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Kyklo-Telechelics:[1] Tailored Synthesis of Cyclic Poly(tetrahydrofuran)s Having Two Functional Groups at Opposite Positions

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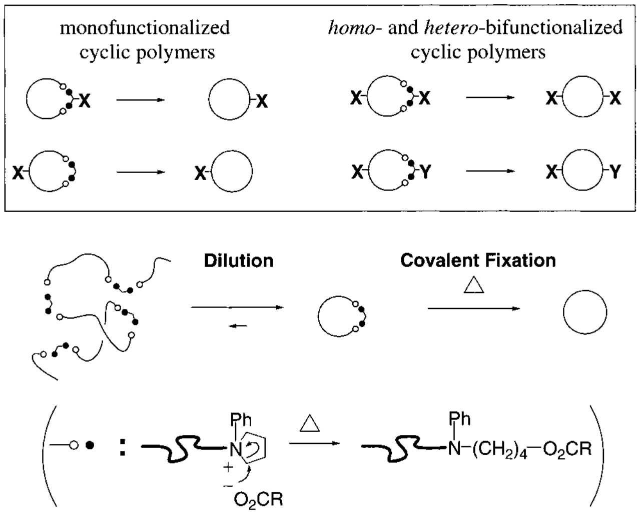
Telechelics and macromonomers generally refer to *linear* and occasionally *branched* polymer precursors having functional end groups, and they have been extensively studied for the controlled synthesis of a variety of branch-shaped and network polymers as well as block and graft copolymers.[2−4] The relevant *cyclic* polymer precursors having functional groups at designated positions, on the other hand, have scarcely been reported,[5] despite their great potential as macromolecular building blocks to construct topologically unique macromolecular architectures containing cyclic polymer units.

We report herein an efficient synthesis of mono- and bifunctionalized cyclic polymers having a single or two functional groups, termed *kyklo*-telechelics,[1] by making use of a poly(teterahydrofuran), poly(THF), with *N*-phenylpyrrolidinium salt end groups, and of another with an additional functional group at the center position of the polymer chain (termed *kentro*-telechelics)[6] (Scheme 1).

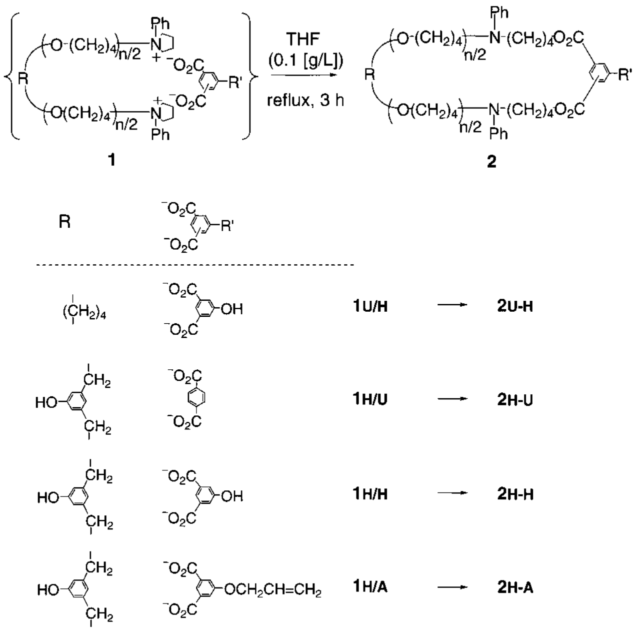
Scheme 1



Our strategy relies on a recently developed “electrostatic self-assembly and covalent fixation” process (Scheme 1),[7] where a telechelic poly(THF) with pyrrolidinium salt groups carrying a dicarboxylate counteranion has been utilized as a key polymer precursor. The ionically linked polymer precursors tend to dissociate in an organic solvent upon dilution, to form a smallest assembly consisting of polymer precursors and counteranions, and having a balanced charge of cations and anions. The subsequent ring-opening reaction of pyrrolidinium salt groups by the nucleophilic attack of the carboxylate counteranion at an appropriately elevated temperature under dilution, can produce a covalently linked, cyclic and multicyclic poly(THF)s in almost quantitative yields.

Thus, first, a telechelic poly(THF) with *N*-phenylpyrrolidinium salt groups carrying a 5-hydroxyisophthalate counteranion (**1U/H**)[8] was prepared through a simple precipitation of a THF solution of a telechelic poly(THF) with *N*-phenylpyrrolidinium salt groups carrying trifluoromethanesulfonate (triflate) counteranions (**1U/CF$_3$SO$_3$$^-$**) into an ice-cooled aqueous solution containing an excess amount of sodium 5-hydroxyisophthalate. The ion-exchange reaction, by replacing the initial triflate with the 5-hydroxyiosphthalte anion, occurred to produce **1U/H** quantitatively, as confirmed by IR and ^{1}H NMR analysis as reported before.[7,9]

Scheme 2



The ionically linked polymer precursor **1U/H** was then subjected to the heat treatment under dilution in THF (0.1 g/L) at 66 °C for 3 h, to cause the ring-opening reaction of pyrrolidinium salt end groups (Scheme 2 and Table 1). The complete ring-opening reaction was confirmed by ^{1}H NMR spectroscopic analysis (in DMSO-d_6 at 100 °C) of the product, which was recovered quantitatively by simply evaporating the solvent. Thus, signals for the *N*-phenylpyrrolidinium salt group were completely replaced, after the heat treatment, by those for an amino−ester group, i.e., a triplet at 4.32 ppm due to ester methylene protons and by signals at 7.09, 6.66, and 6.53 ppm due to the *N*-phenyl protons. The observed signals were totally assignable, showing a singlet at 9.88 ppm due to the hydroxy proton of the 5-hydroxyisophthalate counteranion (see Supporting Information). SEC shows that the product **2U-H** possesses a narrow size distribution (PDI = 1.12) and a notably smaller size in the solution than that of the linear analogue **3U**,

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Table 1. Synthesis of Cyclic Poly(THF)s Having a Single Functional Group or Two Functional Groups

entry	ionic precursor[a,b]	cyclic poly(THF)[a,c]	M_n(**2**) (NMR) × 10^{-3} [d]	PDI[e]	linear analogue[f]	M_n(**3**) (SEC) × 10^{-3} [g]	⟨*G*⟩[h]
1	**1U/H**	**2U-H**	4.9	1.12	**3U**	4.7	0.72
2	**1H/U**	**2H-U**	5.7	1.13	**3H**	5.6	0.73
3	**1H/H**	**2H-H**	5.6	1.13	**3H**	5.6	0.73
4	**1H/A**	**2H-A**	5.5	1.15	**3H**	5.6	0.73

[a] See Scheme 2 for formulas. [b] Ionic precursors were prepared from **1U/CF$_3$SO$_3$$^-$** or **1H/CF$_3SO_3$$^-$** with a series of sodium dicarboxylates through the ion-exchange reaction. [c] Cyclic poly(THF)s were obtained quantitatively from the corresponding ionic precursors by the heat treatment in THF under the concentration of 0.1 g/L at 66 °C for 3 h. [d] Determined by ^{1}H NMR spectroscopy assuming the structure of the product as shown in Scheme 3. [e] Determined by SEC in comparison with polystyrene standard samples. [f] Linear analogues **3U** and **3H** were synthesized from **1U/CF$_3$SO$_3$$^-$** and from **1H/CF$_3SO_3$$^-$** with benzoate counteranions, respectively. PDI(**3U**) = 1.12; PDI(**3H**) = 1.13. [g] Determined by SEC with a calibration using linear polystyrene standards by a conversion factor of 0.556.[16] [h] ⟨*G*⟩ = M_p(**2**)/M_p(**3**). M_p: Apparent peak molecular weight determined by SEC with a calibration using linear polystyrene standards.

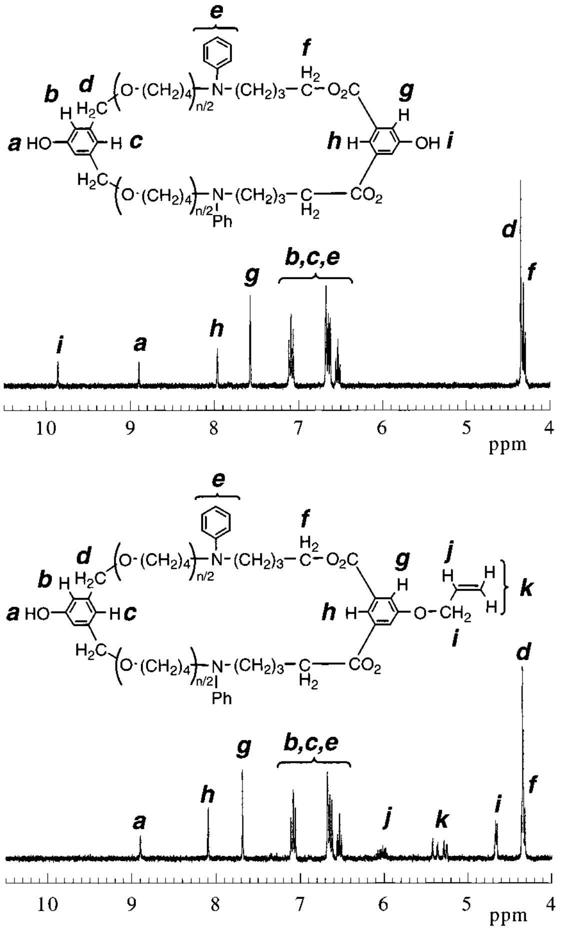

Figure 1. 300 MHz ^{1}H NMR spectra (functional group region) of *homo*- and *hetero*-bifunctionalized cyclic poly(THF)s **2H-H** (top) and **2H-A** (bottom), respectively. Samples: entry 3 and 4 in Table 1, DMSO-d_6, 100 °C.

obtained by the reaction of a common polymer precursor **1U/CF$_3$SO$_3$$^-$** with sodium benzoate (see Supporting Information). A measure of the hydrodynamic volume ratio between **2U-H** and **3U**, ⟨*G*⟩ = M_p(**2U-H**)/M_p(**3U**), estimated by SEC from their apparent peak molecular weights, was 0.72, and this value is in good agreement with those reported before.[10−12] From these results, it is shown that a monofunctionalized cyclic poly(THF) with a hydroxy group, derived from the dicarboxylate counteranion, has efficiently been produced.[13,14]

The relevant hydroxy-functionalized cyclic poly(THF) has been prepared alternatively by using an α,ω,*kentro*-telechelic poly(THF) (**1H/CF$_3$SO$_3$$^-$**),[6] not only having *N*-phenylpyrrolidinium salt groups at both chain ends but also having an additional hydroxy group at the center position of the polymer chain. Thus, the corresponding polymer precursor carrying a terephthalate counteranion **1H/U** was prepared and subjected to heat treatment under dilution in THF (0.1 g/L) at 66 °C for 3 h (Scheme 2 and Table 1). The complete ring-opening reaction of the pyrrolidinium salt end groups was again confirmed by ^{1}H NMR and IR analysis of the quantitatively recovered product. The ^{1}H NMR spectrum (in DMSO-d_6 at 100 °C) shows, in particular, a singlet at 8.90 ppm due to the hydroxy proton derived from the polymer precursor (see Supporting Information). In addition, SEC shows that the obtained cyclic poly(THF) **2H-U** possesses a narrow size distribution (PDI = 1.13) and a notably smaller size in the solution (⟨*G*⟩ = M_p(**2H-U**)/M_p(**3H**) = 0.73) than that of the linear analogue **3H**, obtained by the reaction of a common polymer precursor **1H/CF$_3$SO$_3$$^-$** with sodium benzoate (see Supporting Information).

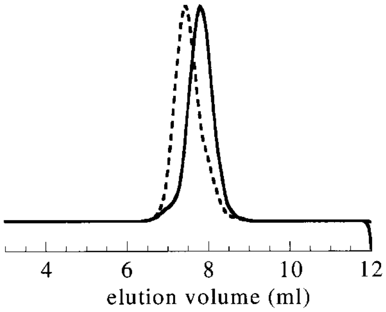

Figure 2. SEC traces (RI) of a *homo*-bifunctionalized cyclic poly(THF) **2H-H** (solid line) and of the linear analogue **3H** (broken line). Sample: entry 3 in Table 1. Column: TSK G3000HXL. eluent: THF, 1 mL/min.

Furthermore, novel *homo*- and *hetero*-bifunctionalized cyclic poly(THF)s having two identical or two different functional groups at the opposite positions, have been synthesized (Scheme 2 and Table 1). Thus, first, a polymer precursor carrying a 5-hydroxyisophthalate counteranion **1H/H** was prepared and subjected to the heat treatment under dilution in THF (0.1 g/L) at 66 °C. The ^{1}H NMR spectrum (in DMSO-d_6 at 100 °C; Figure 1, top) of the quantitatively recovered product **2H-H** shows two singlets at 9.86 ppm and at 8.90 ppm due to hydroxy protons not only from the 5-hydroxyisophthalate counteranion as in **2U-H** but also from the poly(THF) precursor as in **2H-U**. The intensities of these two signals are consistent with each other. SEC shows the product **2H-H** possesses a narrow size distribution (PDI = 1.13), as shown in Figure 2. And by means of a reversed-phase HPLC (RPC) technique (Figure 3), it is shown that the product **2H-H** with a high purity (>98%) was subsequently isolated in 81% recovered yield after the preparative thin-layer chromatography (TLC).[15] It is thus confirmed that a *homo*-bifunctionalized cyclic

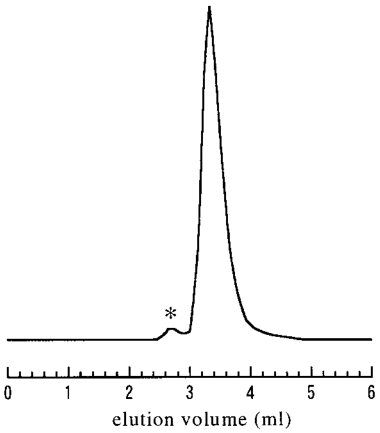

Figure 3. RPC trace (UV) of a *homo*-bifunctionalized cyclic poly(THF) **2H-H**. Sample: entry 3 in Table 1. Column: TSK ODS-80TS. Eluent: THF/CH_3CN/H_2O = 66/25/9, 1 mL/min. The peak marked by an asterisk (<2%) is that of a mixture of cyclic products from multiple polymer precursor units.

poly(THF) having two hydroxy groups at the opposite positions has been effectively produced.

Finally, the polymer precursor carrying a 5-allyloxyisophthalate counteranion **1H/A** was prepared and subjected to heat treatment under dilution in THF (0.1 g/L) at 66 °C for 3 h. A *hetero*-bifunctionalized cyclic poly(THF) having a hydroxy and an allyloxy group at the opposite positions was subsequently produced in a quantitative yield (Scheme 2 and Table 1). The ^{1}H NMR (in DMSO-d_6 at 100 °C; Figure 1, bottom) of the product shows again a singlet at 8.90 ppm due to the hydroxy proton derived from the telechelic poly(THF) precursor, in addition to signals at 5.98−6.08, 5.24−5.44, and 4.65−4.68 ppm due to allyloxy protons from the 5-allyloxyisophthalate counteranion. The proton intensity ratio of these signals agrees with that calculated from the expected molecular formula. SEC shows the obtained *hetero*-bifunctionalized cyclic poly(THF) **2H-A** possesses a narrow size distribution (PDI = 1.15) (see Supporting Information).

In conclusion, mono- and bifunctionalized cyclic poly(THF)s having a single or two functional groups have been effectively synthesized by making use of a novel polymer cyclization process, i.e., an electrostatic self-assembly and covalent fixation process, where a telechelic poly(THF) with pyrrolidinium salt groups and another with an additional functional group at the center position, and carrying functionalized dicarboxylate counteranions, have been utilized. Further studies to construct unusual macromolecular architectures containing cyclic polymer units, including novel polymer networks by a chain threading through large cyclic polymer units are currently in progress in our laboratory by using these functionalized cyclic prepolymers.

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Supporting Information Available: Text giving the detailed experimental procedures and figures showing ^{1}H NMR spectra of mono- and bifunctionalized cyclic poly(THF)s **2U-H**, **2H-U**, **2H-H** and **2H-A**, and SEC traces of **2U-H**, **2H-U** and **2H-A**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) A “*kyklo*-telechelics” refers to a cyclic polymer precursor (Greek “*kyklos*” means cycle), possessing two functional groups at the opposite positions of the chain. We propose the term “*kyklo*-telechelics”, since the usage of the Greek “*kyklo*” is apparently consistent with the Greek-based term “*telechelics*”.

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(6) An “α,*ω*-*kentro*-telechelics” refers to a telechelic (thus, end-reactive) polymer precursor, possessing an additional functional groups at the center (“*kentro*” in Greek) position of the chain. See: Oike, H.; Kobayashi, S.; Tezuka, Y.; Goethals, E. J. *Macromolecules* **2000**, *33*, 8898−8903.

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(8) The suffix (**U**, **H**, and **A**) for the compound number (**1**, **2**, and **3**) indicates the mode of functionalization (**U** = unfunctionalized; **H** = hydroxy functionalized; **A** = allyloxy functionalized). For a series of cyclic poly(THF)s **2U-H**, **2H-U**, **2H-H**, and **2H-A**, the former and the latter suffixes refer to functional groups from a telechelic poly(THF) precursor and from a dicarboxylate counteranion, respectively.

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(13) The molecular weights by both VPO and ^{1}H NMR techniques for an unfunctionalized cyclic poly(THF) and for a linear analogue agree with each other within the experimental error. See ref 7.

(14) Our attempts to characterize cyclic poly(THF)s using MALDI−TOF MS have so far been unsuccessful, presumably due to laser-induced decomposition of the products containing photosusceptible anilinobenzoate groups.

(15) For the product obtained in the higher reaction concentration (above 1.0 g/L), the RPC showed an intense peak corresponding to a mixture of cyclic products from multiple polymer precursor units at the shorter retention time (marked by an asterisk in Figure 3). The RPC showed the purity of a series of *kyklo*-telechelics products, after the purification, to be constantly more than 98%.

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