# Terminal Index: A New Way for Precise Description of Topologic Structure of Highly Branched Polymers Derived from $A_2 + B_3$ Stepwise Polymerization

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Ⓢ Supporting Information

ABSTRACT: Terminal index (TI) was presented as a new characteristic parameter for quantitative description of branched and cyclic topology of highly branched soluble polymers derived from $A_2 + B_3$ stepwise polymerization. TI is defined as the ratio of terminal units of an $A_2 + B_3$ type highly branched polymer to those in its perfect hyperbranched counterpart. TI is concisely represented as $T/(D + L)$, which can be conveniently calculated from a quantitative NMR spectrum. The model of soluble $A_2 + B_3$ type polymers is suggested as an intermediate between multicyclic polymers and perfect hyperbranched polymers. The TI ranges between 0 and 1 where a higher TI indicates a perfect hyperbranched topology while a low TI indicates a multicyclic structure. The analysis of soluble $A_2 + B_3$ type polyesters and polycarbosilanes as model polymers demonstrates that TI as a more precise parameter, along with degree of branching, can be generally applied to understand the fine topology of highly branched polymers derived from $A_2 + B_3$ polymerization.
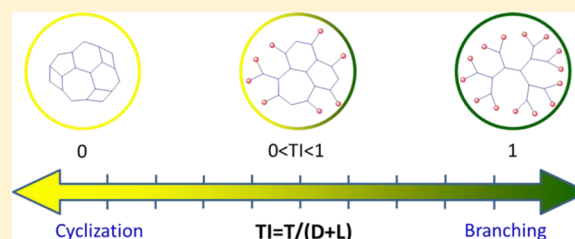
■ INTRODUCTION

Similar to dendrimers, hyperbranched polymers have received considerable attention because of their special features, such as a compact intrinsic structure, numerous functional terminal groups, low viscosity, and high solubility. Normally, hyperbranched polymers can be prepared by a so-called one-pot approach, typically as a stepwise polymerization of AB_n ($n \geq 2$) monomers, which makes it much more suitable for industrial application than dendrimers. For AB_n monomers with latent reactive groups, the inconvenience of synthesis and storage limits their application. So the highly branched polymers, typically derived from $A_2 + B_n$ stepwise polymerization, have emerged as an alternative of hyperbranched polymers in the past two decades.[1,2]

The $A_2 + B_3$ polymerization is a well-known polymerization with a tendency to be cross-linked. By controlling the concentration of monomers and feed ratio of A/B group, or terminating polymerization before gelation point, the gelation can be effectively delayed and avoided. Furthermore, the asymmetric functional monomer strategy, such as $AA^* + B^*B_2$ or $A_2 + CB_2$, was also addressed to avoid gelation to some degree.[3−6] Accordingly, the obtained soluble product was normally regarded as highly branched polymer in order to distinguish from hyperbranched polymer from AB_n monomers. As early as 1929, Kienle and Hovey noticed the branched polymers transiently formed from the polymerization of phthalic anhydride and glycerol.[7] Until the late 1990s, the $A_2 + B_3$ type highly branched polymers had received close attention due to rapid development of hyperbranched polymers. The commercial availability of numerous A_2 and B_3

monomers makes it emerge as an alternative approach to the classic AB_n strategy.[8] Since Russo et al. reported the preparation of highly branched aromatic polyamides using difunctional amines and trifunctional acids,[9,10] various highly branched polymers had been prepared, such as aromatic polyamides,[11,12] aliphatic polyethers,[13−15] polyimides,[16−18] polysulfone-amines,[19] poly(ether sulfone)s,[20,21] polyurethanes,[22,23] aliphatic polyesters,[24,25] polycarbosiloxanes,[26,27] etc.[28−32]

Besides molecular weight and its distribution, R_g/R_h,[33] and the Mark−Houwink−Sakurada equation and contraction factor, $g' = [\eta]_{hyperbranched}/[\eta]_{linear}$,[34] degree of branching (DB) was often employed to quantitatively describe the regularity of hyperbranched polymers. The expressions in eq 1, defined by Fréchet[35] and Frey,[36,37] are most used to calculate the value of DB. For the hyperbranched polymers from the AB_n route, the expression of DB in eq 1 is an effective way to describe the topological structure of hyperbranched polymers, where D, L, and T refer to the fraction of dendritic, linear, and terminal units, respectively. For hyperbranched polymers with long linear chains between branching points,[38,39] Long and his colleagues deduced another effective expression of DB as presented in eq 1c.[40] All these works provided a basis for the design and synthesis of functional hyperbranched polymers and pushed their thriving development over past decades.

$$\begin{cases} DB_{Frey} = \dfrac{2D}{2D + L} & (1a) \\[2ex] DB_{Frechet} = \dfrac{D + T}{D + T + L} & (1b) \\[2ex] DB_{Long} = \dfrac{D + T}{D + L + T + n} & (1c) \end{cases}$$

For highly branched polymers derived from $A_2 + B_3$ polymerization, it is a little different. In a stepwise polymerization, the intramolecular cyclization was usually companied with chain growth according to the classic Flory−Stockmayer statistical theory.[41] The intramolecular cyclization can be negligible for AB_n type hyperbranched polymers. However, for the soluble $A_2 + B_3$ type highly branched polymers, it cannot be neglected because of the existence of multicyclic units. With the aid of MALDI-TOF mass spectrum, Kricheldorf and co-workers proved the formation of bicyclics or multicyclics in almost all cases of $A_2 + B_3$ type highly branched poly(ether ketone)s,[42] polyethers,[43] and poly(ether ester)s.[44] In our previous work, the quantitative determination of intermolecular cyclics in $A_2 + B_3$ type highly branched polycarbosilanes was realized by a combination of NMR and SEC analytics.[45] For the highly branched polymers derived from $A_2 + B_3$ polymerization, the direct application of DB to describe their topological structures is still an open question.[46]

For highly branched polymers with intramolecular cyclics, the pseudodendritic units (D_c) in Figure 1 cannot be
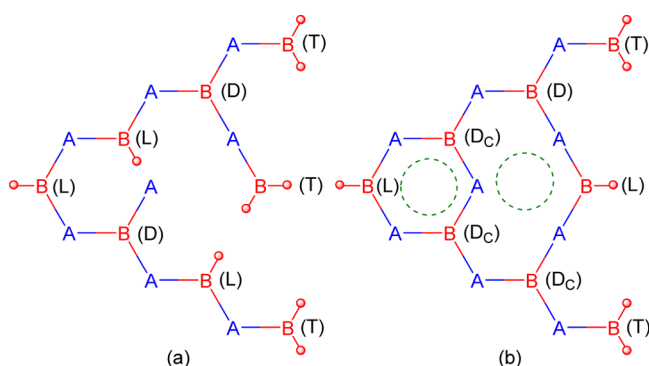

Figure 1. Possible topology of $A_2 + B_3$ type highly branched polymer: (a) acyclic and branched model; (b) multicyclic and branched model.

distinguished from the true dendritic units (D) on the NMR spectrum. When calculating DB according to eq 1, D_c is considered as a dendritic unit and leads to a deviation. In another word, the usage of DB is sensitive to the intramolecular cyclic structure. As shown in Figure 1, the model polymer *b* possesses more pseudodendritic units and the conclusion of higher value of DB than the model polymer *a* can be derived if eq 1 is directly employed. However, the fact is that the polymer *b* is close to a branched structure with multicyclics rather than a hyperbranched structure.

In this contribution, we present a new parameter, named as terminal index (TI), to quantitatively describe the topological structure of soluble $A_2 + B_3$ type highly branched polymers with intramolecular cyclization. The TI is derived as the ratio of terminal units of a soluble $A_2 + B_3$ type polymer to these units in its perfect hyperbranched counterpart. Then, the theoretical derivation and quantitative NMR analyses for model highly

branched polymers, i.e., polyesters and polycarbosilanes are presented to understand the fine topological structures. Since DB mostly reveals the tendency of a formation of branched or linear units, as an addition, TI is suggested to conveniently determine the tendency of branching (to increase terminals) or cyclization (to decrease terminals) for the soluble $A_2 + B_3$ type highly branched polymers.

■ EXPERIMENTAL SECTION

Materials. 1,8-Dibromooctane (98%), dimethylchlorosilane (97%), magnesium powder, platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Karstedt's catalyst), 1,4-cyclohexanedicarboxylic acid (cis + trans, 98%), and 1,1,1-tris(hydroxymethyl)ethane (97%) were purchased from Alfa Aesar China. Trivinylmethylsilane (95%) was purchased from Gelest, Inc. (USA). *p*-Toluenesulfonic acid (PTSA, 99%) was purchased from Acros Organics. The above reagents were used as received without further treatment. Anhydrous hexane, toluene, and THF were freshly distilled under reflux using sodium/benzophenone.

Characterization. The ^1H NMR and ^{29}Si NMR measurement was conducted on a Bruker Avance 600 spectrometer (Bruker BioSpin, Switzerland) operating at 50.7 MHz in $CDCl_3$. The chemical shifts were referenced to the reference of tetramethylsilane (TMS). The quantitative ^{13}C NMR analyses were carried out on Bruker Avance 500 spectrometers (Bruker BioSpin, Switzerland) and recorded using an inverse gated decoupling mode with a 2 s pulse delay, with an addition of chromium acetylacetonate (8 mg). The multiple-bond delay was adjusted to a coupling constant of 5 Hz. The data were collected in an 8192 × 256 matrix with 8 transients per t1 increment. The recycle period was 1.5 s. Sine-bell window functions were applied before Fourier transformation in a 2048 × 1024 matrix. Fourier transform infrared spectroscopy (FT-IR) measurement was carried on a NICOLET iS10 IR spectrometer. Triple-detection size exclusion chromatography (triple-SEC) measurement was conducted on a SEC system equipped a Waters 515 pump (Waters), 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 °C. The three detectors were differential refractometer (OptilabrEX, Wyatt), multiangle light scattering detector (MALS) equipped with a 632.8 nm He−Ne laser (DAWN EOS, Wyatt), and Viscometer (ViscoStar, Wyatt). The refractive index increments of model polymers in THF were measured at 25 °C using a differential refractometer (Optilab rEX, Wyatt). For acquisition and analysis of data, the ASTRA software (Version 5.1.3.0) was employed.

Synthesis Monomers and Polymers. *Synthesis of 1,8-Bis(dimethylsilyl)octane.* Under an argon atmosphere, a 500 mL dried flask was charged with magnesium powder (1.44 g, 60 mmol), iodine crystal (1 mg), and 100 mL of anhydrous THF. 1, 8-Dibromooctane (5.55 g, 20 mmol) in 40 mL of THF was added dropwise to the flask under ultrasonic irradiation. The decolorization of iodine indicated the starting of the reaction. After the addition was completed, the mixture was stirred for 1 h under ultrasonic irradiation at 60 °C and then cooled to 5 °C without ultrasonic irradiation. A solution of chlorodimethylsilane (4.39 g, 45 mmol) in 40 mL of anhydrous THF was added dropwise to the mixture. After that, the reaction mixture was heated to 60 °C and stirred for another 2 h. Upon the completion of reaction, the THF was evaporated and the residue was combined with hexane. After the filtration and

concentration, the crude product was purified by silica column chromatography (hexane as eluent) to yield 1,8-bis-(dimethylsilyl)octane as colorless liquid (3.64 g, 79% yield). ^{1}H NMR (600 MHz, CDCl$_3$, δ): −0.02 (12H, −Si(CH_3)$_2$−H), 0.52 (4H, Si−CH_2−(CH$_2$)$_6$−CH_2−Si), 1.24 (12H, Si−CH$_2$−(CH_2)$_6$−CH$_2$−Si), 3.77 (2H, −Si(CH$_3$)$_2$-H). ^{13}C NMR (500 MHz, CDCl$_3$, δ): −4.97 (4C, −Si(CH$_3$)$_2$−H), 13.70 (2C, Si−CH$_2$−(CH$_2$)$_6$−CH$_2$−Si), 23.88, 29.02, 32.75 (6C, Si−CH$_2$−(CH$_2$)$_6$−CH$_2$−Si). ^{29}Si NMR (600 MHz, CDCl$_3$, δ): −12.95 (−Si(CH$_3$)$_2$−H). FT-IR (KBr, cm^{-1}): 2112 (ν Si−H), 1250 (ν Si−CH$_3$), 836 (ν Si−CH$_2$−).

Preparation of Highly Branched Polyesters (HPE). Highly branched polyesters were synthesized according to a reported procedure with some modification.[47] In a typical synthesis of HPE-1, a dried flask was charged with 1,1,1-tri-(hydroxymethyl)ethane (1.239 g, 10 mmol), 1,4-cyclohexane-dicarboxylic acid (1.757 g, 10 mmol), PTSA (87 mg, 0.5 mmol), and THF (10 mL). An antisplash adapter with two holes (4 mm in diameter) on the bottom was equipped between the flask and a condenser, which played the role of Soxhlet extractor. Ten grams of anhydrous 4 Å molecular sieves were precharged in the adapter. After purging with argon gas, the mixture was heated to keep THF refluxing and stirred overnight. The refluxed THF was returned to the flask through molecular sieves to remove water. The crude product was soluble in THF (5 mL) and precipitated into diethyl ether (50 mL) three times. Then the precipitate was dried in a vacuum oven for 2 days (10 mbar, 60 °C). The soluble product polymers were obtained as white solids (64.3% yield). ^{1}H NMR (600 MHz, CDCl$_3$, δ): 0.80−1.40(C−CH_3), 1.45−3.20 (−cyclohexyl−), 3.30−3.90 (−C−CH_2OH), 3.90−4.55 (C−CH_2−OOC−). 8.18 (−COOH). ^{13}C NMR (500 MHz, DMF-d_7, δ): 16.73 (C−CH$_3$), 26.17, 28.35, 40.79, 42.59 (−cyclo-hexyl−), 39.13 ((−OOC)$_3$−C−CH$_3$), 40.34 ((−OOC)$_2$−C(−CH$_2$OH)−CH$_3$), 41.38 (−OOC−C(−CH$_2$OH)$_2$−CH$_3$), 64.22, 64.83 (−C−CH$_2$OH), 65.5−66.8 (−C−CH$_2$OOC−), 174.4−175.3 (−cyclohexyl−COOC−), 176.46, 176.79, (−cy-clohexyl−COOH). FT-IR (KBr, cm^{-1}): 3461 (ν −OH), 1731 (ν −C=O).

Synthesis of Highly Branched Polycarbosilanes with Vinyl Terminal Groups (HP-oc-Vi). A dried flask was charged with B$_3$ monomer of trivinylmethylsilane (0.262 g, 2 mmol), Karstedt's catalyst (2.0 mg), and toluene (30 mL). At 50 °C, the A$_2$ monomer of 1,8-bis(dimethylsilyl)octane (0.461 g, 2.0 mmol) was added into the solution one time. The reaction mixture was stirred overnight at 50 °C overnight. Then the solvent was removed by rotary evaporation yielding colorless liquid. The crude product was soluble in 5 mL of diethyl ether and precipitated into 50 mL of methanol three times. Then the precipitate was dried in a vacuum oven for 2 days (10 mbar, 60 °C). The soluble product polymers were obtained as colorless, viscous liquids (70.6% yield). ^{1}H NMR (600 MHz, CDCl$_3$, δ): (−0.09)−0.24 (−Si−CH_3), 0.34−0.48 (Si−CH_2−CH$_2$−Si), 0.42−0.70 (Si−CH_2−(CH$_2$)$_6$−CH$_2$−Si), 1.15−1.85 Si−CH$_2$−(CH_2)$_6$−CH$_2$−Si), 5.65−5.90 (−CH=CH$_2$), 5.95−6.40 (−CH=CH_2). ^{13}C NMR (500 MHz, CDCl$_3$, δ): −3.87 (Si−CH$_3$), 4.66, 5.26, 7.18 (Si−CH$_2$−CH$_2$−Si), 14.75 (Si−CH$_2$−(CH$_2$)$_6$−CH$_2$−Si), 23.96, 29.53, 33.82 (Si−CH$_2$−(CH$_2$)$_6$−CH$_2$−Si), 131.91, 132.77 (−CH=CH$_2$), 134.38, 135.47 (−CH=CH$_2$). ^{29}Si NMR (600 MHz, CDCl$_3$, δ): 8.06 [(CH$_3$-)Si(−C$_2$H$_4$-)$_3$], 4.2 [(−C$_8$H$_{16}$−)(CH$_3$−)$_2$$Si$−C$_2H_4$−], −1.31 [(CH$_3$−)(CH$_2$=CH−)$Si$(−C$_2H_4$−)$_2$], −10.91

[(CH$_3$−)(CH$_2$=CH−)$_2$$Si$−C$_2H_4$−]. FT-IR (KBr, cm^{-1}): 3047 (ν −CH=CH$_2$), 1248 (ν Si−CH$_3$), 810 (ν Si−C).

Preparation of Highly Branched Polycarbosilanes with −SiH Terminal Groups (HP-oc-SiH). The preparation proce-dure of HP-oc-SiH-1 was similar to HP-oc-Vi-1, but the feed amounts were changed: 2.0 mmol of 1,8-bis(dimethylsilyl)-octane, 1.0 mmol of trivinylmethylsilane, 35 mL of toluene, and 2.0 mg of catalyst. HP-But-SiH-1 was obtained as a colorless, viscous liquid (68.4% yield). ^{1}H NMR (600 MHz, CDCl$_3$, δ): (−0.10)−0.22 (−Si−CH$_3$), 0.33−0.48 (Si−CH_2−CH$_2$−Si), 0.46−0.72 (Si−CH_2−(CH$_2$)$_6$−CH$_2$−Si), 1.10−1.82 Si−CH$_2$−(CH_2)$_6$−CH$_2$−Si), 3.85−3.95(Si−H). ^{13}C NMR (CDCl$_3$, ppm): −3.87 (Si−CH$_3$), 4.66, 5.26, 7.18 (Si−CH$_2$−CH$_2$−Si), 14.75 (Si−CH$_2$−(CH$_2$)$_6$−CH$_2$−Si), 23.96, 29.53, 33.82 (Si−CH$_2$−(CH$_2$)$_6$−CH$_2$−Si), 131.91, 132.77 (−CH=CH$_2$), 134.38, 135.47 (−CH=CH$_2$). ^{13}C NMR (500 MHz, CDCl$_3$, δ): −3.86 (Si−CH$_3$), 4.56, 7.24 (Si−CH$_2$−CH$_2$−Si), 14.74 (Si−CH$_2$−(CH$_2$)$_6$−CH$_2$−Si), 23.98, 29.39, 33.81 (Si−CH$_2$−(CH$_2$)$_6$−CH$_2$−Si), 131.91, 132.77 (−CH=CH$_2$), 134.38, 135.47 (−CH=CH$_2$). ^{29}Si NMR (600 MHz, CDCl$_3$, δ): −12.90 [(−C$_8$H$_{16}$−)(CH$_3$−)$_2$$Si$−H], 4.20 [(−C$_8H_{16}$−)-(CH$_3$−)$_2$$Si$−C$_2H_4$−], 7.80 [(CH$_3$−)$Si$(−C$_2H_4$−)$_3$]. FT-IR (KBr, cm^{-1}): 2111 (Si−H), 1248 (Si−CH$_3$), 832 (Si−C).

RESULTS AND DISCUSSION

Theoretical Deduction of Terminal Index. In order to introduce the definition of TI, the quantitative relationship between terminal units, and dendritic units, and cyclic units was derived based on the analysis of topological structure in A$_2$ + B$_3$ type highly branched polymer with intramolecular cyclization. As shown in Figure 2, the highly branched polymer can be

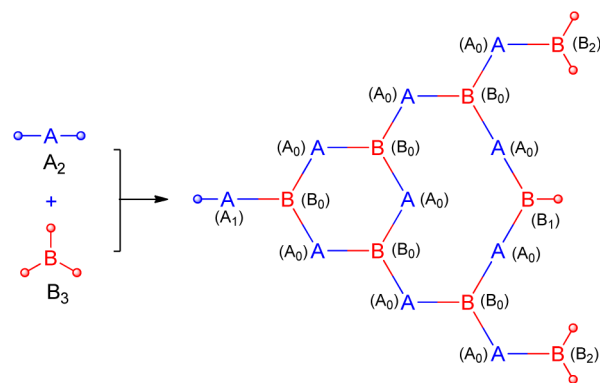**Figure 2.** Topological structure of A$_2$ + B$_3$ type highly branched polymer with intramolecular cyclization.

regarded as a combination of A and B units linked together with covalent bonds, where A units are derived from A$_2$ monomers and B units are derived from B$_3$ monomers. According to the number of unreacted A groups, A units are further divided into A$_0$ and A$_1$, where the A$_0$ unit possesses no unreacted A group and the A$_1$ unit possesses one unreacted A group. Similarly, B units are subdivided into B$_0$, B$_1$, and B$_2$, where B$_0$, B$_1$, and B$_2$ can be regarded as dendritic units, linear units, and terminal units, respectively.

In a typical stepwise polymerization in Figure 3, there exists a competition between chain growth and intramolecular cyclization.[48] Both chain growth and intramolecular cyclization lead to a formation of new covalent bond between the functional groups of A and B. In the chain propagation stage,
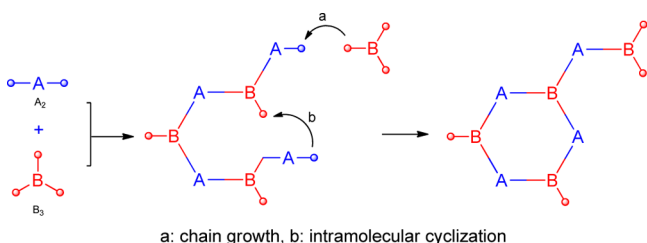
a: chain growth, b: intramolecular cyclization

Figure 3. Schematic of chain growth and intramolecular cyclization in stepwise polymerization of A_2 and B_3 monomers.

the linking of one monomer or an intermediate with another one can form one covalent bond by the reaction between the A group and the B group. So, the number of new covalent bonds (N_{CB}) formed can be expressed as a function of the number of component units (A units and B units) and the number of polymers (N) formed as presented in eq 2a (without intramolecular cyclization).

$$N_{CB} = N_A + N_B - N \qquad (2a)$$

where N_A and N_B refer to the number of A units and B units in all macromolecules. When intramolecular cyclization is considered, the N_{CB} can be expressed as follows.

$$N_{CB} = N_A + N_B - N + N_C \qquad (2b)$$

where N_C refers to the number of intramolecular cyclizations. Normally, one covalent bond links one A unit and one B unit. So the total number of bonds is equal to that of the bonds linked with all A units. Similarly, it is also equal to the number of the bonds linked with all B units. Eqs 3, 4, and 5 also reveal the relationship of component units mentioned above.

$$N_{CB} = 2N_{A0} + N_{A1} = 3N_{B0} + 2N_{B1} + N_{B2} \qquad (3)$$

$$\begin{cases} N_A = N_{A0} + N_{A1} & (4a) \\ N_B = N_{B0} + N_{B1} + N_{B2} & (4b) \end{cases}$$

$$\begin{cases} 2N_{A0} + N_{A1} = N_{A0} + N_{A1} + N_{B0} + N_{B1} & (5a) \\ \qquad\qquad + N_{B2} - N + N_C & \\ 3N_{B0} + 2N_{B1} + N_{B2} & (5b) \\ \quad = N_{A0} + N_{A1} + N_{B0} + N_{B1} + N_{B2} & \\ \quad - N + N_C & \end{cases}$$

Since A units are composed of A_0 units and A_1 units and B units are composed of B_0, B_1, and B_2 units, we can deduce eq 5 by a combination of eq 3 and eq 4. Further, if N_T is defined as the total number of terminal units including N_{A1} and N_{B2}, then eq 6 can be obtained from a sum of eq 5a and eq 5b. It should be

pointed out, the terminal units are different from terminal groups.

$$N_T = N_{A1} + N_{B2} = N_{B0} - 2N_C + 2N \qquad (6)$$

Equation 6 defines the basic relationship among terminal units, dendritic units, and intramolecular cyclics in $A_2 + B_3$ type highly branched polymers with intramolecular cyclization. As a comparsion, for the highly branched counterparts without intramolecular cyclics, the total number of terminal units (N_{TH}) is also related to N_{B2} and N_{A1} (in eq 7). Further, for the perfect highly branched counterpart without intramolecular cyclics, the maximum number of possible terminal units (N_{TD}) is related to N_{B2}, N_{A1}, and N_{B1} as shown in eq 8 and Figure S1 (Supporting Information). It should be pointed out that the terminal units are different from terminal groups. So the N_{TD} can be expressed as eq 8.

$$N_{TH} = N_{A1} + N_{B2} = N_{B0} + 2N \qquad (7)$$

$$N_{TD} = (N_{A1} + N_{B2}) + N_{B1} = N_{B0} + 2N + N_{B1} \qquad (8)$$

As presented in eq 6, the total number of terminal units (N_T) depends on the number of dendritic units (N_{B0}) and intramolecular cyclics (N_C). The conversion of B_3 monomers into dendritic units or the intramolecular cyclic units (D_C) determines the number of terminal units. The former is helpful to increasing regular branched structure while the latter, in fact, decreases terminal units through intramolecular cyclization. In another words, the formation of dendritic units is helpful to yielding a perfect branched polymer (Figure 4a) while intramolecular cyclization tends to generate a multicyclic polymer (Figure 4c). Normally, the topology of $A_2 + B_3$ type highly branched polymer should be an intermediate between perfect branched and multicyclic as presented in Figure 4b. So a precise characteristic parameter needed to be defined to describe the fine topological structure of highly branched polymers. Herein, a new concept of the terminal index (TI) is defined as the ratio of the terminals units in an $A_2 + B_3$ type highly branched polymer with intramolecular cyclization (N_T) to these in its perfect hyperbranched counterpart without any intramolecular cyclics (N_{TD}). The expression of TI in eq 9a can be deduced from a combination of eq 6 and eq 8.

$$TI = \frac{N_T}{N_{TD}} = \frac{N_{A1} + N_{B2}}{N_{B0} + 2N + N_{B1}} \qquad (9a)$$

$$TI \approx \frac{N_{A1} + N_{B2}}{N_{B0} + N_{B1}} = \frac{k_{A1} + k_{B2}}{k_{B0} + k_{B1}} = \frac{T_A + T_B}{D + L} = \frac{T}{D + L} \qquad (9b)$$

When the degree of polymerization is high, the expression of TI can be simplified as eq 9b, where k_{A1}, k_{B0}, k_{B1}, and k_{B2} refer to the mole fraction of N_{A1}, N_{B0}, N_{B1}, and N_{B2}, respectively, which can be calculated from quantitative NMR spectra. Normally,
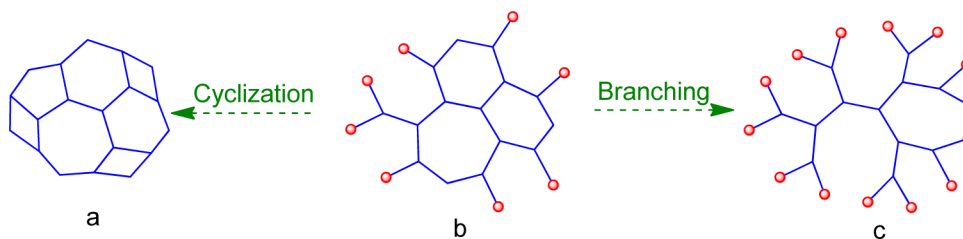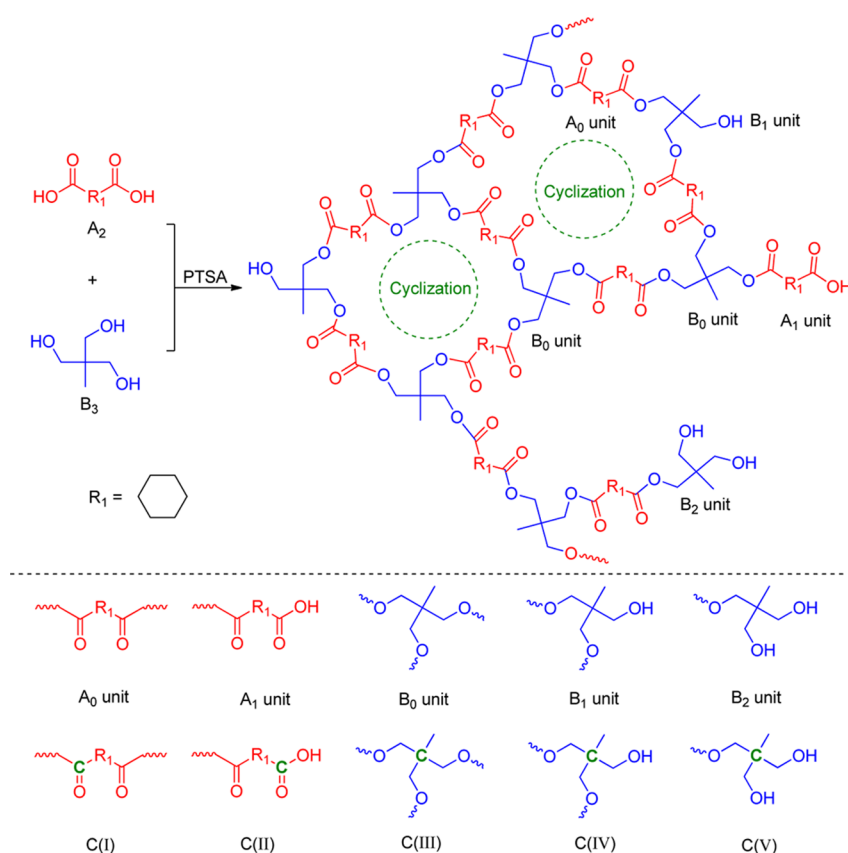

Figure 4. (a) Multicyclic polymer; (b) highly branched polymer; (c) perfect hyperbranched polymer.

Scheme 1. Synthesis Route of the Highly Branched Polyester and Component Units Accompanied with Characteristic Carbon Atoms

the TI value of an A_2 + B_3 type highly branched polymer should be in the range from 0 to 1. The TI value of a perfect branched polymer is equal to 1 while the TI value is close to 0 for a multicyclic polymer even without any terminal units.

Experimental Validation of Terminal Index. Similar to DB, dendritic, linear, and terminal units of polymers must be identified for the determination of TI value. Normally, NMR spectroscopy is a most effective tool. Even for some polymer with overlapped signals in the 1D NMR spectrum, the 2D NMR should be a good choice especially for some complicated hyperbranched polymers synthesized from self-condensation vinyl polymerization (SCVP) or self-condensation ring-opening polymerization (SCROP).[49] Here, as an experimental validation, we report the determination of TI for A_2 + B_3 type highly branched polymers using a quantitative 1D NMR. To ensure the generalization, the aliphatic polyester and polycarbosilane were chosen, which are considered as the representative models for organic polymers[24,25,47,48] and hybrid polymers,[26,27,50] respectivey. Accordingly, two quantitative NMR methods, i.e., ^{13}C NMR with the assistance of relaxation reagent and ^{29}Si NMR, were employed. The detailed information for synthesis and characterization of polymers is presented in the Supporting Information.

Preparation of Model Polymers. As shown in Scheme 1, the highly branched polyesters were synthesized from A_2 monomer, 1,4-cyclohexanedicarboxylic acid containing a rigid cyclohexyl unit, and B_3 monomer, 1,1,1-tris(hydroxymethyl)-ethane. Similarly, the highly branched polycarbosilanes in Scheme 2 were prepared from the A_2 monomer, 1,8-bis(dimethylsilyl)octane containing flexible interval units

(Figures S2−4 in the Supporting Information), and B_3 monomer, trivinylmethylsilane. All the polymers were prepared in a dilute solution with a nonstoichiometric feed ratio of A_2 and B_3 monomers (1:1 or 2:1). By tuning the concentration of solution, polymers with various molecular weights were obtained. The polyesters (HPE) were obtained as white solids (Figure S5−7 in the Supporting Information), and the polycarbosilanes (HP-oc-Vi and HP-oc-SiH) were received as colorless, viscous liquids (Figure S7−10 in the Supporting Information).

The molecular structure parameters of model polymers determined by triple SEC-MALLS are summarized in Table 1. The weight-average molecular weights ($M_{w,SEC}$) of polyesters and polycarbosilanes are in the range from 3,900 to 86,200 g/mol, and the polydispersity index (PDI) is determined to be 1.39−4.64. The parameter of R_g/R_h or the Mark−Houwink−Sakurada equation can also provide a way to describe the topology of polymers. The intrinsic viscosity values, $[\eta]$, is related to the molecular weight as seen in the Mark−Houwink−Sakurada equation, $[\eta] = KM^{\alpha}$. The MHS exponent, α, is a parameter corresponding to the conformation of polymer in a good solvent. As presented in Table 1, the measured α values for model polymers are lower than 0.5, which is a typical value for hyperbranched polymer, whereas their linear analogues normally possess an α value larger than 0.5. It should be noticed that the α value or R_g/R_h describes the compact topology of such polymers, however, it is difficult to identify the branched structure or intramolecular cyclics.

The molecular structures of polyesters and polycarbosilanes were characterized using NMR and FT-IR. From the ^{13}C NMR

Scheme 2. Synthesis Route of the Highly Branched Polycarbosilane and Component Units Accompanied with Characteristic Silicon Atoms
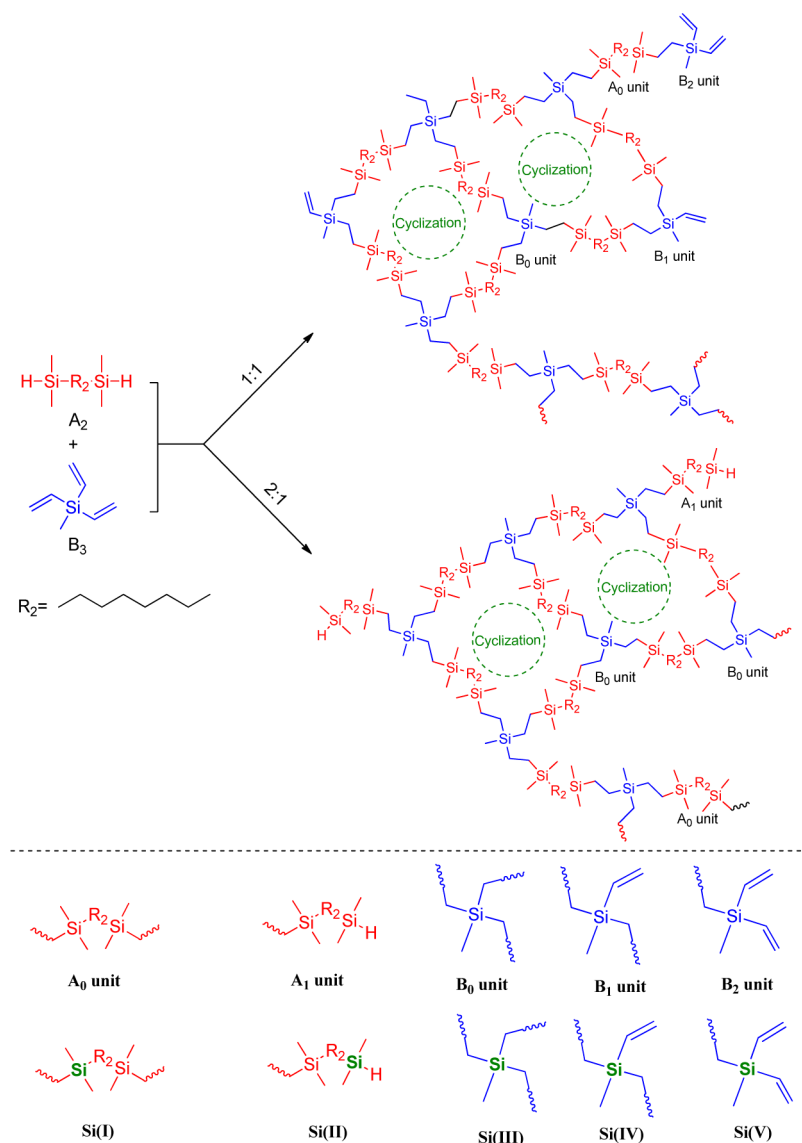
spectrum of HPE-1 (Figure 5), the signals at 174.1−175.3 ppm are attributed to the carbon atoms on ester groups, which confirm the esterification reaction in polymerization. The signals at 176.1−176.7 ppm are assigned to the remaining carbon atoms on carboxyl groups although the feed ratio is set as 1:1 to ensure an excess of hydroxyl groups. The presence of unreacted carbon peaks at 176.1−176.7 ppm suggests incomplete esterification. The phenomenon can be confirmed by ^{1}H NMR spectrum in Figure S6 in the Supporting Information, where the peak at 12.4 ppm assigned for the protons of carboxyl groups did not disappear. Further analysis of NMR showed an incomplete esterification reaction in all polyester samples, resulting in two types of terminal groups, i.e., hydroxyl and carboxyl groups.

For the $A_2 + B_3$ type highly branched polycarbosilanes, the terminal groups were controlled by regulating the feed ratio of monomers. The starting A_2/B_3 of 1:1 and 2:1 resulted in polycarbosilane with vinyl terminals (HP-oc-Vi) or Si−H terminals (HP-oc-SiH), respectively. For HP-oc-Vi, the characteristic signals at 3.77 ppm, assigned to the protons on

Si−H groups, disappeared completely while the signals at 5.65−6.40 ppm for protons on the vinyl groups remained (Figure S9 in the Supporting Information). At the same time, the broad peaks in the region of 0.34−0.48 ppm are in correspondence with the proton peaks of the alkyl bridges formed after the reaction. The Si−H groups have been completely consumed. As verification, the characteristic peak of Si−H bonds at 2110 cm^{-1} disappears as shown in FT-IR spectrum. In contrast, for HP-oc-SiH, the peaks at 5.65−6.40, assigned to the proton on vinyl groups, disappeared completely. At the same time, the characteristic signals of the protons on Si−H groups at 3.85−3.95 ppm can be found (Figure S10 in the Supporting Information), and whose characteristic peak is presented at 2111 cm^{-1} in FTIR spectrum. It reveals a complete hydrosilylation reaction resulting in a consumption of the vinyl groups.

Analysis of Terminal Index. As mentioned above, the quantitative ^{13}C NMR and ^{29}Si NMR spectra were employed to distinguish the structural units of highly branched polyesters and polycarbosilanes, respectively. Here, the ^{13}C NMR spectra

Table 1. Main Molecular Structure Parameters of Highly Branched Polyesters and Polycarbosilanes Determined from SEC-MALLS

sample	feed ratio[a]	$M_{w,SEC}$[b]	$M_{n,SEC}$[b]	PDI[c]	$[\eta]_w$[b] (mL/g)	K[b] (mL/g)	α[b]
HPE-1	1:1	3,900	2,800	1.39	7.8	0.389	0.39
HPE-2	1:1	8,800	4,400	2.01	13.5	0.261	0.43
HPE-3	2:1	4,000	2,300	1.73	5.0	0.252	0.41
HPE-4	2:1	21,200	86,00	2.46	15.2	0.291	0.37
HP-oc-Vi-1	1:1	12,700	4,600	2.76	9.9	0.339	0.34
HP-oc-Vi-2	1:1	37,800	8,100	4.64	17.1	0.978	0.28
HP-oc-SiH-1	2:1	18,600	7,400	2.51	10.4	0.892	0.27
HP-oc-SiH-2	2:1	86,200	21,900	3.94	15.6	0.653	0.25

[a]The refractive index increment (d_n/d_c) value of the sample in THF was determined at 25 °C. [b]The feed ratio refers to the ratio of the concentration of A_2 monomer to the concentration of B_3 monomer. [c]PDI = M_w/M_n.
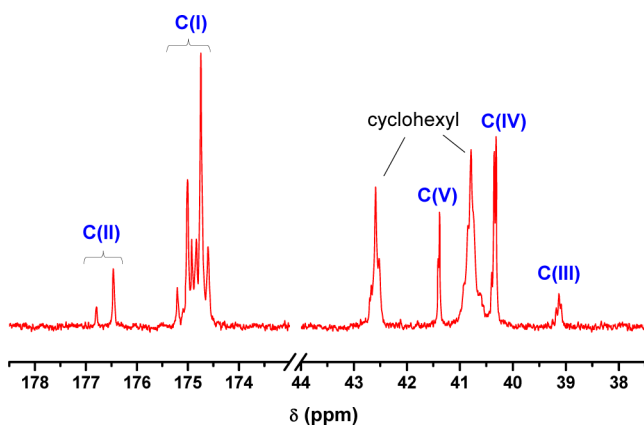

Figure 5. Quantitative ^{13}C NMR spectrum of a typical highly branched polyester of HPE-1 in DMF-d_7.

were recorded using inverse gated decoupling mode with a pulse delay. Chromium acetylacetonate was empolyed as the relaxation reagent for quantitation.[51−53] As shown in the ^{13}C NMR spectrum (Figure 5), the carbon atoms on carbonyl groups are characteristic atoms to identify A_0 and A_1 units of HPE-1. In detail, the carbon atoms (C(II)) on carboxyl groups with signal at 176.1−176.7 ppm belong to A_1 units and the

carbon atoms (C(I)) on ester groups with signals at 174.1−175.3 ppm are assigned to A_0 and A_1 units. Since the 1,1,1-tris(hydroxymethyl)ethane was used as B_3 monomer, the quaternary carbon atoms could identify B_0, B_1, and B_2 units with signals at 39.0−39.2 ppm, 40.2−40.5 ppm, and 41.3−41.5 ppm, respectively. The mole fraction of A_0, A_1, B_0, B_1, and B_2 can be calculated from NMR integral according to eq 10. Accordingly, the TI of highly branched polyesters was conveniently obtained based on eq 9b as presented and summarized in Table 2.

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

$$(10)$$

For highly branched polycarbosilanes, as 1,8-bis(dimethylsilyl)-octane was selected as A_2 monomer, the silicon atoms on −SiH groups could be used to define A_0 and A_1 units. Accordingly, as shown in Figure 6, the silicon atoms (Si(V)) on −SiH groups
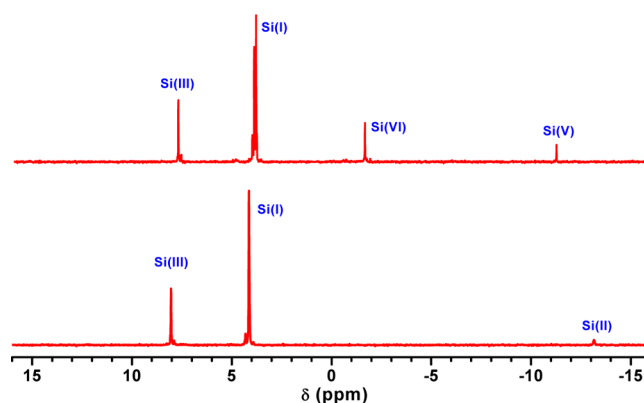
Figure 6. Quantitative ^{29}Si NMR spectra of highly branched polycarbosilanes: (a) HP-oc-Vi-1; (b) HP-oc-SiH-1.

with a signal at −12.90 ppm are attributed to A_1 units. The silicon atoms (Si(VI)) with a signal at 4.20 ppm belong to A_0 and A_1 units. Since the trivinylmethylsilane was selected as B_3 monomer, the silicon atoms with a signal at 7.80 ppm, −1.44 ppm, and −10.91 ppm could define B_0, B_1, and B_2 units, respectively. The HP-oc-Vi includes A_0, B_0, B_1, and B_2 units because all A_2 monomers have been converted into A_0 units. On the other hand, the HP-oc-SiH possesses A_0, A_1, and B_0

Table 2. The Topology Parameters of Highly Branched Polyesters and Polycarbosilanes from Quantitative NMR Spectra and Theoretical Calculation

samples	feed ratio	M_w	content of component units (%)					TI	DB_{Frey}[a]	$DB_{Frechet}$[b]
			k_{A0}	k_{A1}	k_{B0}	k_{B1}	k_{B2}			
HPE-1	1:1	3,900	41.5	8.9	6.6	30.7	12.3	0.57	0.30	0.38
HPE-2	1:1	8,800	43.8	7.2	8.2	29.6	11.2	0.49	0.36	0.40
HPE-3	2:1	4,000	33.7	24.6	15.3	23.4	3.0	0.71	0.57	0.44
HPE-4	2:1	21,200	35.5	26.9	20.7	15.6	1.3	0.78	0.73	0.59
HP-oc-Vi-1	1:1	12,700	55.9	0.0	27.2	14.1	2.4	0.06	0.79	0.68
HP-oc-Vi-2	1:1	37,800	54.6	0.0	23.1	17.9	4.4	0.11	0.72	0.61
HP-oc-SiH-1	2:1	18,600	57.2	3.4	39.4	0.0	0.0	0.09	1.00	1.00
HP-oc-SiH-2	2:1	86,200	59.2	0.8	40.0	0.0	0.0	0.02	1.00	1.00

[a]DB_{Frey} was calculated by the expression of $2k_{B0}/(2k_{B0} + k_{B1})$ from eq 1a. [b]$DB_{Frechet}$ was calculated by the expression of $(k_{B0} + k_{B2})/(k_{B0} + k_{B1} + k_{B2})$ from eq 1b.

units. Similar to HPE, the mole fraction A_0, A_1, B_0, B_1, and B_2 of highly branched polycarbosilane can be calculated from the NMR integral according to eq 11. Hence, the TI of highly branched polycarbosilanes can be obtained from eq 9b as summarized in Table 2.

$$N_{A0}:N_{A1}:N_{B0}:N_{B1}:N_{B2}$$
$$= k_{A0}:k_{A1}:k_{B0}:k_{B1}:k_{B2}$$
$$= \frac{\sum Si(I) - \sum Si(II)}{2} : \sum Si(II) : \sum Si(III) : \sum Si(IV) : \sum Si(V)$$
(11)

As the highly branched polyesters, HPE-1 and HPE-2 synthesized with a low feed ratio of A_2 and B_3 monomer (1:1) possess TI value of 0.57 and 0.49. While HPE-3 and HPE-4 from a high feed ratio of A_2 and B_3 monomer (2:1) show a higher TI value of 0.71 and 0.78. It indicates that the overdose A_2 monomers can promote the conversion of B_3 monomer into dendritic units, accordingly, with few intramolecular cyclics. The reason is that rigid interval units in A_2 monomers decrease intramolecular cyclization, which is in correspondence with the report by Unal and Long[54] where a B_3 monomer containing a rigid phenyl unit is selected. Interestingly, the former two types of polyesters also show low DB value of 0.30 and 0.36 in comparison to those of the latter two types of polyesters with 0.57 and 0.73. In fact, the TI value suggests the tendency of branching or cyclization while the DB illustrates the tendency of forming branched or linear units. So the high TI and high DB show that the polyesters of HPE-3 and HPE-4 have a much more regular highly branched topology than HPE-1 and HPE-2, i.e., a highly branched topology with few intramolecular cyclics and linear units.

For the highly branched polycarbosilanes of HP-oc-Vi and HP-oc-SiH, the TI value lower than 0.20 indicates that they are likely to possess a branched topology with multiple intramolecular cyclics. Especially, for HP-oc-SiH-2, the ultralow TI value even illustrates a multicyclic topology. The multiple cyclization occurs especially when A_2 monomer contains flexible interval units in the $A_2 + B_3$ stepwise polymerization.[45] So the low TI and high DB show the polycarbosilanes that possess a branched topology with multiple intramolecular cyclics.

Obviously, both TI and DB can be employed to well describe the fine topology of highly branched polymers. For DB, it is related to the ratio of dendritic units (B_0 units) and terminal units (B_2 units) in all B units, instead of the expression in terms of the number of actual growth directions compared to the maximum number of possible growth directions.[36] So DB related to B units reflects the tendency of branching or linear units without intramolecular cyclization. When the intramolecular cyclization cannot be ignored in the $A_2 + B_3$ polymerization, the TI value can reflect the tendency of branching (to increase terminals) or cyclization (to decrease terminals). Similar to the well-known DB, the expression of TI, i.e., $T/(D + L)$, is also concise and can be calculated from the quantitative ^{13}C or ^{29}Si NMR spectra rather than molecular weights.[55,56] So it is potential to be a precise characteristic parameter to describe the fine topological structures of highly branched polymers from $A_2 + B_3$ stepwise polymerization.

CONCLUSIONS

Considering the intramolecular cyclization in the polymerization of A_2 and B_3 monomers, a new parameter of terminal index is defined as the ratio of terminals units in a highly branched polymer with intramolecular cyclization to those in its perfect hyperbranched counterpart. Terminal index can be derived using the key parameters T, D, and L, which are calculated from a quantitative NMR spectrum. A high value of TI indicates that the topological structure of polymer is close to a perfect hyperbranched polymer while a low value indicates that it is near to multicyclic polymer. The analysis of results for different highly branched model polymers using quantitative NMR demonstrates that TI, along with DB, can precisely describe the fine topological structures of highly branched polymers.

ASSOCIATED CONTENT

Supporting Information
The ^1H NMR, ^{13}C NMR, ^{29}Si NMR, and FTIR spectra of polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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