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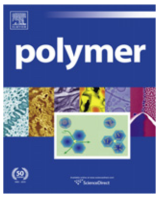

Polymer-based fluorescence sensor incorporating triazole moieties for Hg^{2+} detection via click reaction

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ABSTRACT

The polymer could be obtained by the polymerization of 1,4-dibutoxy-2,5-diethynylbenzene **(M-1)** with 1,4-diazidobenzene (**M-2**) *via* click reaction. The polymer show blue fluorescence. The responsive optical properties of the polymer on various transition metal ions were investigated by fluorescence spectra. Compared with other cations, such as Co^{2+}, Ni^{2+}, Ag^{+}, Cd^{2+}, Cu^{2+} and Zn^{2+}, Hg^{2+} can exhibit the most pronounced fluorescence response of the polymer Hg^{2+} can exhibit the most pronounced fluorescence response of the polymer due to triazole moiety in the polymer main chain as the metal binding ligand. The results indicate this kind of conjugated polymer with triazole moiety synthesized by click reaction can be used as a selective fluorescence sensor for Hg^{2+} detection.

1. Introduction

Conjugated polymers (CPs) used as fluorescence sensors have been gained increased attention due to their high sensitivity and ease of measurement. The high sensitivity of the conjugated polymers originates from the sensory signal amplification which attributed to energy migration along the polymer backbone upon light excitations. An additional advantage of polymer-based fluorescence sensors is that the structure and sequence of the conjugated polymers can be systematically modified to suit for diverse targets by the introduction of the functional groups based on steric and electronic property at well-defined molecular level [1,2]. The research on the polymer-based fluorescence sensor for heavy and transition metal (HTM) ions detection is emerging as an area of current interest in the recent years [3–5]. Among them, mercury and its derivatives are dangerous and widespread global pollutants, and they have caused serious environmental and health problems [6–9]. Many fluorescence sensors for mercury detection have been reported, but most of them are based on small molecules [3,10], and polymer-based chemosensors are very few [11–19]. Therefore, the development of highly selective and sensitive polymer-based chemosensors for HTM ions detection is still attractive.

Click reaction established by Sharpless and co-workers is an efficient tool for the preparation of wide-ranging organic compounds [20,21]. The Copper-catalyzed azide-alkyne click reaction (also termed CuAAC) has had enormous impact on the field of polymer science due to the high efficiency, mild reaction conditions and technical simplicity of the reaction in the last five years. Polymer chemists have widely employed click chemistry in material science and polymer bioconjugation [22–25]. Although a triazole unit which may be used as a potential transition metal coordinating ligand is formed in CuAAC [26], very few polymer-based conjugated fluorescence sensors incorporating triazole moieties examples have been reported. In this paper, we report the synthesis of the conjugated polymer incorporating triazole moieties used as fluorescence sensor for transition metal ions detection via click reaction. Compared with other cations, such as Co^{2+}, Ni^{2+}, Ag^{+}, Cd^{2+}, Cu^{2+} and Zn^{2+}, Hg^{2+} can exhibit the most pronounced fluorescence response of the polymer using triazole moiety as the metal binding sites. The results indicate this kind of polymer with triazole moiety based on click reaction can be used as a selective fluorescence sensor for Hg^{2+} detection.

2. Experimental part

2.1. Materials

All solvents and reagents were commercially available and analytical-reagent-grade. *para*-Phenylenediol and *para*-phenylenediamine

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were purchased from Aldrich and directly used without purification. 1,4-Diazidobenzene (M-2) could be synthesized from *para*-phenylenediamine by a 2-step reaction according to reported literature [27].

2.2. Measurements

NMR spectra were obtained using a 300-Bruker spectrometer 300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR and reported as parts per million (ppm) from the internal standard TMS. FT-IR spectra were taken on a Nexus 870 FT-IR spectrometer. UV–vis spectra were obtained from a Perkin–Elmer Lambda 25 spectrometer. Fluorescence spectra were obtained from a RF-5301PC spectrometer. Thermogravimetric analyses (TGA) was performed on a Perkin–Elmer Pyris-1 instrument under N_2 atmosphere. MS was determined on a Micromass GCT. C, H and N of elemental analyses were performed on an Elementar Vario MICRO analyzer. Molecular weight was determined by GPC with Waters-244 HPLC pump and THF was used as solvent and relative to polystyrene standards. All solvents and reagents were commercially available A. R. grade.

2.3. Preparation of M-1 (Scheme 1)

1,4-Dibutoxybenzene was synthesized according to a reported method [28]. A solution of 1,4-dibutoxybenzene (6.60 g, 29.7 mmol), KIO_3 (2.55 g, 11.9 mmol) and I_2 (8.35 g, 32.9 mmol) in 50 mL acetic acid, 0.9 mL sulphuric acid and 4 mL water was stirred at 80 °C for 24 h. After cooling, solution of $Na_2S_2O_3$ was added until the purple color disappeared, then the reaction mixture was poured into 100 mL water and extracted with petroleum ether (3×50 mL). The organic layer was washed with water, and then dried over anhydrous Na_2SO_4. The solution was evaporated under reduced pressure to give 1,4-dibutoxy-2,5-diiodobenzene (10.3 g, 73.6%) as a white solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.20 (s, 2H), 3.96 (t, 4H, $J = 6.6$ Hz), 1.83–1.76 (m, 4H), 1.59–1.52 (m, 4H), 1.00 (t, 6H, $J = 7.5$ Hz).

A mixture of 1,4-dibutoxy-2,5-diiodobenzene (3.00 g, 6.33 mmol), $Pd(PPh_3)_4$ (366 mg, 0.32 mmol), CuI (241 mg, 1.27 mmol) and trimethylsilyl acetylene (3.58 mL, 25.3 mmol) was dissolved in 15 mL Et_3N and 40 mL THF. The reaction mixture was stirred at 40 °C for 48 h under a N_2 atmosphere. The solution was cooled to room temperature, and then the solvent was removed under reduced pressure. The residue was extracted with CH_2Cl_2 (2×50 mL). The organic layer was washed with cool water, and then dried over anhydrous Na_2SO_4. The solution was evaporated under reduced pressure, and the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) (50:1, v/v) to give 2,5-bis(trimethylsilylethynyl)-1,4-dibutoxybenzene (2.30 g, 87.8%) as a white solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.91 (s, 2H), 3.97 (t, 4H, $J = 6.3$ Hz), 1.84–1.75 (m, 4H), 1.62–1.49 (m, 4H), 0.99 (t, 6H, $J = 7.5$ Hz). 0.27 (s, 18H). A mixture of 2,5-bis(trimethylsilylethynyl)-1,4-dibutoxybenzene (0.85 g, 2.05 mmol) in 1 mol L^{-1} KOH methanol solution (50 mL) was stirred at room temperature for 1 h. The completion of the reaction was determined by TLC. The reaction mixture was poured into water (20 mL) and extracted with $CHCl_3$ (2×30 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and then evaporated in vacuo to dryness to give M-1 (0.50 g, 90.9%) as a pale yellow solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.97 (s, 2H), 4.00 (t, 4H, $J = 6.6$ Hz), 3.35 (s, 2H), 1.83–1.78 (m, 4H), 1.56–1.51 (m, 4H), 0.99 (t, 6H, $J = 7.2$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.9, 117.7, 113.2, 82.3, 79.7, 69.2, 31.1, 19.1, 13.7. FT-IR (KBr, cm^{-1}): 3270, 2962, 2921, 2861, 1498, 1465, 1402, 1384, 1221, 1063, 1025. MS (EI, m/z): 270 (29%), 214 (6%), 158 (100%), 102 (11%), 84 (14%), 49 (23%). Anal. calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.90; H, 8.25.

2.4. Preparation of the conjugated polymer (Scheme 1)

A mixture of M-1 (108.0 mg, 0.40 mmol), M-2 (64.0 mg, 0.40 mmol), 10 mol% sodium ascorbate (7.92 mg, 0.040 mmol) and 5 mol% $Cu_2SO_4.5H_2O$ (4.99 mg, 0.020 mmol) was dissolved in the mixed solvents of 10 mL THF, 10 mL *t*-BuOH, and 10 mL H_2O. The solution was stirred at 30–36 °C for 2 days under N_2. The solvents were removed under reduced pressure and the residue was extracted with $CHCl_3$ (2×50 mL). The organic layer was washed with an aqueous NH_4OH solution, water and then dried over anhydrous Na_2SO_4. After the solution was removed, the resulting polymer was precipitated into methanol, and then filtered and washed with methanol several times. Further purification could be conducted by dissolving the polymer in $CHCl_3$ to precipitate in methanol again. The polymer was dried in vacuum to give 138.0 mg as a yellow solid in 80.2% yield. $M_w = 8400$, $M_n = 7080$, PDI = 1.2. ^{1}H NMR (300 Hz, DMSO-d_6): δ 8.97 (s, 1H), 8.84 (s, 1H), 8.22–7.97 (m, 2H), 7.83–7.22 (m, 4H), 4.35–4.10 (m, 4H), 1.94–1.87 (m, 4H), 1.55–1.46 (m, 4H), 1.02–0.94 (m, 4H). FT-IR (KBr, cm^{-1}): 2956, 2931, 2869, 2093, 1525, 1243, 1029. Anal. calcd for $C_{24}H_{26}N_6O_2$: C, 66.96; H, 6.09; N, 19.52. Found: C, 66.76; H, 6.21; N, 19.43.

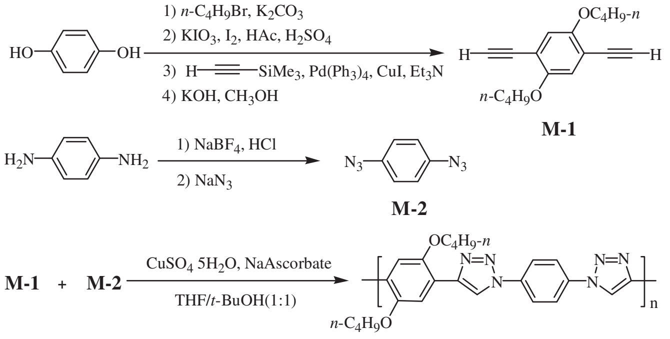
2.5. Metal ion titration

Each metal ion titration experiment was started with a 3.0 mL polymer in $CHCl_3$ solution with a known concentration (1.0×10^{-5} mol L^{-1}). Mercury perchlorate salt and other various metal salts (nitrate, 1.0×10^{-3} mol L^{-1}, CH_3CN) were used for the titration. Polymer–metal complexes were produced by adding aliquots of a solution of the selected metal salt to a $CHCl_3$ solution of the polymer. All kinds of measurements were monitored 2 h after addition of the metal salt to the polymer solutions.

3. Results and discussion

3.1. Synthesis and feature of the conjugated polymer

The synthesis procedures of the monomers 1,4-dibutoxy-2,5-diethynylbenzene (M-1), 1,4-diazidobenzene (M-2) and the conjugated polymer are outlined in Scheme 1. The monomer M-1 could be obtained by a 4-step reaction from the starting material *p*-dihydroxybenzene [28]. M-1 and M-2 could be served as the monomers for the synthesis of the target polymer. In this paper, a typical click reaction condition was applied to the synthesis of the polymer [21,29]. The polymerization could be carried out under mild reaction conditions in THF/*t*-BuOH (1:1, v/v) solution in the presence of a catalytic amount of sodium ascorbate (10%mol) and $CuSO_4 \cdot 5H_2O$ (5%mol) with a good yield as high as 80.2%. The number-average molecular weight (M_n) and the weight-average



Scheme 1. Synthesis procedures of the polymer sensor.

molecular weight (M_w) of the polymer are 7080 and 8400 with polydispersity index of 1.2. The GPC result of the polymer shows the moderate molecular weight. The resulting polymer shows moderate solubility in common solvents, such as toluene, THF, $CHCl_3$, and CH_2Cl_2, which can be attributed to the flexible *n*-butyl group substitutents on phenyl units as side chains of the polymer. TGA of the polymer was carried out under a N_2 atmosphere at a heating rate of 10 °C/min (See Supporting Information, Fig. S1). The results show the polymer has high thermal stability without loss weight before 240 °C.

3.2. *The selective and sensitive recognition of the polymer sensor on Hg^{2+}*

The absorption spectra of the polymer in $CHCl_3$ solution display two absorption peaks at 273 and 339 nm and the fluorescent wavelength of the polymer appears at 377 nm with the excitation at 339 nm (See Supporting Information, Fig. S2). The photoluminescence efficiency (Φ_{PL}) of polymer is 0.24 with reference to quinine sulfate in 0.5 mol L^{-1} H_2SO_4 solution. The effects of the fluorescence response behaviors of the polymer on various transition metal ions have been investigated. Fig. 1 shows the fluorescence spectra of the polymer (1.0×10^{-5} mol L^{-1} in $CHCl_3$) upon the addition of Hg^{2+} in CH_3CN solution. As is evident from Fig. 1, obvious fluorescence quenching could be observed upon the addition of Hg^{2+}. Hg^{2+} leads to about 74.3% fluorescence quenching for the polymer at a concentration of 4:1 molar ratio. Moreover, the fluorescent wavelength of the metal-chelated polymer appears the obvious red shift upon the molar ratio additions from 1:2 to 1:3, which may be attributed to the conjugation effect between triazole moiety and phenyl group while triazole moiety in the polymer main chain coordinates with Hg^{2+}. As shown in Fig. 2, it can be also found the fluorescence intensity of the polymer shows gradual decrease with the concentration mole ratio of Hg^{2+} from 0 to 5.0. A curve equation is got in the range of Hg^{2+} concentrations from 0 to 2.0×10^{-5} mol L^{-1} is $F = 5.65 \times 10^4 – 9.80 \times 10^8$ $[Hg^{2+}]$, $R = -0.997$, $N = 7$ (See Supporting Information, Fig. S3). According to the equation and the standard deviation of the blank, the fluorescence detection limit of the polymer solution for Hg^{2+} was determined to be as low as 4.6×10^{-7} mol L^{-1}. Fluorescence spectra of the polymer (1.0×10^{-5} mol L^{-1}) in $CHCl_3$ with increasing amounts of Hg^{2+} in CH_3CN (5.0×10^{-5} mol L^{-1}) at different time have been investigated in order to get the response time of the fluorescence sensor to Hg^{2+} (See Supporting Information, Fig. S4). The response time of the polymer sensor to Hg^{2+} is 2 h.

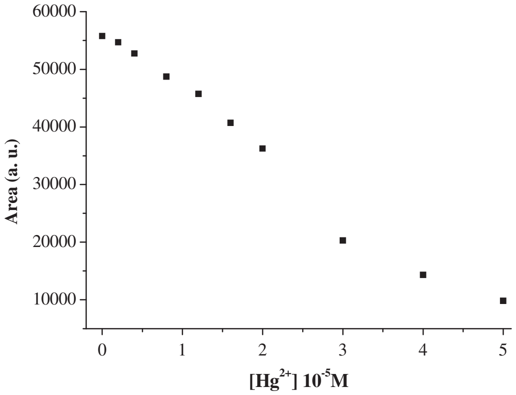


Fig. 2. Fluorescence intensity of the conjugated polymer vs the increasing concentration of Hg^{2+} from 1:0 to 1:5 molar ratios.

The fluorescence response behaviors of the polymer on other transition metal ions were also examined under the same condition as Hg^{2+} ion determination (Fig. 3). The fluorescence intensities of the polymer are not almost affected by the addition of Cd^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} and Cu^{2+}. Although the fluorescence quenching of the polymer detected upon adding Ag^+ ion, the value of the fluorescence quenching efficiency of the polymer for Hg^{2+} ion is approximately 2.8 times higher than that for Ag^+ ion. These results indicate that the polymer possesses specific recognition ability for Hg^{2+} ion. Normally, the excellent fluorescence sensor with highly sensitive and selective feature need meet one of the essential requirements which is minor or no interference from other metal ions. In this paper, we further investigated the utility of the polymer as an ion-selective fluorescence sensor for Hg^{2+}. Herein, we subjected the polymer (1.0×10^{-5} mol L^{-1}) to a mixture of Hg^{2+} (4.0×10^{-5} mol L^{-1}) and each of the metals (4.0×10^{-5} mol L^{-1}) as shown in Fig. 4. The deviations from other transition metals' interference are less than 8% in the coexisted metal experiment. Most importantly, while the fluorescence response was carried out by the Hg^{2+} titrations in presence of the mixed metal ions, such as Co^{2+}, Ni^{2+}, Ag^+, Cd^{2+}, Cu^{2+} and Zn^{2+}, no obvious interference was observed in the fluorescence of the polymer. Herein, the polymer is specifically sensitive toward Hg^{2+}, not toward other metals, which can be arisen from several factors, such as the structural rigidity of the triazole unit, the larger radius of the Hg^{2+} ion and coordination diversification of Hg^{2+}, its soft acid property, the binding ability of triazole unit and strong Hg–N binding [17]. Because of its $5d^{10}6s^2$ electronic configuration and lack of ligand field stabilization energy, Hg(II) can accommodate

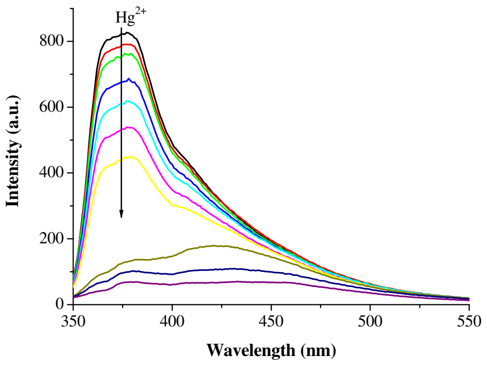


Fig. 1. Fluorescence spectra of the polymer (1.0×10^{-5} mol L^{-1}) in $CHCl_3$ with increasing amounts of Hg^{2+} in CH_3CN (0, 0.2, 0.4, 0.8, 1.2, 1.6, 2.0, 3.0, 4.0, 5.0×10^{-5} mol L^{-1}) ($\lambda_{ex} = 339$ nm).

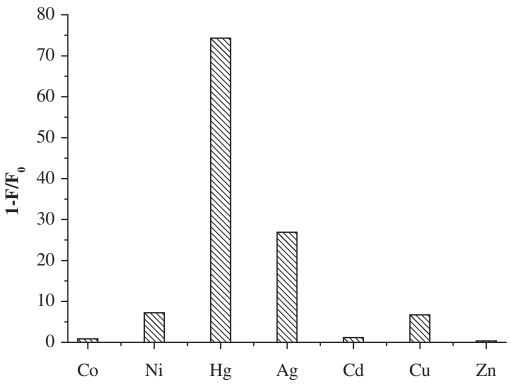


Fig. 3. Fluorescence quenching efficiencies of the polymer (1.0×10^{-5} mol L^{-1}) in the presence of various transition metal ions (each 4.0×10^{-5} mol L^{-1}).

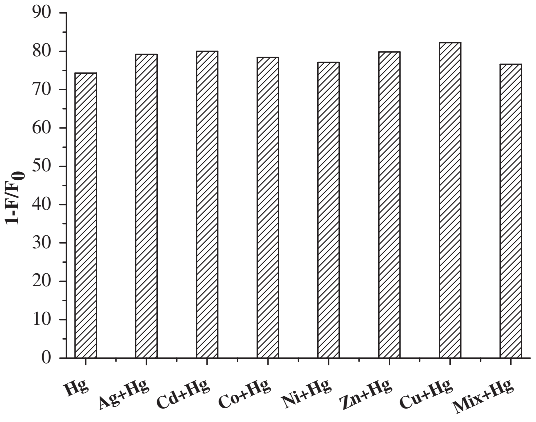


Fig. 4. Metal specificity: the concentration of the polymer is 1.0×10^{-5} mol L^{-1}, Hg^{2+} and other metal ion are used at a concentration of 4.0×10^{-5} mol L^{-1}, respectively. Mix: the mixture of Ag^{+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} and Cu^{2+}.

a range of coordination numbers and geometries. Two-coordinate linear and four coordinate tetrahedral species are common. Hg(II) is a soft acid and the use of soft donor atoms, including nitrogen, sulfur or phosphorus, in a chelating unit will generally increase its affinity and selectivity for Hg(II) [3]. The results indicate that the polymer can also be used as a sole Hg^{2+} probe with high selectivity.

4. Conclusion

The polymer sensor incorporating triazole unit could be synthesized by click reaction. The responsive properties of the polymer on various transition metal ions were investigated by fluorescence spectra. Compared with other cations, such as Co^{2+}, Ni^{2+}, Ag^{+}, Cd^{2+}, Cu^{2+} and Zn^{2+}, Hg^{2+} can exhibit the most pronounced fluorescence response of the polymer due to triazole moiety in the polymer main chain as the metal binding ligand. The results indicate this kind of polymer with triazole moiety can be used as a selective fluorescence sensor for Hg^{2+} detection. This work can further expand the application of click reaction in design and synthesis of the novel fluorescence sensor incorporating triazole unit for metal ion detection.

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Appendix. Supporting information

Supplementary data associated with this article can be found in the online version, at doi: 10.1016/j.polymer.2010.05.001.

References

[1] McQuade DT, Pullen AE, Swager TM. Chem Rev 2000;100:2537–74.
[2] Thomas III SW, Joly GD, Swager TM. Chem Rev 2007;107:1339–86.
[3] Nolan EM, Lippard SJ. Chem Rev 2008;108:3443–80.
[4] Kim IB, Dunkhorst A, Gilbert J, Bunz UHF. Macromolecules 2005;38:4560–2.
[5] Fan LJ, Jones WE. J Am Chem Soc 2006;128:6784–5.
[6] Zhang Z, Wu D, Guo X, Qian X, Lu Z, Zu Q, et al. Chem Res Toxicol 2005;18:1814–20.
[7] Grandjean P, Heihe P, White RF, Debes F. Environ Res 1998;77:165–72.
[8] Boening DW. Chemosphere 2000;40:1335–51.
[9] Harris HH, Pickering IJ, George GN. Science 2003;301:1203.
[10] de Silva AP, Gunaratne HQN, Gunnlaugsson T, Huxley AJM, McCoy CP, Rademacher JT, et al. Chem Rev 1997;97:1515–66.
[11] Fan LJ, Zhang Y, Jones WE. Macromolecules 2005;38:2844–9.
[12] Kim IB, Bunz UHF. J Am Chem Soc 2006;128:2818–9.
[13] Tang Y, He F, Yu M, Feng F, An L, Sun H, et al. Macromol Rapid Commun 2006;27:389–92.
[14] Liu X, Tang Y, Wang L, Zhang J, Song S, Fan C, et al. Adv Mater 2007;19:1471–4.
[15] Li C, Zhou C, Zheng H, Yin X, Zou Z, Liu H, et al. J Polym Sci Part A Polym Chem 2008;46:1998–2007.
[16] Liu X, Zhu J. J Phys Chem B 2009;113:8214–7.
[17] Zou Y, Wan M, Sang G, Ye M, Li Y. Adv Funct Mater 2008;18:2724–32.
[18] Huang X, Xu Y, Miao Q, Zong L, Hu H, Cheng Y. Polymer 2009;50:2793–805.
[19] Huang X, Meng J, Dong Y, Cheng Y, Zhu C. J Polym Sci Part A Polym Chem 2010;48:997–1006.
[20] Kolb HC, Finn MG, Sharpless KB. Angew Chem Int Ed 2001;40:2004–21.
[21] Rostovtsev VV, Green LG, Fokin VV, Sharpless KB. Angew Chem Int Ed 2002;41:2596–9.
[22] Droumaguet BL, Velonia K. Macromol Rapid Commun 2008;29:1073–89.
[23] Lundberg P, Hawker CJ, Hult A, Malkoch M. Macromol Rapid Commun 2008;29:998–1015.
[24] Binder WH, Sachsenhofer R. Macromol Rapid Commun 2008;29:952–81.
[25] Lodge TP. Macromolecules 2009;42:3827–9.
[26] Tamanini E, Katewa A, Sedger LM, Todd MH, Watkinson M. Inorg Chem 2009;48:319–24.
[27] Minato M, Lahti PM. J Am Chem Soc 1997;119:2187–95.
[28] Plater MJ, Sinclair JP, Aiken S, Gelbrich T, Hursthouse MB. Tetrahedron 2004;60:6385–94.
[29] Karim MA, Cho Y, Park JS, Ryu TI, Lee MJ, Song M, et al. Macromol Chem Phys 2008;209:1967–75.