HIGHLIGHT

Topological Polymer Chemistry by Electrostatic Self-Assembly

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ABSTRACT: Recent developments in topological polymer chemistry are outlined. First, nonlinear polymer topologies are systematically classified on the basis of topological considerations of 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.). Various pairs of topological isomers are identified in randomly coiled, flexible polymer molecules with cyclic and branched structures. An electrostatic self-assembly and covalent fixation strategy has subsequently been developed for the efficient synthesis of a variety of topologically unique polymers, including monocyclic and polycyclic polymers, topological isomers, and topological block copolymers. In this process, new telechelics with moderately strained cyclic onium salt groups carrying multifunctional carboxylate counteranions have been designed as key polymeric precursors. Further extensions of topological polymer chemistry have been achieved by the use of cyclic telechelics (*kyklo*-telechelics) and cyclic macromonomers, obtainable also by means of the electrostatic self-assembly and covalent fixation process. © 2003 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 41: 2905–2917, 2003

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Yasuyuki Tezuka was born in Kyoto, Japan, in 1953. He studied synthetic chemistry at the University of Tokyo under the guidance of Professor T. Tsuruta on the subject of asymmetric selective oligomerization of epichlorohydrin. In 1979, he moved to Ghent University (Belgium) to pursue his doctorate with Professor E. Goethals as a promoter on the subject of poly-(tetrahydrofuran)-based telechelic polymers. In 1982, he returned to Japan to start an academic carrier as an assistant professor with Professor K. Imai at Nagaoka University of Technology (Niigata, Japan). He was promoted to associate professor in 1991 and moved to Tokyo Institute of Technology (Department of Organic and Polymeric Materials) in 1994. He has coauthored three books and has published about 150 original publications and review articles. He has served as an associate editor of *Polymer Journal*, which is published by the Society of Polymer Science (Japan). His current research is focused on topological polymer chemistry, particularly on designing topologically unique macromolecular architectures by the development of the electrostatic self-assembly and covalent fixation process.

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POLYMER CHEMISTRY AND TOPOLOGICAL GEOMETRY

The precise control of polymer architectures has been an ongoing challenge in synthetic polymer chemistry because new polymer topologies 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, comb polymers, and dendrimers. Moreover, cyclic, multicyclic, and cyclic–branched polymers, such as ring polymers, 8-shaped polymers, and tadpole polymers, have recently attracted more interest.[1]

These polymer topologies are characterized first by their principal geometric parameters, that is, the absence or presence (and number) of termini (end groups) and junctions (branch points). It is assumed that long-chain polymer segments are allowed to undergo a hypothetical continuous transformation. For example, the topology of a flexible ring polymer molecule is characterized by the absence of a terminus and is regarded as equivalent to a triangle or square, but it can be distinguished from an open-chain linear polymer molecule with two termini. Such a topological graph representation of flexible polymer molecules is in contrast to that of small (or shape-persistent) molecules, in which all bond lengths and bond angles are considered invariant Euclidian geometric parameters. Therefore, unique insights into the intrinsic properties of flexible nonlinear polymer molecules will be obtained through topological elucidation.[2]

In this highlight, recent developments in topological polymer chemistry are outlined. First, a systematic classification of nonlinear polymer topologies is formulated on the basis of the topological consideration of 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.).[3] The topological relationship between different polymer topologies is disclosed, and a rational synthetic protocol for a variety of topologically unique polymers is provided subsequently. It is recognized that polymer topologies are distinguished not only by the terminus/junction numbers, that is, the *first-order topological parameters*, but also by the connectivity or combination of flexible polymer segment components, that is, *the second-order topological parameters*. As a result, various pairs of topological isomers, occurring uniquely on randomly coiled, flexible polymer molecules having cyclic and branched structures, are identified.

An electrostatic self-assembly and covalent fixation strategy has subsequently been developed for the efficient synthesis of a variety of topologically unique polymers, including monocyclic and polycyclic polymers, topological isomers, and topological block copolymers.[4,5] In this process, newly designed telechelic polymer precursors, having moderately strained cyclic onium salt groups carrying multifunctional carboxylate counteranions, have been introduced.[6,7] The unique self-assembly, formed particularly in a dilute solution, has been converted into a covalent form through the ring-opening reaction by heating, to produce a variety of nonlinear polymer architectures with high efficiency.

Further progress in topological polymer chemistry has been achieved by the use of cyclic telechelics (*kyklo*-telechelics) and cyclic macromonomers to construct multicyclic and topologically unique polymer architectures.[8]

SYSTEMATIC CLASSIFICATION OF NONLINEAR POLYMER TOPOLOGIES

The systematic classification of nonlinear (particularly cyclic and multicyclic) polymer architectures composed of sufficiently long and, therefore, flexible segment components has scarcely been documented.[9] We have disclosed a systematic classification process for a series of well-defined cyclic and branched polymer architectures by reference to the constitutional isomerism in alkanes (C_nH_{2n+2}) and in monocycloalkanes and polycycloalkanes (C_nH_{2n}, C_nH_{2n-2}, etc.).[3] The selected results are collected in Table 1. Therein, all alkane and (poly)cycloalkane molecules are employed as sources to generate a unique topological construction. Such Euclidian geometric properties as the distance between two adjacent junctions and that between the junction and terminus are taken as variant parameters. On the contrary, the total number of termini (chain ends) and the total number 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. These conform with the flexible nature of the randomly coiled polymer segments. Furthermore, topological constructions having five or more branches at one junction are included, even though the relevant isomers with the corresponding molecular formulas are absent.

A systematic notation of nonlinear polymer topologies has also been introduced by the division of the main class and subclasses into branched (A), single cyclic (I), dicyclic (II), tricyclic (III), and tetracyclic (IV) constructions with carbon numbers of the respective (cyclo or polycyclo)alkanes (e.g., A_n, I_n, II_n, III_n, and IV_n, respectively). In addition, the total number of termini and junctions is given in parentheses (Table 1).

Alkane molecules of the generic molecular formula C_nH_{2n+2} with $n = 3$–7 and their relevant topological constructions are listed in Table 1(A), which shows the hierarchical order of a series of branched polymer topol-

Table 1. Systematic Classification of Nonlinear Polymer Topologies by Reference to Alkane and Cycloalkane Isomerism

A

Polymer Topology	C_nH_{2n+2}				
	n =3	4	5	6	7
$A_2(2,0)$					
$A_4(3,1)$					
$A_5(4,1)$					
$A_5(4,2)$					
$A_6(5,1)$				$(*)$	$(*)$
$A_7(5,2)$					
$A_7(6,1)$				$(*)$	

I

Polymer Topology	C_nH_{2n}				Polymer Topology	C_nH_{2n}
	n = 3	4	5	6		n = 6
$I_3(0,0)$					$I_6(2,2)$	
$I_4(1,1)$					$I_6(3,1)$	
$I_5(2,1)$					$I_6(3,2)$	
$I_5(2,2)$					$I_6(3,3)$	

III

Polymer Topology	C_nH_{2n-4}			Polymer Topology	C_nH_{2n-4}	Polymer Topology	C_nH_{2n-4}
	n = 4	5	6		n = 6		N = 7
$III_4(0,4)$				$III_6(0,4)$		$III_7(0,1)$	
$III_5(0,2)$				$III_6(0,2)$		$III_7(0,2)$	
$III_5(0,3)$				$III_6(0,3)$			

II

Polymer Topology	C_nH_{2n-2}			Polymer Topology	C_nH_{2n-2}
	n =4	5	6		n =6
$II_4(0,2)$				$II_6(0,2)$	
$II_5(0,1)$				$II_6(1,1)$	
$II_5(1,2)$				$II_6(1,2)$	
				$II_6(2,2)$	
				$II_6(2,2)$	
$II_5(1,3)$				$II_6(2,3)$	
				$II_6(2,3)$	
				$II_6(2,4)$	

IV

Polymer Topology	C_6H_6
$IV_6(0,3)$	
$IV_6(0,6)$	
$IV_6(0,6)$	$K_{3,3}$

ogies. A point from methane (CH_4) and a line construction from ethane (C_2H_6) are omitted because the former corresponds to a point and the latter produces a line construction obtainable also from propane (C_3H_8). Two butane isomers produce a linear construction and a three-armed star construction, respectively. Likewise, pentane isomers produce a four-armed star construction in addition to the previous two from butane isomers. The two new constructions of H-shaped and five-armed star ar-

chitectures are produced from five hexane isomers. Furthermore, heptane isomers produce the two new constructions of super-H-shaped and six-armed star architectures.

A series of a-rings-with-branches structures are also systematically classified by reference to topological constructions produced from monocycloalkane molecules of C_nH_{2n}, and the results up to $n = 6$ are collected in Table 1(I). A simple cyclic topology is produced from cyclo-
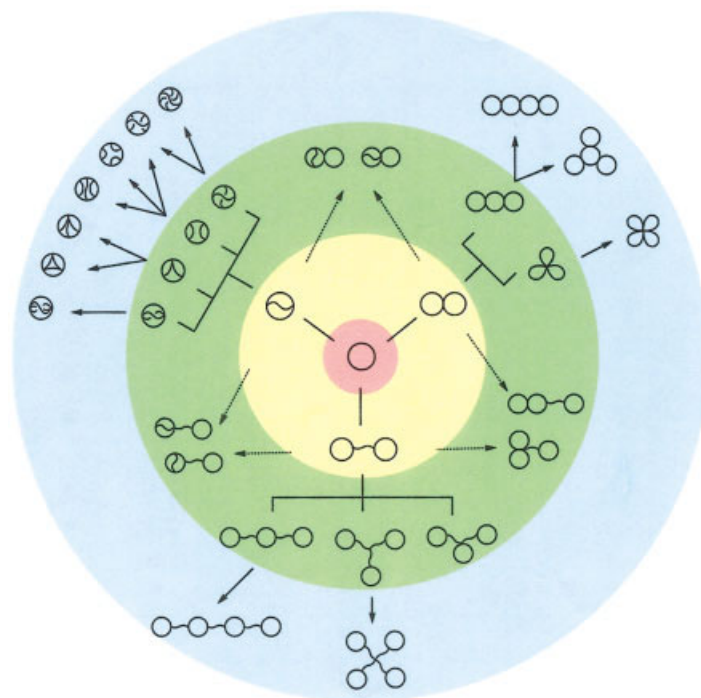
Figure 1.   Ring family tree including monocyclic to tetracyclic constructions.

propane (C_3H_6). The two constructions of a tadpole and a simple ring structures are produced from the two isomers of C_4H_8. Then, the two new constructions are produced from C_5H_{10} isomers and are distinguished from each other by their junction and branch structures; that is, one has two outward branches at one common junction in the ring unit (a twin-tailed tadpole), whereas the other has two outward branches located at two separate junctions in the ring unit (a two-tailed tadpole). Furthermore, the 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).

The constructions formed from bicycloalkanes of C_nH_{2n-2} with up to $n = 6$, including three dicyclic constructions without free branches, that is, θ-ring, 8-ring, and manacle-ring, are listed in Table 1(II). First, a θ-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 emanating from either the θ-ring or the 8-ring shown previously. In this manner, a series of internally and externally linked dicyclic topological constructions can be classified into the corresponding categories by reference to the bicycloalkane isomers.

Furthermore, selected topological constructions from tricycloalkanes of C_nH_{2n-4} and from tetracycloalkanes of C_nH_{2n-6} are shown in Table 1(III,IV), respectively. A variety of topologically significant constructions, such as doubly fused constructions [i.e., α graph, $III_4(0,4)$; β graph, $III_6(0,4)$; γ graph, $III_6(0,3)$; and δ graph, $III_6(0,2)$], as well as spiro-tricyclic constructions are identified in group III. In group IV, moreover, those relevant to a $K_{3,3}$ graph and a prisman are observed.

RING FAMILY

A ring family tree, showing the hierarchical order of polycyclic constructions without free branches, is presented in Figure 1. Starting from a simple ring, 3 dicyclic and 15 tricyclic structures are produced. In addition, a number of topologically significant structures, including a $K_{3,3}$ and a prisman topology, are listed from tetracyclic constructions.[9] Most of these multicyclic polymer structures still elude synthetic polymer chemistry and are, therefore, considered future synthetic targets. The challenge not only is intriguing from a scientific viewpoint, as relevant to the organic chemistry of geometrically challenging compounds, but also will bring new insight into material design by flexible polymers with cyclic and branched structures.
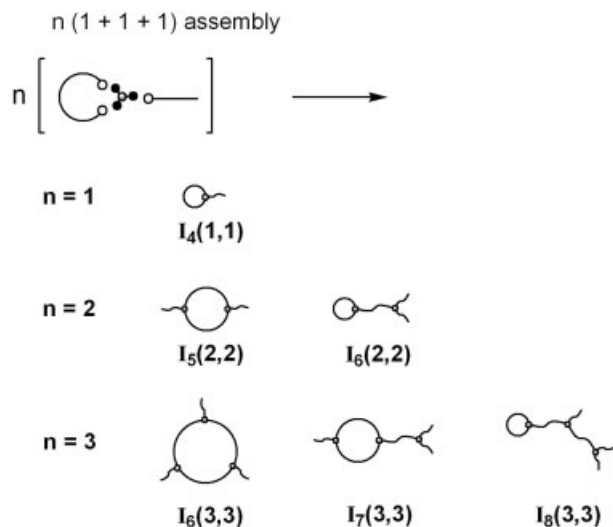
n (1 + 1 + 1) assembly

Figure 2. Topological constructions produced from bifunctional and monofunctional polymer precursors with trifunctional end-linking reagents.

TOPOLOGICAL ISOMERS

The systematic classification of nonlinear polymer topologies has revealed the geometrical relationship of graphically unlike polymers and, consequently, has disclosed the unique constitutional stereoisomerism in flexible polymer molecules. Isomerism,[10] from Greek *isos* (equal) and *meros* (part), is dated back to Berzelius in 1830[11] and has been recognized as a fundamental concept in chemistry. Isomers are a set of compounds possessing the same chemical constitution (and, therefore, the same molar mass) but different properties. The dis-

tinctive properties arise from the uninterconvertible three-dimensional structure of the isomers. Since Kekulé,[12] the recognition of diverse classes in isomerism has continuously brought about a deeper understanding of both static and dynamic structures of chemical substances. In organic chemistry, isomers are divided into constitutional (structural) isomers and stereoisomers. The former refers to those with distinctive connectivity of atoms or atomic groups, whereas the latter refers to those with indistinguishable connectivity, which are still distinguishable from one another by the Euclidian geometric rigidity of the molecules, such as the restriction of bond angle bending and bond rotation.

A set of topological constructions possessing identical terminus and junction numbers as well as branch numbers at each junction is considered to define topological isomers. A two-tailed tadpole, $I_5(2,2)$, and a y-tailed tadpole, $I_6(2,2)$, constitute a typical pair (Fig. 2). Both constructions can be produced from an identical precursor set of telechelic (end-reactive) polymers and end-linking reagents, that is, two bifunctional and two monofunctional polymer precursors and two trifunctional end-linking reagents. Therefore, the pair is assigned as constitutional isomers with topologically distinctive molecular graphs. Among such constitutional isomer pairs identified in the I, II, or III classes, a θ-ring, $II_4(0,2)$, and a manacle-ring, $II_6(0,2)$, are of particular interest (Fig. 3). These are again the products of an identical set of telechelic (end-reactive) polymer precursors and end-linking reagents, that is, three bifunctional polymer precursors and two trifunctional end-linking reagents, or two trifunctional star polymer precursors and three bifunctional end-linking reagents (Fig. 3). It is notable that these
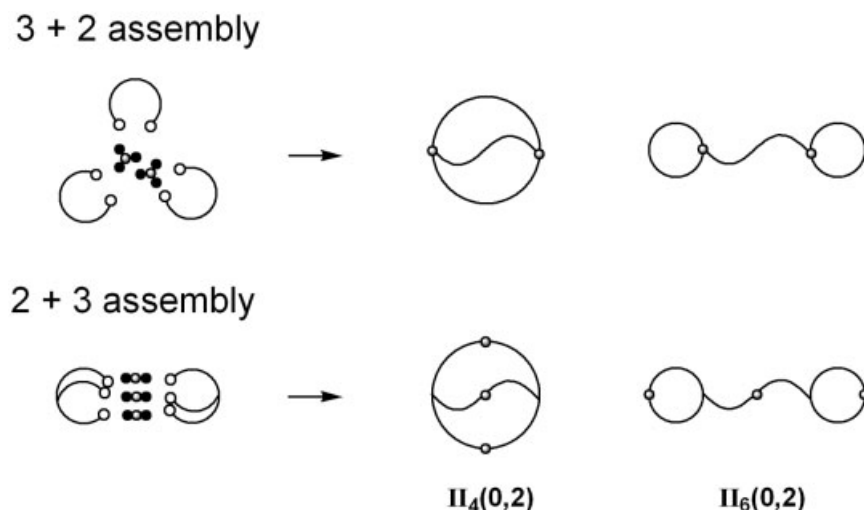

Figure 3. Topological constructions produced from bifunctional polymer precursors with trifunctional end-linking reagents and from trifunctional precursors with bifunctional end-linking reagents.
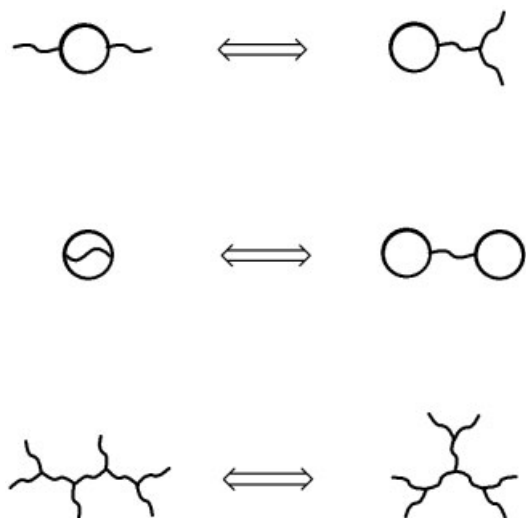
Figure 4. Constitutional isomers with topologically distinctive molecular graphs (different connectivities with identical sets of chains).

isomers are formed from the least common combination of the functionalities of the two components. As a result, the self-assembly synthesis of this particular type of topological isomer has been achieved, as detailed in a later section. Other pairs of such constitutional isomers identified in Table 1(II,III) include the two constructions of $II_5(1,2)$ and $II_6(1,2)$, the two of $III_4(0,4)$ and $III_6(0,4)$, and the two of $III_5(0,2)$ and $III_7(0,2)$. Besides, an example of an isomer pair of branched constructions in the A main class is identified, as shown in Figure 4.

It is remarkable, moreover, that a different class of constitutional isomers is defined from a topological viewpoint. A typical example is a pair of star polymers with the same arm numbers and the same total arm length but with different sets of arm length compositions (Fig. 5). In this case, the two isomers are expressed by a topologically equivalent molecular graph. This is considered an analogy of the constitutional isomerism in 2-methyl and 3-methyl pentane, both made of common atomic groups, that is, three CH_3 groups, two CH_2 groups, and one CH group.

As a result, polymer topologies are characterized not only by the terminus/junction numbers, that is, *the first-order topological parameters*, but also by the connectivity or by the combination of flexible polymer segment compo-

nents. The former corresponds to constitutional isomers with topologically distinctive molecular graphs, whereas the latter refers to constitutional isomers with a topologically equivalent molecular graph. Topological isomers based on such *second-order topological parameters* are unique for randomly coiled, flexible polymer molecules.

Furthermore, a homologous series of polymer topologies can be deduced from the classification of topological constructions, in which their terminus and junction numbers are in a regular order from one to another (Fig. 2). A typical set in class I consists of topologies of $I_4(1,1)$, $I_5(2,2)$, $I_6(2,2)$, $I_6(3,3)$, and $I_7(3,3)$ (Fig. 2). It is recognized that the two topological isomers of $I_5(2,2)$ and $I_6(2,2)$ and the three of $I_6(3,3)$, $I_7(3,3)$, and $I_8(3,3)$ are the respective products of two and three precursor sets for the production of $I_4(1,1)$, that is, one monofunctional polymer precursor, one bifunctional polymer precursor, and one trifunctional end-linking reagent. Likewise, the two constructions of $III_5(0,2)$ and $III_7(0,2)$ are produced from two precursor sets for the production of a construction of $II_5(0,1)$, that is, two bifunctional polymer precursors and one tetrafunctional end-linking reagent (Fig. 6).

Finally, a remarkable feature of the topological isomerism is revealed with three dicyclic polymers having θ, manacle, and intertwined pretzelan constructions (Fig. 7). A pair of θ and manacle polymers are identified as constitutional isomers, as described before. Likewise, a pair of θ and pretzelan polymers are constitutional isomers, and they are interconvertible by the application of chain breaking with two appropriate positions followed by the chain-rearrangement/chain-recombination process, just relevant to the pair of a large single ring and a [2]-catenane. Interestingly, however, a pair of manacle and pretzelan polymers are defined as topological stereoisomers and are topologically relevant to a pair of a ring and a knot, in which the two isomers are interconvertible with each other by the application of chain breaking with an appropriate single position.[1,13,14]

ELECTROSTATIC SELF-ASSEMBLY AND COVALENT FIXATION

Polymer Cyclization

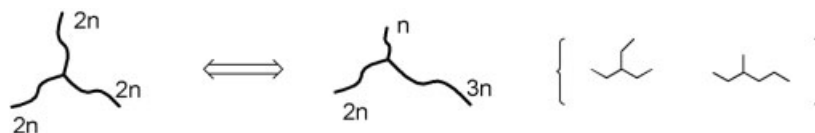The construction of ring polymer topology, crucial in topological polymer chemistry, has been a persistent

Figure 5. Constitutional isomers with a topologically equivalent molecular graph (different chain compositions with identical connectivities).
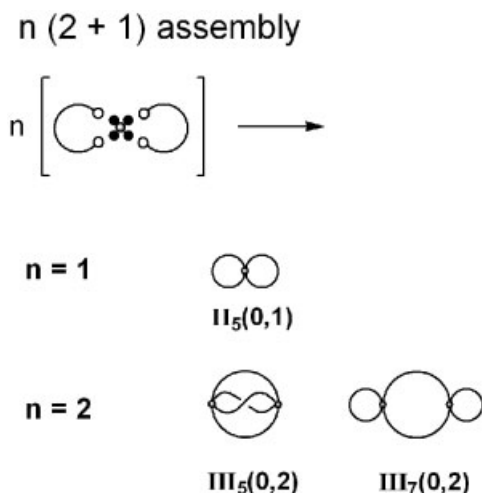
n (2 + 1) assembly

n = 1

II$_5$(0,1)

n = 2

III$_5$(0,2)   III$_7$(0,2)

Figure 6. Topological constructions produced from bifunctional polymer precursors with tetrafunctional end-linking reagents.

research subject.[15] The back-biting and end-biting processes during polycondensation and ring-opening polymerization are known to afford cyclic products, although mainly oligomeric mixtures.[16,17] Ring-expansion polymerization is another direct process. For example, a ring poly(ϵ-caprolactone) was formed with a cyclic stannate initiator.[17] It is notable, however, that the final ring polymer product inherently contains an initiator component, such as Sn, which causes a stability problem during isolation, characterization, and storage. Recently, a ring-opening metathesis polymerization process has been applied with a specifically designed ruthenium catalyst with a monofunctional cyclic ligand, which promotes not only chain propagation but also back-biting chain transfer, to produce cyclic poly(cyclooctene) and subsequently cyclic polyethylene by hydrogenation, free of the catalyst component.[18]

Therefore, ring polymers have so far been prepared through the end-to-end linking reaction of linear polymer precursors, that is, telechelic polymers (Fig. 8). First, the coupling reaction of a bifunctional linear polymer pre-

cursor, such as a bifunctionally living polystyrene, was performed with a complementarily reactive bifunctional reagent, typically dihaloalkanes or dihalosilanes.[19] However, this bimolecular reaction required high dilution to suppress the intermolecular chain-extension reaction and, at the same time, a rigorous stoichiometric balance between large and small molecules. Therefore, the reaction was often kinetically circumvented to limit this straightforward polymer cyclization process from practical synthesis.

An alternative unimolecular polymer cyclization process using an α,ω-heterobifunctional linear polymer precursor was later developed (Fig. 8).[20] In this process, the two end groups of the polymer precursor become complementarily reactive after deprotection or activation, and the reaction under dilution gives a ring polymer product. The cyclization efficiency is notably improved because the inherent stoichiometric balance is maintained between complementarily reactive groups located within the same polymer molecule. The reaction follows unimolecular, first-order kinetics, depending solely on the concentration of the polymer precursor. The synthesis of the heterobifunctional polymer precursor, however, requires laborious multistep processes involving protection/deprotection of reactive end groups.

An improved unimolecular polymer cyclization process has recently been developed with a bifunctional polymer precursor having identical reactive end groups (Fig. 8).[21] Therein, a linear polymer precursor with allyl groups was subjected to a metathesis condensation, also known as a ring-closing metathesis, under dilution in the presence of a Grubbs catalyst, ruthenium(II) dichloride phenylmethylene bis(tricyclohexylphosphine) [RuCl$_2$ (PCy$_3$)$_2$(=CHPh)]. A large ring polymer was effectively produced with a readily accessible precursor, that is, telechelics with allyl groups, in the presence of a commercially available metathesis catalyst.

Moreover, a pseudo-unimolecular reaction by an electrostatic self-assembly and covalent fixation technique has been developed as a novel polymer cyclization process (Fig. 9). In this system, such linear polymer precursors as poly(tetrahydrofuran) (PTHF),[4,22] polystyrene[23]
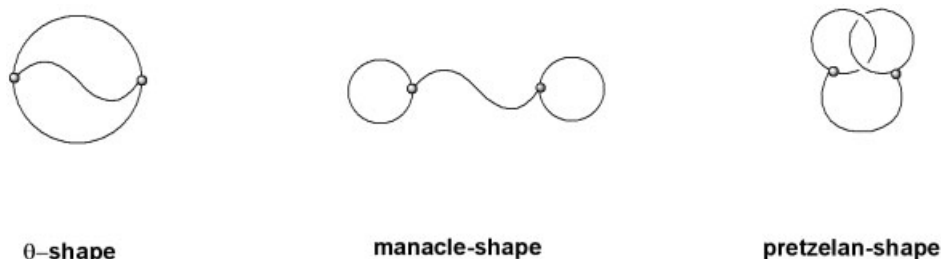

θ−shape   manacle-shape   pretzelan-shape

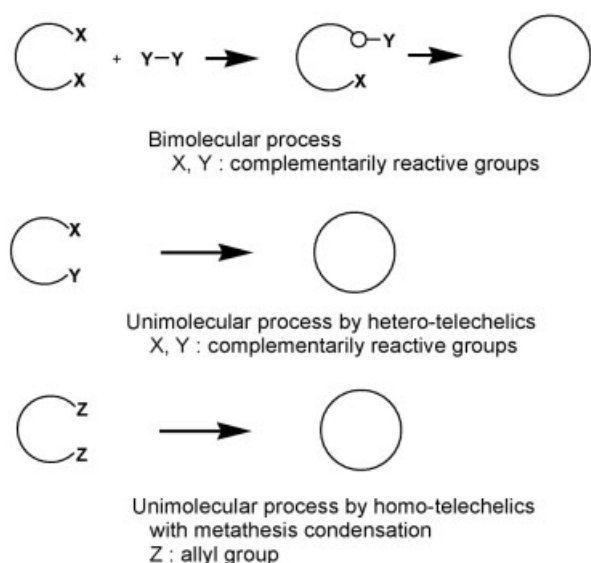**Figure 7.** Constitutional topological isomers and topological stereoisomers.

Figure 8.   Polymer cyclization by the end-to-end linking process.

and poly(ethylene oxide),[24] having moderately strained five-membered cyclic ammonium or six-membered bicyclic ammonium salt groups, that is, N-phenyl or N-ethyl pyrrolidinium as well as quinuclidinium salt groups, carrying an appropriately reactive counteranion such as a dicarboxylate, have been employed. The cations and anions always balance the charges, and the selective nucleophilic ring-opening reaction occurs at an appropriately elevated temperature under dilution, converting the ionic interaction into the permanent covalent linkage.

Dicyclic and Tricyclic Polymer Topologies

Among the three dicyclic polymer topologies, that is, 8-, θ- and manacle-shaped constructions, only the 8-shaped polymer has been a previous synthetic target.[25–27] Recently, the electrostatic self-assembly and covalent fixation process has successfully been applied to the efficient synthesis of a series of multicyclic polymers (Fig. 9).[4,23] Therein, a linear telechelic precursor with moderately strained cyclic ammonium salt groups carrying a tetrafunctional carboxylate counteranion was subjected to covalent conversion through the ring-opening reaction under appropriate dilution. The 8-shaped PTHF and polystyrene were obtained in good yields.

Moreover, the selective synthesis of a θ-shaped polymer has been achieved from a self-assembly composed of a trifunctional star-shaped polymer precursor with cyclic ammonium salt end groups carrying a tricarboxylate counteranion (Fig. 9).[28] Remarkable solvent effects were observed during the covalent conversion process of the electrostatically self-assembled precursor. The iso-

lated θ-shaped polymer product was unequivocally characterized by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MASS) in addition to ^{1}H NMR, size exclusion chromatography (SEC), and reverse-phase liquid chromatography (RPC) techniques.

Furthermore, a tricyclic polymer topology has been constructed from an assembly of three bifunctional linear telechelic precursor carrying a hexafunctional carboxylate counteranion (Fig. 9).[4]

Topological Isomers

In the electrostatic self-assembly and covalent fixation process, cations and anions always balance the charges. As a result, a pair of dicyclic (i.e., θ- and manacle-shaped) polymers were obtained concurrently from an assembly of three bifunctional linear precursors carrying two trifunctional carboxylate counteranions or of two trifunctional star-shaped precursors and three bifunctional carboxylate counteranions (Fig. 9).[4,29] Indeed, the two components were identified by an RPC analysis of the covalent conversion products from these electrostatically self-assembled precursors under dilution and were subsequently isolated by fractionation. The ^{1}H NMR and IR spectra of the two components were identical and showed the quantitative ring-opening reaction of pyrrolidinium salt groups by carboxylate groups in the dicarboxylate and tricarboxylate, respectively. The molecular weights of the product (as a mixture), determined by vapor pressure osmometry and ^{1}H NMR (the quantitative chemical conversion of the polymer end groups being assumed), coincided, within the experimental error, with that of the three-time and two-time linear and star precursor analogues, respectively.

SEC has shown, moreover, that the major component is noticeably larger in size than the minor component. Because the random combination of cations and anions will produce the two constructions of manacle-ring and θ-ring in a ratio of 3:2, and the size, that is, the hydrodynamic volume of the manacle isomer is assumed to be larger than that of the θ-counterpart, the major component is assigned as the manacle isomer.

It is also remarkable that the θ-shaped and manacle-shaped polymers obtained from either linear or three-armed star precursors were distinguished by RPC, despite the identical topology. This is because they are distinctive with respect to the positions of linking groups (aminoester groups) within the identical topological framework (see Fig. 3). Functional polymer design by the precise positioning of specific chemical groups within a flexible but defined polymer framework is considered a promising subject because it is relevant to natural enzymes achieving their molecular recognition and chemoselective catalysis through the fine tuning of
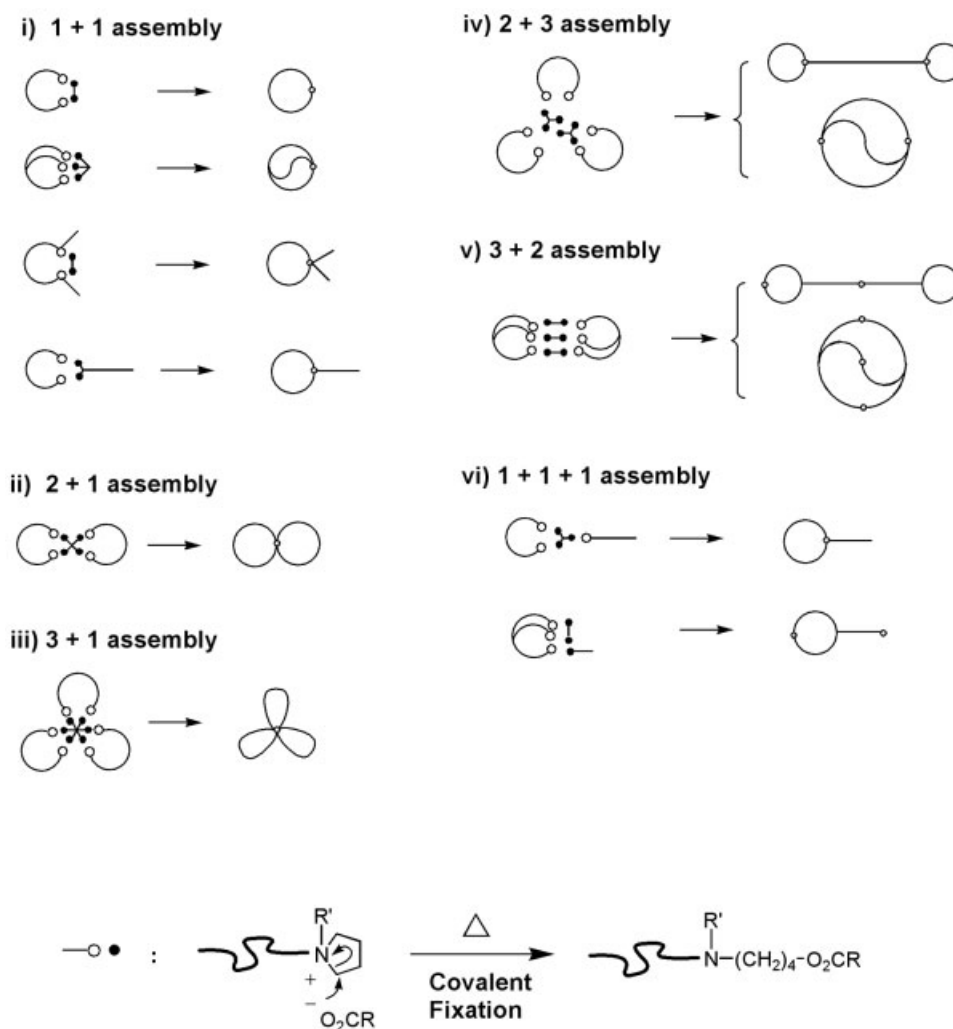
Figure 9. Electrostatic self-assembly and covalent fixation for topologically unique polymers.

the location of functional groups within their polypeptide frameworks.

Topological Block Copolymers

Topological block copolymers, consisting of topologically distinctive linear, branched, cyclic, and multicyclic segments, will offer a broader choice of block copolymer structures, in addition to those from the combination of chemically different polymer in linear topology. A prototype of such topological block copolymers is a tadpole polymer, produced from a simple ring and outward branch segments.[27,30,31] The electrostatic self-assembly and covalent fixation process has been applied to prepare such constructions (Fig. 9). First, a tadpole polymer is prepared from a polymer–polymer electrostatic self-assembly, which consists of one polymer precursor having cyclic ammonium salt groups at both chain ends and

another having a dicarboxylate group at a single chain end, by subsequent covalent fixation through the ring-opening reaction.[32]

In addition, the dynamic equilibrium nature of a noncovalent, electrostatic self-assembly intermediate has been exploited to form a three-component self-assembly of the tadpole structure from bifunctional and monofunctional linear precursors carrying a trifunctional carboxylate counteranion (Fig. 10).[4] An alternative three-component self-assembly, consisting of a trifunctional, star-shaped polymer precursor carrying bifunctional and monofunctional counteranions, could also be employed (Fig. 9).[33] The subsequent covalent conversion under dilution could afford a tadpole polymer product. Furthermore, a twin-tailed tadpole polymer has been constructed effectively from a self-assembly, consisting of an eso-telechelic polymer precursor (Greek *eso* means *inside*) having two cyclic ammonium salt groups at defined
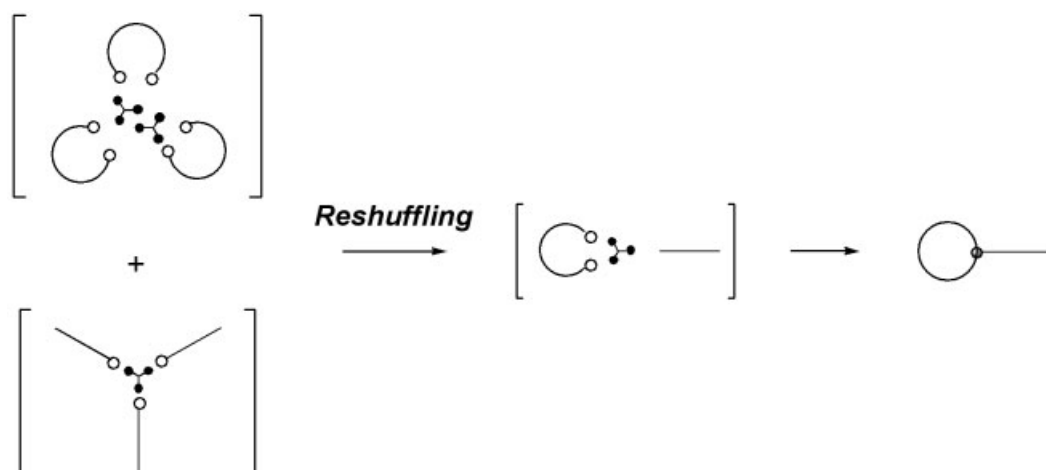
Figure 10.   Formation of a tadpole polymer by dynamic reshuffling of self-assembled precursors.

positions inside the linear segment and carrying a dicarboxylate counteranion, by subsequent covalent conversion under dilution (Fig. 9).[34]

KYKLO-TELECHELICS FOR TOPOLOGICAL POLYMER CHEMISTRY

The electrostatic self-assembly and covalent fixation process has been further applied to designing cyclic polymer precursors with functional groups at the specific locations of the ring polymer structure (*kyklo*-telechelics; Greek *kyklos* means *cyclic*; Fig. 11).[35] *Kyklo*-telechelics are considered versatile macromolecular building blocks for constructing topologically unique and complex macromolecular architectures containing cyclic polymer units and various topological block copolymers. Therefore, a self-assembly consisting of telechelic precursors carrying either a 5-hydroxy or 5-allyloxyisophthalate counteranion (a hydroxy- or allyloxy-functionalized dicarboxylate) has been prepared and subjected to heat treatment under dilution to produce a cyclic PTHF having either a hydroxy or allyloxy group derived from the respective dicarboxylate counteranion.[35]

Homobifunctionalized and heterobifunctionalized cyclic PTHFs with either two identical or two different
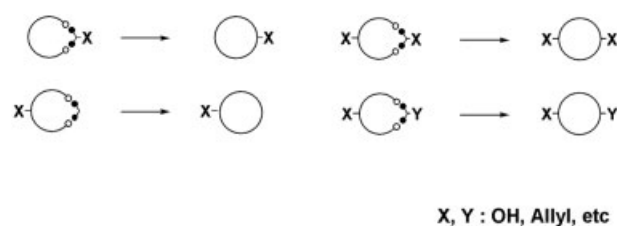
functional groups at the opposite positions, respectively, have also been synthesized. For this purpose, a linear telechelic PTHF having *N*-phenylpyrrolidinium salt groups and having an additional functional group at the center position of the polymer chain (*kentro*-telechelics)[36] has been prepared. The kentro-telechelic precursor carrying a 5-hydroxy- or 5-allyloxyisophthalate counteranion has subsequently been prepared and subjected to heat treatment under dilution to give a homobifunctionalized cyclic PTHF with two hydroxy or allyloxy groups at the opposite positions.

The synthesis of 8-shaped polymers has been performed through the metathesis condensation of cyclic polymer precursors with allyl groups in the presence of a
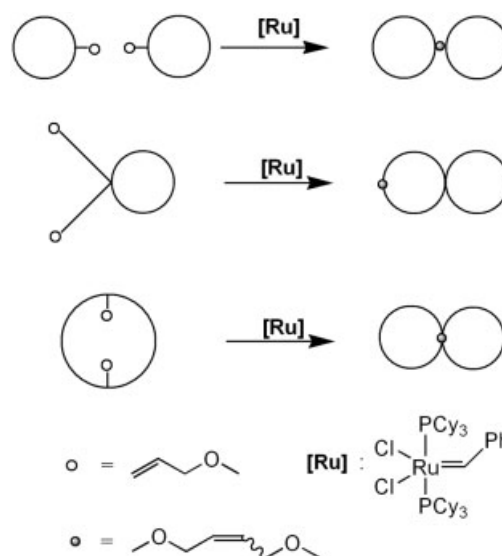

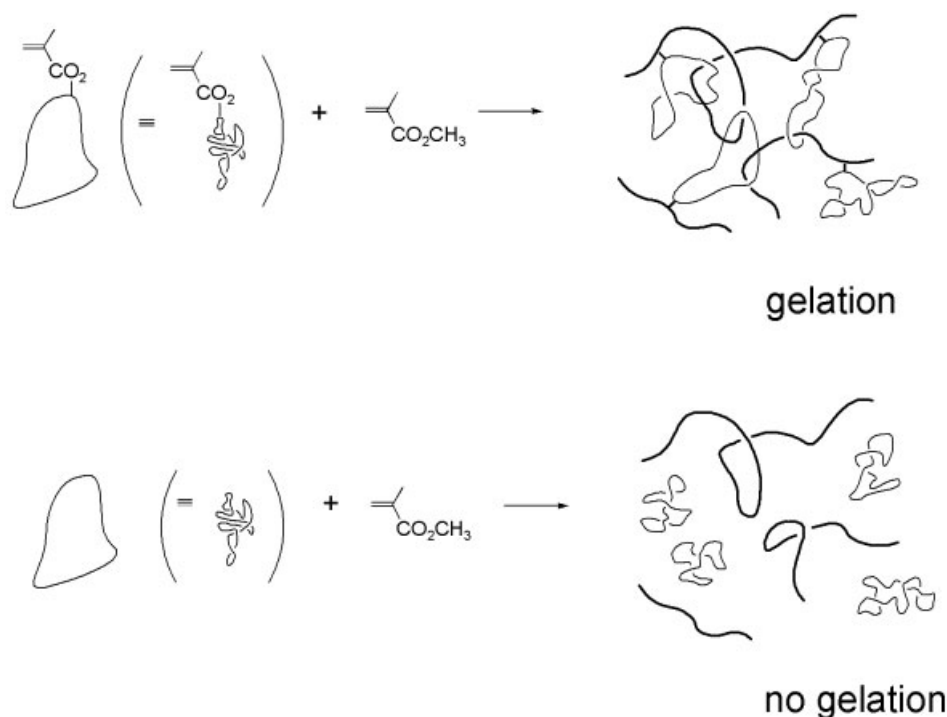**Figure 12.**   Formation of 8-shaped polymers by metathesis condensation.

X, Y : OH, Allyl, etc

Figure 11.   Formation of *kyklo*-telechelic polymers.

Figure 13.   Formation of a topological network by a cyclic macromonomer.

Grubbs catalyst (Fig. 12).[37] First, a cyclic polymer precursor with an allyl group was subjected to an intermolecular metathesis condensation. Second, two types of cyclic polymer precursors, a twin-tailed tadpole PTHF having tail-end allyl groups and a *kyklo*-telechelic PTHF having two allyl groups at opposite positions, were applied to an intramolecular metathesis condensation. The 8-shaped structure of the products produced by metathesis condensation were unequivocally demonstrated by means of spectroscopic and chromatographic techniques and, in particular, by MALDI-TOF-MASS, which allowed the monitoring of the elimination of an ethylene molecule during the condensation. It was found that the intramolecular process was more efficient than the intermolecular counterpart under dilution.

Cyclic polymers are interesting for their potential in constructing physically (noncovalently) crosslinked polymer architectures based on the threading of their loop topology. However, a long and flexible polymer chain tends to assume a randomly coiled and, therefore, constrained three-dimensional structure. Consequently, noncovalent crosslinking processes by threading through flexible and large cyclic polymers have scarcely been observed,[38,39] in contrast to the synthesis of rotaxanes and catenanes by medium macrocyclic compounds having stiff and extended cyclic conformations, such as 30–60-membered crown ethers, bipyridinium-based cyclophanes, cyclodextrins, and macrocyclic amides.[40]

A novel functional cyclic polymer, that is, a cyclic macromonomer as large as a 280-membered ring, has been prepared to design an unusual polymer network structure having both covalent and physical linkages, formed through a chain threading of the propagating polymer segment through large cyclic polymer units attached to the backbone polymer segments (Fig. 13).[38] First, a cyclic macromonomer having a methacryl group was synthesized from hydroxy-functionalized cyclic PTHF in a quantitative yield. A free-radical copolymerization with methyl methacrylate (MMA) resulted in a gel product at the complete monomer conversion. In contrast, no gelation took place either in the relevant quantitative-conversion copolymerization of MMA with an open-chain poly(methyl methacrylate) macromonomer or in a quantitative-conversion homopolymerization of MMA in the presence of a simple cyclic PTHF of the relevant ring size.

These results agree with the physical crosslinking, that is, the threading by the propagating chain through the pendant cyclic branches attached to the polymer backbone. Interestingly, this chain threading through large polymer loops proceeds only when they are covalently attached to the polymer backbone.

CONCLUSIONS

Remarkable progress continues in topological polymer chemistry. By a systematic classification of nonlinear

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polymer topologies, the geometrical relationship between unlike polymer topologies could be disclosed, and eventually their rational synthetic processes were postulated. Topological isomers, uniquely occurring in flexible, nonlinear polymer architectures, were subsequently identified. An electrostatic self-assembly and covalent fixation process has now been developed for the efficient synthesis of various nonlinear polymer topologies, including monocyclic and polycyclic polymers, topological isomers, and topological block copolymers, with newly designed telechelic precursors having moderately strained cyclic ammonium salt groups. Topological polymer chemistry has further been extended with cyclic telechelics (*kyklo*-telechelics) and cyclic macromonomers, again obtainable by the electrostatic self-assembly and covalent fixation process.

Numerous future developments are foreseeable in topological polymer chemistry, as discussed in each section of this article. First, further synthetic challenges will continue to realize such significant polymer topologies as tricyclic α, β, γ, and δ constructions and tetracyclic $K_{3,3}$ and prisman constructions (see Table 1 and Fig. 1). These will undoubtedly become remarkable achievements in synthetic polymer chemistry.

Topological polymer chemistry is expected to disclose unique topological effects in static and dynamic polymer properties that rely, in particular, on *second-order topological parameters*. This will offer a unique opportunity to realize unprecedented control over the functions and properties of flexible polymer molecules. Future research efforts are awaited in theoretics[41] and simulations, which are now ready to be examined experimentally by topologically unique model polymers.

Moreover, topological polymer chemistry will provide various nanosize flexible polymer frameworks, such as θ polymers, having specific functionalities at the designated positions. Such nanosize functional polymer frameworks will be used as adaptable hosts for small to large guest components and will show unique recognition properties as in noncovalent supramolecular chemistry, but with robust covalent structures.

Last but not least, a variety of nanoobjects of a defined nonlinear shape will be constructed from flexible polymer precursors by the stiffening of the initially flexible backbone polymer segment by modification with dendritic branches (dendronized polymers). Such an intriguing integration of topological polymer chemistry by flexible polymers with dendrimer chemistry based on Euclidian geometry will become a crucial step toward future nanotechnology.

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