A Cyclic Macromonomer Designed for a Novel Polymer Network Architecture Having Both Covalent and Physical Linkages

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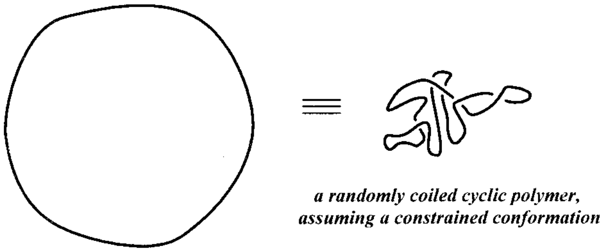
ABSTRACT: A methacrylate-functionalized, cyclic poly(tetrahydrofuran), poly(THF) (**1m**), has been synthesized and copolymerized through a free-radical mechanism involving methyl methacrylate (MMA) and using 2,2′-azobisisobutyronitrile as the initiator in benzene at 65 °C. A copolymer product with cyclic poly(THF) branches was produced initially, with gelation taking place at a later stage of the reaction. In contrast, no gelation was observed either in the quantitative-conversion copolymerization of a related methacrylate-functionalized, open-chain poly(THF) with MMA or in the quantitative homopolymerization of MMA in the presence of a methacrylate-free, cyclic poly(THF). These results demonstrate that the propagating polymer segment threaded the large but constrained cyclic polymer branches covalently attached to the polymer backbone, to produce a novel polymer network architecture having both covalent and physical linkages.

Introduction

Cyclic polymer molecules are of growing interest not only because of their unique physical properties,[1,2] but also because of their potential to form mechanically (noncovalently) linked structures based on their loop topology.[1,3] However, the threading of larger-size, flexible cyclic polymers has scarcely been reported,[4,5] despite its relevance to interpenetrating polymer networks (IPNs).[6] Chain threading through a large cyclic polymer unit is likely to be circumvented, as the randomly coiled cyclic polymer molecules generally assume a constrained structure (Scheme 1). This contrasts with a variety of recently developed noncovalent linkages involving macrocyclic compounds with up to around 100 atoms in the ring. Those include large-size crown ethers,[7−12] bipyridinium-based cyclophanes,[13−16] cyclodextrins,[17−22] and macrocyclic amides,[23−25] and their conformations are generally stiff and extended. The subsequent syntheses of catenanes and rotaxanes[26] involve a variety of noncovalent interactions, such as hydrogen bonding, $\pi-\pi$ stacking, metal-coordinating, and van der Waals interactions to promote chain threading.

Chain threading by propagating polymer segments through macrocyclic compounds has been limited to those with up to around 30 atoms in the ring. Thus, Gibson et al.[27−29] obtained gel products in polycondensation reactions with a macrocyclic diol (a 32-membered bifunctional crown ether) and with a macrocyclic dicarboxylic acid. The threading reportedly took place to produce network polyrotaxanes with polyamide,[27] polyester,[28] or polyurethane[29] backbones. They also obtained branched polyrotaxanes through the complexation of a 32-membered crown ether component attached to one polymer backbone with a dicationic bipyridinium component attached to another polymer backbone.[30] In these cases, a hydrogen-bond interaction and a dipolar−dipolar interaction on the large crown ether moiety provided attractive driving forces for the chain threading.[31]

Scheme 1



a randomly coiled cyclic polymer, assuming a constrained conformation

Also, Zilkha et al.[32−34] recently reported noncovalent cross-linking during vinyl polymerization. They employed 29−32-membered crown ether derivatives having one polymerizable double bond for a bulk radical copolymerization with styrene or methyl methacrylate (MMA). Sufficient chain threading reportedly took place to produce a gel product when the charged amount of vinyl comonomer remained to no more than 40 equiv relative to the macrocyclic monomer. Chain threading was significantly suppressed when the concentration of the macrocyclic monomer was further decreased.

Here, we report efficient chain threading through a macrocycle with as many as 280 members attached to a backbone polymer segment (Scheme 2, bottom). We used a well-defined cyclic poly(tetrahydrofuran), poly(THF), having a methacrylate group (**1m**), namely, a cyclic macromonomer (Schemes 3 and 4). In contrast, no chain-threading products were detected in the quantitative-conversion homopolymerization of MMA in the presence of a methacrylate-free, cyclic poly(THF) (**2**) (Scheme 4).

Results and Discussion

1. Synthesis of Cyclic Poly(THF) Macromonomer. A hydroxy-functionalized cyclic poly(THF) (**1h**) was prepared from an ionically linked precursor that we recently developed,[35,36] as shown in Scheme 4.

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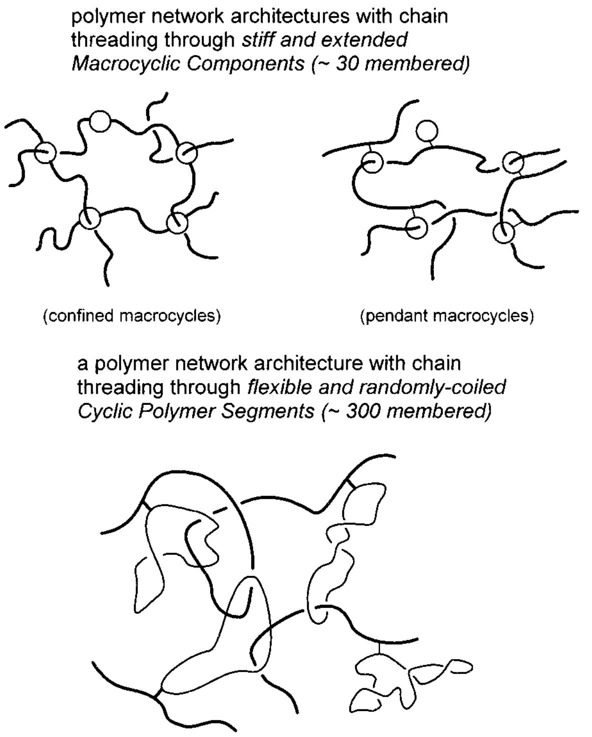
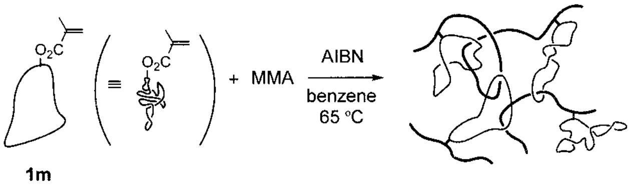
Scheme 2



Scheme 3



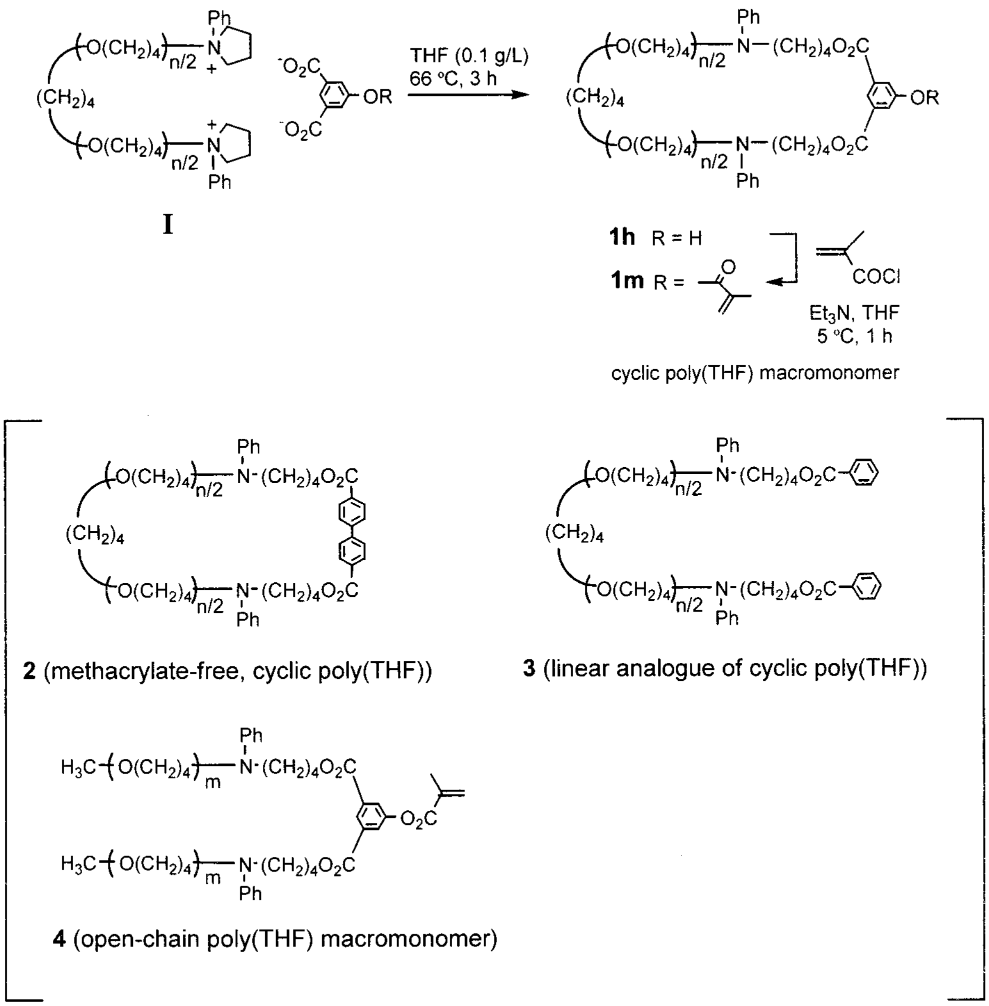
Specifically, a bifunctional poly(THF) having *N*-phenylpyrrolidinium salt end groups and carrying a 5-hydroxyisophthalate counteranion (**I**) was heated under dilution in THF (0.1 g/L) at 66 °C for 3 h to give **1h**. The complete ring-opening reaction of the pyrrolidinium salt end group by a nucleophilic attack of the carboxylate counteranion was evidenced by ^{1}H NMR and IR spectroscopic analyses of the product. The subsequent esterification of **1h** with methacryloyl chloride in the presence of triethylamine produced the cyclic macromonomer **1m** in quantitative yield. As shown in Figure 1 (bottom), size-exclusion chromatography (SEC) indicated that **1m** has a narrow size distribution (PDI = 1.12) and a notably smaller hydrodynamic volume than its linear analogue **3** (Figure 1, top), obtained from the corresponding polymer precursor with benzoate counteranions (Scheme 4). The hydrodynamic volume ratio of **1m** to **3**, $\langle G \rangle = M_p(\mathbf{1m})/M_p(\mathbf{3})$, estimated from the apparent peak molecular weights of **1m** and **3**, was 0.73, which agrees well with values previously reported.[36-41] Moreover, the responses at 6.38, 5.81, and 2.08 ppm in the ^{1}H NMR spectrum (Figure 2, bottom) can be assigned to the methacrylate group, and the signal due to the hydroxy proton at 7.70 ppm in the spectrum of **1h** (Figure 2, top) disappeared completely. By comparing the signal intensities of the ester methylene protons (***d***) and ether methylene protons in the poly(THF) segment at 4.37 ppm and 3.26−3.50 ppm, respectively, the degree of polymerization was estimated to be 70, corresponding to a 280-membered ring (M_n = 5.2 × 10^3 g/mol).

2. Construction of a Polymer Network Architecture Having Covalent and Physical Linkages. A subsequent free-radical copolymerization of **1m** with 150 equiv of MMA was carried out using 2,2′-azobisisobutyronitrile (AIBN) as a radical initiator at 65 °C in benzene. First, the copolymerization was interrupted after 1 h to limit the conversion of MMA (17%). SEC showed a two-peak profile for the recovered mixture (Figure 3, middle), with one peak corresponding to the copolymerization product and another to unreacted **1m** (Figure 3, top). The copolymer fraction (M_w = 5.5 × 10^4 g/mol, M_n = 3.1 × 10^4 g/mol, PDI = 1.80) was isolated by precipitation of the mixture in ice-cooled methanol. SEC of the isolated product showed both ultraviolet (UV, broken line) and refractive index (RI, solid line) responses, with consistent peak shapes, as seen in Figure 3 (bottom). This indicates that the graft component originating from **1m** having a phenyl group distributes statistically along the poly(MMA)-based copolymer backbone. The ^{1}H NMR spectrum (Figure 4) of the product also indicated the presence of the graft component by the poly(THF) resonances in the copolymer, while the methacrylate group signals completely disappeared. On the other hand, no side reactions such as decomposition of the cyclic structure of **1m** were noticeable. The relative molar ratio of the graft units of **1m** in the copolymer was estimated to be 1/164 on the basis of a comparison of the signal intensity of the poly(THF) segment (3.26−3.50 ppm) with that of the poly(MMA) segment (3.50−3.70 ppm). This value is very close to the feed ratio of **1m** to MMA (1/150), in accord with the statistical copolymerization.

Subsequently, a mixture of **1m** and MMA (3.2 × 10^2 equiv) was copolymerized to complete conversion for 5 h in benzene in the presence of AIBN. Most of the recovered product (0.26 g) became insoluble but swelled in benzene, while a small portion (0.03 g) remained soluble in benzene. The gel product also swelled in THF, a good solvent for both poly(MMA) and poly(THF), with a swelling degree of 975%. The latter was confirmed to be a copolymer containing both poly(MMA) and poly(THF) segments (M_w = 23 × 10^4 g/mol, M_n = 8.4 × 10^4 g/mol, PDI = 2.83) by IR and ^{1}H NMR analyses in reference to the soluble copolymer product obtained at lower conversion of MMA. In contrast, no chain-threading products, i.e., gel products or soluble polyrotaxane-type copolymers, were observed in the quantitative-conversion homopolymerization of MMA in the presence of the methacrylate-free, cyclic poly(THF) **2**.

Moreover, no gelation took place in the quantitative-conversion copolymerization of MMA with the open-chain polymer precursor **4** (Scheme 4, M_n = 4.0 × 10^3 g/mol), which was obtained from a monofunctional poly(THF) having a pyrrolidinium salt end group. The recovered product (M_w = 42 × 10^4 g/mol, M_n = 12 × 10^4 g/mol, PDI = 3.33) remained soluble in benzene. The IR and ^{1}H NMR (Figure 5) analyses of the product showed no sign of side reactions responsible for covalent cross-linking by chain-transfer reactions during the copolymerization process. These results indicate that the gelation in the copolymerization of MMA with the cyclic macromonomer **1m** took place through physical cross-linking, i.e., threading by the propagating chain through the pendant cyclic branches attached to the polymer backbone (Scheme 3). The increasing miscibility of the poly(THF) loop incorporated into the propagating chain

Scheme 4



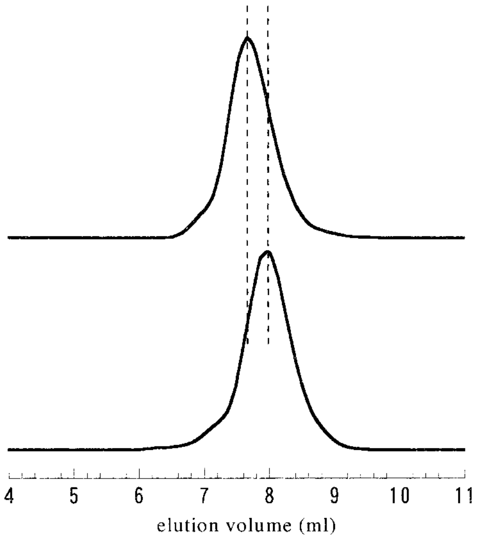


Figure 1. SEC traces (RI) of the methacrylate-functionalized, cyclic poly(THF) **1m** (bottom) and its linear analogue **3**, prepared from the same polymer precursor (column, TSK G3000HXL; eluent, THF, 1 mL/min).

with the poly(MMA) segment presumably assists the chain-threading process.

To conclude, chain threading through large polymer loops can be facilitated by their covalent attachment to the polymer backbone. This discovery will open a convenient and practical process for novel network polymers having both covalent and noncovalent cross-linking structures.

Experimental Section

Reagents. Mono- and bifunctional telechelic poly(THF)s having *N*-phenylpyrrolidinium salt groups carrying trifluoromethanesulfonate (triflate) counteranions were prepared by the method detailed before.[35,42] The methacrylate-free, cyclic poly(THF) **2** ($M_n = 4.0 \times 10^3$ g/mol, PDI = 1.11) and the linear poly(THF) **3** ($M_n = 5.2 \times 10^3$ g/mol, PDI = 1.12) were synthesized by the methods detailed before.[35] Disodium 5-hydroxyisophthalate was prepared quantitatively from the corresponding acid (Tokyo Chemical Industry Co., Ltd., >97%) with two equimolar quantities of sodium hydroxide (Koso Chemical Co., Ltd., 93%) in water. THF (Wako Pure Chemical Industries, Ltd., no stabilizer, >99.5%) was dried over sodium benzophenone ketyl and distilled just before use. Methyl methacrylate (Tokyo Chemical Industry Co., Ltd., stabilized with HQ, >99.8%), benzene (Wako Pure Chemical Industries, Ltd., >99.5%), and triethylamine (Wako Pure Chemical Industries, Ltd., >99%) were distilled over calcium hydride. Methacryloyl chloride (Wako Pure Chemical Industries, Ltd., >97%) was distilled under nitrogen before use. 2,2′-Azobisisobutyronitrile (AIBN, Tokyo Chemical Industry Co., Ltd., 98%) was purified by recrystallization from ethanol. Unless otherwise noted, materials were obtained from commercial sources.

Synthesis of a Hydroxy-Functionalized, Cyclic Poly(THF) (1h).[36] A THF solution (5.0 mL) of a telechelic poly(THF) (MW = 5.2×10^3 g/mol, 0.50 g, 9.6×10^{-2} mmol) having *N*-phenylpyrrolidinium salt groups carrying triflate counteranions was added to an ice-cooled (<5 °C) aqueous solution

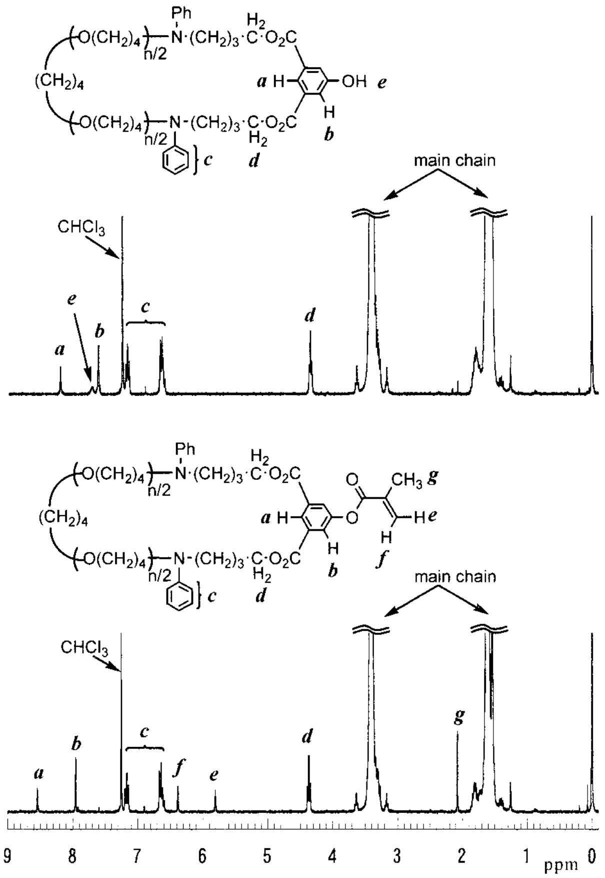


Figure 2. ^{1}H NMR spectra (300-MHz) of the methacrylate-functionalized, cyclic poly(THF) **1m** (bottom) and of the hydroxy-functionalized, cyclic poly(THF) **1h** (top) ($CDCl_3$, 40 °C).

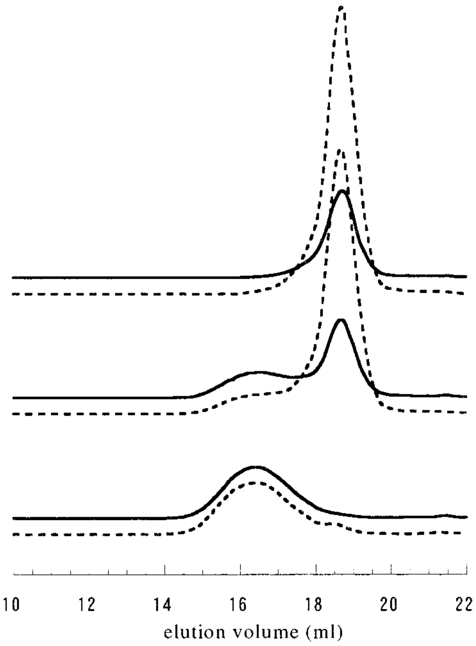


Figure 3. SEC traces of the methacrylate-functionalized, cyclic poly(THF) **1m** (top) and the copolymerization product of **1m** with MMA initiated by AIBN at 65 °C (17% conversion) before (middle) and after (bottom) purification by precipitation in ice-cooled methanol (column, 2 × TSK GMHXL; eluent, THF, 1 mL/min; solid line, refractive index trace; broken line, ultraviolet trace).

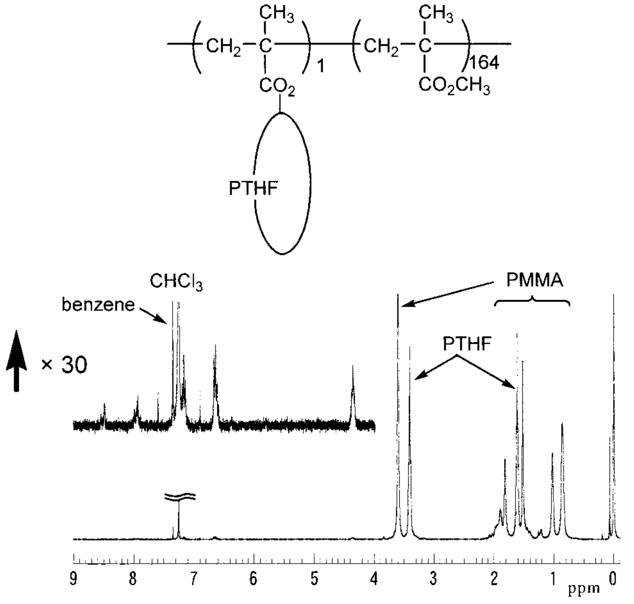


Figure 4. ^{1}H NMR spectrum (300-MHz, $CDCl_3$, 40 °C) of the purified copolymerization product of the methacrylate-functionalized, cyclic poly(THF) **1m** with MMA initiated by AIBN at 65 °C (17% conversion).

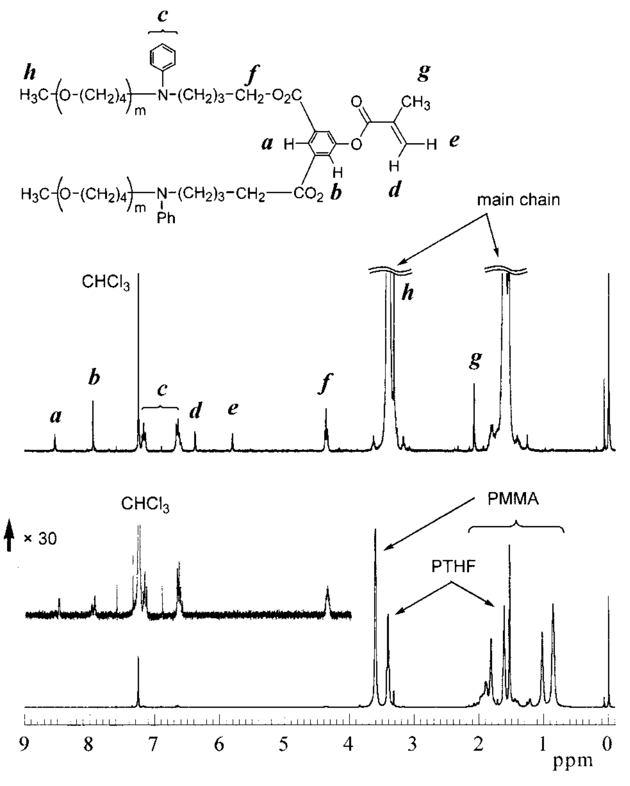


Figure 5. ^{1}H NMR spectrum (300-MHz, $CDCl_3$, 40 °C) of the open-chain poly(THF) macromonomer **4** (top) and the purified copolymerization product of **4** with MMA initiated by AIBN at 65 °C (quantitative conversion) (bottom).

(200 mL) containing an excess amount of disodium 5-hydroxyisophthalate (10 equiv) under vigorous stirring. After 1 h, the precipitated ion-exchange product was collected by filtration and dried in vacuo. This precipitation treatment was repeated three times to complete the reaction. The ion-exchange product **I** was then dissolved in THF (0.1 g/L) and heated at 66 °C for 3 h. The cyclic poly(THF) **1h** was recovered quantitatively by evaporation of the solvent and was further purified by preparative thin-layer chromatography (SiO_2, hexane/acetone = 2/1) (73% isolated yield). ^{1}H NMR: δ 1.50–1.75 (m, CH_2CH_2O), 3.24–3.55 (m, CH_2CH_2O), 4.35 (t, J = 5.7 Hz, 4H), 6.58–6.68 (m, 6H), 7.14–7.20 (m, 4H), 7.62 (br, 2H), 7.72 (br, 1H), 8.21 (br, 1H). IR: 1723 cm^{-1} (ester carbonyl).

Synthesis of a Methacrylate-Functionalized, Cyclic Poly(THF) (1m). Methacryloyl chloride (1.1×10^{-2} g, 5 equiv) was added dropwise to a THF solution (1 mL) containing 9.4×10^{-2} g (1.8×10^{-2} mmol) of **1h** and triethylamine (3.2×10^{-2} g, 15 equiv) at 5 °C. After 1 h, the reaction mixture was added dropwise to water (<5 °C), and the precipitated product **1m** was isolated quantitatively by filtration and dried in vacuo. ^{1}H NMR: δ 1.50−1.75 (m, CH_2CH$_2$O), 2.08 (br, 3H), 3.24−3.55 (m, CH$_2$CH_2O), 4.37 (t, $J = 6.3$ Hz, 4H), 5.81 (dq, $J = 1.5$, 1.5 Hz, 1H), 6.38 (br, 1H), 6.58−6.68 (m, 6H), 7.14−7.20 (m, 4H), 7.96 (d, $J = 1.5$ Hz, 2H), 8.54 (t, $J = 1.5$ Hz, 1H). IR: 1723 cm^{-1} (ester carbonyl).

Synthesis of an Open-Chain, Poly(THF) Macromonomer (4). A THF solution (5.0 mL) of a monofunctional telechelic poly(THF)[42] ($M_n = 2.0 \times 10^3$ g/mol, PDI = 1.11, 0.50 g, 2.5×10^{-1} mmol) having a *N*-phenylpyrrolidinium salt group carrying triflate counteranions was added to an ice-cooled (<5 °C) aqueous solution (200 mL) containing an excess amount of disodium 5-hydroxyisophthalate (10 equiv) under vigorous stirring. After 1 h, the precipitated ion-exchange product was collected by filtration and dried in vacuo. This precipitation treatment was repeated three times to complete the reaction. The ion-exchange product was then dissolved in THF (0.1 g/L) and heated at 66 °C for 3 h. A center-functionalized poly(THF) having a hydroxy group was recovered quantitatively by evaporation of the solvent. Finally, methacryloyl chloride (3.3×10^{-2} g, 5 equiv) was added dropwise to a THF solution (5 mL) containing 2.3×10^{-1} g (5.8×10^{-2} mmol) of the center-functionalized poly(THF) having a hydroxy group and triethylamine (9.1×10^{-2} g, 15 equiv) at 5 °C. After 1 h, the reaction mixture was added dropwise to water (<5 °C), and the precipitated product, i.e., an open-chain poly(THF) macromonomer, was isolated quantitatively by filtration and dried in vacuo. ^{1}H NMR: δ 1.50−1.75 (m, CH_2CH$_2$O), 2.08 (dd, $J = 1.5$, 0.9 Hz, 3H), 3.24−3.55 (m, CH$_2$CH_2O), 3.32 (s, 6H) 4.37 (t, $J = 6.2$ Hz, 4H), 5.81 (dq, $J = 1.5$, 1.5 Hz, 1H), 6.38 (br, 1H), 6.58−6.68 (m, 6H), 7.14−7.20 (m, 4H), 7.92 (d, $J = 1.5$ Hz, 2H), 8.54 (t, $J = 1.5$ Hz, 1H). IR: 1723 cm^{-1} (ester carbonyl).

Copolymerization between 1m and MMA to Low Monomer Conversion. A benzene (0.64 mL) solution of **1m** (3.2×10^{-2} g, 6.4×10^{-3} mmol), MMA (9.7×10^{-2} g, 0.97 mmol), and AIBN (1.2×10^{-2} g, 7.3×10^{-2} mmol) was degassed by three freeze−pump−thaw cycles on a vacuum line and then heated at 65 °C. After 1 h, the solvent and unreacted MMA were removed under reduced pressure to give a crude reaction product mixture (4.7×10^{-2} g). From 4.0×10^{-2} g of the recovered product mixture, the copolymer fraction (1.8×10^{-2} g) was separated from unreacted **1m** (2.2×10^{-2} g) by precipitation in cold methanol (0 °C). ^{1}H NMR: See Figure 4. IR: 1731 (metacrylate ester carbonyl), 1120 (C−O−C) cm^{-1}.

Copolymerization between 1m and MMA to Complete Monomer Conversion. A benzene (0.24 mL) solution of **1m** (3.9×10^{-2} g, 7.8×10^{-3} mmol), MMA (0.25 g, 2.5 mmol), and AIBN (5.0×10^{-3} g, 3.0×10^{-2} mmol) was degassed by three freeze−pump−thaw cycles on a vacuum line and then heated at 65 °C. After 5 h, the solvent was removed under reduced pressure. The product (0.29 g) was extracted with benzene, and both the benzene-insoluble fraction (0.26 g) and the benzene-soluble fraction (0.03 g) were recovered.

Copolymerization between 4 and MMA to Complete Monomer Conversion. A benzene (0.24 mL) solution of **4** (3.9×10^{-2} g, 7.8×10^{-3} mmol), MMA (0.25 g, 2.5 mmol), and AIBN (5.0×10^{-3} g, 3.0×10^{-2} mmol) was degassed by three freeze−pump−thaw cycles on a vacuum line and then heated at 65 °C. After 5 h, the solvent was removed under reduced pressure to give a crude reaction product mixture (0.25 g). From 0.25 g of the recovered product mixture, the copolymer fraction (0.23 g) was isolated by precipitation treatment in cold methanol (0 °C). ^{1}H NMR: See Figure 5 (bottom). IR: 1731 (metacrylate ester carbonyl), 1120 (C−O−C) cm^{-1}.

Measurements. SEC measurements were performed using a Tosoh model CCPS instrument equipped with a refractive index detector (model RI 8020) and a UV detector (model UV 8020) at 254 nm. Either a single TSK G3000HXL column (300 mm × 7.8 mm i.d., 5-μm bead size) or two TSK GMHXL columns (300 mm × 7.8 mm i.d., 5-μm bead size) were employed with THF as the eluent at a flow rate of 1.0 mL/min at 40 °C. The molecular weights of the copolymer products were estimated by SEC relative to polystyrene. IR spectra were recorded on a JASCO FT/IR-410 infrared spectrometer by casting the sample from a chloroform solution onto a NaCl plate. ^{1}H NMR spectra were taken on a JEOL JNM-AL300 apparatus in CDCl$_3$ at 40 °C. The proton chemical shifts (ppm) were referenced to tetramethylsilane. The degree of swelling (by weight) was determined by comparing the weight of the dry product with that of the swollen product after immersion in THF at ambient temperature. The swelling values obtained by three experiments were averaged.

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Supporting Information Available: SEC results and ^{1}H NMR spectra of the copolymerization product of the methacrylate-free, cyclic poly(THF) **2** with MMA, as well as SEC traces of the copolymerization product of the open-chain poly(THF) macromonomer **4** with MMA. This material is available free of charge via the Internet at http://pubs.acs.org.

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