

## Revised (JA0114409)

## Notation Procedures for Nonlinear Polymer Topologies

## 1. Branched Topologies

A systematic notation for a series of branched topologies is performed as follows. First, all constructions produced from alkane isomers are classified as main-class A. A linear construction produced from propane ( $C_3H_8$ ) is termed as a sub-class  $A_3$ , or alternatively  $A_3(2,0)$  by showing the total number of termini and of junctions, respectively, in parentheses. Subsequently, sub-classes  $A_4$  (or  $A_4(3,1)$ ) and  $A_5$  (or  $A_5(4,1)$ ) are uniquely defined as shown in Table 1. On the other hand, sub-classes  $A_6$ ,  $A_7$ ,  $A_8$  and  $A_n$  of higher  $n$  values consist of multiple constructions, and each component are defined by specifying the total number of termini and junctions, respectively, in parentheses as shown in Tables 1 and 2. As a typical example, an  $m$ -armed star polymer topology is labeled as  $A_{m+1}(m,1)$ , as listed in Table 2.

In sub-class  $A_9$ , two of the newly produced constructions of  $A_9(6,3)$  cannot be distinguished by showing merely the total numbers of termini and junctions. The connectivity of junctions for these two constructions is each distinctive, and can be specified by applying the nomenclature rule for substituted alkanes. That is, first a "backbone" chain having the most junctions is identified, and the number of branches at each junction is given in brackets in descending order from the most substituted junction. Thus, the above two  $A_9(6,3)$ 's are designated as  $A_9(6,3)[4-3-3]$  and  $A_9(6,3)[3-4-3]$ , respectively. Another pair of constructions in sub-class  $A_{10}(6,4)$ , namely one having a dendritically branched structure and another having a comb-like branched structure, are defined likewise by specifying their junction connectivity, as  $A_{10}(6,4)[3-3(3)-3]$  for the former and  $A_{10}(6,4)[3-3-3-3]$  for the latter, respectively.

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**2. Cyclic Topologies****2-1. Monocyclic topologies**

A systematic notation for a series of "a ring with branches" constructions has been performed by a similar manner (Table 3 and S-Table 1). First, these are classified as main-class I, since they are produced from monocycloalkanes. A simple ring construction produced from cyclopropane is designated as sub-class  $I_3$ , or alternatively  $I_3(0,0)$  by showing the total number of termini and junctions in parentheses. A new construction from  $C_4H_8$  is labeled likewise as  $I_4$  or  $I_4(1,1)$ . On the other hand, sub-classes  $I_5$ ,  $I_6$ ,  $I_7$  and other  $I_n$  comprise multiple constructions, and each of them can be basically identified by specifying the total number of termini and junctions.

The two sub-classes belonging to  $I_7(3,2)$  and to  $I_7(4,2)$ , however, contain two distinctive constructions. Thus, they are identified by specifying their branch modes on a ring unit. First, the number of outward branches at every junction on the ring unit is identified, and is indicated in the brackets placed after the closing parenthesis. The detailed junction architecture of the outward branches is then identified, according to the procedure applied to the A main-class topology, and is indicated in the parentheses enclosed within the brackets. The two constructions of  $I_7(3,2)$  are thus defined as  $I_7(3,2)[1(4)]$  and  $I_7(3,2)[2(3,0)]$ , respectively. Likewise, the two constructions of  $I_7(4,2)$  are labeled as  $I_7(4,2)[3-1]$  and  $I_7(4,2)[2-2]$ , respectively, where the connectivity of junctions along the ring unit is indicated by connecting the number of the outward branches at each junction with a hyphen.

Fourteen new constructions are produced in sub-class  $I_8$ , in which several sets are again not uniquely assigned by showing merely the total number of termini and junctions (S-Table 1). The three constructions of  $I_8(4,2)$  are distinguished by

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additional parameters, [1(5)], [2(4,0)] and [3(3,0,0)], respectively. Similarly, the three constructions of  $I_8(4,3)$  are distinguished by adding [1(4)-1], [2(3,0)-1], and [2-1(3)], respectively. Furthermore, the two of  $I_8(4,4)$  are labeled with [1(3)-1-1] and with [1-1-1-1], respectively. Finally, the two constructions of  $I_8(5,2)$  and of  $I_8(5,3)$  are labeled by adding [4-1] and [3-2] for the former, and [3-1-1] and [2-2-1] for the latter, respectively.

## 2-2. Multicyclic topologies

A systematic notation for a series of topological constructions from bicycloalkanes is conducted as in the case of A and I main-classes (Table 4). First, these are classified as main-class II, since they are produced from bicycloalkane isomers. A "θ"-shaped ring construction, produced from bicyclo[1,1,0]butane is defined as a sub-class  $II_4$ , or  $II_4(0,2)$  by showing the total number of termini and junctions, respectively, in parentheses. Sub-classes  $II_5$  and  $II_6$  consist of multiple constructions, namely three for  $II_5$  and eight for  $II_6$ , respectively. While they are basically distinguished by specifying the total number of termini and junctions in parentheses, sub-classes  $II_6(2,2)$  and  $II_6(2,3)$  comprise distinctive constructions that require further structural specifications. Thus in the brackets after the closing parenthesis, the number of not only outward branches but also internally linked branches on the ring unit is indicated, and these numbers (thus 0 for the latter, and 1, 2, .. for the former) are linked by hyphens. Moreover, the positions of the two specific junctions internally linked to each other are indicated by giving superscripts (a, b, etc) at the relevant junction numbers. For example, the two  $II_6(2,2)$ 's are designated as  $II_6(2,2)[2^a-0^a]$  and  $II_6(2,2)[1^a-1^a]$ , and the two  $II_6(2,3)$ 's are designated as  $II_6(2,3)[2-0^a-0^a]$  and  $II_6(2,3)[1^a-1-0^a]$ , respectively. Accordingly, any branching modes in an internally linked ring unit can be uniquely defined.

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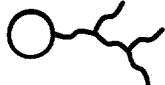

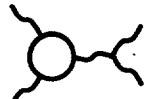


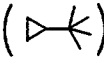








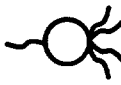





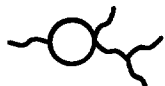



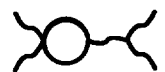



Finally, a systematic notation for a series of topological constructions produced from tri and tetracycloalkanes are presented as in the previous A, I and II main-classes (Tables 5, 6 and 7). These are classified as main-classes III and IV, since they are produced from tri and tetracycloalkane isomers, respectively. A "doubly fused" (internally double-linked) ring construction from tetrahedrane is defined as sub-class  $III_4$  or  $III_4(0,4)$  by showing the total number of termini and junctions, respectively, in parentheses. The two constructions in sub-class  $III_5$  and the three in sub-class  $III_6$  are a few of the large number of possible constructions, in particular those possessing additional branches, which are labeled by reference to the branched topology notation given in the preceding section. Constructions in sub-classes  $III_4(0,4)$ ,  $III_5(0,2)$ ,  $III_5(0,3)$  and  $III_6(0,4)$  commonly possess a "doubly fused" ring unit, while their linking modes on the ring unit are distinctive. They are accordingly labeled by specifying their linking modes as  $[0^a-0^b-0^a-0^b]$ ,  $[0^{a,b}-0^{a,b}]$  and  $[0^{a,b}-0^a-0^b]$ , respectively. Finally, three topologically significant constructions from tetracycloalkanes given in Table 7 commonly possess an "internally triple-linked" ring unit, with distinctive linking modes on the ring unit. They are defined as sub-classes  $IV_6(0,3)$ ,  $IV_6(0,6)$ , and  $IV_6(0,6)$ , respectively, and the latter two are identified by specifying their linking mode within the ring unit as  $[0^a-0^b-0^a-0^c-0^b-0^c]$  and as  $[0^a-0^b-0^c-0^a-0^b-0^c]$ , respectively.

## Supporting Information

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S-Table 1

S-Table 1. Topological Constructions Produced by Reference to  
Cycloalkane Isomers ( $C_nH_{2n}$ :  $n = 7$  and 8)

Topology	$C_8H_{16}$	Topology	$C_8H_{16}$
 $I_8(3,3)$		 $I_8(4,4)[1(3)-1-1]$	
 $I_8(4,2)[1(5)]$		 $I_8(4,4)[1-1-1-1]$	
 $I_8(4,2)[2(4,0)]$		 $I_8(5,1)$	
 $I_8(4,2)[3(3,0,0)]$		 $I_8(5,2)[4-1]$	
 $I_8(4,3)[1(4)-1]$		 $I_8(5,2)[3-2]$	
 $I_8(4,3)[2(3,0)-1]$		 $I_8(5,3)[3-1-1]$	
 $I_8(4,3)[2-1(3)]$		 $I_8(5,3)[2-2-1]$	

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S-Scheme 1

