Topological Polymer Chemistry: Systematic Classification of Nonlinear Polymer Topologies

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Received June 11, 2001

Abstract: Nonlinear polymer topologies composed of cyclic and branched polymer segments are systematically classified 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). Thus, 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 junction. On the other hand, the distance between two adjacent junctions and that between the junction and terminus are taken as variant parameters. On the basis of the classification of polymer topologies, a novel synthetic strategy by an "electrostatic self-assembly and covalent fixation" technique has been proposed to construct a variety of topologically unique polymer architectures.

Introduction

The topology of polymer molecules is often a basis to control their properties and functions at static and dynamic states both in bulk and in solution.[1] Hence, a novel strategy to design unprecedented polymer topologies has been an ongoing challenge in polymer science and technology. Remarkable achievements within recent decades include such branched polymer topologies[2] as "star" polymers, "H-shaped" polymers, "super H-shaped" polymers, "pom-pom shaped" polymers, as well as "comb polymers (polymacromonomers)"[3] and "dendrimers",[4] in addition to such cyclic, multicyclic, and cyclic-branched combined polymers[5] as "ring" polymers, "8-shaped" polymers, and "tadpole" polymers. These have been described in terms of their shapes. Catenanes, rotaxanes, and knots are another class of topologically unique (macro)molecules of growing interest, designed through intriguing noncovalent interactions of precursor components.[5,6]

A systematic classification of topologically unique (macro)molecules, which is often relevant to their terminology, thus provides useful insight for structural relationships between different compounds and eventually for their rational synthesis. In these respects, studies on the classification of "dendrimers",[7] as well as "knots",[8] "catenanes",[9] and "rotaxanes",[10] have been reported so far. In particular, the fundamental mathematical theory of knots has been a subject of active investigation,[11] giving an impetus to elucidate topological features in (macro)molecular chemistry. However, there have been infrequent attempts,[12,13] to the best of our knowledge, on systematic classification of nonlinear and in particular cyclic and multicyclic polymer architectures composed of sufficiently long and thus flexible segment components.[14]

Herein, we propose 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 a series of mono- and polycycloalkanes (C_nH_{2n}, C_nH_{2n-2}, etc). Each alkane and (poly)cycloalkane molecule is taken as a source to generate a unique topological construction according to the procedure of Walba.[15] 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

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[1] For recent studies, see: (a) Gan, Y.; Dahai, D.; Carlotti, S.; Hogen-Esch, T. E. *J. Am. Chem. Soc.* **2000**, *122*, 2130−2131. (b) Adronov, A.; Fréchet, J. M. J. *Chem. Commun.* **2000**, 1701−1710. (c) Sato, T.; Jiang, D.-L.; Aida, T. *J. Am. Chem. Soc.* **1999**, *121*, 10658−10659.

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[8] Schucker, T. *New J. Chem.* **1993**, *17*, 655−660.

[9] Chambron, J.-C.; Dietrich-Buchecker, C.; Sauvage, J.-P. Catenanes and Knots. In *Cyclic Polymers*, 2nd ed.; Semlyen, J. A., Ed.; Kluwer Academic Publishers: Dordorecht, The Netherlands, 2000; p 155.

[10] Gibson, H. W. Rotaxanes. In *Cyclic Polymers*, 2nd ed.; Semlyen, J. A., Ed.; Kluwer Academic Publishers: Dordorecht, The Netherlands, 2000; p 191.

[11] Adams C. C. *The Knot Book: an elementary introduction to mathematical theory of knots*; W. H. Freeman: New York, 1994.

[12] For cycle ranks, see: Armitage, D. H.; Cameron, C.; Fawcett, A. H.; Hetherington, C. R.; McBride, F. V.; Mee, R. A. *Macromolecules* **2000**, *33*, 6569−6577.

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10.1021/ja0114409 CCC: $20.00

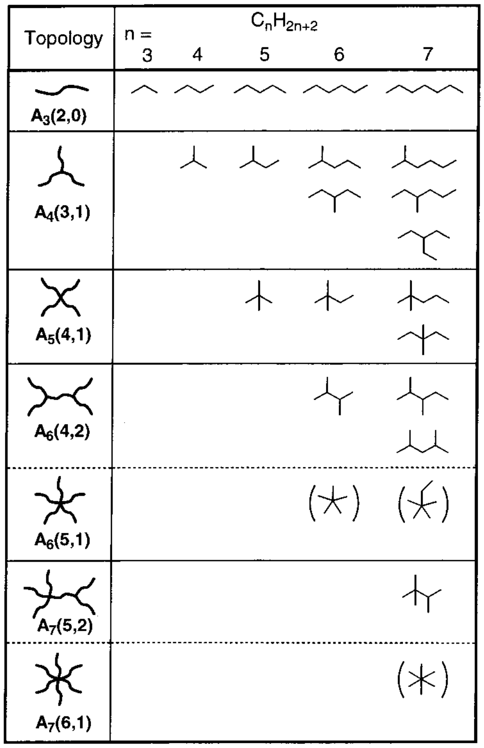
are preserved as invariant parameters as well. On the other hand, such Euclidian geometric properties as the distance between two adjacent junctions and that between the junction and terminus are taken as variant parameters, to conform with the flexible nature of the randomly coiled polymer segments. Furthermore, topological constructions having five or more branches at one junction are produced despite the absence of the relevant isomers having the corresponding molecular formula.

A series of topological constructions comprising, in particular, cyclic polymer units has been classified into different main-classes and sub-classes, and their topological relationships have subsequently been compared. A special emphasis is placed on "topological isomers",[16,17] which are a group of different polymer architectures 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[18] has been proposed to construct a variety of unusual polymer topologies.

Results and Discussion

1. Branched Topologies. A series of alkane molecules of generic molecular formula C_nH_{2n+2} with $n = 3-7$ and their relevant topological constructions (main-class A) are shown in Table 1, in which a systematic notation is also presented (see Supporting Information for the notation procedures). Although a point from methane (CH_4) and a line construction from ethane (C_2H_6) can be produced, they are not included since the former is not significant with respect to polymer topology and the latter produces an equivalent topological construction from propane (C_3H_8). This linear construction is termed A_3, or alternatively $A_3(2,0)$ by showing the total number of termini and of junctions, respectively, in parentheses, and this particular topology is ubiquitous in those from all higher alkanes. Two butane isomers produce a linear and a three-armed star construction, A_4 or $A_4(3,1)$, respectively. Likewise, pentane isomers produce three constructions, namely a four-armed star construction, A_5 or $A_5(4,1)$, and two others equivalent to those from butane isomers. From the five hexane isomers, on the other hand, 2-methyl- and 3-methylpentane produce an identical topological construction. Because no hexane isomer having a molecular formula of C_6H_{14} can form a five-armed star, this hypothetical example is shown in parentheses in Table 1. As a result, the two new constructions of an H-shaped and of a five-armed star architecture, $A_6(4,2)$ and $A_6(5,1)$, respectively, are produced by reference to hexane isomers. And further, heptane isomers produce the two new constructions of a super H-shaped and a six-armed star architecture, i.e., $A_7(5,2)$ and $A_7(6,1)$, respectively. Thus by this process, a series of branched polymer topologies is able to be relevantly ranked.

Table 1. Topological Constructions Produced by Reference to Alkane Isomers (C_nH_{2n+2}: $n = 3-7$)[a]



[a] See Supporting Information for the notation of topological constructions.

In Table 2, moreover, selected topological constructions by reference to their corresponding higher alkane molecules of C_nH_{2n+2} with $n > 7$ are listed. Thus, the two new constructions, i.e., $A_8(5,3)$ and $A_8(6,2)$, are produced from octane isomers having distinctive total numbers of termini and junctions, respectively. On the other hand, two of the newly produced constructions from nonane isomers having identical total numbers of termini and junctions, i.e., $A_9(6,3)[4\text{-}3\text{-}3]$ and $A_9(6,3)[3\text{-}4\text{-}3]$, respectively, are distinct from each other in the connectivity of junctions. This is also the case for another pair of constructions from decane isomers, i.e., $A_{10}(6,4)[3\text{-}3(3)\text{-}3]$

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(14) In this connection, mathematical graph theory has been applied for the enumeration of isomeric structures in various chemical substances. See: (a) Balaban, A. T. In *Chemical Application of Graph Theory*; Balaban, A. T., Ed.; Academic Press: London, 1976; Chapter 5, p 63. (b) Balaban, A. T. *Rev. Roum. Chim.* **1973,** *18,* 635−653. (c) *Graph Theory and Topology in Chemistry*; King, R. B., Rouvray, D. H., Eds.; Elsevier: Amsterdam, The Netherlands, 1987. (d) Rouvray, D. H. *Chem. Soc. Rev.* **1974**, *3*, 355−372. (e) Masinter, L. M.; Sridharan, N. S.; Lederberg, J.; Smith, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 7702−7714. And for chemical utilization of the topological idea, see: (f) Bytautas, L.; Klein, D. J. *Croat. Chem. Acta,* **2000**, *73,* 331−357. (g) Klein, D. J.; Zhu, H. In *Chemical Topology to Three-Dimensional Geometry*; Balaban, A. T., Ed.; Plenum: New York, 1997. Also, nonlinear chain topologies have been elucidated based on theoretical chemical physics. See: (h) Gaunt, D. S.; Lipson, J. E. G.; Martin, J. L.; Sykes, M. F.; Torrie, G. M.; Whittington, S. G.; Wilkinson, M. K. *J. Phys. A: Math. Gen.* **1984,** *17,* 211−236. (i) Martin, J. E.; Eichinger, B. E. *J. Chem. Phys.* **1978,** *69,* 4588−4594. And the nomenclature based on the graph theory has also been proposed. See: (j) Lozac'h, N.; Goodson, A. L.; Powell, W. H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 887−899.

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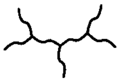
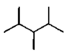
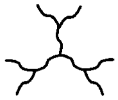
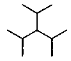
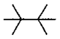
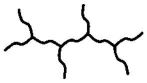
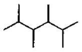
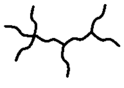
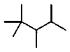
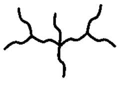
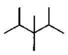
Table 2. Selected Topological Constructions Produced by Reference to Alkane Isomers (C_nH_{2n+2}: $n = 8-10$ and m)[a]

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)**			
Topology	C_9H_{20}	 **A_{10}(6,4)[3-3-3-3]**	
 **A_9(6,3)[4-3-3]**		 **A_{m+1}[m,1]** **m-Arm Star Polymer**	
 **A_9(6,3)[3-4-3]**			

[a] See Supporting Information for the notation of topological constructions.

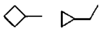
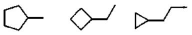
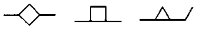
and A_{10}(6,4)[3-3-3-3], respectively. The former corresponds to a dendritically branched structure and the latter to a comblike branched structure. An *m*-armed star polymer topology is designated accordingly as $A_{m+1}(m,1)$.

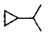
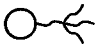
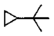
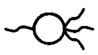
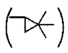
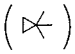
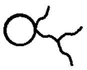
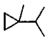
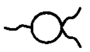
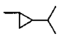
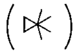
A series of star polymers having 3-, 4-, 5-, or 6-arms,[2,19] an H-shaped polymer, and a super H-shaped polymer[2b,13a] given in Tables 1 and 2 have so far been synthesized as model branched polymers, which are distinct from linear polymers.

It should be stressed that, from a topological viewpoint, a series of branched constructions produced and presented in Tables 1 and 2 are distinct from dendrimers (dendritic polymers possessing well-defined branched structures) and comb-shaped polymers, which are often referred to as the relevant class of model branched macromolecules having well-defined structures. Thus, the topological constructions produced in this study are based on the assumption that the distances between two adjacent junctions and between a junction and a terminus are variable geometric parameters. This assumption conforms to the flexible nature of sufficiently long polymer chains capable of assuming a random coil conformation. In dendrimers, on the other hand, the distances between two adjacent junctions and between the junction and the terminus are regarded as invariant. Consequently, they tend to constitute a stiff, shape-persistent molecule possessing a gradient of structural density.[20] For comb-shaped polymers, likewise, the distances between two junctions along the backbone are regarded as invariant, whereas the branch chain is either flexible (polymacromonomers)[3a,21] or stiff (dendron-jacketed polymers).[3b,22]

2. Cyclic Topologies. a. Monocyclic Topologies. A series of monocycloalkane molecules of C_nH_{2n} with up to $n = 6$ and their relevant topological constructions and additional constructions produced from monocycloalkane isomers of C_7H_{14} (main-class I) are listed in Table 3. Moreover, those produced from C_8H_{16} are shown in S-Table 1 (Supporting Information). In these tables, a systematic notation for each construction is also presented (see Supporting Information for the notation procedures).

Table 3. Topological Constructions Produced by Reference to Cycloalkane Isomers (C_nH_{2n}: $n = 3-7$)[a]

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

Topology	C_6H_{12}	Topology	C_7H_{14}	Topology	C_7H_{14}
 **I_6(2,2)**		 **I_7(3,2)[1(4)]**		 **I_7(4,2)[3-1]**	
 **I_6(3,1)**		 **I_7(3,2)[2(3,0)]**		 **I_7(4,2)[2-2]**	
 **I_6(3,2)**		 **I_7(3,3)**		 **I_7(4,3)**	
 **I_6(3,3)**		 **I_7(4,1)**			

[a] See Supporting Information for the notation of topological constructions.

Topological constructions are produced according to the procedure applied for the A main-class, branched topologies. Thus, a simple cyclic topology, I_3 or $I_3(0,0)$, is produced from cyclopropane (C_3H_6). This topology is ubiquitous among all higher sub-classes in this main-class I. From the two isomers of C_4H_8, i.e., methylcyclopropane and cyclobutane, two constructions, namely one having "a ring with a branch" architecture, I_4 or $I_4(1,1)$, and another having a simple ring structure, respectively, are produced. The latter is topologically equivalent to one produced from cyclopropane. Two new constructions, $I_5(2,1)$ and $I_5(2,2)$, 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., the former, a twin-tailed tadpole, has two outward branches at one common junction in the ring unit, while the latter, a two-tailed tadpole, has two outward

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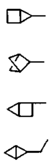
(19) (a) Heise, A.; Nguyen, C.; Malek, R.; Hedrick, J. L.; Frank, C. W.; Miller, R. D. *Macromolecules* **2000**, *33*, 2346−2354. (b) Hecht, S.; Ihre, H.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1999**, *121*, 9239−9240. (c) Wu, X.; Fraser, C. L. *Macromolecules* **2000**, *33*, 4053−4060. (d) Zhang, X.; Xia, J.; Matyjaszewski, K. *Macromolecules* **2000**, *33*, 2340−2345.

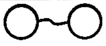
(20) For a brief review of "shape persistent molecule", see: Ober, C. K. *Science* **2000**, *288*, 448−449.

(21) (a) Dziezok, P.; Sheiko, S. S.; Fischer, K.; Schmidt, M.; Möller, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2812−2815. (b) Gerle, M.; Fischer, K.; Roos, S.; Müller, A. H. E.; Schmidt, M.; Sheiko, S. S.; Prokhorova, S.; Möller, M. *Macromolecules* **1999**, *32*, 2629−2637. (c) Beers, K. L.; Gaynor, S. G.; Matyjaszewski, K.; Sheiko, S. S.; Möller, M. *Macromolecules* **1998**, *31*, 9413−9415. (d) Schappacher, M.; Billaud, Paulo, C. C.; Deffieux, A. *Macromol. Chem. Phys.* **1999**, *200*, 2377−2386.

(22) (a) Shu, L.; Schäfer, A.; Schlüter, A. D. *Macromolecules* **2000**, *33*, 4321−4328. (b) Ouali, N.; Méry, S.; Skoulios, A.; Noirez, L. *Macromolecules* **2000**, *33*, 6185−6193.

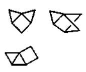
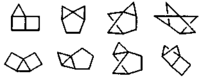
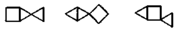
Table 4. Topological Constructions Produced by Reference to Bicycloalkane Isomers (C_nH_{2n-2}: $n = 4-6$)[a]

Topology	C_nH_{2n-2}		
	n = 4	5	6
 **II$_4$(0,2)**			
 **II$_5$(0,1)**			
 **II$_5$(1,2)**			
 **II5(1,3)**			

Topology	C_nH_{2n-2}
	n = 6
 **II$_6$(0,2)**	
 **II$_6$(1,1)**	
 **II$_6$(1,2)**	
 **II$_6$(2,2)[2^a-0^a]**	
 **II$_6$(2,2)[1^a-1^a]**	
 **II$_6$(2,3)[2-0^a-0^a]**	
 **II$_6$(2,3)[1^a-1-0^a]**	
 **II$_6$(2,4)**	

[a] See Supporting Information for the notation of topological constructions.

Table 5. Fused and Spiranic Rings Constructions Produced by Reference to Tricycloalkane Isomers (C_nH_{2n-4}: $n = 4-7$)[a]

Topology	C_nH_{2n-4}			
	n = 4	5	6	7
 **III$_4$(0,4)[0^a-0^b-0^a-0^b]**				
 **III$_5$(0,2)[0^{a,b}-0^{a,b}]**				
 **III$_5$(0,3)[0^{a,b}-0^a-0^b]**				
 **III$_6$(0,4)[0^a-0^a-0^b-0^b]**				
 **III$_6$(0,2)**				
 **III$_6$(0,3)**				
 **III$_7$(0,1)**				
 **III$_7$(0,2)**				

[a] See Supporting Information for the notation of topological constructions.

branches located at two separate junctions in the ring unit. This corresponds to the mode of methyl substitution on the cyclopropane ring unit in the respective C_5H_{10} isomers. Four new topological constructions are subsequently produced by reference to C_6H_{12} isomers; the one having five branches at one junction, $I_6(3,1)$, is hypothetical (and is therefore shown in parentheses in Table 3). It is included even though this particular construction cannot be formed from a chemical compound of molecular formula C_6H_{12}.

Among these polymer architectures, a variety of simple "ring" polymers,[18a−h,23] as well as "tadpole" polymers[18a,24] having "a ring with a branch" architecture and "twin-tailed tadpole" polymers[18f] having "a ring with two branches" architecture, have so far been synthesized.

Also in Table 3, seven new constructions produced from monocycloalkane isomers of C_7H_{14} are collected. Most of them are distinct from each other in the total number of termini and junctions, respectively, shown in parentheses in their notation. However, the two constructions having identical total numbers of termini and junctions, namely a pair $I_7(3,2)[1(4)]$ and $I_7(3,2)$-$[2(3,0)]$ and a pair $I_7(4,2)[3\text{-}1]$ and $I_7(4,2)[2\text{-}2]$, respectively, are distinctive in their branch modes on a ring unit. Moreover, 14 new constructions are produced from cyclooctane isomers, and several sets are again distinctive in their branch modes in the ring unit rather than the total number of termini and junctions (S-Table 1 in Supporting Information).

It is also shown that all constructions initially produced from up to cycloheptane isomers are derived by the relevant isomer containing a *cyclopropane* unit. A topological construction containing four or more junctions on the ring unit, $I_8(4,4)$, is the first one produced by reference to a relevant cyclooctane isomer containing a *cyclobutane* unit (S-Table 1 in Supporting Information),

Thus by this process, as in the A main-class branched topology, a series of "a ring with branches" constructions has been ranked by reference to the constitutional isomerism in monocycloalkanes.

b. Multicyclic Topologies. A series of bicycloalkanes of C_nH_{2n-2} with up to $n = 6$ and their relevant topological constructions (main-class II) are listed in Table 4. Some of topologically remarkable constructions, which are produced by reference to the corresponding tricycloalkanes of C_nH_{2n-4} with $n = 4-10$ (main-class III), are shown in Tables 5 and 6, and those by reference to tetracycloalkanes of C_nH_{2n-6} with $n = 6$ (main-class IV) are also collected in Table 7. In these tables, a systematic notation for each construction is also presented (see Supporting Information for the notation procedures).

In Table 4, the three basic bicyclic constructions without any outward branches are included: namely, an "internally linked (θ-shaped or fused)" ring, $II_4(0,2)$, "8-shaped (spiranic)" rings, $II_5(0,1)$, and "manacle-shaped" rings, $II_6(0,2)$, i.e., two rings externally linked ("bridged") by a linear chain, respectively. And 15 basic tricyclic constructions without any outward branches are shown in Tables 5 and 6: "fused" or "spiranic" rings are collected in Table 5 and externally linked (or "bridged") rings with simple cyclic, "fused", or "spiranic" forms are listed in Table 6, respectively.

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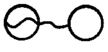
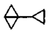
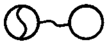
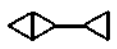
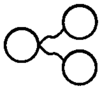
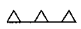
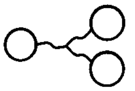
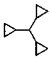
(23) (a) Geiser, D.; Höcker, H. *Macromolecules* **1980**, *13*, 653−656. (b) Vollmert, B.; Huang, J.-X. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 467−472. (c) Hild, G.; Kohler, A.; Rempp, P. *Eur. Polym. J.* **1980**, *16*, 525−527. (d) Roovers, J.; Toporowski, P. M. *Macromolecules* **1983**, *16*, 843−849. (e) Rique-Lurbet, L.; Schappacher, M.; Deffieux, A. *Macromolecules* **1994**, *27*, 6318−6324. (f) Ishizu, K.; Kanno, H. *Polymer* **1996**, *37*, 1487−1492. (g) Kubo, M.; Hayashi, T.; Kobayashi, H.; Tsuboi, K.; Itoh, T. *Macromolecules* **1997**, *30*, 2805−2807.

(24) (a) Beinat, S.; Schappacher, M.; Deffieux, A. *Macromolecules* **1996**, *29*, 6737−6743. (b) Kubo, M.; Hayashi, T.; Kobayashi, H.; Itoh, T. *Macromolecules* **1998**, *31*, 1053−1057.

Table 6. Bridged Ring Constructions Produced by Reference to Tricycloalkane Isomers (C_nH_{2n-4}: $n = 7-10$)[a]

Topology	C_7H_{10}
 $\mathrm{III}_7(0,3)$	
 $\mathrm{III}_7(0,4)$	
Topology	C_8H_{12}
 $\mathrm{III}_8(0,2)$	
 $\mathrm{III}_8(0,3)$	
Topology	C_9H_{14}
 $\mathrm{III}_9(0,3)$	
 $\mathrm{III}_9(0,4)$	
Topology	$C_{10}H_{16}$
 $\mathrm{III}_{10}(0,4)$	

[a] See Supporting Information for the notation of topological constructions.

Table 7. Selected Topological Constructions Produced by Reference to Tricycloalkane Isomers (C_nH_{2n-6}: $n = 6$)[a]

Topology	C_6H_6
 $\mathrm{IV}_6(0,3)[0^{a,c}\text{-}0^{a,b}\text{-}0^{b,c}]$	
 $\mathrm{IV}_6(0,6)[0^a\text{-}0^b\text{-}0^a\text{-}0^c\text{-}0^b\text{-}0^c]$	
 $\mathrm{IV}_6(0,6)[0^a\text{-}0^b\text{-}0^c\text{-}0^a\text{-}0^b\text{-}0^c]$	 $K_{3,3}$

[a] See Supporting Information for the notation of topological constructions.

And so far, the three basic bicyclic polymer architectures, i.e., "8-shaped" polymers,[18a,b,24b,25] a "θ-shaped" ring polymer,[18a] and a "manacle-shaped" polymer,[18a] as well as one of basic tricyclic polymers, i.e., a triple ring polymer,[18a] have been synthesized.

These topological constructions are again produced according to the procedure applied in the previous branched (class A) and monocyclic (class I) systems. Thus first, a "θ-shaped" ring construction, $\mathrm{II}_4(0,2)$, is produced from bicyclo[1.1.0]butane, C_4H_6. This construction is ubiquitous in those produced from all higher bicycloalkanes. From the five bicycloalkane isomers of C_5H_8, the three new constructions, $\mathrm{II}_5(0,1)$, $\mathrm{II}_5(1,2)$, and $\mathrm{II}_5(1,3)$, are produced, while the other two isomers produce an equivalent construction from bicyclo[1.1.0]butane, C_4H_6. The latter two of these three new constructions are obtained from the methyl-substituted derivatives of a bicyclo[1.1.0]butane, and the former one, i.e., an 8-shaped, "spiranic ring" construction, is obtained from spiro[2.2]pentane. These three constructions are distinguished from each other by their total number of termini and junctions as seen in Table 4. By reference to bicyclohexane (C_6H_{10}) isomers, moreover, eight new constructions are produced. All constructions but one from bi(cyclopropane), $\mathrm{II}_6(0,2)$, possess outward branches emanating from either a "θ-shaped" ring or an "8-shaped" ring as noted above. And two of them, i.e., $\mathrm{II}_6(1,1)$ and $\mathrm{II}_6(2,2)[2^a\text{-}0^a]$, have five branches at one junction; these hypothetical examples are included in this group, although they cannot be formed from C_6H_{10} (they are shown in parentheses in Table 4).

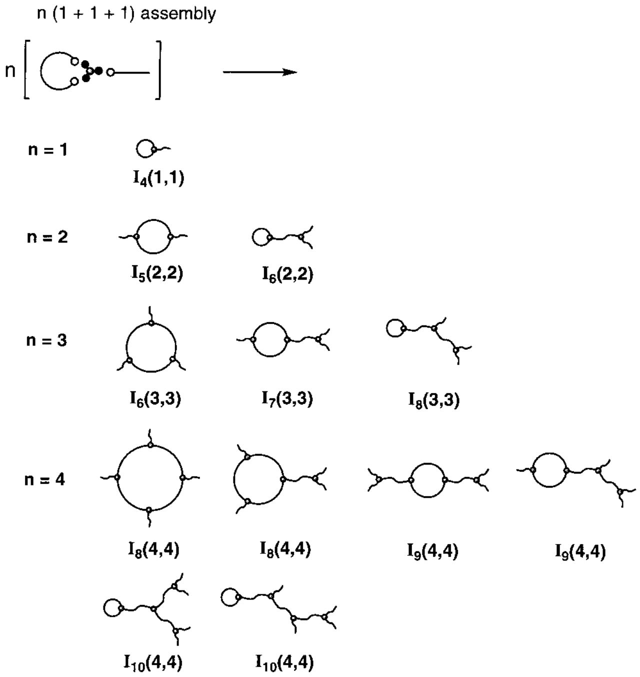
Basically these constructions are distinct from each other in the total number of termini and junctions, respectively, shown in parentheses in their notation. However, the two constructions, namely a pair of $\mathrm{II}_6(2,2)[2^a\text{-}0^a]$ and $\mathrm{II}_6(2,2)[1^a\text{-}1^a]$, and a pair of $\mathrm{II}_6(2,3)[2\text{-}0^a\text{-}0^a]$ and $\mathrm{II}_6(2,3)[1^a\text{-}1\text{-}0^a]$, respectively, are distinctive in the number of outward and internally linked branches on the ring unit, indicated in brackets after the closing parenthesis. The positions of the two specific junctions internally linked to each other are indicated in the notation by giving superscripts (a, b, etc.) at the relevant junction numbers,

Thus, it is shown, as in the previous branched (main-class A) and monocyclic (main-class I) topologies, that a series of internally and externally linked double cyclic topological constructions can be classified into the corresponding categories by reference to the bicycloalkane isomers.

It is important to note that all constructions observed in this main-class II possess one of three types of internally or externally linked ring units, i.e., a "θ-shaped" ring, $\mathrm{II}_4(0,2)$, an "8-shaped" ring, $\mathrm{II}_5(0,1)$ or a "manacle-shaped" ring, $\mathrm{II}_6(0,2)$. A variety of "rings with branches" constructions are also obtainable by emanating from these ring units. They are produced primarily from the corresponding isomers containing cyclopropane units, as was noted in the monocycloalkane (main-class I) topologies. Indeed, all constructions derived from up to C_6H_{10} isomers are produced first by the relevant isomers containing exclusively cyclopropane units, as seen in Table 4.

Furthermore, 15 basic topological constructions produced from the relevant tricycloalkanes of C_nH_{2n-4} with $n = 4-10$ (main-class III) are shown in Tables 5 and 6. 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 a "fused" ring or "spiranic" rings forms as shown in Table 5. Six of them are produced directly from the corresponding tricycloalkanes, and the additional two from the hypothetical molecular formula possessing five or six branches at a junction as given also in Table 5. In particular, a "doubly fused" (internally double-linked) ring construction, III_4 or $\mathrm{III}_4(0,4)$, is produced, in the first place, from tetrahedrane. The two constructions from tricyclopentane isomers and the three from tricyclohexane isomers shown in Table 5 are a few of the large number of possible constructions, in particular those possessing additional branches. It is also notable that four types of "doubly fused" ring constructions, i.e., α-graph, $\mathrm{III}_4(0,4)[0^a\text{-}0^b\text{-}0^a\text{-}0^b]$, β-graph, $\mathrm{III}_6(0,4)[0^a\text{-}0^b\text{-}0^a\text{-}0^b]$, γ-graph, $\mathrm{III}_5(0,3)[0^{a,b}\text{-}0^a\text{-}0^b]$, and δ-graph, $\mathrm{III}_5(0,2)[0^{a,b}\text{-}0^{a,b}]$, respectively,[14b] are included in this class. Moreover, the seven topological constructions of externally linked (or "bridged") rings with simple cyclic, "fused", or "spiranic" forms are obtainable in reference to the relevant tricycloalkane isomers as listed in Table 6. Finally, three particularly notable constructions produced by reference to the relevant tetracycloalkane isomers of C_nH_{2n-6} with $n = 6$ (main-

Scheme 1

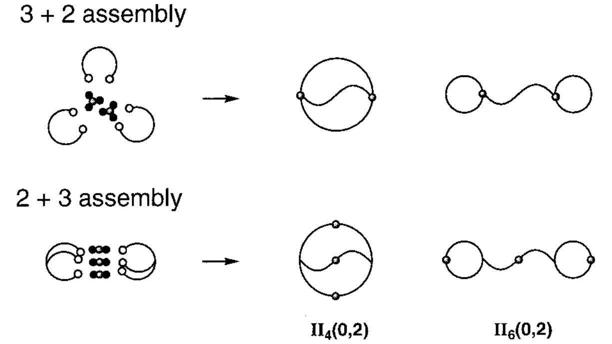


class IV) are listed in Table 7. These include prisman, IV$_6$(0,6)[0^a-0^b-0^a-0^c-0^b-0^c], and K$_{3,3}$ type, IV$_6$(0,6)[0^a-0^b-0^c-0^a-0^b-0^c], constructions,[15,26] which commonly possess an internally triple-linked ring, while their linking modes are distinctive.

3. A Synthetic Strategy of Cyclic and Branched Polymer Topologies: Electrostatic Self-Assembly and Covalent Fixation. On the basis of the classification of nonlinear polymer topologies into a series of main-classes of A, I, II, III, and IV types, and further into respective sub-classes, the structural relationship between different polymer architectures has been investigated. A subsequent rational synthetic strategy has been proposed to construct a variety of topologically unique macromolecular architectures.

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 (Scheme 1). It is readily 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, and 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 "topological isomers".[27] It should be emphasized that topological isomers frequently occur, particularly among constructions comprising ring units belonging to the I, II, III, or IV main-classes; nevertheless, they are also observed in the A main-class topologies, as in A$_9$(6,3) and A$_{10}$(6,4) shown in Table 2. A significant number of topological isomer pairs are observed, on the other hand, in the I main-class. Those given in Tables 3 and S-Table 1 (Supporting Information) include the three in sub-classes I$_6$(3,3), I$_7$(3,3), and I$_8$(3,3), the three in sub-classes I$_6$(3,2), I$_7$(3,2)[1(4)], and I$_7$(3,2)[2(3,0)], the three in sub-classes I$_7$(4,2)[3−1], I$_8$(4,2)[1(5)], and I$_8$(4,2)[3(3,0,0)], and the two in sub-classes I$_7$(4,2)[2-2] and I$_8$(4,2)[2(4,0)], respectively. The four constructions from one I$_7$(4,3) and three I$_8$(4,3)'s, and the two from two I$_8$(4,4)'s, are also pairs of topological isomers in the main-class I.

Scheme 2



Another notable pair of topological isomers is observed in the main-class II, namely the two constructions of II$_4$(0,2) and II$_6$(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 trifunctional 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.[18a] Other pairs of topological isomers in the main-classes II, III, and IV listed in Tables 4, 5, and 6 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), the two of III$_5$(0,2) and III$_7$(0,2), and the two of IV$_6$(0,6).

Second, 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), I$_7$(3,3), I$_8$(3,3), and I$_8$(4,4) is a 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), I$_7$(3,3), and I$_8$(3,3), and the construction of I$_8$(4,4) are the products of two, three, and four times, respectively, of a precursor set for the production of the I$_4$(1,1), namely one monofunctional and one bifunctional polymer precursor and one trifunctional end-linking reagent (Scheme 1).

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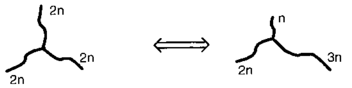
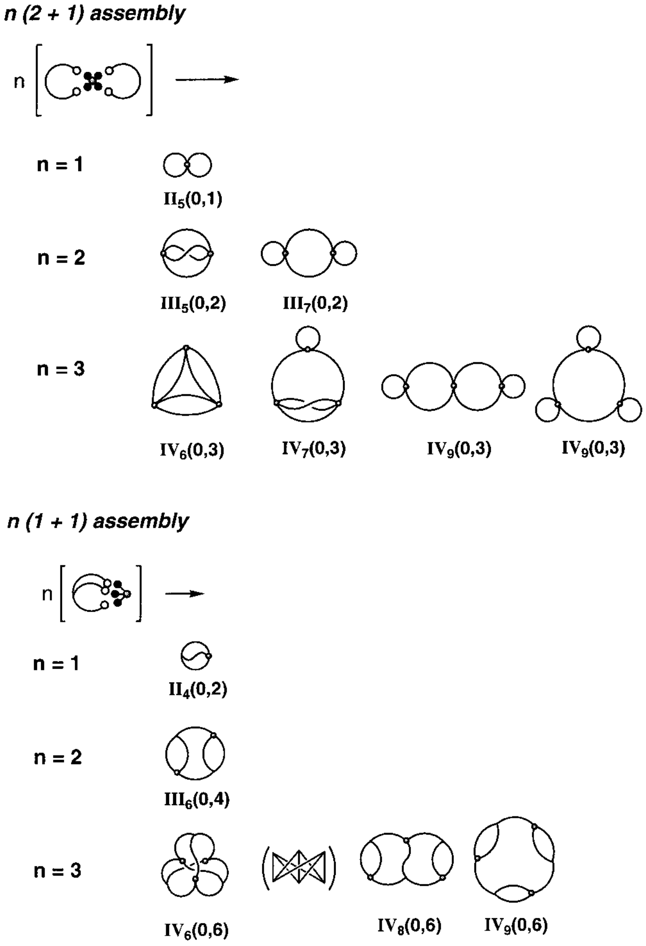
(25) (a) Schappacher, M.; Deffieux, A. *Macromolecules* **1995**, *28*, 2629−2636. (b) El Madani, A.; Favier, J.-C.; Hémery, P.; Sigwalt, P. *Polym. Int.* **1992**, *27*, 353−357. (c) Antonietti, M.; Fölsch, K. J. *Macromol. Chem., Rapid Commun.* **1988**, *9*, 423−430.

(26) Chen, C.-T.; Gantzel, P.; Siegel, J. S.; Baldridge, K.; English, R. B.; Ho, D. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2657−2660.

(27) The set of topological isomers shown here are *constitutional* isomers possessing distinctive topologies, uninterconvertible with each other through conceptual deformation of the molecular graphs. A different *constitutional* isomer class involves a set of those possessing topologically *equivalent* molecular graphs, interconvertible with each other through topological transformation, typically in the case of a pair of star polymers shown below having identical numbers of arms and total arm length but having different sets of arm length composition. Moreover, topological *stereo*isomers[15,16] are distinctive from these *constitutional* isomers. Thus, a pair consisting of a ring and a knot is classified as a typical example of topologically *distinctive stereo*isomers, and more specifically diastereomer. On the other hand, a pair of left- and right-handed knots is classified as topologically *distinctive* enantiomers. Apart from these, a pair consisting of a ring and a square (or triangle etc.) is classified, when these forms are persistently retained, as topologically *equivalent* diastereomers. Likewise, a pair of a right- and left-handed helixes of identical length is classified as topologically *equivalent* enantiomers.



Scheme 3



This reveals a hierarchy of a “homologous” series of polymer topologies obtainable from the classification of nonlinear topological constructions.

Third, a group of topological constructions possessing the relevant terminus and junction numbers, while belonging to different main-classes in either II, III, or IV, has been compared. Thus, the two constructions of $III_5(0,2)$ and $III_7(0,2)$ and another of $IV_6(0,3)$ are produced from twice and three times, respectively, of a precursor set for the production of a construction of $II_5(0,1)$, namely two bifunctional polymer precursors and one tetrafunctional end-linking reagent (Scheme 3). Likewise, the construction of $III_6(0,4)$ and another $K_{3,3}$ type of $IV_6(0,6)$ are produced twice and three times, respectively, of a precursor set for the production of a construction of $II_4(0,2)$, namely one trifunctional star polymer precursor and one trifunctional end-linking reagent (Scheme 3).

Finally, it must be noted that several of the 15 basic topologies in the III class shown in Tables 5 and 6, having either internally or externally linked ring architectures, are simultaneously obtainable again through an appropriate combination of bi- or trifunctional polymer precursors with bi-, tri-, or tetrafunctional end-linking reagents, as shown in S-Scheme 1 (Supporting Information).

By taking into account the hierarchy of a variety of basic topological polymer architectures, we have formulated a synthetic strategy for these polymer topologies by means of an “electrostatic self-assembly and covalent fixation” process.[18a] This can provide an efficient means for the end-linking reaction of various telechelic (end reactive) polymer precursors of mono-, bi-, and 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 proceeded efficiently. And 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, $I_4(1,1)$, and a twin-tailed tadpole, $II_5(2,1)$, as well as a topological isomer pair of a “θ-shaped” ring, $II_4(0,2)$, and “manacle-shaped” rings, $II_6(0,2)$, and a triple ring, $III_7(0,1)$, constructions.[18a−h] Further studies are now in progress, aiming to construct an exceptionally unusual polymer topology such as a $K_{3,3}$ by a stepwise pathway with the relevant cyclic and multicyclic polymer precursors having appropriate functional groups.[18c,d]

Conclusions

A systematic classification of well-defined cyclic and branched polymer topologies has been demonstrated. Thus, a variety of polymer topologies are classified hierarchically by reference to the constitutional isomerism of alkanes and (poly)cycloalkanes. The classification of topological constructions provides insight into the structural relationship among different polymer topologies having, in particular, cyclic or multicyclic polymer units. A number of pairs of “topological isomers” have been accordingly identified. Finally, a rational synthetic strategy by means of an “electrostatic self-assembly and covalent fixation” process has been proposed for constructing a variety of topologically unique polymer architectures.

Acknowledgment. Financial supports from The Iwatani Naoji Foundation’s Research Grant and from a NEDO Nanostructure Polymer Project Grant are gratefully acknowledged. This work was also supported partly by a grant from the Ministry of Education, Science and Culture Japan through the Japan Society of Promotion of Sciences (13450377).

Supporting Information Available: The systematic notation procedure for nonlinear polymer topologies, a table (S-Table 1) for topological constructions produced by reference to monocycloalkane molecules of C_8H_{16}, and a scheme (S-Scheme 1) for the self-assembly and covalent fixation process to provide a variety of tricyclic polymer topologies (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0114409