

# Metathesis Polymer Cyclization with Telechelic Poly(THF) Having Allyl Groups

Yasuyuki Tezuka\* and Ryota Komiya

Department of Organic and Polymeric Materials,  
Tokyo Institute of Technology, O-okayama,  
Meguro-ku, Tokyo, 152-8552 Japan

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**Introduction.** Topologically unique macromolecules comprising a single cyclic and multicyclic polymer units have gained growing interest due to their distinctive behaviors from linear and branched counterparts.<sup>1–5</sup> Polymer cyclization was performed first through the coupling reaction of a bifunctional linear polymer precursor, such as a bifunctionally living polymer like polystyrene, with a complementarily reactive bifunctional reagent, typically dihaloalkanes or dihalosilanes (Scheme 1).<sup>6–9</sup> This bimolecular reaction should be conducted under high dilution to suppress the intermolecular chain extension reaction and at the same time under rigorous stoichiometric balance between large and small molecules. Hence, the process is often kinetically circumvented to limit this straightforward polymer cyclization process from wide applications.

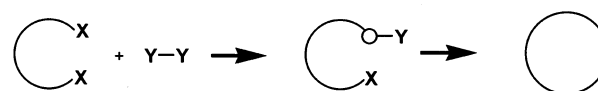
A psuedo-unimolecular reaction by an “electrostatic self-assembly and covalent fixation” technique was recently developed as an alternative polymer cyclization process (Scheme 1).<sup>5,10–14</sup> Thus, a linear polymer precursor having moderately strained onium salt groups, typically five-membered cyclic ammonium or six-membered bicyclic ammonium salt groups, carrying appropriately reactive counteranion like dicarboxylate, was employed. The cations and anions always balance the charges, and the selective nucleophilic ring-opening reaction occurred at an appropriately elevated temperature under dilution, to convert the ionic interaction into the permanent covalent linkage.

A strictly unimolecular polymer cyclization process using an  $\alpha,\omega$ -heterobifunctional linear polymer precursor was developed by Deffieux et al. and applied further by several groups (Scheme 1).<sup>15–19</sup> In this process, the two end groups of the polymer precursor become complementarily reactive with each other after the deprotection or the activation, and the reaction under dilution gives a cyclic polymer product. The cyclization efficiency was notably improved since the inherent stoichiometric balance is maintained between complementarily reactive groups located within the same polymer molecule, and the reaction follows the unimolecular kinetics depending solely on the concentration of the polymer precursor. Nevertheless, the synthesis of the heterobifunctional polymer precursor often requires multistep processes involving protection/deprotection of reactive end groups, limiting its synthetic usefulness.

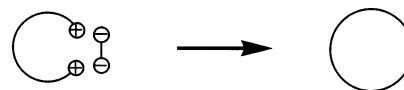
We show here a novel strictly unimolecular polymer cyclization process involving bifunctional polymer precursor having *identical* reactive end groups (Scheme 1). Thus, a linear polymer precursor having allyl groups was prepared and subjected to a metathesis condensa-

Scheme 1

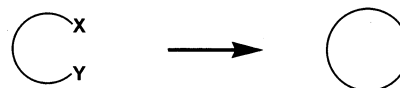
## Polymer Cyclization Processes



Bimolecular process  
X, Y : complementarily reactive groups

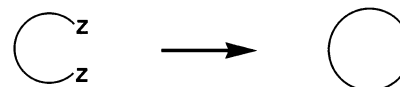


Pseudo-unimolecular process by  
electrostatic self-assembly and covalent fixation



Unimolecular process by hetero-telechelics  
X, Y : complementarily reactive groups

## Present Study

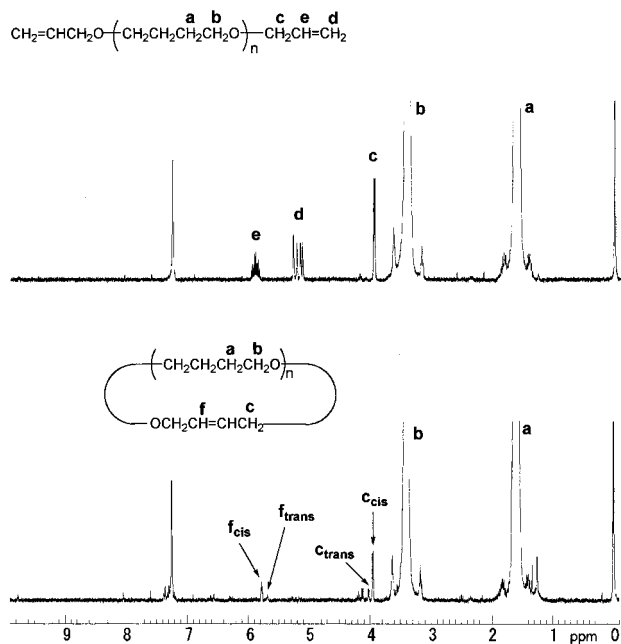


Unimolecular process by homo-telechelics  
with metathesis condensation  
Z : allyl group

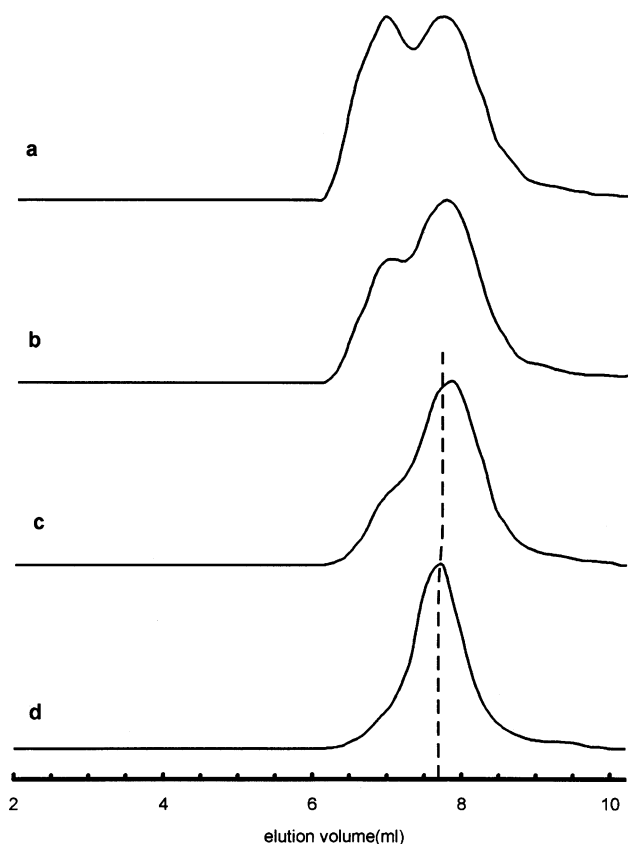
tion, also known as a ring-closing metathesis (RCM), under dilution in the presence of a Grubbs catalyst, ruthenium(II) dichloride phenylmethylene bis(tricyclohexylphosphine)  $[\text{RuCl}_2(\text{PCy}_3)_2(=\text{CHPh})]$ . The metathesis condensation process has so far been successfully applied for the cyclization of small- to medium-sized substrates having terminal allyl groups<sup>20,21</sup> and for the synthesis of a variety of topologically unique molecules like catenanes and knots<sup>22–24</sup> as well as for the polycondensation of acyclic dienes (ADMET) to produce a variety of functional polymer materials.<sup>25–29</sup> Furthermore, the equilibrium between cyclic and linear chains during a ring-opening metathesis polymerization (ROMP) has been a subject of continued studies.<sup>30</sup> In the present communication, we demonstrate a versatile means to produce large-sized cyclic polymers using a readily accessible precursor, i.e., telechelics having allyl groups, in the presence of a commercially available metathesis catalyst.

**Results and Discussion.** Telechelic poly(THF) having allyl end groups, **1**, was prepared by the end-capping reaction of a bifunctionally living poly(THF)<sup>12</sup> with sodium allyloxide (for details, see Supporting Information). <sup>1</sup>H NMR analysis of **1**, having the MW of 5060 and the PDI of 1.27, showed characteristic signals due to allyl protons at 5.17 and 5.90 ppm (Figure 1, top). The metathesis condensation was subsequently performed under reflux in methylene chloride at polymer concentration of 0.2–2.0 g/L in the presence of a Grubbs catalyst. The catalyst was charged in the comparable molar quantity to allyl groups at the polymer chain ends

\* Corresponding author: Tel +81 3/5734-2498, Fax +81 3/5734-2876, e-mail ytezuka@o.cc.titech.ac.jp.

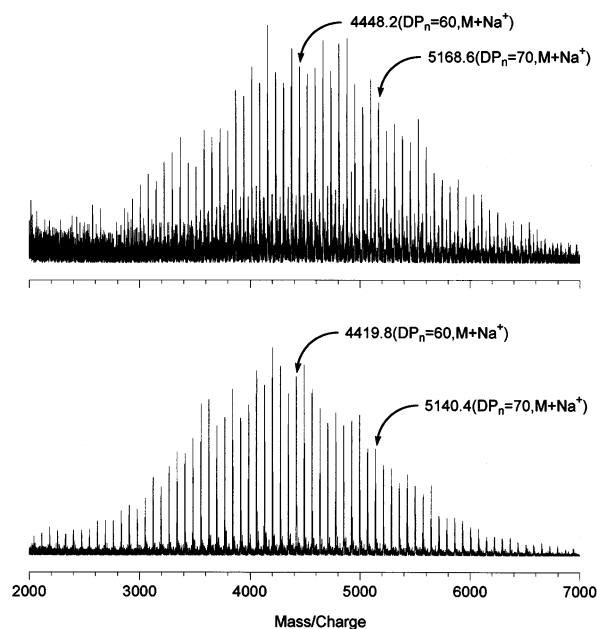


**Figure 1.** The 300 MHz  $^1\text{H}$  NMR spectra of a telechelic poly(THF) having allyl groups (**1**, top) and the metathesis condensation product at 0.2 g/L (**2**, bottom). ( $\text{CDCl}_3$ , 40  $^\circ\text{C}$ ).



**Figure 2.** SEC traces (RI) of the metathesis condensation product (a–c) and of the linear precursor (d). Concentration of **1** in methylene chloride: (a) 2.0, (b) 1.0, and (c) 0.2 g/L (TSK G3000HXL, eluent: THF, 1.0 mL/min).

(ca.  $10^{-5}$  mol/L) in order to achieve quantitative conversion of allyl groups in **1**.<sup>31</sup> The product was recovered after TLC treatment to remove the catalyst residues. The SEC profile of the product (Figure 2) became narrower along with dilution, by eliminating a shoulder fraction at higher molecular weight region. At 0.2 g/L,



**Figure 3.** MALDI-TOF MASS spectra of the cyclic poly(THF) (**2**, bottom) and of the linear precursor (**1**, top) (linear mode, matrix: dithranol with sodium trifluoroacetate).

product **2**, having a nearly symmetrical profile (>95% purity from SEC area ratio), was isolated in 54% yield. Moreover, the hydrodynamic volume of product **2** was noticeably smaller than that of **1** (Figure 2). The hydrodynamic volume ratio of **2** against **1** was estimated by comparing their apparent peak molecular weights by SEC, and the value (0.81) was in good agreement with the previous cases of the cyclic and linear polymers.<sup>32–35</sup> This accords with the effective cyclization by the present metathesis condensation process.

$^1\text{H}$  NMR of product **2** (Figure 1, bottom) showed that the signals due to allyl protons in **1** became scarcely visible, and those due to inner alkene protons (cis and trans signals at 5.79 and 5.68 ppm, respectively)<sup>22</sup> appeared instead. Thus, under dilution, the intramolecular metathesis condensation was confirmed to proceed predominantly.<sup>36</sup>

The cyclic poly(THF), **2**, and its linear precursor, **1**, were also examined by MALDI-TOF MASS spectroscopy (Figure 3). Product **2** showed a uniform series of peaks corresponding to poly(THF) (peak interval of 72 mass units); each peak corresponds exactly to the molar mass summing up the linking structure produced by the metathesis condensation reaction of allyl end groups in **1**. As an example, the peak (assumed to be the adduct with Na<sup>+</sup>) at 4419.8 corresponds to the product with the DP<sub>n</sub> of 60,  $(\text{C}_4\text{H}_8\text{O}) \times 60 + \text{C}_4\text{H}_6\text{O}$ , plus Na<sup>+</sup> as 4419.517. The linear polymer precursor, **1**, also showed a major series of the peaks corresponding to the Na<sup>+</sup> adduct. Thus, the peak (assumed to be the adduct with Na<sup>+</sup>) at 4448.2 corresponds to the product with the DP<sub>n</sub> of 60,  $(\text{C}_4\text{H}_8\text{O}) \times 60 + \text{C}_6\text{H}_{10}\text{O}$ , plus Na<sup>+</sup> as 4447.571. A minor series of peaks were observed in the linear product, presumably corresponding to chains with decomposed end groups. Since the cyclic poly(THF) products are produced from the precursor, **1**, by the elimination of an ethylene molecule, their molecular weights differ by 28 mass units. This was confirmed by the two TOF MASS spectra shown in Figure 3.

To conclude, a metathesis condensation process was proven as a versatile means for polymer cyclization

using a readily accessible precursor, i.e., telechelics having allyl groups, in the presence of a commercially available metathesis catalyst.

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**Supporting Information Available:** Text giving the details of experimental procedures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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