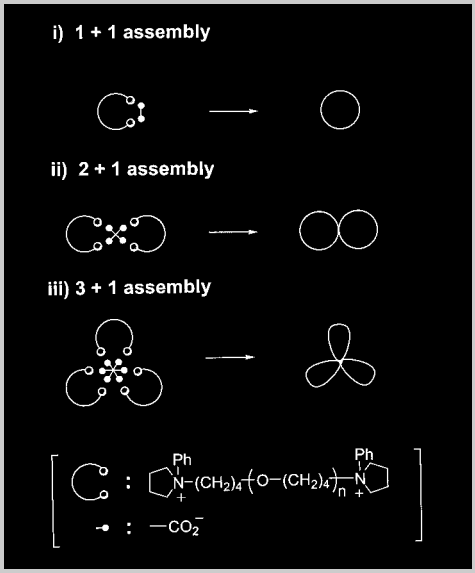
Feature Article: A novel methodology (*electrostatic self-assembly and covalent fixation*) has been proposed for designing various nonlinear polymer topologies, including monocyclic and polycyclic polymers, cyclic macromonomers and cyclic telechelics (kyklo-telechelics), *a-ring-with-a-branch* topology polymers and polymeric topological isomers, as well as branched model polymers, such as star polymers and polymacromonomers. Thus, new telechelic polymer precursors having a moderately strained cyclic onium salt group as single or multiple end groups and carrying multifunctional carboxylates as the counterions were prepared through an ion-exchange reaction. A variety of electrostatic self-assemblies of these polymer precursors, formed particularly in dilute organic solution, was then subjected to heat in order to convert the ionic interactions into covalent linkages by ring-opening reaction, and to produce topologically unique, nonlinear polymer architectures in high efficiency.



Self-Assembly and Covalent Fixation for Topological Polymer Chemistry

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Introduction

Self-assembly of (macro)molecular components through non-covalent interactions plays a critical role in diverse biological events, typically in molecular recognition and molecular communication processes. Any forces weaker than covalent bonds, such as directional hydrogen bonds and metal-coordination bonds as well as non-directional van der Waals forces and Coulombic interactions may be exploited to direct the self-assembly. The self-assembly principle has gained increasing attention in both basic and applied materials sciences, since it will provide a unique means to effectively preorganize (macro)molecular compounds and, subsequently, to convert them into permanent architectures of nanoscopic, mesoscopic and macroscopic scales, which are otherwise difficult or impossible to achieve.[1–3] This will provide important opportunities to realize unprecedented properties and functions, eventually leading to the future nanotechnology.[4]

In this Feature Article, we show a novel methodology to produce various nonlinear polymer architectures in exceptionally high efficiency, by exploiting the self-assembly principle to preorganize linear or star-shaped polymer precursors and to subsequently convert them into covalently linked permanent structures. Thus, we have utilized self-assembly through the Coulombic interaction of hydrophobic macromolecules having specific cationic end groups, namely moderately strained cyclic onium salt groups, which carry multifunctional carboxylates as counterions.[5–7] First, we discuss the synthesis of new telechelic polymer precursors having specific cyclic ammonium groups, and the unique reactivity of end-standing groups against deliberately introduced counterions, namely carboxylate anions. These constitute a basis for the covalent conversion process of the electrostatic self-assembly of telechelic polymer precursors. Then, we demonstrate a variety of topological polymer chemistry by means of *electrostatic self-assembly and covalent fixation* processes to construct unusual nonlinear polymer architectures.

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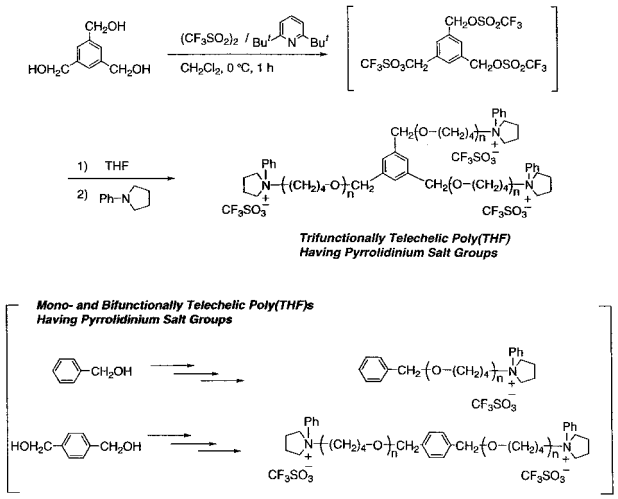
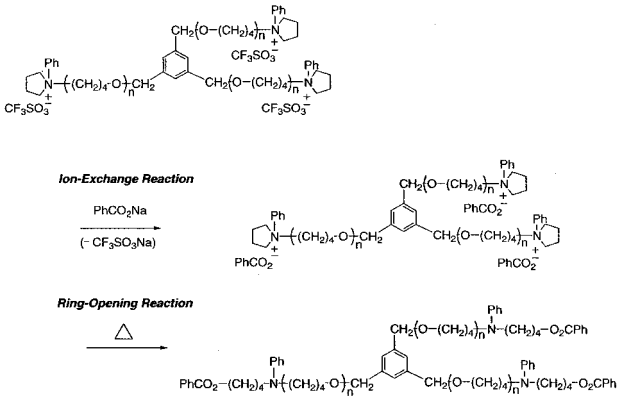


Scheme 1.



Scheme 2.

Novel Telechelic Precursors Designed for Unusual Polymer Topologies

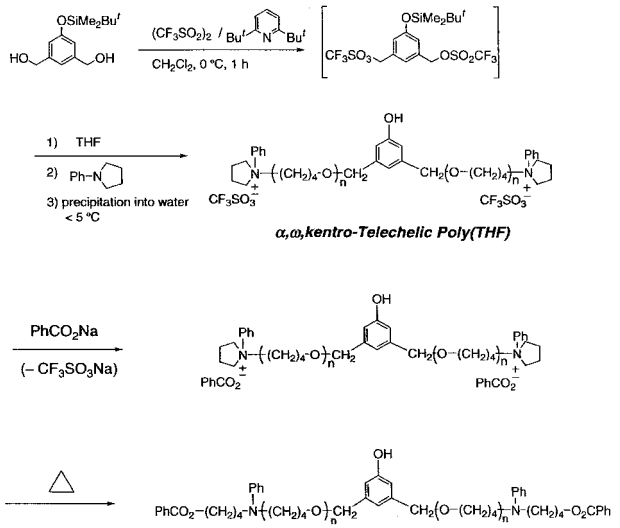
Telechelics with Cyclic Onium Salt Groups

Telechelics, i.e. polymers of uniform size having single or multiple functional end groups, have gained growing interest as macromolecular building blocks to construct various unique polymer architectures.[5, 6, 8] Telechelics having a specific functional group at one or both chain ends are conveniently prepared through the end-group modification of mono- and bifunctionally living polymers, respectively. Moreover, triply and higher functionalized telechelics having star-shaped architectures have been prepared recently on the basis of multifunctional living anionic, cationic, radical as well as ring-opening processes.[9]

We have thus utilized the cationic ring-opening polymerization of tetrahydrofuran (THF) in which mono- and bifunctionally living poly(THF)s can be readily prepared with methyl triflate or triflic anhydride as initiators. Furthermore, we have developed an efficient initiator for the synthesis of a trifunctionally living poly(THF) and the subsequent end-capping reaction for the synthesis of star-shaped telechelic polymers (Scheme 1).[9] This was based on a novel triflate ester, prepared in situ by the reaction of a selected benzylic alcohol, i.e. 1,3,5-tris(hydroxymethyl)benzene, with triflic anhydride in the presence of a proton trap. In benzylic triflate initiators, a phenyl group can stabilize any positive charge that develops at an α-carbon atom during a nucleophilic substitution reaction as in the case of an allyl group.[10, 11] Benzyl triflate, prepared in situ from benzyl alcohol, indeed caused the living polymerization of THF. Likewise, a bifunctional and a trifunctional benzylic triflate (a bis(triflate ester) of 1,4-bis(hydroxymethyl)benzene and a tris-(triflate ester) of 1,3,5-tris(hydroxymethyl)benzene) were prepared accordingly, and were successfully applied in situ as initiators for the living polymerization of THF.[9]

A star-shaped, trifunctionally telechelic poly(THF) and mono- and bifunctionally telechelic poly(THF)s having *N*-phenylpyrrolidinium groups was prepared through the end-capping reaction with *N*-phenylpyrrolidine (Scheme 1). ^{1}H NMR analysis confirmed the quantitative end-capping reaction of the trifunctionally living poly(THF) as well as of the mono- and bifunctional counterparts. The ion-exchange reaction of *N*-phenylpyrrolidinium end groups took place via precipitation into an aqueous solution containing the desired anions, such as sulfonate or carboxylate in their sodium salt form. The ion-exchange products carrying carboxylate counterions were then subjected to heat either in bulk or in solution. The ^{1}H NMR spectra indicated quantitative ion-exchange and the subsequent ring-opening reaction of the *N*-phenylpyrrolidinium initiated by heat (Scheme 2).[9] Size-exclusion chromatography (SEC) confirmed a single peak profile with low polydispersity index. These efficient ion-exchange and selective ring-opening reactions of the terminal pyrrolidinium groups were exploited for a further synthetic application of these telechelic precursors. This will be described in detail later on.

Another type of telechelic poly(THF)s with functional groups not only at the chain ends but also at desired interior positions was prepared.[12] In this case, the benzylic initiator system mentioned above was applied to develop center-functionalized living polymers. The subsequent end-capping reaction provided *α,ω-kentro*-telechelic polymers (Scheme 3). Among a variety of triflates derived from benzylic alcohols, a bis(triflate ester) of 1-(*tert*-butyldimethylsiloxy)-3,5-bis(hydroxymethyl)benzene was found to initiate the living polymerization of THF. The *tert*-butyldimethylsilyl protecting group was readily removed by means of precipitating the reaction mixture into water. The presence of one *tert*-butyldimethylsilyl group was a prerequisite for the living polymerization of THF to occur. The quantitative end-capping reaction of the living poly(THF) with *N*-phenylpyrroli-



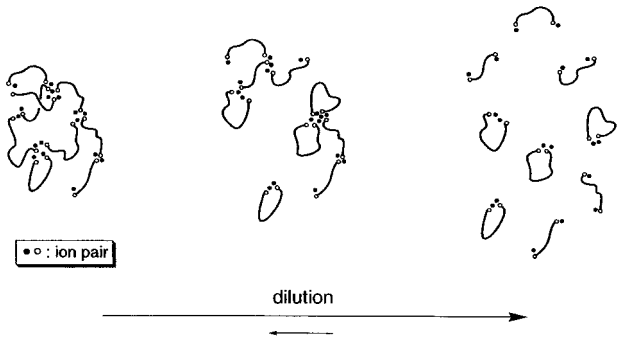
Scheme 3.

dine took place as in the cases of the respective mono- and bifunctionally living poly(THF)s. Subsequent ion-exchange and ring-opening reactions of the *N*-phenylpyrrolidinium end groups having benzoate counterions were selective and quantitative as confirmed by ^{1}H NMR spectroscopy and SEC analysis.[12]

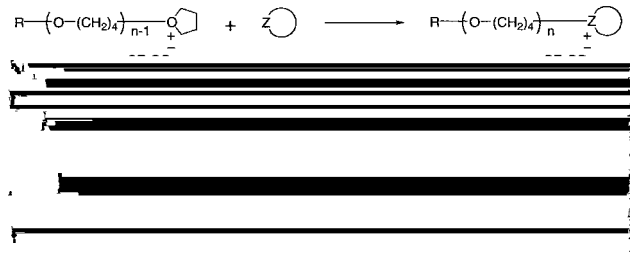
Electrostatic Self-Assembly and Covalent Fixation

Hydrophobic polymers containing small amounts of ionic groups are known to exhibit unique properties both in bulk and in solution. This allows their application in mechanically tough coating materials known as *ionomers*.[13] In organic solution, these polymers tend to aggregate and form clusters (self-assembly) through Coulombic interaction between the ionic groups located along the hydrophobic polymer backbone. The content and location of the ionic groups direct the aggregation (self-assembly) behavior. In this regard, telechelics having ionic groups exclusively at the chain ends might be used as models of ionomers.[14, 15] It was shown that the concentration and the temperature of the solution can significantly influence the aggregation dynamics. Thus in dilute solution, ionic aggregates tend to transform into a small assemblies comprised of a single polymer precursor unit (Scheme 4). Taking into account these features, we have designed a novel polymer reaction process in which such electrostatically self-assembled polymer precursors are utilized for the construction of novel polymer structures by means of subsequent covalent fixation reactions.[16]

A key process in this system is apparently a controlled covalent conversion of ionic species positioned at the end of hydrophobic polymer segments. Hence, we have examined a series of poly(THF)s having a variety of cyclic ammonium groups prepared by means of a direct end-capping reaction of living poly(THF).[5, 7] Thus, a series of three-, four-, five-, and six-membered cyclic ammonium



Scheme 4.

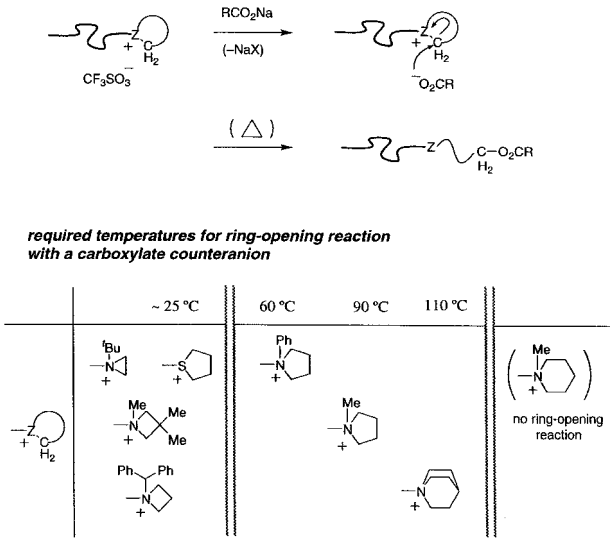


Scheme 5.

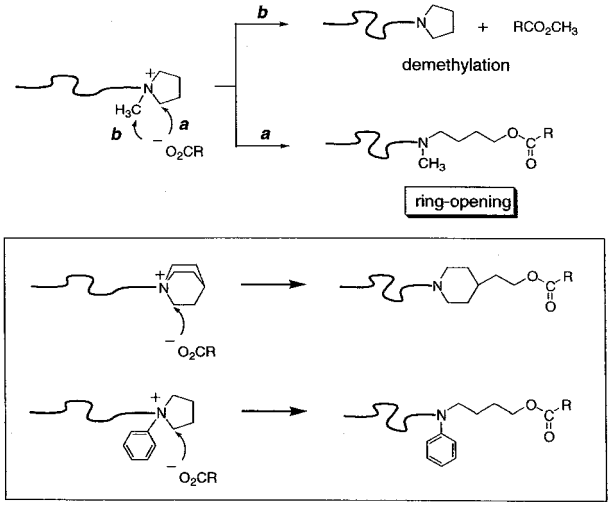
end groups as well as a six-membered bicyclic ammonium end group were synthesized (Scheme 5). The three-membered cyclic ammonium salt end groups are highly reactive and undergo spontaneous ring-opening reactions with the three-membered cyclic amine itself to produce a block copolymer in situ. The four-membered cyclic ammonium end groups, on the other hand, are incapable of initiating ring-opening reactions with the corresponding cyclic amines at ambient temperature. Hence, the telechelic poly(THF) having four-membered cyclic onium groups could be isolated for the relevant spectroscopic and chromatographic characterization. It was subsequently utilized as a reactive polymer precursor to produce block copolymers by the reaction with three- and four-membered cyclic amines at elevated temperature.[17]

It is also interesting to note that the four-membered cyclic ammonium end groups underwent the ion-exchange reaction substituting an originally accompanied weak nucleophile for others like sulfonates or carboxylates through a simple precipitation of the telechelics solution into an aqueous solution containing the desired anions (Scheme 6).[5] When a strong nucleophile, such as a carboxylate counterion, was introduced, a spontaneous ring-opening reaction of the four-membered cyclic ammonium groups took place at ambient temperature.

Telechelic poly(THF)s having modestly strained five-membered cyclic as well as six-membered bicyclic ammonium groups could be isolated even with carboxylates as counterions, but underwent ring-opening reaction at appropriately elevated temperature (Scheme 6). On the other hand, the strain-free six-membered cyclic ammonium group failed to cause selective ring-opening reaction.



Scheme 6.



Scheme 7.

Thus, telechelic poly(THF)s having five-membered cyclic and six-membered bicyclic ammonium groups have been chosen as polymer precursors for the electrostatic self-assembly with appropriate carboxylate counterions. In electrostatic self-assembly, the specific numbers of polymer precursors and counterions are assembled in such a way that cations and anions balance the charges. The subsequent covalent fixation via ring-opening thus can produce covalently linked products of specific architecture.[7]

The relevant telechelics of different main-chain segments, namely polystyrene and poly(dimethylsiloxane) (poly(DMS)) having the five-membered cyclic and six-membered bicyclic ammonium salts as end groups, were also prepared through the sequential end-group derivatization of a living polystyrene and a living poly(DMS) obtainable by an anionic polymerization method.[18, 19] Thus, a direct end-capping reaction of mono- and bifunctionally living polystyrene or poly(DMS) with a chlorosilane derivative having a trimethylsilyl-protected hydroxyl group, followed by tosylation, and eventually by quaternization with a five-membered cyclic amine (*N*-methylpyrrolidine) or a six-membered bicyclic amine (quinuclidine) was performed to produce the telechelic polystyrene and poly(DMS) having moderately strained cyclic onium groups.

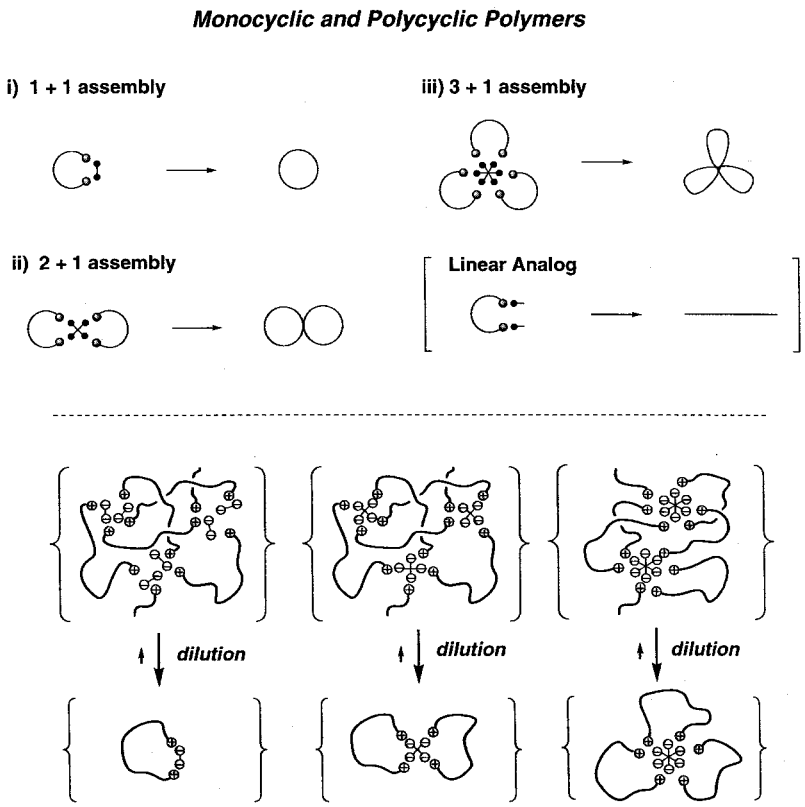
The ring-opening reaction of a series of moderately strained cyclic ammonium groups (*N*-alkylpyrrolidinium, *N*-arylpyrrolidinium and quinuclidinium) was studied in more detail (Scheme 7).[20–22] During the reaction of *N*-methylpyrrolidinium end groups with a variety of carboxylate counterions a noticeable demethylation took place besides ring-opening. This is due to a nucleophilic attack of the carboxylate counterion at the *N*-methyl carbon atom. On the other hand, Hofmann type elimination products were not detected. Moreover, reaction at the *N*-methylpyrrolidinium groups was notably dependent on the pK_a values of the counterions.[20] Electron-donating *p*-methoxybenzoate (pK_a = 4.47) produced the ring-opened product in high yield and with high ring-opening selectivity, while electron-withdrawing *p*-nitrobenzoate (pK_a = 3.42) failed to cause any reaction under the reaction conditions chosen. It was also observed that the higher the reaction temperature, the lower the selectivity of ring-opening over demethylation. On the contrary, quinuclidinium groups underwent comparatively selective ring-opening with a variety of carboxylate counterions, but higher temperatures were required.[23]

Finally, an alternative polymer precursor was designed, in which *N*-methylpyrrolidinium was replaced by *N*-phenylpyrrolidinium.[22] Since nucleophilic substitution at the phenyl group is inherently suppressed, ring-opening at the aliphatic *endo*-methylene groups tends to occur preferentially. Ring-opening will be further promoted by introducing an aniline derivative group, which is a better leaving group than the alkylamino group in nucleophilic substitution reactions.[17] Thus, *N*-phenylpyrrolidine was synthesized and used for the end-capping reaction of living poly(THF).[22] Indeed, the *N*-phenylpyrrolidinium end group underwent quantitative ring-opening even with *p*-nitrobenzoate as the counterion. The reaction takes place exclusively at the *endo*-position of the five-membered pyrrolidinium ring, in contrast to the *N*-methylpyrrolidinium group (Scheme 7). Moreover, unsubstituted benzoate and *p*-methoxybenzoate as counterions caused the quantitative and selective ring-opening of the *N*-phenylpyrrolidinium group without concurrent demethylation reaction, again in contrast to the *N*-methylpyrrolidinium group.

Designing Nonlinear Polymer Topologies

Monocyclic and Polycyclic Polymers

The synthesis of monocyclic and polycyclic polymers[24] has been conducted by using telechelic poly(THF) having *N*-phenylpyrrolidinium groups.[16] The initial triflate



Scheme 8.

counterions were subsequently replaced with carboxylate counterions by precipitating the poly(THF) precursor into an aqueous solution containing excess carboxylate as its sodium salt. ^{1}H NMR spectra of the ion-exchange products with di-, tetra-, and hexacarboxylate indicated the presence of the carboxylate counterions. The balance of the charges between the ammonium groups in the polymer precursor and the carboxylate anions was found to be maintained, corresponding to molar ratios of 1:1, 2:1, and 3:1, respectively.

A series of ionically linked polymer precursors in solution and at different concentrations was then subjected to heat (Scheme 8). When heat treatment was conducted either in bulk or in concentrated solution, an insoluble gel was produced quantitatively, except for the reaction of the bifunctional polymer precursor carrying a dicarboxylate counterion. In dilute solution, on the other hand, the product was totally soluble. Remarkably, the three-dimensional size in solution (hydrodynamic volumes observed by means of SEC) of the quantitatively recovered crude products was nearly as uniform as in the linear polymer analog (Figure 1), which was independently prepared from the bifunctional polymer precursor carrying benzoate as the counterions. These results implicate that a unique form of electrostatic self-assembly was produced from the aggregated polymer precursors upon appropriate dilution, since cations and anions always balance the charges (Scheme 8).

The mono-, bi- and tricyclic poly(THF)s obtained were readily purified using preparative thin layer chromatography, and were fully characterized by spectroscopic and chromatographic techniques. ^{1}H NMR spectra confirmed that all pyrrolidinium groups were converted into amino-ester groups via ring-opening. The IR spectra showed absorptions, which can be assigned to ester carbonyl groups. The molecular weight (corresponding to the total chain length) of the monocyclic product, determined by either vapor pressure osmometry (VPO) or ^{1}H NMR spectroscopy, agreed with that of its linear analog. On the other hand, SEC results showed that the monocyclic product retained a uniform size distribution, and more importantly, its hydrodynamic volume was notably smaller than that of the corresponding linear analog (Figure 1). Besides the SEC results, viscosity measurements of the cyclic and linear poly(THF) revealed an inherent viscosity ratio, $[\eta]_{inh(cyclic)}/[\eta]_{inh(linear)}$, which is very close to the theoretical intrinsic viscosity ratio of 0.66.[25] Furthermore, the cyclic and the corresponding linear product could be distinguished by means of a reversed-phase high pressure liquid chromatography (RPC), where the topology of the polymer product directs the elution properties.[26, 27]

SEC analyses showed that bicyclic and tricyclic poly(THF)s possess significantly larger hydrodynamic volumes than their linear analogs from a single polymer precursor unit, but they are smaller than double (for the

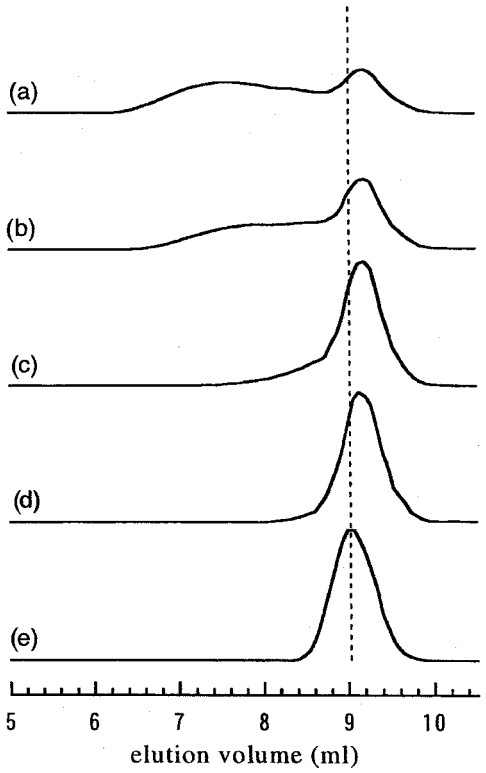


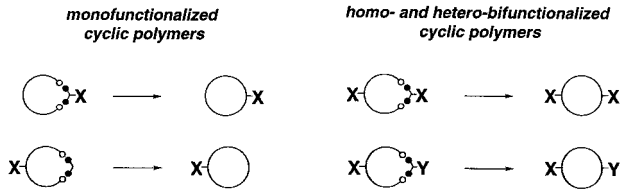
Figure 1. SEC traces (RI) of the quantitatively recovered crude product of a bifunctional poly(THF) precursor carrying dicarboxylate as the counterion after heat treatment (a)–(d), and of the linear analog (e). Concentration of the precursor in THF: (a) 10 g/L, (b) 5.0 g/L, (c) 1.0 g/L, (d) 0.2 g/L (column: TSK G4000HXL; eluent: THF, 1.0 mL/min).

former) and triple the size (for the latter). They retained narrow size distributions. On the other hand, the molecular weights of bicyclic and tricyclic poly(THF)s determined by either VPO or ^{1}H NMR spectroscopy (assuming a quantitative chemical conversion of the polymer end groups) coincided, within experimental error, with twice (for the former) and three times (for the latter) the molecular weight of the linear polymer precursor analogs. Hence, it could be concluded that the unique forms of the corresponding electrostatic polymer assemblies were formed under dilution by balancing the charges between cations and anions, and they are comprised of two or three units of the polymer precursor and one unit of the tetracarboxylate or hexacarboxylate, respectively. A subsequent heat treatment of these precursors led to bicyclic and tricyclic polymer products through covalent fixation by means of the ring-opening reaction of the pyrrolidinium groups (Scheme 8).

Cyclic Polymers with Functional Groups

kyklo-Telechelics

Cyclic polymer precursors having functional groups at designated positions, so-called *kyklo*-telechelics (the

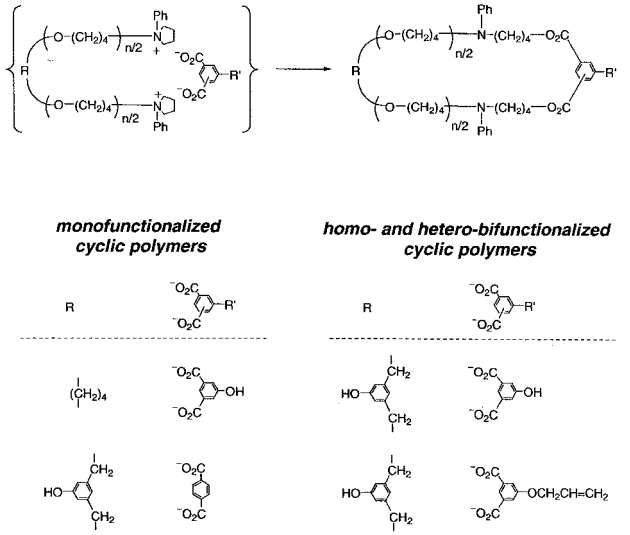


Scheme 9.

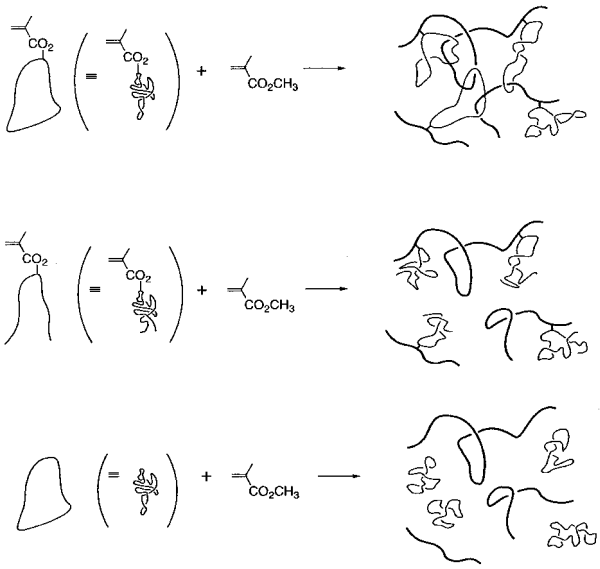
Greek *kyklos* means cyclic), will be of potential importance as macromolecular building blocks to construct topologically unique and complex macromolecular architectures containing cyclic polymer units. Thus, telechelic poly(THF) with *N*-phenylpyrrolidinium groups and, optionally, with an additional functional group at the center position of the polymer chain (termed *kentro*-telechelics[12]) as described in the preceding section, have been utilized to design *kyklo*-telechelics having a single or two functional groups (Scheme 9).[28] The *electrostatic self-assembly and covalent fixation* process was again applied to an efficient polymer cyclization process for telechelic poly(THF)s. The unique self-assemblies were formed by the polymer precursors carrying specific counterions upon dilution in which cations and anions balance the charges.

First, we prepared a telechelic poly(THF) carrying 5-hydroxyisophthalate as the counterion (a hydroxy-functionalized dicarboxylate) via ion exchange (Scheme 10). This ionically linked polymer precursor was then subjected to heat under dilution. Quantitative ring-opening was confirmed by means of ^{1}H NMR analysis of the product, which could be recovered quantitatively after evaporating the solvent. SEC measurements revealed that the product possesses narrow size distribution and a notably smaller hydrodynamic volume than that of the linear analog. The ratio of the hydrodynamic volumes of cyclic to linear products, estimated by means of SEC based on the apparent peak molecular weights, was in good agreement with those reported previously.[29–33] From these results, it could be concluded that a cyclic poly(THF) having a hydroxy group that was derived from the dicarboxylate counterion, was produced efficiently.

Alternatively, the respective hydroxy-functionalized cyclic poly(THF) was prepared by using the *α,ω-kentro*-telechelic poly(THF), which carries not only *N*-phenylpyrrolidinium groups at both chain ends but also an additional hydroxy group at the center position of the polymer chain (Scheme 10). Thus, the corresponding polymer precursor carrying a terephthalate counterion was prepared and subjected to heat under dilution. Again, the ring-opening reaction of the pyrrolidinium end groups took place quantitatively, as was confirmed by ^{1}H NMR and IR analyses of the product. SEC results confirmed that the cyclic poly(THF) obtained possesses narrow size distribution, and a notably smaller hydrodynamic volume than the linear analog.



Scheme 10.



Scheme 11.

Moreover, homo- and hetero-bifunctionalized cyclic poly(THF)s having either two identical or two different functional groups at opposite positions were synthesized (Scheme 10). An *α,ω-kentro*-telechelic polymer precursor carrying 5-hydroxyisophthalate as the counterion was prepared and subjected to heat under dilution. The ^{1}H NMR spectrum of the product showed the two singlets due to the hydroxy protons not only of the 5-hydroxyisophthalate counterion but also of the *kentro*-telechelic poly(THF) precursor. The intensities of these two signals were consistent with each other. SEC results showed that the product possesses narrow size distribution. It is thus confirmed that a homo-bifunctionalized cyclic poly(THF) with two hydroxy groups at opposite positions was produced effectively.

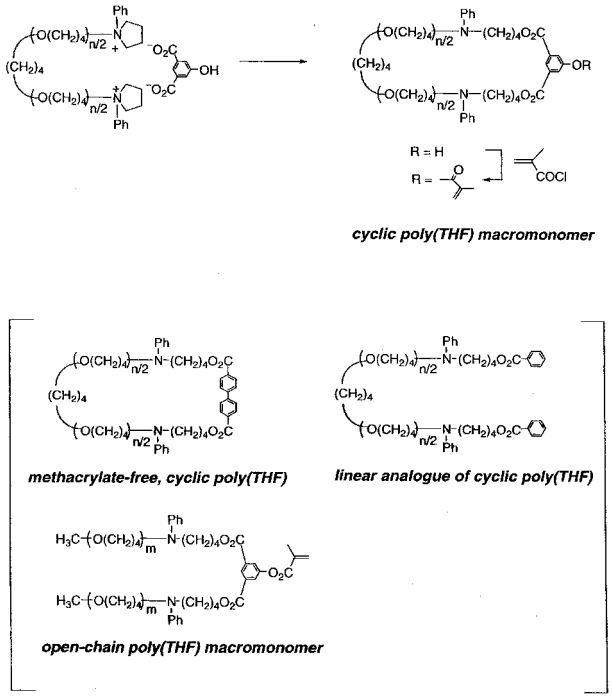
Finally, an *α,ω-kentro*-telechelic polymer precursor carrying 5-allyloxyisophthalate as the counterion was prepared and subjected to heat under dilution. A hetero-bifunctionalized cyclic poly(THF) having a hydroxy and an allyloxy group at opposite positions was produced in quantitative yield (Scheme 10). The ^{1}H NMR spectrum again showed a signal for the hydroxy proton of the *α,ω-kentro*-telechelic poly(THF) precursor, in addition to signals due to allyloxy protons of the 5-allyloxyisophthalate counterion. The proton intensity ratio of these signals agrees with that calculated from the expected molecular formula. SEC showed that the hetero-bifunctionalized cyclic poly(THF) possesses narrow size distribution.

Cyclic Macromonomers

As a further extension to this process, a novel functional cyclic polymer, i.e. a cyclic macromonomer, was designed to construct an unusual polymer network structure having both covalent and physical linkages.[34] This network is formed by a chain threading of the propagating polymer segment through large cyclic polymer units attached to the backbone segments.

Cyclic polymers are of potential interest due to their capability of forming physically (non-covalently) linked architectures based on their loop topology. Despite their relevance with respect to interpenetrating polymer networks (IPNs), a tailored non-covalent linking process by threading through flexible and large cyclic polymers has scarcely been achieved.[35] Since a long and flexible polymer chain tends to assume a randomly coiled and, hence, constrained three-dimensional structure, chain threading of another polymer chain through such a large cyclic polymer unit is unlikely to proceed effectively (Scheme 11). This is contrastive to a variety of medium-sized macrocyclic compounds up to around 100-membered rings, including 30- to 60-membered crown ethers, bipyridinium-based cyclophanes, cyclodextrins and macrocyclic amides.[36–38] They are regarded as configurationally stiff, thus assuming an extended-cyclic conformation. The subsequent intriguing syntheses of (poly)catenanes and (poly)rotaxanes with such macrocycles are noteworthy achievements in which a variety of non-covalent interactions such as hydrogen bonding, π-π stacking, metal-coordinating and van der Waals interactions direct the chain threading events.[38]

We have discovered effective chain threading by the propagating polymer chain through cyclic polymer units of a 280-membered ring, by attaching them to a backbone polymer segment.[34] This has been demonstrated by the copolymerization of a cyclic macromonomer, namely a well-defined cyclic poly(THF) having a methacrylate group. In contrast, no noticeable chain threading was observed in the homopolymerization (quantitative conversion) of methyl methacrylate (MMA) in the presence



Scheme 12.

of a methacrylate-free, cyclic poly(THF) of the relevant ring size (Scheme 11).

The hydroxy-functionalized cyclic poly(THF)[28] described in the preceding section was subjected to esterification with methacryloyl chloride in the presence of triethylamine giving rise to a cyclic macromonomer in quantitative yield (Scheme 12). SEC results revealed a narrow size distribution of the product obtained. The ^{1}H NMR spectrum showed signals due to the methacrylate group, and the degree of polymerization was estimated to be 70, corresponding to a 280-membered ring ($\overline{M}_n$ = 5200).

A free radical copolymerization with MMA was then carried out in solution. The polymerization was first interrupted to keep the conversion of MMA below 20%, and the copolymer fraction was isolated by means of precipitation. SEC measurement showed both ultraviolet (UV) and refractive index (RI) responses of the copolymer, indicating that the graft component (poly(THF) macromonomer having a phenyl group at the precursor chain ends) was distributed statistically along the PMMA-based copolymer backbone. The ^{1}H NMR spectrum also showed the presence of the poly(THF) component in the copolymer, while the signals of the methacrylate group had completely disappeared. No side reactions, such as a decomposition of the cyclic structure, were noticeable. The relative molar ratio of graft units to MMA in the copolymer was estimated to be very close to the feed ratio in agreement with a statistic copolymerization.

Subsequently, a copolymerization was carried out with complete conversion. Nearly the whole portion of recovered product became insoluble but could be swollen in various solvents. On the other hand, no gelation occurred in the copolymerization (quantitative conversion) of MMA with an open-chain polymer precursor, obtained from a monofunctional poly(THF) with a pyrrolidinium end group (Scheme 11). The recovered product was totally soluble. ^{1}H NMR and IR spectra showed no sign of side reactions responsible for a covalent crosslinking by chain-transfer reactions during the copolymerization process. These results indicate that gelation in the copolymerization of MMA with the cyclic macromonomer took place through physical crosslinking, i.e. threading by the propagating chain through the pendant cyclic branches attached to the polymer backbone as shown in Scheme 11. More importantly, chain threading through large polymer loops occurred only when the loops were covalently attached to the polymer backbone.

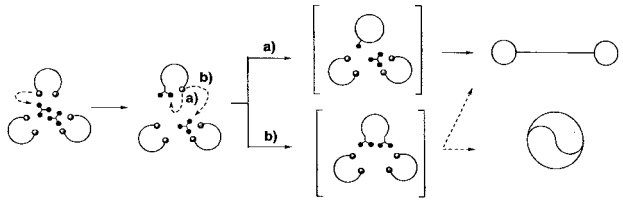
Topological Isomers

Topological isomers typically refer to a pair of molecules having a ring and a knot structure (Scheme 13).[39–42] They are identical in molecular formula and in chemical composition, but their topologies are distinctively different. Thus, they are defined as a special class of isomers. Such topological isomerism is frequently observed, in particular, in macromolecular systems containing cyclic units.

Scheme 13.

A pair of topological isomers can also be produced from an identical precursor set of telechelic (end-reactive) polymers and end-linking reagents, e.g., three bifunctional polymer precursors and two trifunctional end-linking reagents (Scheme 14).[16] Since they are produced from identical precursors by a common chemical reaction, their chemical compositions and molecular weights are identical. They are, on the other hand, topologically distinctive. Hence, they are regarded as a unique pair of topological isomers.

We have attempted to synthesize a pair of polymeric topological isomers by utilizing an ionically linked precursor of the bifunctional poly(THF) precursor carrying tricarboxylates as counterions, which balance the charges between cations and anions.[16] As in the relevant reactions with other polycarboxylates, no gelation occurred as far as under dilution. The covalent linkage between the two pyrrolidinium groups in the bifunctional polymer precursor and the three carboxylate groups in the tricar-



Scheme 14.

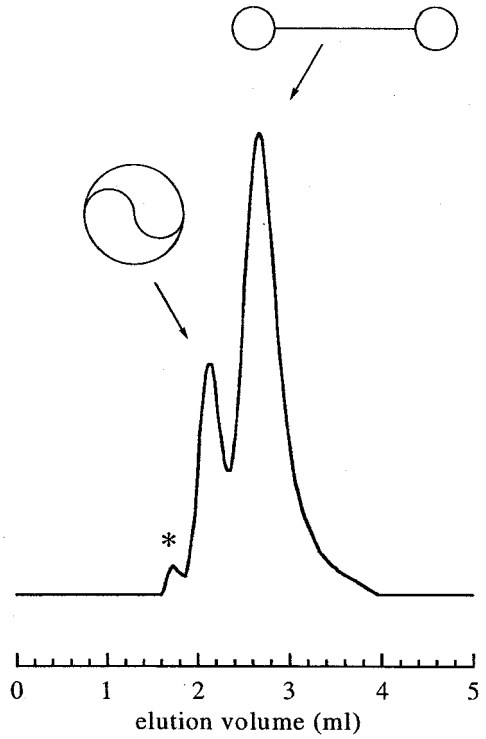
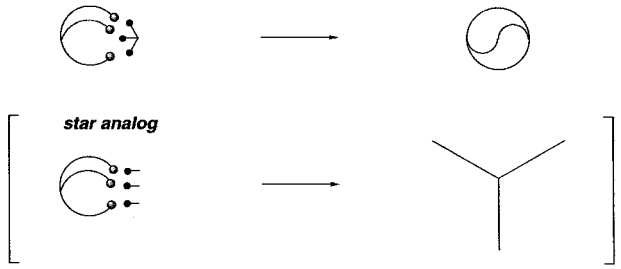


Figure 2. RPC trace (UV) of the product derived from three bifunctional poly(THF) precursors carrying two tricarboxylate counterions after heat treatment under dilution (column: TSK ODS-80TS (80 Å pore, 150 mm × 4.6 mm, 5 μm average particle size); eluent: THF/CH_3CN = 49:51 (v/v), isocratic, 1.0 mL/min). The peak marked with an asterisk (*) is that of the unassigned fraction.

boxylate should produce two topologically distinctive polymer architectures (Scheme 14). The random combination of cations and anions will produce the two constructions, a *manacle* form and a "θ" form, in a ratio of 3:2. The size, i.e. hydrodynamic volume, of the former is considered to be larger than that of the latter. In addition, the dielectric properties of the two topological isomers should be different from each other, since the spatial alignments of the polar groups (*N*-phenyl groups) are different. Indeed, RPC revealed two components in the covalent fixation product, which were subsequently separated by means of fractionation (Figure 2). ^{1}H NMR and IR spectra of the two fractions were identical, indicating the quantitative ring-opening reaction of the pyrrolidinium groups by the carboxylate groups in the tricarboxylate. Although SEC failed to give two distinctly separated peaks, a consistent peak profile was obtained from the



Scheme 15.

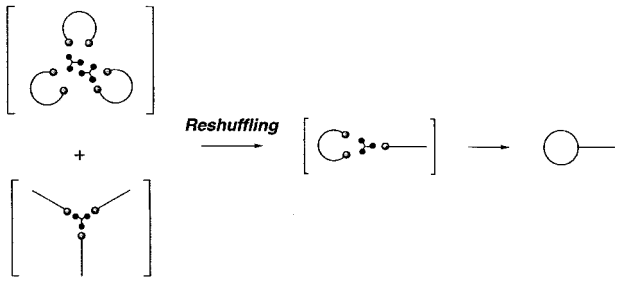
peak convolution of the two isomeric components, 78:22 as estimated by means of RPC, of the respective elution volumes.

The isomer ratio observed indicates that the intramolecular process to produce the *manacle* isomeric form is slightly favored in this covalent fixation process (path **a** in Scheme 14). The molecular weights of these topological isomers (as a mixture) as determined by VPO and by ^{1}H NMR spectroscopy (assuming a quantitative chemical conversion of the polymer end groups) coincided, within experimental error, with that of three times the molecular weight of the linear analog prepared from a single polymer precursor unit. These results are consistent with the formation of a self-assembled product by dilution, consisting of three units of the bifunctional polymer precursor and two units of tricarboxylate. Subsequent heat treatment of the assembled precursor could lead to the two topological isomers through covalent fixation via the ring-opening of the pyrrolidinium groups.

The θ form of these two topological isomers was produced independently.[16] Here, an assembled precursor derived from the trifunctional poly(THF)[9] with *N*-phenylpyrrolidinium end groups carrying three carboxylate groups was subjected to the covalent conversion process (Scheme 15, see also Scheme 1). ^{1}H NMR spectroscopy confirmed that all pyrrolidinium groups in the precursor were converted into amino-ester groups. SEC showed that the product retained uniform size distribution and that its hydrodynamic volume was notably smaller than that of its open-chain analog, i.e. the respective star poly(THF) (Scheme 15).

Reshuffling in Self-Assembly: A Ring-with-a-Branch Topology Polymers

The *electrostatic self-assembly and covalent fixation* strategy has also been applied to the design of a novel polymer architecture comprising both a ring and a branch unit (i.e. possessing a free chain end).[16] We exploited a dynamic reshuffling of the ionic components in an electrostatic self-assembly of the telechelic polymer precursors in solution (Scheme 16). Therefore, equimolar amounts of the two types of ionically linked precursors – one obtained from the bifunctional poly(THF) carrying tricarboxylate as the counterion, and the other one from



Scheme 16.

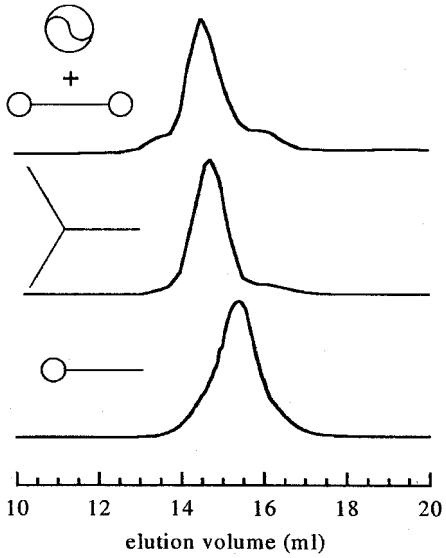
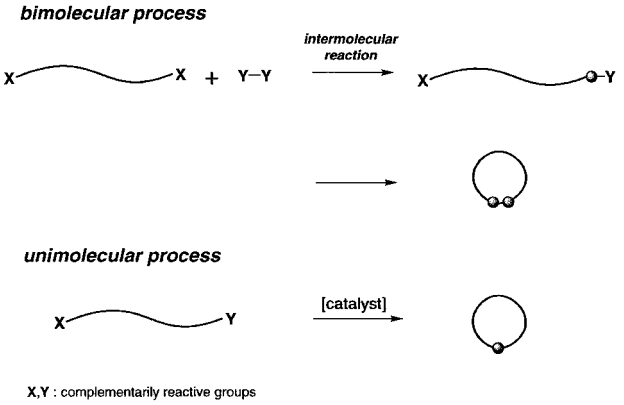


Figure 3. SEC traces (RI) of the polycyclic polymer products derived from three bifunctional poly(THF) precursors carrying two tricarboxylate counterions (top), of the star polymer derived from three monofunctional poly(THF) precursors carrying a tricarboxylate counterion (middle), and of *a-ring-with-a-branch* polymer product derived from mono- and bifunctional poly(THF) precursors carrying a tricarboxylate counterion (column: TSK G4000HXL × 2; eluent: THF, 1.0 mL/min).

the monofunctional poly(THF) also carrying tricarboxylate – were mixed in solution. Under dilution, a spontaneous reshuffling of the ionically linked telechelic polymer precursors took place to form a new thermodynamically favored electrostatic assembly in which the smallest number of polymer components is combined, while the charges between cations and anions are balanced. Subsequent heat treatment under dilution caused the conversion of ionic linkages into covalent bonds, thus producing a new polymer topology (Scheme 16).

The ^{1}H NMR spectrum indicated, as expected, a quantitative ring-opening of the pyrrolidinium group, and SEC resulted in a single peak profile upon reshuffling and subsequent covalent conversion (Figure 3, bottom). The hydrodynamic volume was notably smaller than those of the corresponding pre-reshuffling counterparts, i.e. of the polycyclic polymer products (mixture of the two topological isomers; Figure 3, top) and of the star polymer



Scheme 17.

(obtained separately from the corresponding monofunctional polymer precursor; Figure 3, middle). These results again demonstrate the selective formation of a unique polymer topology comprising both a ring and a branch by the covalent fixation of the corresponding electrostatically assembled polymer precursor. The dynamic reconstruction of ionically linked polymer precursors by means of reshuffling is a conceptually novel methodology providing a versatile means to construct a variety of unusual and complex polymer topologies.

Cyclic Polystyrene

So far we dealt with topological polymer chemistry by specifically using telechelic poly(THF)s. In this section, we show the efficient synthesis of cyclic polystyrenes by means of the *electrostatic self-assembly and covalent fixation* strategy starting from a telechelic precursor with cyclic ammonium groups.[43]

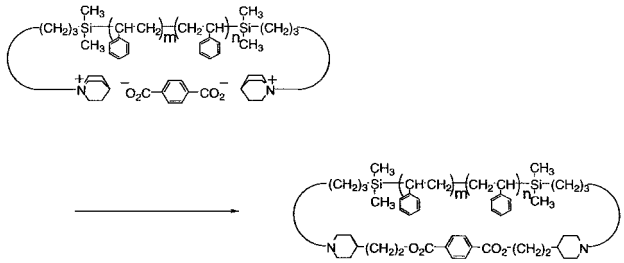
Monocyclic polystyrenes have usually been prepared via the end-to-end linking reaction of a bifunctionally living polystyrene with a bifunctional end-linking reagent (Scheme 17).[44] It should be noted, however, that this bimolecular reaction must be conducted under a strict molar balance between a polymer precursor and a low-molecular weight coupling reagent. Moreover, highly diluted conditions are required to both promote the intramolecular process and to suppress the intermolecular process leading to chain-extension. This, in turn, substantially reduces the reaction rate due to the bimolecular, second-order kinetics of the reaction. Alternatively, the efficiency of the polymer cyclization process can be improved by employing a unimolecular process under high dilution involving α,ω-heterobifunctional polystyrenes (Scheme 17).[32,33] Nevertheless, the selective introduction of complementarily reactive groups at the opposite chain ends inherently requires a multi-step synthesis including protection-deprotection processes. Thus the practical usefulness is limited. An interfacial reaction by using a pair of immiscible liquids has also been applied.[45]

On the contrary, our strategy relies on the *electrostatic self-assembly and covalent fixation* of telechelic polymer precursors with cyclic ammonium groups carrying dicarboxylate as the counterion in a dilute organic medium.[43] As shown in the preceding sections, a telechelic polymer having *N*-phenylpyrrolidinium groups is a versatile choice to this end. However, it was found that the quaternization with *N*-phenylpyrrolidine at the tosylate end groups of polystyrene failed to proceed, apparently due to its substantially weaker nucleophilic reactivity (pK_a = 3.45) than that of aliphatic amines. On the other hand, *N*-methylpyrrolidinium groups can be readily introduced because of the higher reactivity of *N*-methylpyrrolidine (pK_a = 10.3). A series of branched and network polymers consisting of polystyrene and poly(dimethylsiloxane), as well as poly(THF) segments were thus synthesized by an ion-coupling reaction of the respective polymer precursors having *N*-methylpyrrolidinium groups.[18, 19, 23, 46]

However, particularly under dilution, the nucleophilic reaction of the benzoate counterion of the *N*-methylpyrrolidinium end group of polystyrene accompanied the concurrent demethylation, as is in the case of telechelic poly(THF) (see Scheme 7). To address this problem, an alternative telechelic polystyrene containing six-membered bicyclic quinuclidinium groups was selected. The nucleophilic attack of the carboxylate counterion at the quinuclidinium group took place exclusively at the *endo*-methylene position to cause the ring-opening reaction of a strained azabicyclo unit. Thus a reaction at the alternative *exo*-methylene position was excluded. The quinuclidinium group of the telechelic poly(THF) underwent selective ring-opening, while a comparatively higher temperature was required than in the cases of *N*-phenyl- and *N*-methylpyrrolidinium groups.[23]

The subsequent polymer cyclization was conducted with the telechelic polystyrene with quinuclidinium groups carrying terephthalate as the counterion (Scheme 18). The balance between the charges of quinuclidinium cations and terephthalate anions was maintained as confirmed by means of ^{1}H NMR analysis. The ionically linked polymer precursor was then subjected to heat in solution at various concentrations to cause the ring-opening of the quinuclidinium end group. The soluble products were constantly recovered in almost quantitative yield. ^{1}H NMR spectroscopy showed that ring-opening occurred with a selectivity of 90%. Upon dilution, a cyclic polymer product was obtained in up to 90% yield (SEC). As in the poly(THF) systems, an ionic precursor consisting of a single polymer unit having a balance between the charges of cations and anions was formed from the ionically aggregated polymer precursors, which was subsequently converted into the covalently linked product by heat treatment.

After the purification of the product by means of column chromatography (silica gel), SEC showed a single



Scheme 18.

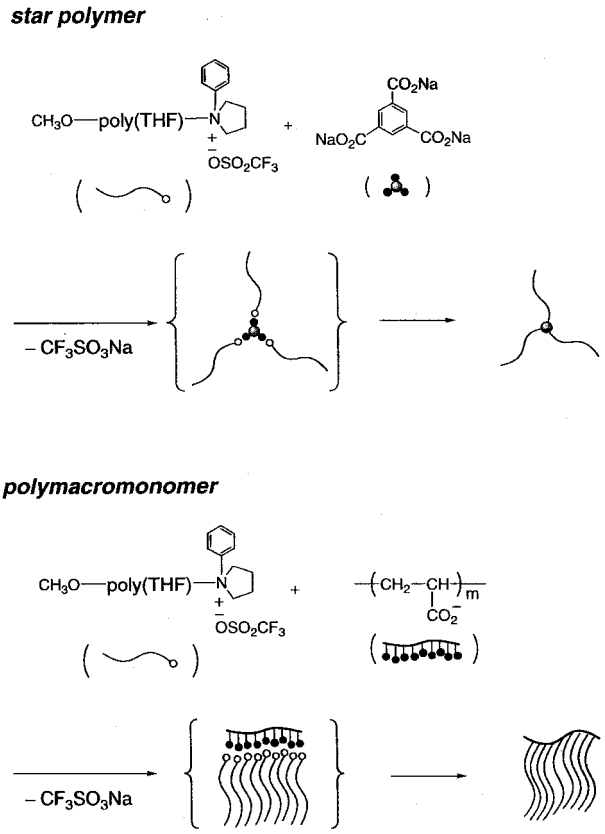
peak profile with narrow size distribution, and more significantly, a notably smaller hydrodynamic volume than that of the linear analog, which was independently prepared from the identical polystyrene precursor carrying benzoate counterions. The hydrodynamic volume ratio between cyclic and linear polymer products was in good agreement with that previously reported for cyclic and linear polymers.[29–33]

Branched Model Polymers

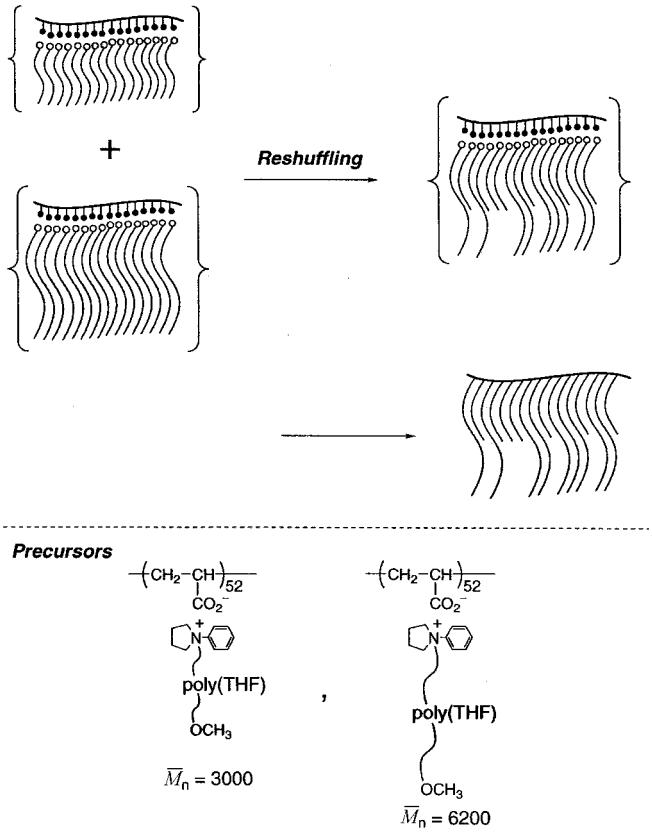
Branched model polymers, such as poly(THF) star polymers and polymacromonomers, were also synthesized. Here no dilution was required in contrast to the preceding polymer cyclization processes (Scheme 19).[22, 47, 48] An efficient ion-exchange reaction of a monofunctional poly(THF) with an *N*-phenylpyrrolidinium end group carrying tricarboxylate as the counterion occurred by repeated precipitation into an aqueous solution containing excess amounts of a sodium tricarboxylate salt. The subsequent heat treatment of the ionically assembled polymer precursor caused selective ring-opening to give a covalently linked three-arm star polymer in high yield.

The telechelic poly(THF) was then utilized in the macromolecular ion-exchange reaction with poly(sodium acrylate) through repeated precipitation (Scheme 19).[47,48] Ion-exchange proceeded quantitatively from triflate to carboxylate, and no signs of ring-opening were detected for the ion-exchanged product isolated, i.e. the electrostatically assembled polymacromonomer precursor. Subsequent heat treatment again caused the selective ring-opening reaction to give a covalently linked polymacromonomer in high yield. By using a uniformly sized poly(sodium acrylate), prepared via the living polymerization of *tert*-butyl acrylate, a well-defined poly(THF) polymacromonomer with controlled length of the backbone segments was obtained having both predetermined branch segment numbers and branch segment lengths.

The isolation of the electrostatically self-assembled precursor provides the unique opportunity for the structural manipulation of star polymers and polymacromonomers. A star *co*polymer and a *co*polymacromonomer with different types of grafted chain segments were produced by the reshuffling of electrostatically self-assembled polymer precursors (Scheme 20).[16]



Scheme 19.



Scheme 20.

In contrast, the reaction with monofunctional poly(THF) having either a four-membered cyclic ammonium or a five-membered cyclic sulfonium (tetrahydrothiophenium) end group suffered from spontaneous ring-opening caused by any carboxylate counterion even at ambient temperature. Thus the ionically assembled polymer precursor, i.e. the intermediate, could not be isolated.[49, 50]

Conclusions and Perspectives

A novel methodology has been reviewed for designing various nonlinear polymer topologies, such as monocyclic and polycyclic polymers, cyclic telechelics (*kyklo*-telechelics), cyclic macromonomers, a pair of polymeric topological isomers, and *a-ring-with-a-branch* topology polymers, as well as branched model polymers, such as star polymers and polymacromonomers. New telechelic prepolymers having moderately strained cyclic ammonium groups as a single or multiple end group(s) were prepared and subjected to ion-exchange reactions to introduce multifunctional carboxylates as counterions. The electrostatically self-assembled products formed in dilute organic solution or in bulk were then treated with heat to convert the ionic interactions into covalent linkages by means of ring-opening. A variety of topologically unique, nonlinear polymer architectures has been thus produced in high efficiency.

A wide variety of future research directions may be envisaged by extending the *electrostatic self-assembly and covalent fixation* strategy: (1) An efficient covalent conversion process not by a thermal reaction as has been described so far, but by a photo-irradiation process will add new synthetic opportunities to this system. This will be achieved by appropriate combinations of cationic/anionic pairs with respect to polymer chain end and counterion. (2) A wider selection of telechelic polymer segments other than poly(THF) and polystyrene could be attained, since, in principle, any polymers obtainable by means of the living polymerization technique can be transformed into the respective telechelics by a few modification steps of the living end groups. This will offer entirely novel multi-component polymer materials not only of contrastive polymer properties but also of different polymer topologies. (3) Reactive cyclic polymer precursors having functional groups at prescribed positions along the polymer chain – not only at the chain end, but also at designated interior positions – will open new ways to design complex and unusual polymer topologies.

Up to now, only a very limited variety of polymer topologies has been realized yet, particularly on a practical scale. A comprehensive topology map to provide a systematic classification of nonlinear polymer topologies should be formulated. This will provide deeper insights into the relationship between different polymer topolo-

gies, and will eventually bring about their rational synthetic strategies. A fascinating synthetic target, such as the well-known $K_{3,3}$ topology,[39,51] will certainly be a challenge in the field of the synthetic polymer chemistry.

The concept of topological isomerism, which is particularly unique and rather common in flexible polymer molecules, will generate a basically new branch in polymer science and technology. Finally, the visualization of various polymer topologies will be achieved either by means of X-ray crystallography using a crystallizable single molecule or by atomic force miscroscopy using a stiffened, discrete polymer object. These will undoubtedly be important steps toward the future nanotechnology.

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[1] D. Philp, J. F. Stoddart, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1154.
[2] V. Balzani, A. Credi, F. M. Raymo, J. F. Stoddart, *Angew. Chem. Int. Ed. Engl.* **2000**, *39*, 3348.
[3] N. C. Seeman, *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 3220.
[4] E. Regis, "*Nano: The Emerging Science of Nanotechnology: Remaking the World – Molecule by Molecule*", Little, Brown and Co., Boston 1995.
[5] Y. Tezuka, *Prog. Polym. Sci.* **1992**, *17*, 471.
[6] Y. Tezuka, "*Telechelic Oligomers (with cyclic onium salt groups)*", in: *Polymeric Materials Encyclopedia,* J. C. Salamone, Ed., CRC, Boca Raton 1996, Vol. 11, p. 8263.
[7] Y. Tezuka, H. Oike, *Macromol. Symp.* **2000**, *161*, 159.
[8] Y. Gnanou, *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1996**, *C36*, 77.
[9] H. Oike, Y. Yoshioka, S. Kobayashi, M. Nakashima, Y. Tezuka, E. J. Goethals, *Macromol. Rapid Commun.* **2000**, *21*, 1185, and references cited therein.
[10] M. F. Debreuil, E. J. Goethals, *Macromol. Chem. Phys.* **1997**, *198*, 3077.
[11] M. F. Debreuil, E. J. Goethals, *Macromol. Rapid Commun.* **1999**, *20*, 383.
[12] H. Oike, S. Kobayashi, Y. Tezuka, E. J. Goethals, *Macromolecules* **2000**, *33*, 8898.
[13] M. Pineri, A. Eisenberg, "*Structure and Properties of Ionomers*", D. Reidel Publishing Co., Dordrecht, The Netherlands 1987.
[14] E. Karayianni, R. Jérôme, S. L. Cooper, *Macromolecules* **1997**, *30*, 7444.
[15] E. Karayianni, R. Jérôme, S. L. Cooper, *Macromolecules* **2000**, *33*, 6473.
[16] H. Oike, H. Imaizumi, T. Mouri, Y. Yoshioka, A. Uchibori, Y. Tezuka, *J. Am. Chem. Soc.* **2000**, *122*, 9592.
[17] H. Oike, M. Washizuka, Y. Tezuka, *Macromol. Chem. Phys.* **2000**, *201*, 1673, and references cited therein.
[18] Y. Tezuka, H. Imai, T. Shiomi, *Macromol. Chem. Phys.* **1997**, *198*, 627.
[19] Y. Tezuka, T. Iwase, T. Shiomi, *Macromolecules* **1997**, *30*, 5220.
[20] H. Oike, H. Hatano, Y. Tezuka, *React. Funct. Polym.* **1998**, *37*, 57.
[21] H. Oike, F. Kobayashi, Y. Tezuka, S. Hashimoto, T. Shiomi, *Macromolecules* **1999**, *32*, 2876.
[22] H. Oike, H. Imamura, H. Imaizumi, Y. Tezuka, *Macromolecules* **1999**, *32*, 4819.
[23] Y. Tezuka, T. Shida, T. Shiomi, K. Imai, E. J. Goethals, *Macromolecules* **1993**, *26*, 575.
[24] J. A. Semlyen, "*Cyclic Polymers Second Edition*", Kluwer Academic Publishers, Dordrecht, The Netherlands 2000.
[25] V. Bloomfield, B. H. Zimm, *J. Chem. Phys.* **1966**, *44*, 315.
[26] H. C. Lee, H. Lee, W. Lee, T. Chang, J. Roovers, *Macromolecules* **2000**, *33*, 8119.
[27] T. Chang, H. C. Lee, W. Lee, S. Park, C. Ko, *Macromol. Chem. Phys.* **1999**, *200*, 2188.
[28] H. Oike, S. Kobayashi, T. Mouri, Y. Tezuka, *Macromolecules* **2001**, *34*, 2742.
[29] J. Roovers, P. M. Toporoski, *Macromolecules* **1983**, *16*, 843.
[30] T. E. Hogen-Esch, J. Sundararajan, W. Toreki, *Makromol. Chem., Macromol. Symp.* **1991**, *47*, 23.
[31] A. Deffieux, M. Schappacher, *Macromol. Symp.* **1995**, *95*, 103.
[32] L. Rique-Lurbet, M. Schappacher, A. Deffieux, *Macromolecules* **1994**, *27*, 6318.
[33] M. Kubo, T. Hayashi, H. Kobayashi, K. Tsuboi, T. Ito, *Macromolecules* **1997**, *30*, 2805.
[34] H. Oike, T. Mouri, Y. Tezuka, *Macromolecules,* **2001**, *34*, 6229.
[35] D. A. Thomas, L. H. Sperling, in: *Polymer Blends*, vol. 2, D. R. Paul, S. Newman, Eds., Academic Press, New York 1978.
[36] C. Gong, H. W. Gibson, *J. Am. Chem. Soc.* **1997**, *119*, 8585.
[37] A. Zada, Y. Avny, A. Zilkha, *Eur. Polym. J.* **2000**, *36*, 359.
[38] "*Molecular Catenanes, Rotaxanes and Knots*", J. P. Sauvage, C. Dietrich-Buchecker, Eds., Wiley-VCH, Weinheim 1999.
[39] D. M. Walba, *Tetrahedron* **1985**, *41*, 3161.
[40] H. L. Frisch, E. Wasserman, *J. Am. Chem. Soc.* **1961**, *83*, 3789.
[41] C. Seel, F. Vögtle, *Chem. Eur. J.* **2000**, *6*, 21.
[42] H. Dodziuk, K. S. Nowinski, *Tetrahedron* **1998**, *54*, 2917.
[43] H. Oike, M. Hamada, S. Eguchi, Y. Danda, Y. Tezuka, *Macromolecules* **2001**, *34*, 2776, and references cited therein.
[44] Y. Gan, D. Dong, S. Carlotti, T. E. Hogen-Esch, *J. Am. Chem. Soc.* **2000**, *122*, 2130, and references cited therein.
[45] K. Ishizu, X. X. Shen, *Polymer* **1999**, *40*, 3251.
[46] Y. Tezuka, Y. Murakami, T. Shiomi, *Polymer* **1998**, *39*, 2973.
[47] H. Oike, H. Imamura, Y. Tezuka, *Macromolecules* **1999**, *32*, 8666.
[48] H. Oike, H. Imamura, Y. Tezuka, *Macromolecules* **1999**, *32*, 8816.
[49] H. Oike, T. Yaguchi, Y. Tezuka, *Macromol. Chem. Phys.* **1999**, *200*, 768.
[50] Y. Tezuka, S. Hayashi, *Macromolecules* **1995**, *28*, 3038.
[51] C.-T. Chen, P. Gantzel, J. S. Siegel, K. K. Baldridge, R. B. English, D. M. Ho, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2657.