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Paper

Topological Analysis and Intramolecular Cyclic Feature Evaluation of Polymers Derived from A_m+B_n Step-Growth Polymerization

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In this contribution, we investigated the evaluation strategy for intramolecular cyclic feature of polymers derived from A_m+B_n ($m\geq 2$ and $n\geq 2$) step-growth polymerization from a topological analysis perspective. The general quantitative relationship between the structural units and cyclic structures was presented regardless of the terminal groups of polymers. Further, two strategies for evaluating cyclic features were developed. First, the general expression of average number of cyclic structures per macromolecule (ANC) for polymers derived from A_m+B_n route was obtained, which could be easily determined by NMR and SEC analytics. The contents of cyclic structures of polymers from step-growth polymerization of monomer pairs were measured especially for the polymers with different terminal groups. Second, a new parameter of cyclic index (CI) was defined as the ratio of terminal units number to dendritic units number in order to determine the extent of intramolecular cyclization in polymers derived from the representative A_2+B_3 route. CI <1 refers to the intramolecular cyclic structures existing in polymers, and a lower CI value indicates a higher degree of intramolecular cyclization. The CI value can be determined by quantitative NMR spectra of polymers, thereby allowing the easy evaluation of their cyclic features. With the validation of model polymer of polycarbosilanes from A_2+B_3 route, the ANC and CI were verified to effectively evaluate their intramolecular cyclic features.

1 Introduction

Step-growth polymerization is an important method for the synthesis of general-purpose and engineering polymers such as polyesters, polyamides, polyurethanes, silicon- and sulfur-containing polymers.[1] In contrast to chain-growth polymerization, the main characteristic of step-growth polymerization is that all the reactive species including monomers, oligomers, and polymers can react with each other at any time and stage during the polymerization process. By selecting monomer pairs, the polymers with various topological structures can be obtained, e.g., linear or cyclic polymers from A_2+B_2 route and highly branched or cross-linked polymers from A_m+B_n ($m\geq 2$ and $n \geq 3$) route.

In the step-growth polymerization of A_m+B_n system, the reaction between A and B functional groups of monomers occurs randomly. The reaction occurring between two reactive species can contribute to chain growth, whereas the reaction occurring in the same one reactive specie results in intramolecular cyclization. The competition between intramolecular cyclization and chain growth affects almost all the important aspects of polymers such as gelation, molecular weight and distribution, terminal groups, and topological structures.[2] Compared to the chain growth, the intramolecular cyclization has received much less attention even in the classical theory of the step-growth polymerization developed by Carothers[3,4] and Flory.[5,6] The main obstacle is that the cyclic structures are hard to be quantitatively distinguished from the acyclic structures. The matrix-assisted laser desorption ionization-time of flight (MALDI-ToF) mass spectrometry is an effective tool to reveal cyclic structures and has confirmed that the cyclic structures widely exist in the step-growth polymerization, e.g., the A_2+B_2,[7] A_2+B_3,[8-13] and AB_2 systems.[14,15]

However, the MALDI-ToF mass spectrometry analysis is not suitable for determining the polymers derived from polyaddition reaction or the polymers without ionized features. Furthermore, for multicyclic structures formed in the A_m+B_n ($m\geq 2$ and $n\geq 3$) system, the analysis of mass spectrum becomes very complicated. In our previous studies,[16,17] the topological structure of highly branched polymers from A_2+B_n ($n\geq 3$) route was analyzed and the cyclic structures were found to depend on the composition of structural units. The average number of cyclics (ANC) and terminal index (TI) were defined to describe the highly branched and multicyclic features of highly branched polymers derived from the representative A_2+B_3 route. These studies are helpful to understand the fine topological structures of polymers in the step-growth polymerization and provide a new perspective to study intramolecular cyclic structures. In general, the step-growth polymerization of the monomer pairs also includes A_3+B_3,[18,19] A_3+B_4 system and some systems with different terminal groups. This study will give a general evaluation strategy for intramolecular cyclic feature of polymers derived from A_m+B_n step-growth polymerization from a topological analysis perspective. And a new parameter of cyclic index (CI) is defined as the ratio of terminal units' number to dendritic units' number in order to determine the extent of intramolecular cyclization.

2 Topological Analyses

At first, the topological structure of macromolecule derived from the A_m+B_n step-growth polymerization can be regarded as a combination of the basic units derived from A_m and B_n monomers linked together by covalent bonds formed in the polymerization. According to the number of unreacted or residual functional groups, the units derived from A_m monomers are subdivided into *m* basic units, i.e., A_0, …, A_i, …, $A_{(m-1)}$ units, where A_i contains *i* functional groups. Similarly, the units derived from B_n monomers are subdivided into *n* basic units, i.e., B_0, …, B_j, …, $B_{(n-1)}$ units, as shown in Fig. 1.

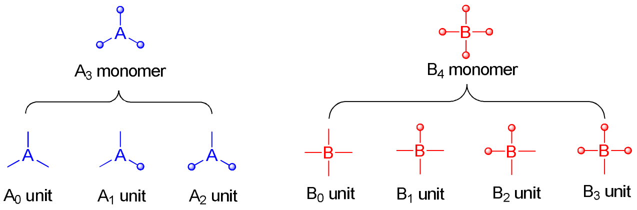


Fig. 1 The division of topological units in A_m+B_n (e.g., A_3+B_4) system

In a typical step-growth polymerization as shown in Fig. 2, there is a competition between the chain-growth and intramolecular cyclization. The former contributes to chain growth, whereas the latter results in cyclic structures. Therefore, the composition of the macromolecule derived from A_m+B_n step-wise polymerization should contain linear, branched, terminal, and cyclic structures.

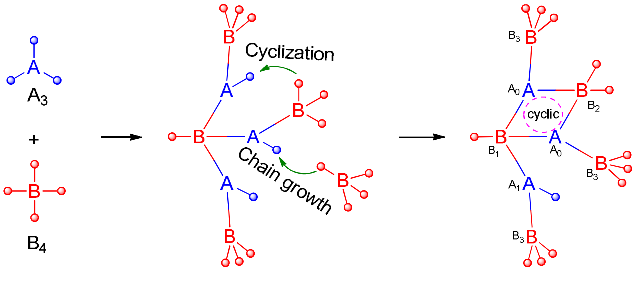


Fig. 2 Chain-growth polymerization and intramolecular cyclization in the A_m+B_n (e.g., A_3+B_4) step-growth polymerization

According to the terminal groups and cyclic structures, the polymers derived from A_m+B_n step-wise polymerization can be divided into three categories: 1) acyclic polymers with same terminal groups, 2) cyclic polymers with same terminal groups, and 3) cyclic polymers with different terminal groups. Based on the macromolecular topological structures, the quantitative relation of the component units and cyclic structures is derived in sequence.

2.1 Acyclic polymers with same terminal groups

The acyclic polymers with B terminal groups was selected to be analyzed firstly, and their macromolecular topological structure was viewed as the two parts, i.e., one unit of "B_1" and *x* repetitive composite units of one A_0 and *m-1* $B_{(n-1)}$ units, as shown in Fig. 3.

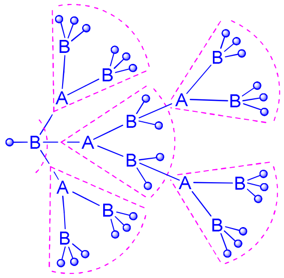


Fig. 3 Topological structure model of acyclic polymers with B terminal groups

The total number of A units (N_A) and total number of B units (N_B) can be obtained as follows:

$$\begin{cases} N_A = x \\ N_B = (m-1)\times x + N \end{cases}$$

where N refers to the total number of macromolecules and obviously,

$$N_B = (m-1)\times N_A + N \quad (1a)$$

Similarly, for the acyclic polymers with A terminal groups,

$$N_A = (n-1)\times N_B + N \quad (1b)$$

2.2 Cyclic polymers with same terminal groups

In the cyclic polymers terminated with B functional groups, the total number of cyclic structures can be set as N_C. If one cyclic structure is supposed to ring-opening by breaking the "A–B" bond, then a "–$B_{(n-1)}$" unit is added to link to the broken A unit. Further, an "–$A_0[B_{(n-1)}]_{(m-1)}$" composite unit is added to link to the broken B unit, resulting in a new acyclic structure as shown in Fig. 4.

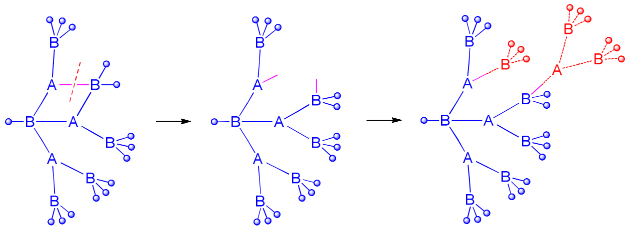


Fig. 4 The supposed scheme from cyclic polymers to acyclic polymers

Similarly, if all the cyclic structures are supposed to ring-opening, followed by adding relative groups as described above, an absolutely acyclic polymer with B functional groups could be obtained. The total number of A units (N_A') and total number of B units (N_B') in the new acyclic polymers can be expressed as follows:

$$\begin{cases} N'_A = N_A + N_C \\ N'_B = N_B + m \times N_C \\ N'_B = (m-1) \times N'_A + N \end{cases}$$

Therefore,

$$N_C = (m-1) \times N_A - N_B + N \qquad (2a)$$

Furthermore, for cyclic polymers with A terminal groups,

$$N_C = (n-1) \times N_B - N_A + N \qquad (2b)$$

2.3 Cyclic polymers with different terminal groups

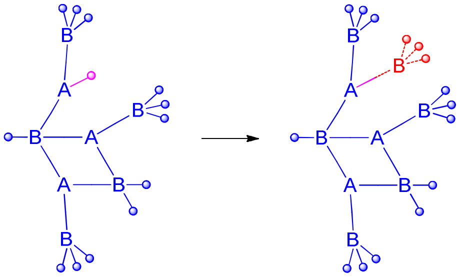


Fig. 5 The supposed scheme from cyclic polymers with different terminal groups to cyclic polymers with same terminal groups

In general, the cyclic polymers with A and B terminal groups should contain various A and B units. If each A_i unit is supposed to be linked to the i corresponding $–B_{(n-1)}$ units to evolve an A_0 unit, the cyclic polymer terminated with two different types of functional groups will evolve into B functional groups-terminating polymer as shown in Fig. 5. For the new B functional groups-terminating polymer, the relationship between its component units can be expressed as follows.

$$\begin{cases} N''_A = \sum_{i=0}^{m} N_{Ai} \\ N''_B = \sum_{j=0}^{n} N_{Bj} + \sum_{i=0}^{m} i \times N_{Ai} \\ N_C = (m-1) \times N''_A - N''_B + N \end{cases}$$

where the N_A'' and N_B'' refer to the total number of A and B units in the new B functional group-terminating polymer, respectively. After the simplification, the following expression is obtained.

$$N_C = \sum_{i=0}^{m} (m-i-1) \times N_{Ai} - \sum_{j=0}^{n} N_{Bj} + N \qquad (3a)$$

Similarly, if the cyclic polymer with both A and B terminal groups is supposed to evolve into an A functional group-terminating polymer, another expression of N_C can be obtained as:

$$N_C = \sum_{j=0}^{n} (n-j-1) \times N_{Bj} - \sum_{i=0}^{m} N_{Ai} + N \qquad (3b)$$

The Eq. 3a and Eq. 3b are both the general expressions of N_C for cyclic polymers with different terminal groups.

$$N_C = \begin{cases} \sum_{i=0}^{m} (m-i-1) \times N_{Ai} - \sum_{j=0}^{n} N_{Bj} + N \\ \sum_{j=0}^{n} (n-j-1) \times N_{Bj} - \sum_{i=0}^{m} N_{Ai} + N \end{cases}$$

The Eq. 3a and Eq. 3b both show the general quantitative relationship between the cyclic structures and structural units. Accordingly, the content of cyclic structures can be determined by comparing the composition of the structural units in polymers where these structural units can be easily identified in NMR spectra.

It should be noted that the equal reactivity or non-equal reactive of A and B groups can affect the content of cyclic structures. However, the only precondition for the analyses mentioned above is that A groups can react with B groups regardless the equal reactivity or non-equal reactive of A and B groups. Thus the conclusion of topological analyses is not only applicable for the A_m+B_n system, where A and B groups possess equal reactivity, but also for the A_2+BB' and A_2+BB'$_2$ system with non-equal reactive species.

Since the Eq. 3a and Eq. 3b are equal to each other, and after the simplification, the following equation is obtained.

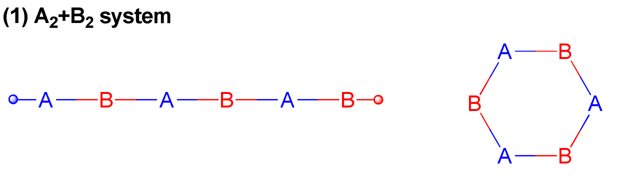
$$\sum_{i=0}^{m} (m-i) \times N_{Ai} = \sum_{j=0}^{n} (n-j) \times N_{Bi} \qquad (4)$$

The Eq. 4 shows the general quantitative relationship between the structural units in the A_m+B_n system including linear, cyclic, highly branched and even cross-linked polymers (beyond critical gelation point). It is important for the relative quantitative analyses of polymers. In some cases, even if the characteristic peaks of different units in NMR spectra overlap together,[20,21] the quantitative relation of Eq. 4 will be helpful to give a solution.

3 Model Validation

Herein, the typical molecular structures in the A_2+B_2, A_2+B_3, and A_3+B_3 systems are presented in Fig. 6–Fig.8 as models to validate the above theoretical deduction. For the A_2+B_2 system, m = 2 and n =2:

$$N_C = \begin{cases} N_{A0} - N_{B0} - N_{B1} + N \\ N_{B0} - N_{A0} - N_{A1} + N \end{cases}$$



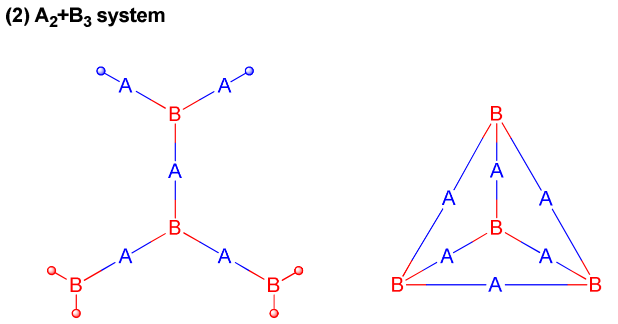
1a. Linear model
N_{A0}=2, N_{A1}=1
N_{B0}=2, N_{B1}=1
N_C=0

1b. Cyclic model
N_{A0}=3, N_{A1}=0
N_{B0}=3, N_{B1}=0
N_C=1

Fig. 6 Linear (1a) and cyclic (1b) structural model in the A_2+B_2 system

For the A_2+B_3 system, m = 2 and n = 3:

$$N_C=\begin{cases}N_{A0}-N_{B0}-N_{B1}-N_{B2}+N\\ 2\times N_{B0}+N_{B1}-N_{A0}-N_{A1}+N\end{cases}$$



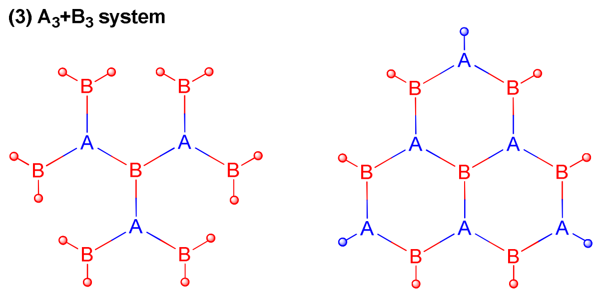
2a. Branched polymer
N_{A0}=3, N_{A1}=2
N_{B0}=2, N_{B1}=0,N_{B2}=2
N_C=0

2b. Multicyclic polymer
N_{A0}=6, N_{A1}=0
N_{B0}=4, N_{B1}=0,N_{B2}=0
N_C=3

Fig. 7 Branched (2a) and multicyclic (2b) structural model in the A_2+B_3 system

For the A_3+B_3 system, m = 3 and n =3,

$$N_C=\begin{cases}2\times N_{A0}+N_{A1}-N_{B0}-N_{B1}-N_{B2}+N\\ 2\times N_{B0}+N_{B1}-N_{A0}-N_{A1}-N_{A2}+N\end{cases}$$



3a. Branched model
N_{A0}=3, N_{A1}=0, N_{A2}=0
N_{B0}=1, N_{B1}=0, N_{B2}=6
N_C=0

3b. Multicyclic model
N_{A0}=3, N_{A1}=3, N_{A2}=0
N_{B0}=1, N_{B1}=6, N_{B2}=0
N_C=3

Fig. 8 Branched (3a) and multicyclic (3b) structural model in the A_3+B_3 system

Table 1 N_C value of the representative structural models

Structural model	N_C[a]	N_C[b]	N_C[c]
1a	0	0	0
1b	1	1	1
2a	0	0	0
2b	3	3	3
3a	0	0	0
3b	3	3	3

[a] The actual number of cyclic structures in the model polymer. [b] N_C values calculated according Eq. 3a. [c] N_C values calculated according Eq. 3b.

As shown in Table 3, all the N_C value in the models agrees well with their calculated value according to Eq. 3a and Eq. 3b, proving that the above mentioned theoretical derivation is correct. In the above models, the linear, branched, and terminal units can be combined together to form linear (1a), branched (2a and 3a), cyclic (1b) or multicyclic (2b and 3b) polymers. The Eq. 3a and Eq. 3b show a clear quantitative relationship between the structural units and cyclic structures and can be contributed to distinguish linear and branched polymers from the multicyclic polymers.

4 Evaluations of Cyclic Features

4.1 Determining the ANC

The average number of cyclic structures per macromolecule (ANC), i.e., the ratio of the intramolecular cyclic structures number (N_C) to the macromolecules number (N), is a key parameter to intuitively describe the cyclic features of polymers. According to Eq. 3a and 3b, the generalized expressions of the ANC for polymers derived from A_m+B_n step-growth polymerization can be obtained as follows.

$$ANC=\frac{N_C}{N}=\begin{cases}\sum_{i=0}^{m}(m-i-1)\times\frac{N_{Ai}}{N}-\sum_{j=0}^{n}\frac{N_{Bj}}{N}+1\\ \sum_{j=0}^{n}(n-j-1)\times\frac{N_{Bj}}{N}-\sum_{i=0}^{m}\frac{N_{Ai}}{N}+1\end{cases}\qquad(6)$$

The number-average molar mass (M_n) of the polymers derived from the A_m+B_n step-growth polymerization can be expressed as follows.

$$M_n=\sum_{i=0}^{m}M_{Ai}\times\frac{N_{Ai}}{N}+\sum_{j=0}^{n}M_{Bj}\times\frac{N_{Bj}}{N}\qquad(7)$$

where M_{Ai} and M_{Bj} are the molar mass of A_i and B_j units, respectively. If the content of each unit is determined, the ratio can be set as follows.

$$\frac{N_{A0}}{N}:\frac{N_{A1}}{N}:\cdots:\frac{N_{Ai}}{N}:\cdots:\frac{N_{A(m-1)}}{N}:\frac{N_{B0}}{N}:\frac{N_{B1}}{N}:\cdots:\frac{N_{Bj}}{N}:\cdots:\frac{N_{B(n-1)}}{N}$$
$$=k_{A0}:k_{A1}:\cdots:k_{Ai}:\cdots:k_{A(m-1)}:k_{B0}:k_{B1}:\cdots:k_{Bj}:\cdots:k_{B(n-1)}\qquad(8)$$

Thus, the expression of ANC can be obtained as the following.

$$ANC=\frac{N_C}{N}=\frac{M_n\times\left[\sum_{j=0}^{n}(n-j-1)\times k_{Bj}-\sum_{i=0}^{m}k_{Ai}\right]}{\sum_{i=0}^{m}M_{Ai}\times k_{Ai}+\sum_{j=0}^{n}M_{Bj}\times k_{Bj}}+1 \qquad (9)$$

In Eq. 9, the parameters of M_n, k_{Ai}, and k_{Bj} can be determined by SEC and NMR spectroscopy. Moreover, M_{Ai} and M_{Bj} are known; therefore, the ANC can be easily determined by the NMR and SEC analytics.

For the A_2+B_2 system, m = 2 and n = 2,

$$ANC=\frac{N_C}{N}=\frac{M_n\times(k_{B0}-k_{A0}-k_{A1})}{M_{A0}\times k_{A0}+M_{A1}\times k_{A1}+M_{B0}\times k_{B0}+M_{B1}\times k_{B1}}+1 \qquad (10a)$$

For the A_2+B_3 system, m = 2 and n = 3,

$$ANC=\frac{N_C}{N} \qquad (10b)$$
$$=\frac{M_n\times(2\times k_{B0}+k_{B1}-k_{A0}-k_{A1})}{M_{A0}\times k_{A0}+M_{A1}\times k_{A1}+M_{B0}\times k_{B0}+M_{B1}\times k_{B1}+M_{B2}\times k_{B2}}+1$$

For the A_3+B_3 system, m = 3 and n = 3,

$$ANC=\frac{N_C}{N} \qquad (10c)$$
$$=\frac{M_n\times(2\times k_{B0}+k_{B1}-k_{A0}-k_{A1}-k_{A2})}{M_{A0}\times k_{A0}+M_{A1}\times k_{A1}++M_{A2}\times k_{A2}+M_{B0}\times k_{B0}+M_{B1}\times k_{B1}+M_{B2}\times k_{B2}}+1$$

Moreover, the structural units can be determined by the degradation method[22] and 2D NMR,[23] and the M_n of cyclic polymers can be determined by size exclusion chromatography (SEC) or SEC-multi-angle light scattering detector (SEC-MALLS),[25] MALDI-ToF mass spectrometry,[4,26] or vapor pressure osmometry.[27]

4.2 Measuring the degree of intramolecular cyclization in A_2+B_3 system

Among numerous monomer pairs systems, the A_2+B_3 system received special attentions in the past two decades for being regarded as an alternative method of AB_m (m≥2) route.[28-34] Meanwhile, some multicyclic polymers, such as poly(ether sulfone)s,[7] poly (ether ketone),[35] and poly(ether esters)s[36] were also prepared in A_2+B_3 system. As shown in Fig. 7, the structural units in the A_2+B_3 system can form highly branched polymer and multicyclic polymer. The multicyclic polymers are vastly different from the hyperbranched polymers that possess large numbers of terminal groups. Until now, the degree of branching (DB) is widely used to describe the structural feature of hyperbranched polymers.[37-40] However, for describing the polymers in the A_2+B_3 system, it is not precise to distinguish the multicyclic polymers from the branched polymers if only the chain growth of the branched structures is considered. Thus, we defined the terminal index (TI) to describe the cyclic and branched dual features of the polymers in the A_2+B_3 system that the chain growth of the branched structures and the formation of cyclic structures are both considered.[17] However, the independent description of cyclic feature is also necessary. In this study, we define cyclic index (CI) as the ratio of terminal unit's number to dendritic unit's number to determine the extent of intramolecular cyclization. As derived above, the simplified expressions of N_C for the A_2+B_3 system are listed as follows.

$$N_C=\begin{cases}N_{A0}-N_{B0}-N_{B1}-N_{B2}+N\\2\times N_{B0}+N_{B1}-N_{A0}-N_{A1}+N\end{cases}$$

Combining the two equations together leads to Eq. 11,

$$\frac{N_{A1}}{N}+\frac{N_{B2}}{N}=\frac{N_{B0}}{N}-2\times\frac{N_C}{N}+2 \qquad (11)$$

According to the Eq. 11, the quantitative relationship between the total number of terminal units (N_{A1} and N_{B2}) and the total number of dendritic units (N_{B0}) is determined by the total number of cyclic numbers (N_C). Therefore, the ratio ((N_{A1}+N_{B2})/N_{B0}) can be viewed as the evaluation criteria of intramolecular cyclization.

$$CI=\frac{N_{A1}+N_{B2}}{N_{B0}}=1-2\times\frac{N_C}{N_{B0}}+2\times\frac{N}{N_{B0}} \qquad (12a)$$

Obviously, when no or less intramolecular cyclizations occur, the CI value is >1 or =1. In comparison to N_C/N_{B0}, the N/N_{B0} is negligible. So,

$$CI\approx 1-2\times\frac{N_C}{N_{B0}} \qquad (12b)$$

When the intramolecular cyclization occurs, the CI value decreases to <1. As shown in Fig. 9, the CI value of the acyclic branched polymer is 1.5, and as cyclic structure forms, the CI value decreases. One cyclic structure decreases CI value to 1, and two cyclic structures further decreases CI value to 0.5. The lower CI value represents the higher degree of intramolecular cyclization.

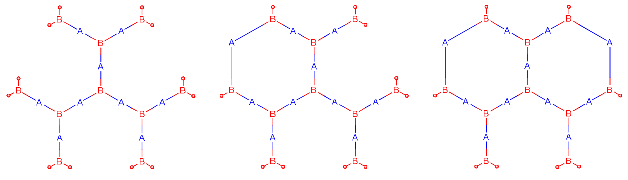
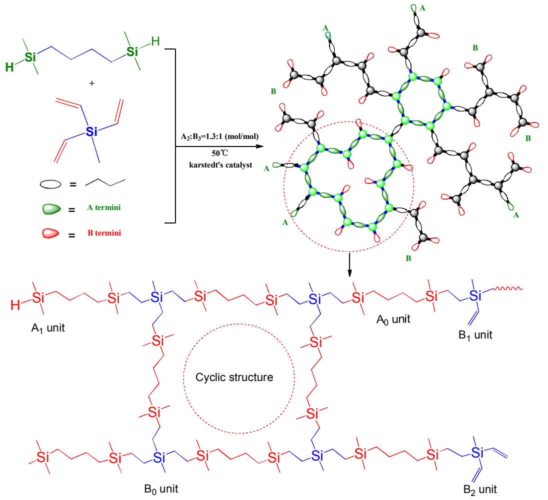

a. Branched polymer
CI=6/4=1.5
b. Branched and cyclic polymer
CI=4/4=1
c. Branched and dicyclic polymer
CI=2/4=0.5

Fig. 9 Structural models of the polymers with different CI values for the A_2+B_3 system

5 Experimental Validation via Highly Branched Polycarbosilanes

5.1 Preparation of highly branched polycarbosilanes via A_2+B_3 route

The highly branched polycarboslianes prepared via A_2+B_3 route was selected as the representative model polymer of the A_m+B_n step-growth polymerization, where A_2 and B_3 monomer were 1, 4-bis(dimethylsilyl)butane and trivinylmethylsilane, respectively. By tuning the feed ratio and terminating the reaction, the highly branched polycarbosilanes with two terminal groups, i.e., silicon-hydrogen bonds and vinyl groups, were prepared as shown in Scheme 1.



Scheme 1 The A_2+B_3 strategy to synthesize polycarbosilanes terminated with silicon-hydrogen bonds and vinyl groups

5.2 Compositional analysis of polycarbosilanes

As shown in Fig. 10, the prepared polycarbosilanes constitute of five component units, i.e., A_0, A_1, B_0, B_1, and B_2 units. All were identified by the quantitative ^{29}Si NMR spectrum as shown in Fig. 10, and the molar ratio of these component units was calculated by the following equation.

$$k_{B0}:k_{B1}:k_{B2}:k_{A0}:k_{A1} = \sum Si(I):\sum Si(II):\sum Si(III):\frac{\sum Si(IV)-\sum Si(V)}{2}:\sum Si(V)$$

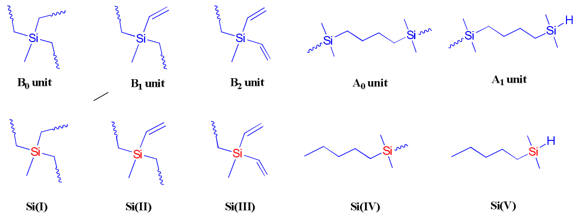


Fig. 10 Constituted units and silicon atoms with different chemical environments

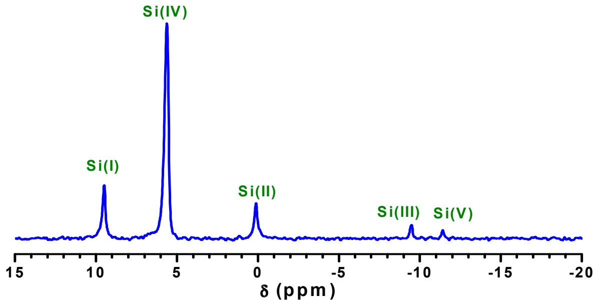


Fig. 11 Quantitative ^{29}Si NMR spectrum of polycarbosilanes terminated with both Si–H bonds and vinyl groups in $CDCl_3$

Table 3 Analysis results of macromolecular composition of polycarbosilanes

Sample	*Content of constituted units (%)*					M_A	M_B	M_n	*ANC*	*CI*
	k_{A0}	k_{A1}	k_{B0}	k_{B1}	k_{B2}					
Polycarbosilanes	52.9	2.0	24.2	16.6	4.3	174.4	124.3	4,200	3.74	0.26

5.3 Evaluating the topologic structure of polycarbosilanes

The polycarbosilanes was synthesized by the hydrosilylation between vinyl groups and silicon-hydrogen bonds; therefore, the molar mass of structural units was same as that of the monomers, i.e., the molar mass of A and B units were 174.4 g/mol and 124.3 g/mol, respectively. The molecular weight of polycarbosilanes was determined to be 4,200 g/mol by the SEC-MALLS measurement, and the ANC value was determined to be 3.74 according to Eq. (10b).

$$ANC = \frac{N_C}{N} = 3.74$$

The ANC of 3.74 demonstrates there are 3.74 cyclic structures existing in each polycarbosilane macromolecule. On the other hand, the CI value is calculated according to the Eq. (12a).

$$CI = \frac{N_{A1}+N_{B2}}{N_{B0}} = \frac{k_{A1}+k_{B2}}{k_{B0}} = 0.26$$

A CI value of 0.26, which is lower than 1, indicates that the intramolecular structures are existing in the polycarbosilanes. Obviously, the CI parameter and ANC value agree well with each other, confirming that the polycarbosilanes prepared by the A_2+B_3 method contain multicyclic structures and are not perfect hyperbranched polymers.

6 Conclusions

In summary, by the topological analyses of the macromolecular structures, we derived the general quantitative relationship between the structural units and cyclic structures for the step-growth polymerization of monomer pairs including A_2+B_2, A_2+B_3, A_3+B_3, and etc. Based on this relationship, the cyclic structures of these polymers from the dimonomer step-growth polymerization were investigated by analyzing the composition of the structural units. The contents of the cyclic structures were determined by the NMR and SEC analytics, and the cyclic features of the macromolecular structure in the A_2+B_3 system were evaluated independently by comparing the terminal to dendritic unit number. This study is helpful to understand the fine macromolecular structure and the relationship between properties and topological structures of high branched polymers.

Experimental Section

Materials. 1,4-dibromobutane (99%), chlorodimethylsilane (97%) and platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Karstedt's catalyst) were purchased from Alfa Aesar China. Trivinylmethylsilane (95%) were purchased from Gelest, Inc. (USA). All the above reagents were used as received without further treatment. Anhydrous hexane, toluene, and tetrahydrofuran (THF) were freshly distilled under reflux using sodium/benzophenone.

Characterization. Nuclear Magnetic Resonance (NMR) measurements were carried on a Bruker Avance 500 spectrometer (Bruker BioSpin, Switzerland) operating at 50.7 MHz in CDCl3. Chemical shifts are referenced to tetramethylsilane (TMS). Fourier transform infrared spectroscopy (FT-IR) measurements were conducted on a FT-IR spectrophotometer (Perkin-Elmer, USA). Size Exclusion Chromatography (SEC) measurements were conducted on a system equipped a Waters 515 pump, an autosampler and two MZ gel columns (10^3 Å and 10^4 Å) with a flow rate of 0.5 mL/min in THF (HPLC grade) at 25 ^{o}C. Detectors were including differential refractometer (Optilab rEX, Wyatt) and multi-angle light scattering detector (MALLS) equipped with a 632.8 nm He–Ne laser (DAWN EOS, Wyatt). The refractive index increments of polymers in THF were measured at 25 ^{o}C using an Optilab rEX differential refractometer. ASTRA software (Version 5.1.3.0) was utilized for acquisition and analysis of data.

Synthesis of Polycarbosilanes via A_2+B_3 Approach. The A_2 monomer of 1, 4-bis(dimethylsilyl)butane was synthesized in our laboratory.[16] Under an insert argon atmosphere, a 500mL flame-dried flask equipped with thermometer, stir bar and condenser was charged with magnesium powder (0.73 g, 30 mmol), iodine crystal (1mg) and 100 mL anhydrous THF at ambient temperature. Then, the 1,4-bis(dimethylsilyl)butane (4.36 g, 20 mmol) was added to the flask dropwise under ultrasonic condition. The starting of reaction was indicated by the decolorization of iodine and the reflux of THF. When the addition was completed, the mixture was stirred for 1h under ultrasonic at 60 °C, and then the mixture was cooled to 5 °C. The chlorodimethylsilane (2.15 g, 22 mmol) in 50 mL THF was added to the mixture dropwise. After the filtration and rotary evaporation, the crude product was purified by silica column chromatography using hexane as an elute, yielding the 1,4-bis(dimethylsilyl)butane as colourless liquid (2.61 g, 75% yield).

^{1}H NMR (500 MHz, $CDCl_3$, δ): 0.06 (12H, $-Si(CH_3)_2-H$), 0.66 (4H, $Si-CH_2CH_2CH_2CH_2-Si$), 1.45 (4H, $-CH_2CH_2CH_2CH_2-$), 3.92 (2H, $-Si(CH_3)_2-H$). ^{13}C NMR ($CDCl_3$, ppm): -4.41 (4C, $-Si(CH_3)_2-H$), 14.22 (2C, $Si-CH_2CH_2CH_2CH_2-Si$), 28.22 (2C, $-CH_2CH_2CH_2CH_2-$). ^{29}Si NMR ($CDCl_3$, ppm): -13.24. FT-IR (KBr, cm^{-1}): 2112 (ν Si-H), 1250 (ν $Si-CH_3$), 836 (ν $Si-CH_2-$).

For the synthesis of polycarbosilanes, a dried flask was charged with B_3 monomer of trivinylmethylsilane (TVMS, 0.262 g, 2 mmol), 2 mg of karstedt's catalyst, and 15 mL of toluene. At 50°C, A_2 monomer of 1, 4-bis(dimethylsilyl)butane (0.468 g, 2.6 mmol) was added into the solution by three-batch addition with an interval of 30 min. In detail, at first, 0.156 g of A_2 monomer was added by a syringe, after 30 min another 0.156 g of reactant was added. And after 30 min the last 0.156 g of reactant was added. The reaction mixture was stirred overnight at 50°C and monitored by FTIR spectroscopy. Before the gel point, the reaction was stopped and the solvent was removed by rotary evaporation (40 mbar, 40 °C) yielding colorless liquids. The crude product was soluble in 5mL of diethyl ether and precipitated into 50 ml of methanol for three times. Then the precipitate was dried in vacuum oven for 2 days (10 mbar, 60°C). The soluble product polymers was obtained as a colourless viscous liquid (74.2% yield). M_n=4200, M_w/M_n=3.87.

^{1}H NMR (500 MHz, $CDCl_3$, δ): (-0.44)-0.22 ($-Si-C\mathit{H}_3$), 0.27-0.43 ($Si-CH_2-CH_2-Si$), 0.43-0.65 ($Si-CH_2CH_2CH_2CH_2-Si$), 1.13-1.41 ($-CH_2-CH_2-CH_2-CH_2-$), 3.81-3.88(Si-H), 5.61-5.78 ($-C\mathit{H}=CH_2$), 5.94-6.24 ($-CH=C\mathit{H}_2$). ^{13}C NMR ($CDCl_3$, ppm): -9.05, -6.40 ($Si-\mathit{C}H_3$), 1.95, 2.68, 4.63 ($Si-\mathit{C}H_2-\mathit{C}H_2-Si$), 11.98 ($-\mathit{C}H_2-CH_2-CH_2-\mathit{C}H_2-$), 25.43, 27.16 ($-CH_2-\mathit{C}H_2-\mathit{C}H_2-CH_2-$), 129.38, 130.24 ($-CH=\mathit{C}H_2$), 134.38, 135.47 ($-\mathit{C}H=CH_2$). ^{29}Si NMR ($CDCl_3$, δ): 9.1-10.1 $[(CH_3-)Si(-C_2H_4-)_3]$, 5.2-6.3 $[(-C_4H_8-)(CH_3-)_2Si-C_2H_4-]$, 0.1 $[(CH_3-)(CH_2=CH-)Si(-C_2H_4-)_2]$, -9.4 $[(CH_3-)(CH_2=CH-)_2Si-C_2H_4-]$, -11.4 $[(-C_4H_8-)(CH_3-)_2Si-H]$. FT-IR (KBr, cm^{-1}): 3047 ($-CH=CH_2$), 2111 (Si-H), 1408, 1248 ($Si-CH_3$), 832 (Si-C).

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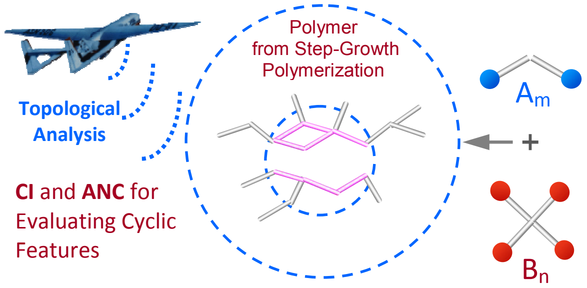
Table of Contents Graphic:

Topological Analysis and Intramolecular Cyclic Feature Evaluation of Polymers Derived from A_m+B_n Step-Growth Polymerization

Heng Chen , Shan Zhang, and Jie Kong*

A table of contents entry:



We presented new and convenient evaluation strategies for intramolecular cyclic feature of polymers derived from A_m+B_n step-growth polymerization.