Polym. Bull. (2010) 65:455–463
DOI 10.1007/s00289-009-0221-1

ORIGINAL PAPER

A one-pot approach to dendritic star polymers via double click reactions

Xing Q. Xiong · Yuan H. Xu

Received: 12 July 2009 / Revised: 31 October 2009 / Accepted: 21 November 2009 /

Abstract A class of well-defined dendritic star polymers with poly (ε-caprolactone) (PCLs) on the periphery has been prepared via one-pot double click reactions (Cu-catalyzed azide/alkyne click chemistry, i.e., CuAAC and Diels–Alder [4+2] cycloaddition reactions). The predecessors for Diels–Alder reaction, maleimide end-functionalized PCLs were produced by ring-opening polymerization (ROP). Obtained dendritic star polymers were characterized by ^{1}H NMR, size exclusion chromatography (SEC), UV/vis, and fluorescence spectroscopy.

Keywords Dendritic star polymers · Double click reactions · One-pot synthesis

Introduction

Dendrimers [1–4] are monodispersed, highly branched, well-defined three-dimensional macromolecules with a large number of reactive end groups. The size, the number of end groups, and the functionality are tailor-made. Star polymers [5, 6] are composed of multiple polymer chains emanating from a central core and have obvious advantages due to their compact structure and higher degrees of chain end functionality.

Dendritic star polymers [7–9], which are the structural hybrids of the dendrimers and star polymers, not only have the common features and properties of both, but also are equipped with the other special functions. Recently, dendritic star polymers have attracted considerable attention from academia and application because of

---

Electronic supplementary material The online version of this article (doi:10.1007/s00289-009-0221-1) contains supplementary material, which is available to authorized users.

X. Q. Xiong (✉) · Y. H. Xu
College of Materials Science & Engineering, Huaqiao University, 361021 Xiamen, China
e-mail: xxqluli@hqu.edu.cn

their unique physical and chemical properties that originated from their inherent branching structures and shapes. They have become attractive nanoscale subjects for various applications such as stabilizers for colloids [10], DNA release [11], electrokinetic capillary chromatography [12], etc.

In general, there are two synthetic strategies, i.e., divergent and convergent methodologies, to synthesize dendritic star polymers. In a divergent strategy, the polymer chains are simultaneously grown from a multifunctional initiator via living polymerization techniques [13–15]. The second route is known as convergent approach [16–18]. By this strategy, perfect polymer chains with a proper end-group functionality are coupled onto a preformed multifunctional core. However, with the stereo-hindrance effect increase, this strategy faces the shortcomings of incomplete grafting and low yields.

In order to obtain defect-free dendritic star polymers, chemical reactions with highly efficient selectivity, strong tolerance of functional groups and quantitative yield are usually introduced into this strategy. At present, the double click reactions concept, namely the orthogonal combination of CuAAC and Diels–Alder [4+2] cycloaddition reactions, has drawn great attention in polymer chemistry because it meets the requirement for the orthogonal synthesis of polymeric materials through accelerated synthetic strategies [19–22]. Tunca et al. studied the synthesis of nonlinear copolymers by CuAAC and Diels–Alder [4+2] cycloaddition reactions first. It was found that one-pot double click reactions were efficient and facile synthetic method for the preparation of well-defined polymeric materials.

In this article, we report an orthogonal approach to synthesize Fréchet-type and PCL-maleimide dendritic star polymers with well-defined structure using double click reactions with a one-pot technique. As showed in Scheme 1, the whole synthetic process of this work was carried out by attachment of anthracene groups onto the multifunctional core by CuAAC and then by postmodification of anthracene-containing core through Diels–Alder [4+2] cycloaddition. By this strategy, PCL-maleimide may be grafted onto the multifunctional core through an accelerated method, and this process can also be monitored easily using UV/vis and fluorescence measurements.

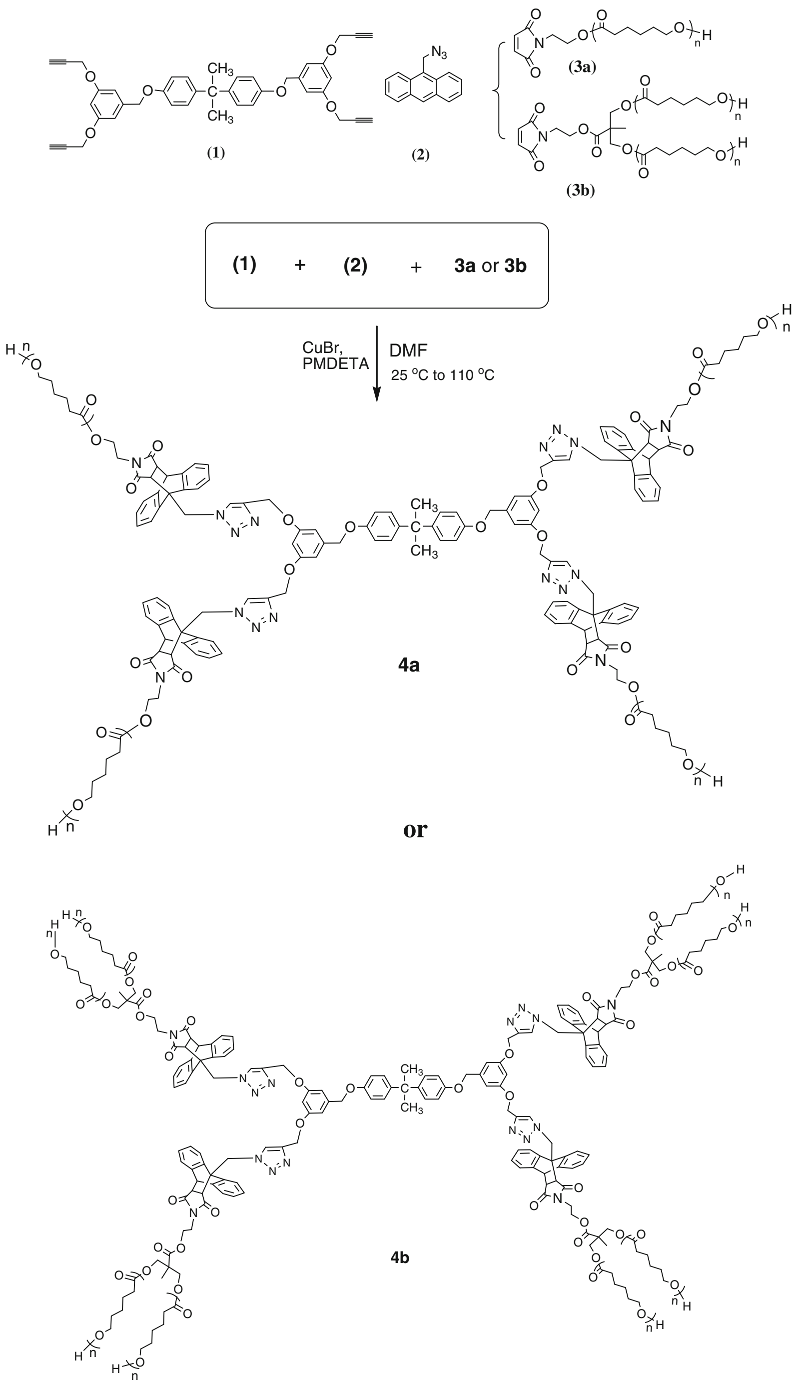
Experimental

Materials

ε-CL (tech 99%, Alfa), $SnOct_2$ (Alfa), and sodium hydride (NaH; 60% dispersed in mineral oil, Aldrich) were used as received. Maleic anhydride (MAn) was recrystallized from benzene. Other reagents were used without further purification. Compounds **1** and **2**, **3a**′, and **3b**′ were prepared (all of purity ≥98%) according to literature procedures [22] and [23], respectively.

Instruments

^{1}H NMR spectra were acquired in $CDCl_3$ on a Bruker DMX-400 spectrometer, the chemical shifts are given in δ values from TMS as an internal standard. SEC using



Scheme 1 Structure of building blocks and strategy to prepare dendritic star polymers **4a** and **4b** by one-pot double click reactions

polystyrene as a standard was obtained on a Waters 2414 instrument with THF as an eluent at a flow rate of 1.0 mL/min. Fluorescence spectra were recorded on a Varian Cary-Eclipse spectrophotometer.

Synthesis of PCL-maleimide **3a** and **3b**

A typical polymerization procedure was as follows. Hydroxyl-terminated initiators **3a**′ or **3b**′ (1.5 mmol), ε-CL (60.0 mmol for **3a**′ and 120.0 mmol for **3b**′, 40.0 equiv), $Sn(Oct)_2$ (5×10^{-3} equiv) and a dried magnetic stirring bar were added into the polymerization tube. The polymerization mixture was degassed with freeze-evacuate-thaw cycle thrice and sealed. The reaction was carried on at 110 °C in an oil bath for 24 h. After being cooled to room temperature, the resultant polymer was dissolved in THF and precipitated twice from ice-cooled ether, affording the purified PCL-maleimide **3a** or **3b**. The obtained products were dried in a vacuum oven until constant weight.

One-pot synthesis of dendritic star polymers **4a** and **4b** via double click reactions

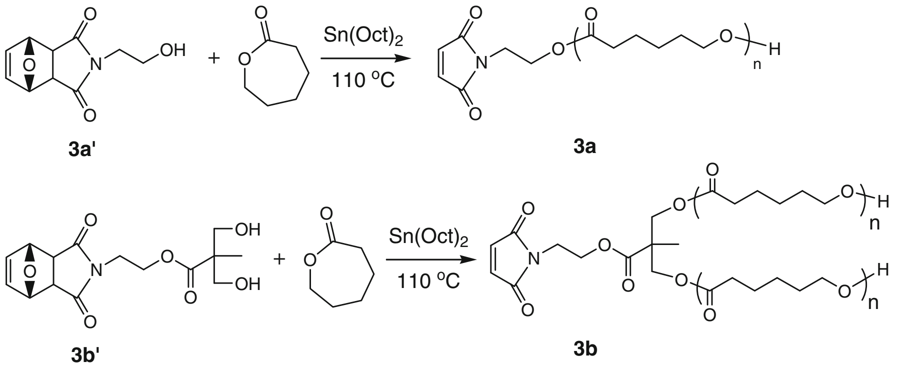
Compound **1** (0.50 g, 0.80 mmol), azide-functionalized anthracene **2** (0.82 g, 3.50 mmol), and PCL-maleimide **3a** or **3b** (6.40 mmol, 2.0 equiv) were dissolved in nitrogen-purged DMF (10 mL) in a Schlenk flask, CuBr (46.0 mg, 0.32 mmol, 0.1 equiv) and PMDETA (55.4 mg, 0.32 mmol, 0.1 equiv) were added, and the reaction mixture was degassed by three freeze-pump-thaw cycles and left under nitrogen and stirred at room temperature for 12 h. Then, the reaction mixture continued to stir at 110 °C for 12 h. When the reaction was completed, the mixture was evaporated under high vacuum. The crude product obtained was then dissolved in 5.0 mL of THF and passed through alumina column to remove copper salt. The solution was evaporated to give a crude product, which was dissolved in THF (5.0 mL) and precipitated thrice from ice-cooled petroleum ether. The dendritic star polymer **4a** or **4b** was isolated as a white solid (the yields were 68 and 55%, respectively).

Results and Discussion

Synthesis of PCL-maleimide **3a** and **3b**

PCL-maleimide **3a** and **3b** were prepared by ROP of ε-CL with hydroxyl-terminated initiators **3a**′ and **3b**′ (the feed molar ratio of ε-CL and hydroxyl groups was 40) in the presence of $SnOct_2$ (5×10^{-3} equiv) as the catalyst at 110 °C for 24 h by one-pot technique (Scheme 2). **3a** and **3b** were synthesized with the yields of 81 and 79%, respectively.

The structures of **3a** and **3b** were confirmed by ^1H NMR. The ^1H NMR spectrum of **3b** was shown in Fig. 1 (see Fig. S1 in Supporting Information for the ^1H NMR spectrum of **3a**). The single peak at 6.70 ppm is assigned to the proton of C*H*=C*H*. The triple peaks at 4.20 and 3.75 ppm, respectively, stands for the protons of H-c



Scheme 2 Synthesis of PCL-maleimide **3a** and **3b**

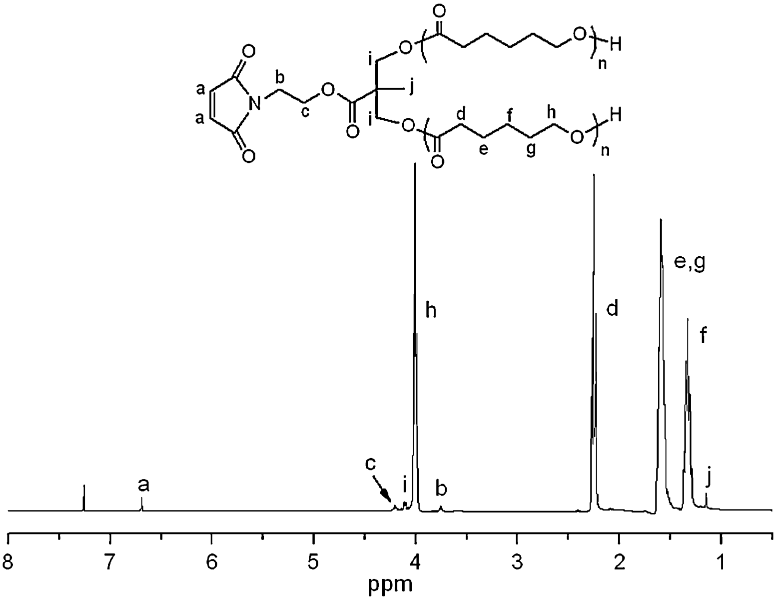


Fig. 1 ^{1}H NMR spectrum of **3b** in CDCl$_3$ with assignment

and H-b of methylene. The peaks at 4.00, 2.25, 1.58, and 1.33 ppm stand for the protons of the PCL chains. The ^{1}H NMR spectrum confirm that ROP of ε-CL can be initiated by hydroxyl-terminated maleimide and the furan groups have been completely removed based on the disappearance of the resonance of signals at 5.30 and 6.50 ppm. The other correlative signals could be assigned to the corresponding protons of **3b** as shown in Fig. 1.

The characterization data of **3a** and **3b** by NMR and SEC are summarized in Table 1. The molecular weights determined by ^{1}H NMR from the ratio of integrated peak areas of the methylene protons next to ether oxygen (h) to the C*H*=C*H* protons

Table 1 Characterization data by molecular weights and polydispersities from NMR and SEC of **3a** and **3b**

Sample	M_n (NMR)	M_n (SEC)	M_w/M_n (SEC)	DP (NMR)
3a	3,600	5,100	1.13	30
3b	9,600	8,400	1.28	40

(a) is about 3,600 g/mol for **3a** (DP $\sim$ 30 per arm) and 9,600 for **3b** (DP $\sim$ 40 per arm), respectively.

One-pot synthesis of dendritic star polymers **4a** and **4b** via double click reactions

Compound **1**, azide-functionalized anthracene **2** and PCL-maleimide **3a** or **3b** were reacted in one pot in order to produce the corresponding dendritic star polymers **4a** or **4b** via the double click reactions (Scheme 1). During the process, excess amounts of **2** (3.5 mmol, 1.1 equiv) and **3a** or **3b** (6.4 mmol, 2.0 equiv) are used to compare to that of **1** (0.8 mmol). A click reaction was accomplished between the azide of 2 and the multifunctional core **1** catalyzed by CuBr/PMDETA in DMF at room temperature. When the reaction was completed, the reaction mixture was heated to 110 °C and continued to stir for 12 h. In this process, a Diels–Alder [4+2] reaction was accomplished between anthracene group of the intermediate and PCL-maleimide **3a** or **3b**.

Evidence for the occurrence of the double click reactions were obtained from ^{1}H NMR, SEC, UV/vis, and fluorescence spectroscopy. The ^{1}H NMR spectrum of dendritic star polymer **4b** was shown in Fig. 2 (see Fig. S2 in Supporting Information for the ^{1}H NMR spectrum of **4a**). As can be seen from Fig. 2, the peaks between 7.60 and 8.40 ppm, characteristic for aromatic protons of anthracene, completely disappeared, which clearly indicated the quantitative efficiency of the process. It revealed that the loss of the aromaticity of the central phenyl units of anthracene as a result of Diels–Alder cycloaddition. Furthermore, a double peak appeared approximately at 4.74 ppm due to the bridgehead proton of the cycloadduct H-m. The peaks at 4.05, 2.29, 1.64, and 1.37 ppm were assigned to H-o, H-h, H-i and H-j of PCLs, respectively. These results revealed that the synthesis of dendritic star polymer **4b** by one-pot double click reactions was achieved efficiently.

UV/vis and fluoroescence spectra might provide further evidence for the efficiency of Diels–Alder reaction. In order to obtain a direct comparison easily, the intermediate anthracene derivative **2′** of the CuAAC reaction was isolated, whose detailed structural analysis was shown in the Fig. S4. In UV/vis measurements (Fig. 3 for **2′** and **4b**, Fig. S5 for **2′** and **4a**), although compound **2′** displayed characteristic five-finger absorbance in the range of 300–400 nm, the dendritic star polymer **4b** showed no absorbance in the same region (Fig. 3b), which was caused by the loss of the aromaticity of central phenyl unit of anthracene.

Figure 3 (right) showed the fluorescence spectra of the intermediate **2′** before and after the reaction with PCL-maleimide. The characteristic fluorescent band of the

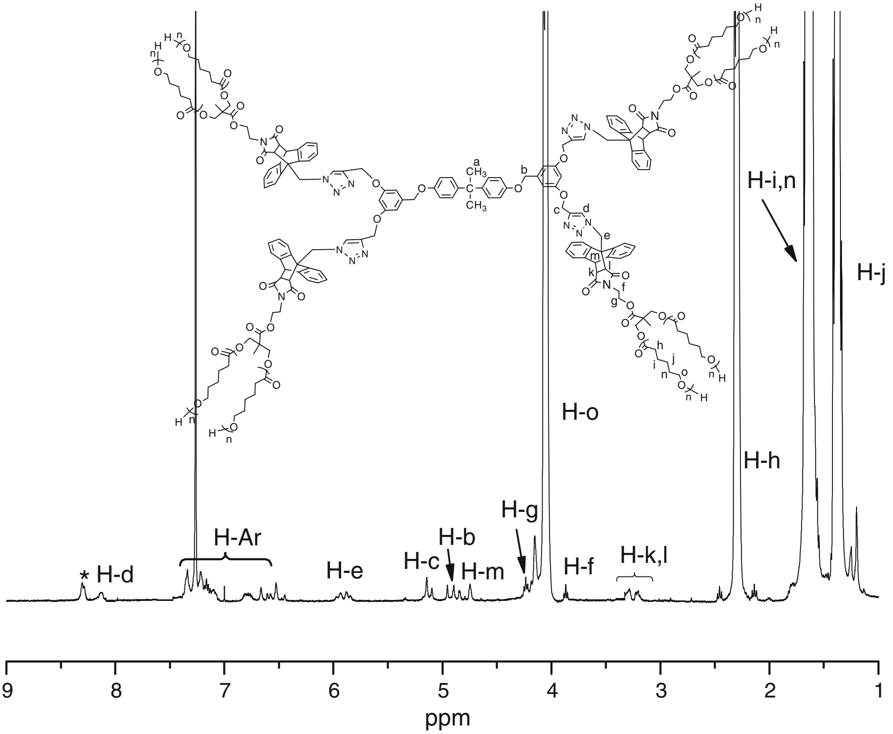


Fig. 2 ^{1}H NMR spectrum of **4b** in $CDCl_3$ with assignment

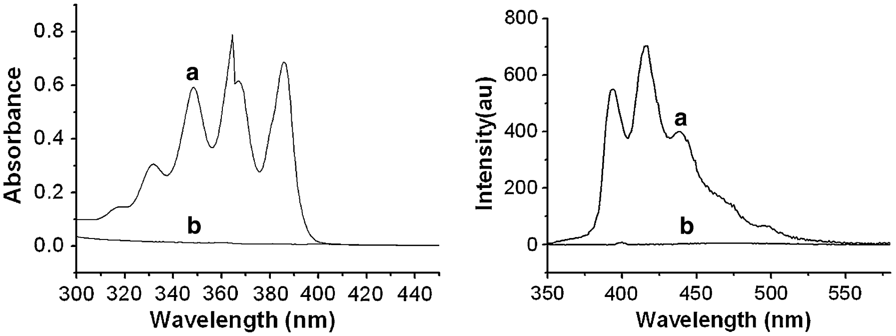


Fig. 3 Comparison of UV/vis (*left*) and fluorescence spectra (*right*, $\lambda_{exc} = 350$ nm) of **2′** (*a*) and **4b** (*b*) in THF (5.0×10^{-5} M for UV/vis and 2.0×10^{-5} M for fluorescence spectra, 25 °C)

anthracene group between 350 and 500 nm disappeared completely after Diels–Alder reaction. From the results of ^{1}H NMR, UV/vis, and fluorescence measurements, a conclusion could be drawn that a quantitative Diels–Alder reaction had happened between anthracene and PCL-maleimide. That is to say, the

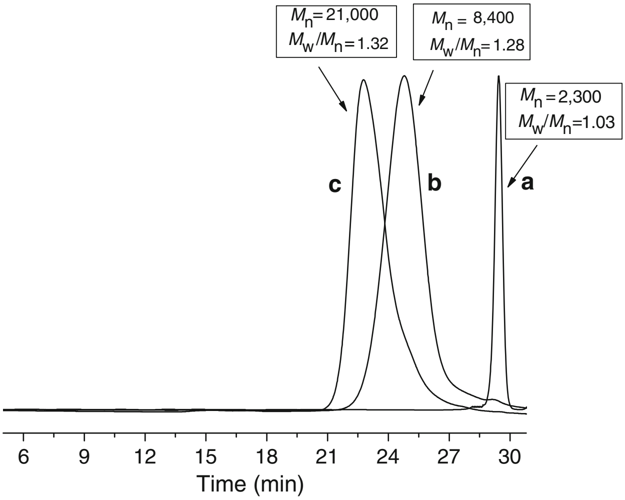


Fig. 4 SEC traces of **1** (trace *a*), **3b** (trace *b*) and dendritic star polymer **4b** (trace *c*)

PCL-maleimide had been attached onto the multifunctional core successfully by Diels–Alder reaction between anthracene and maleimide derivatives.

To demonstrate dendritic star polymers formation, the obtained products were also characterized by SEC (Fig. 4). SEC analysis of **4b** clearly showed an obvious shift to higher molecular weight, implying the grafting of the PCL-maleimide **3b** onto anthracene-functionalized core (see Fig. S3, c for the SEC traces of **4a**).

Conclusions

We have studied one-pot synthesis of dendritic star polymers via combining efficiently CuAAC and Diels–Alder [4+2] cycloaddition strategy. Based on ^{1}H NMR, SEC, UV–vis, and fluorescence analysis, we can know a class of well-defined dendritic star polymers has been prepared. One-pot strategy is a more convenient way to produce dendritic star polymers compared with the conventional synthetic methodologies. This facile synthetic method can furthermore afford production of dendritic star polymers with different compositions and functions.

Acknowledgments Financial support by the Special Foundation for Young Scientists of Fujian Province, China (Grant No. 2008F3067) and the Scientific Research Starting Foundation of Huaqiao University, China (Grant No. 08BS301) are greatly acknowledged.

References

1. Fréchet JMJ, Tomalia DA (2002) Dendrimers and other dendritic polymers. Wiley, New York
2. Newkome GR, Moorefield CN, Vögtle F (2001) Dendrimers and dendrons, concepts, syntheses, applications. Wiley-VCH, Weinheim

3. Matthews OA, Shipway AN, Stoddart JF (1998) Prog Polym Sci 23:1
4. Bosman AW, Janssen HM, Meijer EW (1999) Chem Rev 99:1665
5. Mishra M, Kobayashi S (1999) Star and hyperbranched polymers. Marcel Dekker Inc., New York
6. Inoue K (2000) Prog Polym Sci 25:453
7. Trollsås M, James LH (1998) J Am Chem Soc 120:4644
8. Trollsås M, Kelly MA, Claesson H, Siemens R, Hedrick JL (1999) Macromolecules 32:4917
9. Trollsås M, Atthof B, Würsch A, Hedrick JL (2000) Macromolecules 33:6423
10. Hedden RC, Bauer BJ, Smith AP, Grohn F, Amis E (2002) Polymer 43:5473
11. Yin M, Ding K, Gropeanu RA, Shen J, Berger R, Weil T, Müllen K (2008) Biomacromolecules 9:3231
12. Luo D, Haverstick K, Belcheva N, Han E, Saltzman WM (2002) Macromolecules 35:3456
13. Hovestad NJ, Koten GV, Bon SAF, Haddleton DM (2000) Macromolecules 33:4048
14. Zhao YL, Shuai XT, Chen CF, Xi F (2004) Macromolecules 37:8854
15. Zheng Q, Pan CY (2005) Macromolecules 38:6841
16. Baek KY, Kamigaito M, Sawamoto M (2002) Macromolecules 35:1493
17. Xia JH, Zhang X, Matyjaszewski K (1999) Macromolecules 32:4482
18. Baek KY, Kamigaito M, Sawamoto M (2001) Macromolecules 34:215
19. Durmaz H, Dag A, Hizal A, Hizal G, Tunca U (2008) J Polym Sci A 46:7091
20. Dag A, Durmaz H, Demir E, Hizal G, Tunca U (2008) J Polym Sci A 46:6969
21. Gacal B, Akat H, Balta DK, Arsu N, Yagci Y (2008) Macromolecules 41:2401
22. Xiong XQ (2009) Aust J Chem 62:1371
23. Xiong XQ, Chen YM, Feng S, Wang W (2007) Macromolecules 40:9084