Designing Loop and Branch Polymer Topology with Cationic Star Telechelics through Effective Selection of Mono- and Difunctional Counteranions

Hideaki Oike,[†] Akiko Uchibori, Akiko Tsuchitani, Hyun-Kyoon Kim, and Yasuyuki Tezuka*

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

Received May 20, 2004; Revised Manuscript Received August 3, 2004

ABSTRACT: An "electrostatic self-assembly and covalent fixation" process has been applied with linear and three-armed star telechelic polymer precursors carrying a mixture of mono- and dicarboxylate counteranions. It has been shown that a unimeric polymer assembly is formed exclusively with the linear polymer precursor under appropriate dilution through the effective discrimination of mono- and dicarboxylate counteranions with balancing the charges between cations and anions. Subsequently, a selective synthesis of tadpole polymers has been achieved with the three-armed star telechelic precursor carrying a pair of a mono- and a dicarboxylate counteranion. Moreover, functional tadpole polymers possessing a hydroxy group at the precisely designated position have been prepared by the use of hydroxy-containing mono- and dicarboxylate counteranions.

Introduction

Diverse unique functions and properties programmed in advanced synthetic polymer materials, inspired by the relevant biomacromolecules, are often relied on their geometrical architectures of different dimensions. Nonlinear polymer architectures are basically made by loop and branch (with and without free chain ends) segments,[1−19] and they can be constructed by connecting the chain ends of linear polymer precursors with mono-, di-, and/or multifunctional reagents under precise control. In practice, however, an effective discrimination of those having different numbers of relevant functional groups is hard to achieve. In consequence, complicated product mixtures are usually produced by random linking through the irreversible covalent bond formation.

On the contrary, reversible noncovalent interactions, including hydrogen bonding and metal−ligand coordination as well as interconvertible covalent bond systems such as thiol−sulfide transformation, have offered an alternative opportunity to allow the selective formation of a thermodynamically stable product from equilibrium mixtures. A potential of such noncovalent chemical process, often referred as supramolecular chemistry or dynamic combinatorial chemistry, has been demonstrated as a new materials design principle.[20−25]

We have specifically applied the electrostatic interaction between moderately strained cyclic ammonium cations, placed on chain ends of linear or star telechelic polymer precursors, and appropriately nucleophilic carboxylate counteranions for selective chain-end-linking processes.[17−19,26−33] A significant feature of this process is the selective formation of precursor assemblies through the deassembling from their aggregation forms under dilution with balancing the charges between cations and anions. The subsequent covalent conversion by the ring-opening reaction of cyclic ammonium salt groups by carboxylate counteranions could provide a novel effective means to synthesize single- and multicyclic polymers[26−30] in addition to branched polymers like star and comb polymers.[31−33] We have so far employed single type of multifunctional counteranion in each "electrostatic self-assembly and covalent fixation" process by the combination of either linear or star telechelic cationic precursors. And notably, tadpole-type polymers have been obtained by the combination of one difunctional and one monofunctional telechelic precursors carrying one trifunctional counteranion (Scheme 3d)[26] as well as by the combination of an internally functionalized difunctional linear precursor and one difunctional counteranion (Scheme 3e).[34]

A tadpole (or lasso) topology is regarded as a basic form of a series of "loop and branch" constructions (Scheme 1) and as a useful building block for diverse topologically unique polymers.[13−16,26,34] It is notable also that a certain bacterial peptide possessing the tadpole topology adopts a unique folded structure by threading the tail chain into the loop segment.[35−37] However, attempts to synthesize tadpole-type polymers have so far been limited. Those include, besides our previous studies, an intramolecular polymer cyclization by using a specifically designed linear precursor having two complementary reactive groups at one chain end and at an interior position in the main chain[13] and a bimolecular coupling reaction between complementary functionalized cyclic and linear polymer precursors (Scheme 2).[14]

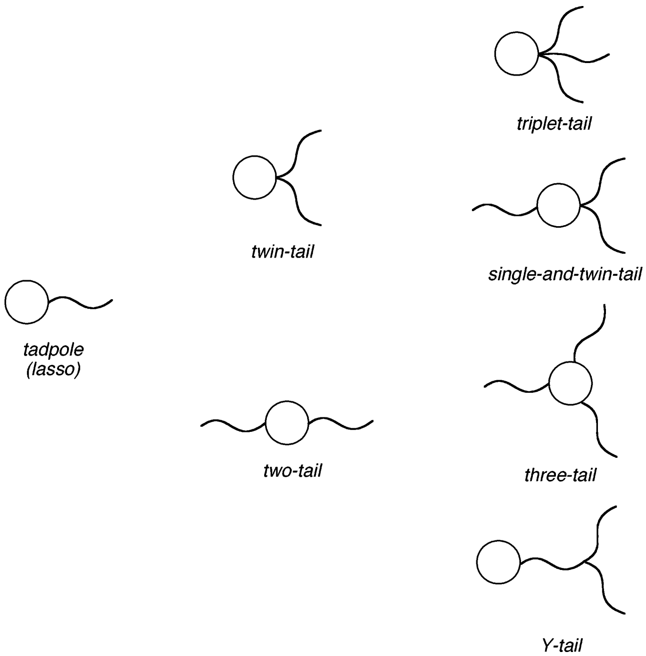
We show in the present paper a new synthetic protocol for a tadpole polymer topology, in which the "electrostatic self-assembly and covalent fixation" process has been integrated with the dynamic equilibrium involving a star telechelic precursors carrying a mixture of two different types of carboxylate counteranions (Scheme 3, see also Chart 1). A tadpole polymer has been exclusively produced with a three-armed star telechelic precursor carrying a pair of a mono- and a

[†] Present address: ERATO Nanospace Project, JST, Aomi 2-41, Koto-ku, Tokyo 135-0064, Japan.

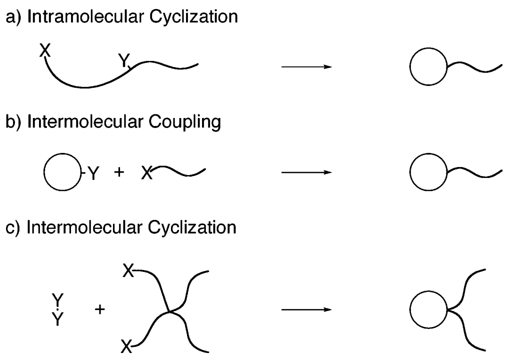
* Address correspondence to this author. E-mail: ytezuka@o.cc.titech.ac.jp.

10.1021/ma049001s CCC: $27.50
Published on Web 09/10/2004

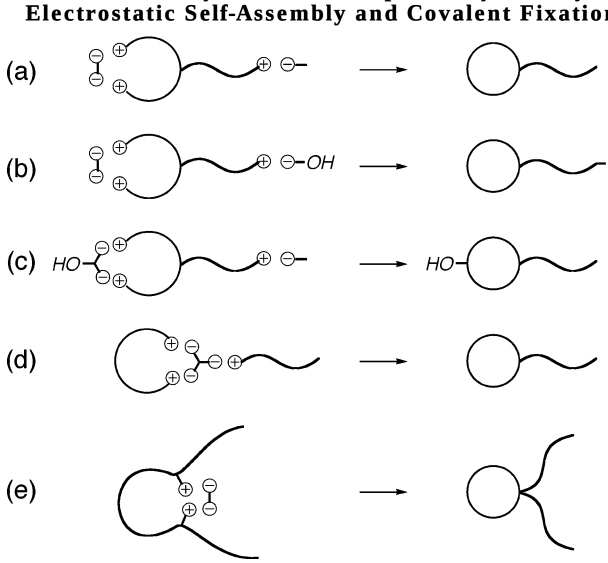
Scheme 1. A Series of Tadpole Constructions



Scheme 2. Synthesis of Tadpole Polymers

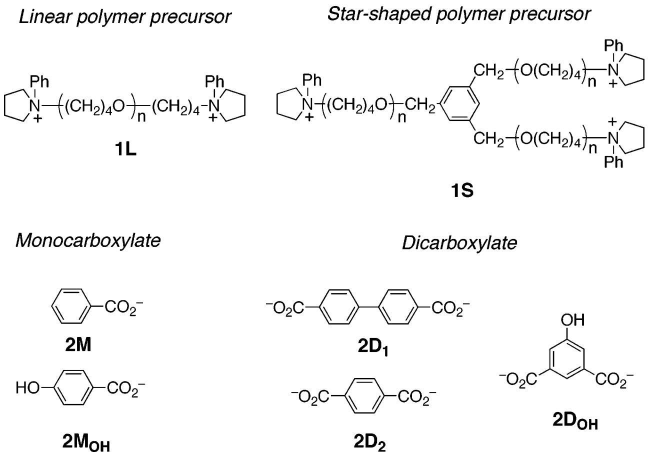


Scheme 3. Synthesis of Tadpole Polymers by Electrostatic Self-Assembly and Covalent Fixation



dicarboxylate counteranions, formed under appropriate dilution (Scheme 3a). Moreover, a series of functional tadpole polymers, in which the location of the functional group is precisely designated, have been obtained by the use of hydroxy-containing mono- and dicarboxylate counteranions, respectively (Scheme 3b,c).

Chart 1. Polymer Precursors and Carboxylate Anions



Experimental Section

Preparation of Polymer Precursors. Linear telechelic poly(THF)s of different chain lengths (M_n(NMR) = 5.3 × 10^3 and 6.6 × 10^3) having *N*-phenylpyrrolidinium salt groups carrying benzoate anions (**1L**/**2M**) and a 4,4′-biphenyldicarboxylate anion (**1L**/**2D$_1$**) were prepared by the method detailed before.[26,38] Trifunctional star-shaped poly(THF)s of different molecular weights (M_n(NMR) = 9.0 × 10^3 and 1.1 × 10^4) having *N*-phenylpyrrolidinium salt end groups carrying trifluoromethanesulfonates (triflates) were also prepared by a similar procedure described previously.[39] Molecular weights of the polymer precursors were determined by ^{1}H NMR based on the signal ratio between the end groups and poly(THF) main chains because of the serious peak tailing in the size exclusion chromatography (SEC) measurements due to the ionic end groups.

Ion-Exchange Reaction. Trifunctional star-shaped poly(THF)s having *N*-phenylpyrrolidinium salt end groups carrying benzoates (**1S**/**2M**), 4-hydroxybenzoates (**1S**/**2M$_{OH}$**), a terephthalate (**1S**/**2D$_2$**), and a 5-hydroxyisophthalate (**1S**/**2D$_{OH}$**) were prepared by a similar procedure for **1L**/**2M** and **1L**/**2D$_1$**. The procedure for **1S**/**2D$_2$** is described as a typical example. Thus, a THF solution (2.0 mL) of 0.40 g (0.036 mmol) of trifunctional star-shaped poly(THF) precursor carrying triflate counteranions was added dropwise to an ice-cooled (<5 °C) aqueous solution (200 mL) containing an excess amount of a sodium terephthalate (10 equiv) under vigorous stirring. After 1 h, the precipitated ion-exchange product was collected by filtration and dried in vacuo for 1.5 h. This precipitation treatment was repeated four times for the completion of ion exchange reaction (confirmed by the disappearance of the peaks due to triflate anions in their IR spectra) to give **1S**/**2D$_2$** in the yield of 0.44 g (containing ca. 10 wt % residual water to avoid uncontrolled ring-opening reaction).

Preparation of Linear and Cyclic Poly(THF). Both THF solutions of **1L**/**2M** and of **1L**/**2D$_1$** (concentration: 1.0 and 0.2 g/L, respectively) were heated at reflux temperature for 3 h, as reported before, to give quantitatively a linear and a cyclic poly(THF), respectively.[26,38] The products were unequivocally characterized by means of MALDI-TOF-MS technique (see Supporting Information) in addition to IR, ^{1}H NMR, and SEC as previously reported.[26,38]

Heat Treatment of a Linear Poly(THF) Precursor Carrying a Mixture of Mono- and Dicarboxylates (1L/2M·2D$_1$). Linear poly(THF) precursors **1L**/**2M** and **1L**/**2D$_1$** were mixed (total 30−50 mg, 1/1 in mol/mol for counteranion) in THF at the prescribed concentration (0.2−10 g/L) and was heated at the reflux temperature for 3 h. The covalently converted product was recovered in an almost quantitative yield by simply evaporating the solvent and was subjected to spectroscopic and chromatographic analyses.

Synthesis of Tadpole-Shaped Poly(THF)s. The procedure with precursor **1S**/**2M**·**2D$_2$** was described as a typical example. Star-shaped poly(THF) precursors **1S**/**2M** and **1S**/

$2D_2$ were mixed (total 30−60 mg, 1/1 in mol/mol for counteranion) in THF at the prescribed concentration (0.05−1.0 g/L) and was heated at the reflux temperature for 3 h. The covalently converted product was recovered in an almost quantitative yield by simply evaporating the solvent and was subjected to spectroscopic and chromatographic analyses. Apparent main peak molecular weights (M_p(SEC)) of the products were determined by SEC relative to linear polystyrene standards by a conversion factor of 0.556.[40]

Tadpole polymer obtained from **1S/2M·2D₂**. ^{1}H NMR: δ 8.10 (s, 4H, Ar-*H ortho* to CO_2CH_2), 8.10−7.94 (m, 2H, Ar-*H ortho* to CO_2CH_2), 7.58−7.38 (m, 3H, Ar-*H meta* and *para* to CO_2-CH_2), 7.30−7.10 (m, 6H, Ar-*H meta* to N), 7.20 (s, 3H, Ar-*H ortho* to CH_2O), 6.80−6.58 (m, 9H, Ar-*H ortho* and *para* to N), 4.44 (s, 6H, ArC*H*$_2$O), 4.36−4.26 (m, 6H, CO_2CH_2), 3.60−3.24 (m, CH_2CH_2O), 1.80−1.40 (m, CH_2CH_2O).

Tadpole polymer obtained from **1S/2M$_{OH}$·2D$_2$**. ^{1}H NMR: δ 8.06 (s, 4H, Ar-*H ortho* to CO_2CH_2), 7.92 (d, J = 9.3 Hz, 2H, Ar-*H meta* to OH), 7.30−7.10 (m, 6H, Ar-*H meta* to N), 7.19 (s, 3H, Ar-*H ortho* to CH_2O), 6.84 (d, J = 9.3 Hz, 2H, Ar-*H ortho* to OH), 6.80−6.58 (m, 9H, Ar-*H ortho* and *para* to N), 4.46 (s, 6H, ArC*H*$_2$O), 4.40−4.26 (m, 6H, CO_2CH_2), 3.54−3.24 (m, CH_2CH_2O), 1.75−1.40 (m, CH_2CH_2O).

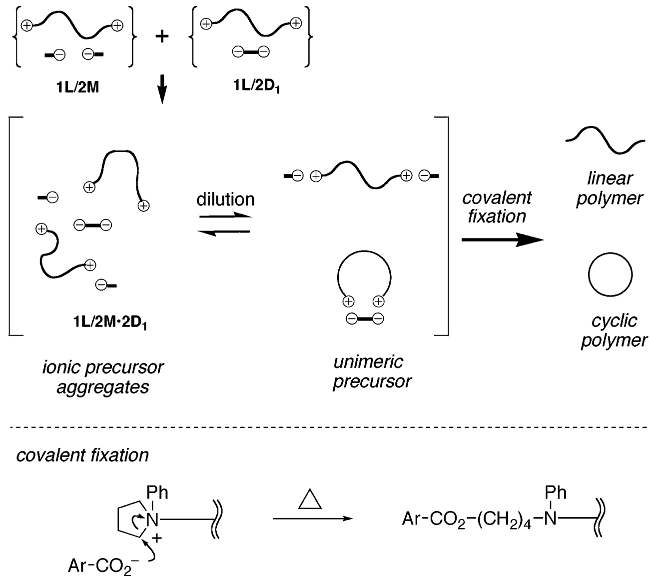
Tadpole polymer obtained from **1S/2M·2D$_{OH}$**. ^{1}H NMR: δ 8.20 (br s, 1H, Ar-*H para* to OH), 8.06−7.98 (m, 2H, Ar-*H ortho* to CO_2CH_2), 7.64 (br s, 2H, Ar-*H ortho* to OH), 7.58−7.38 (m, 3H, Ar-*H meta* and *para* to CO_2CH_2), 7.30−7.10 (m, 6H, Ar-*H meta* to N), 7.20 (s, 3H, Ar-*H ortho* to CH_2O), 6.80−6.58 (m, 9H, Ar-*H ortho* and *para* to N), 4.46 (s, 6H, ArC*H*$_2$O), 4.40−4.28 (m, 6H, CO_2CH_2), 3.60−3.20 (m, CH_2CH_2O), 1.80−1.40 (m, CH_2CH_2O).

Measurements. SEC measurements were performed using a Tosoh model CCPS equipped with a refractive index detector model RI 8020, a UV detector model UV 8020 at 254 nm, and a conductivity detector model CM 8010. A column of either TSK G3000HXL or TSK G4000HXL was employed with THF as an eluent at a flow rate of 1.0 mL/min. In a typical procedure, 40 μL of sample solution (sample concentration of 10 wt %) was injected. Reversed-phase chromatography (RPC) measurements were conducted by an isocratic mode using a Tosoh model CCPS equipped with a UV detector model UV 8020 at 254 nm. A C18 bonded silica column of TSK ODS-80TS (80 Å pore, 150 mm × 4.6 mm i.d., 5 μm average particle size) was employed with a mixture of THF/CH_3CN (50/50 in volume). IR spectra were taken on a JASCO FT/IR-410 infrared spectrometer by casting the sample from the chloroform solution on a NaCl plate. ^{1}H NMR spectra were recorded with a JEOL JNM-AL300 apparatus in $CDCl_3$ at 40 °C. The proton chemical shifts (ppm) were referenced from the signal of tetramethylsilane. MALDI-TOF-MS spectra were taken on a Shimadzu AXIMA-CFR mass spectrometer. The spectrometer was equipped with a nitrogen laser (λ = 337 nm) and with pulsed ion extraction. The operation was performed at an accelerating potential of 20 kV by a linear-positive ion mode. The sample polymer solution (1 g/L) was prepared in THF. The matrix, 1,8-dihydroxy-9(10*H*)-anthracenone (dithranol, Aldrich) and sodium trifluoroacetate (Aldrich), was dissolved in THF (10 and 1 g/L, respectively). The polymer solution (50 μL) was then mixed with 50 μL of the matrix solution. A 1 μL portion of the final solution was deposited onto a sample target plate and allowed to dry in air at room temperature. Mass values were calibrated by the two-point method with insulin β plus H^+ at 3497.96 and α-cyanohydroxycinnamic acid dimer plus H^+ at 379.35.

Results and Discussion

Electrostatic Self-Assembly and Covalent Fixation of Linear Poly(THF) Precursor Carrying a Mixture of Mono- and Dicarboxylates. To obtain basic insights into the electrostatic self-assembly and covalent fixation process involving different types of counteranions, we first studied the reaction of a linear poly(THF) precursor having cyclic ammonium salt end groups carrying a mixture of mono- and dicarboxylate, **1L/2M·2D₁** (Scheme 4).

Scheme 4. Electrostatic Self-Assembly and Covalent Fixation of Linear Poly(THF) Precursor Carrying a Mixture of Mono- and Dicarboxylates



Thus, a linear poly(THF) (M_n(NMR) = 6.6 × 10^3) having *N*-phenylpyrrolidinium salt end groups, carrying trifluoromethansulufonate (triflate) counteranions, was prepared (Chart 1),[26,31,38] and the counteranions were replaced with desired anions such as monofunctional benzoate and difunctional 4,4′-biphenyldicarboxylate anions to give **1L/2M** and **1L/2D₁**, respectively. A telechelic polymer precursor **1L/2M·2D₁** carrying a mixture of mono- and dicarboxylate (1/1 in mol/mol for counteranion) was subsequently prepared by simply mixing **1L/2M** and **1L/2D₁** in THF.

Through the ring-opening reaction of pyrrolidinium salt groups by a nucleophilic attack of carboxylate anions under appropriate heat conditions (>50 °C), the ionic salt end groups can be converted into covalent linkages. Thus, a unimeric linear product was obtained at any concentration with **1L/2M**, having uniquely monofunctional carboxylate. On the other hand, **1L/2D₁**, having exclusively difunctional counterparts, gave an equilibrium mixture of the chain-extended products at high concentration. But under dilution, a cyclic product consisting of a single polymer precursor unit was produced through the deassembly with balancing the charges between cations and anions.

Both linear and cyclic polymer products were isolated after covalent conversion by the ring-opening reaction. The products were unequivocally characterized by means of the MALDI-TOF-MS technique (see Supporting Information) besides IR, ^{1}H NMR, and SEC.[26,38] Both products showed a uniform series of peaks corresponding to poly(THF) (peak interval of 72 mass units), and each peak corresponds exactly to the molar mass summing up the linking structure produced by the ring-opening reaction of *N*-phenylpyrrolidinium end groups in **1L/2D₁** and in **1L/2M**. Since the cyclic and the linear poly(THF) products are produced from the same precursor but with the respective monofunctional and difunctional counteranions, their molecular weights differ by 2 mass units. This was confirmed by the two MALDI-TOF-MS spectra (see Supporting Information).

In the case of **1L/2M·2D₁**, carrying a mixture of mono- and difunctional carboxylate anions, a unimeric selec-

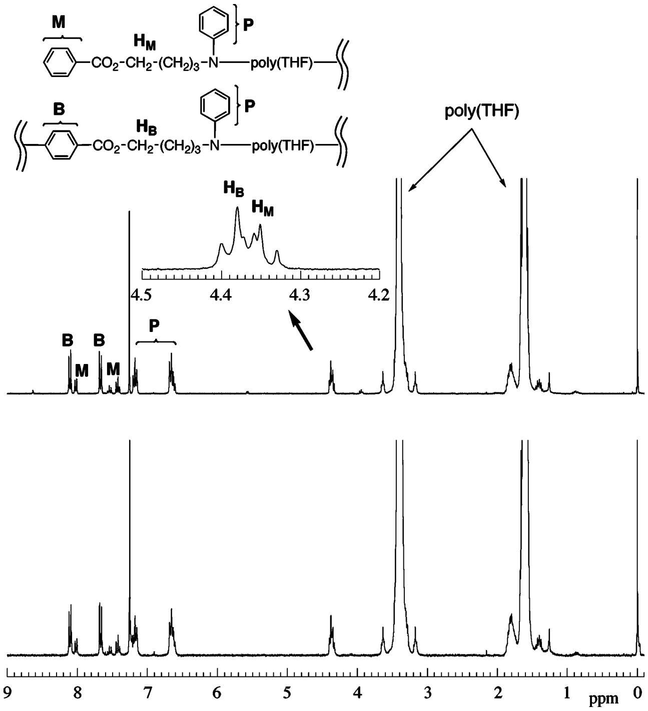


Figure 1. 300 MHz ^{1}H NMR of a linear telechelic poly(THF) carrying a mixture of benzoate and 4,4′-biphenyldicarboxylate counteranions (1/1 in mol/mol for counteranion), **1L/2M·2D$_1$**, after the heat treatment (top) and of a mixed sample of a linear and a cyclic poly(THF) prepared independently from **1L/2M** and **1L/2D$_1$** (bottom) (M_n(NMR) of the sample: 6.6 × 10^3, $CDCl_3$, 40 °C).

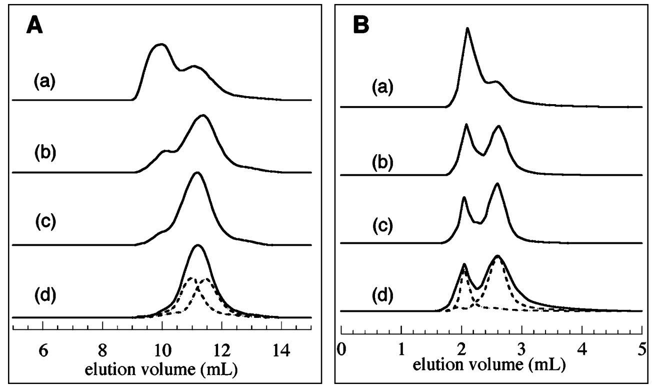


Figure 2. SEC (A, RI detector) and reversed-phase chromatography (RPC, B, UV detector at 254 nm) traces of the quantitatively recovered product after the heat treatment of **1L/2M·2D$_1$** in THF at various concentrations (a−c) and of a 1:1 mixture of a linear and a cyclic poly(THF)s prepared by the heat treatments of **1L/2M** and of **1L/2D$_1$**, respectively (solid line in (d)). Broken lines in (d) correspond to the former at shorter and to the latter at longer retention times, respectively. Concentration of the poly(THF) precursor in THF: (a) 10, (b) 1.0, and (c) 0.2 g/L [M_n(NMR) of the sample: 6.6 × 10^3; SEC: column, TSK G3000HXL; eluent: THF; 1.0 mL/min; RPC: column, TSK ODS-80TS; eluent: THF/CH_3CN = 50/50 (v/v), isocratic, 1.0 mL/min].

tion of the polymer precursor by dilution will result in the discrimination between mono- and difunctional carboxylate anions, leading to the exclusive formation of linear and cyclic polymers consisting of a single polymer precursor unit, respectively (Scheme 4). On the other hand, a series of linear and cyclic polymers of various chain lengths will be formed by kinetically controlled or random selection of mono- and difunctional carboxylates.

When a THF solution of **1L/2M·2D$_1$** was heated at 66 °C for 3 h at different polymer concentrations, the quantitative ring-opening reactions of the pyrrolidinium salt end groups took place as evidenced by ^{1}H NMR and IR spectroscopic analyses. The ^{1}H NMR shows clearly two sets of signals due to both amino-ester groups with benzoate and 4,4′-biphenyldicarboxylate units (Figure 1, top). This spectrum, moreover, coincided with that of a mixture of the linear and the cyclic polymer products, prepared independently from **1L/2M** and from **1L/2D$_1$**, respectively (Figure 1, bottom).

SEC profiles of the covalently converted products from **1L/2M·2D$_1$** obtained under different polymer concentrations are shown in Figure 2A (a−c). At the concentration of 10 g/L (Figure 2A (a)), a major fraction was observed at the higher molecular weight region. This indicates that the polymer precursor with a mixture of mono- and difunctional carboxylate anions tended to form multiple aggregates in the concentrated solution, and the subsequent covalent conversion produced the chain extended linear products containing both carboxylate moieties besides large cyclic products containing solely dicarboxylate moieties. Along with dilution toward 0.2 g/L (Figure 2A (b) and (c), respectively), however, the content of the lower molecular weight fraction prevailed progressively by the expense of the higher molecular weight fraction. And finally, the product obtained at 0.2 g/L showed the SEC profile consistent with that of a mixture of the unimeric polymer products of linear and cyclic forms, prepared independently from **1L/2M** and from **1L/2D$_1$** (Figure 2A (d)), respectively.

Moreover, the reversed-phase chromatography (RPC) technique was applied to separate the unimeric linear product with two monocarboxylates from the relevant cyclic counterpart with one dicarboxylate (Figure 2B).[26,38] Thus, the product obtained at 0.2 g/L showed the two distinguishable peaks, corresponding to the unimeric polymer product of linear and cyclic forms, prepared independently from **1L/2M** and from **1L/2D$_1$**, respectively (Figure 2B (d)).

These results clearly show that the linear and the cyclic polymer products both consisting of a single polymer unit were exclusively formed with the balance of the charges between cations and anions during the deassembly of ionic precursor aggregates, even in the copresence of mono- and dicarboxylate counteranions.

Synthesis of Tadpole Polymer with Three-Armed Star Poly(THF) Precursor. Three-armed star poly(THF) precursors of different molecular weights were synthesized with an “in situ” prepared trifunctional initiator for living cationic polymerization of THF, followed by an end-capping reaction of *N*-phenylpyrrolidine (Chart 1).[39] The subsequent ion-exchange reactions with monofunctional benzoate and with difunctional terephthalate afforded three-armed star poly(THF) precursors **1S/2M** and **1S/2D$_2$** (M_n(NMR) = 1.1 × 10^4), respectively. We have so far applied the “electrostatic self-assembly and covalent fixation” to a three-armed star telechelic poly(THF) in simple combinations with mono-, di-, and trifunctional carboxylate counteranions. It has been found that a star polymer[39] and a pair of topological isomers of manacle- and *θ*-shaped polymers[41] have been produced with mono- and dicarboxylates, respectively, and the doubly cyclized *θ*-shaped polymer has been selectively obtained with a trifunctional carboxylate counteranion.[29]

In the present study, three-armed telechelic polymer precursor **1S/2M·2D$_2$** carrying a mixture of mono- and

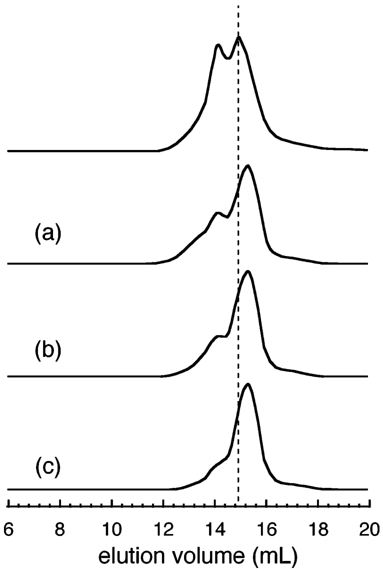


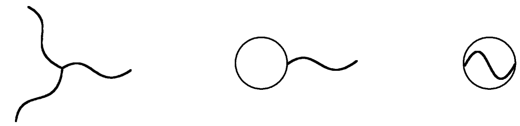
Figure 3. SEC (RI detector) traces (top) of a 1:1 mixture of the products prepared independently from **1S/2M** and **1S/2D$_2$** by the heat treatment in THF (reaction concentration: 0.4 g/L) and (a–c) of the quantitatively recovered product after the heat treatment of **1S/2M·2D$_2$** at various concentrations. Concentration of **1S/2M·2D$_2$** in THF: (a) 1.0, (b) 0.4, and (c) 0.05 g/L [M_n(NMR) of the sample: 1.1 × 10^4; SEC: column, TSK G4000HXL; eluent: THF, 1.0 mL/min].

dicarboxylate (1/1 in mol/mol for counteranion) was prepared by simply mixing **1S/2M** and **1S/2D$_2$** in THF as in the case of the linear polymer precursor. The heat treatment of **1S/2M·2D$_2$** was then conducted in THF under various dilutions in the range 0.05–1.0 g/L. The reaction proceeded homogeneously under these concentrations, while the gelation took place in bulk or at higher concentration. The quantitative ring-opening reaction of the pyrrolidinium salt end groups has been again confirmed by ^{1}H NMR and IR analyses. The ^{1}H NMR shows the two sets of signals due to amino-ester groups formed through the ring-opening reaction with benzoate and with terephthalate anions (see Supporting Information). MALDI-TOF-MS measurements have so far been unsuccessful presumably due to ineffective ionization of the present products having the molecular weights around 10^4.

SEC profiles of the covalently converted products at different concentrations are shown in Figure 3a–c, together with the profile of a mixture of a pair of polymeric topological isomers (manacle- and θ-shaped polymers) and a star-shaped polymer, prepared independently from **1S/2D$_2$** and from **1S/2M**, respectively (Figure 3, top). The lower molecular weight fraction having a narrow size distribution (PDI = 1.27 at the concentration of 0.05 g/L) prevails along with dilution by the expense of the higher molecular weight fraction. Thus, the deassembly of the ionic aggregates of **1S/2M·2D$_2$** tended to proceed, as in the case of the linear precursor system, to form a unique assembly comprising of a unimeric three-armed polymer precursor carrying a pair of a benzoate and a terephthalate anion to balance the charges between cations and anions. The subsequent heat treatment could produce exclusively a tadpole polymer (Scheme 3a).

SEC results in Figure 3 also showed that the tadpole polymer was significantly smaller in its hydrodynamic volume than the relevant star polymer possessing nearly equal molecular weights (thus total chain lengths).

Scheme 5



The relative hydrodynamic volume ratio, corresponding to their three-dimensional sizes, between the tadpole and the star polymers was estimated as 0.83, from their SEC peak molecular weights (M_p(SEC) = 8.6 × 10^3 and 1.04 × 10^4, respectively). The contracted hydrodynamic volume of the former is reasoned because the tadpole polymer is formed through the intramolecular cyclization of the star polymer precursor. It is notable that the relative hydrodynamic volume ratio between θ-shaped and the relevant star-shaped polymers was reported in the range 0.71–0.75.[39] This means that the three-dimensional size of a tadpole polymer is somewhat larger than that of the relevant θ-shaped polymer, since the former is a *singly* cyclized but the latter is a *doubly* cyclized product from the star polymer precursor (Scheme 5).

Synthesis of Functionalized Tadpole Polymers. The "electrostatic self-assembly and covalent fixation" process has been also applied with carboxylate anions possessing such functionalities as hydroxy and allyloxy groups.[42,43] We have so far described cyclic polymers having functional groups at the precisely designated positions, i.e., *kyklo*-telechelics and cyclic macromonomers, for the constructions of eight-shaped polymers as well as polymer networks involving physical linkage (chain-threading). In the present study, we have synthesized two types of hydroxy-functionalized tadpole polymers, one having a hydroxy group at the tail end and another having it at the middle of the loop (or the top of the tadpole head) (Scheme 3, b and c, respectively).

Thus, star poly(THF) precursor **1S/2M$_{OH}$·2D$_2$** (M_n(NMR) = 1.1 × 10^4) carrying a mixture of 4-hydroxybenzoate and terephthalate anions (1/1 in mol/mol for counteranion) was prepared in the manner similar to **1S/2M·2D$_2$**. Another precursor **1S/2M·2D$_{OH}$** (M_n(NMR) = 9.0 × 10^3) carrying a mixture of benzoate and 5-hydroxyisophthalate anions (1/1 in mol/mol for counteranion) was also prepared. As expected, SEC profiles of the recovered products after the heat treatment of **1S/2M$_{OH}$·2D$_2$** and of **1S/2M·2D$_{OH}$** under appropriate dilution (0.05 g/L) showed the unimodal peaks with narrow size distributions (PDI = 1.34 and 1.30, respectively) at the elution volumes corresponding to the tadpole polymers (M_p(SEC) = 9.1 × 10^3 and 7.9 × 10^3, as seen in Figure 4a and Figure 5a, respectively). The quantitative formation of each type of the hydroxy-functionalized tadpole polymers has been further confirmed by the ^{1}H NMR, in which signals due to 4-hydroxybenzoate and 5-hydroxyisophthalate moieties are visible as shown in Figure 4b and Figure 5b, respectively.

Conclusion

An "electrostatic self-assembly and covalent fixation" process has been applied with linear and three-armed star telechelic polymer precursors carrying a mixture of mono- and dicarboxylate counteranions. It has been

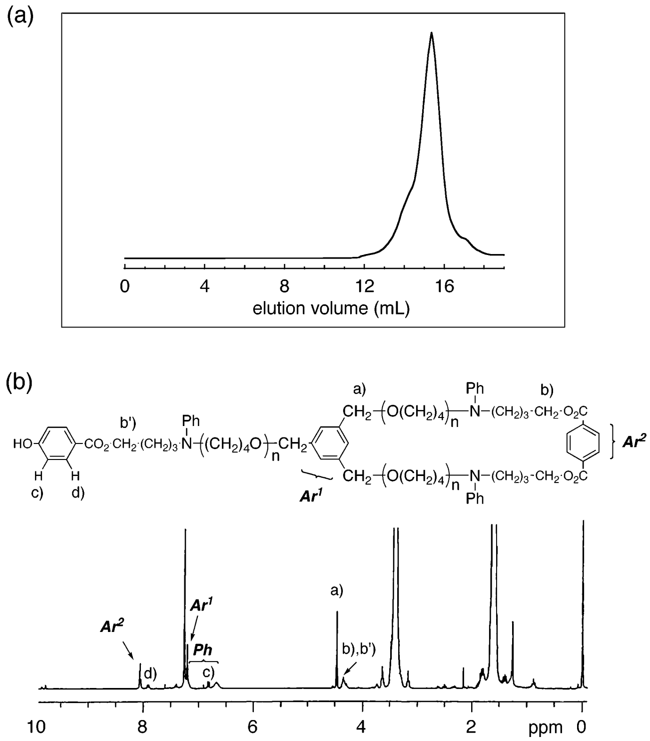


Figure 4. (a) A SEC (RI detector) trace and (b) a ^{1}H NMR spectrum in $CDCl_3$ of the hydroxy-functionalized tadpole polymer obtained by the heat treatment of **1S/2M$_{OH}$·2D$_2$** in THF (reaction concentration: 0.05 g//L) [M_n(NMR) of the sample: 1.1×10^4; SEC: column, TSK G4000HXL; eluent: THF, 1.0 mL/min].

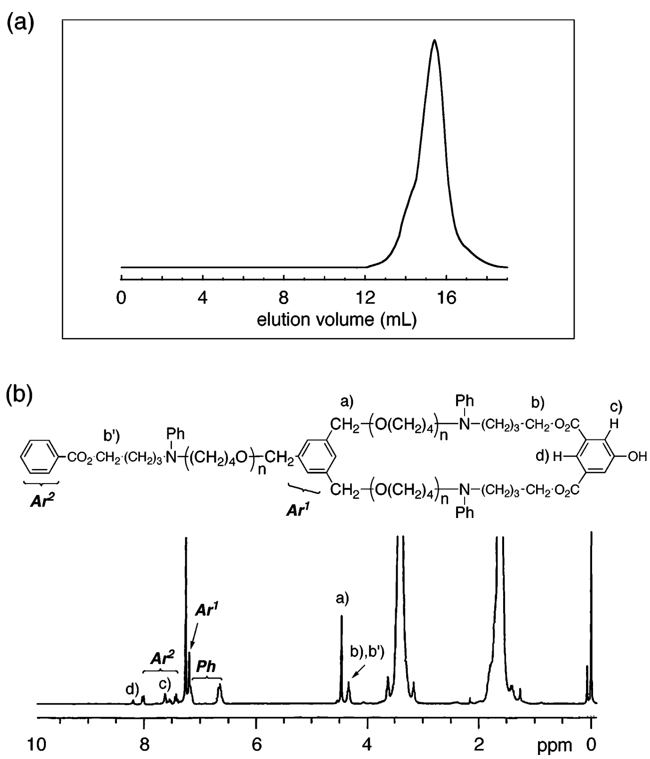


Figure 5. (a) A SEC (RI detector) trace and (b) a ^{1}H NMR spectrum in $CDCl_3$ of the hydroxy-functionalized tadpole polymer obtained by the heat treatment of **1S/2M·2D$_{OH}$** in THF (reaction concentration: 0.05 g//L) [M_n(NMR) of the sample: 9.0×10^3; SEC: column, TSK G4000HXL; eluent: THF, 1.0 mL/min].

shown that a unimeric polymer assembly is formed exclusively with the linear polymer precursor under appropriate dilution through the effective discrimination of mono- and dicarboxylate counteranions with balancing the charges between cations and anions. Subsequently, a selective synthesis of tadpole polymers has been achieved with the three-armed star telechelic precursor carrying a mixture of mono- and dicarboxylate counteranions. Moreover, functional tadpole polymers possessing a hydroxy group at the precisely designated position have been prepared by the use of hydroxy-containing mono- and dicarboxylate counteranions. This dynamic combinatorial strategy based on the electrostatic self-assembly and covalent fixation process is not only useful to construct the tadpole macromolecular building blocks but also will offer further unique opportunities for the rational design of various complex polymer topologies.

Acknowledgment. Authors are grateful to Professor M. Kakimoto for our access to the NMR apparatus. Financial support from The Iwatani Naoji Foundation's Research Grant and from a NEDO Nanostructure Polymer Project is gratefully acknowledged. This work was supported partly by a grant from the Ministry of Education, Science and Culture, Japan (13450377).

Supporting Information Available: MALDI-TOF-MS spectra of a linear and a cyclic poly(THF)s (S-Figure 1) and ^{1}H NMR spectra of the quantitatively recovered product after heat treatment of **1S/2M·2D$_2$** before and after heat treatment in THF (S-Figure 2). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Hadjichristidis, N.; Pitskalis, M.; Pispas, S.; Iatrou, H. *Chem. Rev.* **2001**, *101*, 3747−3792.
(2) *Cyclic Polymers*, 2nd ed.; Semlyen, J. A., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2000.
(3) McLeish, T. *Science* **2002**, *297*, 2005−2006.
(4) Bielawski, C. W.; Benitez, D.; Grubbs, R. H. *Science* **2002**, *297*, 2041−2044.
(5) Alberty, K. A.; Tillman, E.; Carlotti, S.; King, K.; Bradforth, S. E.; Hogen-Esch, T. E.; Parker, D.; Feast, W. J. *Macromolecules* **2002**, *35*, 3856−3865.
(6) Lepoittevin, B.; Hémery, P. *Polym. Adv. Technol.* **2002**, *13*, 771−776.
(7) Singla, S.; Zhao, T.; Beckham, H. W. *Macromolecules* **2003**, *36*, 6945−6948.
(8) Bielawski, C. W.; Benitez, D.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 8424−8425.
(9) Kricheldorf, H. R.; Schwarz, G. *Macromol. Rapid Commun.* **2003**, *24*, 369−381.
(10) Takano, A.; Kadoi, O.; Hirahara, K.; Kawahara, S.; Isono, Y.; Suzuki, J.; Matsushita, Y. *Macromolecules* **2003**, *36*, 3045−3050.
(11) Zhu, Y.; Gido, S. P.; Iatrou, H.; Hadjichristidis, N.; Mays, J. W. *Macromolecules* **2003**, *36*, 148−152.
(12) Helfer, C. A.; Xu, G.; Mattice, W. L.; Pugh, C. *Macromolecules* **2003**, *36*, 10071−10078.
(13) Beinat, S.; Schappacher, M.; Deffieux, A. *Macromolecules* **1996**, *29*, 6737−6743.
(14) Kubo, M.; Hayashi, T.; Kobayashi, H.; Itoh, T. *Macromolecules* **1998**, *31*, 1053−1057.
(15) Ma, J. *Macromol. Symp.* **1995**, *91*, 41.
(16) Tezuka, Y.; Komiya, R.; Washizuka, M. *Macromolecules* **2003**, *36*, 12−17.
(17) Tezuka, Y.; Oike, H. *J. Am. Chem. Soc.* **2001**, *123*, 11570−11576.
(18) Tezuka, Y.; Oike, H. *Prog. Polym. Sci.* **2002**, *27*, 1069−1122.
(19) Tezuka, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 2905−2917.
(20) Lehn, J.-M. *Science* **2002**, *295*, 2400−2403.
(21) Badjic, J. D.; Balzani, V.; Credi, A.; Silvi, S.; Stoddart, J. F. *Science* **2004**, *303*, 1845−1849.
(22) Seeman, N. C. *Nature (London)* **2003**, *421*, 427−431.

(23) Shin, W. M.; Quispe, J. D.; Joyce, G. F. *Nature (London)* **2004**, *427*, 618−621.
(24) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071−4098.
(25) Rowan, S. J.; Cantrill, S. J.; Cousins, G. R. L.; Sanders, J. K. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2002**, *41*, 898−952.
(26) Oike, H.; Imaizumi, H.; Mouri, T.; Yoshioka, Y.; Uchibori, A.; Tezuka, Y. *J. Am. Chem. Soc.* **2000**, *122*, 9592−9599.
(27) Oike, H.; Hamada, M.; Eguchi, S.; Danda, Y.; Tezuka, Y. *Macromolecules* **2001**, *34*, 2776−2782.
(28) Tezuka, Y.; Mori, K.; Oike, H. *Macromolecules* **2002**, *35*, 5707−5711.
(29) Tezuka, Y.; Tsuchitani, A.; Yoshioka, Y.; Oike, H. *Macromolecules* **2003**, *36*, 65−70.
(30) Tezuka, Y.; Tsuchitani, A.; Oike, H. *Polym. Int.* **2003**, *52*, 1579−1583.
(31) Oike, H.; Imamura, H.; Imaizumi, H.; Tezuka, Y. *Macromolecules* **1999**, *32*, 4819−4825.
(32) Oike, H.; Imamura, H.; Tezuka, Y. *Macromolecules* **1999**, *32*, 8666−8670.
(33) Oike, H.; Imamura, H.; Tezuka, Y. *Macromolecules* **1999**, *32*, 8816−8820.
(34) Oike, H.; Washizuka, M.; Tezuka, Y. *Macromol. Rapid Commun.* **2001**, *22*, 1128−1134.
(35) Bayro, M. J.; Mukhopadhyay, J.; Swapna, G. V. T.; Huang, J. Y.; Ma, L.-C.; Sineva, E.; Dawson, P. E.; Montelione, G. T.; Ebright, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 12382−12383.
(36) Wilson, K.-A.; Kalkum, M.; Ottesen, J.; Yuzenkova, J.; Chait, B. T.; Landick, R.; Muir, T.; Severinov, K.; Darst, S. A. *J. Am. Chem. Soc.* **2003**, *125*, 12475−12483.
(37) Rosengren, K. J.; Clark, R. J.; Daly, N. L.; Göransson, U.; Jones, A.; Craik, D. J. *J. Am. Chem. Soc.* **2003**, *125*, 12464−12474.
(38) Oike, H.; Mouri, T.; Tezuka, Y. *Macromolecules* **2001**, *34*, 6592−6600.
(39) Oike, H.; Yoshioka, Y.; Kobayashi, S.; Nakashima, M.; Tezuka. Y.; Goethals, E. J. *Macromol. Rapid Commun.* **2000**, *21*, 1185−1190.
(40) Burgess, F. J.; Cunliffe, A. V.; Dawkins, J. V.; Richards, D. H. *Polymer* **1977**, *18*, 733−740.
(41) Tezuka, Y.; Tsuchitani, A.; Oike, H. *Macromol. Rapid Commun.* **2004**, *25*, 1531−1535.
(42) Oike, H.; Kobayashi, S.; Mouri, T.; Tezuka, Y. *Macromolecules* **2001**, *34*, 2742−2744.
(43) Oike, H.; Mouri, T.; Tezuka, Y. *Macromolecules* **2001**, *34*, 6229−6234.

MA049001S