

Topological Polymer Chemistry in Pursuit of Elusive Polymer Ring Constructions

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Abstract: Current challenges and future perspectives of topological polymer chemistry have been reviewed. A variety of novel cyclic and multicyclic macromolecular topologies has now been realized by intriguing synthetic protocols. In particular, the electrostatic polymer self-assembly of telechelic precursors having cyclic ammonium salt groups accompanying polyfunctional carboxylate counteranions has been exploited in dilution to produce topologically significant, non-covalent constructions of a dynamic nature. The subsequent covalent conversion through the ring-opening or through the ring-emitting reaction of cyclic ammonium salt groups by carboxylate counteranions provides cyclic and multicyclic polymer products effectively. Furthermore, the metathesis condensation process with functional cyclic polymer precursors has been demonstrated as a promising synthetic means to construct a variety of complex polymer topologies.

1. Introduction

There are frequent examples in the macroscopic world where the form of objects underlies the basis of their functions and properties.¹ On the other hand, the fabrication of extremely small objects having precisely defined structures has only recently become an attractive challenge, which is now opening the door to nanoscience and nanotechnology.² In the field of synthetic polymer chemistry, the form of macromolecules has long been restricted to a linear or a randomly branched topology. In the last decade, however, a variety of precisely controlled, branched topologies has been realized by the introduction of intriguing synthetic techniques, based on living polymerization as well as on self-assembly protocols.³ Nevertheless, the synthesis of a variety of cyclic and multicyclic polymers (Scheme 1) has still been a formidable challenge, and even the practical means for

constructing simple ring polymers has only recently become a subject of intensive research.⁴

In this review, we show recent progress in this area, with particular emphasis on a new concept of *topological polymer chemistry*⁵ to provide new insights for polymer science and polymer materials engineering.

2. New Synthetic Protocols for Ring Polymers

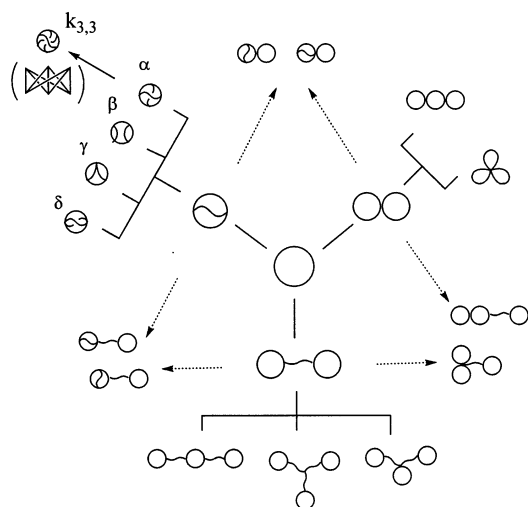
Ring polymers are distinctive from their linear and branched counterparts by the absence of chain-ends (terminus) and branch points (junctions), and their unique properties are often due to this particular topology.^{5,6} A number of new processes have been developed in recent years through either a ring-expansion polymerization,⁷ or an end-linking of telechelic precursors.⁸

2.1 Ring-expansion Polymerization

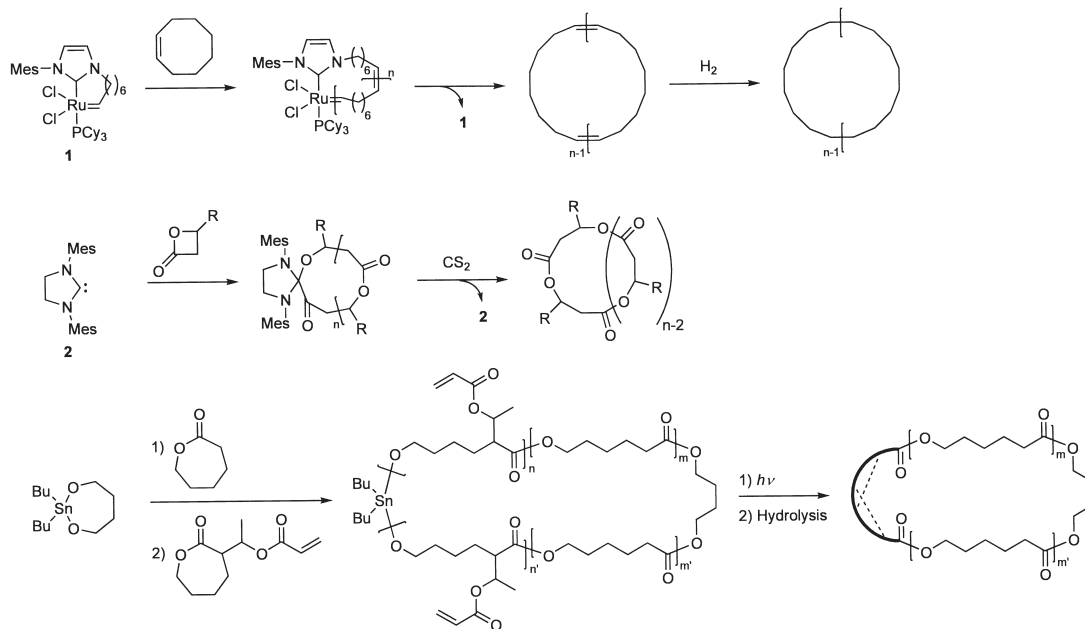
A ring-expansion polymerization proceeds through the repetitive insertion of a monomer into a deliberately designed, cyclic initiator, and this polymerization does not require the dilution condition, in contrast with the end-linking process using telechelic precursors. On the other hand, the initiator fragment remains as a structural component within the main chain segment during the polymerization. The ring topology of the product, however, is often not preserved during the subsequent chemical treatment to remove or to deactivate the initiator species.⁹ Thus, it has been a challenge to address this problem for the ring-expansion process to be employed as a practical means for ring polymer synthesis.

A novel Ru catalyst having a specifically designed cyclic ligand has been developed for a ring-opening metathesis polymerization of cyclo-alkenes like a cyclooctene (Scheme 2).^{7a-d} The catalyst promotes not only the propagation to form a ring poly(cyclooctene) but also the end-biting chain transfer reaction to regenerate the catalyst species to reinitiate the polymerization. By the subsequent hydrogenation, a ring polyethylene has been obtained, which exhibits distinct

Scheme 1. Single and multicyclic polymer topologies (ring family tree).



Scheme 2. New developments in the ring-expansion polymerization process.



tive properties in comparison with conventional linear or branched polyethylenes.^{7a} The "end-biting" chain transfer to eliminate the initiator species is a key to producing stable ring polymers. However, the chain transfer occurs concurrently during the propagation, and the chain length distribution (MWD) of the polymer products could not be controlled rigorously. By this ring-expansion process using a bulky, dendronized monomer, a ring-shaped nano-object has also been produced.^{7e}

Ring poly(sulfide)s, free of the initiator fragment and having controlled size distributions have also been reported, in which the repetitive insertion of thiirane, a three-membered cyclic sulfide monomer into the thioester unit of a cyclic initiator proceeds with the concurrent chain transfer by intermolecular ester exchange reactions.^{7f} More recently, ring polyesters with narrow size distributions have been obtained by a zwitterionic ring-opening polymerization of cyclic lactones and lactides with an *N*-heterocyclic carbene initiator (Scheme 2).^{7g-i} In this process, the "end-biting" chain transfer is assumed to take place after the rapid propagation to eliminate the initiator species.⁷ⁱ

Furthermore, ring-expansion polymerization has been combined with the end-linking reaction for the practical synthesis of ring polymers of high molar mass (Scheme 2).¹⁰ Thus, a cyclic initiator of stannous dialkoxide has been employed for the ring-opening polymerization of ϵ -caprolactone. By taking advantage of the living nature of this process, a few units of a photo-crosslinkable, acrylate-functionalized ϵ -caprolactone derivative have subsequently been introduced. Thereafter the intramolecular photo-crosslinking of acrylic groups has been conducted under dilution, and the stannous dialkoxide initiator fragment has finally been removed by hydrolysis, to produce ring polymers free of the initiator fragments.^{10a} By this process, a *twin-tail* tadpole polymer comprised of a ring and two outward branch segments, has also been prepared by the re-initiation of ring-opening polymerization of ϵ -caprolactone from a stannous dialkoxide unit before its removal.^{10a} The process has successfully been

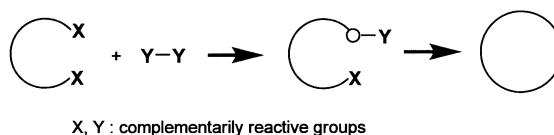
applied to the preparation of ring polymers having high molecular weights, while the precise cross-linking structures are inherently obscure. A ring-shaped nano-object, directly observable by AFM has been produced by this process through the subsequent grafting reaction onto the polymer backbone.^{10b} Furthermore, a ring polymer with pendant functional groups prepared by this method has been applied to the polymer drug carrier to study the topological effect on its pharmacokinetic behavior.^{10c}

2.2 End-linking of Telechelic Precursors

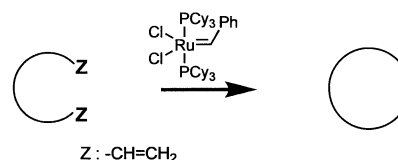
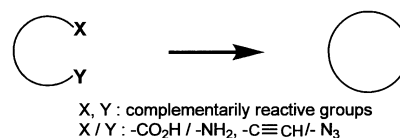
A direct end-to-end linking reaction of an α,ω -bifunctional linear polymer precursor with a bifunctional coupling reagent is thought to be a straightforward means to preparing ring polymers (Scheme 3).^{4a,b} In practice however, this *bimolecular* process has rarely been adopted as a convenient synthetic means to provide ring polymers of high purity with

Scheme 3. End-linking of telechelic polymers for ring polymer synthesis.

Bimolecular process



Unimolecular process



high yields. This is because, during this bimolecular process, the first step product, i.e., asymmetric telechelics, thus the desired precursor for the cyclization, tends to also react with the coupling reagent to form symmetric telechelics, incapable of proceeding to the cyclization. The prerequisite strict stoichiometry between a large polymeric and a small coupling compound is often hard to achieve in practice. Moreover, the high dilution to promote the intramolecular chain-extension process over a concurrent intermolecular one causes serious suppression of the reaction rate upon second-order kinetics. Thus inevitably, the cumbersome fractionation/purification treatment is needed to isolate the ring polymer product from the linear counterpart of the same chain length.¹¹ Due to these practical problems, the preparation of ring polymers by the end-linking method has been limited until recently to model polymers of significant academic interest.⁶

An alternative *unimolecular* polymer cyclization process using α,ω -heterobifunctional polymer precursors has been introduced to achieve remarkably improved efficiency (Scheme 3).^{8a-c} Thus, an α -vinyl- ω -acetal heterotelechelic polymer has been prepared by the living polymerization technique, and subjected to the end-to-end reaction under dilution in the presence of Lewis acid catalyst to give a ring polymer in higher yield.^{8a} Other hetero-telechelic polymer precursors having an amino and a carboxylic acid group at each polymer end, have been prepared through the living anionic polymerization of styrene or of *tert*-butyl acrylate by using an initiator having a protected amino group and succinic anhydride as a terminator, respectively.^{8b} The subsequent intramolecular amidation has been performed under dilution to give ring polymers in good yield. In particular, the obtained ring poly(*tert*-butyl acrylate) has further been hydrolyzed to produce a ring poly(acrylic acid), applicable to a less viscous polyelectrolyte.^{8c} More recently, a "click" process, i.e., a highly efficient alkyne-azide addition reaction, has also been applied to the ring polymer synthesis.^{8d-i} Thus, a ring poly(styrene) was synthesized effectively by the "click" chemistry with a heterotelechelic polymer precursor having an alkyne group and an azide group at each end, obtainable through the ATRP process. The "click" process has also been applied to the synthesis of a variety of ring polymers, including a ring poly(*N*-isopropyl acrylamide) to reveal a topological effect on its phase transition^{6h-j} and a ring block copolymer.^{8e}

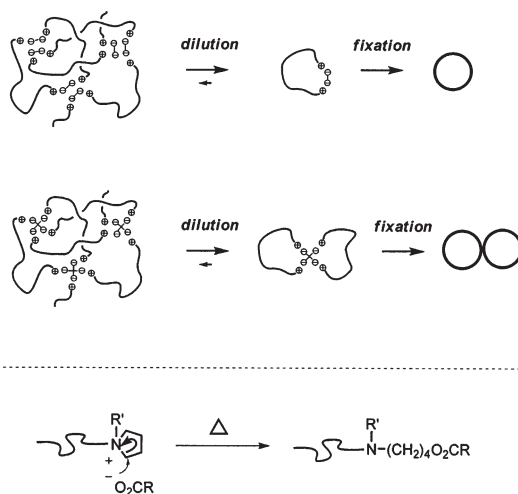
It is notable, however, that multiple synthetic steps are needed for the preparation of α,ω -heterobifunctional polymer precursors, involving protection-deprotection, prior to the cyclization step. Alternative homo-coupling, i.e., a ring-closing metathesis (RCM) process in the presence of a Grubbs catalyst has subsequently been introduced with α,ω -bifunctional polymer precursors prepared more conveniently (Scheme 3).¹² Further details are discussed later in Sec. 5.

3. Electrostatic Polymer Self-assembly and Covalent Fixation for Topological Polymer Chemistry

We have developed an *electrostatic self-assembly and covalent fixation* technique for designing non-linear polymer architectures (Scheme 4).^{5,13} Linear or star telechelic precursors, such as poly(tetrahydrofuran, THF), poly(ethylene oxide), poly(styrene), and poly(dimethylsiloxane), obtainable

through the living polymerization technique, and having moderately strained, 5-membered cyclic ammonium salt groups, carrying counteranions of appropriate nucleophilic reactivity, like carboxylates, have been employed as key polymer precursors. It is also notable that not only small (low molecular weight and water-soluble) but also large (polymeric and water-insoluble) carboxylates can be employed in this *electrostatic self-assembly and covalent fixation* process.¹⁴ By simple precipitation of a telechelic precursor having cationic end-groups into aqueous solution containing small carboxylate salts, or by coprecipitation of an equimolar mixture of cationic and anionic polymer precursors, the corresponding electrostatic polymer complexes are formed in high yields. Also importantly, the cations and anions always balance the charges even under dilution, and the selective nucleophilic ring-opening reaction occurred at an elevated temperature, to convert the ionic interaction into permanent covalent linkage (Scheme 4).

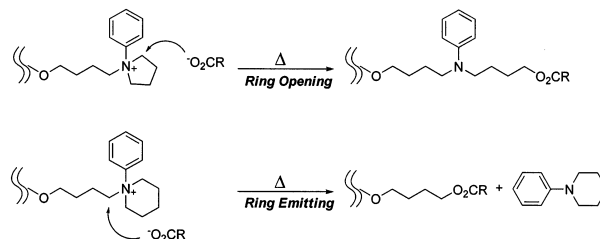
Scheme 4. Electrostatic polymer self-assembly and covalent fixation.



3.1 Ring-opening and Ring-emitting Processes for Covalent Conversion

The amino-ester group, formed by the above *ring-opening* process, tends to become unstable especially at elevated temperatures by undergoing inter- and intramolecular substitution reactions. Therefore, an alternative covalent conversion process to give a stable linking structure would be of particular interest for practical applications. To meet this challenge, an alternative covalent conversion process has been developed by using a telechelic precursor having *unstrained* cyclic ammonium salt end groups (Scheme 5).¹⁵ Thus, telechelic poly(THF)s having 6-membered, *N*-phenylpiperidinium salt

Scheme 5. Ring-opening and ring-emitting processes for covalent conversion.

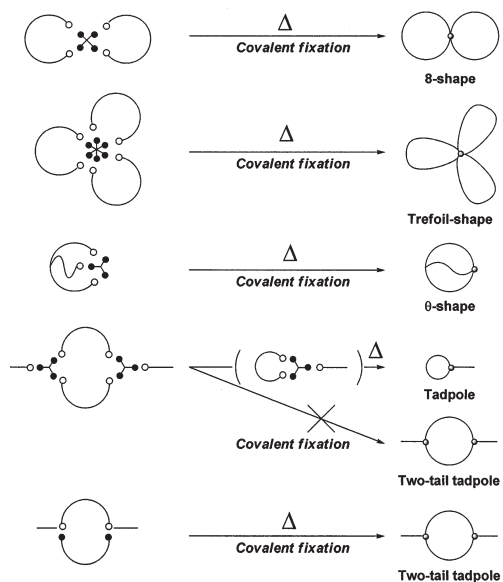


groups carrying either monofunctional benzoate or bifunctional biphenyldicarboxylate counteranions were prepared. Upon subsequent heating, the carboxylate counteranion undergoes selective nucleophilic attack at the *exo*-position of the cyclic ammonium salt group, to form a simple ester group by eliminating *N*-phenylpiperidine units from the polymer chain ends (Scheme 5). In addition, the *ring-emitting* covalent conversion under dilution afforded ring polymers containing simple ester linking groups. Though such ring polymers could also be produced by an equimolar reaction between a polymeric diol and a dicarboxylic acid under dilution, such an ineffective bimolecular process appears impractical for routine synthesis of ring polymers.

3.2 Multicyclic Polymer Constructions by Electrostatic Polymer Self-assembly and Covalent Fixation

The *electrostatic self-assembly and covalent fixation* protocol has been applied successfully for the efficient synthesis of various ring polymers, optionally having specific functional groups at the designated positions of the ring polymer structures (*kyklo*-telechelics and cyclic macromonomers).⁵ In addition, a variety of ring-and-branch polymers, i.e., a simple tadpole as well as twin-tail and two-tail tadpole forms, have been constructed.⁵ Moreover, *spiro*-dicyclic 8-shaped polymers are obtainable from two units of telechelic precursor carrying one unit of tetracarboxylate counteranion.⁵ A fused-dicyclic θ -shaped polymer was also synthesized from a three-armed, star telechelic precursor carrying a tricarboxylate counteranion.¹³ Moreover, a tricyclic polymer having a trefoil topology has been produced from the self-assembly consisting of three units of a linear telechelic precursor carrying a hexafunctional carboxylate counteranion (Scheme 6).¹³

Scheme 6. Cyclic polymer topologies constructed by electrostatic self-assembly and covalent fixation.



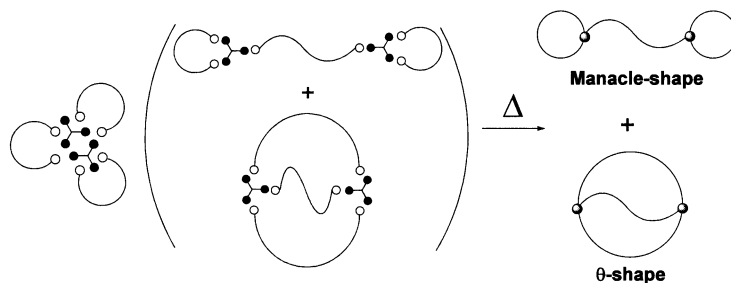
4. Polymeric Topological Isomers: Concept, Synthesis and Separation

Isomerism,¹⁶ a term from the Greek "*isos*" (equal) and "*meros*" (part), is a key concept in chemistry, dating back to Berzelius in 1830.¹⁷ Isomers are a set of compounds having the same chemical constitution (thus, molar mass) but differ-

ent properties. The evolution of constitutional (structural) isomerism by Kekulé¹⁸ has remarkably extended rational understanding of both the static and dynamic structures of organic substances with carbon skeletons, in which non-interconvertible three-dimensional structures of the isomers have distinctive properties. The term "constitutional (structural) isomers" refers to those with distinctive *connectivity* of atoms or atomic groups. In contrast, the term "stereoisomers" refers to isomers with indistinguishable *connectivity*, but which are distinctive from each other in terms of the Euclidean geometric rigidity of the molecules, such as the restriction of bond angle, bond bending and bond rotation.

In case of flexible polymer molecules, a pair of isomeric products can be formed from an identical set of telechelic (end-reactive) polymer precursors and end-linking reagents. As a typical example, three units of a bifunctional polymer precursor and two units of a trifunctional end-linking reagent, or two units of a trifunctional star polymer precursor and three units of a bifunctional end-linking reagent could produce *topological isomers* possessing identical terminuses and junction numbers as well as branch numbers at each junction, referring to manacle- and θ -shaped polymers (Scheme 7).^{1,19} It is noteworthy that these isomers are formed from the least common combination of the functionalities of the two components.

Scheme 7. Polymeric topological isomers formed by electrostatic self-assembly and covalent fixation.



A pair of θ - and manacle-shaped polymers have indeed been obtained simultaneously from an assembly comprised of bifunctional linear precursors carrying trifunctional carboxylates, or from trifunctional star-shaped precursors carrying bifunctional carboxylates.^{5,13} They are regarded as a first example of deliberately produced *polymeric topological isomers*, or more precisely *topologically distinctive polymeric constitutional isomers*, in which not only their molecular weights but also their chemical compositions are identical, but their topological connectivity is distinctive.

These polymeric topological isomers as well as polymers having distinctive topologies, such as linear and ring polymers, could be resolved by means of the reversed-phase chromatography (RPC) technique.¹³ A theoretical study has shown the basis of the separation of topologically distinctive polymers by means of size-exclusion chromatography (SEC), liquid adsorption chromatography, and liquid chromatography at the critical condition.²⁰ In particular, the separation of θ -shaped polymers from their three-armed star analogues has been discussed in detail (Figure 1).²⁰ The simulation chromatogram has first been produced for model mixtures of θ - and star- polymers, and subsequently been compared with

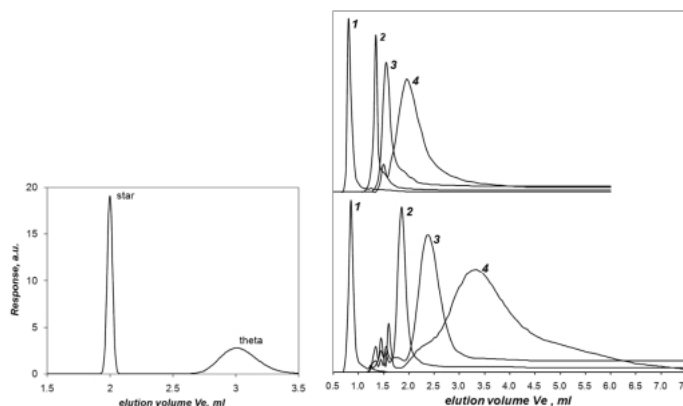
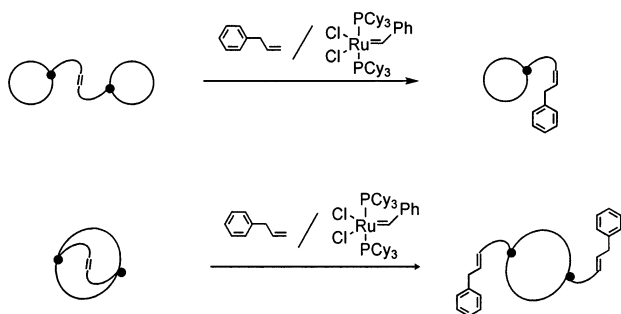


Figure 1. (Left) Theoretical RPC chromatogram for a mixture of star- and θ -shaped poly(THF)-under the condition of critical interaction, and (Right) Measured RPC chromatograms of star- (top) and θ -shaped (bottom) polymers (of $M_w = 9,600$) at different eluent compositions of THF/acetonitrile of 100/0 (1), 52/48 (2), 50/50 (3) and 48/52 (4). Column: TSK ODS-80TS; flow rate: 0.75 mL/min.

the experimental results on star- and θ -shaped poly(THF)s in RPC. A good qualitative agreement between theory and experiment has been observed (Figure 1). Hence, the chromatography under the critical and near-critical interaction conditions is shown as a promising means for the separation of topologically distinctive polymers.

Furthermore, each of the polymeric topological isomers having either θ - or manacle- constructions were chemically assigned by employing those containing a cleavable olefinic group in a backbone segment (Scheme 8).²¹ Thus, a pair of θ - and manacle-shaped polymeric isomers having olefinic groups at the designated positions has purposely been synthesized using linear precursors having an inner olefinic group. The subsequent metathesis cleavage of the inner olefinic group placed at the specific position of the two isomer frameworks allowed the chemical assignment by SEC analysis of the products, since the θ -shaped isomer is transformed into a two-tailed tadpole product having a similar 3D size, in contrast to the manacle-isomer which is transformed into two units of a tadpole product having a significantly smaller 3D size.

Scheme 8. Chemical assignment process of polymeric topological isomers.



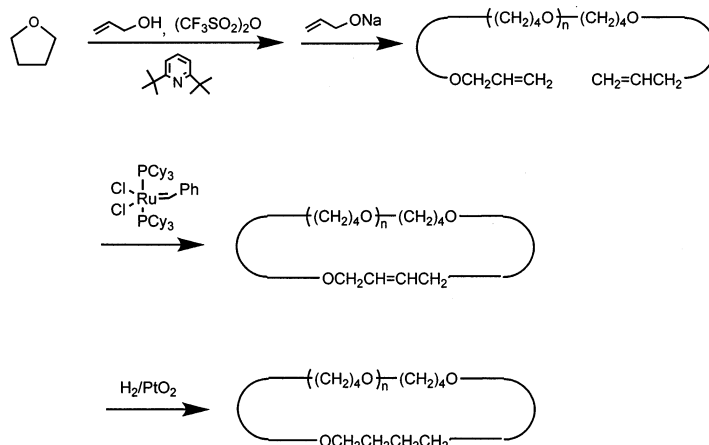
5. Metathesis Polymer Cyclization (MPC) for Topological Polymer Chemistry

5.1 Polymer Cyclization through RCM Process

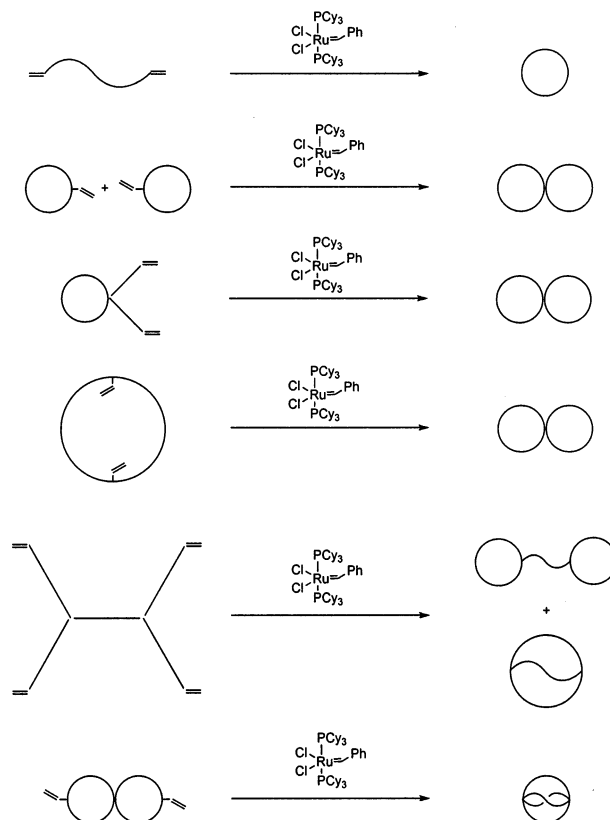
Based on the *electrostatic self-assembly and covalent fixa-*

tion process, a variety of cyclic as well as multicyclic polymers, having such functional groups as allyl, hydroxyl and others by further derivatization, have been prepared.⁵ They are subjected to further topological transformation by taking advantage of effective inter- and intramolecular covalent-linking processes, such as a ring-closing metathesis (RCM) in the presence of a Grubbs catalyst,^{12,22} a palladium-mediated coupling reaction,²³ or the "click" process.²⁴ As for the latter two processes, the introduction of the relevant functional groups could be achieved by the esterification of the hydroxyl groups with the corresponding carboxylate derivatives.

Scheme 9. Synthesis of defect-free ring poly(THF) through metathesis polymer cyclization process.



Scheme 10. Cyclic and multicyclic polymer topologies constructed by inter- and intramolecular metathesis condensation.



In particular, the metathesis condensation has been proven as a versatile means to cause effective polymer cyclization even under dilution with functional group tolerance (Scheme 3). Thus first, a telechelic poly(oxytetramethylene), poly(THF), having allyl groups has been subjected to metathesis polymer cyclization (MPC) to produce a ring polymer having a linking butenoxy group,¹² which has subsequently been hydrogenated to form the oxytetramethylene unit, identical to the monomer unit structure (Scheme 9). In consequence, a unique *defect-free* ring poly(THF), consisting exclusively of monomer units with controlled size distributions, has been produced for the rigorous examination of the topological effect in their polymer crystallization behavior. (Scheme 9).²⁵

The metathesis condensation has further been applied to produce an 8-shaped polymer (Scheme 10). Thus, a ring prepolymer having an allyloxy group, a twin-tailed tadpole polymer precursor, and ring polymer precursors having two allyloxy groups at opposite positions have been employed.²⁶ The metathesis condensation has also been applied with an H-shaped precursor having allyloxy end groups at each chain end, to produce dicyclic polymeric topological isomers having θ and manacle constructions (Scheme 10).²⁷

Moreover, an 8-shaped kyklo-telechelic precursor having two allyl groups at opposite positions has been prepared by the *electrostatic self-assembly and covalent fixation* with a self-assembly consisting of two units of a cationic linear precursor having an allyl group and tetracarboxylate counteranion, and subjected to the metathesis condensation to construct a polymeric δ -graph having a doubly-fused tricyclic topology (Scheme 10).²²

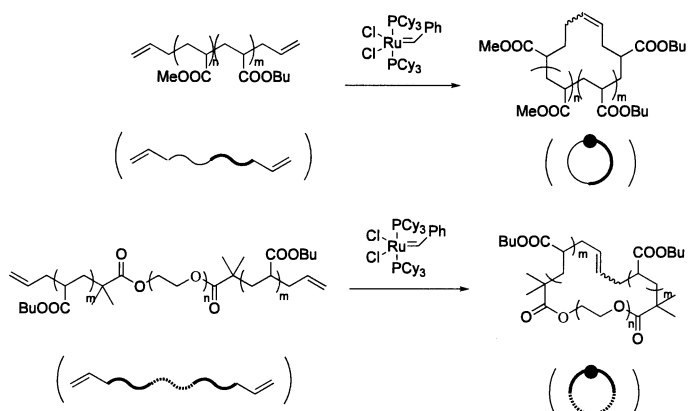
5.2 ATRP-RCM for New Cyclic and Multicyclic Polymer Architectures

By combining an atom-transfer radical polymerization (ATRP) process, which has now been recognized as an effective means to design a variety of chain architectures,^{3e} with the RCM reaction using a telechelic precursor having allyl groups, ring polyacrylates have been prepared in a convenient procedure. Thus, in this process, a key telechelic prepolymer having allyl groups has been prepared by quantitative conversion of the terminal bromoalkyl groups, formed in the ATRP process, through the Keck allylation with allyltributylstan-

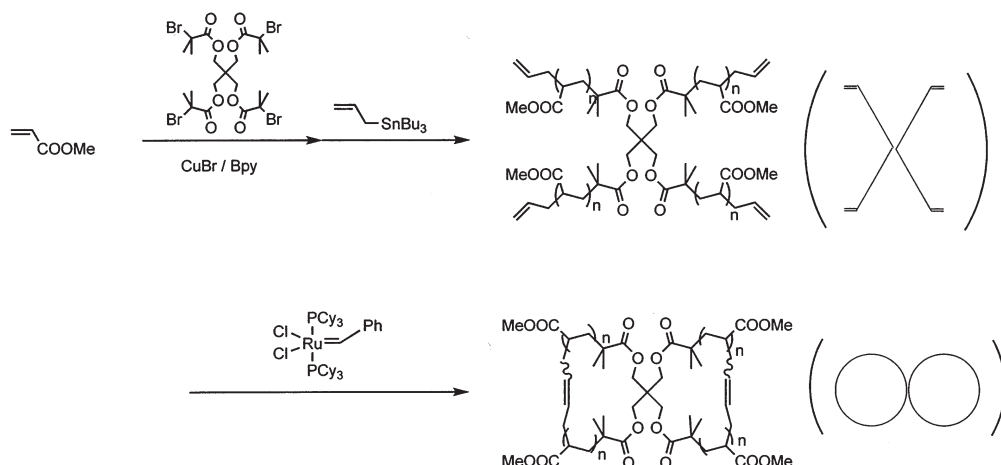
nane. In addition, an 8-shaped polyacrylate has been obtained through the double RCM using a 4-armed star polymer precursor, prepared with a tetrafunctional initiator (Scheme 11).²⁹ Since the ATRP will readily produce various star polymers by making use of multi-functional initiators, the combination with the RCM process will offer unique opportunities to construct further complex multicyclic polymer topologies.

Moreover, cyclic diblock copolymers have been synthesized by means of the ATRP/RCM technique (Scheme 12).³⁰ Thus first, an A-B type allyl-telechelic diblock copolymer comprised of two different acrylate ester segments, i.e., poly(methyl acrylate)-*b*-poly(butyl acrylate), has been prepared via the ATRP of methyl acrylate by allyl bromide as an initiator, followed by the addition of the second monomer, butyl acrylate, and with allyltributylstannane as an end-capping reagent. Alternatively, an A-B-A type allyl-telechelic triblock copolymer comprised of poly(butyl acrylate) and poly(ethylene oxide), poly(EO), segments has been prepared via the ATRP of butyl acrylate using a poly(EO) macroinitiator having 2-bromoisobutyryl end groups, followed by the end-capping reaction by the Keck allylation. The subsequent RCM of the allyl-telechelic block copolymers under dilution in the presence of a Grubbs catalyst could afford the corresponding A-B type cyclic diblock copolymers.

Scheme 12. Synthesis of cyclic diblock copolymers through the ATRP/RCM process.



Scheme 11. Synthesis of 8-shaped poly(methyl acrylate) through the ATRP/RCM process.



6. Concluding Remarks and Future Perspectives

Numerous future opportunities are anticipated with ongoing progress in *topological polymer chemistry*.¹ A new concept of topological isomerism has now been introduced, and a pair of topological isomers uniquely occurring in flexible, non-linear polymer architectures have been synthesized by an *electrostatic self-assembly and covalent fixation* process with newly designed telechelic polymer precursors having cyclic ammonium salt groups. Further synthetic challenges should include such topologically significant polymers as tri-cyclic α , β , γ and δ -graph constructions as well as a tetra-cyclic $K_{3,3}$ construction by employing specifically designed telechelic precursors having appropriate Cayley-tree constructions. In addition, *topological polymer chemistry* is now offering unique opportunities in the exploration of any topological effects in polymer materials, since a variety of topologically defined polymers have now become available systematically. Together with the progress in theories and simulations, we expect to achieve unique topological control in static and dynamic properties that rely on conjectures of topological geometry, in particular, but not limited by those intuitively envisaged from common Euclidian geometry.

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