

## Topological Polymer Chemistry: Classification and Construction of Nonlinear Polymer Architectures

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**Summary:** A systematic classification of nonlinear polymer architectures is formulated 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). And a variety of topologically unique polymers, such as monocyclic and polycyclic polymers, cyclic telechelics (kyklo-telechelics), cyclic macromonomers and polymeric topological isomers have been constructed by means of an "electrostatic self-assembly and covalent fixation" strategy. In this process, new telechelic polymer precursors having moderately strained cyclic onium salt groups carrying multifunctional carboxylate counteranions have been prepared as key polymer precursors. The unique electrostatic self-assembly, formed particularly in a dilute solution, was covalently fixed through the ring-opening reaction by heating, to produce a variety of nonlinear polymer architectures in high efficiency.

### Introduction

The precise control in polymer architectures has been an ongoing challenge in synthetic polymer chemistry, since new polymer topologies will realize unprecedented properties and functions in polymeric materials. A variety of branched polymer structures have so far been constructed, including star polymers, H-shaped polymers, super H-shaped polymers, pom-pom shaped polymers, as well as comb polymer and dendrimers. Moreover, cyclic, multicyclic and cyclic-branched combined polymers, such as ring polymers, 8-shaped polymers as well as tadpole polymers have recently gained increasing interests.<sup>[1]</sup>

We show first a systematic classification of nonlinear 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).<sup>[2]</sup> Subsequently, a novel methodology has been proposed to produce various non-linear polymer architectures in high efficiency, by exploiting the self-assembly principle to preorganize linear polymer precursors, prior to convert them into covalently linked permanent structures. Thus, we have utilized Coulombic self-assembly of hydrophobic macromolecules having moderately strained cyclic onium salt groups carrying

multifunctional carboxylates as counteranions.<sup>[3,4]</sup>

## Systematic Classification of Nonlinear Polymer Topologies

A rational classification of nonlinear polymer topologies will indicate their structural relationships, and eventually provide their convenient synthetic pathways. There have been, however, few attempts on the systematic classification of nonlinear, and in particular cyclic and multicyclic, polymer architectures composed of sufficiently long and thus flexible segment components.

We have formulated a systematic classification of a series of well-defined cyclic and branched polymer architectures by reference to constitutional isomerism in alkanes ( $C_nH_{2n+2}$ ) and in mono- and polycycloalkanes ( $C_nH_{2n}$ ,  $C_nH_{2n-2}$ , etc).<sup>[2]</sup> Each alkane and (poly)cycloalkane molecule is taken as a source to generate a unique topological construction. The total number of termini (chain ends) and of junctions (branch points) are taken as invariant (constant) geometric parameters. The total number of branches at each junction and the connectivity of each junction are maintained as invariant parameters as well. On the other hand, such Euclidian geometric properties as the distance between two adjacent junctions and that between the junction and terminus are taken as variant parameters. This conforms to the flexible nature of the randomly-coiled polymer segments. Furthermore, topological constructions having five or more branches at one junction is allowed while the relevant isomers having the corresponding molecular formula are absent.

In Table 1-A, alkane molecules of generic molecular formula of  $C_nH_{2n+2}$  with  $n = 3-7$  and their relevant topological constructions are listed. 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 and propane ( $C_3H_8$ ) produce an equivalent line construction. 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 produced already 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. Accordingly, a series of branched polymer topologies are hierarchically ranked as shown in Table 1-A.

Topological constructions from monocycloalkane molecules of  $C_nH_{2n}$  with up to  $n = 6$  are collected in Table 1-I. Cyclopropane ( $C_3H_6$ ) produces a simple cyclic topology. From the two

Table 1. Systematic Classification of Nonlinear Polymer Topologies. (Reprinted with permission from ref [2]. Copyright, 2001 by American Chemical Society)

A					
Polymer Topology	$C_nH_{2n+2}$				
	n=3	4	5	6	7

I					
Polymer Topology	$C_nH_{2n}$				Polymer Topology
	n=3	4	5	6	$C_nH_{2n}$ n=6

II					
Polymer Topology	$C_nH_{2n-2}$			Polymer Topology	$C_nH_{2n-2}$ n=6
	n=4	5	6		

III					
Polymer Topology	$C_nH_{2n-4}$			Polymer Topology	$C_nH_{2n-4}$ N=7
	n=4	5	6		

isomers of  $C_4H_8$ , a tadpole and a simple ring structures are produced. Two constructions are newly produced from  $C_5H_{10}$  isomers, and 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 the other has two outward branches located at two separate junctions in the ring unit. Further, four new topological constructions are produced from  $C_6H_{12}$  isomers; one having five branches at one junction is hypothetical and is therefore shown in parentheses in Table 1-I. A series of "a ring with branches" constructions have been thus classified as summarized in Table 1-I.

Topological constructions from bicycloalkanes of  $C_nH_{2n-2}$  with up to  $n = 6$  are listed in Table

1-II, where basic three bicyclic constructions free of outward branches are included. Those are  $\theta$ -ring, 8-ring and manacle-ring, respectively. First, a  $\theta$  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 an 8-shaped construction from spiro[2,2]pentane. By reference to bicyclohexane ( $C_6H_{10}$ ) isomers, moreover, eight new constructions are produced. All constructions but one from bi(cyclopropane) possess outward branches emanated from either  $\theta$ -ring or 8-ring shown above. 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.

Selected topological constructions produced from tricycloalkanes of  $C_nH_{2n-4}$  are also shown in Tables 1-III. A large number of "rings with branches" constructions are produced in this group. Eight topological constructions are derived from  $\theta$ - or 8-forms. 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 1-III. Moreover, the seven topological constructions of externally linked (or "bridged") rings with a simple cyclic,  $\theta$ - or 8-forms are obtainable in reference to the relevant tricycloalkane isomers.

## Single Cyclic and Multicyclic Polymers

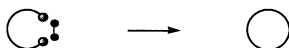
We have developed an "electrostatic self-assembly and covalent fixation" strategy to construct a variety of topologically unique, nonlinear polymer architectures, where new telechelic polymer precursors having a moderately strained cyclic onium salt group carrying multifunctional carboxylate counteranions have been employed as key polymer intermediates. The unique electrostatic self-assembly, formed particularly in a dilute solution, has been subsequently converted to permanent covalent product through the ring-opening reaction by heating, to produce a variety of nonlinear polymer architectures in high efficiency.<sup>[3,4]</sup>(Scheme 1)

Thus, a polymer cyclization was carried out using a telechelic poly(THF) having N-phenylpyrrolidinium salt groups carrying a dicarboxylate counteranion.<sup>[5-7]</sup> Typically, the reaction proceeded by heating under dilution at the concentration of 0.2 [g/L] in as high as 93 % yield, and the cyclic poly(THF) of more than 98 % purity was obtained in 74 % yield after the purification with preparative thin-layer-chromatography (TLC) technique.<sup>[5]</sup>

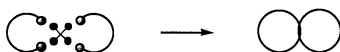
Bicyclic and tricyclic polymer topologies were also constructed by using the telechelic

poly(THF) having N-phenylpyrrolidinium salt groups, and carrying a tetra and a hexacarboxylate counteranion, respectively.<sup>[4]</sup> The balance of the charges between the ammonium salt groups in the polymer precursor and the carboxylate anions was maintained,

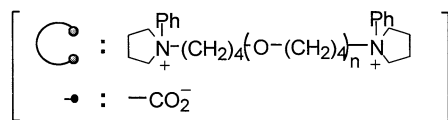
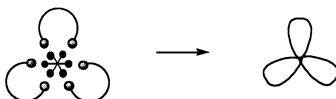
**i) 1 + 1 assembly**



**ii) 2 + 1 assembly**



**iii) 3 + 1 assembly**



**Scheme 1**

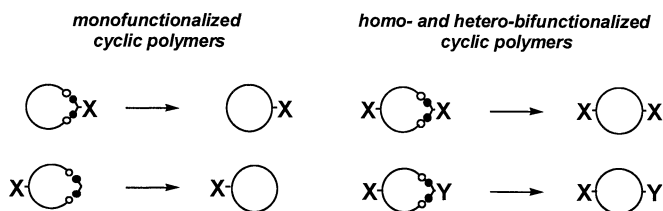
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corresponding to the molar ratio of 2:1 and 3:1, respectively. (Scheme 1) These polymer precursors were then subjected to the heat treatment under appropriate dilution. The bi- and tricyclic poly(THF)s were readily obtained after the preparative thin layer chromatography. These results indicate that the electrostatic polymer assemblies formed under dilution 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 could lead to bicyclic and tricyclic polymer products, through the covalent fixation by the ring-opening reaction of pyrrolidinium salt groups.

## Kyklo-Telechelics

Cyclic polymer precursors having functional groups at the designated positions, termed *kyklo-*

telechelics (the Greek “*kyklos*” means cyclic), will be of a potential importance as a macromolecular building block to construct topologically unique and complex macromolecular architectures containing cyclic polymer units. 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) has been utilized to design *kyklo*-telechelics having a single or two functional groups.<sup>[8]</sup> (Scheme 2) The "electrostatic self-assembly and covalent fixation" process was applied for an efficient polymer cyclization process by the linear telechelic poly(THF)s, where a unique self-assembly is formed under dilution by polymer precursors carrying specific counteranions, while balancing the charges between cations and anions.



**Scheme 2**

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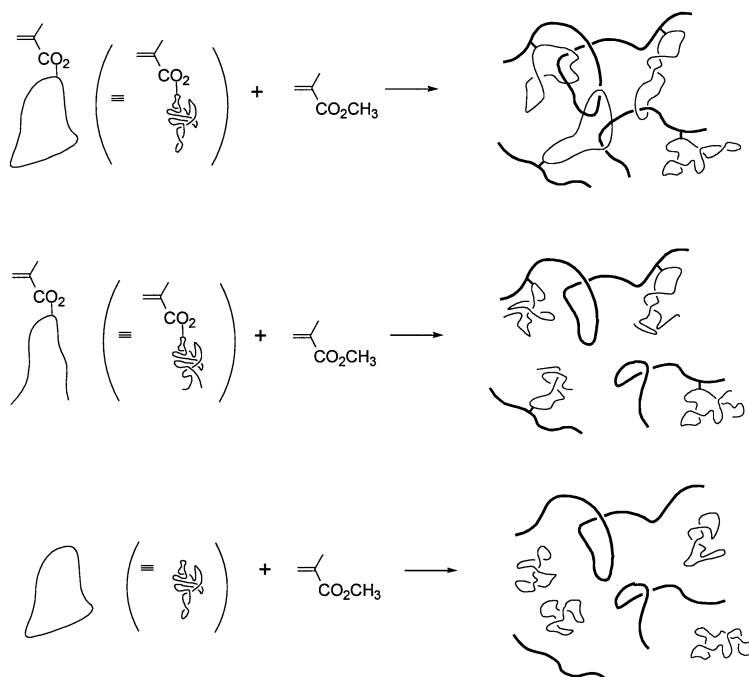
Thus, a telechelic poly(THF) carrying a 5-hydroxyisophthalate counteranion (a hydroxy-functionalized dicarboxylate) was prepared. This ionically-linked polymer precursor was subjected to the heat treatment under dilution to produce a cyclic poly(THF) having a hydroxy group, derived from the dicarboxylate counteranion. Homo- and hetero-bifunctionalized cyclic poly(THF)s having either two identical or two different functional groups at the opposite positions, respectively, have subsequently been synthesized by using the relevant hydroxy-functionalized cyclic poly(THF) obtained alternatively from an  $\alpha,\omega$ ,*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. Thus, the  $\alpha,\omega$ ,*kentro*-telechelic polymer precursor carrying a 5-hydroxyisophthalate counteranion was subjected to the heat treatment under dilution to give a homo-bifunctionalized cyclic poly(THF) having two hydroxy groups at the opposite positions. Similarly, an  $\alpha,\omega$ ,*kentro*-telechelic poly(THF) carrying a 5-allyloxyisophthalate counteranion was prepared as a precursor to produce a hetero-bifunctionalized cyclic poly(THF) having a hydroxy and an

allyloxy group at the opposite positions.

### Cyclic Macromonomer

Cyclic polymers will be utilized to construct physically (non-covalently) cross-linked polymer architectures based on its loop topology. However, a tailored non-covalent cross-linking process by threading through flexible and large size cyclic polymers has scarcely been achieved. Since a long and flexible polymer chain tends to assume a randomly coiled and hence constrained three-dimensional structure, the threading by another polymer chain through such a large cyclic polymer unit is unwilling to proceed. 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. They assume stiff and extended cyclic conformation and are used for the synthesis of rotaxanes and catenanes.

We have succeeded in synthesizing a novel functional cyclic polymer, i.e., a cyclic macromonomer of 280-membered ring, to design an unusual polymer network structure



**Scheme 3**

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having both covalent and physical linkages. This network is formed by a chain threading of the propagating polymer segment through large cyclic polymer units attached to the backbone polymer segments.<sup>[9]</sup> (Scheme 3)

A cyclic macromonomer having a methacryl group with the degree of polymerization of 70, corresponding to 280-membered ring ( $M_n = 5200$ ), was obtained from the hydroxy-functionalized cyclic poly(THF), in a quantitative yield. A free radical copolymerization with methyl methacrylate (MMA) to a complete-conversion resulted in a gel product. In contrast, no gelation took place either in the relevant quantitative-conversion copolymerization of MMA with an open-chain poly(MMA) macromonomer, or in a quantitative-conversion homopolymerization of MMA in the presence of a simple cyclic poly(THF) of the relevant ring size. (Scheme 3)

These results indicate that the gelation 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. And interestingly, this chain threading through large polymer loops occurred only when they are covalently attached to the polymer backbone.

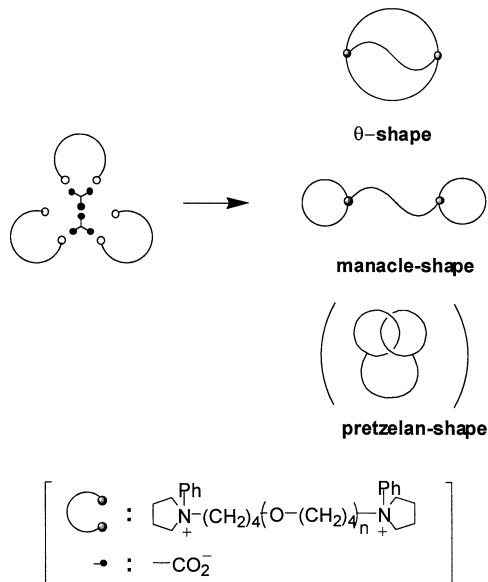
## Topological Isomers

The covalent conversion of an electrostatically self-assembled precursor, obtained from the bifunctional poly(THF) having N-phenylpyrrolidinium salt groups carrying tricarboxylate (trimesate) counteranions, was also performed under dilution.<sup>[4]</sup> (Scheme 4) The reversed-phase chromatography (RPC) showed the presence of two components in the covalent fixation product. The <sup>1</sup>H NMR and IR of the two fractions isolated by RPC fractionation were identical each other, and showed the quantitative ring-opening reaction of pyrrolidinium salt groups by carboxylate groups in the tricarboxylate. The molecular weights of the product (as a mixture) determined by the VPO and by the <sup>1</sup>H NMR (assuming quantitative chemical conversion of polymer end groups) coincided, within an experimental error, with that of the three times of its linear precursor analogue. The SEC showed, however, that one fraction is larger in its size than another.

These results indicate that a pair of topological isomers, i.e.  $\theta$ - and manacle-constructions, were formed simultaneously from three bifunctional polymer precursors and two trifunctional end-linking reagents.<sup>[1,10]</sup> (Scheme 4) 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  $\theta$ -ring in the ratio of 3:2. The size, i.e., hydrodynamic volume of the manacle-form isomer is considered to be larger than that of the  $\theta$ -form counterpart. The observed isomer ratio (78:22) indicates that the intramolecular process to produce the manacle-type isomer is slightly favored in this covalent fixation process.



**Scheme 4**

## Conclusions

We have formulated a systematic classification of nonlinear polymer topologies. It provides useful insights for the relationship between different polymer topologies, and eventually for the rational synthetic pathway. Thus, an "electrostatic self-assembly and covalent fixation" process has been devised for constructing various non-linear polymer topologies, including monocyclic and polycyclic polymers, cyclic telechelics (*kyklo*-telechelics), cyclic macromonomers and a pair of polymeric topological isomers. New telechelic prepolymers having moderately strained cyclic ammonium salt group were prepared as key intermediates. The electrostatic self-assemblies, formed in particular under dilution, were subsequently converted into the permanent covalent products by the selective ring-opening reaction.

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