Topological polymer chemistry

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Abstract

Recent developments in designing non-linear polymer topologies comprising cyclic and branched segments are reviewed. Thus first, a systematic classification of non-linear polymer topologies is presented by reference to constitutional isomerism in a series of alkanes (C_nH_{2n+2}), monocycloalkanes (C_nH_{2n}) and polycycloalkanes (C_nH_{2n-2}, C_nH_{2n-4}, etc.). A special emphasis is placed on constitutional isomerism as well as stereoisomerism occurring uniquely in such non-linear polymer molecules as cyclics, knots and catenanes. Secondly, a novel strategy based on an 'electrostatic self-assembly and covalent fixation' process is described to realize a variety of topologically unique polymer architectures. Those include monocyclic and polycyclic polymers, polymeric topological isomers, cyclic macromonomers and cyclic telechelics (*kyklo*-telechelics) and 'a ring with a branch' topology polymers, as well as such model branched polymers as star polymers and polymacromonomers. In this process, new telechelic polymer precursors having a moderately strained cyclic onium salt group as single or multiple end groups carrying multifunctional carboxylate counteranions have been prepared through an ion-exchange reaction. The unique electrostatic self-assembly directed by these polymer precursors, particularly in a diluted organic solution, is transformed into the covalent product by the heat treatment of the polymer precursor, causing the ring-opening reaction to produce a variety of topologically unique, non-linear polymer architectures in high efficiency. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer topology; Telechelics; Self-assembly; Review

Contents

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1. Introduction

The precise architectural control in polymer molecules has been a principal subject in synthetic polymer chemistry, since new polymer topologies can provide unprecedented properties and functions in polymeric materials. Thus, such branched polymer topologies [1–15] have been constructed as 'star' polymers, 'H-shaped' polymers, 'super H-shaped' polymers, 'pom–pom shaped' polymers, as well as 'comb' polymers (polymacromonomer) [16–23] and 'dendrimers' [24–28], in addition to such cyclic, multicyclic and cyclic-branched combined polymers [29] as 'ring' polymers, '8-shaped' polymers as well as 'tadpole' polymers. Other topologically unique (macro)molecules as catenanes, rotaxanes and knots have also gaining a growing interest, and intrigued self-assembly processes through non-covalent interactions of precursor components have been applied to construct these supramolecules [29–31].

The 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 drawn 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 make [32–34]. And this will provide important opportunities to realize unprecedented properties and functions, eventually leading to the future 'nanotechnology' [35–37].

In this review article, we first present a systematic classification of non-linear polymer topologies by reference to constitutional isomerism in a series of alkanes (C_nH_{2n+2}), monocycloalkanes (C_nH_{2n}) and polycycloalkanes (C_nH_{2n-2}, C_nH_{2n-4}, etc.). In this classification, the total number of chain ends (termini) and of branch points (junctions) are maintained as invariant parameters, as well as the number of branches at each junction and the connectivity of junctions. On the other hand, the distance between two adjacent junctions and that between the junction and terminus are taken as variant parameters. A special emphasis is placed on constitutional and stereoisomerism occurring uniquely in non-linear polymer molecules, such as cyclics, knots and catenanes. We show subsequently a novel methodology to produce various non-linear polymer architectures in exceptionally high efficiency, by exploiting the self-assembly principle to preorganize linear or star-shaped polymer precursors, prior to convert them into covalently linked permanent structures. Thus, we have utilized a self-assembly through a Coulombic interaction of hydrophobic macromolecules having specific cationic end groups, namely moderately strained cyclic onium salt groups, carrying multifunctional carboxylates as counteranions [38–41].

## 2. Systematic classification of non-linear polymer topologies

A classification of non-linear polymer topologies will lay a basis for the elucidation of structural relationships between different macromolecular compounds, and eventually of their rational synthetic pathways. A rational classification can also give a systematic nomenclature. Thus, the classification of dendrimers [42–44], as well as 'knots' [45], 'catenanes' [46] and 'rotaxanes' [47] have so far been reported. The fundamental mathematical theory of knots has also been a subject of active investigations [48], giving unique insights in topological features of (macro)molecular architectures. However, there have been few attempts [49–51] on the systematic classification of non-linear, and in particular cyclic and multicyclic polymer architectures composed of sufficiently long and thus flexible segment components.[2]

A systematic classification of a series of well-defined cyclic and branched polymer architectures is presented by reference to constitutional isomerism in alkanes (C_nH_{2n+2}) and in a series of mono- and polycycloalkanes (C_nH_{2n}, C_nH_{2n-2}, etc.) [56]. Each alkane and (poly)cycloalkane molecules is taken as a source according to the procedure by Walba [57], in order to generate a unique topological construction. Thus first, the total number of termini (chain ends) and of junctions (branch points) are maintained as invariant (constant) geometric parameters. The total number of branches at each junction and the connectivity of each junction are preserved as invariant parameters as well. Such Euclidian geometric properties as the distance between two adjacent junctions and that between the junction and terminus are taken, on the other hand, as variant parameters, to conform with the flexible nature of the randomly coiled and constrained polymer segments. Furthermore, topological constructions having five or more

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[2] In this connection, the mathematical graph theory has been applied for the enumeration of isomeric structures in various chemical substances [52–54] and the nomenclature based on the graph theorem has also been proposed [55].

Table 1

Topological constructions produced by reference to alkane isomers (C_nH_{2n+2}: $n = 3$–7) (Reprinted with permission from Ref. [56]. Copyright, 2001 by American Chemical Society)

branches at one junction can be produced while the relevant isomers having the corresponding molecular formula are absent.
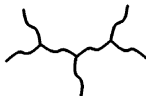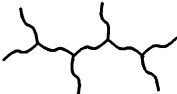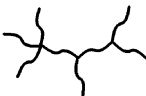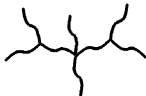
Topological constructions having, in particular, cyclic polymer units have been classified into different main-classes and sub-classes, and their topological relationships have subsequently been compared. Especially, a set of 'topological isomers' [58–69] is of a particular interest, since they possess topologically different architectures although produced from an identical set of polymer precursors and chain-linking reagents. Finally, a rational synthetic strategy by an electrostatic self-assembly and covalent fixation process [70–78] has been presented to produce a variety of non-linear polymer topologies.

2.1. Branched topologies

Alkane molecules of generic molecular formula C_nH_{2n+2} with $n = 3$–7 and their relevant topological constructions are shown in Table 1. A point from methane (CH_4) and a line construction from ethane (C_2H_6) are not included since the former is not significant with respect to polymer topology and the latter

Table 2
Selected topological constructions produced by reference to alkane isomers (C_nH_{2n+2}: $n = 8-10$ and m) (Reprinted with permission from Ref. [56]. Copyright, 2001 by American Chemical Society)

Topology	C_8H_{18}	Topology	$C_{10}H_{22}$
$A_8(5,3)$		$A_{10}(6,4)[3-3(3)-3]$	
$A_8(6,2)$		$A_{10}(6,4)[3-3-3-3]$	
Topology	C_9H_{20}		
$A_9(6,3)[4-3-3]$		$A_{m+1}[m,1]$ **m-Arm Star Polymer**	
$A_9(6,3)[3-4-3]$			

produces an equivalent topological construction from propane (C_3H_8). In Table 2, selected topological constructions by reference to their corresponding higher alkane molecules of C_nH_{2n+2} with $n > 7$ are listed. A series of star polymers having 3, 4, 5 or 6-arms [1–15,79–82], an H-shaped polymer and a super H-shaped polymer [2,50] given in Tables 1 and 2 have so far been synthesized as model branched polymers as distinct from linear polymers.

As seen in Table 1, two butane isomers produce a linear and a three-armed star construction, respectively. Likewise, pentane isomers produce a four-armed star construction in addition to the two already produced from butane isomers. From five hexane isomers, two new constructions of an H-shaped and of a five-armed star architecture are produced. And further, heptane isomers produce the two new constructions of a super H-shaped and a six-armed star architectures. Thus by this process, a series of branched polymer topologies can be relevantly ranked as shown in Table 1.

A systematic notation for a series of branched topologies is thus introduced as listed in Table 1. All these constructions are classified as A main-class, since they are produced from alkane isomers. A linear construction is produced from propane (C_3H_8) and this particular topology is ubiquitous in those from all higher alkanes. This sub-class construction is thus termed A_3, or alternatively $A_3(2,0)$ by showing the total number of termini and of junctions, respectively, in parentheses. Likewise, sub-classes A_4 (or $A_4(3,1)$) and A_5 (or $A_5(4,1)$) are uniquely defined as shown in Table 1. On the other hand, sub-classes A_6, A_7 and A_n of higher n values consist of multiple constructions, and each component can be defined by

specifying the total number of termini and junctions, respectively, in parentheses as shown in Table 1. As a typical example, an *m*-armed star polymer topology is classified $A_{m+1}(m, 1)$, as listed in Table 2.

Also in Table 2, selected constructions from octane and higher alkane isomers are collected. Thus in sub-class A_8, the two new constructions are defined again by specifying their total numbers of termini and junctions, respectively, in parentheses, i.e. $A_8(5,3)$ and $A_8(6,2)$. In sub-class A_9, on the other hand, two of the newly produced constructions of $A_9(6,3)$ cannot be distinguished by showing merely the total numbers of termini and junctions. The connectivity of junctions for these two constructions is each distinctive, and can be specified by applying the nomenclature rule for substituted alkanes. That is, first a 'backbone' chain having the most junctions is identified, and the number of branches at each junction is given in brackets in descending order from the most substituted junction. Thus, the above two $A_9(6,3)$s are designated as $A_9(6,3)[4-3-3]$ and $A_9(6,3)[3-4-3]$, respectively. Another pair of constructions in sub-class $A_{10}(6,4)$ in Table 2, namely one having a dendrimer-like star polymer structure [9] and another having a comb-like branched structure, are defined by specifying their junction connectivity, as $A_{10}(6,4)[3-3(3)-3]$ for the former and $A_{10}(6,4)[3-3-3-3]$ for the latter, respectively.

From a topological viewpoint, it is important to note that a series of branched constructions in Tables 1 and 2 is distinct from dendrimers (dendritic polymers possessing well-defined branched structures) and comb-shaped polymers, although they are also referred as model branched macromolecules having well-defined structures. Thus, the topological constructions produced above are based on the assumption that the distance between two adjacent junctions and between the junction and the terminus are variable geometric parameters. This conforms to the flexible nature of sufficiently long polymer chains capable of assuming a random coil conformation. In dendrimers, on the other hand, the distance between two adjacent junctions and between the junction and the terminus are regarded to be invariant. Consequently, they tend to constitute a stiff, shape-persistent molecule possessing a gradient of structural density [19,83]. For comb-shaped polymers, likewise, the distance between two junctions along the backbone are regarded as invariant, whereas the branch chain is either flexible (polymacromonomers) [16,84–87] or stiff (dendron-jacketed polymers) [19,88,89].

2.2. Cyclic topologies

2.2.1. Monocyclic topologies

Monocycloalkane molecules of C_nH_{2n} with up to $n = 6$ and their relevant topological constructions are listed in Table 3. Additional constructions produced from higher monocycloalkane isomers of C_7H_{14} and C_8H_{16} are shown in Table 4. They are produced according to the procedure applied for the A main-class, branched topologies. Among these polymer architectures, a variety of simple 'ring' polymers [70–72,90–97], tadpole polymers having 'a ring with a branch' architecture [70,98–100] as well as 'a ring with two branches' architecture [77,101] have so far been synthesized.

A simple cyclic topology is produced from cyclopropane (C_3H_6). From the two isomers of C_4H_8, two constructions, namely one having a ring with a branch architecture and another having a simple ring structure, respectively, are produced. The latter is topologically equivalent to one produced from cyclopropane. Two new constructions are produced from C_5H_{10} isomers, in addition to those observed either from C_3H_6 or C_4H_8 isomers. These two constructions are distinguished from each other by their junction and branch structures, i.e. one has two outward branches at one common junction in the ring unit while

Table 3
Topological constructions produced by reference to cycloalkane isomers (C_nH_{2n}: $n = 3$–6)
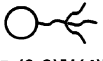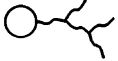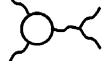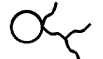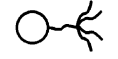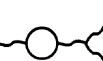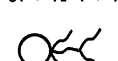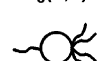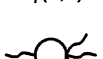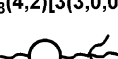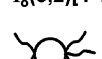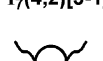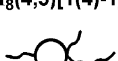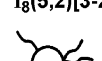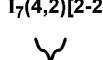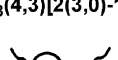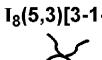
the other has two outward branches located at two separate junctions in the ring unit. Four new topological constructions are subsequently produced by reference to C_6H_{12} isomers; the one having five branches at one junction is hypothetical (and is therefore shown in parentheses in Table 3). Thus by this process, a series of 'a ring with branches' constructions has been ranked by reference to the constitutional isomerism in monocycloalkanes.

Table 4

Topological constructions produced by reference to cycloalkane isomers (C_nH_{2n}: $n = 7$ and 8)
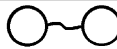
Topology	C_7H_{14}	Topology	C_8H_{16}	Topology	C_8H_{16}
$I_7(3,2)[1(4)]$		$I_8(3,3)$		$I_8(4,4)[1(3)\text{-}1\text{-}1]$	
$I_7(3,2)[2(3,0)]$		$I_8(4,2)[1(5)]$		$I_8(4,4)[1\text{-}1\text{-}1\text{-}1]$	
$I_7(3,3)$		$I_8(4,2)[2(4,0)]$		$I_8(5,1)$	
$I_7(4,1)$		$I_8(4,2)[3(3,0,0)]$		$I_8(5,2)[4\text{-}1]$	
$I_7(4,2)[3\text{-}1]$		$I_8(4,3)[1(4)\text{-}1]$		$I_8(5,2)[3\text{-}2]$	
$I_7(4,2)[2\text{-}2]$		$I_8(4,3)[2(3,0)\text{-}1]$		$I_8(5,3)[3\text{-}1\text{-}1]$	
$I_7(4,3)$		$I_8(4,3)[2\text{-}1(3)]$		$I_8(5,3)[2\text{-}2\text{-}1]$	

A systematic notation for a series of 'a ring with branches' constructions has been accordingly introduced as given in Table 3. First, these are classified into a I main-class topology, since they are produced from *mono*cycloalkanes. Then, a simple ring construction produced from cyclopropane is designated as sub-class I_3, or alternatively $I_3(0,0)$ by showing the total number of termini and junctions in parentheses. This topology is ubiquitous among all higher sub-classes in the I main-class. A new construction from C_4H_8 is labeled likewise as I_4 or $I_4(1,1)$. As is evident from Table 3, sub-classes I_5, I_6 and other I_n comprise multiple constructions, and each of them can be basically identified by specifying the total number of termini and junctions.

In Table 4, the newly produced constructions from monocycloalkane isomers of C_7H_{14} and of C_8H_{16} are shown. Seven new constructions are produced in sub-class I_7, and most of them are uniquely defined again by specifying the total number of termini and junctions, respectively, in parentheses. The two sub-classes $I_7(3,2)$ and $I_7(4,2)$, however, contain two distinctive constructions. Thus, they are identified by specifying their branch modes on a ring unit. First, the number of outward branches at each junction on the ring unit is identified, and is indicated in the brackets placed after the closing parenthesis. The detailed junction architecture of the outward branches is then identified, according to the procedure applied to the A main-class topology, and is indicated in the parentheses enclosed within the brackets. The two constructions of $I_7(3,2)$ are thus defined as $I_7(3,2)[1(4)]$ and $I_7(3,2)[2(3,0)]$, respectively.

Table 5
Topological constructions produced by reference to bicycloalkane isomers (C_nH_{2n-2}: $n = 4$–6) (Reprinted with permission from Ref. [56]. Copyright, 2001 by American Chemical Society)

Likewise, the two constructions of $I_7(4,2)$ are labeled as $I_7(4,2)[3-1]$ and $I_7(4,2)[2-2]$, respectively, where the connectivity of junctions along the ring unit is indicated by connecting the number of the outward branches at each junction with a hyphen.

It is also shown that all constructions up to sub-class I_7 are produced initially from the relevant isomer containing a cyclopropane unit. In the higher sub-class I_8, a topological construction containing four or more junctions on the ring unit is first produced by reference to a relevant isomer containing a cyclo-butane unit, i.e. $I_8(4,4)$.

2.2.2. Multicyclic topologies

Bicycloalkanes of C_nH_{2n-2} with up to $n = 6$ and their relevant topological constructions are listed in Table 5, where three basic bicyclic constructions without any outward branches are included; namely,

Table 6

Fused and spiranic ring constructions produced by reference to tricycloalkane isomers (C_nH_{2n-4}: $n = 4–7$) (Reprinted with permission from Ref. [56]. Copyright, 2001 by American Chemical Society)
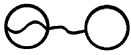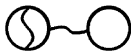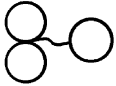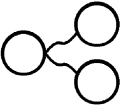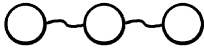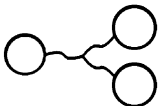
‘θ-shaped’ or internally linked (fused) rings, ‘8-shaped’ or spiranic rings and ‘manacle-shaped’ rings, i.e. two rings externally linked (or ‘bridged’) by a linear chain. Moreover, 15 basic tricyclic constructions without any outward branches, which are produced by reference to the corresponding tricycloalkanes of $C_nH_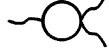{2n-4}$ with $n = 4–10$, are shown in Tables 6 and 7, respectively. And so far, the three basic bicyclic polymer architectures, i.e. ‘8-shaped’ polymers [70,71,99,101–104], a ‘θ ring’ polymer [70] and a manacle-shaped polymer [70] as well as one of basic tricyclic polymers, i.e. triple ring polymer [70] have been synthesized.

First, a ‘θ ring’ construction is produced from bicyclo[1,1,0]butane, C_4H_6. From the five bicycloalkane isomers of C_5H_8, three new constructions are produced. One of them is a ‘spiranic (8-shaped) rings’ construction from spiro[2,2]pentane. These three constructions are distinguished from each other by their total number of termini and junctions as compared in Table 5. By reference to bicyclohexane

Table 7
Bridged rings constructions produced by reference to tricycloalkane isomers (C_nH_{2n-4}: $n = 7-10$) (Reprinted with permission from Ref. [56]. Copyright, 2001 by American Chemical Society)

(C_6H_{10}) isomers, moreover, eight new constructions are produced. All constructions but one from bi(cyclopropane) possess outward branches emanated from either θ rings or spiranic (8-shaped) rings shown earlier. In this manner, a series of internally and externally linked double cyclic topological constructions can be classified into the corresponding categories by reference to the bicycloalkane isomers.

A systematic notation for a series of topological constructions in Table 5 is then introduced, as in the A and I main-classes. These are classified into a II main-class topology, since they are produced from

*bi*cycloalkane isomers. A θ form construction, which is produced from bicyclo[1,1,0]butane, and is often observed in those from higher bicycloalkanes, is defined as sub-class II_4, or $II_4(0,2)$ by showing the total number of termini and junctions, respectively, in parentheses. Sub-classes II_5 and II_6 consist of multiple constructions as shown in Table 5, namely three for II_5 and eight for II_6, respectively. While they are basically distinguished by specifying their total number of termini and junctions in parentheses, sub-classes $II_6(2,2)$ and $II_6(2,3)$ comprise distinctive constructions that require further structural specifications. Thus in the brackets after the closing parenthesis, the number of not only outward branches but also internally linked branches on the ring unit is indicated, and these numbers (thus 0 for the latter, and 1, 2,… for the former) are linked by hyphens. Moreover, the positions of the two specific junctions internally linked to each other are indicated by giving superscripts (a, b, etc.) at the relevant junction numbers. For examples, the two $II_6(2,2)$s are designated as $II_6(2,2)[2^a\text{-}0^a]$ and $II_6(2,2)[1^a\text{-}1^a]$, and the two $II_6(2,3)$s are designated as $II_6(2,3)[2\text{-}0^a\text{-}0^a]$ and $II_6(2,3)[1^a\text{-}1\text{-}0^a]$, respectively. Accordingly, any branching modes in an internally linked ring unit can be uniquely defined.

All constructions in the II main-class contain one of either three types of internally or externally linked ring units, i.e. θ rings like a construction $II_4(0,2)$, spiranic (8-shaped) rings like $II_5(0,1)$ or manacle-shaped rings like $II_6(0,2)$. A variety of 'rings with branches' constructions is also obtainable by emanating from these ring units. They are produced primarily from the corresponding isomers containing cyclopropane units, as was noted in the I main-class topologies. Indeed, all constructions up to sub-class II_6 are produced first from the relevant isomers containing exclusively cyclopropane units, as seen in Table 5.

Furthermore, 15 basic topological constructions produced from the relevant tricycloalkanes of C_nH_{2n-4} with $n = 4$–10 are shown in Tables 6 and 7. A large number of rings with branches constructions are also produced in this group, but are omitted for brevity. Thus, eight topological constructions are produced as θ or spiranic (8-shaped) forms as shown in Table 6. The six of them are produced directly from the corresponding tricycloalkanes, and the additional two from hypothetical molecular formula possessing five or six branches at a junction as given also in Table 6. Moreover, the seven topological constructions of externally linked (or bridged) rings with a simple cyclic, θ or spiranic (8-shaped) forms are obtainable in reference to the relevant tricycloalkane isomers as listed in Table 7.

A systematic notation for a series of topological constructions in Tables 6 and 7 is then introduced as in the previous A, I and II main-classes. These are classified into III main-class, since they are produced from tricycloalkane isomers, respectively. A 'doubly fused' (internally double-linked) ring construction is produced, in the first place, from tetrahedrane and is defined as sub-class III_4 or $III_4(0,4)$ by showing the total number of termini and junctions, respectively, in parentheses. The two constructions in sub-class III_5 and the three in sub-class III_6 shown in Table 6 are a few of the large number of possible constructions, in particular those possessing additional branches. Constructions in sub-classes $III_4(0,4)$, $III_5(0,2)$, $III_5(0,3)$ and $III_6(0,4)$ commonly possess a doubly fused ring unit, while their linking modes on the ring unit are distinctive. In mathematical graph theory, they are named as α, δ, γ and β ring, respectively [105]. Their notations are accordingly given in Table 6. For instance, the architectures of $III_4(0,4)$, $III_5(0,2)$ and $III_5(0,3)$ are further specified by indicating their linking modes as $[0^a\text{-}0^b\text{-}0^a\text{-}0^b]$, $[0^{a,b}\text{-}0^{a,b}]$ and $[0^{a,b}\text{-}0^a\text{-}0^b]$, respectively. On the other hand, bridged rings constructions listed in Table 7 are defined distinctively by showing merely the total number of termini and junctions respectively in parentheses.

2.3. Topological Isomers and homologues

On the basis of the classification of non-linear polymer topologies into A, I, II and III main-classes, and further into sub-classes, the structural relationship between different polymer architectures and a subsequent rational synthetic strategy for a variety of topologically unique macromolecular architectures has been elucidated.

First, a set of different topological constructions belonging to different sub-classes, but possessing identical terminus and junction numbers, has been compared. A set of $I_5(2,2)$ and $I_6(2,2)$ is a typical example. It is intuitively recognized that these two constructions are produced from an identical precursor set of telechelic (end-reactive) polymers and end-linking reagents, i.e. two bifunctional and two monofunctional polymer precursors and two trifunctional end-linking reagents (Scheme 1). Since they are produced from the identical precursors by common chemical reactions, their chemical compositions are identical with each other, since they possess an identical molecular weight. They are, on the other hand, distinctive from each other with respect to their topologies. They are thus regarded as a pair of constitutional isomers, and more specifically as 'topologically distinctive constitutional isomers' (Further discussion is given in Section 3). Such topological isomerism frequently occurs among
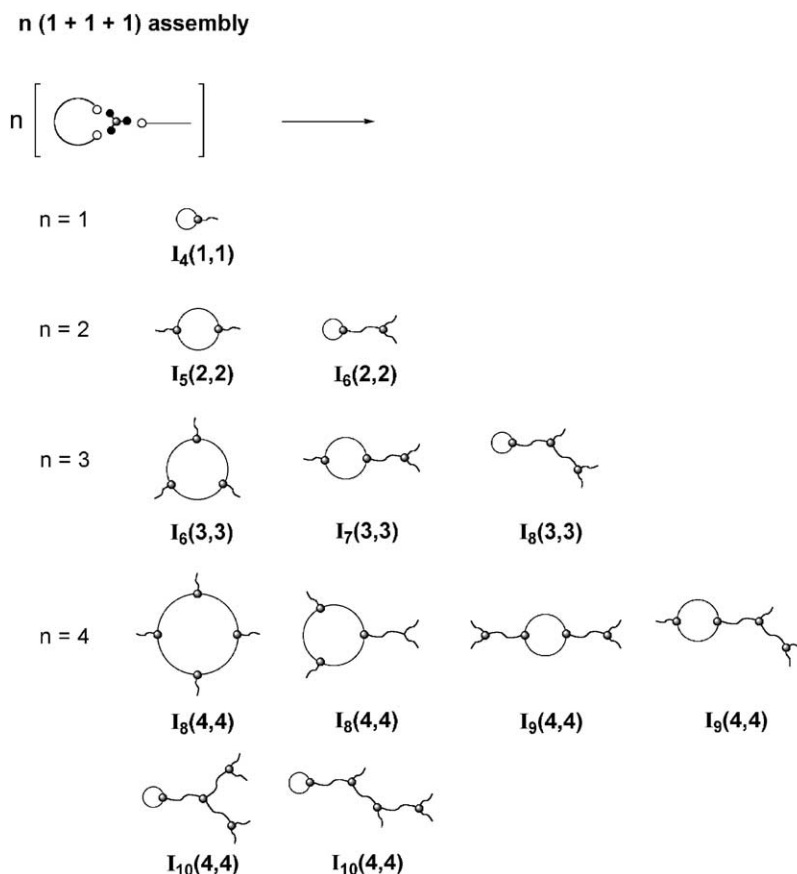
Scheme 1. Reprinted with permission from Ref. [56]. Copyright, 2001 by American Chemical Society.

3 + 2 assembly

2 + 3 assembly

$\Pi_4(0,2)$　　　　　　　　$\Pi_6(0,2)$
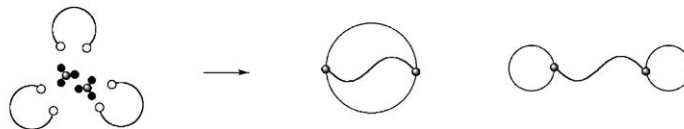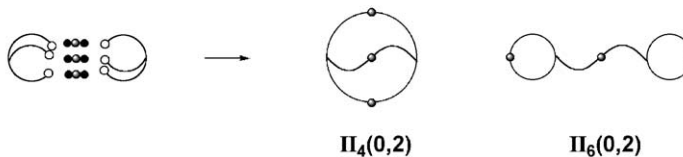
Scheme 2. Reprinted with permission from Ref. [56]. Copyright, 2001 by American Chemical Society.

constructions in the I, II or III main-classes; though also observed in the A main-class topologies, as in $A_9(6,3)$ and $A_{10}(6,4)$ shown in Table 2. A number of topological isomer pairs are observed in the I main-class listed in Tables 3 and 4, including the three in sub-classes $I_6(3,3)$, $I_7(3,3)$ and $I_8(3,3)$, and the three in sub-classes $I_6(3,2)$, $I_7(3,2)[1(4)]$ and $I_7(3,2)[2(3,0)]$.

Another notable pair of topological isomers is observed in the II main-class, namely the two constructions of $\Pi_4(0,2)$ and $\Pi_6(0,2)$. These are again the product of an identical set of telechelic (end-reactive) polymer precursors and end-linking reagents, i.e. three bifunctional polymer precursors and two tri-functional end-linking reagents, or two trifunctional star polymer precursors and three bifunctional end-linking reagents (Scheme 2). We have recently succeeded in the synthesis and the subsequent chromatographic separation of this particular type of topological isomer [70]. Other pairs of topological isomers in the II and III main-classes listed in Tables 5–7 include: the two constructions of $\Pi_5(1,2)$ and $\Pi_6(1,2)$, the two of $\text{III}_4(0,4)$ and $\text{III}_6(0,4)$, and the two of $\text{III}_5(0,2)$ and $\text{III}_7(0,2)$.

Secondly, a series of constructions belonging to different sub-classes, while their terminus and junction numbers are in a regular order from one to another, has been compared. A group of sub-classes $I_4(1,1)$, $I_5(2,2)$, $I_6(2,2)$, $I_6(3,3)$, and $I_7(3,3)$ is an typical example to note (Scheme 1). It is recognized that the two topological isomers of $I_5(2,2)$ and $I_6(2,2)$, the three of $I_6(3,3)$ and $I_7(3,3)$ are the products of twice and three times, respectively, of a precursor set for the production of the $I_4(1,1)$, namely one mono-functional and one bifunctional polymer precursors and one trifunctional end-linking reagent (Scheme 1). This reveals a hierarchy of a 'homologous' series of polymer topologies deduced from the classification of non-linear topological constructions.

Thirdly, a group of topological constructions possessing the relevant terminus and junction numbers, while belonging to different main-classes in either II or III has been compared. Thus, the two constructions of $\text{III}_5(0,2)$ and $\text{III}_7(0,2)$, are produced from twice of a precursor set for the production of a construction of $\Pi_5(0,1)$, namely two bifunctional polymer precursors and one tetrafunctional end-linking reagent (Scheme 3).

By taking into account for the hierarchy of a variety of basic topological polymer architectures, a synthetic strategy for these polymer topologies has been formulated by an electrostatic self-assembly and covalent fixation process [70]. This provides an efficient means for the end-linking reaction of

n (2 + 1) assembly
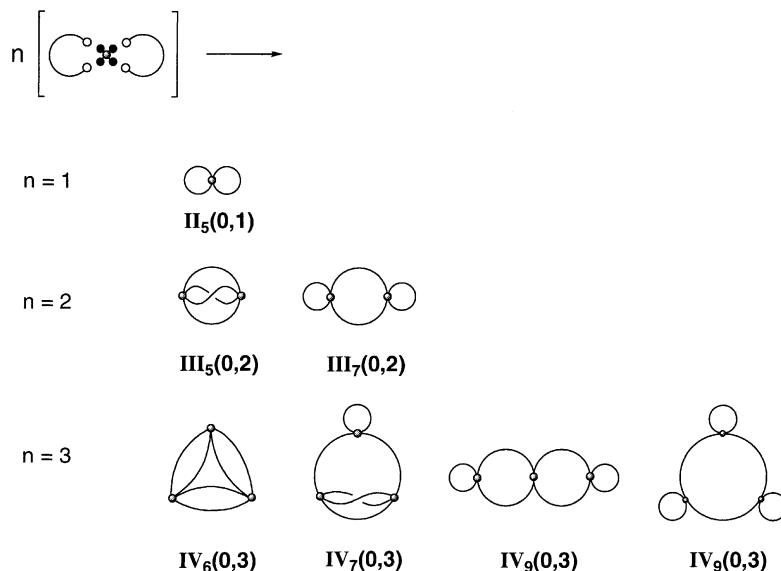
Scheme 3. Reprinted with permission from Ref. [56]. Copyright, 2001 by American Chemical Society.

various telechelic (end-reactive) polymer precursors of either mono-, bi-, or trifunctionalities having moderately strained cyclic ammonium salt groups. Thus, the introduction of multifunctional carboxylates as counteranions, followed by the covalent conversion through the ring-opening reaction of strained cyclic ammonium salt groups by carboxylate counteranions under appropriate dilution in organic medium, has been proceeded efficiently. And as detailed in the following sections, we have so far succeeded in synthesizing such unique polymer topologies as a simple ring, $I_3(0,0)$, an 8-shaped, $II_5(0,1)$, a tadpole, $I_4(1,1)$, a twin-tailed tadpole, $I_5(2,1)$ as well as a topological isomer pair of a θ ring $II_4(0,2)$ and 'manacle'-shaped rings $II_6(0,2)$ and a triple ring, $III_7(0,1)$ constructions [70–73,77].

3. Topological isomerism in macromolecular cyclics, knots and catenanes

Isomerism [106], termed from Greek 'isos' (equal) and 'meros' (part) by Berzelius in 1830 [107], has been a fundamental concept in chemistry. Isomers are a set of compounds possessing the same chemical constitution (thus molar mass) but different properties. The distinctive properties arise from uninterconvertible 3D structure of the isomers. Since Kekulé [108], the recognition of diverse classes in the isomerism has continuously brought about deeper insights in both static and dynamic structures of chemical substances. In organic chemistry, isomers are basically classified into constitutional (structural) isomers and stereoisomers. The former are the isomers of distinctive 'connectivity' with respect to atoms or atomic groups, while the latter are the isomers of indistinguishable *connectivity*, but distinctive each other based on the Euclidian geometric rigidity of molecules, such as the restriction of bond angle bending and of bond rotation. Recently, an increasing number of topologically unique molecules such as

cyclics [29], knots [30,31] and catenanes [30,31] have been synthesized not merely from scientific attraction by their forms but also from technological quest for molecular devices and molecular machines [33]. Topological properties uniquely attainable by these molecules have been conjectured by mathematic theories of knots, links and graphs [48], and remarkably topological chirality of a trefoil knot molecule has been experimentally verified [109]. A new conception is presented to account for the isomerism in flexible macromolecular cyclics, knots and catenanes [110], in reference with the classical constitutional isomerism and stereoisomerism, for which the molecular graphs are expressed based on Euclidian geometric invariants.

In contrast with extensive studies on the topological *stereo*isomerism occurring in cyclics, knots and catenanes [57–59], the *constitutional* isomerism has been received comparatively less attention from the topological viewpoint. In classical constitutional isomers, the *connectivity* of compositional atoms or atomic groups is distinctive each other. For example, dimethyl ether, CH_3OCH_3, and ethanol, CH_3CH_2OH, are distinctive in their links between atoms. Likewise, *n*-butane and *iso*-butane are distinctive in the variety of compositional atomic groups, namely two CH_3 and two CH_2 groups for the former, and three CH_3 and one CH groups for the latter. Moreover, and to be significant in topological viewpoint, another class of constitutional isomerism occurs, as typically observed in hexane. Among constitutional isomers of hexane, 2-methyl and 3-methyl pentanes are made of common atomic groups, i.e. three CH_3, two CH_2 and one CH groups. The isomerism arises from the distinctive linking mode of these groups. These show diverse classes of the *connectivity* conception in the classical constitutional isomerism. And it is notable that the molecular graphs of 2-methyl and 3-methyl pentane are topologically equivalent, i.e. interconvertible by the topological transformation by conceptual continuous deformation of lines (chains) in the molecular graph. This corresponds to a pair of star polymers having the same arm numbers and the same total arm length, but having different sets of arm length composition (Scheme 4). Since the total chain length of the molecular graphs corresponds to the molar mass, it should be maintained as well as the number of junctions and terminus during this topological transformation process, though this is not exactly conforming with the theorem of topological geometry. The molecular graphs of other hexane isomers are, on the other hand, topologically distinctive each other, as they are distinctive in the variety of compositional atomic groups (CH_3, CH_2, CH and C groups).

There exist another class of constitutional isomers made of the same variety of atomic groups but having topologically distinctive molecular graphs. An example observed in alkanes is shown in Scheme 4. A dendritic type and a comb type decane molecules are isomers both comprised of six CH_3 and four CH groups, but possess topologically distinctive molecular graphs. Thus, we call this particular type of constitutional isomers as topologically distinctive constitutional isomers in contrast to another set of constitutional isomers of 2-methyl and 3-methyl pentanes as 'topologically equivalent constitutional isomers'. As we will show later, topologically distinctive constitutional isomers are often observed in macromolecular cyclics, knots and catenanes (Scheme 4).

The interconversion (or isomerization) process in classical constitutional isomers and in classical stereoisomers intrinsically differs each other in the expression of the molecular graphs. Since the former are distinctive in their *connectivity*, the chain-breaking with at least two appropriate positions is required, followed by the chain-rearrangement and the chain-recombination to complete the process. On the other hand, for the interconversion in the molecular graphs of a pair of classical stereoisomers, the chain-breaking process is not required but the conceptual unrestricted deformation of bond angles and the freedom of bond rotation are sufficient to complete the process.

Constitutional Isomerism in Polymers

(a) Different connectivity of atoms

$$X-(CH_2-\underset{OH}{CH})_n-X \iff X-(CH_2-CH_2-O)_n-X \quad \{ CH_3CH_2OH \quad CH_3OCH_3 \}$$
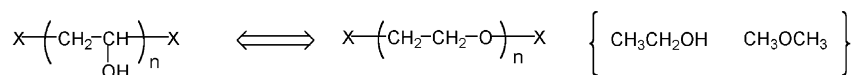
(b) Different sets of atomic groups

$$X-(CH_2-CH_2)_{3n}-X \iff X-(CH_2-\underset{CH_3}{CH})_{2n}-X \quad \{ \sim \quad Y \}$$
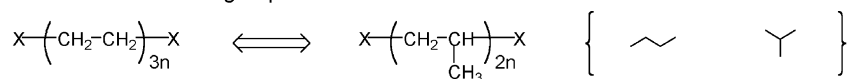
(c) Identical connectivity by different sets of chains

"topologically equivalent constitutional isomers"
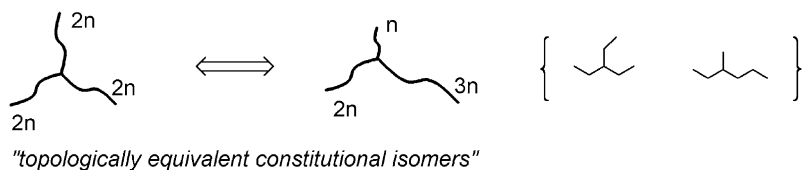
(d) Different connectivity by identical sets of chains

"topologically distinctive constitutional isomers"
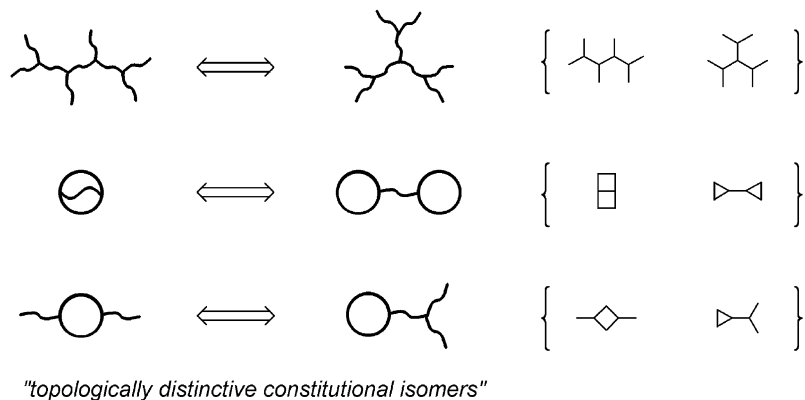
Scheme 4.

A pair of compounds possessing a simple ring (or a trivial knot in topology term) molecular graph and a knot (typically a trefoil knot) counterpart has been referred as a typical example of 'topological stereoisomers' [60]. It should be noted that an open ring compound is also a stereoisomer of a triangle, a square or a randomly constrained ring compound. The distinction in these two isomerism is recognized by comparing the topological property of the respective isomer molecular graphs. Thus, a ring and a triangle (and a square, etc.) are topologically equivalent to each other, interconvertible through the

"topologically distinctive diastereomers"

"topologically equivalent diastereomers"
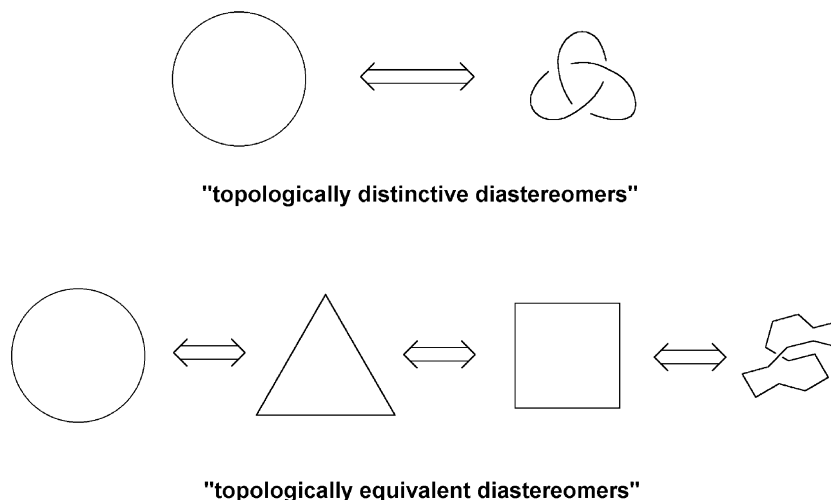
Scheme 5.

conceptual continuous chain deformation with retaining the total chain length, but without chain-breaking process. On the other hand, a ring and a knot can only be interconvertible each other by applying the chain-breaking process. And significantly, the chain-breaking with a SINGLE position and the subsequent chain-rearrangement/chain-recombination is required to complete interconversion of this isomer pair. This is contrastive to the constitutional isomers, where the chain-breaking with at least TWO positions (appropriately chosen) is required to complete the process. By this distinction, we call a ring and knot as 'topologically distinctive stereoisomers' or more specifically, since they are not mirror images each other, as 'topologically distinctive diastereomers', in contrast to a ring and a triangle (or a square, etc.) as 'topologically equivalent diastereomers' (Scheme 5).

A trefoil knot compound is known to be resolved into a right-handed and a left-handed enantiomeric isomer. It is remarkable again that these isomers are interconvertible only by applying the chain-breaking process with a SINGLE position, in contrast to the classical enantiomeric isomers, where the molecular graphs are interconvertible simply by the conceptual continuous chain-deformation, but without subjecting the chain-breaking process. Thus, we call a right and a left-handed knots as 'topologically distinctive enantiomers' in contrast to another relevant isomers such as a right and a left handed open-helix chain compounds as 'topologically equivalent enantiomers' (Scheme 6).

The isomerism in a catenane (more precisely [2]-catenane) and two separated rings has often been quoted since the pioneering study by Wasserman [60], and even in several recent articles [111]. It must be emphasized, however, that the isomerism refers, in itself, to a set of compounds possessing the same chemical formula. Hence for example, a [2]-catenane molecule consisting of two rings of 30 methylene units is an isomer of a simple ring molecule of 60 methylene units, and more importantly, either is not an isomer but a product of two molecules of a ring of 30 methylene units. This is just chemically valid as that a cyclohexane is not an isomer of TWO cyclopropanes! The confusion on this particular isomerism is apparently caused by the fact that a [2]-catenane is interconvertible to two rings by applying the chain-breaking with a SINGLE position and the subsequent chain-rearrangement/chain-recombination process, just as in the isomerization between a ring and a knot. Nevertheless,
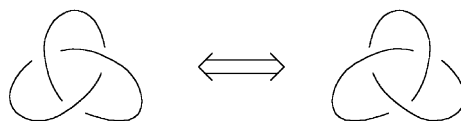
"topologically distinctive enantiomer"
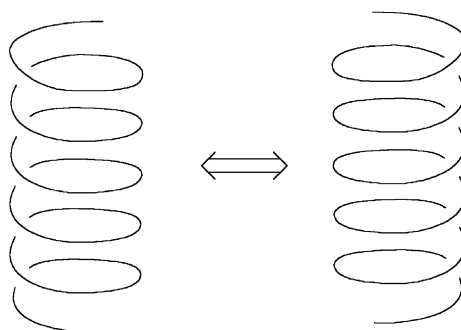
"topologically equivalent enantiomers"

Scheme 6.

this process-based analogy is chemically inappropriate for a basis of the isomerism involving a catenane. Likewise, a rotaxane molecule is a product but not an isomer of a separated axle and a ring component (Scheme 7).

Thus, a large single ring and a catenane is interconvertible by applying the chain-breaking with at least appropriate TWO positions followed by the chain-rearrangement/chain-recombination. This exactly conforms to the criterion of the constitutional isomers. Therefore, a set of a ring and a catenane is classified as topologically distinctive constitutional isomers as in the previous dendritic and comb-type branched decane isomers. Likewise, a [2]-catenane is a 'topologically distinctive constitutional isomer' of a [3]-catenane. On the other hand, a set of [2]-catenanes possessing different ring sizes is classified into 'topologically equivalent constitutional isomers'.

Finally, the isomerism of three bicyclic molecules, namely a θ-shaped molecule [70], **A**, a manacle-shaped molecule [70], **B**, and a 'pretzelan'-shaped, catenane molecule [112], **C**, is of interest to note (Scheme 8). It is evident that **A** and **B** are isomers, since both are products of an identical set of the chain precursors and the linking reagents [70] as outlined in Scheme 2 (Section 2.3). As in the cases of a large single ring, and a [2]-catenane, **A** and **B** (or **A** and **C**) are topologically distinctive constitutional isomers, since they are interconvertible by applying the chain-breaking with appropriate TWO positions followed by the chain-rearrangement/chain-recombination process. On the other hand, **B** and **C** are interconvertible each other by applying the chain-breaking with an appropriate SINGLE position. Thus, they are classified into, as in the case of a ring and a knot, 'topologically distinctive diastereomers'.
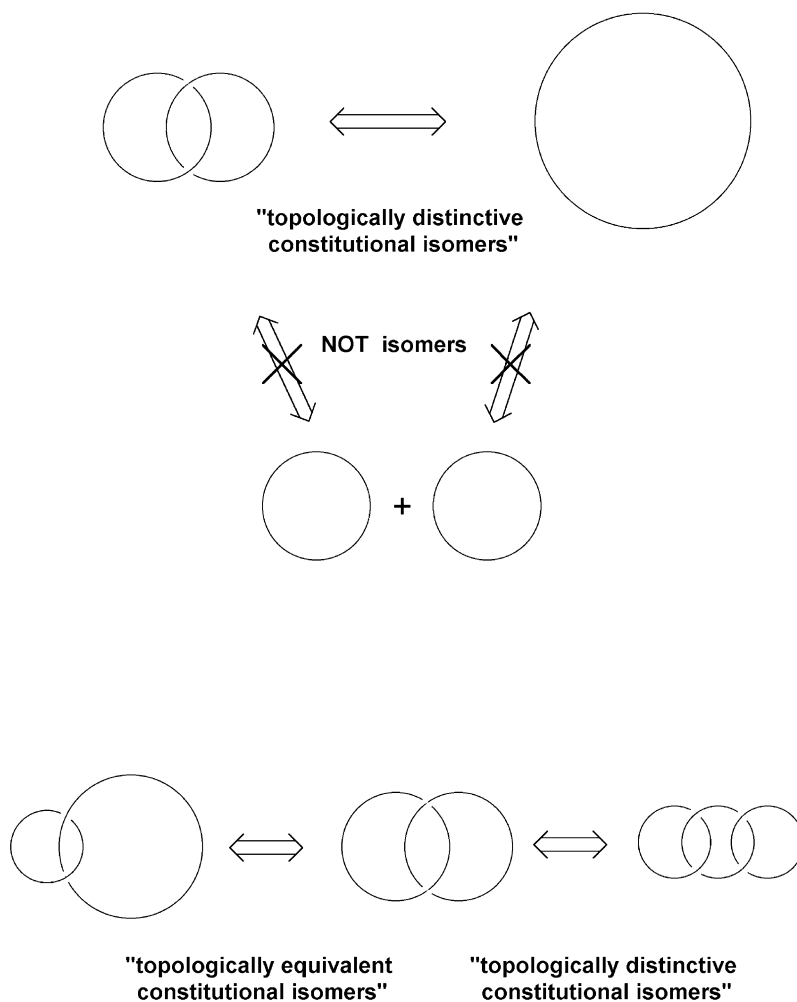
Scheme 7.

4. Designing non-linear polymer topologies

4.1. Branched topologies

Branched polymer architectures are classified into three categories from the topological respect. First one includes, as shown in Section 2.1, star polymers and multijunctional branched polymers comprised of flexible and long segments both between junctions and between junction and terminus. Second one, such as dendrimers and dendronized polymers, are made of stiff and short segments both between junctions and junction and terminus. Finally, polymacromonomers comprised of long and flexible segments between junction and terminus, while short segments between junctions are classified into a third category. Synthetic strategies so far developed for these branched topologies are summarized in the following sections.

"topologically distinctive constitutional isomers"

"topologically distinctive diastereomers"
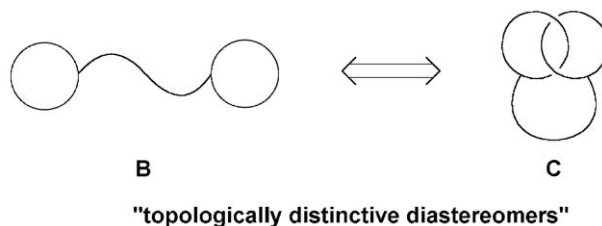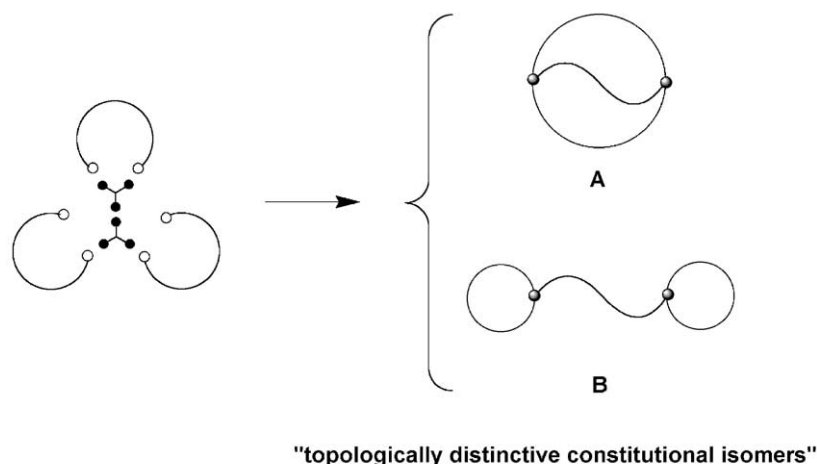
Scheme 8.

4.1.1. Star polymers

Star polymers are synthesized by means of a living polymerization technique [1–15]. Three processes shown in Scheme 9 are typically employed [3].

First one involves the deactivation of a monofunctional living polymer by a plurifunctional coupling reagent. When the reaction proceeds under exact stoichiometry to complete conversion, the formed star polymer will be perfectly well defined with respects to both the number of branches at the junction, since the star polymer has only one junction, and the number of branches emanating from the junction corresponds to the functionality of the coupling reagent. The branch length (the segment length between the junction and terminus) is controlled since they are prepared by the living polymerization process. In practice, however, an excess of the living polymer must be charged against the coupling reagent to promote the coupling reaction to cope with the increasing steric effect and the decreasing concentration of reactive groups in the course of the reaction, particularly for the star polymer having many branches. The cumbersome fractionation is sometimes required to isolate the pure star polymer product.

The second one involves a sequential living polymerization by a small amount of plurifunctional

1)

X* : living end group

Y : complementary reactive group

2)

"nodule"

X* : living end group

X : plurifunctinal monomer

3)

I : initiating group
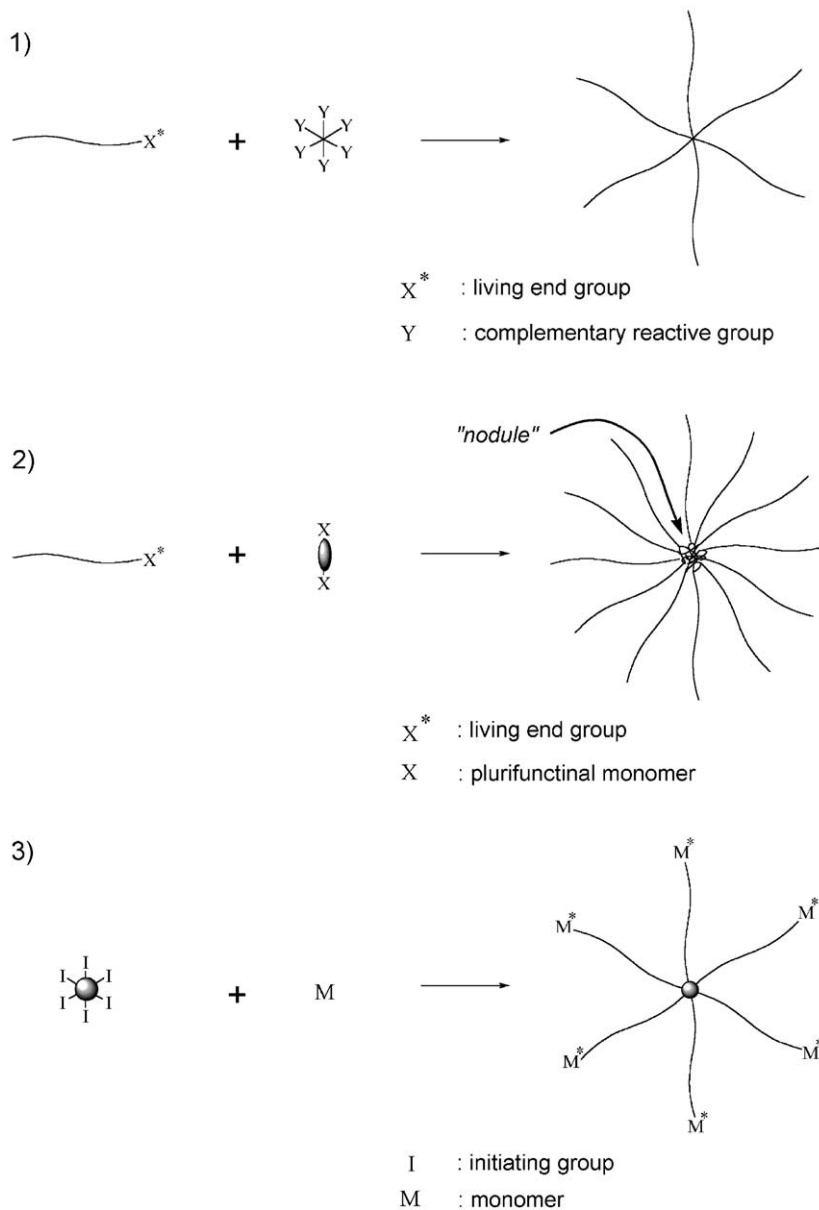
M : monomer

Scheme 9.

monomer. A typical example is a living polymerization of styrene and subsequent addition of divinyl-benzene, to form a small 'nodule' as a core junction. Though the exact structure of the core is not readily accessible due to the complicated nature of the divinyl coupling reaction to form the core (nodule). However, the product is soluble and the number of branches attached to the nodule may be empirically estimated by the ratio of added divinylbenzene over the living prepolymer chain end. This process has been often applied to prepare star polymers having many (over 100) branches. The length of the branch

segments is controllable since they are prepared by the living process. On the other hand, the number of branches emanated from the core (nodule) is not exactly prescribed but in average by nature. The distribution in the branch number should be taken into account.

In the third process, plurifunctional initiators are applied. Such initiators are either a compound of the defined number of functionalities or a nodule species produced from a plurifunctional monomer under diluted condition. These can produce star polymers having very long branch segments, having block copolymer segments or having mixed branch segments [12,13]. On the other hand, the length of branch segments is often difficult to control since the initiation of plurifunctional initiators is seldom instantaneous [14]. Moreover, the poor solubility of plurifunctional initiators, in particular polymetallated compounds for the living anionic process, circumvents the efficient initiation.

4.1.2. Multijunctional branched polymers

Branched polymers having multiple junctions such as H-shaped and super H-shaped polymers (Table 1 in Section 2.1) are distinctive to star polymers from topological viewpoint. Such polymer structures have so far been designed as a model of graft copolymers comprised of different polymer segments [1–15,50,51], in which one type of linear polymer components is linked by their end groups onto another type of polymer segment along the main chain. Thus in comparison with linear block copolymers, there exist excessive structural diversity in graft copolymers with respect to junction structures.

Graft copolymers are prepared by the following three processes [4], namely a graft-onto method, a graft-from method and a macromonomer method, respectively (Scheme 10). These will provide versatile means to combine different polymer segments by a covalent linkages, and the branch segment length and the average number of junctions along the main chain may be controlled. The precise control in such junction architectures as the number of junctions as well as the number of branches at each junction is still a challenge [15]. The step-by-step approach involving the end-modification of living polymers and subsequent coupling reactions has been applied for the construction of H-shaped and super H-shaped topologies. Further research efforts are awaited to achieve the substantial progress in this area.

4.1.3. Dendrimers and polymacromonomers

Dendrimers, polymacromonomers and dendronized polymers are of increasing current interest (Scheme 11) [16–28]. They tend to form stiff and shape-persistent 3D mesostructures, and this is particularly distinctive to above-described branched polymers forming soft and random coil 3D structures. A variety of synthetic processes has been developed for the preparation of dendrimers [24–28]. They are principally classified into a divergent and a convergent process, in which highly selective reactions are applied to construct the target molecule either from the core or from the periphery, respectively, by step-by-step process. Details of the synthesis of dendrimers, polymacromonomers and dendronized polymers are often the subject of recent reviews and book chapters [16–28].

4.2. Cyclic topologies

Cyclic polymer architectures have gained increasing interests both in fundamental and in applied fields of polymer science and technology, since their absence of end groups is expected to realize diverse novel polymer properties [29]. An efficient and practical means to construct cyclic polymer architectures, however, has been an ongoing challenge in contrast to remarkable achievements in the synthesis of

1) "graft from"

I   : initiating group

M   : monomer

2) "graft onto"

X,Y   : complementary reactive group

3) "macromonomer"

M'   : polymerizable group

M   : monomer

Scheme 10.

such well-defined branched polymer architectures having plural end groups, as star polymers [1–15], polymacromonomers [16–23], hyperbranched polymers [1–15], and dendrimers [24–28] shown in Section 4.1.

Straightforward polymer cyclization has so far been performed through an end-to-end linking reaction of an α,ω-bifunctional linear polymer precursor. This bimolecular process, however, requires strict stoichiometry between a polymer precursor and a small coupling reagent [90–94]. And in order to avoid a concurrent intermolecular chain-extension, the high dilution of a reaction solution is a prerequisite for promoting the intramolecular process. This, in turn, seriously reduces the rate of the bimolecular reaction of the second-order kinetics. An alternative means to improve the polymer

dendrimer   **polymacromonomer**   **dendronized polymer**

Scheme 11.

Scheme 12.

cyclization efficiency includes a unimolecular, high dilution process by use of α,ω-*hetero*bifunctional polymer precursors [95–97]. Nevertheless, the selective introduction of complementarily reactive groups at the opposite chain ends inherently requires a multistep process involving protection–deprotection reactions, and thus its practical usefulness will be limited.

We have developed an electrostatic self-assembly and covalent fixation process for an efficient construction of a variety of unusual macromolecular architectures containing cyclic polymer units, in which telechelic poly(THF)s having cyclic ammonium salt groups carrying various pluricarboxylate counteranions have been synthesized and utilized [70–78]. Upon diluting in an organic medium below a gram per liter, the ionically aggregated polymer precursors completely dissociate into a smallest assembly while cations and anions balance the charges (Scheme 12). The subsequent covalent fixation through the ring-opening reaction of a cyclic ammonium salt group by a carboxylate counteranion produces a variety of unconventional polymer architectures comprising mono- and multicyclic polymer units. In the following sections, this exceptionally efficient polymer cyclization process is described with using a variety of telechelic poly(THF)s having pyrrolidinium salt groups carrying different dicarboxylate counteranions.

5. Electrostatic self-assembly and covalent fixation

5.1. Telechelics having cyclic onium salt groups

5.1.1. Preparation

Telechelic polymers, referring to those possessing single or multiple functional end groups, have gained a growing interest as macromolecular precursors for a variety of novel polymer architectures [38,39,113]. In most cases, linear telechelics possessing a specific functional group at one or at both chain ends have been involved, since they are readily prepared through the end-capping of increasingly available mono- and bifunctionally living polymers, respectively. Recently, moreover, star-shaped telechelics having triple and more functionalities have been prepared by taking advantage of the progress in multifunctional anionic, cationic, radical as well as ring-opening living processes [114].

We have employed mono- and bifunctionally living poly(THF)s, which are readily produced by methyl triflate and by triflic anhydride as an initiator, respectively. Moreover, a trifunctionally living poly(THF) by a novel triflate ester initiator, prepared in situ from benzylic triol, i.e. 1,3,5-*tris*(hydroxy-methyl)benzene, has been prepared and subjected to a subsequent end-capping reaction to produce star-shaped telechelic polymers (Scheme 13). In benzylic triflate initiators, a phenyl group can stabilize any positive charge that develops on an α-carbon atom during a nucleophilic substitution reaction as in
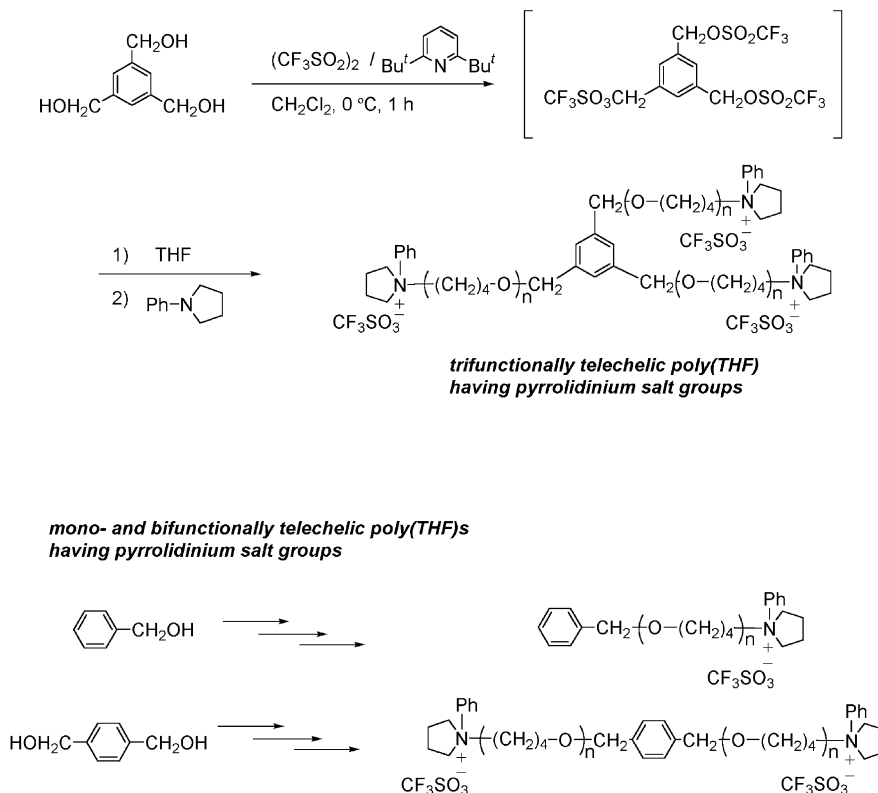
Scheme 13.

the case of an allyl group [115,116]. Therefore, a monofunctional benzyl triflate and a bifunctional benzylic triflate, i.e. a bis(triflate ester) of 1,4-bis(hydroxymethyl)benzene, were successfully applied as in situ initiators for the living polymerization of THF.

By the subsequent end-capping reaction with *N*-phenylpyrrolidine, mono-, bi- and trifunctional star-shaped, telechelic poly(THF)s having *N*-phenylpyrrolidinium salt groups were obtained (Scheme 13). The quantitative end-capping reaction was confirmed by the ^{1}H NMR analysis of the products. The formed *N*-phenylpyrrolidinium salt end groups initially accompany triflate counteranions, and the ion-exchange reaction was found to occur by simply precipitating the prepolymer solution into aqueous solution containing desired anions, such as a sulfonate or a carboxylate in sodium salt form. The heat treatment of the ion-exchange products carrying carboxylate counteranions were then performed either in bulk or in solution to cause a quantitative ring-opening reaction of *N*-phenylpyrrolidinium group (Scheme 14). SEC confirmed, meanwhile, the covalently converted product retained a low polydispersity index. In the following sections, a series of synthetic application with these telechelic precursors will be demonstrated by exploiting their efficient ion-exchange and selective ring-opening reactions at the end-standing pyrrolidinium salt groups.

Another class of telechelic poly(THF)s have also been prepared, in which functional groups are located not only at the chain ends but also at the desired interior positions [117]. Thus, a center-functionalized living poly(THF) was prepared by a particular benzylic initiator, i.e. a bis(triflate ester) from 1-(*tert*-butyldimethylsiloxy)-3,5-bis(hydroxymethyl)benzene. The protection by a *tert*-butyldimethylsilyl group of the phenolic group was a prerequisite for the living polymerization of THF to occur. The end-capping reaction of the living end groups with *N*-phenylpyrrolidine took place quantitatively as in the cases of the relevant mono- and bifunctionally living poly(THF). And the *tert*-butyldimethylsilyl protecting group was removed during the precipitation of the reaction
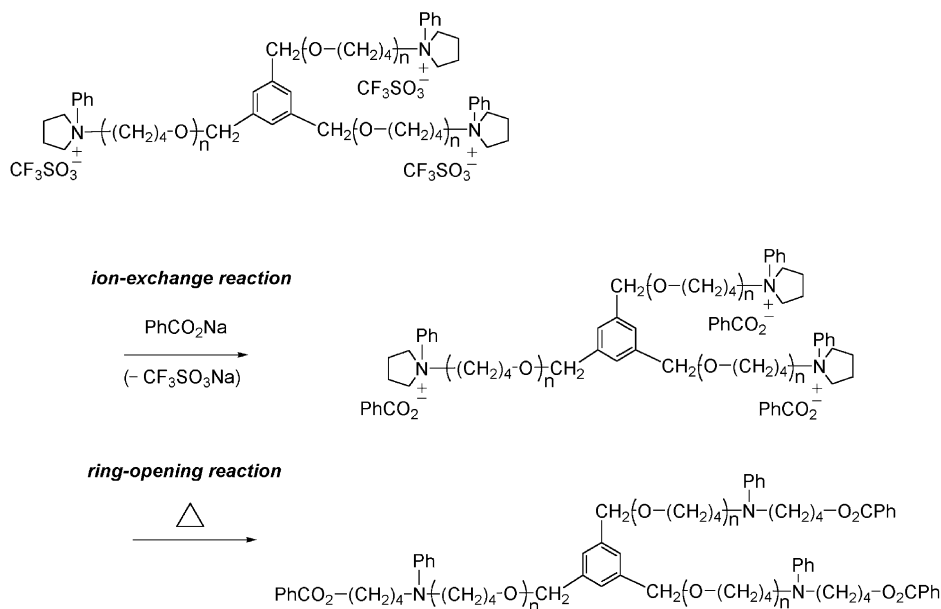
Scheme 14.
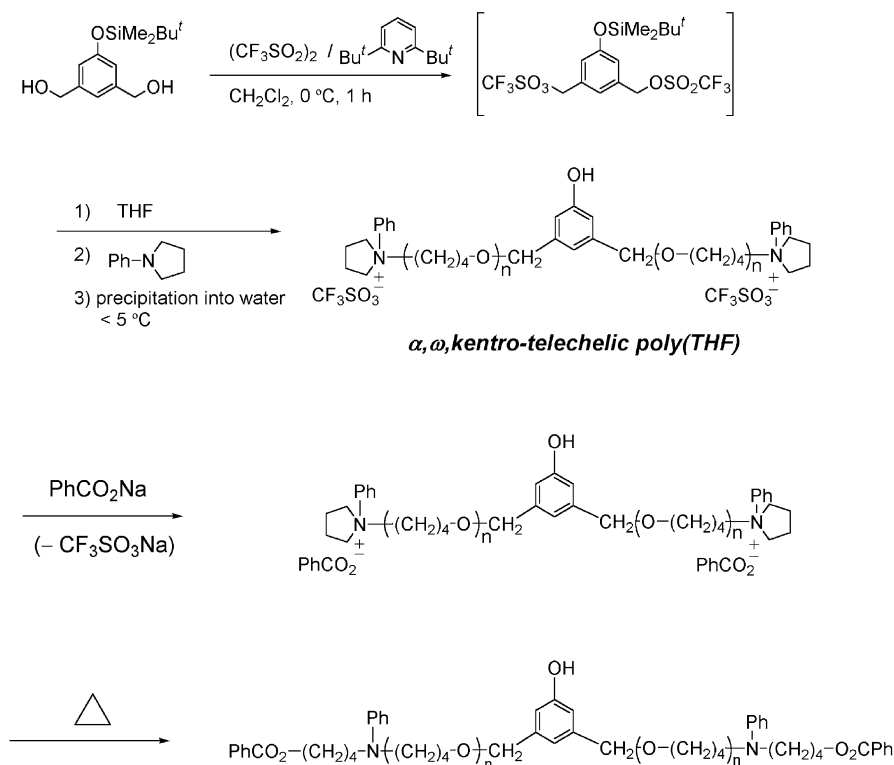
Scheme 15.

mixture into water, to produce an α,ω-*kentro*-telechelic polymers (Scheme 15). The subsequent ion-exchange and ring-opening reactions of *N*-phenylpyrrolidinium salt end groups by a benzoate counter-anion were selective and quantitative as confirmed by the ^{1}H NMR and SEC analysis.

Moreover, *eso*-telechelic poly(THF)s having pyrrolidinium salt groups at the prescribed inner positions were prepared [77]. The two types of *eso*-poly(THF) having pyrrolidinium salt groups at the prescribed interior positions were thus synthesized by a two-stage procedure (Scheme 2 and Table 1). Thus in the first stage, monofunctionally living poly(THF)s having either a methyl or an allyl end group were prepared either by methyl triflate or by allyl triflate [115,116]. They were subsequently terminated with a secondary amine, i.e. pyrrolidine to produce the corresponding poly(THF)s having a tertiary amine, i.e. *N*-substituted pyrrolidine end group, respectively. And in the second stage, they were subjected to the end-capping reaction of a bifunctionally living poly(THF), prepared by triflic anhydride. The reaction products were readily recovered after the precipitation into water. The ^{1}H NMR spectra of the recovered products showed the formation of interiorly functionalized, *eso*-telechelic poly(THF)s having pyrrolidinium salt groups.

The relevant telechelics with different main chain segments, namely telechelic polystyrene and poly(dimethylsiloxane), poly(DMS), having the 5-membered cyclic and 6-membered bicyclic ammonium salt end groups, have also been prepared through the sequential end-group modification of a living polystyrene and of a living poly(DMS) obtainable by an anionic polymerization method, respectively [118,119]. 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 eventual quaternization with 5-membered cyclic amine (*N-methyl*pyrrolidine) or with 6-membered bicyclic amine (quinuclidine) was performed to produce the telechelic polystyrene and the poly(DMS) having moderately strained cyclic onium salt groups, respectively.

It is notable, on the other hand, that the quaternization by *N-phenyl*pyrrolidine at the tosylate end groups of polystyrene failed to proceed, apparently due to its substantially weaker nucleophilic reactivity ($pK_a = 3.45$) than aliphatic amines with higher reactivities like *N-methyl*pyrrolidine ($pK_a = 10.3$).

5.1.2. Ring opening reactivity

Hydrophobic polymers having up to a few mol% of ionic groups are known typically as 'ionomers' applicable to mechanically tough coating materials [120]. These polymers tend to form clusters by aggregation (self-assembly) in organic solutions through Coulombic interaction between ionic groups located along hydrophobic polymer backbone. In this connection, telechelics having ionic groups exclusively at the chain ends have drawn an attention, since the control of the content and the location of ionic groups in the polymer chain may dictate their aggregation (self-assembly) behaviors, and eventually their properties [121,122]. Moreover, it has been shown that the aggregation dynamics is significantly influenced by the concentration and by the temperature of ionomer solution. Thus in a diluted solution, ionic aggregates tend to de-assembly into the dispersion of a single polymer component (Scheme 16). We have devised a novel polymer reaction process based on these characteristics of telechelics having ionic end groups, where such telechelics are allowed to form a thermodynamically favored electrostatic self-assembly, and subsequently converted to permanently fixed covalent structures [70–78].

In order to optimize the key process of this system, we have performed a systematic study on the covalent conversion process of ionic species with using a series of poly(THF) having a variety of cyclic ammonium, i.e. 3-, 4-, 5-, 6-membered cyclic as well as 6-membered bicyclic ammonium salt end
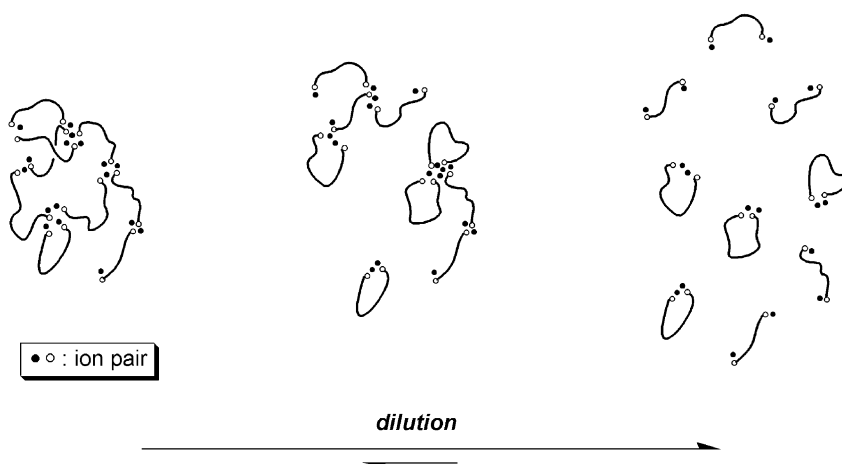
Scheme 16. Reprinted with permission from Ref. [41]. Copyright, 2001 by Wiley-VCH Verlag GmbH, D-69451 Weinheim (FRG).
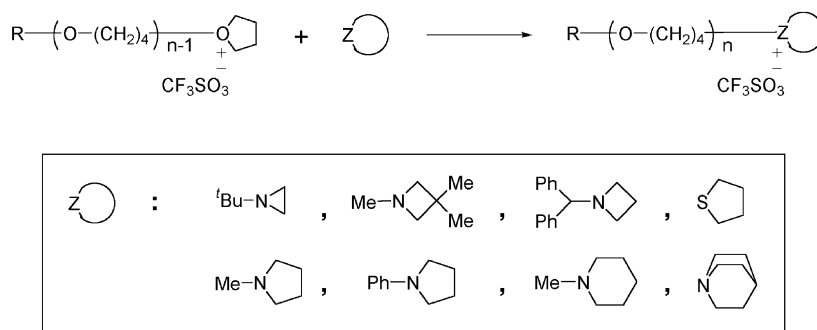
Scheme 17. Reprinted with permission from Ref. [41]. Copyright, 2001 by Wiley-VCH Verlag GmbH, D-69451 Weinheim (FRG).

groups [38,40,41] (Scheme 17). The 3-membered cyclic ammonium salt end groups were found to be so reactive as to undergo a spontaneous ring-opening reaction with 3-membered cyclic amine itself, forming a block copolymer in situ. The 4-membered cyclic ammonium salt end groups, on the other hand, were observed to be less reactive, and the ring-opening reaction did not occur with 4-membered cyclic amines at ambient temperature. Thus, the telechelic poly(THF) with 4-membered cyclic onium salt groups could be isolated, and was subsequently utilized to produce block copolymers by the reaction with 3- and 4-membered cyclic amines at an elevated temperature [123].

A remarkable feature of the 4-membered cyclic ammonium salt end groups is the ion-exchange reaction from an originally accompanied weak nucleophile of a triflate to others like sulfonates or carboxylates. The reaction proceeds through a simple precipitation of the telechelics solution into an aqueous solution containing desired anions as a salt form (Scheme 18) [38]. And when a strong nucleophile such as a carboxylate was introduced as a counteranion, a spontaneous ring-opening reaction of the 4-membered cyclic ammonium salt groups took place at an ambient temperature.

Moreover, it has been noticed that modestly strained 5-membered cyclic as well as 6-membered bicyclic ammonium salt end groups were unreactive with carboxylates as a counter-anion at ambient temperature, but underwent the selective ring-opening reaction by heating to elevated temperatures (Scheme 18). In contrast, the strain-free 6-membered cyclic ammonium salt group failed to cause the selective ring-opening reaction. Based on these findings, we have chosen such telechelic poly(THF)s as having 5-membered cyclic and 6-membered bicyclic ammonium salt groups as polymer precursors for the 'electrostatic self-assembly' with appropriate carboxylate counteranions, and for the subsequent 'covalent fixation' by the ring-opening reaction to produce covalently linked products [40,41].

Further details of the ring-opening reaction were studied with *N*-alkyl and *N*-arylpyrrolidinium salt groups and quinuclidinium salt groups (Scheme 19) [76,124,125]. Thus, in the reaction of the *N*-methyl*pyrrolidinium salt end groups, not only the ring-opening reaction but also a noticeable demethyl-ation reaction was observed through the nucleophilic attack of the carboxylate counteranion at the *N*-methyl*carbon. On the other hand, any noticeable Hofmann type elimination reactions were observed. And, the nature of the counteranion was found to influence significantly on the course of the reaction at the *N*-methyl*pyrrolidinium groups [124]. Thus, a ring-opening reaction took place predominantly by an
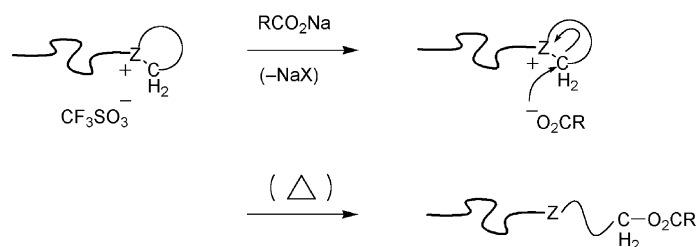
required temperatures for ring-opening reaction with a carboxylate counteranion
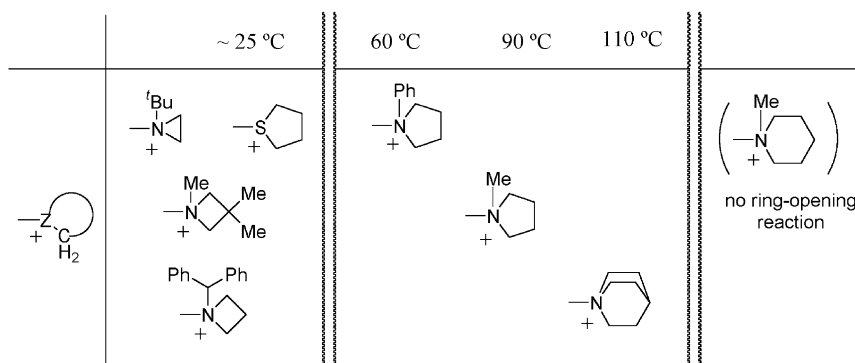
Scheme 18. Reprinted with permission from Ref. [41]. Copyright, 2001 by Wiley-VCH Verlag GmbH, D-69451 Weinheim (FRG).

electron-donating *p*-methoxybenzoate ($pK_a = 4.47$), while no reaction at all by an electron-withdrawing *p*-nitrobenzoate ($pK_a = 3.42$) at the relevant reaction condition. It was also observed that the higher the reaction temperature, the lower the selectivity for the ring-opening reaction over the demethylation. On the other hand, the nucleophilic attack of the carboxylate counteranion at the 6-membered bicyclic, quinuclidinium salt groups was found to take place at a comparatively higher temperature than in the case of *N-methyl*pyrrolidinium groups. It is remarkable to note that the ring-opening reaction occurred exclusively at the *endo*-methylene position of a strained azabicyclo unit, and a reaction at the alternative *exo*-methylene position was excluded.

Based on these results, a new poly(THF) precursor has been designed, in which *N-methyl* group on a pyrrolidinium salt group was replaced by *N-phenyl* group [76]. Since the nucleophilic substitution reaction on the phenyl group is apparently suppressed, the ring-opening reaction on aliphatic *endo*-methylene groups tends to occur preferentially. Furthermore, the ring-opening reaction will be promoted by introducing an aniline derivative group, which is a better leaving group than the alkylamino group in the nucleophilic substitution reaction [123]. Thus, *N-phenyl*pyrrolidine was newly synthesized and used for the end-capping reaction of the living poly(THF) [76]. Indeed, the *N-phenyl*pyrrolidinium salt end group underwent a complete ring-opening reaction even with *p*-nitrobenzoate counteranion and exclusively at the *endo*-position of the 5-membered pyrrolidinium ring, in contrast with the *N-methyl*-pyrrolidinium salt group (Scheme 19). Moreover, unsubstituted benzoate and *p*-methoxybenzoate
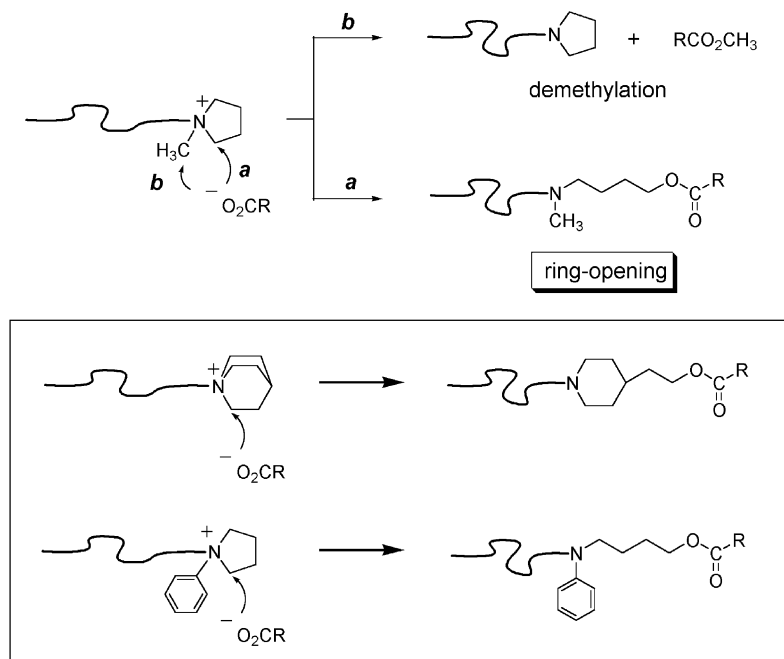
Scheme 19. Reprinted with permission from Ref. [41]. Copyright, 2001 by Wiley-VCH Verlag GmbH, D-69451 Weinheim (FRG).

counteranions caused a quantitative and selective ring-opening reaction of an *N-phenyl*pyrrolidinium salt group without concurrent dephenylation reaction, again in contrast with the *N-methyl*pyrrolidinium salt group.

5.2. Polymer cyclization

5.2.1. Ring poly(THF)

The polymer cyclization reaction was extensively studied by using the telechelic poly(THF) having *N-phenyl*pyrrolidinium salt groups [70,72]. This telechelics initially accompanied triflate counteranions, which were subsequently replaced by a desired carboxylate counteranion, through a simple precipitation of a poly(THF) precursor into an aqueous solution containing excess amount of a carboxylate as a sodium salt form. The ^{1}H NMR spectra of the ion-exchange products with dicarboxylate showed signals due to the corresponding carboxylate counteranions. The charges between the quaternary ammonium cations at the ends of the polymer precursor and the carboxylate anions balance each other, corresponding to the molar ratio of 1:1.

This ionic polymer precursor tends to self-assemble electrostatically in an organic solution. The dissociation/association of ionic species depends on the solution concentration, while the cations and anions balance the charges throughout the process (Scheme 12 in Section 4.2). A cyclic poly(THF) with a narrow size distribution (PDI < 1.10), corresponding to the polymer precursor, was obtained after the heat treatment in an appropriately diluted THF solution ([C] = 0.2 g/l). The cyclic structure of the product was unequivocally confirmed by means of SEC, and viscosity measurements, as well as [1]H

NMR, and VPO analyses [70]. Thus, the SEC and viscosity measurements showed the agreement between theoretical and experimental hydrodynamic volume ratios for the cyclic product against its linear analogue, prepared from an identical telechelic poly(THF) but carrying benzoate counteranions. The VPO and ^{1}H NMR, on the other hand, confirmed that the absolute molecular weights (thus corresponding to the total chain length) of the cyclic and of the linear poly(THF)s coincide with each other within an experimental error.

Furthermore, the cyclic product and the relevant linear counterpart could be distinguished by means of a reversed-phase high pressure liquid chromatography (RPC), where the topology of the polymer product directs the elution property [70,95,97,126–129]. The RPC technique was also found to separate a mixture of cyclic products from multiple polymer precursor units from a cyclic product from a single polymer precursor unit, and was shown to provide more accurate yield values than the conventional SEC. Thus, it was confirmed that the content of the latter was found to increase along with the dilution of the reaction solution. Typically, the polymer cyclization proceeded with as high as 93% yield at the concentration of 0.2 g/l, and the cyclic poly(THF) of more than 98% purity was obtained in 74% yield by the subsequent purification with preparative thin-layer-chromatography (TLC) technique.

Based on the statistics for an intramolecular cyclization and intermolecular chain extension processes by the end-reactive polymer precursor [130], the ratio of the respective products formed at different concentrations can be estimated from the corresponding probability ratios, P_c and P_e, respectively, and is given by the following equation,

$$P_c/P_e = [3/2p\langle r_0^2 \rangle]^{2/3} \times \text{MW}/[\text{C}]N_A$$

where $\langle r_0^2 \rangle$ (cm^2), [C] (g/ml), and N_A are a mean square end-to-end distance of the polymer precursor, a polymer concentration in the cyclization reaction, and the Avogadro's number, respectively. For instance, the theoretical yields of cyclic poly(THF) at different concentrations from the linear precursor (MW = 4700 g/mol) were thus estimated by assuming the end-to-end distance per unit mass for poly(THF), $r_0/\text{MW}^{1/2}$, to be 0.09 nm(mol/g)$^{1/2}$ [131], at a theta condition. The experimental yields were indeed very close to the theoretical ones, conforming with the cation/anion stoichiometry in the electrostatically self-assembled polymer precursor system, and the quantitative and selective chemical conversion process at the polymer precursor chain end.

Another poly(THF) precursor having *N-methyl*pyrrolidinium salt groups, in place of *N-phenyl*pyrrolidinium salt groups, has also been subjected to the polymer cyclization reaction. Since a ring-opening reaction of the *N-methyl*pyrrolidinium salt group takes place only at the higher temperature than around 80 °C [124], the heat treatment of an ionic poly(THF) precursor, prepared by the ion-exchange reaction with sodium 4,4'-biphenyldicarboxylate, was performed in a toluene solution. The ring-opening reaction was confirmed to occur, as evidently shown by ^{1}H NMR and IR spectroscopic analysis of the quantitatively recovered crude product by evaporating the solvent. The SEC showed a unimodal profile with a narrow size distribution (PDI = 1.15) for the product. A cyclic poly(THF) could be isolated in a pure form with a high yield (72%) by the subsequent preparative TLC treatment.

The effective polymer cyclization was found to proceed under appropriate dilution (0.2 g/l) in THF for a series of telechelic poly(THF)s having the molecular weight ranging from 4000 to 12 000, corresponding to the 260–800-membered ring.

The polarity of the reaction solvent was found to affect on the cyclization process. Thus, the covalent conversion reaction proceeded quantitatively in toluene, in chloroform, and in acetone. In contrast, no

⊖ : carboxylate

☐ : triflate

assembly by multiple polymer units

dilution

assembly by a single polymer unit

covalent fxation
(exclusively with carboxylate
counteranions)
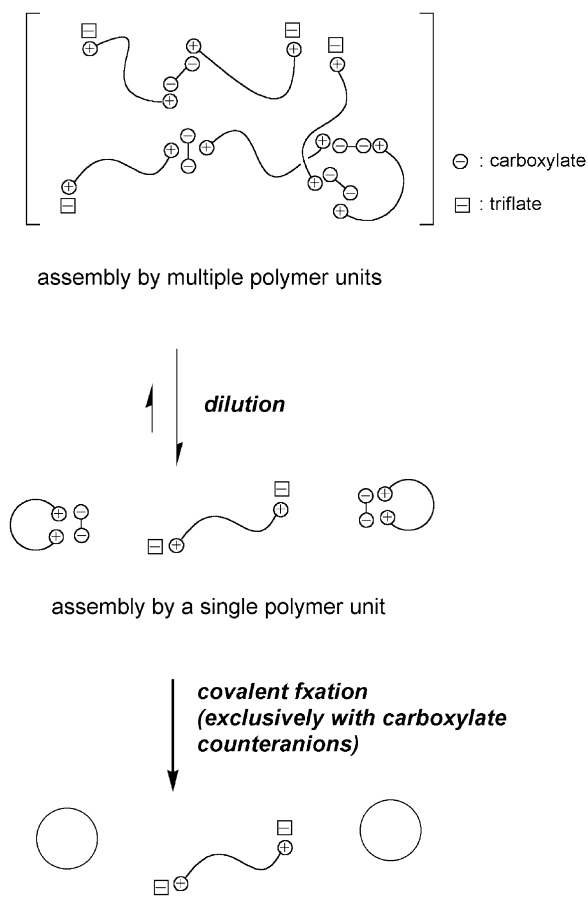
Scheme 20.

reaction was observed at all in ethanol. The solvation of ethanol to carboxylate anions through the hydrogen bond is presumably suppress their nucleophilic reactivity. The SEC showed that the products obtained in chloroform and in acetone possess narrow size distributions as observed in THF. On the other hand, the SEC peak profile was comparatively broader (PDI > 1.5) for the product obtained in toluene. And the cyclic polymer yield of a single polymer precursor unit estimated by RPC was slightly lower (80% against 89–93% in THF, chloroform and acetone). These imply that the ionically aggregated polymer precursor is unwilling to dissociate in a less-polar toluene solution.

Furthermore, the type of dicarboxylate counteranion was found to affect on the extent of the ion-exchange reaction of telechelic polymer precursors. Thus, a series of aromatic and aliphatic dicarboxylate counteranions, i.e. terephthalate, *o*-phthalate, succinate, adipate and *trans*-2-butene-1,4-dicarboxylate, in addition to 4,4$'$-biphenyldicarboxylate, were examined. The ion-exchange reaction of a telechelic poly(THF) having *N*-phenylpyrrolidinium salt groups proceeded easily with 4,4$'$-biphenyldicarboxylate and terephthalate, while sluggish with *o*-substituted phthalate. And for aliphatic dicarboxylates, the ion-exchange yield reached off at most 70–80% after the five-times precipitation treatment. From these results, aromatic dicarboxylates are preferred to aliphatic ones in the ion-exchange process, and 1,2-dicarboxylates are less

efficient presumably due to the steric hindrance. On the other hand, the ring-opening reaction of pyrrolidinium salt groups proceeded quantitatively by each of the carboxylate counteranion.

Finally, notable feature of the present covalent conversion process is stressed. That is, the cyclic poly(THF) products having narrow size distributions were obtained in proportional yields even in the reaction employing a partially ion-exchanged polymer precursor, i.e. carrying mixed counteranions of a dicarboxylate anion and a triflate anion. This is uniquely ascribed to the exclusive formation of an electrostatically self-assembled single polymer precursor unit in dilution, in which cations and anions balance the charges (Scheme 20). In consequence, the remarkable efficient polymer cyclization has been achieved by the present electrostatic self-assembly and covalent fixation process.

5.2.2. Ring/branch poly(THF)

A dicarboxylate, i.e. a terephthalate counteranion was introduced at the interiorly located pyrrolidinium salt groups in *eso*-telechelic poly(THF)s, through a simple precipitation of a prepolymer solution

Scheme 21.

an interiorly-functionalized
prepolymer with cyclic
ammonium salt groups

2 × ⊟

[1+1] assembly

covalent
fixation

a polymer product of
"A Ring with Two Branches"
topology
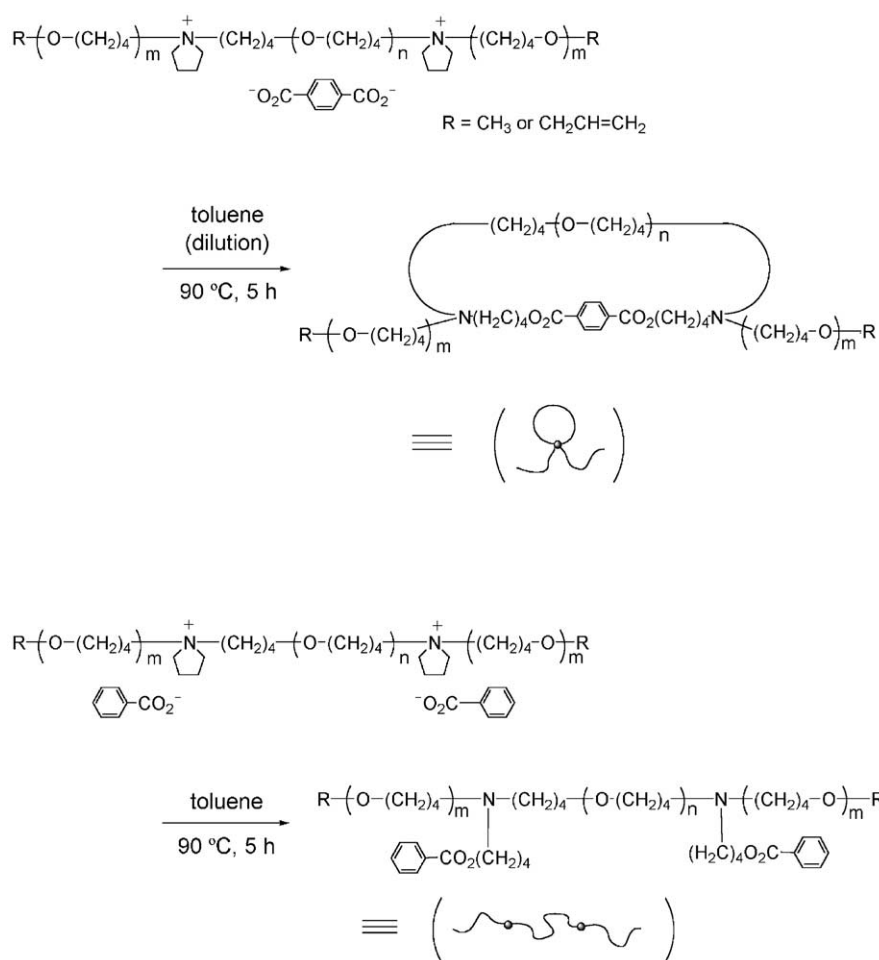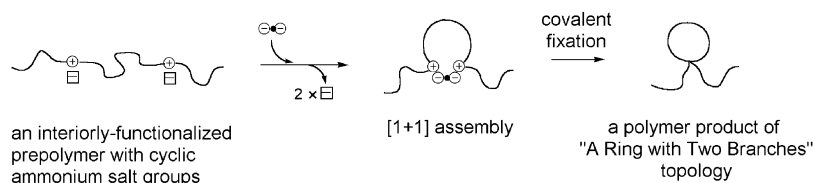
Scheme 22. Reprinted with permission from Ref. [77]. Copyright, 2001 by Wiley-VCH Verlag GmbH, D-69451 Weinheim (FRG).

into water (<5 °C) containing an excess amount of sodium terephthalate [77] (Scheme 21). The ion-exchange reaction from the initial triflate anions toward the dicarboxylate anion was readily confirmed by IR and ^{1}H NMR spectroscopic analyses, as in the case of the previous telechelic poly(THF) having pyrrolidinium salt groups [70,72].

The subsequent heat treatment of the polymer precursor was performed in a toluene solution, to cause a ring-opening reaction of the interiorly located pyrrolidinium salt group by a nucleophilic attack of a carboxylate counteranion (Scheme 21). The ^{1}H NMR analysis of the quantitatively recovered product showed that the nucleophilic attack of a carboxylate counteranion occurred exclusively at the *endo*-methylene position of the pyrrolidinium salt group. Thus, during the present nucleophilic reaction by carboxylate counteranions, the attack at the *exo*-methylene position on the interiorly located pyrrolidinium salt group did not take place at all [70,72]. The IR spectrum of the product also showed an absorption at $1720 \, \text{cm}^{-1}$ assignable to the ester carbonyl group of the ring-opening product.

The SEC of the isolated poly(THF)s of a ring with two branches structure showed narrow size distributions (PDI $= 1.08 - 1.13$), and the smaller hydrodynamic than those of their linear analogues, prepared from the identical polymer precursors but carrying benzoate counteranions.

These results indicate that a unique form of the electrostatic self-assembly was selectively produced under dilution at 1.0 g/l, with balancing the charges between cations and anions (Scheme 22), and was effectively converted into a permanent polymer structure of a ring with two branches topology.

In comparison with the case of the *end*-functionalized poly(THF) [70,72], the selective cyclization with a single polymer precursor unit was found to proceed even at the higher concentration. This implies that the complete disaggregation of polymer precursors having *interiorly located* pyrrolidinium salt groups takes place at the higher concentration than the *end*-functionalized telechelics. The location of ionic groups either at the interior or at the end positions of the polymer chain appears to direct the equilibrium state of the ionically aggregated polymer precursors, in which the steric (exclusion-volume) effect by polymer chain segments is considered to play an important roll.

5.2.3. Ring polystyrene

The polymer cyclization was conducted also with the telechelic polystyrene having quinuclidinium salt groups carrying a terephthalate counteranion (Scheme 23) [71]. The balance of the charges between the quinuclidinium cations and the terephthalate anions was maintained as confirmed by the ^{1}H NMR analysis. This ionically linked polymer precursor was then subjected to the heat treatment in an organic solution at various concentrations, to cause a ring-opening reaction of the quinuclidinium salt end group by a nucleophilic attack of the terephthalate anion. The soluble products were constantly recovered in almost quantitative yields. The ^{1}H NMR showed the ring-opening reaction occurred with as high as 90%
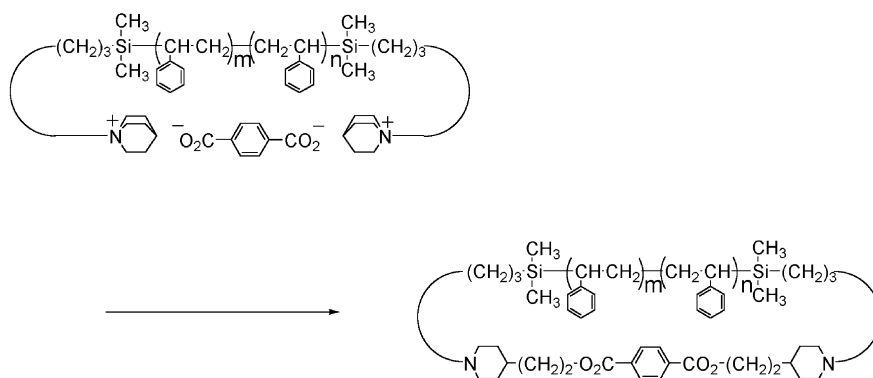
Scheme 23.

selectivity. Besides, the SEC showed that a cyclic polymer product was obtained up to 90% yield upon dilution. This shows, as in the poly(THF) systems, that an ionic precursor comprising single polymer unit was formed from the ionically aggregated polymer precursors, while balancing the charges between cations and anions. And it was subsequently converted to the covalently linked product by the heat treatment.

After the purification of the product by means of a silica gel chromatography, the SEC showed a single peak profile with narrow size distribution, and more significantly, a notably smaller hydrodynamic volume than that of the linear analogue, independently prepared from the identical polystyrene precursor carrying benzoate counteranions. The hydrodynamic volume ratio between the cyclic and the linear polymer products by SEC was in a good agreement with previously reported ones for cyclic and linear polystyrenes [90–97].

5.3. Multicyclics and topological isomers

5.3.1. Multicyclics

Bicyclic and tricyclic polymer topologies were also constructed by using the telechelic poly(THF) having *N-phenyl*pyrrolidinium salt groups [70]. Initially accompanied triflate counteranions of this telechelics were replaced by a tetra and hexacarboxylate counteranions, through a simple precipitation of a poly(THF) precursor into an aqueous solution containing excess amount of a carboxylate as a sodium salt form. The ^{1}H NMR spectra of the ion-exchange products with tetra- and hexacarboxylate showed signals due to the corresponding carboxylate counteranions. The balance of the charges between the ammonium salt groups in the polymer precursor and the carboxylate anions was found to be maintained, corresponding to the molar ratio of 2:1 and 3:1, respectively.

These polymer precursors were then subjected to the heat treatment in solution at different concentrations (Scheme 24). When the reaction was conducted either in bulk or in concentrated solution, insoluble gel products were produced. Along with dilution, on the other hand, the product became totally soluble. And remarkably, the 3D size in solution (hydrodynamic volumes observed by SEC) of the quantitatively recovered crude products, approached to be as uniform as in the linear polymer analogue, which was independently prepared from the bifunctional polymer precursor carrying benzoate counteranions. These results implicate, as was the case of the simple polymer cyclization described in

2 + 1 assembly　　　　　　　　　　**3 + 1 assembly**
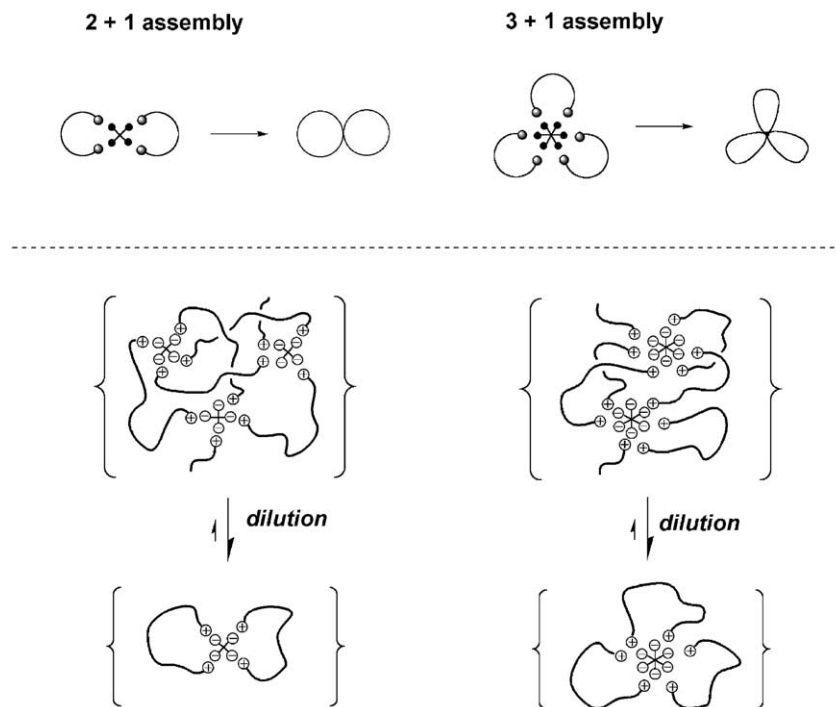
Scheme 24. Reprinted with permission from Ref. [41]. Copyright, 2001 by Wiley-VCH Verlag GmbH, D-69451 Weinheim (FRG).

the preceding sections, that a unique form of an electrostatic self-assembly has been produced upon appropriate dilution from the aggregated polymer precursors, while cations and anions balance the charges (Scheme 24).

The obtained bi- and tricyclic poly(THF)s were readily purified by the preparative thin layer chromatography, and were fully characterized by spectroscopic and chromatographic techniques. Thus, the ^{1}H NMR confirmed that all pyrrolidinium salt groups were converted into amino-ester groups through the ring-opening reaction. The IR spectra showed the absorption assignable to ester carbonyl groups.

The SEC analysis of the bicyclic and tricyclic poly(THF)s showed that they possess significantly larger hydrodynamic volumes than that of the linear analogue from a single polymer precursor unit, but smaller than those of the twice (for the former) and of the three times (for the latter), respectively. They retained narrow size distributions. On the other hand, the actual molecular weights of the bicyclic and tricyclic poly(THF)s determined either by the VPO or by the ^{1}H NMR (assuming quantitative chemical conversion of polymer end groups) coincided, within experimental error, with those of the twice (for the former) and of the three times (for the latter) of the linear polymer precursor analogue, respectively. Hence, it is concluded that the unique forms of the corresponding electrostatic polymer assemblies were formed under dilution, and they are comprised of two units of the polymer precursor and one unit of tetracarboxylate, and of three units of the polymer precursor and one unit of hexacarboxylate, respectively. Subsequent heat treatment of these precursors could lead to bicyclic and tricyclic polymer products, through the covalent fixation by the ring-opening reaction of pyrrolidinium salt groups (Scheme 24).

5.3.2. Topological isomers

Among topological isomers discussed in Sections 2.3 and 3, a pair of topological isomers, i.e. a θ-shaped and a manacle-shaped constructions, were produced simultaneously from three bifunctional polymer precursors and two trifunctional end-linking reagents (Scheme 2 in Section 2.3, see also Scheme 8 in Section 3) [70]. Since they are produced from the identical precursors by a common chemical reaction, their chemical compositions are identical each other, possessing an identical molecular weight. They are, on the other hand, topologically distinctive each other. The random combination of cations and anions will produce the two constructions of manacle ring and θ ring in the ratio of 3:2. As described in Section 3, they are classified as a pair of topologically distinctive constitutional isomers. The size, i.e. hydrodynamic volume of the manacle form isomer is considered to be larger than that of the θ form counterpart. In addition, the dielectric property of the two topological isomers may be distinct from each other, since the spatial alignments of polar groups (*N*-phenyl groups) are different.

The covalent conversion of the electrostatically assembled precursor comprising the bifunctional poly(THF) having pyrrolidinium salt groups carrying tricarboxylate counteranions proceeded without any sign of gelation under diluted conditions. And remarkably, the RPC showed the presence of two components in the covalent fixation product, which were subsequently separated by means of fractionation (Fig. 1). The ^{1}H NMR and IR of the two fractions were identical each other, and showed the
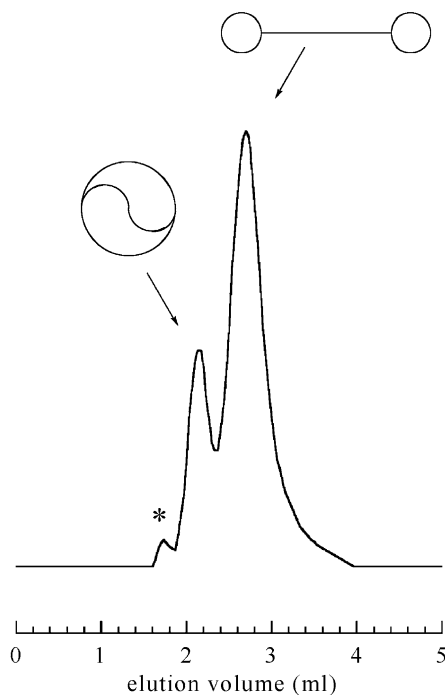
Fig. 1. RPC trace (UV) of the product from three bifunctional poly(THF) precursors carrying two tricarboxylate counteranions after the heat treatment under dilution. (Column: TSK ODS-80TS (80 Å pore, 150 mm × 4.6 mm, 5 μm average particle size); eluent: THF/CH$_3$CN = 49/51 (v/v), isocratic, 1.0 ml/min). The peak marked by (∗) is that of unassigned fraction. Reprinted with permission from Ref. [41]. Copyright, 2001 by Wiley–VCH Verlag GmbH, D-69451 Weinheim (FRG).
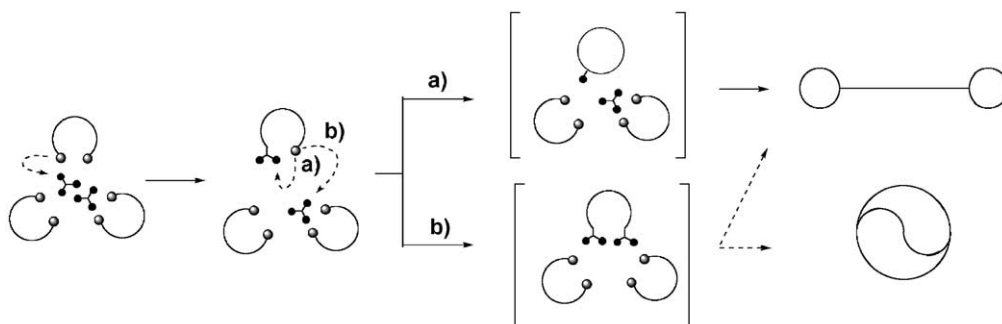
Scheme 25. Reprinted with permission from Ref. [41]. Copyright, 2001 by Wiley-VCH Verlag GmbH, D-69451 Weinheim (FRG).

quantitative ring-opening reaction of pyrrolidinium salt groups by carboxylate groups in the tricarboxylate. The SEC showed, although it failed to give the two distinctly separated peaks, a consistent peak profile convoluted from the two isomer components of the respective elution volumes with the ratio of 78:22, estimated by the RPC.

The observed isomer ratio indicates that the intramolecular process to produce the manacle type isomer is slightly favored in this covalent fixation process (path **a** in Scheme 25). The molecular weights of the topological isomers (as a mixture) determined by the VPO and by the ^{1}H NMR (assuming quantitative chemical conversion of polymer end groups) coincided, within an experimental error, with that of the three times of its linear analogue 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 the covalent fixation by the ring-opening reaction of pyrrolidinium salt groups.

An exclusively single form in these two topological isomers, namely an identical topology of the θ ring, has been produced by an alternative process [70]. Thus, an assembled precursor from the trifunctional, star-shaped poly(THF) having *N*-phenylpyrrolidinium salt end groups [114] carrying a trifunctional carboxylate was subjected to the covalent conversion process (Scheme 26). The ^{1}H NMR confirmed that all pyrrolidinium salt groups in the precursor were converted
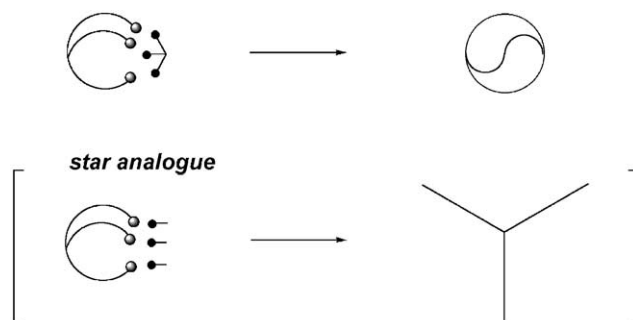
Scheme 26. Reprinted with permission from Ref. [41]. Copyright, 2001 by Wiley-VCH Verlag GmbH, D-69451 Weinheim (FRG).

into amino-ester groups. In addition, the SEC showed that the product retained uniform size distribution, and its hydrodynamic volume was notably smaller than that of its open-chain analogue, i.e. the relevant star poly(THF).

5.4. Cyclics with functional groups

5.4.1. kyklo-Telechelic poly(THF)

Cyclic polymer precursors having functional groups at the designated positions, termed *kyklo*-telechelics (the Greek 'kyklos' means cyclic), will be of potential importance as a macromolecular building block to construct topologically unique and complex macromolecular architectures containing cyclic polymer units [73]. Thus, the linear telechelic poly(THF) having *N*-phenylpyrrolidinium salt groups, and optionally with an additional functional group at the center position of the polymer chain (termed *kentro*-telechelics [117]), described in the preceding section, have been utilized to design *kyklo*-telechelics having a single or two functional groups (Scheme 27). The electrostatic self-assembly and covalent fixation process was again successfully applied for an efficient polymer cyclization process of the linear telechelic poly(THF)s, through the formation of a unique self-assembly by polymer precursors carrying specific counteranions upon dilution, while balancing the charges between cations and anions.

First, a telechelic poly(THF) carrying a 5-hydroxyisophthalate counteranion (a hydroxy-functionalized dicarboxylate) was prepared through the relevant ion exchange reaction detailed in Section 5.2.1 (Scheme 28). This ionically linked polymer precursor was then subjected to the heat treatment under dilution. The complete ring-opening reaction was confirmed by the ^{1}H NMR of the product quantitatively recovered after simply evaporating the solvent. And the SEC showed that the product possesses a narrow size distribution and a notably smaller hydrodynamic volume than that of the linear analogue. The ratio of the hydrodynamic volumes between the cyclic and the linear products, estimated by the SEC with their apparent peak molecular weights was in good agreement with those previously reported. From these results, it is concluded that a cyclic poly(THF) having a hydroxy group, derived from the dicarboxylate counteranion, has been effectively produced.

The relevant hydroxy-functionalized cyclic poly(THF) has been prepared alternatively by using an α,ω,*kentro*-telechelic poly(THF), which carries not only *N*-phenylpyrrolidinium salt groups at both chain ends but also an additional hydroxy group at the center position of the polymer chain (Scheme 28). Thus, the corresponding polymer precursor carrying a terephthalate counteranion was prepared and subjected to the heat treatment under dilution. The complete ring-opening reaction of the pyrrolidinium
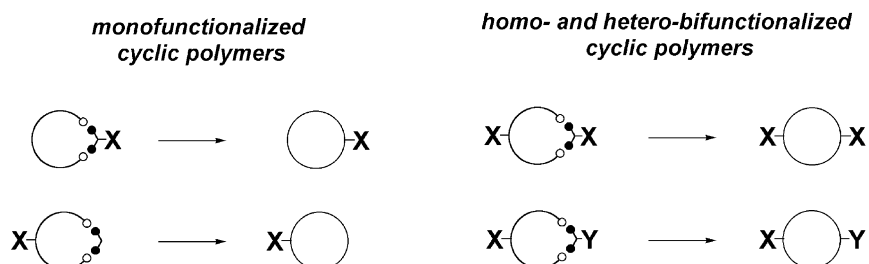
Scheme 27. Reprinted with permission from Ref. [41]. Copyright, 2001 by Wiley-VCH Verlag GmbH, D-69451 Weinheim (FRG).

**monofunctionalized
cyclic polymers**

**homo- and hetero-bifunctionalized
cyclic polymers**
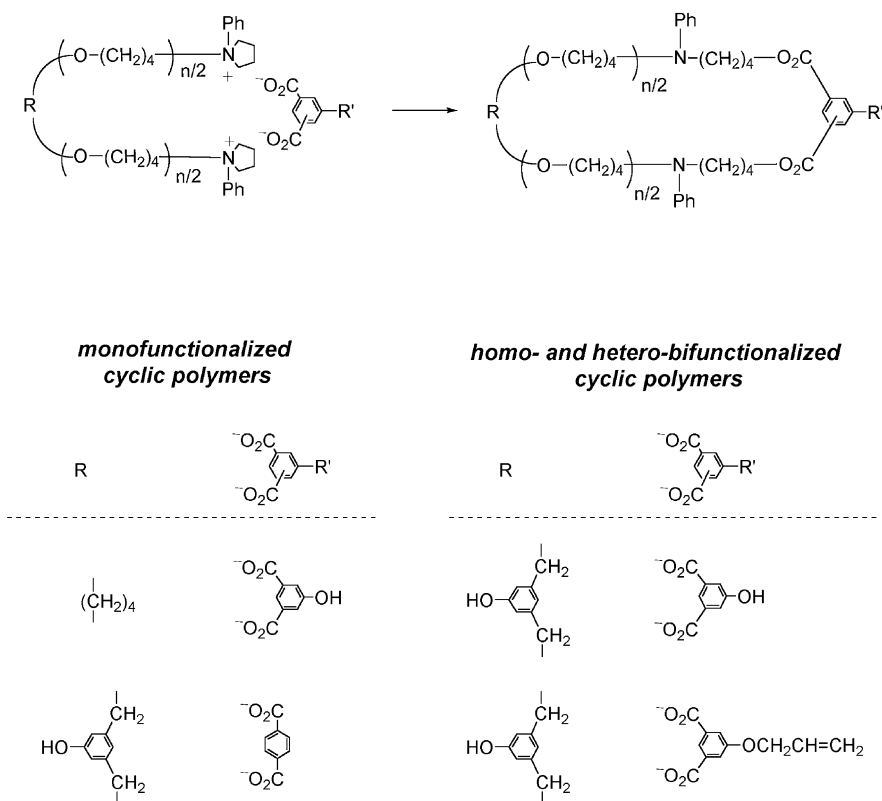
Scheme 28. Reprinted with permission from Ref. [41]. Copyright, 2001 by Wiley-VCH Verlag GmbH, D-69451 Weinheim (FRG).

salt end groups again took place, as was confirmed by the ^{1}H NMR and the IR. Besides, the SEC showed that the obtained cyclic poly(THF) possesses a narrow size distribution, and a notably smaller hydrodynamic volume than that of the linear analogue.

Moreover, homo- and hetero-bifunctionalized cyclic poly(THF)s having either two identical or two different functional groups at the opposite positions, respectively, have been synthesized (Scheme 28). Thus, the $\alpha,\omega,kentro$-telechelic polymer precursor carrying a 5-hydroxyisophthalate counteranion was prepared and subjected to the heat treatment under dilution. The ^{1}H NMR of the product showed the two singlets due to hydroxy protons not only from the 5-hydroxyisophthalate counteranion but also from the *kentro*-poly(THF) precursor. The intensities of these two signals were consistent with each other. Also, the SEC showed that the product possesses a narrow size distribution. It is thus confirmed that a homo-bifunctionalized cyclic poly(THF) having two hydroxy groups at the opposite positions has been effectively produced. And finally, an $\alpha,\omega,kentro$-telechelic polymer precursor carrying a 5-allyl-oxyisophthalate counteranion was prepared and subjected to heat treatment under dilution. A hetero-bifunctionalized cyclic poly(THF) having a hydroxy and an allyloxy group at the opposite positions was subsequently produced in a quantitative yield (Scheme 28). The ^{1}H NMR showed again a signal due to the hydroxy proton derived from the $\alpha,\omega,ketro$-telechelic poly(THF) precursor, in addition to signals due to allyloxy protons from the 5-allyloxyisophthalate counteranion. The proton intensity ratio of these

Scheme 29. Reprinted with permission from Ref. [41]. Copyright, 2001 by Wiley-VCH Verlag GmbH, D-69451 Weinheim (FRG).

signals agrees with that calculated from the expected molecular formula. The SEC showed the obtained hetero-bifunctionalized cyclic poly(THF) possesses a narrow size distribution.

5.4.2. Cyclic poly(THF) macromonomers

A novel functional cyclic polymer, i.e. a cyclic macromonomer, was prepared to design an unusual polymer network structure having both covalent and physical linkages [78]. This network is formed by a chain threading of the propagating polymer segment through large cyclic polymer units attached to the backbone polymer segments.

Although cyclic polymers are of a potential interest due to its capability to construct physically (non-covalently) linked architectures based on its loop topology, a tailored non-covalent linking process by threading through flexible and large size cyclic polymers has scarcely been achieved despite its relevance to interpenetrating polymer networks (IPNs) of wide applications [132]. Since a long and flexible polymer chain tends to assume a randomly coiled and hence contracted 3D structure, the chain threading by another polymer chain through such a large cyclic polymer unit is unwilling to proceed (Scheme 29). This is contrastive with a variety of medium size macrocyclic compounds up to around 100-membered ring, including 30–60-membered crown ethers, bipyridinium-based cyclophanes, cyclodextrins and macrocyclic amides [30,31,133,134]. They are regarded as configurationally stiff,

cyclic poly(THF) macromonomer

methacrylate-free, cyclic poly(THF)

linear analogue of cyclic poly(THF)

open-chain poly(THF) macromonomer

Scheme 30. Reprinted with permission from Ref. [41]. Copyright, 2001 by Wiley-VCH Verlag GmbH, D-69451 Weinheim (FRG).

and thus assuming an extended-cyclic conformation. The subsequent intriguing synthesis 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 [30,31].

An effective chain threading by the propagating polymer chain through cyclic polymer units of even as large as 280-membered ring has been achieved, by attaching them to a backbone polymer segment [78]. This has been confirmed by a copolymerization of a well-defined cyclic poly(THF) having a methacrylate group, namely a cyclic macromonomer (Scheme 29). In contrast, no noticeable chain threading was observed in a quantitative-conversion homopolymerization of methyl methacrylate (MMA) in the presence of a methacrylate-free, cyclic poly(THF) of the relevant ring size (Scheme 29).

Thus, the hydroxy-functionalized cyclic poly(THF) [73], described in Section 5.4.1, was subjected to the esterification by methacryloyl chloride in the presence of triethylamine (Scheme 30). A cyclic

macromonomer was obtained in a quantitative yield. The SEC showed that the obtained product possesses a narrow size distribution. Moreover, the ^{1}H NMR spectrum showed the signals due to the methacrylate group, and the degree of polymerization to be 70, corresponding to be as large as 280-membered ring (Mn = 5200).

A free radical copolymerization with MMA was then carried out in solution. First, the polymerization was interrupted to keep a limited conversion of MMA at less than 20%. The copolymer fraction was isolated by the precipitation treatment. The SEC of the copolymer product showed both ultraviolet (UV) and refractive index (RI) responses, to indicate that the graft component by the poly(THF) macromonomer, having a phenyl group at the precursor chain ends, distributes statistically along the poly(MMA)-based copolymer backbone. The ^{1}H NMR also showed the presence of the poly(THF) component in the copolymer, while the methacrylate group signals are completely disappeared. No side reactions such as a decomposition of the cyclic structure were detectable. The relative molar ratio of the graft units in the copolymer was estimated to be very close to the feed ratio against MMA, in accord with the random copolymerization to occur.

Subsequently, a complete-conversion copolymerization was carried out. A nearly whole portion of the recovered product became insoluble but swollen in various solvents. No gelation, on the other hand, took place in the relevant quantitative-conversion copolymerization of MMA with a relevant open-chain polymer precursor, obtained from a monofunctional poly(THF) with a pyrrolidinium salt end group (Scheme 29). The recovered product was totally soluble, and the ^{1}H NMR and IR showed no sign of side reactions, responsible for the covalent cross-linking by chain transfer reactions during the copolymerization process. These results indicate that the gelation in the copolymerization of MMA with the cyclic macromonomer took place through the physical cross-linking, i.e. the threading by the propagating chain through the pendant cyclic branches attached to the polymer backbone as shown in Scheme 29. And more importantly, the chain threading through large polymer loops occurred only when they are covalently attached to the polymer backbone.

5.5. Reshuffling in self-assembly

The electrostatic self-assembly and covalent fixation strategy has also been applied to design of a novel polymer architecture comprising of both a ring and a branch units (i.e. possessing a free chain end)
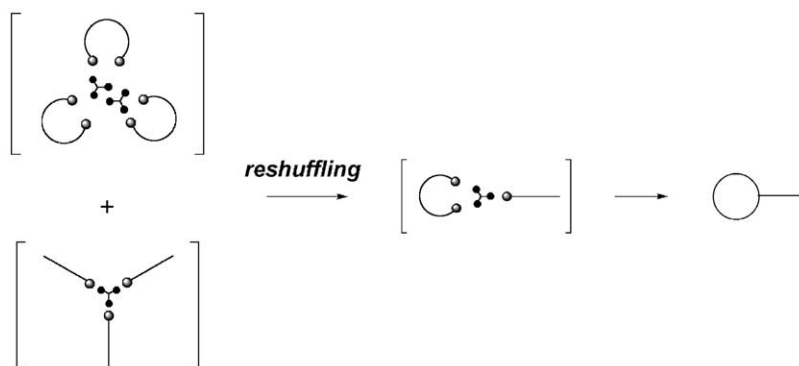
Scheme 31.
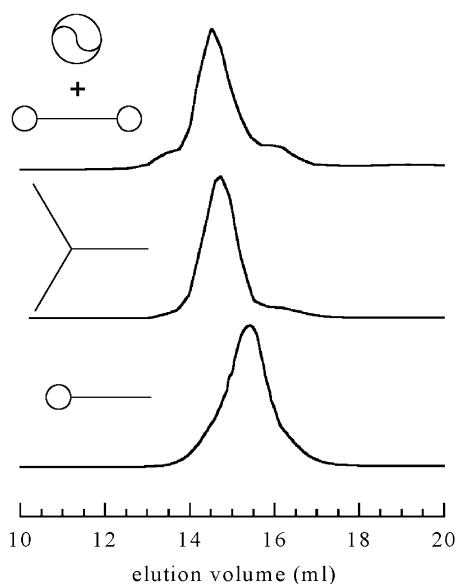
Fig. 2. SEC traces (RI) of the polycyclic polymer products from three bifunctional poly(THF) precursors carrying two tricarboxylate counteranions (top), of the star polymer product from three monofunctional poly(THF) precursors carrying a tricarboxylate counteranion (middle), and of 'a ring with a branch' polymer product from a mono- and a bifunctional poly(THF) precursors carrying a tricarboxylate counteranion. (Column: TSK G4000HXL × 2; eluent: THF, 1.0 ml/min). Reprinted with permission from Ref. [41]. Copyright, 2001 by Wiley–VCH Verlag GmbH, D-69451 Weinheim (FRG).

[70]. Thus, dynamic reshuffling of the ionic components has been exploited in an electrostatic self-assembly of the telechelic polymer precursors in solution (Scheme 31). More specifically, an equimolar amount of the two types of the self-assembled precursor, namely one obtained from the bifunctional poly(THF) carrying tricarboxylate counteranions, and another obtained from the monofunctional poly(THF) carrying again tricarboxylate, were mixed in solution. Under dilution, the spontaneous reshuffling of the telechelic polymer precursors in the electrostatic self-assembly tends to take place to form a new thermodynamically favored assembly, where the smallest number of polymer components is combined, while balancing the charges between cations and anions. The subsequent heat treatment under the relevant dilution could convert their ionic linkage into covalent bond, and a new polymer topology was produced (Scheme 31).

The ^{1}H NMR showed, as expected, a quantitative ring-opening reaction of the pyrrolidinium salt, and the SEC showed a single peak profile upon the reshuffling by the two self-assembled polymer precursors under dilution and the subsequent covalent conversion (Fig. 2, bottom). In addition, its hydrodynamic volume was notably smaller than those of the relevant pre-reshuffling counterparts, i.e. the polycyclic polymer products (mixture of the two topological isomers detailed in Section 5.3.2) and of the star polymer product, obtained separately from the corresponding monofunctional polymer precursor (Fig. 2, top and middle, respectively). These results demonstrate that a unique polymer topology comprising of both a ring and branch units was produced selectively by the covalent conversion from the corresponding electrostatically assembled polymer precursor. The reconstruction of ionically self-assembled polymer precursors can be readily achieved through the reshuffling in a diluted solution, to form a new self-assembled product with the smallest number of the components with balancing the charges of cations
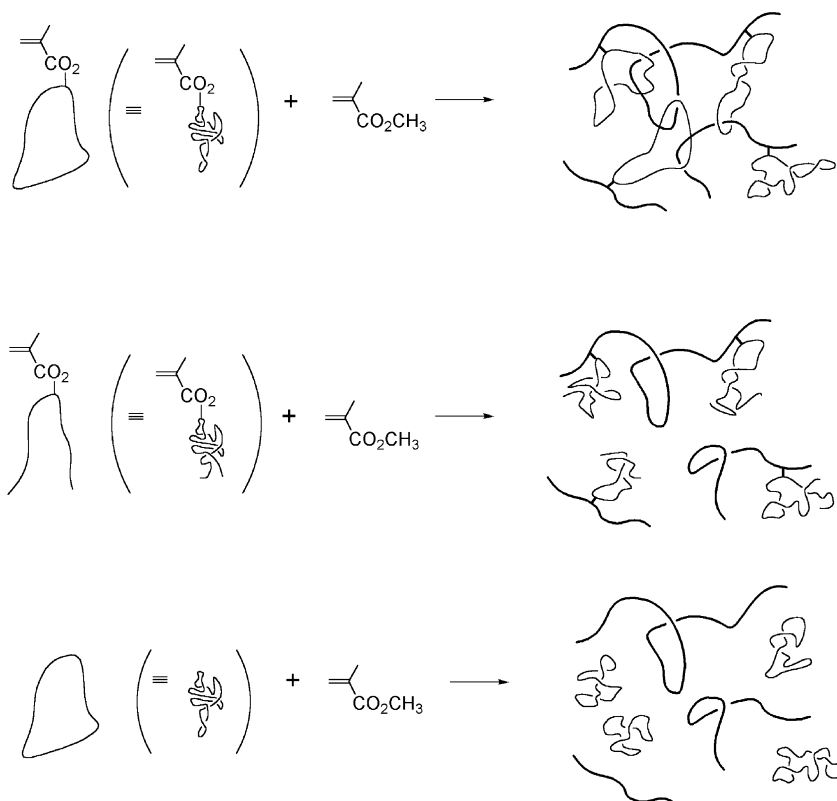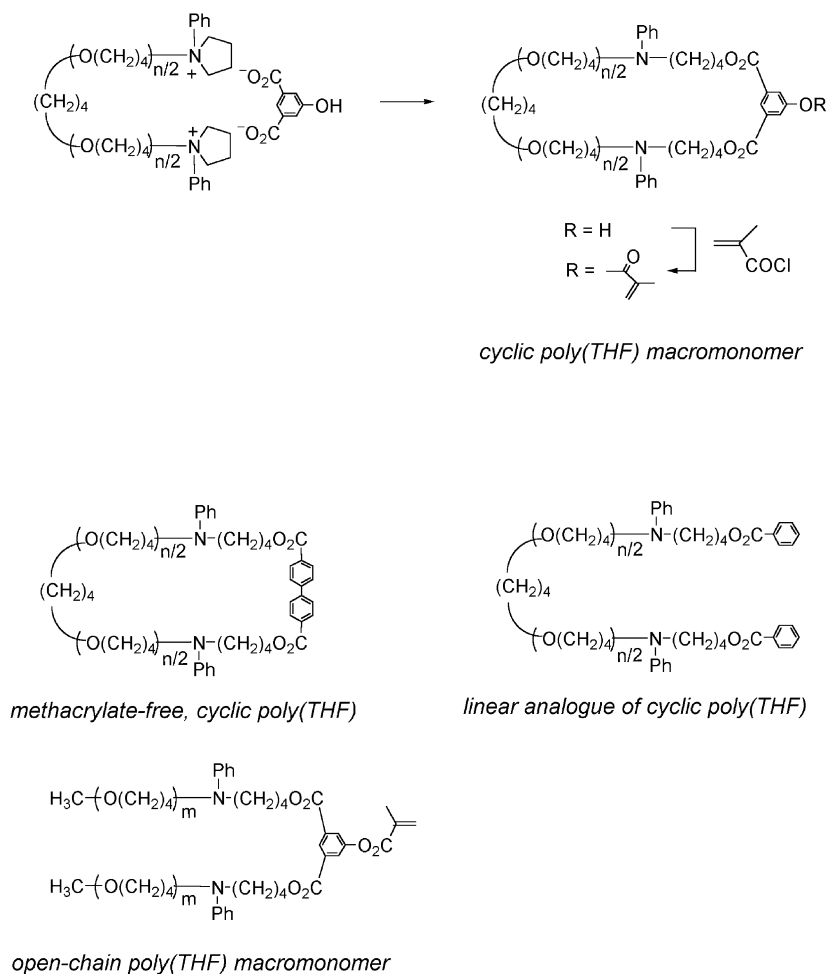
star polymer
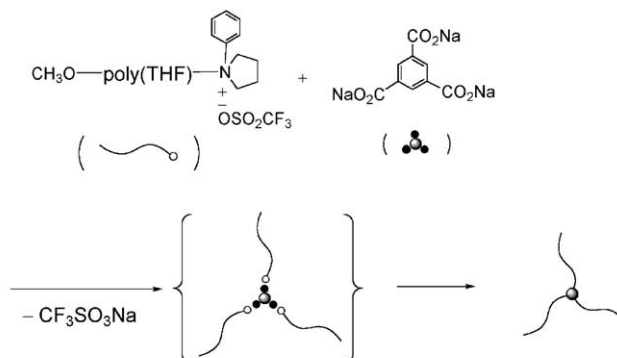
polymacromonomer
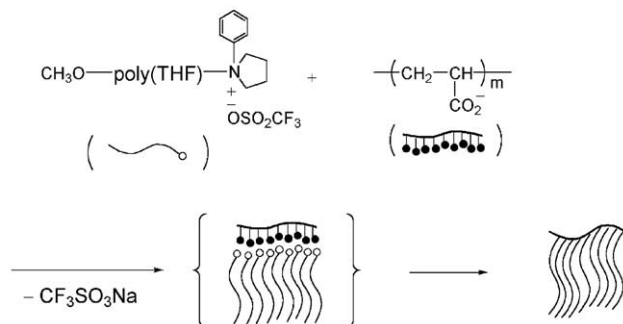
Scheme 32. Reprinted with permission from Ref. [41]. Copyright, 2001 by Wiley-VCH Verlag GmbH, D-69451 Weinheim (FRG).

and anions. This conceptually novel methodology will afford a versatile means to construct a variety of unusual and complex polymer topologies.

5.6. Star polymers and polymacromonomers

Various model branched polymers such as poly(THF) star polymers and polymacromonomers have also been produced, while no dilution condition was required in contrast to the preceding polymer cyclization processes (Scheme 32) [74–76]. Thus, an efficient ion-exchange reaction of a monofunctional poly(THF) having an *N-phenyl*pyrrolidinium salt end group carrying a tricarboxylate was found to occur by the repeated precipitation into an aqueous solution containing an excess amount of a tricarboxylate sodium salt. The subsequent heat treatment of ionically assembled polymer precursor caused the selective ring-opening reaction to give a covalently linked star polymer of three arms in a high yield.

The telechelic poly(THF) was then utilized in the macromolecular ion-exchange reaction with poly(sodium acrylate) through the repeated precipitation (Scheme 32) [74–75]. The ion-exchange
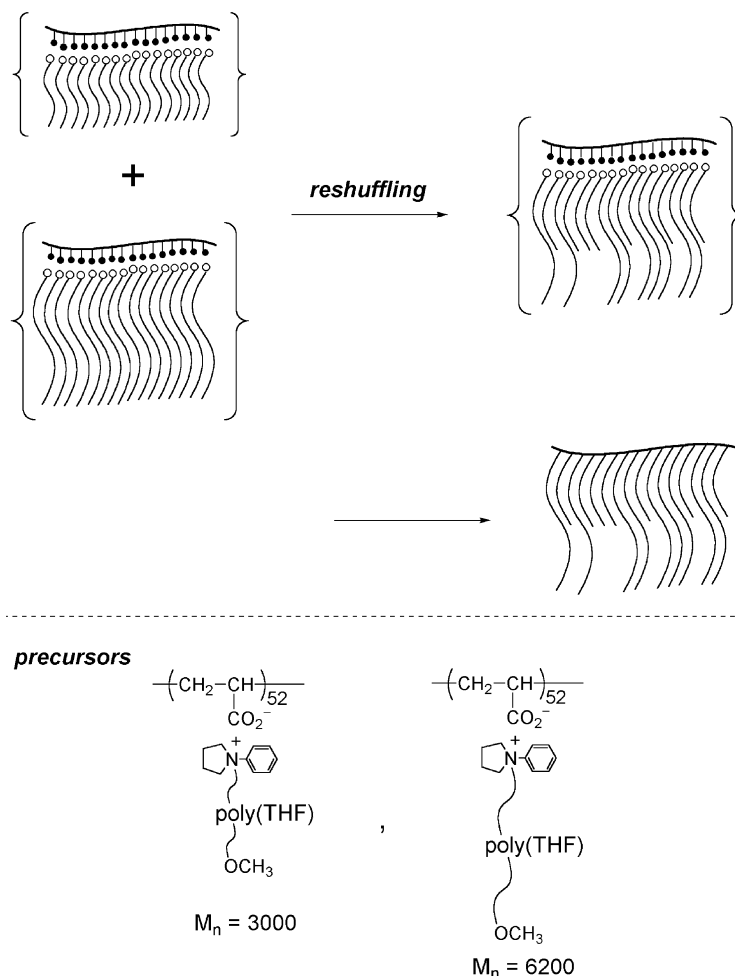
Scheme 33. Reprinted with permission from Ref. [41]. Copyright, 2001 by Wiley-VCH Verlag GmbH, D-69451 Weinheim (FRG).

reaction proceeded quantitatively from triflate to carboxylate, and no sign of the ring-opening reaction was detected for the isolated ion-exchanged product, i.e. the electrostatically assembled polymacromonomer precursor. The subsequent heat treatment again caused the selective ring-opening reaction to give a covalently linked polymacromonomer in a high yield. Furthermore, by using a uniform size poly(-sodium acrylate), prepared via a living polymerization of *tert*-butyl acrylate, a well-defined poly(THF) polymacromonomer with controlled backbone segment length having both predetermined branch segment numbers and branch segment length was obtained.

The isolation of the electrostatically self-assembled precursor can also provide a unique opportunity for the structural manipulation of star polymers and polymacromonomers, and a star copolymer and a copolymacromonomer having different types of graft chain segments were produced by the reshuffling of electrostatically self-assembled polymer precursors (Scheme 33) as in the case of the synthesis of a polymer having a ring with a branch architecture [70].

In contrast, the reaction with monofunctional poly(THF) having either a 4-membered cyclic ammonium or a 5-membered cyclic sulfonium (tetrahydrothiophenium) salt end group caused the spontaneous ring-opening reaction by any carboxylate counteranions even at an ambient condition, and the ionically assembled polymer precursor could not be isolated as an intermediate [135,136].

6. Conclusions and perspectives

In the first part of this review, we have formulated a comprehensive classification of non-linear polymer topologies. It will provide useful insights for the relationship between different polymer topologies, and can eventually show their rational synthetic strategies. A special emphasis is placed on the concept of topological isomerism, which is particularly unique and often encountered in flexible non-linear polymer molecules. These may evolve into a new branch in polymer science and technology.

In the second part, we have shown a novel methodology for designing various non-linear polymer topologies, such as monocyclic and polycyclic polymers, a pair of polymeric topological isomers, cyclic telechelics (*kyklo*-telechelics) and cyclic macromonomers, and a ring with a branch topology polymers, as well as such model branched polymers as star polymers and polymacromonomers. Thus, new telechelic prepolymers having moderately strained cyclic ammonium salt group as a single or multiple end groups were prepared. In addition, the polymer precursor having functional groups at the designated interior positions have been prepared. They were subjected to an ion-exchange reaction to introduce multifunctional carboxylate as a counteranion. The electrostatically self-assembled products formed in a diluted organic solution or in bulk were then subjected to the heat treatment to convert the ionic interaction into the permanent covalent linkage by the ring-opening reaction. A variety of topologically unique, non-linear polymer architectures has been thus produced in high efficiency.

Wide options for the future directions are envisaged by extending the electrostatic self-assembly and covalent fixation strategy. Those include; first, an efficient covalent conversion process not by a thermal reaction so far described, but by a photo-irradiation process, which will implement further synthetic opportunities of this system. This will be achieved by an appropriate combination of cationic/anionic pairs for the polymer chain end and the counter ion. Secondly, a wider selection of telechelic polymer segment other than poly(THF) and polystyrene can be attained, since, in principle, any polymers besides polystyrene obtainable by means of a living polymerization technique can be transformed to the relevant telechelics by the subsequent modification of the living end groups. This will offer entirely novel multicomponent polymer materials of the combination of not only contrastive polymer properties but also different polymer topologies.

Finally, the visualization of various polymer topologies will be achieved either by X-ray crystallography with a crystallizable, single large molecule, or by AFM with a stiffened, discrete polymer object. These will undoubtedly become important steps toward the future 'nanotechnology'.

Acknowledgements

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