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Click polymerization: Synthesis of novel σ - π conjugated organosilicon polymers

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ABSTRACT

Poly[silylene-1,4-phenylene-(1,2,3-triazol-4-yl)-1,4-phenylene]s were prepared via step-growth Click coupling polymerization of bis(*p*-ethynylphenyl)silanes and 1,4-diazidobenzene. The organosilicon units in the backbones may contribute to an electronic communication among the π -conjugated units and improve the solubility of the polymers. Fourier transform infrared spectroscopy (FT-IR) and nuclear magnetic resonance spectroscopy (NMR) were used to confirm the polymers structure. The UV–vis absorption wavelength of silicon-containing compounds red-shifted ca. 15 nm when compared with the compounds without silicon atoms. The fluorescence emission of polymers in CHCl₃ solutions was observed in visible blue region (ca. 440 nm), and the intensity and quantum yield (Φ) were enhanced due to the influence of σ - π interaction. The results of the absorption and emission supported the weak σ - π conjugation between the silylene and aromatic segments, and these polymers can be potentially applied in organic light emitting devices (OLEDs).

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1. Introduction

The Cu(I)-Catalyzed Azides and Alkynes Cycloaddition (CuAAC), which is defined as "Click Chemistry", has been intensively applied in polymer synthesis since its discovery by Sharpless and Meldal groups in 2002 [1,2]. This kind of reactions exhibit a lot of advantages, including benign reaction conditions, simple workup, high reaction rate, good solvent tolerance and excellent yield. So the powerful and efficient synthetic method has gained popularity in polymer synthesis and material science over the last decade [3–6].

Recently, many works have been done to prepare the π -conjugated polymers by the Click reaction [7–11]. Meudtner's group report the synthesis of Poly[(1,2,3-triazol-4-yl-1,3-pyridine)-alt-(1,2,3-triazol-1-yl-1,3-phenylene)]s via the Click reaction of 2,6-diethynylpyridines and 3,5-diazidobenzoate monomers. In addition, the heterocycles in the polymer backbones can serve as ligands to coordinate with Zn^{2+} , Fe^{2+} and Eu^{3+} ions. Thus metallosupramolecular gels are obtained and can be potentially used as magnetic and emissive materials [12]. Another π -conjugated Click polymer is synthesized from diethynyl- and diazido-based fluorene monomers. The dye-sensitized solar cell (DSSC) fabricated from the fluorene-based Click polymers shows high power conversion efficiency of 4.62% and can be used as electronic materials in future [13,14].

However, the π -conjugated polymers are always insoluble due to the rigid backbone structures, and the method of the above published papers is to introduce long alkyl or other flexible groups as side chain. As we know, incorporating silicon atoms into the π -conjugated polymer backbone is another choice to effectively improve the flexibility, solubility, and processability [15,16]. As a Group 14 element, the silicon atoms have unique *d*-orbital and exhibit electron-donating properties to the adjacent π -conjugated organic structure, and the interaction between the σ -orbital and the π -orbital is named σ - π conjugation, can influence the electron delocalization between the organosilicon and π -conjugated units. The σ - π conjugated polymers mean the polymers composed of silylene or oligosilylene group as σ units and arylene, ethynylene, thienylene, vinylene or other aromatic heterocycle groups as π units, and the optical properties of the polymers will be influenced by the electron delocalization. Therefore, the σ - π conjugated organosilicon polymers can be potentially applied in organic light emitting devices (OLEDs), electroluminescent display, semiconductors, optical sensor and ceramic precursors [17–21]. But most of the σ - π conjugated polymers are synthesized via Sonogashira reaction, Heck reaction, Stille reaction, Suzuki reaction, Hydrosilylation and so on. Expensive metal catalysts (Palladium, Rhodium or Platinum complexes) and extreme conditions (isolation of humidity and oxygen) are required, which limit the development of the σ - π conjugated polymers. So we attempt to introduce the Click polymerization to synthesize the σ - π conjugated organosilicon polymers.

We prepared Poly[silylene-1,4-phenylene-(1,2,3-triazol-4-yl)-1,4-phenylene]s (**P1**, **P2**) by step-growth Click polymerization of





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bis(*p*-ethynylphenyl)silanes and 1,4-diazidobenzene (Scheme 1). The Click coupling reaction was carried out in DMF/pyridine mixture using Cul as a catalyst. The obtained σ - π conjugated organosilicon polymers in dilute CHCl₃ solutions exhibited emission in visible blue region (ca. 440 nm) with moderate quantum yields (Φ > 0.4). So these polymers may be potentially applied as emission materials in OLEDs.

2. Results and discussion

2.1. Polymer synthesis

Poly[silylene-1,4-phenylene-(1,2,3-triazol-4-yl)-1,4-phenylene]s (**P1**, **P2**) were prepared from bis(*p*-ethynylphenyl)silanes and 1,4diazidobenzene under typical Click coupling reaction. The structures were characterized by FT-IR and NMR spectra. In Fig. 1, the peaks of corresponding to ethynyl (3270 cm⁻¹) and azide (2125 cm⁻¹) groups disappear after the reaction, and a new resonance (3128 cm⁻¹) belongs to C–H stretching vibration of triazole group is observed in the spectra. The ¹H NMR spectrum of the polymers shows a characteristic signal of triazole group at about 9.40 ppm (C \equiv C–H), and the peak of phenyl attached to triazole shift to 7.97 ppm (Fig. 2). Fig. 3 shows the ¹³C NMR spectra of **P1**, two vinyl carbons from triazole unit are clearly shown at 149.2 and 140.5 ppm. The peaks around 120–140 ppm are due to the benzene rings in the polymer backbone. These results confirm the Click reaction has occurred.

The average molecular weight of polymers was evaluated using GPC and the results were summarized in Table 1. The average molecular weights of **P1** and **P2** were 6200 and 7150, respectively. The molecular weights were only low to moderate due to the rigid structure in the main chains. The degrees of polymerization calculated from the number average molecular weights were over 15, which indicate that the polymers were prepared successfully via the Click polymerization.

2.2. Optical properties

In order to understand the nature of the polymers, two model compounds (**M1**, **M2**) were synthesized (Scheme 2). The **M2**, whose structure was similar with one repeating unit of the polymers, was prepared to verify whether the silylene can contribute electronic communication or insulation in the backbones. On the other hand, the structure of **M1** was similar with **M2** but without organosilicon units and we attempt to find out the effect of organosilicon units through comparing the optical properties of **M1** and **M2**.

In Table 2 the UV–vis absorption and emission data of the polymers and model compounds in CHCl₃ solution were



Scheme 1. Synthesis of P1, P2.



Fig. 1. FT-IR spectra of diazide (a), dialkyne (b) and polymer (c).

summarized. The UV-vis spectra were shown in Fig. 4. All the compounds exhibit a similar absorption maximum at around 230 nm due to π - π * transition of triazole groups [22]. In addition, the phenyl unit in M1 shows absorption at 246 nm, while the absorption of the phenyl unit in M2 is around 261 nm, which is ca. 15 nm red-shift compared to that of M1. As we know, silicon atom has empty 3d-orbitals which can conjugate with adjacent π -conjugated systems, so the red-shift can be ascribed to the π -to- σ charge transition between phenyl and silvlene units. The phenyl units in P1 and P2 exhibit similar absorption at 262 and 259 nm, respectively. No obvious wavelength shift is found between the polymers and M2. The above results illuminate the silicon atom can influence the electron delocalization of the π -electron segments, but the electronic transitions is not strong enough to connect the adjacent π -conjugated units, and only weak σ - π conjugation occurred along the main chain.



Fig. 2. ¹H NMR spectra ^a of P1 ^a DMSO- d_6 as solvent as solvent, solvent peaks are marked with asterisks.



Fig. 3. ¹³C NMR spectra ^a of P1 ^a DMSO- d_6 as solvent as solvent, solvent peaks are marked with asterisks.

Table 1	
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The yields and GPC results of P1, P2.

	Yield (%) ^a	$M_n \left(\mathrm{g/mol} \right)^\mathrm{b}$	$M_w \left(\mathrm{g/mol} \right)^\mathrm{b}$	PDI ^b	DP ^b
P1	67	6200	8620	1.39	15
P2	62	7150	10500	1.47	17

^a Isolated yield after reprecipitation into petroleum ether.

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

The polymers were further investigated by photoluminescence (PL) spectrum (Fig. 5). The emission maximum of the polymers and M2 in CHCl₃ solutions are observed at around 440 nm excited at 350 nm, while the emission maximum of M1 is 461 nm. All the compounds show fluorescence emission in visible blue region, and the emission maximum wavelength of silicon-containing compounds is about 20 nm blue-shifted compared with that of M1, which can be attributed to charge transition between the silicon atoms and aromatic rings. Similar results were described by Suzuki et al. [23]. The authors have synthesized polymers with terfluorene and organosilicon groups in the backbones, and the emission maximum wavelengths of the polymers are ca. 400 nm while polyfluorene is 418 nm, the blue-shift reveals that the silylene units contribute an electronic communication between connected fluorenes. However, no obvious emission wavelength difference between M2 and the polymers was observed, which illuminate the charge communication is not strong enough to connect the whole backbones of the polymer and only partial σ - π conjugation occurred along the main chain. The relative intensities of the polymers were stronger than that of M1 and M2 due to the polymeric structure. The quantum yields (ϕ) of **P1** and **P2** were 0.45

Table 2

JV—vis and emission results of M1 , M2 , P1 and P

	λ_{ab} [nm]	$\lambda_{ab \ 2nd}[nm]$	$\lambda_{em} \left[nm \right]$	$\Phi^{\rm a}$	condition (298K)
P1	231	262	439	0.45	CHCl ₃ , $\lambda_{ex} = 350 \text{ nm}$
			455		solid state, $\lambda_{ex} = 300 \text{ nm}$
P2	229	259	440	0.47	CHCl ₃ , $\lambda_{ex} = 350 \text{ nm}$
			457		solid state, $\lambda_{ex} = 300 \text{ nm}$
M1	229	246	461	0.13	CHCl ₃ , $\lambda_{ex} = 350 \text{ nm}$
M2	228	261	445	0.19	CHCl ₃ , $\lambda_{ex} = 350 \text{ nm}$

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

and 0.47, higher than that of **M1** and **M2**. Thus, the results suggest that the σ - π conjugation can effectively enhance the emission efficiency.

In addition, the emission spectra of polymers in different solvents and solid state were shown in Fig. 6(a) and (b), respectively. The solubility of polymers was better in polar solvents, such as DMSO and DMF, may be ascribe to the polar structure in the main chain. The Fig. 6(a) shows that the emission region in different solvents are near 400–435 nm, insensitive to the solvent polarity. The emission of **P1** in solid state is observed around 445–460 nm, which is considerably red-shifted compared with that in solution, presumbly due to the π - π stacking interactions of the fluorophores.

In summary, the results of both UV–vis and PL measurements revealed that the silicon atoms have a little electronic communication with the adjacent π -conjugated units. Although the σ - π conjugation of the polymers was too weak to influence the emission wavelength, the emission and quantum yields were still enhanced under the σ - π conjugation. Finally, the similar spectra suggest that the side groups on the silicon atom had little effect on the photoproperties of the σ - π conjugated organosilicon polymers.

2.3. Thermal properties

The thermal stability of the polymers with heating rate of 10 °C/ min under N₂ atmosphere was shown in Fig. 7. The polymers exhibit good heat-resistant properties, the 5 and 10% weight loss temperatures (T_{d5} and T_{d10}) are almost the same for **P1** (322, 350 °C) and **P2** (325, 370 °C). The TGA profiles of **P1** and **P2** are composed of two similar decomposed stages. The first degradation (ca. 260–400 °C) is due to the thermal decomposition of Si–CH₃ groups. Then the backbone begins to break down when the temperature is higher than 400 °C. The residue after 800 °C pyrolysis of **P2** is 59.8%, slightly higher than that of **P1** (52.1%). This is probably due to the crosslinking reaction between vinyl groups in **P2**. The DSC measurement had also been done, but no obvious glass transition temperature (*T_g*) was found for any polymer.

3. Conclusion

Poly[silylene-1,4-phenylene-(1,2,3-triazol-4-yl)-1,4-phenylene]s were successfully synthesized from bis(*p*-ethynylphenyl)silanes and 1,4-diazidobenzene via Click step-growth polymerization. The



Scheme 2. Synthesis of M1, M2.



Fig. 4. UV-vis absorption spectra of M1, M2, P1 and P2 (CHCl₃, 10^{-5} M).

polymers showed unique UV–vis and PL properties, which indicated that the weak σ - π conjugation occurred between the silylene and aromatic segments. The present results provided a reliable and cheap method to modify the solubility, processability and optical properties of the π -conjugated polymers. The obtained novel σ - π conjugated organosilicon polymers were observed in visible blue region (ca. 440 nm) in the fluorescence emission spectrum. The emission intensity and quantum yield were also enhanced due to the σ - π interaction of the polymer main chains. Therefore, these polymers could be used as potential optical materials in OLEDs. Other σ - π conjugated organosilicon polymers with different organosilicon or aromatic segments in backbone are currently investigated in progress.

4. Experimental

4.1. General

Anhydrous tetrahydrofuran (THF) and diethyl ether (Et₂O) were freshly distilled over sodium and benzophenone before use. n-Butyllithium (n-BuLi, 2.5 mol/L, in hexane) was purchased from Mayer. 1,4-diazidobenzene was prepared by modifying the reported procedure [24,25]. 1-bromo-4-trimethylsilylethynylbenzene was obtained according to the published literatures [16,20,26]. Petroleum ether (PE), ethyl acetate (EtOAc), dimethyl sulfoxide (DMSO), dimethylformamide (DMF) and other chemicals were purchased from Aldrich and used as received unless otherwise noted.

FT-IR spectra were 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. High-resolution mass spectra were obtained using positive mode on Aglient Technologies Q-TOF 6510. Elemental analysis (C, H, N) 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 waters515 liquid chromatograph equipped with the refractiveindex detector and three Styragel columns, and using the standard polystyrene (PS) 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 EtOAc (200 ml), washed with H₂O (3 \times 100 ml), dried over MgSO₄, filtered and distilled under reduced pressure. The crude product was purified by a silica gel



Fig. 5. Emission spectra of M1, M2, P1 and P2 (CHCl₃, 10^{-5} M).



Fig. 6. Emission spectra of P1. (a) in different solution (10^{-5} M, $\lambda_{ex} = 350$ nm); (b) in the solid state ($\lambda_{ex} = 300$ nm).

column (PE as 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($-N_3$); HRMS (*m*/*z*): calcd for C₆H₄N₆ 160.1382, found 160.1374.

4.3. Preparation of p-(trimethylsilyl) phenylacetylene

The mixture of 1-bromo-4-trimethylsilylethynylbenzene (2.52 g, 10 mmol) and dry Et₂O (100 ml) was cooled at -78 °C under argon atmosphere, and *n*-BuLi solution (4.8 ml, 12.0 mmol) was dropped slowly and kept for 2 h. Then trimethylchlorosilane (1.09 g, 10 mmol) was added in 10 min. The mixture was allowed to warm to room temperature overnight. After quenching with NH₄Cl solution, the mixture was extracted with Et₂O (100 ml) and washed with H₂O (3 × 50 ml), dried over MgSO₄, filtered and distilled under reduced pressure. Then the residue and K₂CO₃ (0.14 g, 1 mmol) were dissolved in THF/MeOH (50/50 ml) mixture, and stirred for 12 h at room temperature. Then solvent was distilled and the residue was purified by a silica gel column (PE as eluent) to give *p*-(trimethylsilyl) phenylacetylene 1.34 g (Yield: 77%) as colorless liquid.

¹H NMR (δ in CDCl₃) 7.49 (s, 4H), 3.10 (s, 1H), 0.28 (s, 9H); ¹³C NMR (δ in CDCl₃) 138.5, 133.7, 131.7, 122.9, 84.3, 77.2, –3.8 ppm; FT-



Fig. 7. TGA profile of P1, P2 (10 °C/min, N₂).

IR (KBr plate) 3300, 2109, 1250 cm⁻¹; HRMS (m/z): calcd for C₁₁H₁₄Si 174.3177, found 174.3165.

4.4. Preparation of bis(p-ethynylphenyl)silanes

The bis(*p*-ethynylphenyl)silanes were prepared from dichlorodimethylsilane and dichloromethylvinylsilane similar to *p*-(trimethylsilyl) phenylacetylene.

Data for bis(*p*-ethynylphenyl)dimethylsilane: colorless solid (Yield: 70%);

¹H NMR (δ in CDCl₃) 7.47 (s, 8H), 3.10 (s, 2H), 0.55 (s, 6H); ¹³C NMR (δ in CDCl₃) 138.8, 133.6, 131.4, 123.4, 84.0, 79.2, -4.0 ppm; FT-IR (KBr plate) 3270, 2113, 1255 cm⁻¹; HRMS (*m*/*z*): calcd for C₁₈H₁₆Si 260.4105, found 260.4119.

Data for bis(*p*-ethynylphenyl)methylvinylsilane: colorless liquid (Yield: 68%);

¹H NMR (δ in CDCl₃) 7.49 (s, 8H), 6.46 (m, 1H), 6.25 (m, 1H), 5.82 (m, 1H) 3.13 (s, 2H), 0.65 (s, 3H); ¹³C NMR (δ in CDCl₃) 137.4, 136.2, 135.3, 135.1, 131.9, 123.7, 84.3, 78.5, -3.9 ppm; FT-IR (KBr plate) 3296, 2108, 1253 cm⁻¹; HRMS (*m*/*z*): calcd for C₁₉H₁₆Si 272.4215, found 272.4207.

4.5. Preparation of model compound (M1, M2)

Phenylacetylene (0.20 g, 2 mmol), 1,4-diazidobenzene (0.16 g, 1 mmol), copper iodide (0.02 g, 5 mol %), pyridine (1 ml) and DMF (4 ml) was stirred for 24 h at 60 °C under dark. Then the mixture was poured into EtOAc (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 (PE: EtOAc = 3:2) to give **M1** as a pale yellow solid (Yield: 53%).

¹H NMR (δ in DMSO-*d*₆) 9.44 (s, 2H), 7.97 (s, 4H), 7.72 (d, 4H), 7.45 (m, 6H); ¹³C NMR (δ in DMSO-*d*₆) 149.3, 140.6, 137.2, 135.6, 130.1, 129.3, 122.5, 120.7 ppm; FT-IR (KBr plate) 3125, 3051, 1508, 847, 823 cm⁻¹; Anal. Calc. for $C_{22}H_{16}N_6$: C, 72.53; H, 4.40; N, 23.07. Found: C, 72.77; H, 4.55; N, 22.68%.

The **M2** were prepared from *p*-(trimethylsilyl) phenylacetylene in a similar procedure.

Data for M2: pale yellow solid (Yield: 56%);

¹H NMR (δ in DMSO-*d*₆) 9.47 (s, 2H), 7.95 (s, 4H), 7.74 (d, 4H), 7.35 (m, 6H), 0.28 (s, 18H); ¹³C NMR (δ in DMSO-*d*₆) 149.6, 140.2, 137.8, 134.3, 130.2, 128.5, 122.5, 120.7, -3.5 ppm; FT-IR (KBr plate) 3127, 3069, 1511, 1253, 843, 820 cm⁻¹; Anal. Calc. for C₂₈H₃₂N₆Si₂: C, 66.14; H, 6.30; N, 16.54. Found: C, 65.65; H, 6.53; N, 16.71%.

4.6. Preparation of polymers (P1, P2)

The mixture of bis(*p*-ethynylphenyl)dimethylsilane (0.13 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 EtOAc (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 PE (100 ml) to afford **P1** as yellow precipitate (Yield: 67%).

¹H NMR (δ in DMSO-*d*₆) 9.40 (s, 2H), 7.97 (m, 4H), 7.56 (m, 4H), 7.49 (m, 4H), 0.63 (m, 6H); ¹³C NMR (δ in DMSO-*d*₆) 149.2, 140.5, 138.4, 135.3, 129.7, 128.1, 121.5, 120.9, -4.5 ppm; FT-IR (KBr plate) 3128, 3065, 1521, 1251, 845, 819 cm⁻¹; Anal. Calc. for ($C_{24}H_{20}N_6Si_{n}$: C, 68.57; H, 4.76; N, 20.00. Found: C, 67.42; H, 4.67; N, 19.20%.

The **P2** were prepared from bis(*p*-ethynylphenyl)methylvinylsilane in a similar procedure.

Data for **P2**: beige solid (Yield: 62%);

¹H NMR (δ in DMSO-*d*₆) 9.47 (s, 2H), 7.98 (m, 4H), 7.66 (m, 4H), 7.51 (m, 4H), 6.53 (m, 1H), 6.25 (m, 1H), 5.80 (m, 1H), 0.65 (m, 3H); ¹³C NMR (δ in DMSO-*d*₆) 149.7, 144.3, 138.4, 136.7, 135.8, 135.2, 129.7, 129.1, 121.5, 120.9, -4.3 ppm; FT-IR (KBr plate) 3129, 3051, 1517, 1252, 840, 817 cm⁻¹; Anal. Calc. for (C₂₅H₂₀N₆Si)_n: C, 69.44; H, 4.63; N, 19.44. Found: C, 69.13; H, 4.75; N, 19.65%.

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References

- V.V. Rostovtsev, L.G. Green, V.V. Fokin, K.B. Sharpless, Angew. Chem. Int. Ed. 41 (2002) 2596–2599.
- [2] C.W. Tornoe, C. Christensen, M. Meldal, J. Org. Chem. 67 (2002) 3057-3064.
- [3] M. Meldal, C.W. Tornoe, Chem. Rev. 108 (2008) 2952-3015.
- [4] V.D. Bock, H. Hiemstra, J.H. Maarseveen, Eur. J. Org. Chem. (2006) 51-68.
- [5] J.F. Luta, Angew. Chem. Int. Ed. 46 (2007) 1018–1025.
 [6] J.A. Johnson, M.G. Finn, J.T. Koberstein, N.J. Turro, Macromol. Rapid Commun.
- 29 (2008) 1052–1072.
- [7] L. Liang, C.D. Frisbie, J. Am. Chem. Soc. 132 (2010) 8854-8855.
- [8] D.J. Steenis, O.R. David, G.P. Strijdonck, J.H. Maarseveen, J.N. Reek, Chem. Commun. (2005) 4333–4335.
- [9] A.J. Qin, J.W.Y. Lam, B.Z. Tang, Macromolecules 43 (2010) 8693-8702.
- [10] B.Z. Tang, Macromol. Chem. Phys. 209 (2008) 1303-1307.
- [11] B.B. Ni, C. Wang, H.X. Wu, J. Pei, Y.G. Ma, Chem. Commun. 46 (2010) 782-784.
- [12] R.M. Meudtner, S. Hecht, Macromol. Rapid Commun. 29 (2008) 347–351.
- [13] M.A. Karim, Y.R. Cho, J.S. Park, T.I. Ryu, M.J. Lee, M. Song, S.H. Jin, J.W. Lee, Y.S. Gal, Macromol. Chem. Phys. 209 (2008) 1967–1975.
- [14] M.A. Karim, Y.R. Cho, J.S. Park, S.C. Kim, H.J. Kim, J.W. Lee, Y.S. Gal, S.H. Lin, Chem. Commun. (2008) 1929–1931.
- [15] G. Kwak, T. Masuda, Macromolecules 35 (2002) 4138-4142.
- [16] F. Wang, B.R. Kaafarani, D.C. Neckers, Macromolecules 36 (2003) 8225-8230.
- [17] T. Sasano, H. Sogawa, K. Tamura, M. Shiotsuki, T. Masuda, F. Sanda, J. Polym. Sci. Part A: Polym. Chem. 48 (2010) 1815–1821.
- [18] J. Ohshita, S. Kangai, H. Yoshida, A. Kunai, S. Kajiwara, Y. Ooyama, Y. Harima, J. Organomet. Chem. 692 (2007) 801–805.
- [19] M. Kakimoto, H. Kashihara, Y. Yamaguchi, T. Takiguchi, Macromolecules 33 (2000) 760-765.
- [20] J. Liu, R. Zheng, Y.H. Tang, M. Ha1ussler, J.W.Y. Lam, A.J. Qin, M.X. Ye, Y.N. Hong, P. Gao, B.Z. Tang, Macromolecules 40 (2007) 7473-7486.
- [21] J. Liu, J.W.Y. Lam, B.Z. Tang, Chem. Rev. 109 (2009) 5799-5867.
- [22] J.T. Fletcher, B.J. Bumgarner, N.D. Engels, D.A. Skoglund, Organometallics 27 (2008) 5430–5433.
- [23] K. Takagi, H. Kakiuchi, Y. Yuki, M. Suzuki, J. Polym. Sci. PartA: Polym. Chem. 45 (2007) 4786–4794.
- [24] D.W. Ma, W. Zhu, Chem. Commun. 7 (2004) 888.
- [25] A.K. Feldman, B. Colasson, V.V. Fokin, Org. Lett. 6 (2004) 3897-3899.
- [26] R. Wang, L. Fang, C.H. Cang, Eur. Polym. J. 46 (2010) 465-471.