Polymer Chemistry

PAPER

View Article Online
View Journal | View Issue

Cite this: *Polym. Chem.*, 2015, **6**, 6880

Received 19th July 2015,
Accepted 7th August 2015

DOI: 10.1039/c5py01131k

www.rsc.org/polymers

A fixable supramolecular cyclic polymer based on the cucurbit[8]uril-stabilized π–π interaction†

Zhongwei Ji,[a] Yipeng Li,[b] Yu Ding,[b] Guosong Chen*[a] and Ming Jiang[a]

A novel reversible unimolecular cyclization method based on the CB[8]-stabilized interaction in an aqueous environment has been investigated. The dynamic properties of the cyclic PEG chain were monitored by viscometry and DLS. Upon photo-irradiation, the cyclic PEG was covalently fixed and utilized for GPC characterization.

Introduction

Preparation of polymers with different topological structures has been a long-term goal for polymer chemists, as properties of the resulting materials are intimately related to their architectures. With elaborate design and synthesis, a variety of precisely controlled polymer topologies have been attained.[1] Among them, cyclic polymers have attracted considerable interest, owing to their unique physical properties compared to their linear or branched counterparts.[2] Despite the difficulties in synthesis, cyclic polymers with various chemical structures[3] have been realized due to the development of novel synthetic protocols, which are mainly based on controlled polymerization techniques as well as coupling reactions with high efficiency. One of the most explored and versatile routes utilized to prepare a cyclic architecture is cyclization of a linear precursor, which typically involves a bimolecular or unimolecular end group coupling reaction. In the last few decades, efforts have been made to solve problems in ring closure, such as low yields and polycondensation byproduct formation, most of which were based on different chemical reactions forming covalent bonds.

Being a research group devoted to macromolecular assembly, we have great interest in cyclizing polymers *via* non-covalent bonds, since the properties of the resulting materials could be tuned directly by their dynamic topologies, which is quite attractive for novel materials with special applications.[3c,f,4] Although there has been great success in cyclizing polymers *via* various covalent bonds, non-covalently cyclized polymers with reversible switching between their linear and ring state are still very rare. Two major problems have hindered their development: (1) the instability of the non-covalent bond in solvent and its concentration-dependency make the resulting polymers difficult to be characterized by Gel Permeation Chromatography (GPC) and Maldi-TOF as traditional polymers; (2) a relatively strong non-covalent interaction is required to obtain cyclic polymers in a highly diluted solution. Until now, although a couple of supramolecular interactions have been employed, including hydrogen bonding,[5] inclusion complexation,[6] and electrostatic interaction,[7] as far as we know, there have been only two reported reversible cyclic polymers with clear GPC evidence of showing a different elution time from their linear precursors, which were formed by dynamic covalent bonds in organic solvents.[8] In fact, such bonds under some circumstances are featured by covalent bonds. Thus it is still quite demanding to employ new supramolecular interactions for efficient polymer cyclization.

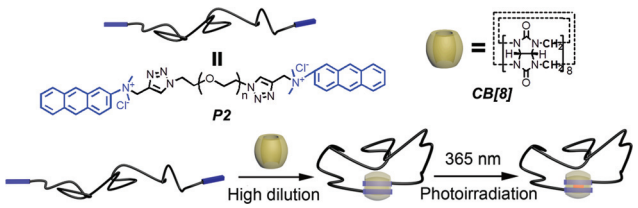
The pumpkin-shaped host, cucurbit[8]uril (CB[8]), has become very popular since the convenient synthetic protocol was published by Kim.[9] Its cavity is capable of encapsulating two guest molecules at the same time through hydrophobic and ion–dipole interactions, when it is employed to connect two molecules or polymers. A plethora of supramolecular structures have been prepared through the CB[8]-based host–guest complexation, including oligomers,[10] supramolecular polymers,[11] hydrogels,[12] microcapsules,[13] micelles[14] and responsive surfaces.[15] Moreover, the binding motif has induced protein dimerization in a highly diluted solution (20 μM).[16] Thus, CB[8]-based complexation is quite suitable to construct a polymeric ring, considering its high association constant (10^{10}–10^{13} M^{-2}), as one of the highest ones among all the synthetic non-covalent interactions.

Herein, this paper reports a novel reversible unimolecular cyclization method based on CB[8]-stabilized π–π interactions. Ring closure of naphthalene (or anthracene)-functionalized

[a]*State Key Laboratory of Molecular Engineering of Polymers, and Department of Macromolecular Science, Fudan University, Shanghai, 200433, China. E-mail: guosong@fudan.edu.cn*

[b]*Department of Physiology and Biophysics, School of Life Sciences, Fudan University, Shanghai 200438, China*

† Electronic supplementary information (ESI) available: Synthesis and characterization of **P1**, **P2** including ^{1}H NMR and GPC results, as well as details of UV-Vis, ITC and photoreaction. See DOI: 10.1039/c5py01131k



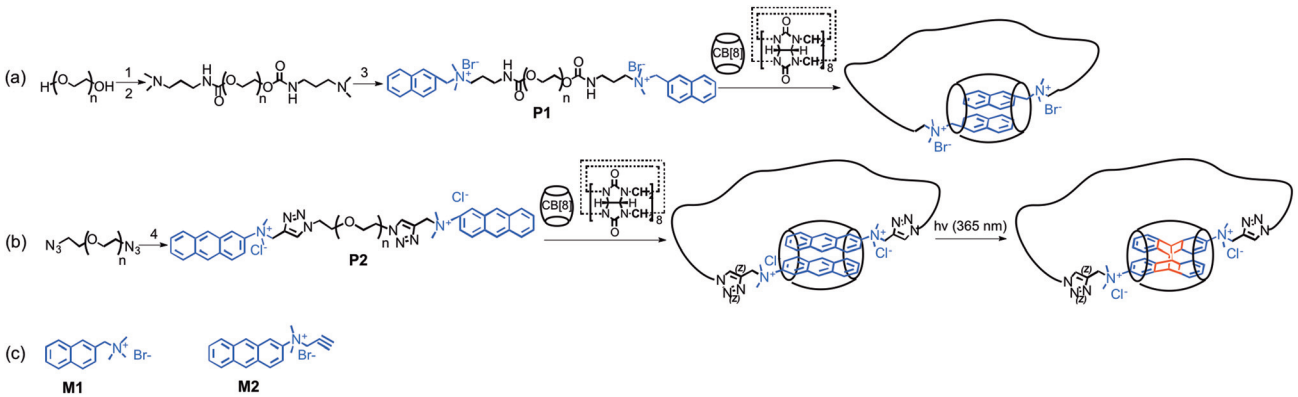
Scheme 1 Schematic representation of reversible cyclization based on the CB[8]-stabilized π–π interaction in a highly diluted aqueous solution, and the following covalent fixation through photo-irradiation at 365 nm.

polyethylene glycol (PEG, M_n = 20 000) was achieved in a highly diluted solution through addition of an equimolar amount of CB[8], which brought the two naphthalene (or anthracene) ends to a really close position in its cavity. More importantly, the π–π stacking of anthracene groups was further fixed to a covalent bond after irradiation under UV light (Scheme 1). Thus direct characterization of the cyclic polymer by GPC was achieved, which is very rare for this type of polymer linked by supramolecular interactions. It is also worth noting that the whole process occurred in water, thus this environmentally friendly cyclization may find further applications as a new concept of dynamic topologies and properties.

Results and discussion

To synthesize naphthalene (Np) end-functionalized PEG (**P1**, Scheme 2, S1†), a ternary amine terminated PEG chain was achieved through amidation between the carbonyldiimidazole (CDI) activated hydroxyl end of PEG and 3-dimethylaminopropylamine (Fig. S1†), followed by the electrophilic attack of 2-(bromomethyl)naphthalene. GPC showed the resulting cationic naphthalene telechelic PEG (**P1**, $M_{n,SEC}$ = 14 400, PDI = 1.12) shifted to a higher elution volume compared to the unmodified PEG ($M_{n,SEC}$ = 19 000, PDI = 1.11), probably due to the electrostatic interaction with the stationary phase (Fig. S2†). Successful incorporation of Np groups was confirmed by ^{1}H NMR spectroscopy (Fig. S3†). The relative peak area of the PEG backbone to the Np group indicated that more than 90% hydroxyl end was transferred to Np functionalization. Successive addition of CB[8] into an aqueous solution of **P1** resulted in a decrease of the intensities of the peaks corresponding to free Np and growth of a new set of signals assigned to CB[8]-encapsulated Np, which exhibited a significant broadening and upfield shift (Fig. S4†). The peaks of free Np disappeared when the molar ratio of **P1** and CB[8] reached 1 : 1, suggesting the successful formation of CB[8]-based host–guest complexes, in which the opposite alignment of the two singly charged guests was more favorable, although the two Np groups with the same direction could not be fully excluded.[17]

To provide more detailed information on the CB[8] enhanced π–π interaction, the naphthalene derivative *N*,*N*,*N*-trimethyl-1-(naphthalen-2-yl)methanaminium bromide (**M1**, ^{1}H NMR in Fig. S5†) was chosen as a model molecule and its binding ability with CB[8] was investigated by isothermal titration calorimetry (ITC).[18] In the experiment, an aqueous solution of **M1** (2 mM) was consecutively titrated into a solution of CB[8] (0.1 mM) at 25 °C (Fig. S6†). The binding stoichiometry of **M1** to CB[8] was confirmed to be 2 : 1, as indicated by the abrupt change in the titration curve. The generated exothermic binding isotherm fitted the two-site binding mode well yielding an overall binding constant of 1.30 × 10^{12} M^{-2}, which indicated that the host-enhanced π–π interaction between two cationic Np groups promoted by CB[8] could be strong enough for the fabrication of a cyclic polymer in a highly diluted solution. To further confirm the stoichiometry of the polymer to CB[8], several portions of CB[8] were continuously titrated into a diluted aqueous solution of **P1** (0.25 mg mL^{-1}), and the absorption change at 220 nm was recorded, showing a turning point at 0.5 equiv. of CB[8] to the Np group (Fig. S7†), and indicating a 1 : 1 binding between **P1** and CB[8]. Thus, the CB[8]-stabilized π–π stacking of the Np group retained its association in highly diluted solution.



Scheme 2 (a) Synthetic route to **P1** and its cyclization upon addition of CB[8] in a highly diluted aqueous solution: (1) CH_2Cl_2, CDI, rt; (2) 3-dimethylaminopropylamine, CH_2Cl_2, 35 °C; (3) 2-(bromomethyl)naphthalene, CH_3CN, reflux. (b) Synthetic route to **P2**, its cyclization and the following photo-irradiation at 365 nm: (4) **M2**, $CuSO_4$, sodium ascorbate, H_2O, 30 °C. (c) Model molecules **M1** and **M2**.

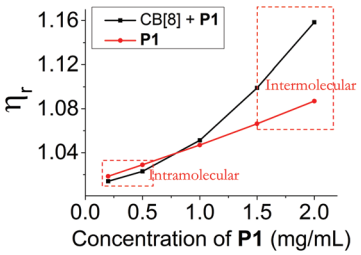


Fig. 1 Relative viscosity of CB[8]+**P1** and **P1** alone at different concentrations.

With the telechelic polymer in hand, the first problem we were facing was the competition between intramolecular cyclization and intermolecular polymerization, which could be mainly controlled by the solution concentration.[3b] The critical concentration for the formation of a cyclic polymer was first established *via* viscometry experiments by varying the concentration of the CB[8]+**P1** complex in comparison with **P1** alone as a control. As shown in Fig. 1, in the high concentration region (>1 mg mL^{-1}), the CB[8]+**P1** complex provided a higher relative viscosity compared to **P1**, indicating the favorable intermolecular polymerization. The non-linear plot type of the CB[8]+**P1** complex was very similar to our previous results in CB[8]-mediated supramolecular polymerization,[19] which also demonstrated the successful incorporation of Np groups at both chain ends of PEG. When the concentration gradually decreased, the relative viscosity of the complex CB[8]+**P1** decreased much faster than that of **P1** until 0.5 mg mL^{-1} was reached, where the former exhibited a relatively lower value than the latter. It is known that the intrinsic viscosity of the cyclic polymer was lower than the linear one with the same molecular weight. We deduced here that the viscosity decrease at low concentrations was caused by the conformation transformation of **P1** from linear to cyclic. The calculated inherent viscosity ratio $[\eta]_{c,exp}/[\eta]_{l,exp}$ of CB[8]+**P1** at 0.5 mg mL^{-1} was 0.79, close to but larger than the theoretical value of 0.66,[20] probably due to the supramolecular nature of the cyclic PEG.

The hydrodynamic distribution of the CB[8]-based host–guest complex at different concentrations was examined by DLS. As shown in Fig. 2a, at concentrations of 2 mg mL^{-1} and 1.5 mg mL^{-1}, in the range giving a high viscosity, besides the main peak around 4 nm, a small peak corresponding to the large-sized species was observed, which was obviously corresponding to the intermolecular aggregates.[19] While at concentrations of 1 mg mL^{-1} and 0.5 mg mL^{-1}, CB[8]+**P1** giving a similar viscosity value to **P1** alone, in the R_h distributions no signal associated with such large species was observed. Then 0.5 mg mL^{-1} was selected as a critical concentration for further study of the host–guest complex system. Detailed investigation at this concentration was performed (Fig. 2b). After the addition of equimolar CB[8] to 0.5 mg mL^{-1} **P1** solution, the number-weighted radius distribution ($<R_h>$) shifted to a lower value, indicating the hydrodynamic volume decrease of CB[8]+**P1** compared to **P1**, which is a typical characteristic of a cyclic polymer. Furthermore, the distribution curve of CB[8]+**P1** returned when the solution was treated by either heating to 60 °C or adding 10 equiv. 1-amantadine (Ad). This confirmed the supramolecular nature of the CB[8]-based cyclic polymer.

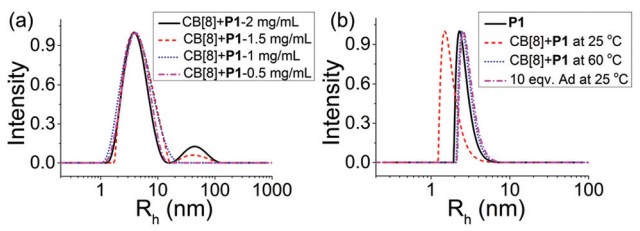


Fig. 2 (a) Unweighted R_h distribution of the CB[8]+**P1** complex with different concentrations at 25 °C. (b) Number-weighted R_h distribution (0.5 mg mL^{-1}) of CB[8]+**P1** and **P1** alone at 25 °C, CB[8]+**P1** at 60 °C, and CB[8]+**P1** at 25 °C with 10 equiv. Ad.

GPC is one of the most powerful methods in demonstrating cyclization of a linear polymer, as the cyclic one exhibits a longer retention time than its linear counterpart due to the more compact chain structure of the former. However, our attempt to demonstrate the cyclic structure of CB[8]+**P1** in aqueous solution by GPC failed, probably due to the dynamic nature of inclusion complexation which underwent association–dissociation equilibrium under highly diluted conditions. This phenomenon is quite common in other supramolecular systems. Previous work proved that Np groups could be dimerized in the cavity of CB[8] by photoirradiation.[21] Compared to the lifetime of the excited singlet state of Np, the exchange between free and complexed Np can be neglected, thus major conformation of the non-covalent system should be retained in the resulting covalent system.[17] This encouraged us to perform the photoreaction for transferring the labile non-covalent bond into a stable covalent bond. Unexpectedly, the photo-irradiation of CB[8]+**P1** with UV light (wavelength >280 nm) only resulted in white precipitates from aqueous solution. ^{1}H NMR (Fig. S8†) showed that Np groups were cleaved from the PEG backbone, leading to the formation of the byproduct. We supposed that here the methylene linkage was not suitable for photo-dimerization, as previous work had only shown successful photo-induced dimerization when the carbonyl group was utilized.[21,22]

To solve this problem, the cationic Np group was substituted by the cationic anthracene (An) group with much higher photo-activity on the PEG backbone. The polymer named **P2** for clarity (Scheme 2) was prepared through a click reaction between an alkyne modified An group and azide-modified PEG (M_n = 20k, Scheme S2, Fig. S9–S12†).[23] To efficiently click the An group to the end of PEG_{20k}, PEG_{2k} was first selected as a model reactant. Different reaction conditions were screened. And finally we found that by using chloride as the counter ion for quaternary ammonium and water as the solvent after 24 h reaction, no azide was found in the Fourier transform infrared spectrum (FT-IR) (Fig. S13†). Then the azide-modified PEG_{20k}

was charged into the reaction under the same conditions. The obtained crude product was further loaded into a cation exchange column, and eluted with an aqueous NaCl gradient for purification. ^{1}H NMR of the final product of **P2** showed that more than 90% hydroxyl end was transferred to the An group (Fig. S14†). ^{1}H NMR of **P2** exhibited a significant upfield shift of the An protons after the addition of CB[8] (Fig. S15†), very similar to the result of **P1**. Consecutive titration of the model molecule **M2** (2 mM) into CB[8] (0.1 mM) at 25 °C indicated a 2 : 1 binding ratio of An to CB[8] (Fig. S16†), yielding an overall binding constant of 1.14×10^{13} M^{-2}. Besides, UV-Vis titration of **P2** (0.25 mg mL^{-1}) with CB[8] showed that CB[8]-stabilized π–π stacking of the An group was also retained in highly diluted solution (Fig. S17†).

Supramolecular cyclization is mainly controlled by the molecular weight of the linear polymer precursor and its concentration. When a very similar supramolecular interaction is employed, the dynamic system should exhibit similar properties. This assumption was supported by the viscosity test of CB[8]+**P2**, which showed a similar viscosity change *vs.* concentration to that of CB[8]+**P1**, yielding an inherent viscosity ratio $[\eta]_{c,exp}/[\eta]_{l,exp}$ of 0.8 at 0.5 mg mL^{-1} (Fig. S18†). Then photoreaction of CB[8]+**P2** was conducted in a highly diluted solution, with **P2** alone as the control at the same concentration. Photo-irradiation of CB[8]+**P2** led to a rapid decrease of the absorbance centred around 254 nm (Fig. S19†), resulting from the close stacking of two An groups in the cavity of CB[8], while **P2** alone showed a much slower decrease at the same interval (Fig. S20†).[23]

The crude product from photo-irradiation was freeze-dried and subjected to GPC characterization. As shown in Fig. 3a, the main peak of the photo-irradiated CB[8]+**P2** complex at 0.5 mg mL^{-1} ($M_{n,SEC}$ = 15 300, PDI = 1.26, M_p = 14 000) appeared at a larger elution volume than the **P2** precursor ($M_{n,SEC}$ = 15 500, PDI = 1.12, M_p = 17 800), which provided direct evidence of the formation of a covalent cyclic polymer from GPC. Besides, there was also a small quantity of oligomers in the final product, due to the relatively long PEG precursor. As predicted by theory, for the same precursor concentration, a long chain length can lead to the formation of oligomers.[24] Here the content of oligomers could be decreased by decreasing the precursor concentration to 0.2 mg mL^{-1} ($M_{n,SEC}$ = 13 900, PDI = 1.19, M_p = 13 700). The cyclic *vs.* linear ratio of the apparent peak molar mass ($M_{p,c}/M_{p,l}$) from GPC, denoted as $\langle G \rangle$, was 0.77 at 0.2 mg mL^{-1} and 0.5 mg mL^{-1}, which is in good agreement with the value previously reported for cyclic PEG.[25] On the contrary, irradiating the CB[8]+**P2** complex at 1 mg mL^{-1} as expected led to a great increase in both the content of oligomers and the polydispersity ($M_{n,SEC}$ = 20 300, PDI = 1.45, M_p = 15 100) and meanwhile the cyclization efficiency was apparently decreased.

Fig. 3b shows the GPC profile of photo-irradiated **P2** at 0.2 mg mL^{-1} without CB[8], which exhibited a much broader molecular weight distribution ($M_{n,SEC}$ = 11 400, PDI = 1.40, M_p = 11 500), compared to that of the cyclized CB[8]+**P2** at the same concentration. The apparently decreased M_n and the broad peak indicated chain cleavage of **P2** after photo-irradiation without CB[8]. This was reasonable since in the absence of CB[8], either the intra- or intermolecular dimerization of two An groups was really difficult for the long chain at such a low concentration, thus part of energy from the excited An groups was transferred to the PEG backbone, resulting in polymer structure destruction. ^{1}H NMR results also supported this assumption. The peaks corresponding to the aromatic part of the reacted **P2** in ^{1}H NMR without CB[8] became disordered and weak (Fig. S21†). Meanwhile, the ^{1}H NMR (Fig. S15†) of the photo-irradiated CB[8]+**P2** showed a distinctively different result, indicating a typical covalent An dimer in the cavity of CB[8], which was linked to the PEG backbone through the triazole unit (8.2 ppm).[23]

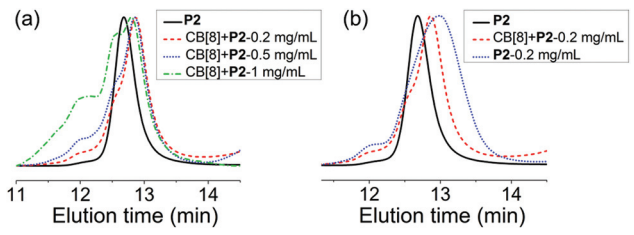


Fig. 3 (a) GPC profiles of **P2**, product after photo-irradiation of CB[8]+**P2** at different concentrations. (b) GPC profiles of **P2**, product after photo-irradiation of **P2** and CB[8]+**P2** at 0.2 mg mL^{-1}.

Conclusion

In conclusion, we have demonstrated a selective and reversible unimolecular cyclization method based on the CB[8]-stabilized π–π interaction. The detailed molecular structure distribution of the resultant polymers in a labile non-covalent system at various dilute concentrations was explored for the first time through GPC by photo-irradiation which led to covalent bonds between two An groups at the chain ends of PEG within the CB[8] cavity. Viscometry, DLS, NMR and GPC strongly indicated the formation of a cyclic polymer. We believe the idea of tuning the properties of materials by a controlled topological change between cyclic and linear polymers will find further applications in many research fields.

Acknowledgements

The Ministry of Science and Technology of China (2011CB932503), the National Natural Science Foundation of China (no. 21474020, 91227203, 31470764 and 51322306) and the Innovation Program of the Shanghai Municipal Education Commission are acknowledged for their financial support.

Notes and references

1 Y. Tezuka and H. Oike, *J. Am. Chem. Soc.*, 2001, **123**, 11570.

2 (*a*) K. Endo, *Adv. Polym. Sci.*, 2008, **217**, 121; (*b*) T. Yamamoto and Y. Tezuka, *Polym. Chem.*, 2011, **2**, 1930; (*c*) B. A. Laurent and S. M. Grayson, *Chem. Soc. Rev.*, 2009, **38**, 2202; (*d*) H. R. J. Kricheldorf, *Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 251; (*e*) Z. Jia and M. J. J. Monteiro, *Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 2085.

3 (*a*) C. W. Bielawski, D. Benitez and R. H. Grubbs, *Science*, 2002, **297**, 2041; (*b*) B. A. Laurent and S. M. Grayson, *J. Am. Chem. Soc.*, 2006, **128**, 4238; (*c*) J. N. Hoskins and S. M. Grayson, *Macromolecules*, 2009, **42**, 6406; (*d*) M. Glassner, J. P. Blinco and C. Barner-Kowollik, *Macromol. Rapid Commun.*, 2011, **32**, 724; (*e*) K. Ishizu and Y. Akiyama, *Polymer*, 1997, **38**, 491; (*f*) X. P. Qiu, F. Tanaka and F. M. Winnik, *Macromolecules*, 2007, **40**, 7069; (*g*) A. J. Boydston, T. W. Holcombe, D. A. Unruh, J. M. J. Frechet and R. H. Grubbs, *J. Am. Chem. Soc.*, 2009, **131**, 5388.

4 (*a*) X. Xu, N. C. Zhou, J. Zhu, Y. F. Tu, Z. B. Zhang, Z. P. Cheng and X. L. Zhu, *Macromol. Rapid Commun.*, 2010, **31**, 1791; (*b*) H. Karatas, S. Y. Lee, E. C. Townsend, F. Cao, J. Xu, D. Bernard, L. Liiu, Y. Dou and S. Wang, *Chin. Chem. Lett.*, 2015, **26**, 455; (*c*) S. Honda, T. Yamamoto and Y. Tezuka, *Nat. Commun.*, 2013, **4**, 1574; (*d*) N. Nasongkla, B. Chen, N. Macaraeg, M. E. Fox, J. M. J. Fréchet and F. C. Szoka, *J. Am. Chem. Soc.*, 2009, **131**, 3842.

5 O. Altintas, P. Gerstel, N. Dingenouts and C. Barner-Kowollik, *Chem. Commun.*, 2010, **46**, 6291.

6 (*a*) J. Willenbacher, B. V. K. J. Schmidt, D. Schulze-Suenninghausen, O. Altintas, B. Luy, G. Delaittread and C. Barner-Kowollik, *Chem. Commun.*, 2014, **50**, 7056; (*b*) T. Ogawa, K. Nakazono, D. Aoki, S. Uchida and T. Takata, *ACS Macro Lett.*, 2015, **4**, 343.

7 H. Oike, H. Imaizumi, T. Mouri, Y. Yoshioka, A. Uchibori and Y. Tezuka, *J. Am. Chem. Soc.*, 2000, **122**, 9592.

8 (*a*) M. R. Whittaker, Y. K. Goh, H. Gemici, T. M. Legge, S. Perrier and M. J. Monteiro, *Macromolecules*, 2006, **39**, 9028; (*b*) M. Schappacher and A. Deffieux, *J. Am. Chem. Soc.*, 2011, **133**, 1630.

9 J. Kim, I. S. Jung, S. Y. Kim, E. Lee, J. K. Kang, S. Sakamoto, K. Yamaguchi and K. Kim, *J. Am. Chem. Soc.*, 2000, **122**, 540.

10 Y. H. Ko, K. Kim, J. K. Kang, H. Chun, J. W. Lee, S. Sakamoto, K. Yamaguchi, J. C. Fettinger and K. Kim, *J. Am. Chem. Soc.*, 2004, **126**, 1932.

11 Y. L. Liu, Y. Yu, J. Gao, Z. Q. Wang and X. Zhang, *Angew. Chem., Int. Ed.*, 2010, **49**, 6576.

12 E. A. Appel, F. Biedermann, U. Rauwald, S. T. Jones, J. M. Zayed and O. A. Scherman, *J. Am. Chem. Soc.*, 2010, **132**, 14251.

13 J. Zhang, R. J. Coulston, S. T. Jones, J. Geng, O. A. Scherman and C. Abell, *Science*, 2012, **335**, 690.

14 (*a*) Y. Wang, D. D. Li, H. Wang, Y. J. Chen, H. J. Han, Q. Jin and J. Ji, *Chem. Commun.*, 2014, **50**, 9390; (*b*) F. Sakai, Z. Ji, J. Liu, G. Chen and M. Jiang, *Chin. Chem. Lett.*, 2013, **24**, 568.

15 Q. An, J. Brinkmann, J. Huskens, S. Krabbenborg, J. D. Boer and P. Jonkheijm, *Angew. Chem., Int. Ed.*, 2012, **51**, 12233.

16 H. D. Nguyen, D. T. Dang, J. L. J. V. Dongen and L. Brunsveld, *Angew. Chem., Int. Ed.*, 2010, **122**, 907.

17 A. Nakamura and Y. Inoue, *J. Am. Chem. Soc.*, 2003, **125**, 966.

18 Y. L. Liu, R. C. Fang, X. X. Tan, Z. Q. Wang and X. Zhang, *Chem. – Eur. J.*, 2012, **18**, 15650.

19 Z. W. Ji, J. H. Liu, G. S. Chen and M. Jiang, *Polym. Chem.*, 2014, **5**, 2709.

20 V. Bloomfield and B. H. Zimm, *J. Chem. Phys.*, 1966, **44**, 315.

21 X. L. Wu, L. Luo, L. Lei, G. H. Liao, L. Z. Wu and C. H. Tung, *J. Org. Chem.*, 2008, **73**, 491.

22 L. Luo, G. H. Liao, X. L. Wu, L. Lei, C. H. Tung and L. Z. Wu, *J. Org. Chem.*, 2009, **74**, 3506.

23 F. Biedermann, I. Ross and O. A. Scherman, *Polym. Chem.*, 2014, **5**, 5375.

24 L. Rique-Lurbet, M. Schappacher and A. Deffieux, *Macromolecules*, 1994, **27**, 6318.

25 Y. N. Zhang, G. W. Wang and J. L. Huang, *Macromolecules*, 2010, **43**, 10343.

