *J* = 9.0 Hz), 7.34 (d, 2H, *J* = 9.0 Hz), 0.32 (s, 9H); ¹³C NMR (δ in DMSO-*d*₆) 147.2, 140.4, 134.5, 129.6, 122.7, 121.4, -0.11 ppm; FT-IR (KBr plate) 3143, 3071, 2103, 1508, 1253 cm⁻¹; Anal. Calc. for C₁₁H₁₄N₆Si: C, 51.16; H, 5.43; N, 32.56. Found: C, 51.25; H, 5.23; N, 32.81%.

4.4. Preparation of polymers (P1–P4)

The mixture of diethynyldimethylsilane (0.05 g, 0.5 mmol), 1,4-diazidobenzene (0.08 g, 0.5 mmol), copper iodide (0.01 g, 5 mol %), pyridine (0.5 ml) and DMF (2 ml) was stirred for 24 h at 60° C under dark. The mixture was poured into ethyl acetate (200 ml) and washed with H_2O (3 × 100 ml), and the organic layer was dried over MgSO₄, filtered and distilled under reduced pressure. The residue was poured into vigorously stirred petroleum ether (100 ml) to afford **P1** as beige precipitate (Yield: 71%).

¹H NMR (δ in DMSO-*d*₆) 8.88 (s, br, 2H), 8.00 (m, 4H), 0.43 (s, 6H); ¹³C NMR (δ in DMSO-*d*₆) 148.5, 141.6, 135.9, 121.8, -2.5 ppm; FT-IR (KBr plate) 3121, 1661, 1517, 1259, 837, 800 cm⁻¹; Anal. Calc. for (C₁₂H₁₂N₆Si)_n: C, 53.73; H, 4.48; N, 31.34. Found: C, 53.47; H, 4.63; N, 31.76%.

The polymers **P2**, **P3**, **P4** were prepared in a similar procedure to **P1**. Data for **P2**: yellow solid (Yield: 65%); ¹H NMR (δ in DMSO- d_6) 8.92 (s, br, 2H), 7.96 (m, 4H), 7.53 (m, 2H), 7.39 (m, 3H), 0.43 (m, 3H); ¹³C NMR (δ in DMSO- d_6) 149.2, 142.1, 137.5, 135.2, 134.8, 129.5, 127.9, 122.5, -2.8 ppm; FT-IR (KBr plate) 3130, 3070, 1667, 1510, 1258 cm⁻¹; Anal. Calc. for ($C_{17}H_{14}N_6Si_{n}$: C, 61.82; H, 4.24; N, 25.45. Found: C, 61.25; H, 4.43; N, 25.87%.

Data for **P3**: yellow solid (Yield: 62%); ¹H NMR (δ in DMSO- d_6) 8.97 (s, br, 2H), 7.99 (m, 4H), 7.34 (m, 10H); ¹³C NMR (δ in DMSO- d_6) 149.7, 141.5, 137.7, 135.6, 134.8, 129.2, 127.6, 123.8 ppm; FT-IR (KBr plate) 3132, 3071, 1663, 1519 cm⁻¹; Anal. Calc. for (C₂₂H₁₆N₆Si)_n: C, 67.35; H, 4.08; N, 21.43. Found: C, 67.06; H, 4.53; N, 21.73%.

Data for **P4**: yellow solid (Yield: 70%); ¹H NMR (δ in DMSO- d_6) 8.23 (s, br, 2H), 7.96 (m, 4H), 7.59 (m, 4H), 7.37 (m, 6H), 2.89 (m, 2H); ¹³C NMR (δ in DMSO- d_6) 142.7, 140.3, 137.2, 135.8, 132.8, 128.5, 127.2, 121.7, 66.0 ppm; FT-IR (KBr plate) 3136, 3070, 1608, 1521 cm⁻¹; Anal. Calc. for (C₂₄H₂₀N₆Si)_n: C, 68.57; H, 4.76; N, 20.00. Found: C, 68.16; H, 4.49; N, 20.56%.

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