Topology Transformation

Star/Linear Polymer Topology Transformation Facilitated by Mechanical Linking of Polymer Chains**

Daisuke Aoki, Satoshi Uchida, and Toshikazu Takata

Abstract: *Topology transformation of a star polymer to a linear polymer is demonstrated for the first time. A three-armed star polymer possessing a mechanical linking of two polymer chains was synthesized by the living ring-opening polymerization of δ-valerolactone initiated by a pseudo[2]rotaxane having three hydroxy groups as the initiator sites on the wheel component and at both axle termini. The polymerization was followed by the propagation end-capping reaction with a bulky isocyanate not only to prevent the wheel component deslippage but also to introduce the urethane moiety at the axle terminal. The resulting rotaxane-linked star polymer with a fixed rotaxane linkage based on the ammonium/crown ether interaction was subjected to N-acetylation of the ammonium moiety, which liberated the components from the interaction to move the wheel component to the urethane terminal as the interaction site, eventually affording the linear polymer. The physical property change caused by the present topology transformation was confirmed by the hydrodynamic volume and viscosity.*

Structure or topology transformation and the resulting property change often seen in molecular switches or machines have attracted much attention because of their potential applicability to the macroscopic change of appearance or properties.[1] Because such a transformation is mainly limited to small molecules, a topology-transformable polymer would be attractive for bulk property control. In comparison with linear polymers, corresponding topological polymers,[2] such as star polymers,[3] cyclic polymers,[4] dendrimers,[5] and hyperbranched polymers,[6] generally provide smaller hydrodynamic volume, lower solution viscosity, and less polymer entanglement in the bulk. These properties are useful in solid materials that can help not only in reducing solvent use as sustainable products but also making the molding process easy because of low melt viscosity.

However, most topological polymers[7] reported to date are not transformable, because they are constructed by covalent bonds. There are a few reports on topology

reconstruction using weak and reversible interactions to change polymer properties.[8] Meanwhile, we have recently reported[9] the synthesis of mechanically linked block/graft copolymers as a shape-transformable polymer in which the two polymer chains are tied by the rotaxane structure; one polymer chain is threaded into the crown ether wheel to which the other is connected. Because we have found that the urethane moiety placed in the rotaxane axle has some attractive interaction with the crown ether wheel,[9c] which is consistent with Gibson's reports,[10] crown ether based rotaxanes having both ammonium and urethane moieties can be regarded as two-station-type molecular switches. Namely, the rotaxane structure plays a key role as a controllable movable linking unit, thereby being applicable to more sophisticated transformable systems. This paper describes the synthesis of a star polymer characterized by the rotaxane linking of the polymer chains and its conversion to a linear polymer by a topology transformation (Figure 1).
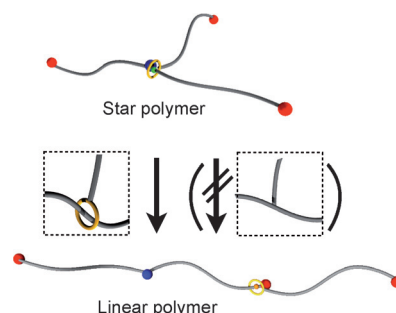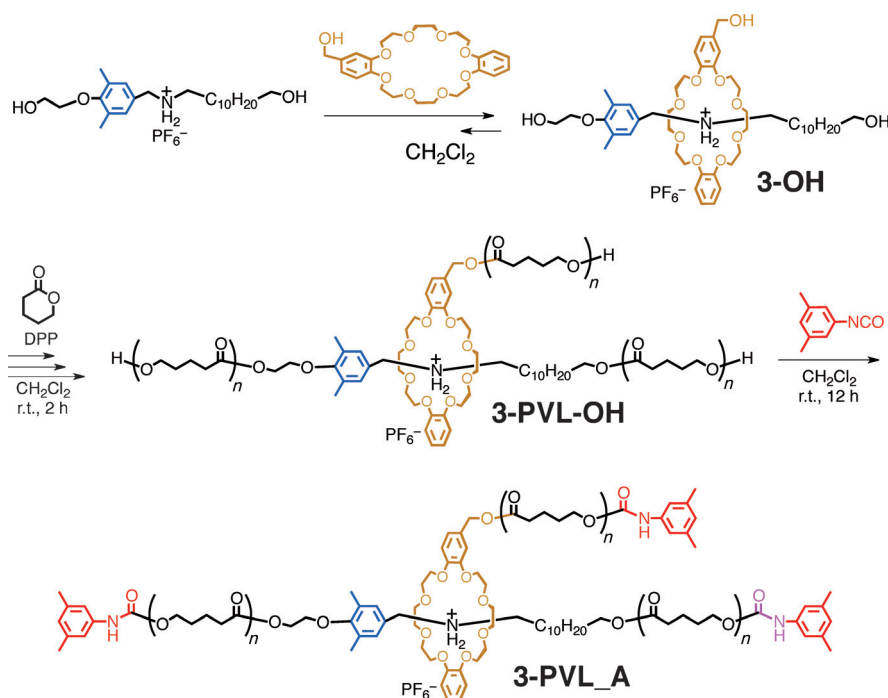

Figure 1. Polymer topology transformation from star to linear shape using a mechanically linked polymer system.

The rotaxane-linked star polymer (**3**-PVL_A) having a polymer chain fixed at the center of another polymer chain via the mechanical linkage by using the strong interaction between the *sec*-ammonium moiety and crown ether wheel was designed as shown in Scheme 1. To ensure the synthesis of the well-defined three-armed star polymer in which the arm polymer chains have the same degree of polymerization (DP), a trifunctional pseudo[2]rotaxane initiator having three primary hydroxy groups as the initiating sites (**3**-OH) was designed for living ring-opening polymerization (ROP) of a lactone. Diphenyl phosphate (DPP)-catalyzed living ROP of δ-valerolactone (δ-VL) (ratio of [δ-VL]$_0$/[initiator]$_0$/[DPP]$_0$ = 80/1.0/0.7) was carried out at ambient temperature. An excess amount of 3,5-dimethylphenyl isocyanate was added to the polymerization mixture after 2 h for both the propagation end-capping with the bulky stopper

[*] Dr. D. Aoki, Dr. S. Uchida, Prof. Dr. T. Takata
Department of Organic and Polymeric Materials
Tokyo Institute of Technology
2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552 (Japan)
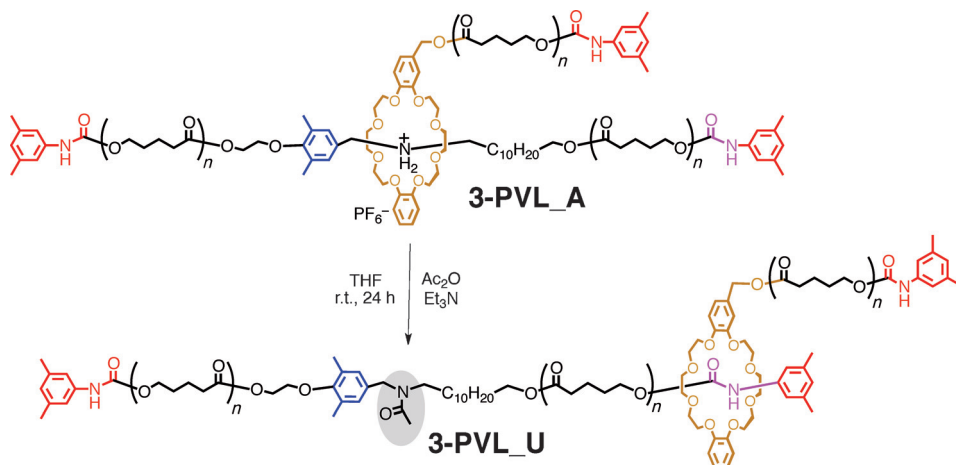E-mail: ttakata@polymer.titech.ac.jp

Scheme 1. Synthesis of the rotaxane-linked star polymer **3**-PVL_A.

as shown in Figure 2 and the Supporting Information, Figures S3 and S4. A series of peaks with a clear interval of 100.05 Da corresponding to the molecular weight of δ-VL agreed well with the structure of **3**-PVL_A in Figure 2a. The result supported the progress of the DPP-catalyzed living ROP and the subsequent propagation end-cap to afford **3**-PVL_A. Conversely, a similar series of peaks with the same m/z interval was recorded for **3**-PVL_U, as shown in Figure 2b. All of the peaks were shifted to the higher m/z region with the difference of 65 Da, the sum of thr acetyl group and sodium. It is obvious that the acetylation proceeded successfully to give **3**-PVL_U. The ^{1}H NMR spectra of **3**-PVL_A and **3**-PVL_U showed the signals characteristic of their structures, including the typical split signals of the methylene protons next to the nitrogen group (Supporting Information, Figure S4).

To answer the question as to whether the wheel component having the polymer chain can really translate from the center to the end of the axle polymer, the following control experiment was carried out. A rotaxane-linked star polymer having no bulky end-cap group, **3**-PVL-OH (Scheme 1), could be isolated by the direct precipitation of the polymerization reaction mixture into an ethanol/hexane mixed solvent (1:9 vol/vol). The MALDI-TOF-MS result (Supporting Information, Figure S5) supports well the proposed structure of **3**-PVL-OH. The *N*-acetylation of **3**-PVL-OH under similar conditions to that of **3**-PVL_A was performed.

The reaction mixture after the acetylation was directly subjected to MALDI-TOF-MS and ^{1}H NMR[11] measurements. Two series of peaks with the same interval of about 100.05 Da were observed in the MALDI-TOF-MS (Supporting Information, Figure S5b); one series of peaks corresponded to PVL with the crown ether, while the other corresponded to PVL with the axle polymer. These results unambiguously showed that the wheel component having a PVL chain could travel from the ammonium moiety to the open end to afford the individual PVLs by acetylation.

Figure 3 shows the GPC profiles of the products from **3**-PVL-OH by *N*-acetylation, along with **3**-PVL_A and **3**-

and the introduction of the urethane moiety at the polymer end. The resulting mixture was purified by reprecipitation and fractionation to afford the star polymer **3**-PVL_A. The ammonium moiety of **3**-PVL_A was then *N*-acetylated with an excess amount of acetic anhydride in the presence of triethylamine to give the linear polymer **3**-PVL_U (Scheme 2). The formation of **3**-PVL_U is supported by the

Scheme 2. Transformation of star polymer **3**-PVL_A to linear polymer **3**-PVL_U by *N*-acetylation.

fact that the interaction of the urethane linkage/crown ether is stronger than that of the ester linkage/crown ether, and the acetylated moiety no longer interacts with the crown ether wheel.[10]
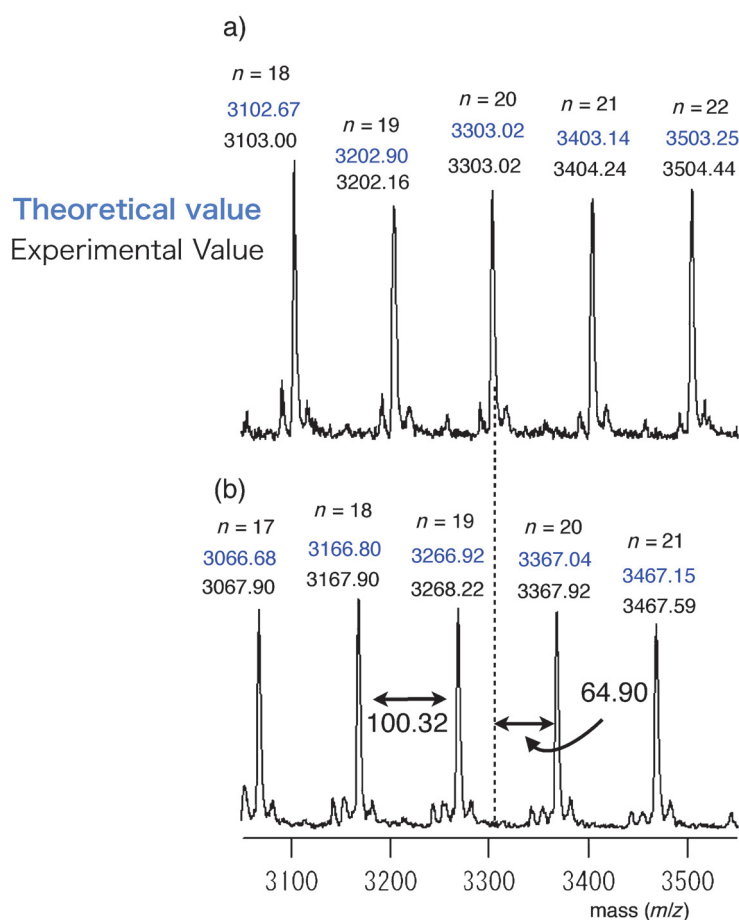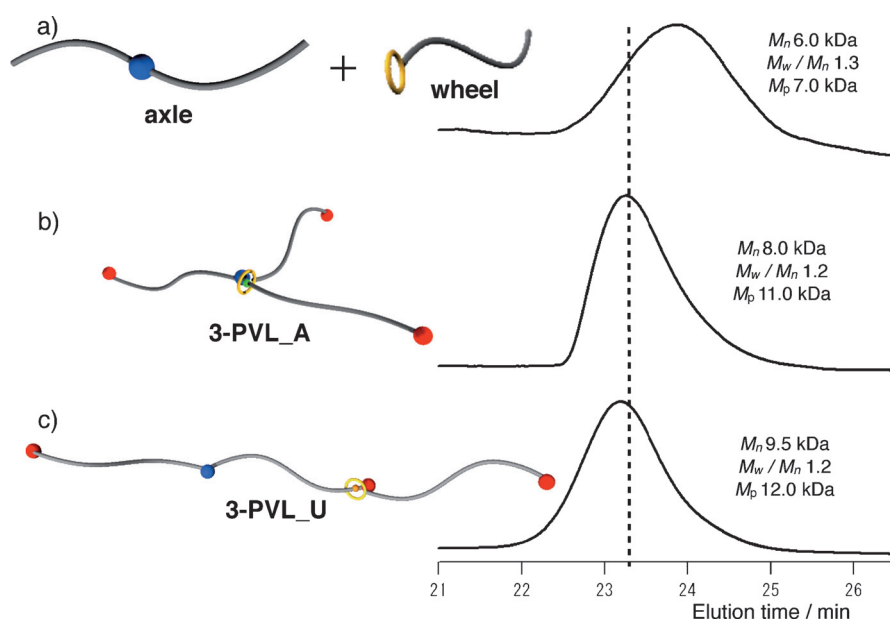
The chemical structures of **3**-PVL_A and **3**-PVL_U were characterized by MALDI-TOF-MS and ^{1}H NMR spectra,[11]

Figure 2. MALDI-TOF-MS of a) 3-PVL-A and b) 3-PVL-U formed after *N*-acetylation. Black: experimental, blue: theoretical values.


Figure 3. GPC profiles of a) acetylated **3**-PVL-OH, b) **3**-PVL_A, c) **3**-PVL_U calibrated with polystyrene standards (eluent CHCl₃; flow rate: 0.85 mL min⁻¹; detected by RI).

PVL_U. A broad GPC peak of the products from **3**-PVL-OH observed at a later elution time (M_p 7.0 kDa) compared with those of **3**-PVL_A and **3**-PVL_U also supported the dissociation of the **3**-PVL-OH fragments to two polymers, the axle polymer and the polymer with the wheel. Focusing on the GPC profiles of linear **3**-PVL_U, the unimodal peak (M_p 12 kDa) was slightly shifted to an earlier elution time region compared with that of star **3**-PVL_A (M_p 11 kDa) without change in M_w/M_n, as shown in Figure 3. It is known that the star polymers generally show a smaller hydrodynamic volume compared with the corresponding linear polymer with the same molecular weight. Therefore, this peak shift indicates an increase in hydrodynamic volume, that is, the occurrence of the topology transformation from star to linear shape. Since a similar result was obtained with higher molecular weight arm-containing star polymers **3**-PVL_A₁₅₀ and **3**-PVL_U₁₅₀ (Supporting Information, Figure S6), it is obvious that the topology transformation from star to linear shape caused an increase in hydrodynamic volume.

GPC measurement is the most common and facile method to evaluate the hydrodynamic volume for various polymers. However, **3**-PVL_A possesses the ammonium moiety, and therefore an electrostatic interaction with the GPC column or other effect based on the ionic moiety cannot be ruled out. Thus, a viscosity measurement was conducted to verify the difference in hydrodynamic volume between **3**-PVL_A and **3**-PVL_U.

To undertake the viscosity measurement, two star- and linear-model polymers having covalently connected polymer chains with the same molecular weight were prepared,[11] named the Star-Model (M_n 8.3 kDa by NMR) and Linear-Model (8.5 kDa by NMR), respectively (Figure 4).

Figure 4 shows the Huggins plots of **3**-PVL_A, **3**-PVL_U, Star-Model, and Linear-Model. In comparison of the rotaxane-linked polymers with the model polymers, the plots of the star polymers (**3**-PVL_A and Star-Model) and the linear polymers (**3**-PVL_U and Linear-Model) were in good agreement with each other, whereas the intrinsic viscosity value of the star polymers was lower than those of the linear polymers, independent of the presence of the ammonium moiety; the results demonstrated that the presence of the ammonium group has no extra effect in this case. Although the slope of the Huggins plots of **3**-PVL_U was slightly different from that of Linear-Model, which might be caused by the effect of the rotaxane linkage, the
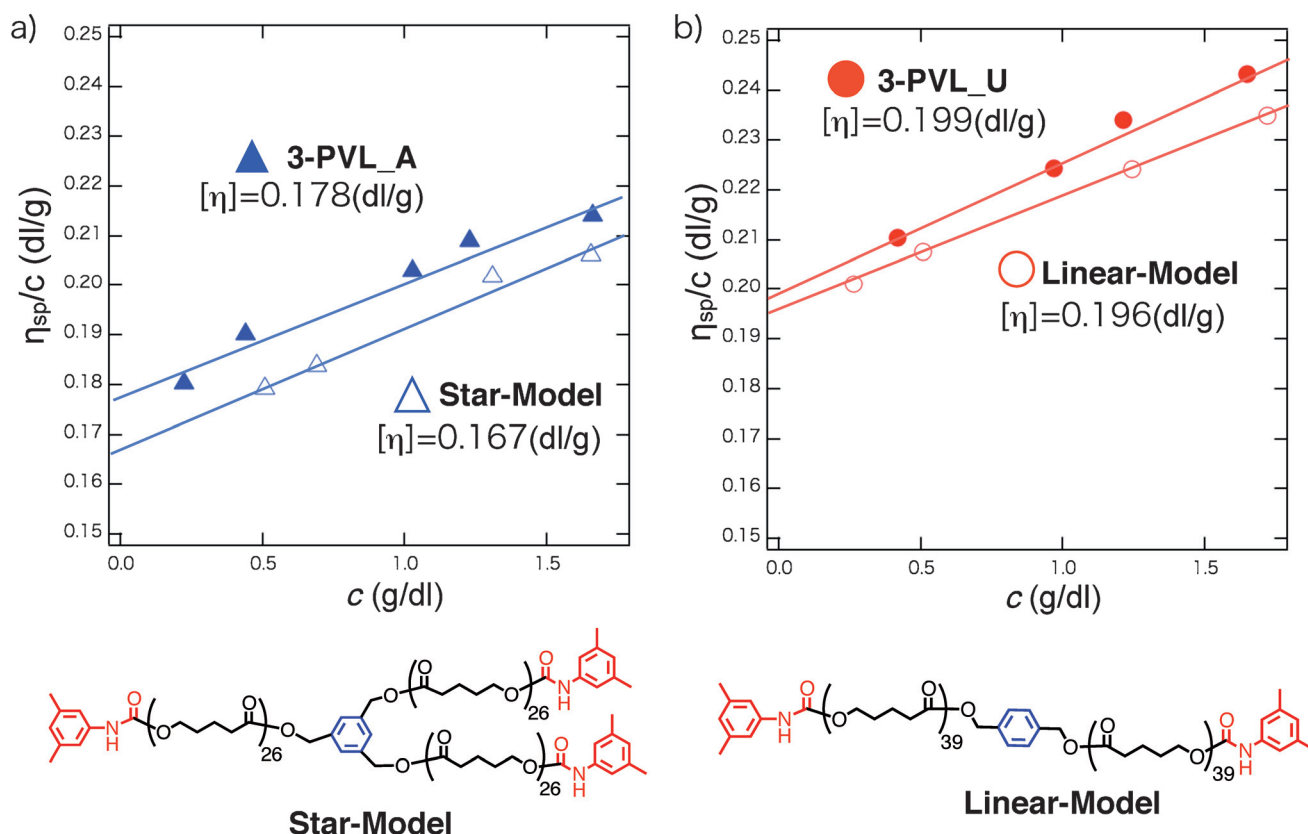
Figure 4. Huggins plot of a) **3**-PVL_A and Star-Model, b) **3**-PVL_U and Linear-Model.

intrinsic viscosities [η] of **3**-PVL_A and **3**-PVL_U were very similar to those of the model polymers. The g' value, which is defined as the ratio of the intrinsic viscosity of branched polymer to linear polymer with the same molecular weight, is generally used to theoretically evaluate the extent of branching. The g' value of **3**-PVL_A to **3**-PVL_U was calculated as $g' = 0.89$, which agrees well with the reported value for the covalently bonded three-armed star polymers.[12] This result also demonstrates the actual topology transformation of the rotaxane-linked polymers.

In conclusion, we have successfully achieved the synthesis of rotaxane-linked star polymer and its topology transformation to the corresponding linear polymer, which is facilitated by the movable junction generated by the rotaxane-linking of the polymer chains. The trifunctional pseudo[2]rotaxane initiator based on the ammonium/crown ether interaction and the precise living ROP were the keys for the synthesis of the rotaxane-linked star polymer. The *N*-acetylation of the ammonium moiety caused the movement of the crown ether wheel having a polymer chain along the axle polymer to reach the urethane moiety at the ω-end, leading to the topology transformation. The topology transformation was reflected by the physical property change in not only hydrodynamic volume but also in viscosity. Thus, it has been demonstrated that the present rotaxane system provides a useful method for effective polymer topology transformation. The fusion of rotaxane chemistry and polymer chemistry opens up further new possibilities in material science.

[1] a) C. X. Yuan, S. Saito, C. Camacho, S. Irle, I. Hisaki, S. Yamaguchi, *J. Am. Chem. Soc.* **2013**, *135*, 8842–8845; b) C. Romuald, A. Arda, C. Clavel, J. Jimenez-Barbero, F. Coutrot, *Chem. Sci.* **2012**, *3*, 1851–1857; c) L. Fang, M. Hmadeh, J. S. Wu, M. A. Olson, J. M. Spruell, A. Trabolsi, Y. W. Yang, M. Elhabiri, A. M. Albrecht-Gary, J. F. Stoddart, *J. Am. Chem. Soc.* **2009**, *131*, 7126–7134; d) S. Kobatake, S. Takami, H. Muto, T. Ishikawa, M. Irie, *Nature* **2007**, *446*, 778–781.

[2] a) J. E. Poelma, K. Ono, D. Miyajima, T. Aida, K. Satoh, C. J. Hawker, *ACS Nano* **2012**, *6*, 10845–10854; b) J. H. Lee, P. Driva, N. Hadjichristidis, P. J. Wright, S. P. Rucker, D. J. Lohse, *Macromolecules* **2009**, *42*, 1392–1399; c) S. Aoshima, S. Kanaoka, *Chem. Rev.* **2009**, *109*, 5245–5287; d) J. H. Lee, K. Orfanou, P. Driva, H. Iatrou, N. Hadjichristidis, D. J. Lohse, *Macromolecules* **2008**, *41*, 9165–9178; e) S. Aoshima, T. Yoshida, A. Kanazawa, S. Kanaoka, *J. Polym. Sci. Part A* **2007**, *45*, 1801–1813; f) Z. F. Jia, H. Chen, X. Y. Zhu, D. Y. Yan, *J. Am. Chem. Soc.* **2006**, *128*, 8144–8145; g) S. M. Grayson, J. M. J. Frechet, *Chem. Rev.* **2001**, *101*, 3819–3867; h) Z. B. Guan, P. M. Cotts, E. F. McCord, S. J. McLain, *Science* **1999**, *283*, 2059–2062; i) G. Floudas, S. Pispas, N. Hadjichristidis, T. Pakula, I. Erukhimovich, *Macromolecules* **1996**, *29*, 4142–4154.

[3] a) Y. Deng, S. Zhang, G. L. Lu, X. Y. Huang, *Polym. Chem.* **2013**, *4*, 1289–1299; b) H. H. Liu, S. X. Li, M. J. Zhang, W. Shao, Y. L. Zhao, *J. Polym. Sci. Part A* **2012**, *50*, 4705–4716.

[4] a) B. A. Laurent, S. M. Grayson, *Chem. Soc. Rev.* **2009**, *38*, 2202–2213; b) J. N. Hoskins, S. M. Grayson, *Macromolecules* **2009**, *42*, 6406–6413; c) S. Honda, T. Yamamoto, Y. Tezuka, *Nat. Commun.* **2013**, *4*, 1574.

[5] S. Hecht, J. M. J. Frechet, *Angew. Chem. Int. Ed.* **2001**, *40*, 74–91; *Angew. Chem.* **2001**, *113*, 76–94.

[6] B. I. Voit, A. Lederer, *Chem. Rev.* **2009**, *109*, 5924–5973.

[7] a) M. Igari, H. Heguri, T. Yamamoto, Y. Tezuka, *Macromolecules* **2013**, *46*, 7303–7315; b) J. A. Castro-Osma, C. Alonso-Moreno, J. C. Garcia-Martinez, J. Fernandez-Baeza, L. F. Sanchez-Barba, A. Lara-Sanchez, A. Otero, *Macromolecules* **2013**, *46*, 6388–6394; c) B. T. Dong, Y. Q. Dong, F. S. Du, Z. C. Li, *Macromolecules* **2010**, *43*, 8790–8798; d) H. S. Wan, Y. Chen, L. Chen, X. Y. Zhu, D. Y. Yan, B. Li, T. Liu, L. Zhao, X. L. Jiang, G. Z. Zhang, *Macromolecules* **2008**, *41*, 465–470.

[8] a) Y. Zhao, L. Tremblay, Y. Zhao, *Macromolecules* **2011**, *44*, 4007–4011; b) M. Schappacher, A. Deffieux, *J. Am. Chem. Soc.* **2011**, *133*, 1630–1633; c) O. Altintas, P. Gerstel, N. Dingenouts, C. Barner-Kowollik, *Chem. Commun.* **2010**, *46*, 6291–6293.

[9] a) D. Aoki, S. Uchida, T. Takata, *ACS Macro Lett.* **2014**, *3*, 324–328; b) D. Aoki, S. Uchida, K. Nakazono, Y. Koyama, T. Takata, *ACS Macro Lett.* **2013**, *2*, 461–465; c) D. Aoki, S. Uchida, T. Takata, *Polym. J.* **2014**, *46*, 546–552.

[10] a) C. G. Gong, H. W. Gibson, *J. Am. Chem. Soc.* **1997**, *119*, 8585–8591; b) C. G. Gong, H. W. Gibson, *J. Am. Chem. Soc.* **1997**, *119*, 5862–5866; c) H. W. Gibson, S. Liu, C. G. Gong, Q. Ji, E. Joseph, *Macromolecules* **1997**, *30*, 3711–3727.

[11] See the Supporting Information.

[12] a) L. M. Van Renterghem, E. J. Goethals, F. E. Du Prez, *Macromolecules* **2006**, *39*, 528–534; b) F. Sanda, H. Sanada, Y. Shibasaki, T. Endo, *Macromolecules* **2002**, *35*, 680–683; c) R. P. Quirk, Y. S. Tsai, *Macromolecules* **1998**, *31*, 8016–8025.