ELSEVIER

Polymer 43 (2002) 203–222

polymer

www.elsevier.com/locate/polymer

Long chain branch polymer chain dimensions: application of topology to the Zimm–Stockmayer model☆

Danail Bonchev[a,*], Eric J. Markel[b], Armenag H. Dekmezian

[a]*Department of Marine Sciences, Program for Theory of Complex Systems, Texas A & M University, Fort Crockett Campus, 5007 Avenue U, Galveston, TX 77551, USA*
[b]*ExxonMobil Chemical, Baytown Polymers Center, P.O. Box 52000, Baytown, TX 77522, USA*

Abstract

An explicit topological approach to the dimensions of LCB polymers is presented. It is based on the Wiener number, a topological descriptor which is shown in this study to be related to the topological radius of the macromolecule, the mean-square radius of gyration, the *g*-ratio, and the intrinsic viscosity within the Rouse–Zimm range. The new theory enables the treatment of the highly complex hyperbranched polymers, which are difficult to handle by the classical theory of Zimm and Stockmayer. The agreement with the measured *g*-values of model polyethylenes, synthesized by Hadjichristidis et al., is fairly good for star-like polymers and satisfactory for pom–pom type of structures, whereas for crowded comb-type species the calculated *g*-values are underpredicted. Extension of the approach is shown to cyclic structures for which the Kirchhoff number replaces the Wiener number. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Radius of gyration; *g*-Ratio; Wiener number

---

1. Introduction

In their seminal paper 'The Dimensions of Chain Molecules Containing Branches and Rings' [1], Zimm and Stockmayer presented a theory for the mean square radius of various branched and ringed polymer molecules proceeding from a statistical treatment of the polymer chain conformations in θ-solvent. For more than fifty years this theory has been regarded as a paradigm standing at the very heart of polymer science and engineering. (Some recent appeals to reduce the importance of this theory at the expense of some modern ideas, based on scaling and percolation arguments [2], would in our opinion only contribute to a better interplay of the classical and modern theories). One of the major developments in polymer theory during these fifty years was the recognition of the fact that the basic interactions in polymers are topological in nature, i.e. they do not depend on specific chemistry. Eichinger [3–6] and Yang [7] used the mathematical formalism of graph theory [8–10] in the analysis of the radius of gyration of polymers. Both studies proceed from the equivalence of the Rouse and Zimm matrices [11,12] in the theory of viscoelasticity to the adjacency matrix and admittance (or Kirchhoff) matrix in graph theory, and they are centered on solving the eigenvalue problem of these matrices [3–6] and finding the polynomial coefficients [7]. Albeit producing elegant formulas for linear and cyclic polymers, these methods become cumbersome for highly branched systems. It is therefore worthwhile to apply a different graph theoretical technique that would further simplify the description of polymer dimensions. Such is the technique based on the distance matrix of the graph, and *the Wiener number* [13,14], which counts all the distances in the graph. The distance matrix and the Wiener number of graphs have been widely used in characterizing molecular branching and cyclicity as the most essential features of molecular topology [15–19]. The Wiener number is one of the most commonly used topological descriptor of molecular structure with broad applications in areas ranging from drug design and material design to characterization of polymers and crystals [20–26]. Recently, three journals covering the area of theoretical and mathematical chemistry marked by special issues the 50th anniversary of the Wiener number (see e.g. Ref. [27]). The Wiener number is a much more powerful descriptor of polymer topology than the degree of branching [28–30], (defined with respect to the branching in a perfect dendrimer, taken as a standard for

---

☆ This paper was originally submitted to *Computational and Theoretical Polymer Science* and received on 9 January 2001; received in revised form on 9 March 2001; accepted on 14 March 2001. Following the incorporation of *Computational and Theoretical Polymer Science* into *Polymer*, this paper was consequently accepted for publication in *Polymer*.

* Corresponding author.

E-mail address: bonchevd@aol.com (D. Bonchev).

PII: S0032-3861(01)00589-4

maximum branching), which could be the same for polymers with quite different topology [31].

A careful analysis of the Zimm–Stockmayer paper has shown that it uses parameters that are implicitly graph-theoretical ones: branch units for branched graph vertices, and functionality for vertex degree. Moreover, as it will be demonstrated in Section 2, in deriving the formulae of Zimm–Stockmayer theory other intermediate parameters may be interpreted (though not originally identified) as important graph invariants, such as the *vertex distance* (the sum of the integer distances from a vertex to all the other vertices in the graph) and the graph distance, which is the Wiener number itself. Thus, one may qualify the Zimm–Stockmayer theory as an *implicit* topological theory of polymers.

This study presents the fundamentals of an *explicit* topological Zimm–Stockmayer theory. It will be shown that the formulae of the Zimm–Stockmayer theory, as well as new formulae for complex hyperbranched polymers, which are difficult to handle within the classical theory, can be derived on a purely topological basis, proceeding from the distance invariants of three fundamental polymer graphs we introduce. The *random distribution polymer graph* (RDG) is the smallest graph mapping the basic topology of any ensemble of polymers having a given number of branch units, at a variable molar mass, spacer length, branch length and branch position along the polymer backbone (branch centrality). The *uniform polymer graph* (UPG) represents the set of polymers with the same number of branch units *and the same branch lengths* at a variable molar mass, spacer length, and branch centrality. In the *long chain branch graphs* (LCBG) the spacer length is also kept the same but different from the constant branch length. In deriving the formulae for the RDGs we do not introduce any approximations, whereas those for the UPGs and LCBGs are obtained both with and without simplifications. This allowed an evaluation of the effect of the approximations made by Zimm–Stockmayer. The theory presented in this paper is applicable to monodisperse polymers and narrow distribution fractions. This is a necessary preliminary step to understanding polydisperse LCB systems and their molar mass (molecular weight) and branching distributions [32–35].

2. Re-examining the Zimm–Stockmayer formula for the radius of gyration of linear polymers

The Zimm–Stockmayer formula for the mean square distance, X^2, of the rest of the chain from a reference segment is

$$X^2 = (b^2/N)\sum_{i=1}^{N} n_i = (b^2/N)\sum_{i=1}^{N} i \tag{1}$$

where n_i is the number of segments between the reference terminal segment l, and the ith segment, and N is the total number of segments (a segment is defined as a small unit which by repetition may be considered to generate the chain). In deriving Eq. (1) Zimm and Stockmayer proceed from the basic assumption that for flexible chains the mean square distance $\langle x_i^2\rangle$ from the reference segment to any segment i is proportional to the number of segments n_i between them:

$$\langle x_i^2\rangle = b^2 n_i \tag{2}$$

the proportionality constant b being determined by the detailed structure of the chain, especially the length and flexibility of its bonds. It is through Eq. (2) that topology and graph theory become involved because the number of segments n_i may be interpreted as the number of vertices in the graph representing the polymer structure. Eq. (2) makes thus possible the use of the graph theory formalism in reexamining the Zimm–Stockmayer formulae.

After representing the segments by the vertices in the chain graph shown above, Eq. (1) may be reinterpreted and modified as follows:

(i) $n_i = i$ is in fact the integer distance between vertices 1 and i, d_{1i},

(ii) the summation starts with the distance to the second vertex. Thus, the total number of distances is $N-1$;

(iii) the sum itself is a well-known graph invariant called vertex distance [3,4] or distance sum [19], d_{1i}, calculated for the terminal vertex 1 in the linear graph. Dividing by the number of distances $(N-1)$, the average distance $N/2$ of the reference vertex 1 is obtained

$$X^2 = \frac{b^2}{N-1}\sum_{i=1}^{N-1} i = b^2\frac{N}{2}. \tag{3}$$

Eq. (3), derived without any simplifications, coincides with the Zimm–Stockmayer [1] formula (10), which however was obtained by dropping terms of order unity, at which a chance canceling of the dropped terms occurs.

The revisiting of the Zimm–Stockmayer formula for the average mean square distance, $\langle Z^2\rangle$, from the reference segment to the center of mass

$$\langle Z^2\rangle = (2b^2/N^2)\sum_{i=1}^{N}(N-n_i)n_i \tag{4}$$

(i) identifies (for acyclic graphs only) the sum as the well-known graph-invariant termed *graph distance* [8] or *Wiener number*, W [13,14], which for linear graphs (chains) is calculated by the formula

$$W_{\text{chain}} = \sum_{i=1}^{N}(N-n_i)n_i = N(N-1)(N+1)/6 \tag{5}$$

(ii) the correct averaging in this case is to divide by the total number of distances in the graph which is $N(N-1)/2$ (instead of $N^2/2$).

After substituting (i) and (ii) into Eq. (4) one obtains

$$\langle Z^2\rangle = b^2\frac{2N(N-1)(N+1)}{6N(n-1)} = b^2\frac{N+1}{3} \tag{6}$$

instead of the Zimm–Stockmayer approximate result $b^2N/3$.

Combination of these results yields the mean square radius of gyration, r_g^2

$$\langle r_g^2\rangle = X^2 - \langle Z^2\rangle = b^2\frac{N-2}{6} \tag{7}$$

Dividing by the total end-to-end length square distance, $R^2 = b^2(N-1)$, one arrives at the expression

$$\frac{\langle r_g^2\rangle}{R^2} = \frac{1}{6}\frac{N-2}{N-1} \tag{8}$$

the numerical estimate of which shows that the Zimm–Stockmayer value 1/6 is correct to the third decimal point for linear polymers containing more than 1000 segments, which for polyethylenes (assuming the 'segment' of the Zimm–Stockmayer theory to be a synonym of a $-CH_2-CH_2$ group) means more than 2000 carbon atoms or molar mass higher than 30 000. Thus, for precise calculations with *oligomers*, Eq. (8) might be preferred rather than the value 1/6.

For branched species we will not revisit the Zimm–Stockmayer analysis of polymers with one to five branch units, because this analysis strongly relies on the specific choice of a reference segment in the macromolecule. Rather, we will reinterpret the Kramers theorem [36], used in the second part of the Zimm–Stockmayer paper [1], as a general approach to the problem of the macromolecule dimension. To start with we show that there is no need of a specific fragment when one proceeds from our more general concept for the topological radius of a molecule.

3. Topological radius of a molecule. Random distribution polymer graph (RDG)

3.1. Preliminary information on the graph-theoretical formalism

Industrial polymers are a complex mixture of macromolecules with different molar mass and branching, as described by the branch number, length and positioning along the main chain. All this variety makes difficult the calculation and prediction of polymer properties. However, the problem can be greatly alleviated by introducing the concept of the polymer *random distribution graph* (RDG). These graphs present the highest degree of abstract generalization for the variety of random distribution polymers having a constant number of branches. All such polymers irrespective of the length, spacing, and positioning of their branches are modeled by a single connected graph for polymers having up to three branches and by a set of 'isomeric' graphs for polymers with four or more branches for which more than one macromolecule architecture is available. Thus, what is actually preserved in the polymer random distribution graph (RDG) of acyclic polymers is the basic topology, the branching patterns of the polymer skeleton.

In describing polymer topology we proceed from the following definitions:

Definition 1. A graph G is a mathematical structure composed of points called *vertices*, which are connected by lines termed *edges*. *Simple connected graphs* have no isolated vertices, as well as no loops or multiple edges.

Definition 2. A vertex degree, a_i, is the number of edges emanating from the vertex i.

Definition 3. The distance d_{ij} between graph vertices i and j is an integer counting the number of edges along the shortest path between them. The *distance matrix* of a graph, **D(G)** having N vertices is a square NxN matrix symmetric with respect to the main diagonal. The diagonal elements $d_{ii} = 0$.

Definition 4. The graph distance, commonly known as the *Wiener number*, $W(G)$, is the sum of the distances between all pairs of vertices in the graph. It is equal to the half-sum of the distance matrix entries d_{ij}.

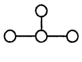
$$W(G) = \frac{1}{2}\sum_{j=1}^{N}\sum_{i=1}^{N} d_{ij} \tag{9}$$

The Wiener number was shown to be an effective measure of the degree of branching of molecular skeleton [15,18].

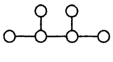
Definition 5. A proper graph is a graph, which contains only two types of vertices–terminal (with vertex degree one) and branched (with vertex degree ≥3) ones.

Definition 6. (New): A random distribution polymer graph (RDG) is a proper graph representing the smallest homomorphic image of each of the polymers in an ensemble of polymers having a constant number of branches, and a variable molar mass, as well as variable length, spacing, and positioning of their branches. (Two structures having the same connectivity are called *homomorphic*.)

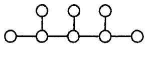
An illustration is shown below with the RDGs of acyclic polymers with one, two, and three branches, as well as with the distance matrix and the Wiener number of RDG(2).



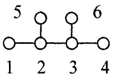
1



2



3



W(**2**) = 29

$$\mathbf{D(2)} = \begin{Vmatrix} 0 & 1 & 2 & 3 & 2 & 3 \\ 1 & 0 & 1 & 2 & 1 & 2 \\ 2 & 1 & 0 & 1 & 2 & 1 \\ 3 & 2 & 1 & 0 & 3 & 2 \\ 2 & 1 & 2 & 3 & 0 & 3 \\ 3 & 2 & 1 & 2 & 3 & 0 \end{Vmatrix}$$

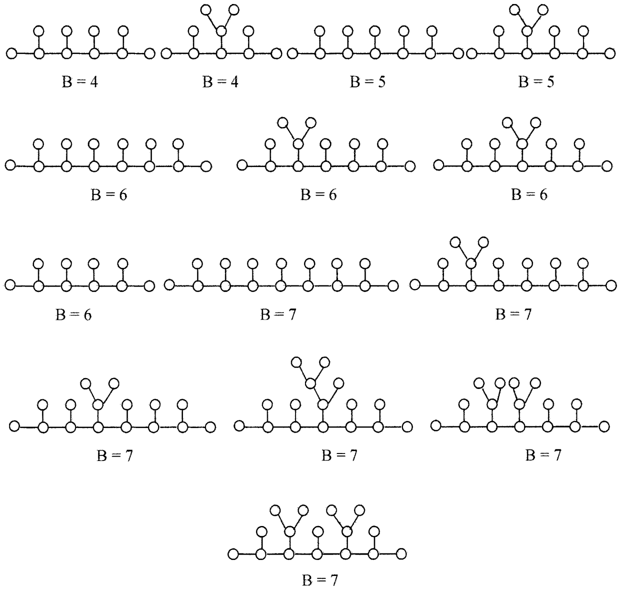


Fig. 1. Isomeric random distribution polymer graphs (RDGs) having four to seven branch units.

Definition 7. (New): *Isomeric random distribution polymer graphs* are nonisomorphic RDGs having the same total number of vertices N and the same number of branched vertices (branch units) B (see Fig. 1).

Definition 8. (New): The topological radius of an acyclic (see Section 9 for a more general definition) macromolecule having N atoms is the average distance in its corresponding polymer graph, i.e. the Wiener number W of the graph divided by the total number of distances in the graph, $N(N-1)/2$:

$$R_{\text{top}} = \frac{2W}{N(N-1)} \tag{10}$$

Definition 9. The normalized Wiener number W' of a graph is the Wiener number W divided by that number W_{lin} of the linear graph having the same number of atoms N:

$$W' = W/W_{\text{lin}} \tag{11}$$

It should be mentioned that the Wiener number of a macromolecule is a polynomial of degree three in the number of vertices [23–26]. Therefore, the topological radius of a macromolecule is linearly proportional to the number of atoms N, whereas the normalized Wiener number W' is a dimensionless number equal to one for linear species and less than one for branched ones.

In earlier applications of graph theory to polymers [23–26] its dimensionless measure of macromolecule branching, W_∞, was introduced. The Wiener number of a polymer homologue series was doubly normalized by dividing it by the total number of distances $N(N-1)/2$ (as in Eq. (10)), and then by dividing by the number of bonds $N-1$. The limit of the ratio of the two polynomials, W_∞, has the meaning of the average topological distance per bond in an infinite macromolecule. It was used as a structural descriptor for the real polymers, correlating highly with different physicochemical properties and electron energies. However, it is only in the present study that the real meaning of the first averaging is understood as defining the topological radius of the (macro)molecule. Moreover, as it will be shown below, the new dimensionless parameter of molecule branching W' has a direct interpretation as the Zimm–Stockmayer branching index g, which defines the dimension of a branched macromolecules relative to that of linear polymer with the same number of atoms.

3.2. Two theorems relating the radius of gyration to the topological radius and the Wiener number of the corresponding polymer graph

Theorem 1. *The mean square radius of gyration* $\langle r_g^2\rangle$ *of a macromolecule containing no atomic rings is linearly proportional to the topological radius of the macromolecule* R_{top}:

$$\langle r_g^2\rangle = b^2 R_{\text{top}}/2 = \frac{b^2 W}{N(N-1)} \tag{12}$$

where the proportionality constant b^2 *has the same meaning as in the Zimm–Stockmayer theory* [1], i.e. it depends on the length and flexibility of the bonds in the structure.

Proof. From Kramers' theorem [36], cited as formula (35) in Ref. [1], the mean square radius of gyration $\langle r_{\text{g}}^2\rangle$ of a macromolecule containing any number of branches but no rings is given by

$$\langle r_{\text{g}}^2\rangle = b^2\langle N_L N_R\rangle_{\text{Av}}/N \tag{13}$$

where N is the total number of atoms, N_{L} and N_{R} are the number of atoms in the left and right fragments, respectively, obtained by cutting the molecule at one bond, and the averaging is taken over all bonds.

Wiener [13] defined his 'path number' W in a similar manner as

$$W = \sum_{\text{all bonds}} N_{\text{L}} N_{\text{R}} \tag{14}$$

(It was only 24 years later that Hosoya [37] proved that for acyclic graphs Eq. (14) is equal to the half-sum of the distance matrix entries, Eq. (9). The proof is briefly as follows: Eq. (9) may be transformed for acyclic graphs into the sum of all paths lengths in the graph, and then be partitioned into the sum of the lengths of the paths traversing each edge, the latter being presented a the products $N_{\text{L}}N_{\text{R}}$.)

Averaging Eq. (14) by dividing by the number of graph edges $N-1$, substituting into Eq. (13), and using Definition 9, one arrives at

$$\langle N_{\text{L}} N_{\text{R}}\rangle_{\text{Av}} = \frac{W}{N-1} \qquad \text{and}$$

$$\langle r_{\text{g}}^2\rangle = \frac{b^2 W}{N(N-1)} = \frac{b^2}{2} R_{\text{top}}$$

which proves the theorem. A general proof and generalization of Theorem 1 is given in Section 9 based on the relation between the Wiener number and the eigenvalues of the Laplacian matrix of the graph. □

Theorem 2. *The normalized mean square radius of gyration of a set of acyclic polymers with a constant number of branch units B and random distribution (r.d.) of molar mass, branch length, and branch position (the Zimm–Stockmayer branching index g) is equal to the normalized Wiener number W' of the random distribution polymer graph for B =1, 2 or 3 and to the average normalized Wiener number $\langle W'\rangle$ of the respective isomeric RDGs with $B \geq 4$.*

$$\textit{for } B = 1,2,3 \qquad g(r.d.) = W'(RDG) \tag{15a}$$

$$\textit{for } B \geq 4 \qquad g(r.d.) = \langle W'\rangle(RDG) \tag{15b}$$

Proof. Equality (15a) follows from Eq. (12) and Definition 8 (Eq. (10)), the constants in which are canceled when applied both to the macromolecules in question and the linear structure having the same number of atoms N.

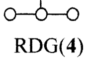
$$g(r.d.) = \frac{\langle r_g^2\rangle}{\langle r_{g,0}^2\rangle} = \frac{W(N)}{W_{\text{lin}}(N)} = \frac{W(RDG)}{W_{\text{lin}}(RDG)} = W'(RDG) \tag{15c}$$

The validity of our Theorem 2 is verified by the mathematical *identity* of the formulas derived by us for W' and those of Zimm and Stockmayer for g of the simplest classes of branched polymers, and by those derived later by Kurata and Fukatsu [38] for the major classes of acyclic polymers. □

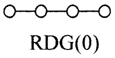
Due to the extremely simple graphical representation of the random distribution polymers, the calculations of g in our approach are also very simple. An example for random distribution 3-arm stars is given below with the Wiener number calculated by Eq. (9) as a sum of distances of different length:

$$\begin{aligned} g_{3\text{-star}}(\text{r.d.}) &= W(\text{RDG}(4))/W(\text{RDG}_{\text{lin}}) \\ &= (3\times 1 + 3\times 2)/(3\times 1 + 2\times 2 + 1\times 3) = 0.9, \end{aligned}$$

where $W(\text{RDG}_{\text{lin}})$ is the Wiener number of the linear graph having the same number of four vertices like RDG(4).



RDG(**4**)

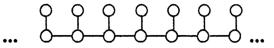


RDG(0)

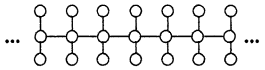
3.3. The g-ratio (the normalized Wiener number) for RDGs having simple branches (first-order branches, 'normal' RDGs)

Consider a random distribution graph with N vertices and B branch units having branches of length one (first-order branches). As stated above, such a graph contains only two types of vertices: terminal vertices of degree one and branched vertices of degree (or *functionality*) f. The three parameters are related by the equation

$$N = B(f-1) + 2 \tag{16}$$



f = 3



f = 4

The general formula for the Wiener number of a RDG having B first-order branch units of functionality f is (see Appendix A):

$$W = B(f^2 - 1) + 1 + \tfrac{1}{6}(f-1)^2 B(B^2 + 6B - 7) \tag{17}$$

The Wiener number is normalized by dividing by the value W_{lin} it has for the chain graph with the same number of vertices. Taking into account the relation (16) between N, B, and f, and the formula (5) for the Wiener number of a path graph, one obtains:

$$\begin{aligned} g = W' &= \frac{W}{W_{\text{lin}}} \\ &= \frac{6[B(f^2-1)+1] + (f-1)^2 B(B-1)(B+7)}{[B(f-1)+1][B(f-1)+2][B(f-1)+3]} \end{aligned} \tag{18}$$

This is a general formula valid for any number of branch units B and any vertex degree (atom functionality) f within the class of polymers having first-order branches (unbranched branches) only. It is a purely topological formula because it does not contain any parameter related to the real metric of polymers. It is important to point out that substituting $B = 1, 2$, and 3 in Eq. (18) produces formulae that are *identical* with the Zimm–Stockmayer [1] formulas (22)–(24) for the normalized radius of gyration g of branched materials with one, two, and three branch units, respectively, distributed at random. For $B > 3$, some numerical data have been presented [1] along with a scheme for their calculation. Analytical expressions for g and radius of gyration models have been presented later by Wales, Marshall, and Weissberg [39], by Orofino [40], Berry and Orofino [41], Kurata and Fukatsu [38], Gordon and Dobson [42–44] and others. The closed-form formula derived by Kurata and Fukatsu [38] is:

$$g(\text{r.d.}) = \frac{6p^2 + (f-1)^2 B(B^2-1)}{p(p+1)(p+2)} \tag{19}$$

where p is the total number of subchains (spacers, branches, and main chain ends):

$$p = N - 1 = (f-1)B + 1 \tag{20}$$

It can be shown that our independently derived Eq. (18)

can be transformed into Eq. (19), and these two formulae produce the same g-values.

Eq. (18) may be used to determine the limit of the g-ratio as approached from above (the upper limit obtained for $B = 1$ is given by the well known values of $g = 0.9$ for $f = 3$ and $g = 0.8$ for $f = 4$):

$$\lim_{B\to\infty} \frac{W}{W_{\mathrm{lin}}} = \lim_{B\to\infty} \frac{B(f^2-1)+1+(f-1)^2B(B-1)(B+7)/6}{[B(f-1)+1][B(f-1)+2][B(f-1)+3]/6} = \frac{(f-1)^2B^3}{(f-1)^3B^3} = \frac{1}{f-1} \tag{21}$$

Corollary 1. The normalized mean square radius of gyration g of random distribution acyclic polymers having only first-order branch units cannot be smaller than 1/2 for branch units of functionality three, and it can not be smaller than 1/3 for branch units of functionality four.

3.4. The g-ratio for polymers having singly-branched branches (first- and second-order branches)

There is more than one random distribution polymer graph for a number of branch units B larger than three, and the variety of such isomeric RDGs increases fast with B. Below, we present the formula derived for the RDGs with any number of singly-branched branch units (termed here *second-order branches*) and any functionality f (see Appendix B for details).

$$W(2) = B(f^2-1)+1+\frac{1}{6}(f-1)^2\left[B(B-1)(B+7) - 6\sum_{i=j}^{t} B_i\left(i-1+\sum_{s=j-1}^{i-1} B_s\right)\left(B-i-\sum_{s=j}^{i} B_s\right)\right] \tag{22}$$

In Eq. (22), the positions of the branches along the main chain are denoted by $i, j, k, \ldots, t$, respectively, B_i and B_s denote the number of branched units in the respective branched branches i and s. As seen from Eq. (22), the Wiener number of the polymer random distribution graphs having second-order branches is obtained from the Wiener number of the random distribution graph with the same number of branch units B having first-order branches only (the first two terms in Eq. (22)), with a negative corrective term. Thus, the appearance of second-order branches, which increases the degree of branching of the respective statistical polymers, diminishes the Wiener number, i.e. reduces the normalized radius of gyration g.

Specific cases of Eq. (22), describing the RDGs with one and two branched branches, are given below.

$$W_j = B(f^2-1)+1+\tfrac{1}{6}(f-1)^2[B(B-1)(B+7) - 6B_j(j-1)(B-j-B_j)] \tag{23}$$

$$W_{jk} = B(f^2-1)+1+\tfrac{1}{6}(f-1)^2[B(B-1)(B+7) - 6B_j(j-1)(B-j-B_j) - 6B_k(B_j+k-1) \times (B-k-B_j-B_k)]. \tag{24}$$

In calculating $g = W' = W/W_{\mathrm{lin}}$ of these cases, W_{lin} is taken as used in Eq. (18).

3.5. Ranges of g-values and their averaging

It is easily assessed that when the number of branches is small, the normalized Wiener number varies within a relatively narrow range of values. However, when the number of branches is large, the variety of isomers spans over a very broad range of values. Thus, for functionality-three polymers and $B = 5$, W' ranges only from 0.703 to 0.675; for $B = 15$, the range spans from 0.587 to 0.437; for $B = 50$, the variation is a substantial one (0.529–0.249). In the last two cases, the highly branched isomers strongly dominate thus making the average W' value closer to the lower limit of the respective ranges. These examples

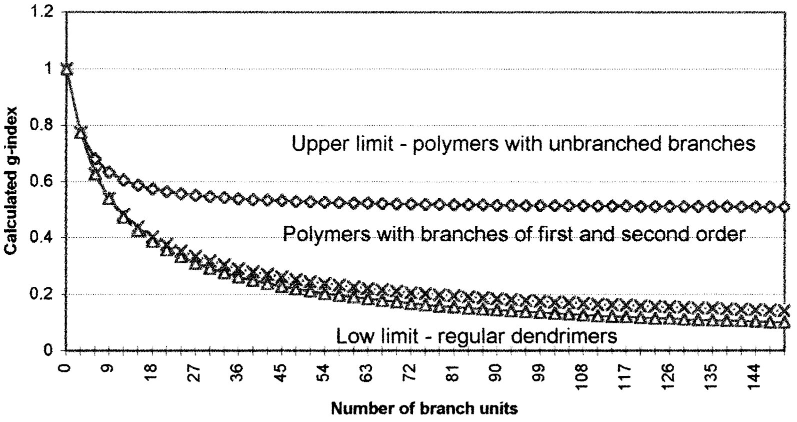


Fig. 2. Ranges of the g-ratio in statistical polymers having up to 150 branch units of functionality three.

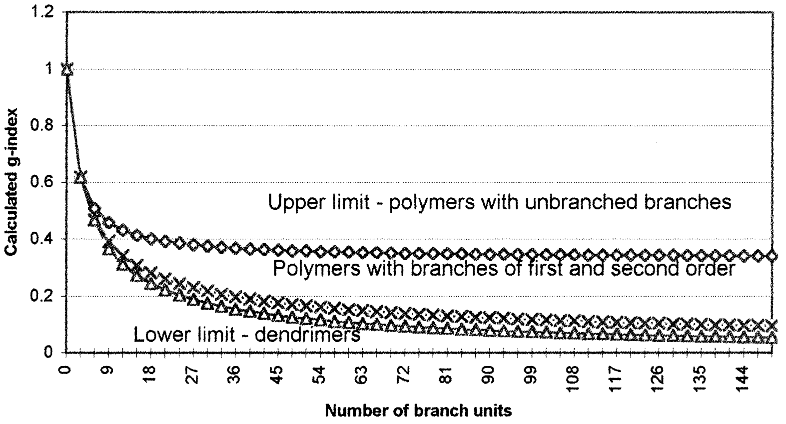


Fig. 3. Ranges of the g-ratio in statistical polymers having up to 150 branch units of functionality four.

emphasize also how strongly topology influences macromolecule size at a constant molecular weight. In full detail the effect of branching on polymer dimension can be evaluated in Figs. 2 and 3 by comparing the two limits of g-values at a given molecular weight.

It may be shown that the limit of the normalized Wiener number for RDGs having branch units of both first and second order is zero. This limit, however, could be reached with an accuracy of 0.001 only in polymers having more than a million branch units. For real-life statistical hyperbranched polymers of functionality three, $W' = g$ is always larger than 0.100 for polymers with less than 250 branch units; it is larger than 0.200 for polymers with less than 80 branch units, and larger than 0.300 for polymers having less than 34 branch units. For hyperbranched polymers having branch units of functionality four, $W' = g$ remains always larger than 0.100 for structures with less than 135 branch units; it is larger than 0.200 for polymers having less than 35 branch units, and larger than 0.300 for polymers having less than 16 branch units.

Detailed information about the ranges of g-values (the normalized Wiener number) is presented in Figs. 2 and 3. The upper limit of these ranges is determined by the values for the RDGs having first-order branches. Two lower limits are shown. The first one refers to polymers having branches of first and second order, as defined above. The absolute lower limit is the one for the dendrimers, the polymers with the highest degree of branching. In the last case, we made use of the formula for the Wiener number of regular dendrimers, derived by Gutman et al. [45]. After expressing the total number of atoms in terms of branching vertex functionality f and the dendrimer radius r (the number of edges from the core vertex to any of the terminal vertices):

$$N = [f(f-1)^r - 2]/(f-2) \tag{25}$$

and after applying Eq. (5), the following g-ratio results for dendrimers:

$$g(\text{dendrimers}) = \frac{6\{(f-1)^{2r}[rf^2 - 2(r+1)f + 1] + 2f(f-1)^r - 1\}}{[(f-1)^r - 1][f(f-1)^r - 2][f(f-1)^r + f - 4]} \tag{26}$$

As seen from Figs. 2 and 3, the g-values for regular dendrimers are lower than the lower limit for the respective polymers having branches of first and second order only. In fact, the dendrimer curves in Figs. 2 and 3 are interpolations from the discrete points obtained by formula (26): for $f = 3$, and generation radius $r = 1$ to 5, $g = 0.900$, 0.709, 0.513,

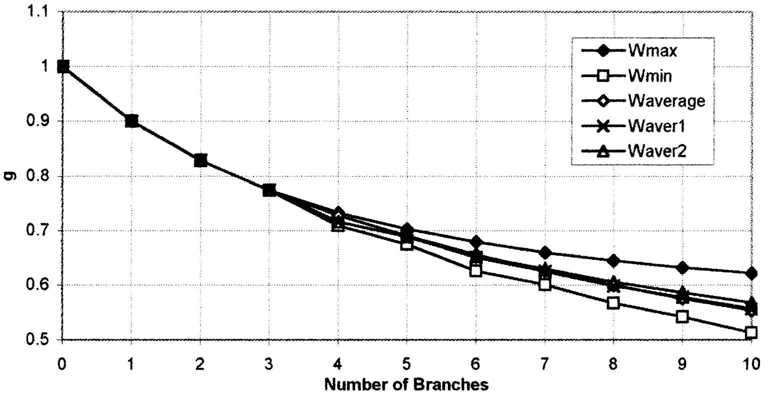


Fig. 4. Ranges and average values of g-ratio for statistical polymers having 0–10 branch units of functionality three.

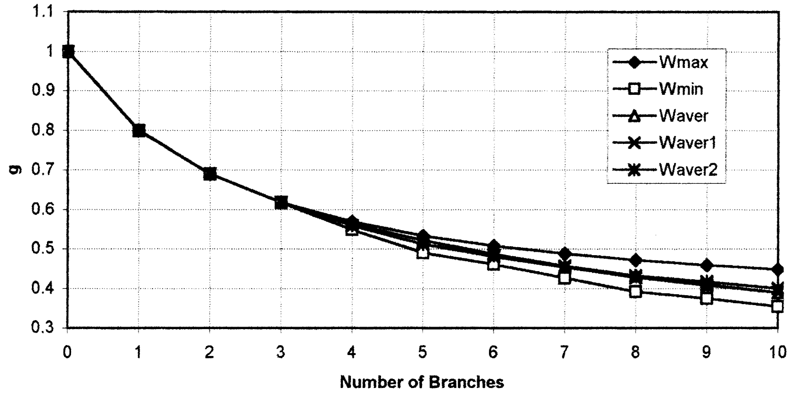


Fig. 5. Ranges and averages values of g-ratio for statistical polymers having 0–10 branch units of functionality four.

0.349, and 0.226; and for $f = 4$, $g = 0.800$, 0.490, 0.254, 0.118, 0.051, respectively.

Figs. 4 and 5 contain some information on the averaging of the g-index in statistical polymers. Three different average values are presented and compared: the first average makes use of specified isomer ratios based on the RDG symmetry, the second one is an arithmetic mean of the values for all isomers, and the third estimate is the median of the lower and upper g-boundaries. As shown in these figures, the difference between the first two estimates decreases and at 10 branch units it disappears for the polymers with tetrafunctional units, while remaining negligibly small (0.003) for those with $f = 3$. This trend allows one to avoid for $B > 10$ the calculation of isomer concentrations (ratios) and to proceed with the arithmetic mean of the g-values of isomers only. The third average deviates from the first two when the number of branches exceeds eight.

3.6. Polymers having branches of third and higher order

The emergence of branches on branched branches diminishes further the Wiener number as compared to a parent isomeric structure having only branches of first and second order at the same total number of branch units B, the same number B_j of branch units in the branch j. The formula for these complex cases can be presented by subtracting from Eq. (22) a corrective term C_j for each third order branch at the first order branch j:

$$W'(\text{3rd order}) = W'(\text{2nd order}) - \sum_j \Delta W'(C_j) \tag{27}$$

The formula for the ΔC_j term is derived in Appendix C. The same strategy can be followed for polymers having branches of any higher order. Thus, for the RDGs with fourth order branches, the formula for W' can be obtained from Eq. (27) with an additional corrective term $\Delta W'(C_{j'})$ for each fourth order branch starting with vertex j' of the second order branch. If fourth order branches are available at different j's, each one is accounted for by a separate $C_j{}'$ term, etc.

$$W'(\text{4th order}) = W'(\text{3rd order}) + \sum_j \Delta W'(C_{j'}) \tag{28}$$

Eqs. (27) and (28) show the way to calculate the Wiener number of the random distribution polymer graphs with any degree of branching. The formulas may be applied to generate a standard table with $W' = g$ values of branched polymers, as well as for the change in the Wiener number upon a recursive procedure of generating RDGs with an increasing number of branch units. Due to the very complex architecture of such hyperbranched polymers, the formulae for the Wiener number also become rather complex. However, the calculation of the Wiener number and g of *individual* isomers makes sense only up to a certain limited number of branches B, because not only complexity of macromolecules increases rapidly with B but so does the number of isomeric species. Due to this, *average* estimates of g for higher levels of branching are needed. In Figs. 4 and 5 we have already shown such estimates obtained from the calculations of all individual species having up to 10 branch units.

The calculation of average g values for larger number of branches requires a different approach. Such an approach based on generating series has been developed recently [46] for calculating the average values of molecular properties. Calculations of the Wiener number have been performed up to a hundred branch units of functionality three and four [47]. In the present study, the average Wiener numbers from [47] were used as a basis in calculating the average g values, with the Wiener number of the corresponding linear polymer used as a normalizing factor. The results are shown in Table 1. For $B = 4 - 10$ the values in Table 1 are the average g-values of the individual isomeric structures calculated according to our formulae. In the averaging, the generation probabilities of each species was taken into account. When the averaging is done as an arithmetic mean, as for all other data in Table 1, the values obtained diverge slightly from the more exact averages: for $B = 4 - 10$ and $f = 3$ these are 0.721, 0.689, 0.651, 0.625, 0.599, 0.579, 0.557, and for $f = 4$ they are correspondingly 0.558, 0.512, 0.481, 0.453, 0.428, 0.407, and 0.390. As seen from the comparison with Table 1, for $f = 4$ the difference vanishes at $B = 10$, whereas for $f = 3$ and $B = 10$ it is reduced to 0.003. Evidently, for $B > 10$ the averaged g-values produced by the generating function method are accurate enough and

Table 1
Average g-values of random distribution polymers having up to 101 branch units obtained by using generation functions

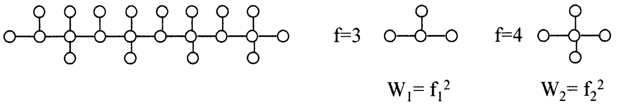
B	g ($f = 3$)	g ($f = 4$)	B	g ($f = 3$)	g ($f = 4$)	B	g ($f = 3$)	g ($f = 4$)
1	0.900	0.800	35	0.347	0.2199	69	0.259	0.157
2	0.829	0.690	36	0.343	0.2166	70	0.257	0.156
3	0.774	0.6188	37	0.339	0.2144	71	0.255	0.155
4	0.728	0.5644	38	0.335	0.2111	72	0.254	0.154
5	0.690	0.5222	39	0.332	0.2088	73	0.252	0.153
6	0.656	0.4877	40	0.328	0.2066	74	0.251	0.152
7	0.626	0.4577	41	0.325	0.2033	75	0.249	0.151
8	0.600	0.4322	42	0.321	0.2011	76	0.248	0.150
9	0.576	0.4101	43	0.318	0.1988	77	0.246	0.149
10	0.554	0.3909	44	0.315	0.1966	78	0.245	0.148
11	0.539	0.3744	45	0.312	0.1944	79	0.243	0.147
12	0.524	0.3606	46	0.309	0.1922	80	0.242	0.146
13	0.510	0.3488	47	0.306	0.1909	81	0.241	0.145
14	0.497	0.3366	48	0.303	0.1888	82	0.239	0.144
15	0.485	0.3266	49	0.301	0.1866	83	0.238	0.143
16	0.473	0.3177	50	0.298	0.1844	84	0.237	0.143
17	0.463	0.3088	51	0.295	0.1833	85	0.235	0.142
18	0.453	0.3003	52	0.293	0.1811	86	0.234	0.141
19	0.444	0.2933	53	0.291	0.1799	87	0.233	0.140
20	0.435	0.2866	54	0.288	0.1788	88	0.232	0.139
21	0.427	0.2808	55	0.286	0.1766	89	0.231	0.139
22	0.419	0.2744	56	0.284	0.1744	90	0.229	0.138
23	0.412	0.2688	57	0.281	0.1733	91	0.228	0.137
24	0.405	0.2633	58	0.279	0.1711	92	0.227	0.136
25	0.398	0.2588	59	0.277	0.1707	93	0.226	0.136
26	0.392	0.2533	60	0.275	0.1699	94	0.225	0.135
27	0.386	0.2488	61	0.273	0.1677	95	0.224	0.134
28	0.381	0.2444	62	0.271	0.1666	96	0.223	0.133
29	0.375	0.2404	63	0.269	0.1644	97	0.222	0.133
30	0.370	0.2366	64	0.267	0.1633	98	0.221	0.132
31	0.365	0.2333	65	0.265	0.1622	99	0.220	0.131
32	0.360	0.2299	66	0.264	0.1611	100	0.219	0.131
33	0.356	0.2266	67	0.262	0.1606	101	0.218	0.130
34	0.351	0.2222	68	0.260	0.1588			

there is no need to calculate the values of the numerous individual isomers.

4. Acyclic statistical polymers with mixed functionalities

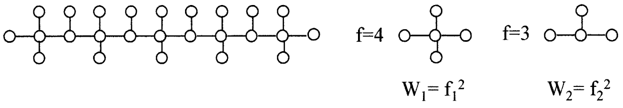
The Zimm–Stockmayer theory [1] does not offer formulas for mixed branching types. We present explicit formulas for a regular mixing of B branch units with two different functionalities f_1 and f_2. The examples given deal with the most common functionalities, $f = 3$ and $f = 4$.

4.1. Even number of first-order branches



$$W(B\text{-even}) = \frac{B}{2}(f_1^2 + f_2^2) - (B - 1) + \frac{1}{12}(f_1 - 1)(f_2 - 1)B(B^2 + 6B + 2) + \frac{1}{24}[(f_1 - 1)^2 + (f_2 - 1)^2]B(B - 2)(B + 8). \quad (29)$$

4.2. Odd number of first-order branches



$$W(B\text{-odd}) = \frac{B + 1}{2}f_1^2 + \frac{B - 1}{2}f_2^2 - (B - 1) + \frac{1}{12}(f_1 - 1) \times (f_2 - 1)(B - 1)(B + 1)(B + 6) + \frac{1}{24}(f_1 - 1)^2(B - 1) \times (B + 1)(B + 9) + (f_2 - 1)^2(B - 1)(B - 3)(B + 7). \quad (30)$$

Eqs. (29) and (30) reduce to Eq. (17) for the case of (normal) single branching type with $f_1 = f_2$.

In order to calculate the normalized Wiener index we present below the formulae for the Wiener number of the linear chain with the same total number of vertices as that of the even and odd normal polymers with mixed functionalities.

$$W_{lin}(B\text{-even}) = (5B + 2)(5B + 4)(5B + 6)/48 \quad (31)$$

The class of polymers with mixed branching and an odd

Table 2
The calculated g-ratio (the normalized Wiener number) of normal even and odd acyclic polymers with regularly mixed branching functionalities (the meaning of a 'normal' polymer here is the same as in Section 3, i.e. these are polymers having first-order branches only)

Number of branch units	Functionalities of branch units	$W' = g$
2	3,4	0.750
3	3,4,3	0.700
	4,3,4	0.673
4	3,4,3,4	0.640
5	3,4,3,4,3	0.613
	4,3,4,3,4	0.600
6	3,4,3,4,3,4	0.581

number of branch units divides into two subclasses depending on whether the terminal branch unit has a functionality larger than that of the next-to-terminal one or vice versa: for $f_1^2 < f_2^2$, $n' = (5B+3)/2$, and for $f_1^2 > f_2^2$, $n'' = (5B+5)/2$.

$$W'_{\mathrm{lin}}(B\text{-odd}) = (5B+1)(5B+3)(5B+5)/48 \tag{32}$$

$$W''_{\mathrm{lin}}(B\text{-odd}) = (5B+3)(5B+5)(5B+7)/48 \tag{33}$$

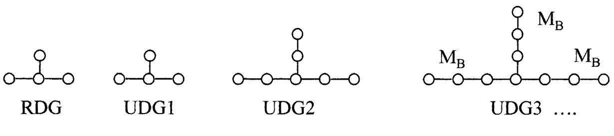
From Eqs. (29)–(33), one can directly calculate the normalized Wiener index for the examined cases of 'normal' polymer with mixed branching. According to our Theorem 1, the values obtained are equal to those of the radius of gyration g, averaged over a random distribution of branch lengths and positions along the polymer backbone. The numerical results are presented in Table 2.

5. The concept of uniform distribution graph (UDG) and its relation to the polymers having equal chain lengths

The class of polymers having equal chain lengths [1], called also *uniform distribution polymers* [38], is modeled by another type of polymer graphs.

Definition 10. The uniform distribution polymer grap (UDG) with N vertices is a symmetric graph having all chains (branches, branch spacers, and chain ends) of equal length l edges (or of equal molar mass M_1).

A set of UDGs corresponding to one RDG is shown below.

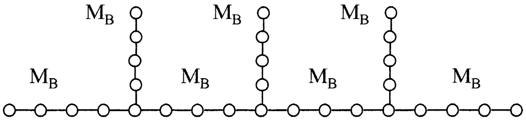


The UDG differs from the random distribution polymer graph (RDG) in having one more structural variable in addition to the number of branch units B and functionality f. This is the size of the chains l, which varies depending on the number of unbranched vertices of degree two the chain contains. (Such vertices are not allowed in the RDGs, which characterize the most general topological properties of polymers.)

The following relations exist between the UDG parameters (M and M_B are the total mass and the mass of a single chain, respectively):

$$N = [(f-1)B+1]l + 1; \qquad l = (M_B - 2)/14; \qquad N = (M-2)/14. \tag{34}$$

Example:



B = 3, f = 3, l = 4, N = 29, M$_B$= 57

Theorem 1, proved in Section 3, can be applied to uniform distribution polymer graphs as well: The mean square radius of gyration $< r_g^2 >$ of a set of macromolecules having no rings whereas having a uniform number of branch units and equal chain length (e.c.l), is proportional to the mean topological radius R_{top} of the uniform distribution polymer graph of these macromolecules:

$$\left\langle r_g^2(\text{e.c.l.})\right\rangle = b^2 R_{\mathrm{top}}/2 \tag{35}$$

Theorem 3. *The Zimm–Stockmayer g-ratio of acyclic statistical polymers having a constant number B of branch units and equal chain lengths (e.c.l) is equal to the normalized Wiener number* $W' = W/W_{\mathrm{lin}}$ *of the corresponding uniform distribution polymer graph (UDG).*

$$\text{for } B \le 3 \qquad g(\text{e.c.l.}) = W'(UDG) \tag{36a}$$

$$\text{for } B > 3 \qquad g(\text{e.c.l.}) = <W'>(UDG) \tag{36b}$$

□

The proof of Theorem 3 is analogous to that of Theorem 2, Section 3. Below, we present a general formula (derived in Appendix D) for the Wiener number permitting a calculation of g(e.c.l.) for any number and length of the branches, as well as for any functionality of the branch units in this class of polymers.

$$\begin{aligned} W(\mathrm{UDG}) = {} & \frac{1}{12\times 14^3}(M_B - 2)\{(M_B+12)(6M - 4M_B - 32) \\ & \times[(f-1)B+1] + (M_B-2)(B-1)(B+1)(f-1) \\ & \times[3(M-M_B) - B(f-1)(M_B-2) - 42]\}. \end{aligned} \tag{37}$$

For polymers, Eq. (37) may be simplified by neglecting the terms of order unity and those of order ten, which are small relative to M and M_1

$$W(\mathrm{UDG}) \approx \frac{M_\mathrm{B}^3}{6\times 14^3}[B^3(f-1)^2 + 3B^2(f-1)^2 - B \times (f-1)(f-5) + 1] \quad (38)$$

To normalize W(UDG) we divide it to the Wiener number of the linear graph having the same number of vertices N:

$$W_\mathrm{lin}(\mathrm{UDG}) = \frac{1}{6}(N^3 - N) = \frac{[(f-1)B+1]^3 M_\mathrm{B}^3 - 196[(f-1)B+1]M_\mathrm{B}}{6\times 14^3} \approx \frac{M_\mathrm{B}^3[(f-1)B+1]^3}{6\times 14^3} \quad (39)$$

By dividing Eqs. (39) and (40), and following Theorem 3, we arrive at a result which no more depends on the size of the macromolecule and its branches; it depends on its topology only:

$$g(\mathrm{e.c.l.}) = W'(\mathrm{UDG}) \approx \frac{[B^3(f-1)^2 + 3B^2(f-1)^2 - B(f-1)(f-5) + 1]}{[(f-1)B+1]^3} \quad (40)$$

Simple formulas result for g(e.c.l) for any specific functionality:

$$f = 3 \Rightarrow g(\mathrm{e.c.l.}) = W'(\mathrm{UDG}) = \frac{(4B^3 + 12B^2 + 4B + 1)}{(2B+1)^3} \quad (41)$$

$$f = 4 \Rightarrow g(\mathrm{e.c.l.}) = W'(\mathrm{UDG}) = \frac{(9B^3 + 27B^2 + 3B + 1)}{(3B+1)^3} \quad (42)$$

On the other hand, substituting $B = 1$ in Eq. (40) produces the formula [38] for the g-ratio of uniform (regular) stars:

$$g(\mathrm{star}) = (3f-2)/f^2 \quad (43)$$

The exact, more complicated formula for W' is also obtained from Eq. (37) by dividing it to Eq. (39), thus providing the opportunity to assess the accuracy of Eq. (40) for a wide range of MWs. The analysis shows that Eq. (40) is a limit that is reached with an exact third decimal place at MWs ranging from 6000 to 25000 for polymers having from ten to twenty five branch units of functionality three; for polymers having ten to fifty branch units of functionality three this limit is reached at MW = 30000–100000.

It might be mentioned that Zimm and Stockmayer present formulae (15a), (18) and (19) for polymers having one, two and three branch units only, whereas for more complex molecules their ‘formulas become excessively unwieldy’ [1]. Later, Kurata and Fukatsu [38] derived a general formula:

$$g(\mathrm{e.c.l.}) = \frac{3p-2}{p^2} + \frac{1}{p^3}(f-1)^2 B(B^2-1) \quad (44)$$

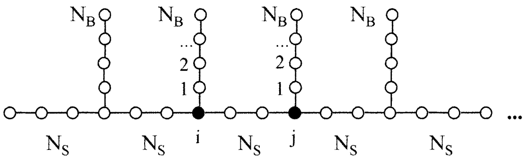
where $p = (f-1)B + 1$ is the total number of chains (spacers, branches, and main chain ends). Our independently derived two-parametric formula (40) can be transformed into the three-parametric Eq. (44).

Eqs. (41) and (42) provide the opportunity to prove the following:

Corollary 2. The Zimm–Stockmayer g-ratio of acyclic statistical polymers having equal chain lengths and unbranched trifunctional and tetrafunctional branch units, cannot be smaller than 1/2 and 1/3, respectively.

The corollary follows directly from Eqs. (41) and (42) for $B \gg 1$, in which case only the ratios of the third power coefficients remain.

6. The long chain branch graph (LCBG) for acyclic polymers having a variable ratio of the branch length and spacer length



The comb-like long-chain branch polymers are synthesized with the same branch length N_B and a random distribution of the spacing between the branch points. A generally accepted model assumes the same spacer length N_S, and uses the branch/spacer length ratio $a = N_\mathrm{B}/N_\mathrm{S}$ as a basic parameter. Formulae for g of this class of polymers have been obtained by Berry and Orofino [41]. Our topological description of these polymers proceeds from a graph having B branching points of degree f, as well as having branches and spacers with N_B and N_S vertices, respectively. Such a graph, shown above may be called *long chain branch graph* (LCBG).

We derived a formula for the Wiener number of such a polymeric macromolecule (see Appendix E):

$$W_\mathrm{comb}(f,B,a,N_\mathrm{S}) = N_\mathrm{S}^3\{(B+1)^3 + aB(f-2)[a^2 + (B+1) \times (2B+3a+1) + a(f-2)(B-1)(3a+B+1) + 3a^2(f-3)]/6\}. \quad (45)$$

Denoting the total number N of vertices in *LCBG* by

$$N = (B+1)N_\mathrm{S} + (f-2)N_\mathrm{S} = N_\mathrm{S}[B + 1 + aB(f-2)] \quad (46)$$

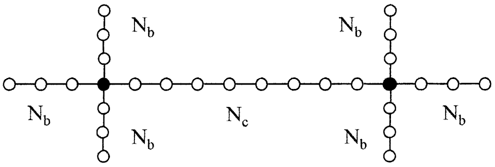
and applying Eq. (5) for the Wiener number of a linear polymer with $N_S \gg 1$, one obtains the formula for the normalized Wiener number or for its equivalent, the g-ratio:

$$g(\mathrm{LCBG}) = \frac{(B+1)^3 + aB(f-2)[a^2 + (B+1)(2B+3a+1) + a(f-2)(B-1)(3a+B+1) + 3a^2(f-3)]}{[a(f-2)B+B+1]^3} \quad (47)$$

For $a = 1$ ($N_S = N_B$), Eq. (47) reduces to Eq. (41). It can be shown that Eq. (47) is equivalent to Berry and Orofino's [41] Eq. (22), and these two equations produce the same g-values.

Figs. 6 and 7 illustrate the trends of variations in the g-ratio with varying parameter a within the 0.1–10 range for polymers having up to 10 branch units of functionality three and four, respectively. Both figures show a sharp decrease in g when the parameter a varies from 0.1 to 1.0. When a continues to grow from 1 to 10, the g-ratio of polymers having more than four branch units decreases, although in a much slower rate. Polymers with two branch units show clearly expressed minimum at 1.20 ($f = 3$) and 1.80 ($f = 4$), respectively. The functionality-three combs with three and four branch points have rather flat minimum, whereas the functionality-four combs with three arms form a plateau. The figures enable a variety of choices for designing polymers with a prescribed g-ratio, e.g. for LCB polymers having branch units of functionality three the value $g = 0.4$ can be obtained from species either having eight branches and branch length/spacer length ratio of 4.6:1 or having nine branches with a 3.6:1 ratio or having ten branches with a 3.1:1 ratio.

7. The Wiener number of $\alpha-\omega$ polymers



These polymers may be regarded as two stars of functionality f and branches of length N_b connected by a linear chain of length N_c. When $N_c = 1$, pom–pom polymers result. This class of polymers is a useful theoretical model because polymer properties converge at short chain to those of a star, whereas for very long chain macromolecules approximate linear polymers. We derived the following formula for the normalized Wiener number $W' = g$:

$$g(\alpha - \omega) = \frac{N_c^2 + 2fN_B[N_B^2(3f-2) + 3(N_c+N_B)(N_c+fN_B)]}{(N_c+2fN_B)^3} \quad (48)$$

It can be shown that Eq. (48) can be transformed into Milner's [48] expression which is given in terms of the mole fraction of the backbone, $k = M_{bb}/\mathrm{MW}$:

$$g(\text{pom–pom}) = k^3 + 3k^2(1-k) + \frac{3(f+1)}{2f}k(1-k)^2 + \frac{3f-1}{2f^2}(1-k)^3 \quad (49)$$

8. Comparison with measured g-ratios

The comparison between theory and experiment became possible after a series of model long chain branched polyethylenes have recently been synthesized by using anionic polymerization techniques, and some of their properties have been measured [49]. In Table 3 we compare the g-values calculated by our theory with the experimental and calculated ones given in reference [49]. In analyzing the results, one should take into account the insufficient accuracy of the measurements, what may be inferred, for

Table 3
Experimental versus calculated g-ratios of some model star, comb, and $\alpha-\omega$ polyethylenes

MW data	g (this paper)	g (measured)[41]	g (calculated)[41]
Stars			
$(27)_3$	0.78	0.78	0.78
$(43)_3$	0.78	0.73	0.78
$(45)_3$	0.78	0.70	0.78
$(49)_3$	0.78	0.76	0.78
$(51)_3$	0.78	0.76	0.78
$(53)_3$	0.78	0.77	0.78
$(50)_2 5$	0.93	0.91	0.93
$(51)_2 5$	0.94	0.91	0.94
$(51)_2 15$	0.85	0.84	0.85
$(51)_2 25$	0.81	0.78	0.81
$(19)_2 83$	0.90	0.96	0.90
$(15)_2 85$	0.90	0.91	0.92
$(40)_2 60$	0.79	0.84	0.79
$\alpha-\omega$ polyethylenes			
$(6)_2 27(6)_2$	0.87	0.94	0.95
$(12)_2 27(12)_2$	0.79	0.90	0.95
$(10)_2 95(10)_2$	0.94	0.97	0.95
$(10)_3 107(10)_3$	0.87	0.94	0.95
$(10)_5 92(10)_5$	0.74	0.80	0.74
Combs			
101-$(7)_{30}$	0.36	0.46	0.31
97-$(23)_{26}$	0.22	0.32	0.25
100-$(5)_2$	0.89	1.00	0.88
100-$(5)_{12}$	0.64	0.70	0.58
100-$(6)_{12}$	0.62	0.75	0.63

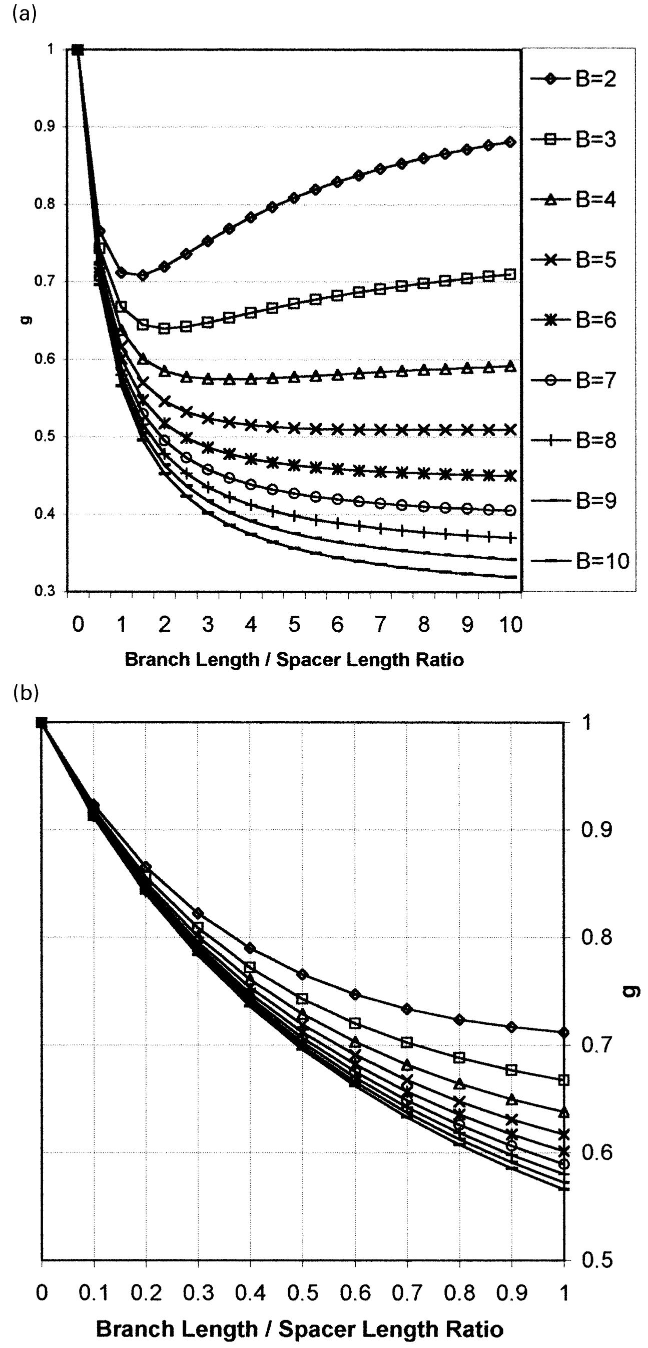


Fig. 6. Variations in the g-values of LCB polymers having 2–10 branch units of functionality three and a variable branch length/spacer length ratio.

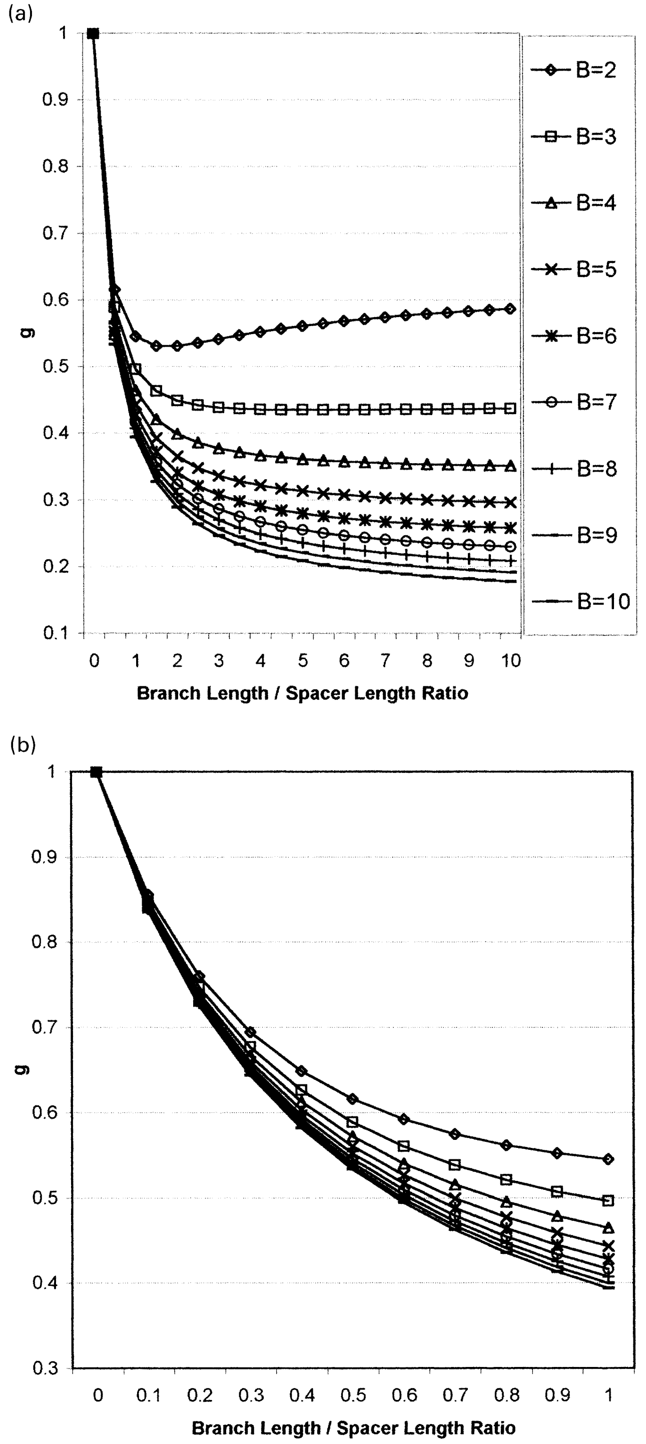


Fig. 7. Variations in the g-values of LCB polymers having 2–10 branch units of functionality four and a variable branch length/spacer length ratio.

example, from the strongly overestimated value $g = 1.00$ for the comb with two branches of MW = 5000 each, as well as from the irregular variations in the g-values for the six symmetrical 3-arm stars. In the light of the above, the agreement between the values calculated by the topological theory and the experimental ones may be assessed as very good for stars and satisfactory for $\alpha-\omega$ polyethylenes. However, for the highly branched combs the calculated values are systematically lower than the experimental ones, as found also in [49]. This finding is not a surprising one, particularly for the highly crowded combs with 26 and 30 arms. Some of the differences between calculated and measured g-values may be due to solvent effects that, to our knowledge, have not been studied in detail with these model polymers.

9. The Wiener number in the viscoelastic theory of polymers of Rouse [11] and Zimm [12]

This paper was almost completed when we were acquainted with the graph theoretical analysis of Eichinger [3–6] and Yang [7] of the bead-and-spring theory of polymer viscoelasticity of Rouse [11] and Zimm [12]. We show below that the Wiener number, though unidentified by these authors, is also contained in the Rouse–Zimm theory of polymers having no cycles, and thus a new light on the significance of the Wiener number for the polymer theory could be shed. In addition, the generalization of our approach is shown to polymers containing rings, for which the Wiener number fails to produce correct results. The extension of the method is based on another important graph invariant, the Kirchhoff number, which for acyclic graphs coincides with the Wiener number. A rigorous proof and generalization of Theorem 1 to molecules containing cycles is thus presented.

The dimensions and viscoelastic properties of polymers are obtained within the Rouse and Zimm bead-and-spring model by finidng the eigenvalues of the Rouse matrix **R** and the Zimm matrix **Z**. The very high rank of these matrices causes difficulties in the solution of the eigenvalue problem for polymers with complicated topology. Eichinger [3–6] has shown in 1980 that the mean-square radius of gyration $\langle r_g^2 \rangle$ of a macromolecule with N atoms can be expressed by the formula:

$$\langle r_g^2 \rangle = \frac{b^2}{N} \sum_{i=1}^{N-1} \frac{1}{\lambda_i} = \frac{b^2}{N} \mathrm{tr}(Z^+) = \frac{b^2}{N} \mathrm{tr}(R^{-1}) \tag{50}$$

where λ_i is the ith eigenvalue of the Zimm matrix, and $\mathbf{Z}^+$ is the Moore–Penrose generalized inverse of the Zimm matrix **Z** (the Zimm matrix contains one zero eigenvalue and has no inverse). $\mathbf{Z}^+$ contains all nonzero eigenvalues of the initial matrix **Z**, which are simultaneously eigenvalues of the Rouse matrix **R**.

In a paper summarizing his work since 1985, Yang [7] emphasized the equivalence of the Rouse and Zimm matrices to the adjacency matrix and admittance (or Kirchhoff) matrix in graph theory, respectively. The Kirchhoff matrix is also called the Laplacian matrix because it is a matrix of a discrete Laplacian operator. (The Laplacian matrix applications in chemistry have been reviewed by Trinajstić and coworkers [50]). This matrix has vertex degrees (or functionalities) as diagonal elements, whereas the off diagonal entries are -1 for neighboring vertices and zero for nonadjacent vertices. Yang developed graph theoretical techniques for solving the eigenvalue problem of the **R** matrix, and proved that the trace of the inverse Rouse matrix can be calculated from the ratio of two of the Rouse polynomial coefficients:

$$a_2/a_1 = -\mathrm{tr}(R^{-1}) \tag{51}$$

This relationship enables the calculation of the chain dimension from the derivatives of the characteristic polynomials without knowing the generalized inverse $\mathbf{Z}^+$, which is difficult to find for polymers with complicated topologies. In the example presented by Yang [10] for the calculation of a_1 and a_2 of the linear chain, the expression for the second coefficient is $N(N-1)(N+1)/6$ which is the well known formula for the Wiener number of linear chains [13,15]. However, it has not been identified by Yang and the opportunity to find the relationship with the Wiener number has thus been missed.

Such simple relationships, however, have already been found *for trees* (*acyclic graphs*) by Mohar [51,52] in 1991:

$$a_2 = (-1)^{N-2} W \tag{52}$$

$$W = N \sum_{i=1}^{N-1} \frac{1}{\lambda_i} \tag{53}$$

Inserting Eq. (53) into Eq. (50) we therefore obtain

$$\langle r_g^2 \rangle = \frac{b^2}{N^2} W \tag{54a}$$

Similar dependence of the mean-square radius of gyration and the Wiener number has recently been obtained by Widmann and Davies [31] for linear polymers only, proceeding from Flory statistical theory [53]. Our formula (54a) is valid for any branched polymer as well, and as shown below it can be generalized so as to include cyclic polymers.

Eq. (54a) just found is almost identical with Eq. (12), the only difference being the denominator $N(N-1)$ instead of N^2. Another unsolved problem was the failure of the Wiener number approach to reproduce the correct radius of gyration of a simple cyclic polymer (3/4 of the $\langle r_g^2 \rangle_{\mathrm{lin}}$ value was obtained instead of the correct 1/2 ratio). The literature search helped to find the missing pieces of the puzzle (amazingly, one of us co-authored in 1994 a paper [54] that could provide an earlier clue).

In 1995, Gutman and coworkers [55] made use of the right-hand side of Eq. (53) as a molecular descriptor *for cyclic graphs* and called it 'quasi-Wiener index', W^*.

$$W^* = -N \sum_{i=1}^{N-1} \frac{1}{\lambda_i} \tag{54b}$$

The correlation between W and W^* has been studied [55] in the case of benzenoid molecules and found to be linear, though not particularly good.

In 1993, Klein and Randić [56] advanced the concept for a new metric imposed on graphs, according to the electrical resistance rules of Kirchhoff. The newly defined distances between graph vertices i and j were termed 'resistance distances', $(rd)_{ij}$. The sum over all resistance distances in the graph has been defined by analogy with the Wiener number, and in a later paper [54] this sum was termed the *Kirchhoff number*, *Kf*. Klein and Randić [56] have also shown that the sum of the resistance distances of a graph

G is proportional to the trace of the generalized inverse $\mathbf{L}^+$ of the Laplacian (Kirchhoff) matrix $\mathbf{L}$:

$$Kf(G) = \sum_{i=1}^{N}\sum_{j=1}^{N}(rd)_{ij} = Ntr(L^+) \tag{55}$$

In 1996, almost simultaneously, Klein and coworkers [57] and Gutman and Mohar [58] have shown the equivalence of the quasi-Wiener number and the Kirchhoff number. The Kirchhoff number for acyclic polymers is equivalent to the Wiener number, because in tree-graphs the resistance distances coincide with the graph distances (the resistances in a series are additive just as the graph distances; it is only in cyclic graphs where resistances in parallel are added according to the inverse-proportional law). More precisely, $Kf = 2W$ because the Kirchhoff number is calculated as the sum of *all* matrix entries of the resistance distance matrix, whereas the Wiener number is defined by Eq. (9) as a sum of the upper-right submatrix of the distance matrix. Therefore, Eq. (54a) for the mean-square radius of gyration of an acyclic structure, can be generalize for species containing cycles as well:

$$\langle r_g^2\rangle = \frac{b^2}{2N^2}Kf \tag{56}$$

The mismatch in the denominator of Eqs. (54a) and (12), (N^2 vs. $N(N-1)$), is now traced down to the fact that Kf is averaged by dividing to the *total* number N^2 of the Kirchhoff matrix entries, whereas the Wiener number is averaged by dividing by $N(N-1)/2$ Eq. (56) also produces the correct value for the radius gyration of monocyclic polymers to be 1/12 of the mean square end-to-end distance of the linear polymer having the same number of non-hydrogen atoms.

This analysis enables the more precise definition of the topological radius of a molecule we presented in Definition 8, and may be regarded as a proof for a generalized Theorem 1 for the relation between the mean-square radius of gyration and the topological radius.

Generalized Definition 8: *The topological radius* of any (macro) molecule having N (non-hydrogen) atoms is the average resistance distance in its molecular graph, i.e. the Kirchhoff number Kf of the graph divided by the total number of entries in the resistance distance matrix:

$$R_{\text{top}} = \frac{Kf}{N^2} \tag{57a}$$

For acyclic structures Eq. (10) thus modifies to

$$R_{\text{top}} = \frac{2W}{N^2} \tag{57b}$$

Generalized Theorem 1. The mean-square radius of gyration of a (macro) molecule is proportional to its topological radius, i.e. it is proportional to the average resistance distance in the corresponding molecular graph:

$$\langle r_g^2\rangle = \frac{b^2}{2}R_{\text{top}} = \frac{b^2Kf}{2N^2} \tag{58}$$

Besides the better elucidation of the topological fundament of the macromolecule dimension, the analysis presented in this section may be extended to the interpretation of viscoelastic properties of polymers. Proceed from the formula relating the zero-shear viscosity, η_0, to the mean-square radius of gyration [59]:

$$\eta_0 = \frac{c\xi}{6}\langle r_g^2\rangle \tag{59}$$

where ξ is the friction coefficient, and c is the number of polymer chains in a unit volume. Inserting Eq. (56) or (54a) into Eq. (59) produces formulae in which the zero-shear viscosity in the Zimm–Rouse range is directly related to the Kirchhoff number, and the Wiener number, respectively:

$$\eta_0 = \frac{cb^2\xi}{12N^2}Kf \tag{60a}$$

and for polymers without atomic rings

$$\eta_0 = \frac{cb^2\xi}{6N^2}W \tag{60b}$$

An approximate relationship, showing that for polymers of equal molecular weight but different topology intrinsic viscosity scales like $W^{3/2}$, has been recently reported by Widmann and Davies [31] proceeding from the Kirkwood and Riseman theory [60]:

$$\eta_0 \propto W^{3/2}/M^4 \tag{61}$$

10. Conclusion

This study started with revealing the implicit topological essence of the Zimm–Stockmayer theory of the dimensions of macromolocules. Introducing the concept of the random distribution polymer graph, as the smallest structure preserving the connectivity of all macromolecules that have a uniform number of branch units, we avoided the tedious and necessarily approximate averaging over molar mass and branch distribution by size and positioning along the polymer backbone. Combining this concept with the definition of the topological radius of a molecule on a graph theoretical basis resulted in an explicit topological theory. The latter rationalizes the calculations of the radius of gyration and the g-ratio of polymers containing no cycles enabling thus the calculations for statistical polymers having any complex branch architecture. As specific cases it reproduces the explicit formulas given for the simpler types of structures in the classical paper of Zimm and Stockmayer [1], and those of Berry and Orofino [41] and Kurata and Fukatsu [38]. The extension of the topological theory to statistical polymers having equal chain length was enabled by another useful concept — that of the uniform distribution polymer graph. The general formulas derived allowed the evaluation of the approximations of the earlier theory. Formulae were obtained for the first time for calculating the *g*-index of hyperbranched polymers with different level of complexity, as well as for calculating the *g*-ratio of polymers having branch units of mixed functionality. LCB polymers with a variable branch length/spacer length raio and model pom–pom polymers were also investigated. The comparison of our theory with the experimental *g*-values of the model star-, comb-, and pom–pom type polyethylenes is satisfactory. The results obtained also confirm the conclusion made recently [49] about the necessity of corrections to the theory of polymer dimensions for highly branched polymer structures.

Combining our approach with recent relevant theoretical work on the properties of the Kirchhoff matrix and the resistance distance matrix [50–58] confirmed the importance of the topological index of Wiener in determining the dimensions of polymers having no rings. In addition, with the use of the Kirchhoff number, the way to extend the method is shown so as to include polymers containing atomic rings. The two topological single number descriptors of the polymer structure, the Wiener number and the Kirchhoff number, were included directly in Rouse–Zimm type equations determining the radius of gyration and zero-shear viscosity of polymers. The use of Wiener's and Kirchhoff's numbers, compared to the eigenvalue- and polynomial-coefficients-based approaches [3–7], has the advantage to enable the deduction of exact general formulas that include very wide classes of polymers with complex topology. The extension to other viscoelastic properties is also possible and is a part of our ongoing project. These results, supplementing the important previous work of Eichinger [3–6], Yang [10], and Widmann and Davies [31], indicate the feasibility of a 'first principle' theory of polymer dynamics based entirely on polymer topology.

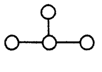
Finding some answers in this study has also prompted us to ask two very general questions that go beyond polymer science and chemistry. The first one is about the real meaning of molecular topology. How is it possible that a simple 4-vertex graph can successfully model the radius of gyration and *g*-ratio of statistical starlike polymers with any possible size and configuration? Is topology nothing else than an averaged metric? The second question is related to the metric itself. The Wiener number is based on a 'constant' metric; the distance between two neighboring points in this metric is always the same. In case of molecules containing cycles, however, the Wiener number fails and has to be replaced by the Kirchhoff number, which is the sum of 'resistance' distances that are no more constant but depend on the molecule as a whole. Is then the space metric only a specific case of a more general metric, based on the electrical resistance rules of Kirchhoff, and if the answer were 'Yes' what would that mean?

Acknowledgements

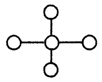
The authors are indebted to Dr P. Jiang, and Dr T. Sun (ExxonMobil Chemical, Baytown) for the acquaintance with the publications of Yang [7] and Kurata and Fukatsu [38], respectively. The constructive remarks of the referees are gratefully acknowledged.

Appendix A. Derivation of the formula for the Wiener number of random distribution polymer graphs (RDG) having branches of first order

The general formula for the Wiener number of a RDG having *B* first-order branch units of functionality *f* can be obtained proceeding from the Wiener number of the respective random distribution graphs having one branch unit:



$W_1 = 3.1 + 3.2 = 9$



$W_1 = 4.1 + 6.2 = 16$

Both cases can be described by the simple formula

$$W_1 = f \times 1 + \frac{f(f-1)}{2} \times 2 = f^2 \tag{A1}$$

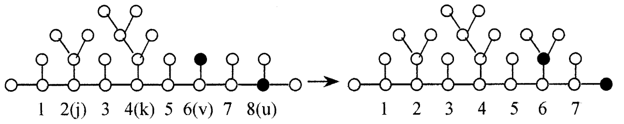
In calculating the Wiener number for *B* branch units, the sum of all ones and twos will be $BW_1 - (B-1) = Bf^2 - (B-1) = B(f^2-1)+1$. The number of distances three, four, etc., calculated between two branch units will be $(f-1)^2$. For a graph with *B* branch units, the number of the distances larger than two will be found by multiplying the $(f-1)^2$ factors by the number of pairs of branch units between which such distances occur. There are $(B-1)$ such pairs for distances three, $(B-2)$ pairs for distances four, etc. Therefore,

$$\begin{aligned} W &= B(f^2-1)+1+(f-1)^2[(B-1)\times 3+(B-2)\times 4 \\ &\quad + \cdots + 1\times(B+1)] \\ &= B(f^2-1)+1+(f-1)^2\sum_{i=3}^{B+1} i(B-i+2) \\ &= B(f^2-1)+1+\frac{1}{6}(f-1)^2B(B^2+6B-7) \end{aligned} \tag{A2}$$

Appendix B. Derivation of the formula for the Wiener number of random distribution polymer graphs (RDG) having branches of first and second order

We proceed from a theorem proved in 1990 by Polansky and Bonchev [14]. According to this theorem, if we transfer a subgraph in a graph from a terminal vertex *u* to a vertex *v*, the change in the Wiener number of the graph upon the transfer equals the product of the number of vertices n_{11} in the transferred subgraph and the difference in the distance numbers d_v and d_u of vertices v and u respectively.

Example:



B=11; f=3; B_j=1; B_k=2; B_v(final) = 1; u > v > k > j ; u = B - B_j - B_k - B_v+1

$$\Delta W = n_{11}(d_v - d_u) \tag{B1}$$

$$d_u = 1 + (f-1) \times \left[\sum_{i=2}^{u} i + \sum_{i=1}^{B_j} (u - j + 1 + i) + \sum_{i=1}^{B_k} (u - k + 1 + i) \right] \tag{B2}$$

$$d_v = 1 + (f-1)\left[2 + \sum_{i=3}^{v+1} i + \sum_{i=3}^{u-v+1} i + \sum_{i=1}^{B_j} (v - j + 2 + i) + \sum_{i=1}^{B_k} (v - k + 2 + i \right] \tag{B3}$$

From Eqs. (B1)–(B3), as well as substituting $n_{11} = B_v(f-1)$, one arrive at

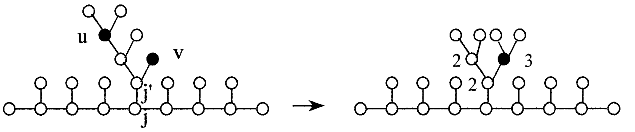
$$\Delta W = -B_v(f-1)^2(B_j + B_k + v - 1)(B - B_j - B_k - B_v - v) \tag{B4}$$

or, more generally;

$$\Delta W = -(f-1)^2 \sum_{i=j}^{t} B_i(i - 1 + \sum_{s=j-1}^{i-1} B_s)(B - i - \sum_{s=j}^{i} B_s) \Bigg] \tag{B5}$$

where t is the number of branched vertices along the main chain. From here, adding ΔW to the Wiener number of the normal RDG (Eq. (17)), one arrives at formula (22).

Appendix C. Derivation of the formula for the Wiener number of random distribution polymer graphs (RDG) having branches of third and fourth order



Seven first-order branches and three second-order branches

Two second-order branches and one third-order branch

We proceeded from the Polansky–Bonchev theorem [14] (See Eq. (B1) in Appendix B), and described the macromolecule with a third order branch as obtained from a parent structure having branches of only first and second order after transferring t atoms from a second order branch j between two points u and v of this branch. Denote by j' the branching point on branch j at which the third order branch is attached. The difference in the distance d_v and d_u of vertices v and u is composed of two types of components. The first one is characterized by a constant difference $\Delta_1 = d_{uj'} - d_{vj'}$ between the distances from u and from v to all vertices not belonging to the branch j, as well as to all vertices from the branch j that are between j and j' (including j'). Therefore one needs only to multiply Δ_1 by the number of these vertices, which is $n - (f-1)k_j$, k_j being the number of branched vertices between u and v, excluding vertex j', as well as excluding vertices u and v; n is the total number of vertices diminished by $t + 2$ (vertices u and v and the transferred vertices t are excluded). The second component of $\Delta W'$ (C_j) accounts for the difference in the distances between the pairs of vertices u, k and v, k, where $k \neq j'$ is a branched vertex belonging to the path uv. The same difference $d_{uk} - d_{vk}$ characterizes the $f - 2$ single-vertex branches attached to vertex k. One thus arrives at the formula:

$$\Delta W'(C_j) = t(d_u - d_v) = t\left\{ (d_{uj'} - d_{vj'})[n - (f-1)k_j] + (f-1) \sum_{k=j'+1}^{u-1} (d_{uk} - d_{vk}) \right\} \tag{C1}$$

For the example shown, $n = 18$, $t = 2$, $k_j = 1$, $d_{j'v} = 1$, $d_{j'u} = 2$, wherefrom $\Delta W'(C_j) = 28$ results. By dividing Eq. (28) by the Wiener number of the corresponding linear isomer with $n = 18$, the correction for g is obtained ($\Delta g = -0.029$).

Appendix D. Derivation of the formula for the Wiener number of acyclic statistical comb-like polymers having arms of uniform length

In deriving the formula for the Wiener number of a UDG, representing this class of polymers, we consider it composed by contributions from the UDG *shell*, including all branches and chain ends, and contributions from the UDG *core*, which incorporates the rest of the main chain. These two terms were calculated by the procedure used by Wiener [12] namely, by summing over all bonds the products of the total number of vertices, N_L and N_R, in the left and right molecular fragments the current bond connects.

$$W(\mathrm{UDG}) = \sum_{\text{all edges}} N_{\mathrm{L}} N_{\mathrm{R}} = W_{\mathrm{shell}} + W_{\mathrm{core}}$$

$$= [(f-2)B+2]\sum_{i=1}^{l} i(N-1)$$

$$+ 2\sum_{j=1}^{(B-1)/2}\sum_{i=1}^{l}[j(f-1)l+i][N-j(f-1)l-i]$$

$$= \frac{1}{12} l\{2(l+1)[(f-1)B+1](3N-2l-1)$$

$$+ l(B-1)(B+1)(f-1)[3N-Bl(f-l)$$

$$-3l-3]\} \qquad \text{(D1)}$$

Substituting l and N from Eq. (34) into Eq. (D1) one obtains the explicit formula for the Wiener number of an UDG in terms of molar mass of the equal chains M_B, the total molar mass M, the number of branch units B, and their functionalities f.:

$$W(\mathrm{UDG}) = \frac{1}{12\times 14^3}(M_{\mathrm{B}}-2)\{(M_{\mathrm{B}}+12)(6M-4M_{\mathrm{B}}-32)$$

$$\times[(f-1)B+1] + (M_{\mathrm{B}}-2)(B-1)(B+1)(f-1)$$

$$\times[3(M-M_{\mathrm{B}}) - B(f-1)(M_{\mathrm{B}}-2) - 42]\} \qquad \text{(D2)}$$

Appendix E. Derivation of the formula for the Wiener number of acyclic statistical comb-like polymers having a variable branch length/spacer length ratio

Denote the constant branch length by N_{B}, the constant spacer length by N_{S}. Their ratio a, the total number of atoms N, and the number of atoms in the main polymer chain N_{C} are then expressed as

$$N_{\mathrm{C}} = (B+1)N_{\mathrm{S}};$$

$$N = (B+1)N_{\mathrm{S}} + (f-2)BN_{\mathrm{B}} = N_{\mathrm{S}}[B+1+(f-2)aB];$$

$$a = N_{\mathrm{B}}/N_{\mathrm{S}} \qquad \text{(E1)}$$

The Wiener number of such a comb can be calculated as a sum of four terms accounting for the LCBG graph distances within the main chain, W_{c}, within the branches, W_{b}, as well as between the vertices of the main chain and the branches, $W_{\mathrm{c/b}}$, and between the vertices of different branches, $W_{\mathrm{b/b}}$:

$$W_{\mathrm{comb}}(f,B,a) = W_{\mathrm{c}} + W_{\mathrm{b}} + W_{\mathrm{c/b}} + W_{\mathrm{b/b}} \qquad \text{(E2)}$$

The first two terms in Eq. (E2) can be readily calculated by using the formula (5) for the Wiener number of a linear graph, and neglecting terms of order unity:

$$W_{\mathrm{c}} = N_{\mathrm{C}}(N_{\mathrm{C}}-1)(N_{\mathrm{C}}+1)/6 \approx N_{\mathrm{C}}^3/6 = (B+1)^3 N_{\mathrm{S}}^3/6 \qquad \text{(E3)}$$

$$W_{\mathrm{b}} = (f-2)BW_{\mathrm{b},i} = (f-2)BN_{\mathrm{B}}(N_{\mathrm{B}}-1)(N_{\mathrm{B}}+1)/6$$

$$= (f-2)BN_{\mathrm{B}}^3/6 = (f-2)Ba^3N_{\mathrm{S}}^3/6 \qquad \text{(E4)}$$

The third term may be presented as the sum of distances between the main chain vertices and those of the $(f-2)$ branches attached to each branch vertex:

$$W_{\mathrm{c/b}} = (f-2)\sum_{i=1}^{B} W_{\mathrm{c/b},i} = (f-2)\sum_{i=1}^{B}\{D_{ii} + (D_{ii}+N_{\mathrm{C}})$$

$$+ (D_{ii}+2N_{\mathrm{C}}) + \cdots + [D_{ii} + (N_{\mathrm{B}}-1)N_{\mathrm{C}}]\}$$

$$= (f-2)\sum_{i=1}^{B}\left[\left(D_{ii}N_{\mathrm{B}} + N_{\mathrm{C}}\sum_{j=1}^{N_{\mathrm{B}}-1} j\right)\right]$$

$$= (f-2)\sum_{i=1}^{B}[N_{\mathrm{B}}D_{ii} + N_{\mathrm{C}}N_{\mathrm{B}}(N_{\mathrm{B}}-1)/2] \qquad \text{(E5)}$$

where the D_{ii} term describes the sum of distances between the first vertex of branch i and all the N_{C} vertices of the main chain, whereas the summation over j accounts for all the distances between the remaining $N_{\mathrm{B}}-1$ vertices of the branch and those of the main chain. The D_{ii} term can be calculated as the sum of distances between vertex 1 of branch i, and all the vertices left and right of the branching vertex i:

$$D_{ii} = \sum_{l=1}^{iN_{\mathrm{S}}} l + \sum_{m=1}^{N_{\mathrm{C}}-iN_{\mathrm{S}}} m$$

$$= [(iN_{\mathrm{S}}+2)iN_{\mathrm{S}} + (N_{\mathrm{C}}-iN_{\mathrm{S}}+1)(N_{\mathrm{C}}-iN_{\mathrm{S}})]/2 \qquad \text{(E6)}$$

After substituting Eqs. (E6) and (E1) into Eq. (E5), and neglecting terms of order unity, one obtains

$$W_{\mathrm{c/b}} = (f-2)aB(B+1)(2B+3a+1)N_{\mathrm{S}}/6 \qquad \text{(E7)}$$

The branch /branch component of the Wiener number for this class of combs can be presented as a sum over all distances between the vertices of the branches attached to different branch vertices i and j, and those attached to the same branching vertex i:

$$W_{\mathrm{b/b}} = (f-2)^2\sum_{i=1}^{B-1}\sum_{j=1}^{B} W_{ij} + (f-2)(f-3)BW_{ii}/2 \qquad \text{(E8)}$$

The derivations for $W_{i,j}$ and W_{ii} are similar to those of

Eqs. (E5) and (E6)

$$W_{ii} = W_1 + (W_1 + N_B) + (W_1 + 2N_B) + \cdots + [W_1 + (N_B - 1)N_B] = N_B\left(W_1 + \sum_{i=1}^{N_B-1} i\right) = (N_B - 1)N_B^2 \approx N_B^3 = a^3N_S^3 \qquad \text{(E9)}$$

where

$$W_1 = 2 + 3 + \cdots + N_B + 1 = (N_B + 3)N_B/2$$

describes the sum of distances between the first vertex of one of the branches attached to vertex i, and all the N_B vertices of another branch attached to the same vertex i. Similarly, for D_1, which is the sum of distances between the first vertex of one of the branches attached to vertex i, and all the N_B vertices of another branch attached to the vertex j, one has

$$D_1 = [(j - i)N_S + 2] + [(j - i)N_S + 3] + \cdots + [(j - i)N_S + N_B + 1] = \sum_{k=2}^{N_B+1} [(j - i)N_S + k] = (j - i)N_SN_B + (N_B + 3)N_B/2 \qquad \text{(E10)}$$

$$W_{ij} = D_1 + (D_1 + N_B) + (D_1 + 2N_B) + \cdots + [D_1 + (N_B - 1)N_B] = N_B\left(D_1 + \sum_{i=1}^{N_B-1} i\right) = N_B^2[(j - i)N_SN_B + N_B + 1] \qquad \text{(E11)}$$

After substituting Eqs. (E9), (E11), and (E1) into Eq. (E8), and neglecting terms of order unity one obtains

$$W_{b/b} = (f - 2)a^2BN_S^3[(f - 2)(B - 1)(3a + B + 1) + 3a(f - 3)]/6 \qquad \text{(E12)}$$

Substituting now Eqs. (E3), (E4), (E7), and (E12) into Eq. (E2) one arrives to

$$W_{\mathrm{comb}}(f, B, a, N_S) = N_S^3\{(B + 1)^3 + aB(f - 2)[a^2 + (B + 1) \times (2B + 3a + 1) + a(f - 2)(B - 1)(3a + B + 1) + 3a^2(f - 3)]/6 \qquad \text{(E13)}$$

References

[1] Zimm BH, Stockmayer WH. J Chem Phys 1949;17:1301.
[2] Janzen J, Colby RH. J Mol Struct 1999;485:569.
[3] Eichinger BE. Macromolecules 1977;10:671.
[4] Eichinger BE. Macromolecules 1980;13:1.
[5] Eichinger BE, Martin JE. J Chem Phys 1978;69:4595.
[6] Eichinger BE. Macromolecules 1980;1:80.
[7] Yang Y. Macromol Theory Simul 1998;7:521.
[8] Harary F. Graph theory. Reading, MA: Addison-Wesley, 1969.
[9] Bonchev D, Rouvray D, editors. Chemical graph theory. Introduction and fundamentals, Mathematical chemistry series, vol. 1. Reading, UK: Gordon & Breach, 1991.
[10] Trinajstić N. Chemical graph theory. 2nd ed. Boca Raton, FL: CRC Press, 1992.
[11] Rouse PE. J Chem Phys 1953;21:1272.
[12] Zimm BH. J Chem Phys 1956;24:269.
[13] Wiener HJ. Am Chem Soc 1947;69:17.
[14] Polansky OE, Bonchev D. Commun Math Chem (MATCH) 1987;21:133.
[15] Bonchev D, Trinajstić N. J Chem Phys 1977;67:4517.
[16] Bonchev D, Knop JV, Trinajstić N. Commun Math Chem (MATCH) 1979;6:21.
[17] Bonchev D, Mekenyan O, Trinajstić N. Int J Quant Chem 1980;17:845.
[18] Bonchev D. Theochem 1995;336:137.
[19] Balaban AT, Motoc I, Bonchev D, Mekenyan O. Topics Curr Chem 1983;114:21.
[20] Rouvray DH. In: Trinajstić N, editor. Mathematics and computational concepts in chemistry. Chichester: Horwood, 1986. p. 295.
[21] Bonchev D, Mekenyan O, Fritsche H. J Cryst Growth 1980;49:90.
[22] Bonchev D, Mountain CF, Seitz WA, Balaban AT. J Med Chem 1993;36:1562.
[23] Bonchev D, Mekenyan O. Z Naturforsch 1980;35a:739.
[24] Bonchev D, Mekenyan O, Polansky OE. Z Naturforsch 1981;36a:643, see also page 647.
[25] Mekenyan O, Dimitrov S, Bonchev D. Eur Polym J 1983;12:1185.
[26] Bonchev D, Mekenyan O, Kamenska V. J Math Chem 1992; 11:107.
[27] Gutman I, Klavžar S, Mohar B, editors. Commun Math Comput Chem (MATCH) 1997;35:259.
[28] Hawker CJ, Lee R, Fréchet JMJ. J Chem Soc 1991;113:4583.
[29] Hölter D, Burgath A, Frey H. Acta Polym 1997;48:30.
[30] Hölter D, Frey H. Acta Polym 1997;48:298.
[31] Widmann AH, Davies GR. Comput Theoret Polym Sci 1998;8:191.
[32] Stejskal J, Kratochvil P. Macromolecules 1987;20:181.
[33] Soares JBP, Hamielec AE. Macromol Theory Simul 1996;5:547.
[34] Muller AHE, Yan D, Wulkow M. Macromolecules 1997;30:7015.
[35] Zhu S. Macromolecules 1998;31:7519.
[36] Kramers HA. J Chem Phys 1946;14:415.
[37] Hosoya H. Bull Chem Soc Jpn 1971;44:2332.
[38] Kurata M, Fukatsu M. J Chem Phys 1964;41:2934.
[39] Wales M, Marshall PA, Weissberg SG. J Polym Sci 1953;10:229.
[40] Orofino TA. Polymer 1961;2:305.
[41] Berry GC, Orofino , T A. J Chem Phys 1963;40:1614.
[42] Gordon M. Proc R Soc Lond, Ser A 1963;272:54.
[43] Dobson GR, Gordon M. J Chem Phys 1964;41:2389.
[44] Dobson GR, Gordon M. J Chem Phys 1965;43:705.
[45] Gutman I, Yeh YN, Lee SL, Chen JC. Commun Math Chem (MATCH) 1994;30:103.
[46] Bytautas L, Klein DJ. J Chem Inf Comput Sci 2000;40:471.
[47] Bytautas L, Bonchev D, Klein DJ. MATCH (Commun Math Comput Chem) 2001, in press.
[48] Milner S. Private communication.
[49] Hadjichristidis N, Xenidou M, Iatrou H, Pitsikalis M, Poulos Y, Avgeropoulos A, Sioula S, Paraskeva S, Velis, Lohse D, Schulz DN, Fetters LJ, Wright P, Mendelson RA, Garcia-Franco CA, Sun T, Ruff CJ. Macromolecules 2000;33:2424.
[50] Trinajstić N, Babić D, Nikolić S, Plavšić D, Mihalić Z. J Chem Inf Comput Sci 1994;34:368.
[51] Mohar B. Graph Combin 1991;7:53.
[52] Mohar B, Babić D, Trinajstić N. J Chem Inf Comput Sci 1993;33:153.
[53] Flory PJ. Statistical mechanics of chain molecules. New York: Wiley, 1969.

[54] Bonchev D, Balaban AT, Liu X, Klein DJ. Int J Quant Chem 1994;50:1.
[55] Marković S, Gutman I, Banćević Ž. J Serb Chem Soc 1995;60:633.
[56] Klein DJ, Randić M. J Math Chem 1993;12:81.
[57] Zhu HY, Klein DJ, Lukovits I. J Chem Inf Comput Sci 1996;36:420.
[58] Gutman I, Mohar B. J Chem Inf Comput Sci 1996;36:982.
[59] Yang Y, Yu T. Macromol Chem 1985;186:513.
[60] Kirkwood JG, Riseman J. J Chem Phys 1948;16:565.