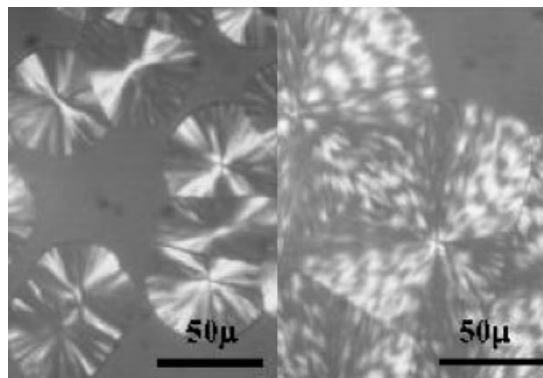


A Defect-Free Ring Polymer: Size-Controlled Cyclic Poly(tetrahydrofuran) Consisting Exclusively of the Monomer Unit^a

Dedicated to Professor Eric J. Goethals on the occasion of his 70th birthday

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A series of size-controlled, cyclic poly(tetrahydrofuran)s ($\overline{M}_{n,NMR}$ of 4 400–8 600) that consist exclusively of the monomer, i.e., oxytetramethylene, unit (I) have been prepared in high yield through the metathesis polymer cyclization of a telechelic precursor having allyl groups, **1**, in the presence of a Grubbs catalyst, and the subsequent hydrogenation of the linking, i.e., 2-butenoxy, unit in the presence of an Adams' catalyst (PtO₂). A remarkable topology effect has subsequently been observed upon the isothermal crystallization of these two model polymers, showing distinctive spherulite growth rates and spherulite morphologies in comparison with the relevant linear poly(tetrahydrofuran) counterpart that has ethoxy end groups (II).



Introduction

Ring polymers are distinctive from their linear and branched counterparts by the absence of chain-ends (terminus) and branch points (junctions), and their unique properties often rely on this particular topology.^[1–9] Moreover, size-controlled ring polymers that consist

exclusively of the monomer unit, in which not only chemically but also geometrically irregular, chain-end or branched structures are completely eliminated, are considered to be *defect-free*, and are valuable for the study of the fundamental physical chemistry and physics of randomly coiled long-chain polymers both in solution and in bulk in a more exacting manner than had been possible previously.^[10]

The practical synthesis of ring polymers of a defined, *defect-free* structure, however, has been an ongoing challenge either through a ring-enlarging chain polymerization,^[11–14] through a back-biting reaction in polycondensation,^[15] or through an end-linking reaction of telechelic precursors.^[16] Thus in the ring-enlarging process, an initiator or a catalyst fragment within the growing cyclic polymer intermediate is inherently included as an

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^a Supporting information for this article is available at the bottom of the article's abstract page, which can be accessed from the journal's homepage at <http://www.mrc-journal.de>, or from the author.

irregular structure, and the ring topology of the polymer product scarcely remains intact upon removing the initiator or catalyst fragment.^[11a,11b,12a]

The formation of ring polymers by a back-biting reaction has often been observed in polycondensation processes.^[15] However, size-control in the polymer products has rarely been achieved because the back-biting reaction tends to occur randomly.^[15d] The subsequent separation of ring polymer products from linear counterparts is, moreover, a cumbersome task, especially as both products possess a broad chain length distribution.^[17]

Recently, a new ring-opening metathesis polymerization of cyclooctene with a Ru catalyst that contains a specifically designed cyclic ligand has been developed.^[13,14] A ring poly(cyclooctene) was thus produced by the catalyst promoting not only the propagation but also the end-biting chain transfer reaction. A ring polyethylene comprising exclusively of the monomer unit was subsequently obtained, though its chain-length distribution was not strictly controlled.^[18]

It has been documented that, to avoid an intermolecular chain extension reaction in the polymer cyclization process, the end-linking reaction of telechelic precursors should be conducted under dilution.^[16,19] In general, the chemical structure of the resulting linking unit is different from the monomer unit. We have found, on the contrary, that a ring poly(tetrahydrofuran) (poly(THF)) that has a linking structure of a 2-butenoxy group, **2**, could be formed through the elimination of ethylene by means of the intramolecular metathesis condensation of a uniform-size, telechelic poly(THF), poly(oxytetramethylene), that has allyl end groups, **1**.^[19] Remarkably, the subsequent hydrogenation reaction is capable of transforming the linking unit into an oxytetramethylene group, identical to the monomer unit (Scheme 1). Thus in the present study, we have prepared a series of *defect-free* ring poly(THF)s that have different molecular weights, and their relevant linear counterparts with inert end groups, whose structure corresponds to one formed through the bond-breaking at the middle position of the butane (tetramethylene) unit of the ring polymer and the subsequent addition of two hydrogen atoms (Scheme 1). We have also

examined the isothermal crystallization of these model polymers, since a distinctive polymer topology effect is anticipated in the dynamics of the ring polymer as opposed to the linear counterpart as a result of the absence of chain ends as well as the entropic restriction of chain conformations.^[20,21]

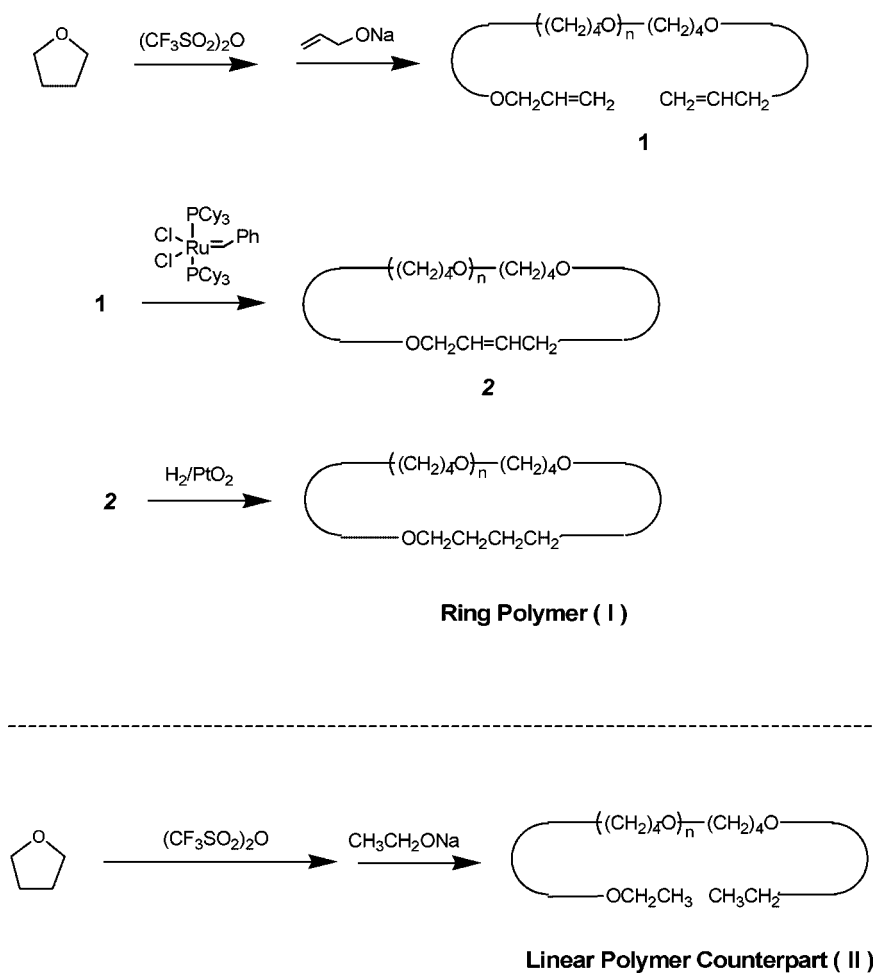
Experimental Part

Detailed information about materials, synthetic procedures, and characterization methods can be found in the supporting information.

Results and Discussion

Synthesis of Cyclic Poly(THF) that Consists Exclusively of the Monomer Unit

A series of ring poly(THF)s that have a 2-butenoxy linking group, **2**, was first synthesized through a metathesis polymer cyclization with telechelic precursors having allyl



■ Scheme 1. Synthesis of a defect-free ring poly(THF).

groups, **1**, $\overline{M}_{n,NMR}$ of 4 400–8 600 with a polydispersity index (PDI) of 1.08–1.17.^[19] The subsequent intramolecular condensation was performed under dilution at the polymer concentration of 0.2 g · L⁻¹ ($\approx 10^{-5}$ mol · L⁻¹) in dichloromethane in the presence of a Grubbs catalyst, charged in the comparable molar quantity to allyl end groups.^[19,22] The cyclized products, **2**, were recovered in high yields (>85%), and fully characterized by means of ¹H NMR spectroscopy and matrix-assisted laser desorption-ionization time-of-flight mass spectrometry (MALDI-TOF MS). (See Supporting Information for experimental procedures, and ¹H NMR (S-Figure 1) and MALDI-TOF MASS (S-Figure 2) spectra, respectively.)

The subsequent hydrogenation reaction was conducted in THF under a H₂ atmosphere in the presence of either a Pd/C catalyst, a Wilkinson catalyst (RhCl(PPh)₃), or an Adams' catalyst (PtO₂). While noticeable chain-degradation was accompanied during the reaction with Pd/C, the size-controlled products were recovered after the hydrogenation by using either the Wilkinson or the Adams' catalyst. In particular, the latter could be removed conveniently by a simple filtration with a celite-packed column to give almost colorless products in high yields (>80%). (See Supporting Information for experimental procedures.)

A relevant linear poly(THF) counterpart having ethoxy end groups (**II**, $\overline{M}_{n,NMR}$ of 4 900–5 800, PDI = 1.07–1.14) was also prepared by a simple end-capping reaction of a bifunctional living poly(THF) with sodium ethoxide. The linear counterpart, **II**, whose structure corresponds to one formed through the bond-breaking at the middle position of a tetramethylene unit of the above-obtained ring poly(THF), **I**, and the subsequent addition of two hydrogen atoms, therefore, is regarded as a unique reference sample for the study of the polymer topology effects.

The ring and linear products, **I** and **II**, were fully characterized by ¹H NMR, MALDI-TOF MS, and size exclusion chromatography (SEC) techniques. SEC traces of the linear telechelic poly(THF) precursor, **1**, the metathesis polymer cyclization product, **2**, as well as the crude and the purified hydrogenated products, **I**, are compared in Figure 1. The metathesis product, **2**, showed a reduced hydrodynamic volume compared to that of the starting linear telechelic precursor, **1**, in agreement with the occurrence of an intramolecular polymer cyclization^[19] (Figure 1A and B). The metathesis product, **2**, obtained under dilution at an applied polymer concentration of 0.2 g · L⁻¹, showed a nearly symmetrical peak profile but with a noticeable shoulder at the higher molecular weight region, ascribed to the products of the intermolecular chain-extension reaction. This minor fraction remained to be observed even after the hydrogenation reaction (Figure 1C), but could be removed by preparative SEC fractionation to give a purified ring polymer (Figure 1D).

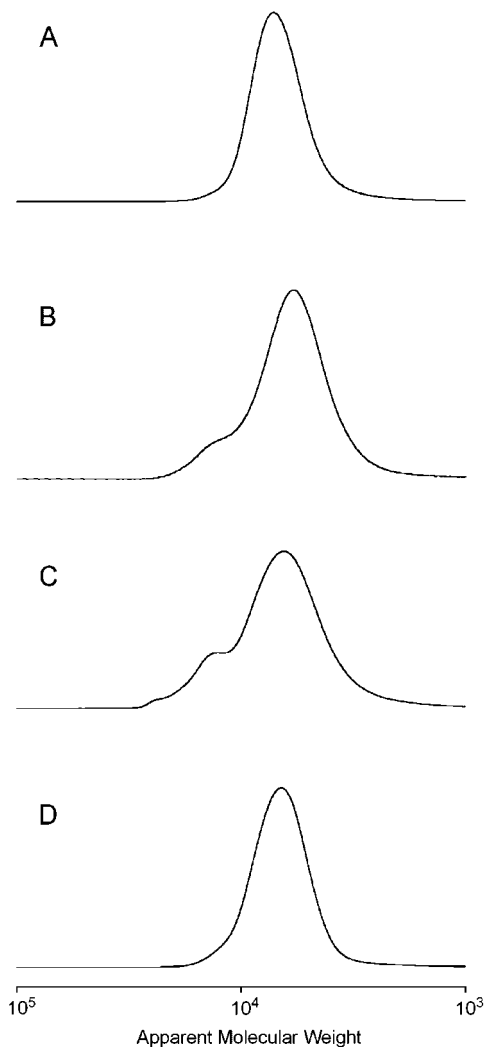


Figure 1. SEC traces of a linear poly(THF) precursor that has allyl end groups (A), a ring poly(THF) that has a 2-butenoxy linking group (B), a hydrogenated ring poly(THF), **I**, before (C) and after (D) the purification by SEC fractionation. (TSKG3000HXL, eluent: THF 1.0 mL · min⁻¹.)

The obtained ring and linear poly(THF)s **I** and **II**, were compared by means of ¹H NMR and MALDI-TOF MS techniques (S-Figure 3 in Supporting Information and Figure 2, respectively). The ¹H NMR of the ring polymer **I** (S-Figure 3, top) showed no signals except for those arising from the main-chain methylene units, while the spectrum of the linear counterpart, **II** (S-Figure 3, bottom) showed a triplet signal at 1.20 ppm due to methyl protons of ethoxy end groups.

MALDI-TOF MS analysis (Figure 2) showed a uniform series of peaks that correspond to poly(THF) (peak interval of 72 mass units), and each peak corresponds exactly to the molar mass summing up solely the monomer units for **I**,

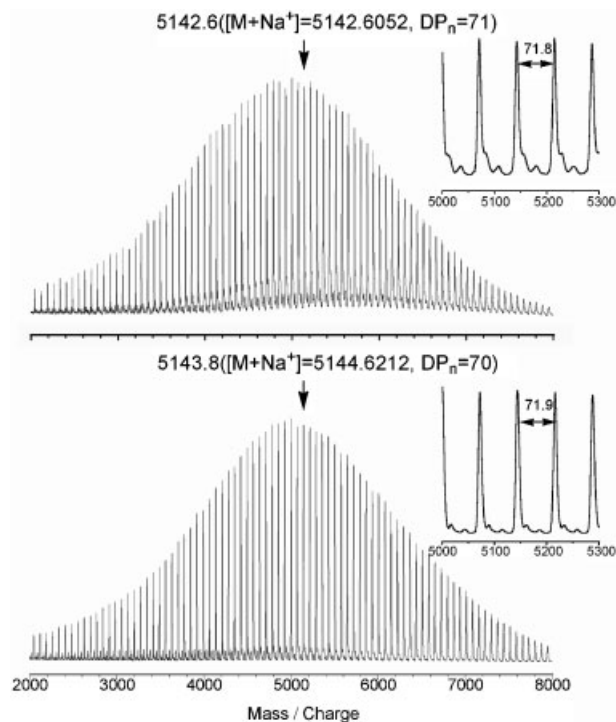


Figure 2. MALDI-TOF mass spectra of a *defect-free* ring poly(THF), **I** (top) and a linear poly(THF) counterpart that has ethoxy end groups, **II** (bottom). (Linear mode, matrix: dithranol with sodium trifluoroacetate, DP_n denotes the number of monomer units in the product.)

and additional ethoxy end groups for **II**, respectively. As an example, the peak (assumed to be the adduct with Na^+) at 5142.6 corresponds to the ring product, **I**, with a degree of polymerization (DP_n) of 71 [$(C_4H_8O) \times 70 + C_4H_8O$, plus $Na^+ = 5142.605$]. On the other hand, the linear analogue, **II**, showed a peak (assumed to be the adduct with Na^+) at 5143.8, which corresponded to a DP_n of 70 [$(C_4H_8O) \times 70 + C_4H_{10}O$, plus $Na^+ = 5144.621$]. The molecular weight of the linear analogue that has ethoxy end groups, **II**, should differ by two mass units from the ring poly(THF), **I**. This was indeed confirmed by comparing the two MALDI-TOF MS spectra shown in Figure 2.

Topology Effect Revealed in the Crystallization of Ring and Linear Poly(THF)s

We have subsequently examined the isothermal crystallization using the obtained *defect-free* ring polymers in comparison with the relevant linear polymer counterparts having a nearly identical molecular weight, to observe the distinctive polymer topology effect due to the absence of chain ends as well as the entropic restriction of chain conformations.^[20,21]

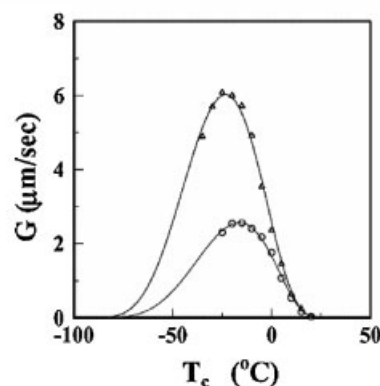
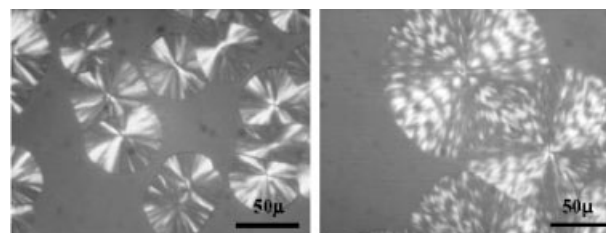


Figure 3. Optical micrographs of spherulites for linear (left) and ring (right) poly(THF)s crystallized at 10 °C from the melts (top), and crystallization temperature (T_c) dependence of spherulite growth rates (G) for linear (Δ) and ring (\circ) poly(THF)s (bottom). (Samples: a ring poly(THF) with an $\bar{M}_{n,NMR}$ of 5100 with PDI = 1.14, a linear poly(THF) of $\bar{M}_{n,NMR}$ of 4900 with PDI = 1.14.)

Figure 3 (top) shows typical polarized optical micrographs of spherulites crystallized at 10 °C for linear (left) and ring (right) poly(THF)s. The spherulite of the former shows a negative birefringence, as normally observed in polymer spherulites. On the contrary, the latter shows a negative spherulite with a banded structure with a concentric ring pitch of about 7 μm . The banded spherulites indicate rotation of the optical indicatrix along a radial direction. This rotation is caused by the lamellae twisting, which is associated with cumulative reorientation of lamellae at successive screw dislocation^[23,24] or different surface stresses on opposite fold surfaces of individual lamellae.^[25,26] The surface stress tends to be developed by the fold structures, such as uneven fold volume, and the morphological difference observed between the linear and the ring poly(THF)s might be caused by the distinctive chain folding structures. The ring polymer can build up the sharp chain folding but the linear polymer might construct additional chain-folding structures, such as sharp and loose loops. The sharp (tight) chain folding can produce surface stresses on the lamella surface.

The spherulite growth rates of the linear and the ring poly(THF)s at various crystallization temperatures are shown in Figure 3 (bottom). In both the ring and linear

poly(THF)s, the bell-shaped curves were observed with the maximum growth rates (G_{\max}) at around $-20\text{ }^{\circ}\text{C}$. Solid lines in the figure are the results for the best fit of the experimental data based on Hoffman–Laouritzen theory.^[27] G_{\max} is a characteristic intrinsic value in a polymer crystallization mechanism.^[28,29] For example, the molecular weight dependence of G_{\max} is scaled and expressed by power laws as $G_{\max} \propto M^{-0.5}$. The maximum growth rate of the ring poly(THF) reduces significantly against the linear counterpart (from 6.0 to 2.6 $\mu\text{m} \cdot \text{s}^{-1}$). The reduction of the growth rate in the ring polymer samples might be ascribed either to the conformational entropy in the molten state, to the adsorption mechanism on the crystal growth front in the secondary nucleation process, or to the chain folding surface energy. In fact, the melting temperature of the ring poly(THF) ($34.5\text{ }^{\circ}\text{C}$) is lower than that of the linear counterpart ($39.6\text{ }^{\circ}\text{C}$). The differences might be accounted for by the difference between entropic contributions, since the enthalpy can be the similar contribution to the melting temperature. Further studies on the topology effect in the spherulite morphology and crystallization mechanism are in progress.

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