

Communications to the Editor

Telechelics Having Unstrained Cyclic Ammonium Salt Groups for Electrostatic Polymer Self-Assembly and Ring-Emitting Covalent Fixation

Kaoru Adachi, Hajime Takasugi, and Yasuyuki Tezuka*

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

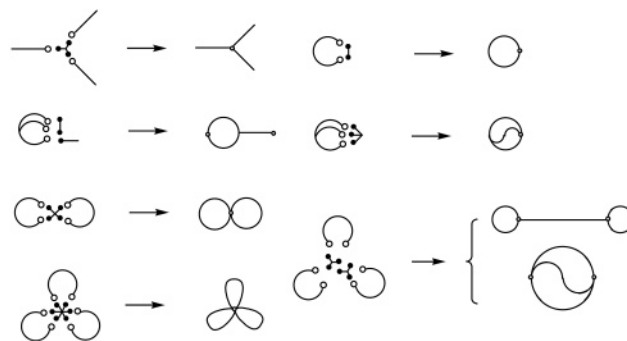
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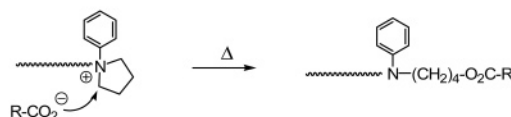
Introduction. Self-assembly of polymer precursors through noncovalent interactions, such as hydrogen bond,^{1,2} metal coordination,^{3,4} van der Waals interaction,⁵ and ionic (electrostatic) forces,⁶ has now been recognized as a promising protocol to provide a novel polymeric and supramolecular materials having unprecedented architectures, properties, or functions.

We have proposed an *electrostatic self-assembly and covalent fixation* process,^{7–10} in which temporary stable, but specifically programmed noncovalent structures are constructed through electrostatic interaction with polymer precursors containing ionic groups and are subsequently transformed into robust and stable products of totally covalent linkages (Scheme 1). In this process, we have purposely employed telechelic precursors having moderately strained cyclic ammonium such as five-membered cyclic (pyrrolidinium) or six-membered bicyclic (quinuclidinium), salt groups at the designated position of a polymer chain.¹¹ The subsequent covalent conversion process has been relied on the *ring-opening* reaction of the cyclic ammonium salt group by appropriately nucleophilic counteranions such as a carboxylate, occurring at an elevated temperature. In particular, by using telechelics having five-membered, *N*-phenylpyrrolidinium salt groups, a highly controlled ring-opening reaction proceeds to form covalent aminoester groups,¹² and the *electrostatic self-assembly and covalent fixation* process has been successfully applied for the synthesis of a variety of topologi-

Scheme 1. Construction of Multicyclic Polymer Topologies by Electrostatic Polymer Self-Assembly and Ring-Opening Covalent Fixation



Covalent Fixation



cally unique polymers having cyclic and multicyclic constructions (Scheme 1).^{6–10,13}

It is notable, however, that aminoester groups, formed by the *ring-opening* process, tend to undergo inter- and intramolecular substitution reactions, especially at elevated temperatures.^{14–16} Therefore, an alternative covalent conversion process to form a more stable linking structure should be not only of scientific interest but also of practical importance because cyclic and multicyclic polymers having the linking group free of amino groups could exhibit superior thermal stability and oxidation resistance.

From this context, we show here a new covalent conversion process using a telechelic precursor having *unstrained* cyclic ammonium salt end groups. Reactive polymers having such cyclic ammonium salt groups have so far been employed for grafting¹⁷ and for cross-linking/decross-linking¹⁸ reactions. Moreover, it has been reported that the reaction of six-

* Corresponding author. E-mail: ytezuka@o.cc.titech.ac.jp.

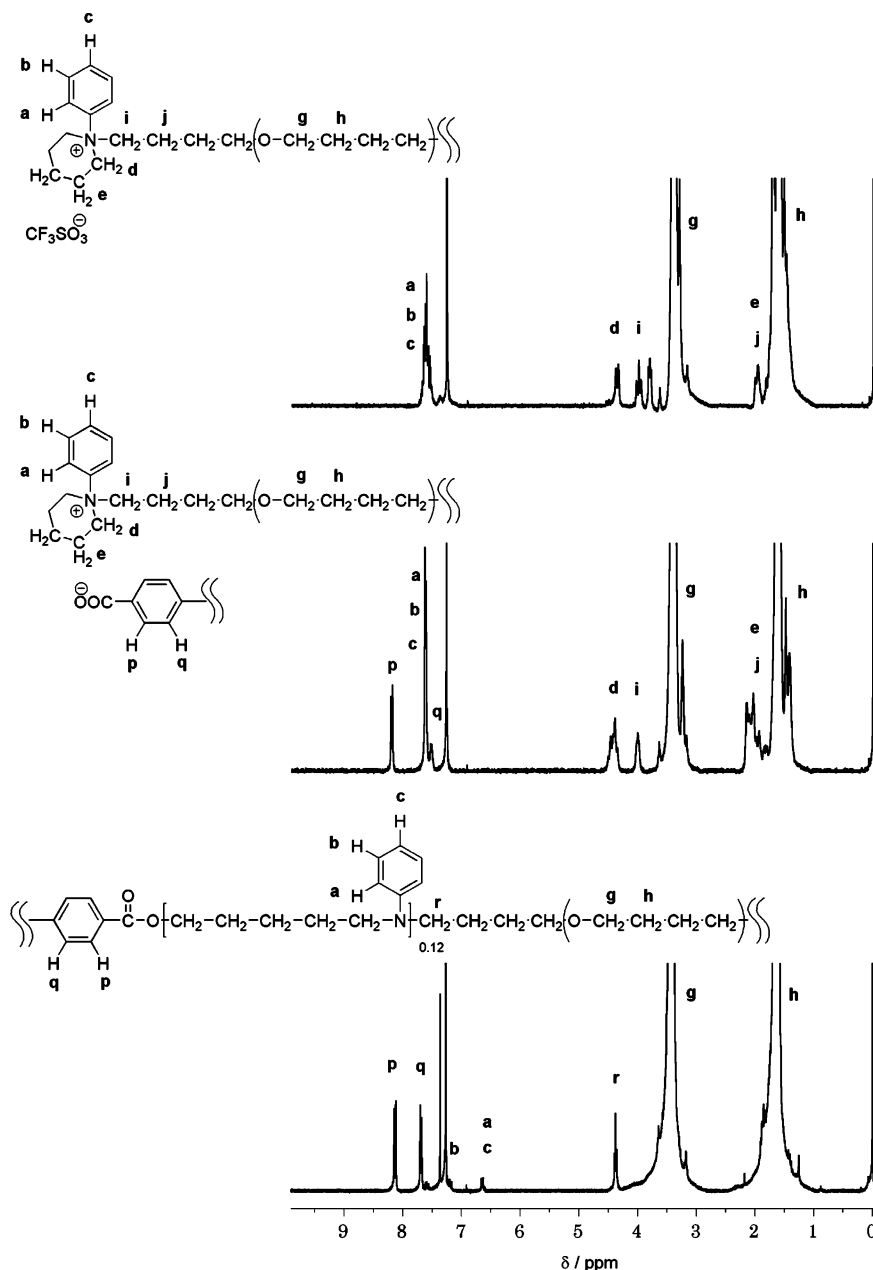
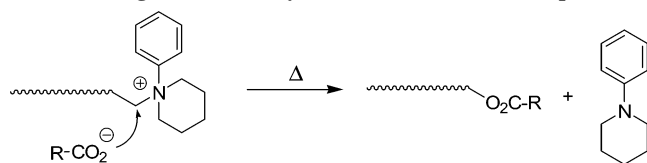


Figure 1. 300 MHz ^1H NMR spectra of poly(THF) having *N*-phenylpiperidinium salt end groups carrying triflate counteranions (top) and the ion-exchange product with a biphenyldicarboxylate counteranion before (middle) and after (bottom) the heat treatment. (CDCl_3 , 40 $^\circ\text{C}$, the assignment of the *N*-phenylalkyl group due to the minor ring-opening reaction is shown in a square bracket.).

Scheme 2. Ring-Emitting Covalent Fixation by Telechelics Having Unstrained Cyclic Ammonium Salt Groups



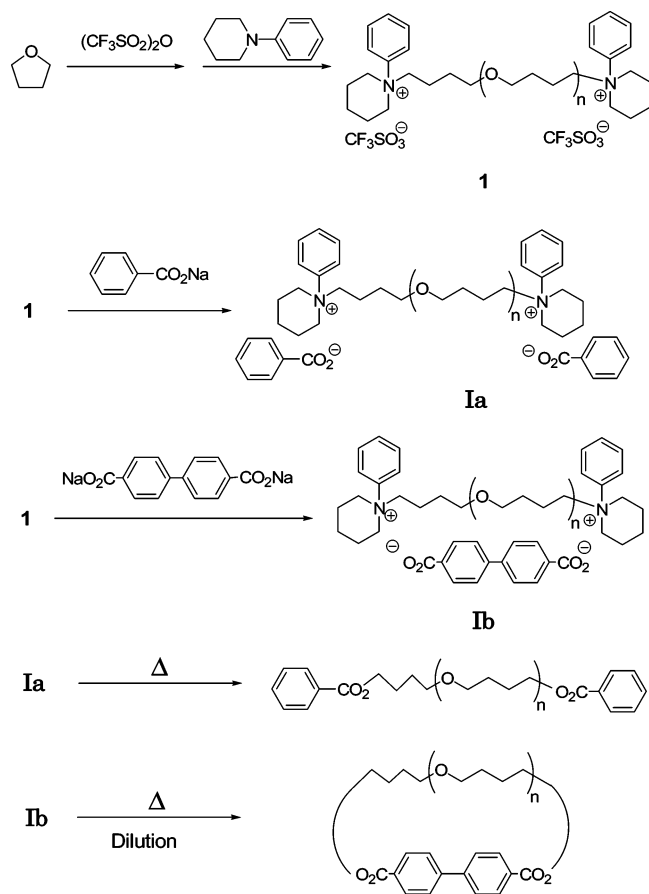
membered, *N,N*-dimethylpiperidinium and *N*-methyl-*N*-phenylpiperidinium salts by an alkoxide proceeds through the nucleophilic attack at a methyl group on the quaternized nitrogen to eliminate *N*-methylpiperidine in as high as 90% selectivity,¹⁹ and *N*-phenylpiperidine almost quantitatively.²⁰ These studies have prompted us to prepare a telechelic poly(THF) having six-membered, *N*-phenylpiperidinium salt groups carrying either monofunctional benzoate or bifunctional biphenyldicarboxylate counteranions. Upon the subsequent heating treatment, the carboxylate counteranions are expected to attack selectively at

the exo position of a cyclic ammonium salt group to form a simple ester group by eliminating *N*-phenylpiperidine units from the polymer chain ends (Scheme 2).

Through the *ring-emitting* covalent conversion using the telechelics carrying a bifunctional carboxylate under dilution, cyclic polymers containing exclusively a simple ester linking group are formed. The relevant cyclic polymers might be obtained by an equimolar reaction between a polymeric diol and a dicarboxylic acid under dilution. In practice, however, such a bimolecular process is hardly applicable as a routine synthetic means because the reaction becomes severely slow under high dilution.²¹ Hence, to the best of our knowledge, this work demonstrates a unique example of practical synthesis of cyclic polymers containing a simple ester linking group.²²

Results and Discussion. A telechelic poly(THF) having *N*-phenylpiperidinium groups carrying triflate counteranions, **1**, was conveniently produced by the end-capping reaction of a bifunctionally living poly(THF) with *N*-phenylpiperidine (Scheme

Scheme 3. Synthesis of Linear and Cyclic Poly(THF) by Electrostatic Polymer Self-Assembly and Ring-Emitting Covalent Fixation



3). The triflate counteranions were then replaced by a more nucleophilic benzoate or biphenyldicarboxylate by the ion-exchange reaction through the precipitation of the polymer precursor into an aqueous solution containing the desired counteranion as sodium salt form (Scheme 3).¹²

¹H NMR spectra of the telechelic poly(THF), **1**, and the ion-exchange product with a biphenyldicarboxylate (**1b**) are shown in Figure 1 (top and middle, respectively). The relevant spectra for poly(THF) carrying benzoate counteranions (**1a**) are shown in S-Figure 1 (Supporting Information). The effective ion exchange from **1** to **1b** was confirmed by the appearance of signals attributed to a biphenyldicarboxylate group at 8.20 and 7.63 ppm. The subsequent heat treatment of the precursors having benzoate (**1a**) or biphenyldicarboxylate (**1b**) counteranions was performed in THF at 66 °C for 5 h at the concentration of 2.0 g/L for the former, and at the dilution of 0.2 g/L for the latter, respectively.²³ The covalently converted products were recovered both from **1a** and from **1b** in 80% and in 65% yields, respectively. ¹H NMR spectra of **1b** before and after the heat treatment are shown in Figure 1 (middle and bottom). The relevant spectra for **1a** are shown in S-Figure 1 (Supporting Information). By the heat treatment, signals attributed to the *N*-phenylpiperidinium salt group of **1a** and **1b** at 7.45–7.70, 3.90–4.10, and 4.30–4.55 ppm were replaced by a triplet signal arising from ester methylene protons at 4.38 ppm. It is particularly remarkable that signals assignable to an *N*-phenyl group at 6.63 and 7.20 ppm became scarcely visible, indicating the predominant elimination (88% for both **1a** and **1b**) of *N*-phenylpiperidine units.

MALDI-TOF mass analysis unequivocally confirmed the exact structures of the covalently converted products from **1a**

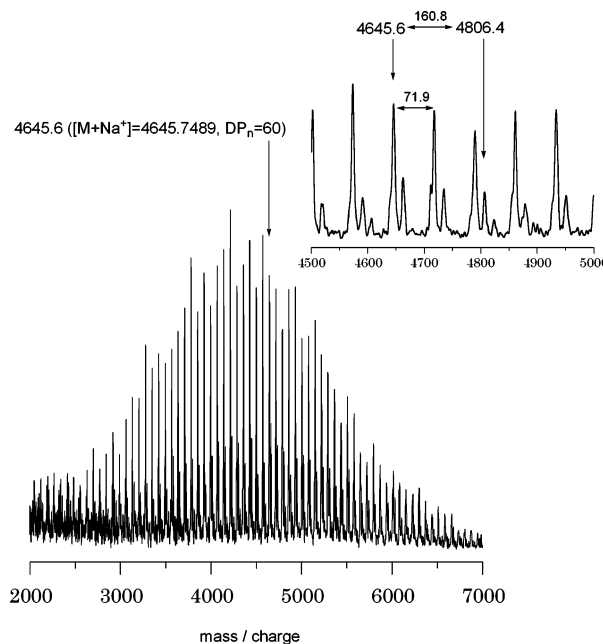


Figure 2. A MALDI-TOF mass spectrum of a ring poly(THF) obtained after the heat treatment of the poly(THF) precursor having *N*-phenylpiperidinium salt end groups carrying a biphenyldicarboxylate counteranion (linear mode; matrix: dithranol with sodium trifluoroacetate).

and **1b**, i.e., a ring poly(THF) from **1b**, and of a linear counterpart from **1a**, respectively (Figure 2 for the covalently converted product from **1b**, and S-Figure 2 (Supporting Information) for that from **1a**, respectively). A series of major and minor peaks are observed corresponding to poly(THF) (peak interval of 72 mass units) having specific linking or end group structures.²⁴ Thus, a peak at 4645.6 (assumed to be the adduct with Na⁺) in the major series corresponds to the product having the number of THF unit (DP_n) of 60 and having simple ester end groups formed by the elimination of *N*-phenylpiperidine units, i.e., (C₄H₈O) × 60 + C₁₈H₁₆O₄, plus Na⁺ as 4645.749. On the other hand, a peak at 4806.4 (assumed to be the adduct with Na⁺) in the minor series corresponds to the product having also the number of THF units (DP_n) of 60 and having an aminoester end group at one chain end formed by the ring opening of an *N*-phenylpiperidinium group, i.e., (C₄H₈O) × 60 + C₂₉H₃₁NO₄, plus Na⁺ as 4806.997. The difference of the molecular weights between two peaks was 160.8, exactly corresponding to the molecular weight of *N*-phenylpiperidine (161.3). As for the covalently converted product from **1a** (S-Figure 2 in Supporting Information), a peak at 4647.3 was observed in the major series, corresponding to a linear poly(THF) having benzoate end groups. The molecular weights differ by just two mass units from the relevant cyclic product obtained from **1b**. No signals were detected for the product having aminoester groups at both chain ends formed by the ring-opening reaction.

SEC traces of the covalently converted product from **1b**, i.e., a ring poly(THF), and of the product from **1a**, a linear analogue, were then compared (Figure 3). Both products showed narrow size distribution (PDI = 1.14 from the former and 1.13 from the latter, respectively), and the linear product showed the apparent peak molecular weight of *M*_p = 6000 as a measure of the hydrodynamic volume, and the value was notably higher than that of the ring polymer product (*M*_p = 4500) despite both products being derived from the common poly(THF) precursor, **1**. The hydrodynamic volume ratio of the product from **1b** against that from **1a** was thus estimated to be 0.75 and was in

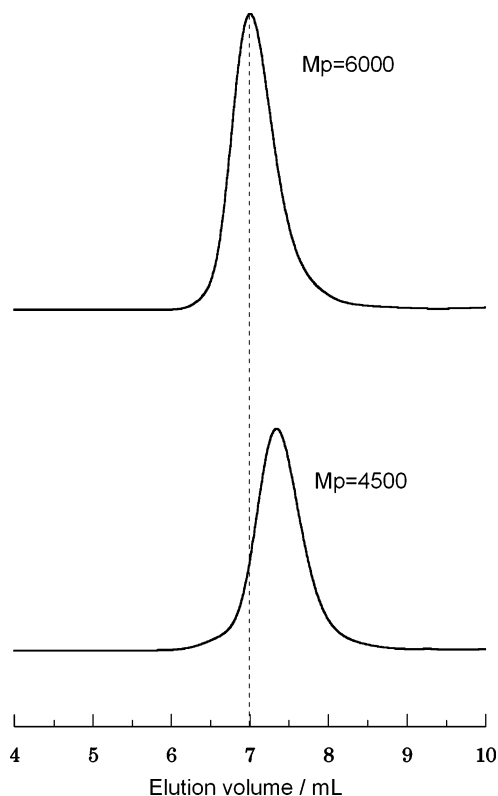


Figure 3. SEC traces of a linear poly(THF) (top) and a ring poly(THF) (bottom), obtained after the heat treatment of poly(THF) precursors having *N*-phenylpiperidinium salt end groups carrying benzoate and biphenyldicarboxylate counteranions, respectively (TSKG3000HXL; eluent: THF 1.0 mL/min).

good agreement with the previous examples comparing the size of a ring polymer and a linear counterpart.^{25–29} These results demonstrate the effective polymer cyclization by **1b** through the *ring-emitting* covalent conversion by the elimination of *N*-phenylpiperidine units at both chain ends. Moreover, the *ring-emitting* process, forming a simple ester linkage group, has been readily applicable as in the preceding *ring-opening* process for the covalent conversion because the anion-exchange reaction of cyclic ammonium groups proceeds efficiently from triflate to carboxylate, and cyclic polymer products are obtainable under the similar dilution and heating conditions regardless of the type of ammonium groups of the telechelic precursors.

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Supporting Information Available: Text giving the details of experimental procedures, ¹H NMR spectra of **1a** before and after the heat treatment (S-Figure 1), and MALDI-TOF mass spectrum of the covalently converted product from **1a** (S-Figure 2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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