An Efficient Route to Cyclic Polymers by ATRP–RCM Process

Shotaro Hayashi, Kaoru Adachi, and Yasuyuki Tezuka*
Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8552

(Received April 23, 2007; CL-070436; E-mail: ytezuka@o.cc.titech.ac.jp)

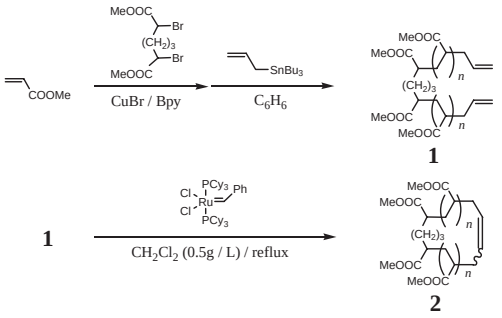
An efficient synthetic route to cyclic polymers has been demonstrated through atom-transfer radical polymerization (ATRP) and subsequent ring-closing metathesis (RCM) reaction. Thus, telechelic poly(methyl acrylate) (PMA) having allyl groups was synthesized by ATRP of methyl acrylate with a difunctional initiator and the subsequent end-capping reaction with allyltributyltin. The following RCM reaction proceeded even under dilution in the presence of the Grubbs catalyst to give a cyclic PMA in a high yield.

Cyclic polymers, free of the chain ends on their topology in contrast to common linear and branched counterparts, are recognized as a promising polymer material to attain unique properties both in dynamic and static states.[1] Therefore, effective preparation of cyclic polymers has become a subject of increasing attention. And recent remarkable achievements include, in particular, the highly effective end-to-end cyclization process with purposely designed linear, telechelic precursors,[2] and the controlled ring-expansion process with intriguing initiator/catalyst components.[3]

We have so far reported a metathesis polymer cyclization (MPC) process, i.e., a ring-closing metathesis (RCM) with polymer precursors in dilution, as a convenient means to provide cyclic polymers.[4] In order to extend the synthetic scope of this process, we show here a versatile polymer cyclization method by combining an atom-transfer radical polymerization (ATRP) with the RCM process using telechelic poly(methyl acrylate) (PMA) obtainable by the end-capping of the ATRP.[5]

ATRP has allowed the remarkable control in radical polymerization process, and has been widely applied for the preparation of a variety of polymers having functional groups, telechelic polymers, and star polymers as well as block and graft copolymers.[6] By integrating ATRP with RCM, a wider variety of functional cyclic polymers, which are not readily accessible through cationic or anionic processes, could become available for practical application.

A linear telechelic PMA was prepared by the ATRP of methyl acrylate (MA) with a difunctional initiator ([MA]:[dimethyl-2,6-dibromoheptanedioate]:[Cu^{I}Br]:[bpy] = 72:1.0:0.81:2.2, 80 °C, 60 min), followed by a radical addition (Keck) reaction with allyltributyltin.[6] The polymer product was subjected to alumina column chromatography and isolated after reprecipitation into hexane. The subsequent RCM reaction was performed in the presence of the Grubbs catalyst 1st generation under dilution (0.5 g/L in CH_2Cl_2, [allyl group of PMA]:[Grubbs catalyst] = 1.0:1.2) (Scheme 1). The product still including noticeable residual catalyst components (by ^{1}H NMR, not shown) was recovered in good yield (98%) upon alumina colum chromatography, and was subsequently purified by SEC fractionation.



Scheme 1. The preparation of telechelic PMA by ATRP and the subsequent RCM.

^{1}H NMR spectra of the telechelic PMA having allyl groups, **1**, and the product obtained by the RCM reaction, **2**, are shown in Figure 1 (top and bottom, respectively). Along with the RCM reaction, the signals due to allyl end groups in **1** at 5.02 and 5.65 ppm are replaced by those due to the inner olefinic unit (trans and cis signals both at about 5.3 ppm).[7] The efficient RCM reaction was thus confirmed to take place even under applied dilution.

The cyclic PMA, **2**, and its linear PMA precursor, **1**, were then compared by MALDI-TOF/MS spectrometry (Figure 2, bottom and top, respectively).[8] The cyclic product, **2**, showed a uniform series of peaks corresponding to PMA (peak interval

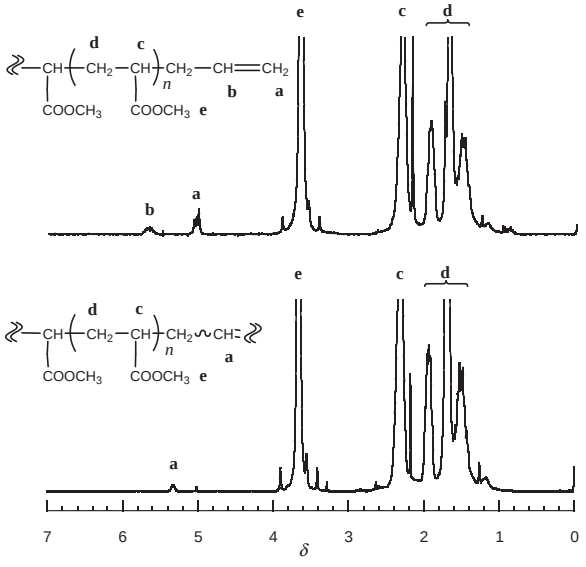


Figure 1. 300-MHz ^{1}H NMR spectra of the telechelic PMA having allyl groups (**1**; top), and the cyclic PMA obtained by the RCM reaction purified by SEC fractionation, (**2**; bottom), ($CDCl_3$).

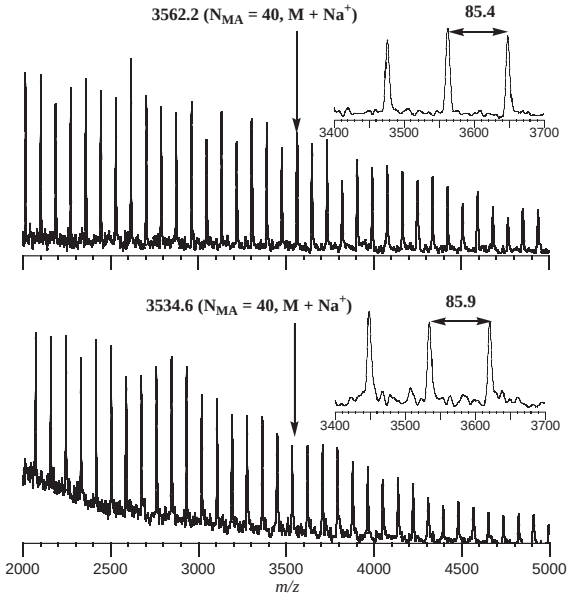


Figure 2. MALDI-TOF-MS spectra of the telechelic PMA precursor having allyl groups (**1**; top) and the cyclic PMA obtained by the RCM reaction (**2**; bottom). (linear mode, matrix: dithranol, with sodium trifluoroacetate).

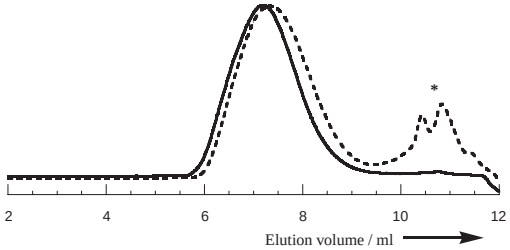


Figure 3. SEC traces (RI) of a telechelic PMA precursor having allyl end groups (**1**; —), and the cyclic PMA obtained by the RCM reaction (**2**; - - -). (TSK G3000HXL, eluent: THF, 1.0 mL/min) ∗: unassignable products including residual catalyst components.

of 86 mass units); each peak corresponds exactly to the molar mass summing up the linking structure produced by the RCM reaction of allyl groups in **1**. As an example, the peak (assumed to be the adduct with Na^+) at m/z 3534.6 corresponds to the product with the number of monomer MA units, N_{MA} of 40, $(C_4H_6O_2) \times 40 + C_5H_8$, plus Na^+ as 3534.73. The linear precursor, **1**, also showed a major series of the peaks corresponding to the Na^+ adduct. Thus, the peak (assumed to be the adduct with Na^+) at m/z 3562.2 corresponds to the product with the N_{MA} of 40, $(C_4H_6O_2) \times 40 + C_7H_{12}$, plus Na^+ as 3562.79. Since the cyclic product, **2**, is produced from **1** by the elimination of an ethylene molecule, their molecular weights differ 28 mass units. This was confirmed by two MALDI-TOF/MS spectra shown in Figure 2. Moreover these show unequivocally the formation of a cyclic PMA, **2**, free from the precursor, **1**.

SEC measurements were carried out to confirm the topology of the obtained polymer product (Figure 3). The peak molecular weight, M_p, as a measure of the hydrodynamic volume in solution, of the cyclic product, **2** (dashed line, $M_w/M_n = 1.58$, $M_p = 8000$, polystyrene standard) was indeed 84% of the linear precursor, **1** (solid line, $M_w/M_n = 1.51$, $M_p = 9500$, polystyrene standard). This agrees with the formation of the cyclic product having the smaller 3D size (70–90%) than the linear counterpart of the relevant chain length.[1b,2,4a]

In conclusion, cyclic PMA has been produced efficiently by the RCM under dilution from linear telechelic precursor having allyl groups, which was obtained by the ATRP and subsequent end-capping reaction. This new synthetic protocol for cyclic polymers will be applied to various monomers for the synthesis of cyclic functional polymers.

References and Notes

1 *Cyclic polymers*, 2nd ed. by J. A. Semlyen, Kluwer Academic Publishers, Dordrecht, The Netherlands, **2000**. b) J. Roovers, P. M. Toporowski, *Macromolecules* **1983**, *16*, 843. c) G. Hild, C. Strazielle, P. Rempp, *Eur. Polym. J.* **1983**, *19*, 721. d) K. A. Alberty, T. E. Hogen-Esch, S. Carlotti, *Macromol. Chem. Phys.* **2005**, *206*, 1035. e) N. Chen, N. Maeda, M. Tirrell, J. Israelachvili, *Macromolecules* **2005**, *38*, 3491. f) K. Hur, R. G. Winker, D. Y. Yoon, *Macromolecules* **2006**, *39*, 3975.

2 a) H. Oike, H. Imaizumi, T. Mouri, Y. Yoshioka, A. Uchibori, Y. Tezuka, *J. Am. Chem. Soc.* **2000**, *122*, 9592. b) M. Kubo, T. Nishigawa, T. Uno, T. Itoh, H. Sato, *Macromolecules* **2003**, *36*, 9264. c) B. A. Laurent, S. M. Grayson, *J. Am. Chem. Soc.* **2006**, *128*, 4238. d) H. Li, A. Debuigne, R. Jerome, P. Lecomte, *Angew. Chem., Int. Ed.* **2006**, *45*, 2264.

3 a) C. W. Bielawski, D. Benitez, R. H. Grubbs, *J. Am. Chem. Soc.* **2003**, *125*, 8424. b) P. Hodge, S. D. Kawau, *Angew. Chem., Int. Ed.* **2003**, *42*, 2412. c) H. Kudo, S. Makino, A. Kameyama, T. Nishikubo, *Macromolecules* **2005**, *38*, 5964. d) D. A. Culkin, W. Jeong, S. Csihony, E. D. Gomez, N. P. Balsara, J. L. Hedrick, R. M. Waymouth, *Angew. Chem., Int. Ed.* **2007**, *46*, 2627.

4 a) Y. Tezuka, R. Komiya, *Macromolecules* **2002**, *35*, 8667. b) Y. Tezuka, K. Fujiyama, *J. Am. Chem. Soc.* **2005**, *127*, 6266.

5 Telechhelic PMA and other polyacrylates are obtainable through the ATRP,[6a] while telechelic poly(*t*-butyl acrylate) through anionic process and cyclic polymers therefrom were reported previously.[2b]

6 a) K. Matyjaszewski, J. Xia, *Chem. Rev.* **2001**, *101*, 2921. b) V. Coessens, J. Pyun, J. Miller, S. G. Gaynor, K. Matyjaszewski, *Macromol. Rapid Commun.* **2000**, *21*, 103.

7 a) R. H. Grubbs, S. Chang, *Tetrahedron* **1998**, *54*, 4413. b) C. Pascual, J. Meier, W. Simon, *Helv. Chim. Acta* **1966**, *49*, 164.

8 The effective ionization of the higher molecular weight part of the polymer product was not achieved under the applied conditions.

Published on the web (Advance View) June 30, 2007; doi:10.1246/cl.2007.982