

# Topological Analysis of Long-Chain Branching Patterns in Polyolefins

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Patterns in molecular topology and complexity for long-chain branching are quantitatively described. The Wiener number, the topological complexity index, and a new index of 3-starness are used to quantify polymer structure. General formulas for these indices were derived for the cases of 3-arm star, H-shaped, and B-arm comb polymers. The factors affecting complexity in monodisperse polymer systems are ranked as follows: number of arms  $\gg$  arm length  $>$  arm central position  $\approx$  arm clustering  $>$  total molecular weight  $\approx$  backbone molecular weight. Topological indices change rapidly and then plateau as the molecular weight of branches on a polyolefin backbone increases from 0 to 5 kD. Complexity calculations relate 2-arm or 3-arm comb structures to the corresponding 3-arm stars of equivalent complexity but much higher molecular weight. In a subsequent paper, we report the application of topological analysis for developing structure/property relationships for monodisperse polymers. While the focus of the present work is on the description of monodisperse, well-defined architectures, the methods may be extended to the description of polydisperse systems.

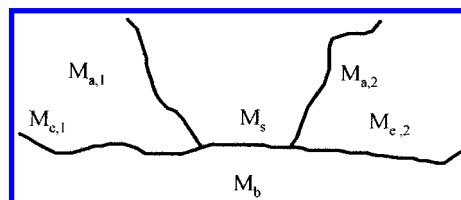
## INTRODUCTION

Long-chain branching (LCB) in polymers has become an area of academic<sup>1–3</sup> and commercial interest since it can greatly influence polymer properties. The presence of different types of long-chain branch structures in a polymer, such as stars,<sup>4–10</sup> H-shaped structures,<sup>11–13</sup> combs,<sup>14–16</sup> and hyperbranched structures,<sup>7,17</sup> have been shown to affect melt and solid-state properties to various extents. To understand how they work, model monodisperse polymers from anionic polymerization have been synthesized and subjected to select studies.<sup>18</sup> But perhaps one of the most dramatic demonstrations of how branching influences a property is illustrated by the recent work of Wagener, Valenti, and Hahn.<sup>19</sup> They have shown that a polyethylene with regularly spaced methyl groups at every ninth carbon on the chain reduces the peak melting point from 134 °C to –2 °C. Even stronger effects might be anticipated for longer branches. It has already been shown that long-chain branches, even at much less than 0.1LCB/1000C, can cause dramatic effects on both rheological and mechanical properties, all depending on the topological details of the branched species.<sup>20–23</sup>

The development of quantitative structure–property relationships for long-chain branched (LCB) polymers requires a new quantitative language that can describe polydisperse systems. Such is the language of molecular topology,<sup>24–30</sup> which provides the mathematical tools to describe how the structural units in a system are connected to one another. Typical topological variables include the number of branch units as well as branch length, spacer length (branch–branch distance), and branch position. Other patterns are related to structures containing atomic rings and are termed molecular

cyclicity.<sup>31</sup> Both branching and cyclicity contribute to molecular complexity.<sup>32–36</sup>

Until recently, molecular topology/complexity analysis was limited mainly to small molecules, the pioneering work in polymer applications of Gordon and Dobson,<sup>37,38</sup> Klein and Seitz,<sup>39</sup> and a few others being a fortunate exception. In the 1980s, a topological extrapolation procedure was developed for predicting the properties of commercial polymers proceeding from data for the initial members of the polymer homologue series.<sup>40,41</sup> Bicerano<sup>42</sup> reported a detailed study on the prediction of polymer properties using molecular connectivity indices of monomers. Topological analysis of dendrimers has been a subject of a recent study.<sup>43,44</sup> An independent process of quantifying the degree of branching by polymer scientists is also underway.<sup>45–47</sup> The present work aims at building further bridges between molecular topology theory and polymer science by presenting a theoretical basis for polymer structure–property relationships. We derive herein the analytical formulas for several selected descriptors of branching and complexity for starlike, H-shaped, and comblike polyolefins and present a theoretical analysis of the branching and complexity patterns in these polymers.



## TOPOLOGICAL DESCRIPTORS

Branched polymers are usually described using molecular weight of the macromolecule ( $MW$ ), and its backbone ( $M_b$ ), arms ( $M_a$ ), spacers ( $M_s$ ), and the backbone end part ( $M_e$ ). Considering the complexity of structural distributions in a

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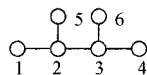
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polydisperse system, it may be necessary to develop criteria for finding average  $MW$  values and moments of the distribution for each of these structural descriptors. A more general approach is based on polymer topology and complexity.

Branching can be quantitatively characterized using topological indices, which are numbers uniquely derived from a molecular graph. The latter is a structure composed of vertices (symbolizing atoms) and edges (standing for covalent chemical bonds). As a rule, molecular graphs do not include hydrogen atoms. A large number of topological indices have been introduced during the last 25 years for the modeling of various properties and biological activities of chemical compounds.<sup>27–30,48–51</sup> Based on earlier work, two basic indices were selected as convenient measures of polymer branching, the Wiener index,  $W$ ,<sup>24,52,53</sup> and the complexity index,  $K$ .<sup>54–56</sup>

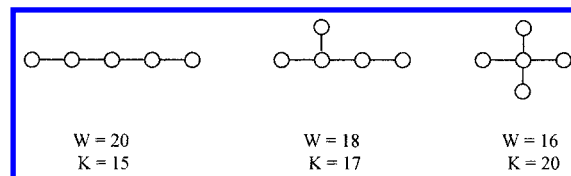
The Wiener number is the sum of the distances between all vertices in a molecular graph.<sup>57</sup> The graph distances are integers, starting with the distance one between any pair of neighboring atoms, then distance two for the second neighbors, etc. The Wiener index of structures with the same number of atoms has a maximum value for a linear chain, and it decreases with the branching of the molecular skeleton due to the shorter distances in the more complex and more compact branched structures. The Wiener number thus measures the compactness of branched polymer and decreases with the degree of branching, just like the polymer branching indices based on viscometric ( $g'$ ) and laser light scattering ( $g$ ) measurements.

The  $K$  index is the sum of all connected subgraphs of a molecular graph. The subgraphs of a certain size form a hierarchical series that begins with graph vertices, then graph edges, then two-edge subgraphs, etc., and ends with the graph itself. Thus, the  $K$  index reflects the intuitive idea that the more complex the molecule, the larger the number of components into which the molecule can be decomposed. The two indices are illustrated below with the graph of 2,3-dimethylbutane, which may be used as a representation of asymmetric 3-arm star polymer.



Distances 1: 1–2, 2–3, 2–5, 3–4, 3–6; distances 2: 1–3, 1–5, 2–4, 2–6, 3–5, 4–6; distances 3: 1–4, 1–6, 4–5, 5–6; the Wiener number  $W = (5 \times 1) + (6 \times 2) + (4 \times 3) = 29$ . Subgraphs: (a) vertices – 6 (1, 2, 3, 4, 5, 6); (b) edges – 5 (1–2, 2–3, 2–5, 3–4, 3–6); (c) two-edge subgraphs – 6 (1–2–3, 1–2–5, 2–3–4, 2–3–6, 3–2–5, 4–3–6); (d) three-edge subgraphs – 6 (1–2–3–4, 1–2–3–5, 1–2–3–6, 2–3–4–6, 5–2–3–4, 5–2–3–6); (e) four-edge subgraphs – 4 (1–2–3–4–5, 1–2–3–4–6, 1–2–3–5–6, 2–3–4–5–6); and (f) five-edge subgraph – 1 (the entire graph); the complexity index  $K = 6 + 5 + 6 + 4 + 6 + 4 + 1 = 28$ .

We constructed a third index using the symmetrical 3-arm starlike structure as a standard for branched polyethylene. The new descriptor termed starness,  $S$ , measures the similarity of a singly branched polyethylene to a symmetrical 3-arm star. The starness is the product of the length of the three arms in the singly branched polymer, expressed by the



**Figure 1.** The decrease in the Wiener number  $W$  and the increase in the topological complexity index  $K$  with the increasing branching in the (simplified) graphs of three isomeric macromolecules.

number of bonds  $e_i$  and normalized by dividing by the total number of graph edges  $E = e_1 + e_2 + e_3$ . For polyethylene, one may introduce the arm molecular weights  $M_i$  and the total molecular weight  $M = M_1 + M_2 + M_3 + 12$ , making use of the relation between the number of carbon atoms  $n_i$ , the number of arm bonds  $e_i$ , and molecular weight  $M_i$  of the  $i$ th arm:  $e_i = n_i - 1 = [(M_i - 2)/14] - 1 = (M_i - 16)/14$ ;  $n = n_1 + n_2 + n_3 + 1$ ,  $M = M_1 + M_2 + M_3 + 13$ .

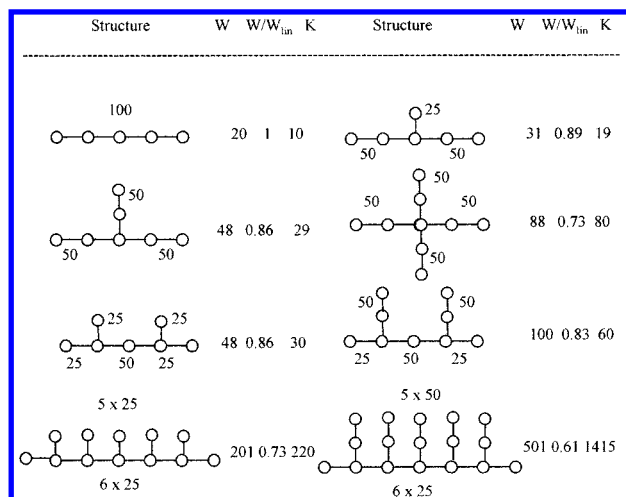
$$S = \frac{27e_1e_2e_3}{(e_1 + e_2 + e_3)^3} = \frac{27(M_1 - 16)(M_2 - 16)(M_3 - 16)}{(M - 35)^3} \quad (1)$$

The index  $S$  is equal to 1 for a symmetric 3-arm star and equal to 0 for a linear polymer. For the graph of 2-methylbutane, shown above, one obtains  $S = 27 \cdot 1 \cdot 1 \cdot 2 / 4^3 = 0.843$  or 84.3% of starness. One may thus obtain for 2-methylpentane, 2-methylhexane, and 2-methylheptane  $S = 0.648$ , 0.5, and 0.394, respectively, in agreement with the intuitive idea for an increased asymmetry in this series of 3-arm stars. The index of starness may be generalized to any  $k$ -arm star,  $k = 3, 4, 5, 6, \dots$ , preserving the 0 to 1 range of values showing the degree of similarity of the  $k$ -arm star to the symmetric  $k$ -arm star.

$$S(k) = \frac{k^k \prod_{i=1}^k e_i}{(\sum_{i=1}^k e_i)^k} = \frac{k^k \prod_{i=1}^k (M_i - 16)}{[\sum_{i=1}^k (M_i - 16k + 13)]^k} \quad (2)$$

The Wiener number is an inverse measure of molecular branching; at a constant number of atoms  $n$  (or molecular weight  $M$ ), it decreases with an increase in the number of branches, with the branch length, and with their more central positions.<sup>24,26</sup> Thus, for acyclic macromolecules of the same molecular weight, this index has its largest value for the linear chains and its lowest value for the symmetrical starlike polymers. This is exemplified in Figure 1 in which the basic topology of the polymers is preserved only.

The Wiener index can also be regarded as a measure of molecular compactness; the more compact the molecule, the smaller the index. When applied to a series of compounds with different numbers of atoms, however, this topological index needs some modification because it increases with molecular size. Due to this feature, we normalized the Wiener index by dividing it by the Wiener index,  $W_{lin}$ , of the linear (nonbranched) polyethylene of the same total molecular weight. The resulting index,  $W/W_{lin}$ , ranges from 1 for linear structures to values approaching zero for highly branched species. A second normalization,  $(W_{lin} - W)/W_{lin}$ , reverses the range from zero to one, thus producing a normalized



**Figure 2.** Illustration of the Wiener number and complexity index for various polyethylene main-chain topologies. The numbers shown with the main-chain ends and with the branches stand for the respective molecular weights in kD.

molecular descriptor that increases with branching. For the three isomeric structures shown above, the  $W/W_{lin}$  index decreases from 1, to 0.90, to 0.80, whereas  $(W_{lin} - W)/W_{lin}$  increases from 0, to 0.1, to 0.2, respectively.

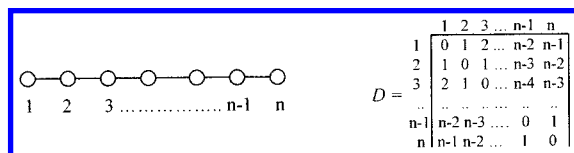
The complexity index  $K$  increases very rapidly with both size and branching.<sup>51</sup> For this reason, it was used both in logarithmic and normalized form (dividing  $K$  by the complexity index  $K_{lin}$  of a linear molecule of the same molecular weight). In this way, for the three isomeric species of Figure 1, the values for  $K/K_{lin}$  increase from 1, to 1.133, to 1.333, respectively. A more detailed illustration of the branching descriptors is presented in Figure 2. The values of the topological indices shown there are obtained by “coarse-graining” the polymers, i.e., by regarding a unit length in the polymer graph to correspond to  $MW = 25$  kD. (This choice was made for the sake of simplicity. A physically significant coarse-graining length would be the entanglement molecular weight,  $M_e$ .) The first four polymer structures are ordered according to the increasing degree of their branching, as reflected by the topological indices  $W/W_o$  and  $K$ . (Due to the increase in the polymer size, the Wiener number is increased in this and the subsequent series of polymers). The next two pairs of structures illustrate the increase in branching in combs, caused by the increased number and length of the branches. From the last four examples, it is clear that combs are considerably more branched, or considerably more complex, than 3-stars. Equivalence between the symmetric 3-arm star polyethylene and the simplest comb—the H-shaped polymer, was found for structures 3 and 5, for which the Wiener number is the same and the complexity index is very close.

In the next section, we present formulas for the two basic topological descriptors of polyethylene structure,  $W$  and  $K$ , derived without the simplifying coarse-graining of Figure 2, but instead with the real number of atoms or with the corresponding molecular weight.

#### FORMULAS FOR THE WIENER INDEX $W$ AND THE COMPLEXITY INDEX $K$ OF POLYOLEFINS

**(i) Linear Polymers.** Wiener defined his index in an empirical way, and he derived the formula for linear acyclic

hydrocarbons without any recourse to graph theory.<sup>52</sup>



In 1971, Hosoya<sup>57</sup> has shown that the Wiener number can be derived as the half sum of the distance matrix entries of the molecular graph of any molecule:

$$W_{lin} = \frac{1}{2} \sum_{i=1}^n \sum_{j=1}^n d_{ij} = \frac{n^3 - n}{6} = \frac{1}{6} n(n-1)(n+1) = \binom{n+1}{3} \quad (3)$$

For linear polyethylene the number of carbon atoms  $n = (M - 2)/14$ ,  $M$  being the total molecular weight. One thus obtains

$$W_{lin} = \frac{M^3 - 6M^2 - 184M + 384}{16,464} \quad (3a)$$

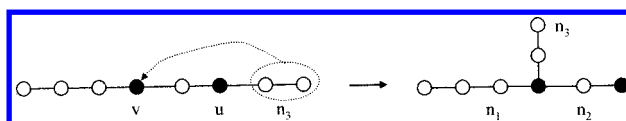
In linear chains, the number of subgraphs having 1, 2, 3, ...,  $n-1$ ,  $n$ -vertices (or 0, 1, 2, ...,  $n-2$ ,  $n-1$  edges) is equal to  $n, n-1, n-2, \dots, 2, 1$ , respectively. Therefore,

$$K_{lin} = \sum_{i=0}^{n-1} (n-i) = \frac{n(n+1)}{2} = \frac{M^2 + 10M - 24}{392} \quad (4)$$

As seen from eqs 3 and 4, the Wiener number of the linear polyethylene is a cubic function of the total molecular weight, whereas the complexity index  $K$  is only a quadratic one. It will be shown below that with the appearance of branches the Wiener index preserves its third power dependence on molecular weight, whereas the  $K$  index raises its power with each new branch.

**(ii) Starlike Polymers.** In graph theory stars are structures of  $n$ -vertices having a single nonterminal vertex and  $(n-1)$  branches of one terminal vertex each. Graphs having  $f$ -branches attached to a single vertex of degree  $f$  are called starlike. In this paper, we use for starlike polymers the terms  $f$ -arm stars, as accepted in polymer science. We also denote the number of vertices in the arms by  $n_1, n_2, \dots, n_f$ . By definition, they do not contain the branching vertex, thus one has  $n = n_1 + n_2 + \dots + n_f + 1$ .

The Wiener index  $W$  of a general (asymmetric) 3-arm star may be presented as the index of the linear chain having the same number  $n$  of vertices reduced by the change in the Wiener number  $\Delta W$  upon the transformation of the linear graph into a starlike one.  $\Delta W$  is determined from the theorem of Polansky and Bonchev<sup>53</sup> from the number of vertices in the transferred subgraph (the third star-arm,  $n_3$ )



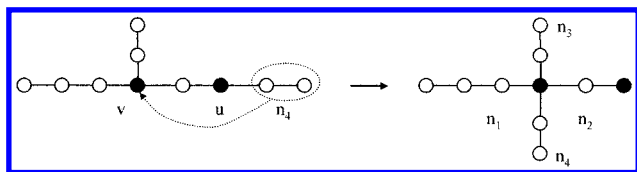
and the distance numbers  $d_u$  and  $d_v$  of the vertices  $u$  and  $v$  between which the transformation occurs (the branching

vertex  $v$  and the terminal vertex  $u$  of the second arm):

$$W_{3\text{-arm star}} = W_{lin} - n_3(d_u - d_v) = \frac{(n+1)n(n-1)}{6} - n_3 \left( \sum_{i=1}^{n_1+n_2} i - \sum_{i=1}^{n_1} i - \sum_{i=1}^{n_2} i \right) = \binom{n+1}{3} - n_1 n_2 n_3 \quad (5a)$$

$$W_{3\text{-arm star}} = \frac{(M-2)(M-16)(M+12) - 6(M_1-2)(M_2-2)(M_3-2)}{16,464} \quad (5b)$$

The Wiener index of a 4-arm star can be similarly derived by applying the Polansky-Bonchev theorem



to the transformation of a 3-arm star into a 4-arm one:

$$W_{4\text{-arm star}} = W_{3\text{-arm star}} - \Delta W = \binom{n+1}{3} - n_1 n_2 (n_3 + n_4) - n_4 (d_u - d_v)$$

$$d_u = \sum_{i=1}^{n_3} i + \sum_{i=1}^{n_1} (n_3 + i) + \sum_{i=1}^{n_2} (n_3 + i)$$

$$d_v = \sum_{i=1}^{n_1} i + \sum_{i=1}^{n_2} i + \sum_{i=1}^{n_3} i$$

$$W_{4\text{-arm star}} = \binom{n+1}{3} - n_1 n_2 (n_3 + n_4) - n_3 n_4 (n_1 + n_2) \quad (6)$$

Extending the derivation to a star having  $f$ -arms one arrives at

$$W_{f\text{-arm star}} = \binom{n+1}{3} - n_1 n_2 (n_3 + n_4 + \dots + n_f) - (n_1 + n_2) n_3 (n_4 + n_5 + \dots + n_f) - (n_1 + n_2 + n_3) n_4 (n_5 + n_6 + \dots + n_f) - \dots - (n_1 + n_2 + \dots + n_{f-2}) n_{f-1} n_f \quad (7)$$

or

$$W_{f\text{-arm star}} = \binom{n+1}{3} - \sum_{1 \leq i < j < k \leq f} n_i n_j n_k \quad (7a)$$

Formulas 5a, 6, and 7a have been independently derived very recently by Gutman, Rada, and Araujo<sup>58</sup> proceeding from Doyle-Graver theorem.<sup>59</sup>

The formula for the specific case of the symmetric (uniform arm length)  $A_3$  stars can be easily obtained from (7a) after imposing the condition  $n_i = n_j = n_k = n_1$  and expressing the total number of vertices  $n$  by means of the branching vertex degree  $f$  (from “functionality”, the term

equivalent to vertex degree in polymer science),  $n = fn_1 + 1$ :

$$W_{\text{uniform } f\text{-star}} = \binom{n+1}{3} - n_1^3 [1(f-2) + 2(f-3) + 3(f-4) + \dots + (f-2) \cdot 1] = \binom{n+1}{3} - n_1^3 \sum_{i=1}^{f-2} i(f-i-1) = \binom{fn_1+2}{3} - n_1^3 \binom{f}{3} = \frac{1}{6} fn_1 (n_1 + 1) (3fn_1 - 2n_1 + 2) \quad (8)$$

From (8) one obtains the specific cases of the most common 3-arm stars and 4-arm stars:

$$W_{\text{uniform } 3\text{-star}} = \frac{1}{2} n_1 (n_1 + 1) (7n_1 + 2) = \frac{1}{784} (M_1^2 - 4)(M_1 + 12) \quad (9)$$

$$W_{\text{uniform } 4\text{-star}} = \frac{4}{3} n_1 (n_1 + 1) (5n_1 + 1) = \frac{1}{2058} (M_1 - 2)(M_1 + 12)(5M_1 + 4) \quad (10)$$

Assuming  $n_1 = 1$  in (8), one obtains the simple formula for the Wiener index of a random-arm star (modeling statistical or random distribution starlike polymers is discussed in detail in another publication of this series<sup>60</sup>):

$$W_{\text{random star}} = f^2 \quad (11)$$

To derive the complexity index  $K$  of the asymmetric  $f$ -arm star we redefine the lengths of the arms  $n_i$  so as to include their common vertex; thus they are larger by one than the  $n_i$  used in the derivation of the Wiener number formulas. The total number of substructures  $K$  can be presented as a sum of their number in all single-arm, double-arm, triple-arm, etc. combinations,  $K_i$ ,  $K_{ij}$ ,  $K_{ijk}$ , etc., respectively.  $K_i$  are determined by eq 4, whereas  $K_{ij}$ ,  $K_{ijk}$ , etc., are calculated as products of the number of the corresponding arm edges,  $e_i = n_i - 1$ , because any subgraphs of arm  $i$  having any given number of edges  $e$  can be combined with any subgraph from the other arms, thus producing more complex subgraphs. The correction of  $-(f-1)$  in the single-arm terms is introduced to compensate for the inclusion of the common core vertex in counting the vertices in each of the arms.

$$K_{f\text{-arm star}} = \sum_{i=1}^f K_i - (f-1) + \sum_{i=1}^{f-1} \sum_{j=2}^f K_{ij} + \sum_{i=1}^{f-2} \sum_{j=2}^{f-1} \sum_{k=3}^f K_{ijk} + \dots + K_{ij\dots f} = \sum_{i=1}^f \frac{n_i(n_i+1)}{2} - f + 1 + \sum_{i=1}^{f-1} \sum_{j=2}^f (n_i-1)(n_j-1) + \sum_{i=1}^{f-2} \sum_{j=2}^{f-1} \sum_{k=3}^f (n_i-1)(n_j-1)(n_k-1) + \dots + (n_i-1)(n_j-1)(n_k-1)\dots(n_f-1) = \frac{1}{2} \sum_{i=1}^f n_i(n_i-1) + n_1 n_2 n_3 \dots n_f = \sum_{i=1}^f \binom{n_i}{2} + n_1 n_2 n_3 \dots n_f \quad (12)$$

For polyethylenes, the specific form of eq 12 is



$$K_{3\text{-arm star}} = n_1 n_2 n_3 + \sum_{i=1}^3 n_i (n_i - 1) \quad (13a)$$

$$K_{3\text{-arm star}} = \frac{1}{2744} \left[ \prod_{i=1}^3 (M_i - 2) + 7 \sum_{i=1}^3 (M_i - 2)(M_i - 16) \right] \quad (13b)$$

For the uniform arm distribution,  $n_1 = n_2 = n_3 = \dots = n_f$ :

$$K_{\text{uniform } f\text{-arm star}} = n_1^f + \frac{1}{2} f n_1 (n_1 - 1) \quad (14)$$

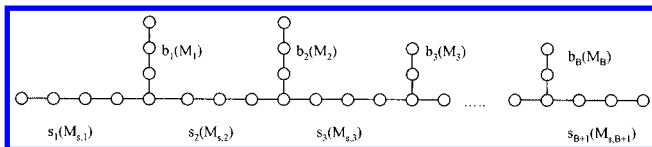
for polyethylene:

$$K_{\text{uniform } 3\text{-arm star}} = n_1^3 + \frac{3}{2} n_1 (n_1 - 1) = \frac{(M - 2)(M^2 + 17M - 332)}{2744} \quad (14a)$$

The formulas derived in this section for the Wiener number  $W$  and complexity index  $K$  of 3-arm stars are applied to modeling polyethylene properties in another publication of this series.<sup>61</sup>

### (iii) The Wiener Number of Combs with B-Arms.

Combs are acyclic graphs which have branch units of vertex degree three and unbranched (first-order) branches, regarded as models of polyolefins.



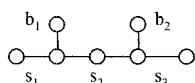
Let the comb polyolefin of molecular weight  $M$  has  $B$  branches and  $B+1$  backbone segments of molecular weight  $M_{b,i}$  and  $M_{s,i}$ , respectively. The corresponding polymer graph has  $n$  vertices and  $B$  branches of  $b_i$  vertices and  $B+1$  chains of  $s_i$  vertices each. The formula for the Wiener index of  $B$ -combs can be derived from the Doyle-Graver formula<sup>59</sup> for branched acyclic graphs

$$W = \binom{n+1}{3} - \sum_u \sum_{1 \leq i < j \leq k} n_i n_j n_k \quad (15)$$

where the first summation is over all branched vertices  $u$ , and the second summation is over all  $i, j$ , and  $k$  branches emanating from  $u$ . In the comb-graph the number of vertices  $n_i$  from eq 15 corresponds either to  $b_i$  or to  $s_i$ . Substituting in (15) the specifics of the comb graph one obtains

$$W_{B\text{-comb}}(b_i, s_i) = \binom{n+1}{3} - \sum_{i=1}^B \left\{ \sum_{k=1}^i (s_k + b_{k-1}) b_i \left[ n - 1 - \sum_{k=1}^i (s_k + b_k) \right] \right\} \quad (16)$$

After substituting the number of atoms  $n = (M - 2)/14$ ,  $s_k = (M_{s,k} - 2)/14$ , and  $b_k = (M_{b,k} - 2)/14$  in (15),



and omitting the terms of order unity and  $10 (M \gg 10)$ , one obtains

$$W_{B\text{-comb}}(M_{s,i}, M_{b,i}) \approx \frac{\binom{M}{3} - \sum_{i=1}^B \left\{ \sum_{k=1}^i (M_{s,k} + M_{b,k-1}) M_{b,i} \left[ n - 1 - \sum_{k=1}^i (M_{s,k} + M_{b,k}) \right] \right\}}{2744} \quad (16a)$$

Equations 15 and 16 are illustrated below for the H-shape (2-arm comb) polymer:

$$W_{H\text{-comb}}(s_i, b_i) = \binom{n+1}{3} - s_1 b_1 (s_2 + s_3 + b_2) - s_3 b_2 (s_1 + s_2 + b_1) \approx \frac{1}{2744} \left[ \binom{M}{3} - M_{s1} M_{b1} (M_{s2} + M_{s3} + M_{b2}) - M_{s3} M_{b2} (M_{s1} + M_{s2} + M_{b1}) \right] \quad (17)$$

The random distribution of arm lengths and arm positions along the polymer backbone is commonly replaced in theoretical models by the distribution of equally long branches into equally spaced positions. The formula for the Wiener number of such model polymers is obtained from eq 15 after substituting  $s_1 = s_2 = \dots = s$ ,  $b_1 = b_2 = \dots = b$ , and  $n = (B + 1)s + Bb + 1$ :

$$W_{B\text{-comb}}(s, b) = \binom{n+1}{3} - \sum_{i=1}^B [is + (i-1)b] b [n - i(s+b) - 1] = \binom{n+1}{3} - \frac{1}{6} b B \{ (s+b)[(s+b)(B+1)(B+2) - 6bB] - 6bs \} \approx \frac{M^3 - BM_b \{ (M_s + M_b)[(M_s + M_b)(B+1)(B+2) - 6BM_b] - 6M_b M_s \}}{16464} \quad (18)$$

For the H-shape polymer (18) reduces to

$$W_{H\text{-comb}}(s, b) = \binom{n+1}{3} - 2sb(2s+b) \approx \frac{1}{16464} [M^3 - 12M_s M_b (2M_s + M_b)] \quad (19)$$

A further simplification of the expression for the Wiener number is obtained for the idealized comb polymers with uniform chain distribution characterized by relations  $s = b$  (or, respectively,  $M_s = M_b$ ), and  $n = (2B + 1)b + 1$ :

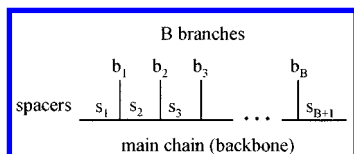
$$W_{\text{uniform } B\text{-arm comb}} = \binom{n+1}{3} - \frac{1}{3} b^3 B (2B^2 + 1) \approx \frac{M_b^3}{16464} (4B^3 + 12B^2 + 4B + 1) \quad (20)$$

For a uniform H-shape polymer the expression is

$$W_{\text{uniform H-comb}} = \binom{n+1}{3} - 6b^3 \approx \frac{89}{16464} M_b^3 \quad (21)$$

**(iv) The Complexity Index K of Combs with B-Arms.**

The complexity index  $K$  of a comb polymer with  $B$ -arms is calculated as a sum of four terms counting the total number of subgraphs in (a) the backbone,  $K_c$ , (b) the individual branches (end chains),  $K_{br}$ , (c) all subgraphs containing main chain spacers  $s$  (separating the pairs of neighboring branches) and one or more branches,  $K_{c/br}$ , and (d) all subgraphs incorporating any combinations of two or more branches together with the connecting part of the main chain (the latter plays only the role of a connector but does not generate new subgraphs),  $K_{br/br}$ . Denote the number of vertices in the  $i$ th branch by  $b_i$ , the root vertex of the branch not being included.



Denote the number of vertices in the  $i$ th spacer by  $s_i$ . Let also by definition,  $s_i$  to include only one of its two end vertices, thus making the number of backbone vertices  $n_c = \sum s_i + 1$ .

$$K_{B-arm comb} = K_c + K_{br} + K_{br/br} + K_{c/br} \quad (22)$$

The first two terms are obtained from eq 4 describing linear chains:

$$K_c = \frac{1}{2}n_c(n_c + 1); K_{br} = \sum_{i=1}^{B+2} \left( \frac{b_i(b_i + 1)}{2} + b_i \right) \quad (23a,b)$$

The second term “ $+b_i$ ” in (21b) accounts for the additional subgraphs that include the edge connecting the branch with the main chain.

The third term in eq 22 includes all path type subgraphs that start and end with branch(es) and have one or more connecting spacers:

$$K_{br/br} = \sum_{1 \leq i < j}^{B+2} b_i b_j + \sum_{1 \leq i < j < k}^{B+2} b_i b_j b_k + \dots + \sum_{1 \leq i < j < \dots < v \leq B+1}^{B+2} b_i b_j \dots b_v + b_1 b_2 b_3 \dots b_{B+1} b_{B+2} \quad (24)$$

The fourth term in eq 22 can be further divided into linear and branched core/branch subgraphs. The terminal chains in linear substructures are a spacer and branch, and more spacers might be incorporated in between.



The branched type substructures include two terminal spacers and one or more branches to the intermediate part of the main chain:

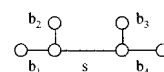
$$K_{c/br}' = \sum_{i=1}^{B-1} s_i \left[ \left( \sum_{j=1}^{i+1} b_j + \sum_{1 \leq j < k}^{i+1} b_j b_k + \sum_{1 \leq j < k < l}^{i+1} b_j b_k b_l + \dots + b_j b_k \dots b_{i+1} \right) + \left( \sum_{p=i+2}^{B+2} b_p + \sum_{i+2 \leq p < r}^{B+2} b_p b_r + \sum_{i+2 \leq p < r < s}^{B+2} b_p b_r b_s + \dots + \sum_{i+2 \leq p < r < \dots < v}^{B+2} b_p b_r \dots b_v + b_{i+2} b_{i+3} \dots b_{B+2} \right) \right] \quad (25)$$

$$K_{c/br}'' = \sum_{i=2}^{B-1} \sum_{i=1}^{B-1-t} s_i s_{i+t-1} \left( \sum_{j=i+2}^{t+1} b_j + \sum_{i+2 \leq j < k}^{t+1} b_j b_k + \sum_{i+2 \leq j < k < l}^{t+1} b_j b_k b_l + \dots + \sum_{i+2 \leq j < k < \dots < v}^{t+1} b_j b_k \dots b_v + b_j b_k \dots b_{i+1} \right) \quad (26)$$

After substituting eqs 23 to 26 into eq 22 one obtains

$$K_{B-comb} = \frac{1}{2}n_c(n_c + 1) + \frac{1}{2} \sum_{i=1}^{B+2} b_i(b_i + 3) + \sum_{1 \leq i < j < \dots < v}^{B+2} \prod_{f=i}^{i+B+1} b_f + \sum_{i=1}^{B-1} s_i \left( \sum_{1 \leq j < k < \dots < m}^{i+1} \prod_{f=j}^{j+i} b_f + \sum_{i+2 \leq p < r < \dots < v}^{B+2} \prod_{f=p}^{p+B-i-2} b_p \right) + \sum_{i=2}^{B-1} \sum_{i=1}^{B-1-t} s_i s_{i+t-1} \left( \sum_{i+2 \leq j < k < \dots < v}^{t+1} \prod_{f=j}^{j+B+1} b_f \right) \quad (27)$$

Equation 27 is rather complex, but it can be easily handled by a computer. The formula for the simplest case of 2-combs (H-shape polymers) is shown below



with the four end chains treated as branches  $b_i$  and the single nonterminal chain as the spacer  $s$  separating the branches:

$$K_{H-shape} = \frac{1}{2}(s+1)(s+2) + \frac{1}{2} \sum_{i=1}^4 b_i(b_i + 3) + \sum_{i=1}^3 \sum_{j=2}^4 b_i b_j + \sum_{i=1}^2 \sum_{j=2}^3 \sum_{k=3}^4 b_i b_j b_k + b_1 b_2 b_3 b_4 + s \left( \sum_{i=1}^4 b_i + b_1 b_2 + b_3 b_4 \right) \quad (28)$$

For polyethylene, after substituting the number of carbon atoms  $n_i = (M_i - 2)/14$ , denoting the molecular weights of the branches and spacer by  $M_i$  and  $M_s$ , respectively, and neglecting the terms of order unity and 10 ( $M_i \gg 10$ ), eq 29 results

$$K_{H\text{-shape}} \approx \frac{1}{392}[(M_C + 1)(M_C + 2) + \sum_{i=1}^4 M_i(M_i + 3)] + \frac{1}{14^2} \sum_{i=1}^3 \sum_{j=2}^4 M_i M_j + \frac{1}{14^3} \sum_{i=1}^2 \sum_{j=2}^3 \sum_{k=3}^4 M_i M_j M_k + \frac{1}{14^4} M_1 M_2 M_3 M_4 + \frac{1}{14^3} M_s (14 \sum_{i=1}^4 M_i + M_1 M_2 + M_3 M_4) \quad (29)$$

For molecules with equally spaced branches of equal lengths ( $b_1 = b_2 = \dots = b$ ;  $s_1 = s_2 = \dots = s$ ;  $n_c = (B - 1)s + 1$ ), eq 27 reduces to

$$K_{B\text{-comb}}(s, b) = \frac{1}{2}[(Bs - s + 1)(Bs - s + 2) + (B + 2)b(b + 3)] + \sum_{k=2}^{B+2} \binom{B+2}{k} b^k + s(B - 1) \sum_{k=1}^B b^k \sum_{i=1}^{B-1} \left[ \binom{i+1}{k} + \binom{B-i+1}{k} \right] + s^2 \sum_{t=2}^{B-1} (B - t) \sum_{k=1}^{B-t+1} b^k \binom{B-t+1}{k} \quad (30)$$

For H-shape polymers ( $B = 2$ ):

$$K_{H\text{-shape comb}} = \frac{1}{2}(s + 1)(s + 2) + b(b^3 + 4b^2 + 8b + 6) + 2sb(b + 2) \quad (31)$$

For the idealized comb model with uniform chain distribution,  $s = b$  and eq 31 modifies to

$$K_{B\text{-comb}}(s = b) = \frac{1}{2}[Bs^2(B - 1) + 3s(2B + s + 1) + 2] + \sum_{k=2}^{B+2} \binom{B+2}{k} s^k + (B - 1) \sum_{k=1}^B s^{k+1} \sum_{i=1}^{B-1} \left[ \binom{i+1}{k} + \binom{B-i+1}{k} \right] + \sum_{t=2}^{B-1} (B - t) \sum_{k=1}^{B-t+1} s^{k+2} \binom{B-t+1}{k} \quad (32)$$

wherefrom the expression for the H-shape polymer turns into a polynomial of a single variable—the uniform chain length  $b$ :

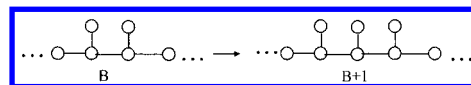
$$K_{\text{uniform H-shape polymer}} = b^4 + 6b^3 + \frac{25}{2}b^2 + \frac{15}{2}b + 1 \quad (33)$$

Equations 30–33 can also be expressed in terms of molecular weight as shown in the foregoing.

#### BRANCHING PATTERN ANALYSIS

The formulas presented in the previous section allow to prove rigorously the structural patterns that increase the degree of branching and complexity of polymers. The proof consists of deriving inequalities showing the increase in the topological complexity index  $K$  and the decrease in the Wiener index  $W$  with the change in the corresponding branching factor. The Wiener index based analysis complements previous analysis of molecular branching.<sup>24,26</sup>

**(i) Adding a New Branch.** It suffices to consider the isomeric transformation of a linear polymer to a 3-arm star isomer to a 4-arm star isomer. From eqs 3 and 5a, as well as from eqs 4 and 12a



one obtains the corresponding change in the  $W$  and  $K$  indices (with the number of vertices in each star arm  $n_i$  not including the branched vertex), respectively:

$$\Delta W = W_{3\text{-arm star}} - W_{\text{linear}} = -n_1 n_2 n_3 < 0; \Delta K = K_{3\text{-arm star}} - K_{\text{linear}} = n_1 n_2 n_3 > 0 \quad (34a, b)$$

$$\Delta W = W_{4\text{-arm star}} - W_{3\text{-arm star}} = -n_3 n_4 (n_1 + n_2) < 0 \quad (35a)$$

$$\Delta K = K_{4\text{-arm star}} - K_{3\text{-arm star}} = n_3 n_4 (n_1 n_2 + n_1 + n_2) > 0 \quad (35b)$$

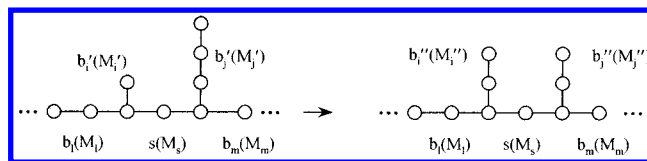
Thus, every new branch will increase the complexity index and will decrease the Wiener index. The comparison of the two starlike structures illustrates the pattern of a stronger effect on the topological branching measures, when the formation of a new branch occurs at already branched structure. One may also see from eqs 34 and 35 that the changes in the two topological indices are closely related

$$\Delta K = -\Delta W \quad (34c)$$

$$\Delta K = -\Delta W + n_1 n_2 n_3 n_4 \quad (35c)$$

with the change in the complexity index becoming larger than that of the Wiener index with each next branch.

**(ii) Variation in the Branch Length.** At a constant total molecular weight, the increase in the length of a branch can occur at the expense of the shortening of another branch or main chain end. To reveal the trend in branch length variations it suffices to consider 2-arm combs, because the pattern is valid for any two branches or any branch/main-chain-end combination in the comb. Let two of the four arms in such a H-shape polymer,  $b_i$  and  $b_j$ , adjacent to different carbons vary their length.

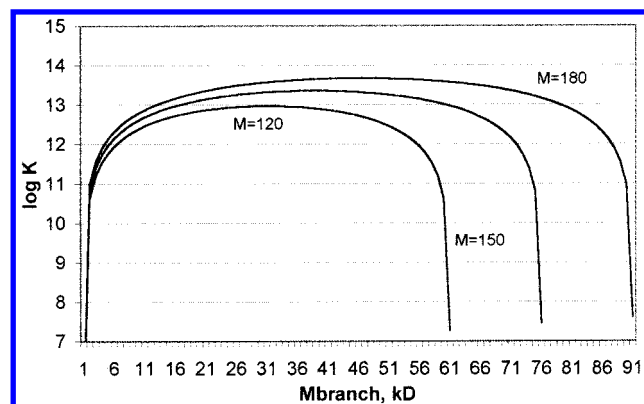


To keep the molecular size the same, one has  $b_j'' = b_j' + k$  and  $b_i'' = b_i' - k$ . The other two arms  $l$  and  $m$  remain unchanged. One thus obtains from eq 27 and respectively eq 17:

$$\Delta K = K_{H\text{-shape}}'' - K_{H\text{-shape}}' = k(b_i'' - b_j')(s + b_l + b_m + b_l b_m) > 0 \text{ for } b_i'' > b_j' \quad (36)$$

$$\Delta W = W_{H\text{-shape}}'' - W_{H\text{-shape}}' = -k(b_i'' - b_j')(b_l + b_m) + ks(b_m - b_l) > 0 \text{ for } b_i'' > b_j' \text{ and } b_m \geq b_l \quad (37)$$

This proves that at a constant total molecular weight the lengthening of a branch at the expense of the shortening of



**Figure 3.** Variations in the topological complexity index with the branch molecular weight for three series of 2-arm comb polymers with evenly spaced arms of equal length.

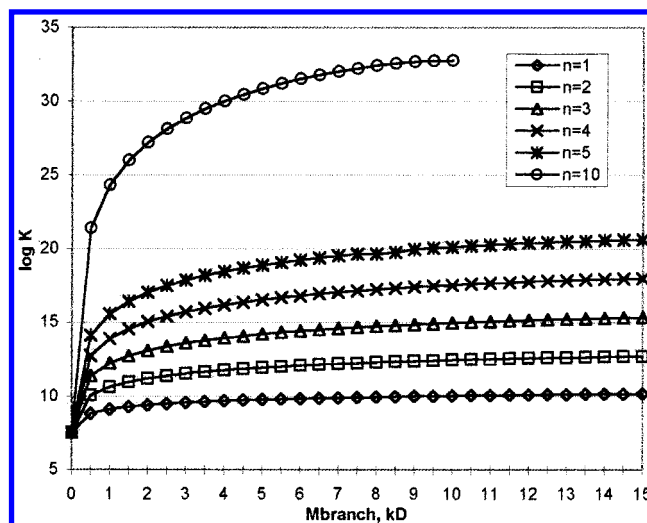
a longer branch increases the degree of polymer branching (complexity). The inequality  $b_i'' > b_j'$  shows that this trend keeps until the two branches become equally long. Thus, at fixed total molecular weight, the symmetric structures that have all branches of the same length are the species with the highest complexity. The complexity index would also increase any time a shortened backbone end chain remains longer than the elongated arm. When the Wiener number is used as a criterion, an additional condition  $b_m \geq b_l$  appears to account simultaneously for the centricity factor (see the next subsection). When  $b_m = b_l$  the two branches are positioned symmetrically to the backbone center and  $b_i'' > b_j'$  suffices to prove the pattern.

The starness index also mirrors the pattern of higher complexity related to the equalizing of the arm lengths. If  $k$  edges are transferred from arm 2 to arm 3 in the 3-arm star graph, i.e., if  $e_3 = e_3 + k$  and  $e_2 = e_2 - k$ , then one obtains from eq 1

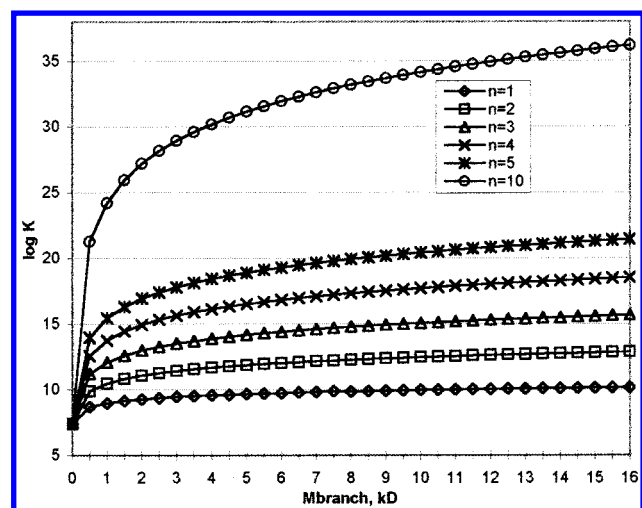
$$\Delta S = S'' - S' = -\frac{ke_1(e_2'' - e_3')}{(e_1 + e_2 + e_3)^3} < 0 \text{ for } e_2'' > e_3' \quad (38)$$

Some illustrations of this branching pattern are given in Figures 3 and 4 with the  $\log K$  descriptor plotted against the branch molecular weight. In Figure 3, the  $\log K/M_{\text{branch}}$  dependence is shown for three series of 2-arm polyethylene with molecular weight of 120 kD, 150 kD, and 180 kD, i.e., branch length increases at the expense of the backbone shortening. In Figure 4, molecular weight is kept constant at MW = 120 kD, and the number of arms varies from 1 to 10, the curves being shown up to the symmetry point.

Both figures show a dramatic increase in polymer complexity when the branch molecular weight increases from zero to about 5 kD. The further arm lengthening has a lesser effect and nearly plateau areas are formed. The starting point of the plateau depends on the number of comb teeth. As illustrated by Figure 3, arm length is much more important for polymer complexity than the total molecular weight: the increase in MW from 120 kD to 180 kD increases the complexity index by less than an order of magnitude whereas the increase in the branch length shown produces a change in complexity of up to 5 orders of magnitude. On the other hand, Figure 4 indicates that the number of branches is the most important factor; the complexity index increases by more than 20 orders of magnitude for an increase in the



**Figure 4.** Variations in the topological complexity index with the branch molecular weight for six series of  $n$ -arm comb polymers with MW = 120 kD having evenly spaced arms of equal length.



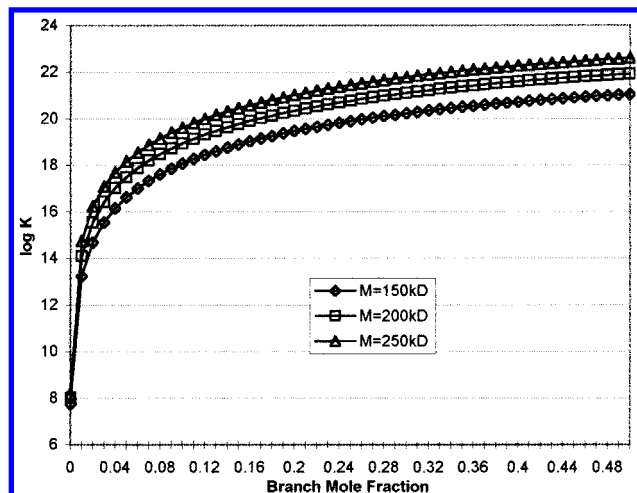
**Figure 5.** The topological complexity index versus branch molecular weight for six series of  $n$ -arm comb polymers with a backbone molecular weight of 100 kD having evenly spaced arms of equal length.

number of arms from 1 to 10. The rapid increase in the degree of polymer branching in  $n$ -combs with  $n$  at fixed molecular weight in Figure 4 also indicates the presence of a "star-effect", i.e., the large plateaus available for low values of  $n$  are less pronounced for  $n \geq 10$ , and an  $n$ -arm comb reduces to an  $(n+2)$ -arm star in the limit of  $nM_{br} \approx M$ .

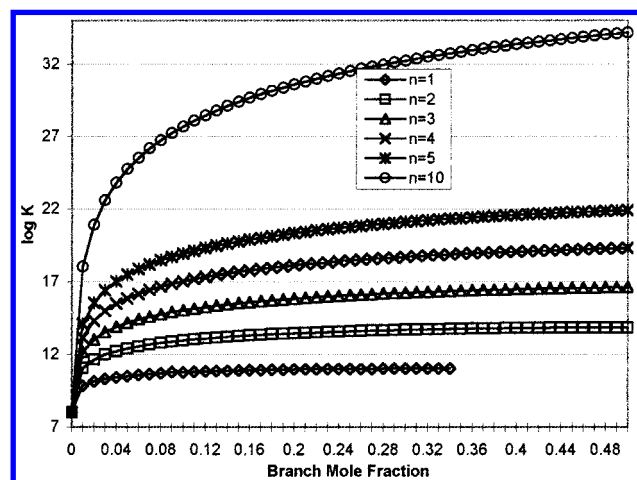
When the backbone molecular weight is kept constant and branch lengthening increases the total molecular weight, polymer complexity increases with each new carbon atom in the arms. As exemplified in Figure 5, the polymer complexity increases faster relative to the cases of constant MW ( $K$  increases with more than 30 orders of magnitude when the number of arms rises from 1 to 10).

The results could be generalized by plotting the complexity index versus the overall branch mole fraction  $f = \sum_i M_{br,i} / MW$ . Figures 6 and 7 show that the major changes in polymer complexity occur at  $f < 0.10$ . The three curves in Figure 6, corresponding to total molecular weights of 150 kD, 200 kD, and 250 kD, come very close to each other, thus emphasizing the small effect of MW on polymer complexity,





**Figure 6.** The topological complexity index versus branch mole fraction for three series of 5-arm comb polymers with a backbone molecular weight of 200 kD having evenly spaced arms of equal length.

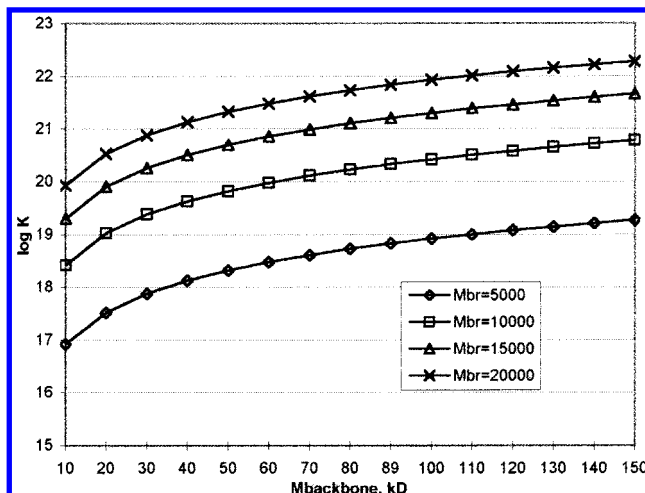


**Figure 7.** The topological complexity index versus branch mole fraction for six series of  $n$ -arm comb polymers with a backbone molecular weight of 200 kD having evenly spaced arms of equal length.

as compared with the mole fraction of branches. Although failing to merge in a single master curve, the three curves indicate the possibility to deal with the broad polyethylene MWDs by decomposing them into a series of closely lying curves characterizing the narrow distribution polymers.

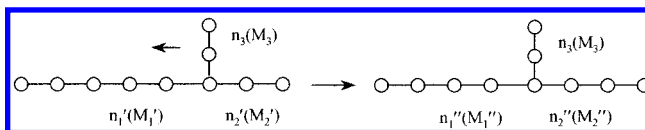
When the arm length is kept constant and the backbone length increases, polymer complexity increases weakly, as evidenced by Figure 8. Thus, for four series of 5-arm polymer with arm molecular weight ranging from 5 kD to 20 kD, the increase in the backbone molecular weight from 50 kD to 150 kD causes a variation in the polymer complexity index within only 1 order of magnitude. Thus, a hierarchy of the complexity factors examined so far is established with the number of arms being the most important component, the arm length coming next and the weakest ones being the total molecular weight and that of the polymer backbone.

**(iii) The Central Position of Branches as a Complexity Factor.** To find this pattern of centrality (or centrality), it suffices to analyze the asymmetrical 3-arm star (eq 5a) one of the arms in which is displaced to a more central position. This changes the number of vertices  $n_1$  and  $n_2$  in the two arms that form the polymer backbone:  $n_1'' = n_1' + k$ ,  $n_2'' =$



**Figure 8.** Variations in the topological complexity index with the increase in the backbone molecular weight of four series of 5-arm comb polymers having evenly spaced arms of equal molecular weight ranging from 5 to 20 kD.

$= n_2' - k$  (and the respective number of edges  $e_1'' = e_1' + k$ ,  $e_2'' = e_2' - k$ ),



while keeping constant the size of the shifted arm  $n_3$ . One thus obtains from eqs 5a and 12a for the change in the Wiener number  $W$ , the complexity index  $K$ , and the starness index  $S$ :

$$\Delta W = W'' - W' = -kn_3(n_2'' - n_1') < 0 \text{ for } n_2'' > n_1' \quad (39)$$

$$\Delta K = K'' - K' = kn_3(n_2'' - n_1') > 0 \text{ for } n_2'' > n_1' \quad (40)$$

$$\Delta S = S'' - S' = -\frac{ke_3(e_2'' - e_1')}{(e_1 + e_2 + e_3)^3} > 0 \text{ for } e_2'' > e_1' \quad (41)$$

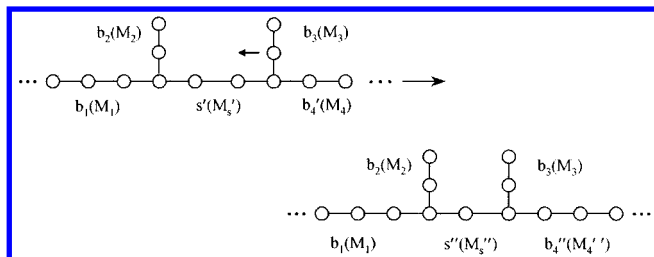
Thus, the more central branch position corresponds to a higher degree of branching or higher complexity of the polymer graph. The variations in the two branching measures again show a close relationship ( $\Delta K = -\Delta W$ ). An illustration of the general trend is shown below for 3-arm star polyethylene with  $M = 150$  kD,  $M_3 = 10$  kD,  $k = 10$  kD,  $M_1 = 10$  kD to 70 kD, and  $M_2' = 130$  kD to 70 kD ( $n \approx M/14$  for  $M \gg 1$ ). The complexity index increases with each branch displacement toward the backbone center, despite the diminishing magnitude of the  $\Delta K$ :

$$M_1/M_2 = 20/120 \ 30/110 \ 40/100 \ 50/90 \ 60/80 \ 70/70$$

$$\Delta K \times 10^{10} = 4.009 \ 3.280 \ 2.551 \ 1.822 \ 1.093 \ 0.364$$

It may be seen by comparison with the data in Figures 3 and 4 that the branch central position affects complexity considerably less than the number of branches and the branch length. However, when more branches are displaced toward the center, the overall effect on complexity is large enough and can considerably exceed that of molecular weight.

**(iv) Branch Clustering and Complexity.** The impact of branch clustering on complexity of polymers having no atomic rings can again be evaluated from the analysis of 2-arm combs (H-shape polymers) since the results obtained can be applied to any pair of branches. We proceed for the change in the Wiener number from eq 17, keeping constant all parameters ( $n$ ,  $b_1$ ,  $b_2$ , and  $b_3$ ) but the position of branch 3, lengthening thus branch 4, and shortening the spacer  $s$ :  $s'' = s' - k$  and  $b_4'' = b_4' + k$ . Equation 27 is used for the calculation of the change in the complexity index  $K$



under this structure transformation, which forms clusters of closely positioned branches. For uniformity of presentation with that of the Wiener number, the quantities in eq 27 are relabeled as follows:  $s_2 \Rightarrow s$ ,  $s_1 \Rightarrow b_1$ ,  $s_3 \Rightarrow b_4$ ,  $b_2 \Rightarrow b_3$ , and  $b_3 \Rightarrow b_4$ . The following relationships are obtained:

$$\Delta W = W'' - W' = -kb_3(b_1 + b_2 + s'' - b_4') < 0$$

for  $b_1 + b_2 + s'' > b_4'$  (42)

$$\Delta K = K'' - K' = kb_3(b_1 + b_2 + b_1b_2 + s'' - b_4') > 0$$

for  $b_1 + b_2 + b_1b_2 + s'' > b_4'$  (43)

Again, the changes in the two topological indices closely match each other:

$$\Delta K = -\Delta W + kb_1b_2b_3 \quad (44)$$

It follows from eqs 42 and 43 that the pattern of clustering branches together increases branching complexity, except for the cases when a very long chain end ( $b_4 \gg b_1, b, s$ ) exists.

An illustration is presented below for H-shape polyethylene ( $n \approx M/14$  for  $M \gg 1$ ) with  $M = 120000$ ,  $M_{br} = 10$  kD,  $M_s'' = 80$  kD to 10 kD,  $M_{b4}' = 10$  kD to 80 kD, and  $k = 10$  kD.

$$M_s \times 10^3 =$$

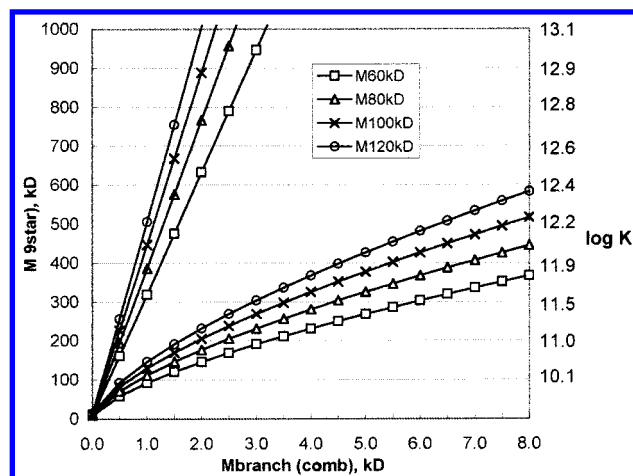
80	70	60	50	40	30	20	10
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$$\Delta K \times 10^{12} =$$

3.690	3.680	3.670	3.660	3.649	3.593	3.491	3.389
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As seen from the data shown, for long chain branches with molecular weight higher than the entanglement molecular weight, branch clustering always increases branching complexity. The clustering effect becomes stronger with the cluster size, i.e., with the increasing number of branches grouping together.

**(v) Complexity Equivalence between Star and Comb Polyolefins.** A correspondence in topological complexity between 2-arm combs with branch molecular weights  $M_{br} = 0$  to 8 kD (total molecular weight  $M = 100$  kD to 116 kD) and symmetrical 3-arm stars with a molecular weight within the 50 kD to 600 kD range is summarized in Figure



**Figure 9.** Topological equivalence of four series of symmetric 2-arm and 3-arm comb polymers (having a constant backbone molecular weight and equally spaced arms of equal length) to symmetric 3-arm star polymers with considerably higher molecular weight.

9. The correspondence is based on equal  $\log K$  values. (As mentioned in the foregoing, the Wiener number decreases with the degree of branching and increases with the size of molecule what limits its application when both changes occur at a time.) This is useful in that the properties of H-shape structures may be modeled using symmetrical 3-arm star equivalents, which are well studied. Indeed, different properties depend to a different degree on polymer complexity, and the calibration to each property would require a different transformation coefficient. The narrow "window" of  $M_{br} = 0.2$  kD to 2.5 kD for 3-arm combs, showing their equivalence to 3-arm stars with molecular weights up to  $10^3$  kD, indicates that the use of the 3-arm star models should not be extended beyond 3-arm comb structures, due to the very different structural complexity of starlike and comblike polymers.

## CONCLUDING REMARKS

This study presents a mathematical framework for the description of branching in polymers based on polymer topology and complexity. Two topological indices were selected based on previous experience as convenient measures of the degree of polymer branching, the Wiener number  $W$  (used in a normalized form), and the topological complexity  $K$  (usually used in a logarithmic form). An index of 3-starness was constructed to describe the similarity of an asymmetrical 3-arm star to the standard symmetrical 3-star with the same total molecular weight. Formulas were derived for these indices, using total molecular weight, number of branches, branch length, and branch positioning as independent variables. These two basic descriptors show similar behavior, the complexity index varying much faster with the number of branches than the Wiener number.

The detailed mathematical analysis presented above and illustrated in Figures 3–9 has led to the identification of the following branching patterns:

(i) At the same total molecular weight the complexity index  $K$  increases and the Wiener index decreases with the number of branches:

$$K_{\text{linear}} < K_{3\text{-star}} < K_{2\text{-comb}} < K_{3\text{-comb}} < \dots < K_{n\text{-comb}}$$

$$W_{\text{linear}} > W_{3\text{-star}} > W_{2\text{-comb}} > W_{3\text{-comb}} > \dots > W_{n\text{-comb}}$$

(ii) At the same total molecular weight and the same number of branches the degree of branching (as measured by the complexity index  $K$  and the Wiener index  $W$ ) increases with the increase in the branch length up to a maximum value that correspond to a uniform branch/chain length as well as with the more central position and the clustering of branches.

(iii) For a given family of topologically similar branched homologues, molecular complexity is dominated by the effect of total molecular weight, both for the case in which the backbone molecular weight increases (at constant branch MW) and when the branch MW increases (at constant backbone MW).

(iv) A hierarchy of factors influencing complexity was established: number of branches  $\gg$  branch length  $>$  branch centrality  $\approx$  branch clustering  $>$  total molecular weight  $\approx$  backbone molecular weight.

As a result of this hierarchy, the level of structural complexity that for 3-arm star polymers is attained at high molecular weight can be reached by 2-arm and particularly 3-arm combs at much lower molecular weights. Branch length, centrality, and clustering additionally favor this trend. The equivalence in complexity found between 3-arm stars and 2-arm and 3-arm combs could, after specific calibration, be reformulated for modeling of their rheological properties.

Another interesting result of our purely mathematical analysis of branching in polymers (and, more specifically, in polyolefins) is the behavior of the complexity index. It increases dramatically with branch lengths over a relatively narrow range ( $M_{branch}$  up to 2 to 5 kD), then reaching a plateau and eventually decreasing again as the majority of polymer mass is composed of branches. Along with the potential of the  $\log K$ /branch-molecular-weight plots to account for the effect of polymer branching on MW-distributions, one may anticipate that a first principles theory of the entanglement in polymer melts and solutions may emerge along this avenue. Another application of the developed mathematical formalism could be in the area of polymer structure–property relationships, provided a set of model structures is available for validation and calibration.<sup>61</sup> Taking into account that many molecular properties depend strongly on molecular branching,<sup>62</sup> a successful step in this direction would prompt further efforts toward a major goal: to use the identified and quantitatively expressed branching and complexity patterns to control the properties of polyolefins.

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