

Topology–Rheology Regression Models for Monodisperse Linear and Branched Polyethylenes

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ABSTRACT: Several quantitative descriptors of polymer topology—the Wiener number W , complexity index K , and the index of 3-starness S —were shown to relate well the measured rheological properties of linear and 3-arm star monodisperse polyethylene samples to their structure. The complexity index K (the substructure count) provided single-variable models with correlation coefficients r ranging from 0.95 to 0.98 for zero-shear viscosity, activation energy, and the parameters λ and α from the Cross equation, which describes the shape of the viscosity/shear rate curve. The regression models with two and three topological variables were characterized by $r > 0.99$ and low standard deviations.

The models were used to predict the values of these rheological parameters for branched monodisperse polyethylenes not yet synthesized, thus indicating the potential of this topology-based methodology for industrial applications. The study also presents a statistical confirmation for the much stronger effect that long-chain branching has on shear rheology than that of molecular weight. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2648–2656, 2003

Key words: rheology; polymer topology; linear and star polyethylenes; structure–property relations; branched

INTRODUCTION

The effect of branching on the rheology of polymer melts and solutions has been extensively studied over the past 15 years.^{1–11} GPC-MALLS and ¹³C-NMR techniques have been used to assess the degree of branching in commercial polymers,^{12,13} although they cannot yet describe satisfactorily structural details of branched polymers. Monte Carlo simulations¹⁴ have also been used to deconvolute broad molecular weight distributions (MWDs) into a series of distributions corresponding to a given number of branches. It has been shown that it is not only the number of branches that influences polymer rheology but also the branch length and their position along the backbone. On the other hand, broad MWD polymers exhibit properties somewhat similar to long-chain branching (e.g., the recoverable compliance J_e^0 increases with MWD), and the two effects are difficult to separate. However, anionic polymerization has made it possible to synthesize nearly monodisperse molecular weight polymers and well-defined macromolecular architectures, paving the way to model quantitative structure–property relationships (QSPR). The effective QSPR analysis of branched polymers requires descriptors of polymer

structure that go beyond the number of branches or the degree of branching.^{15,16} It was previously shown¹⁷ that at a given degree of branching the immense variety of architectures possible in a real polymer shifts polymer properties over a wide range of values.

Graph theory^{18,19} could be used to describe structural diversity in branched polymers by offering quantitative descriptors, called *topological indices*. Over the last 25 years, molecular branching has been the subject of intensive studies, and topological indices have been shown to mirror even the subtlest branching patterns.^{20–22} Some polymer physical properties have been correlated with topological descriptors.^{23–28} The comparative analysis of topological indices as tools for evaluating branching complexity²⁹ has shown the Wiener number W ³⁰ and complexity index K ^{31–35} to be some of the best descriptors. In addition, they are relatively simple to calculate and have a clear physical interpretation.

In the first part of this study,³⁶ we performed a topological/complexity analysis of branching in polymers and derived formulas for the Wiener number W and complexity index K for different classes of branched polymers. The basic patterns of polymer structure were identified and quantitatively characterized using these descriptors. The second paper in the series³⁷ reexamined the Zimm–Stockmayer theory of dimension of polymers. It introduced the concept for a topological radius of a molecule and showed the di-

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TABLE I
Experimental Data for the Examined Rheological Properties of 13 Monodisperse Linear and 3-Arm Star Polyethylenes

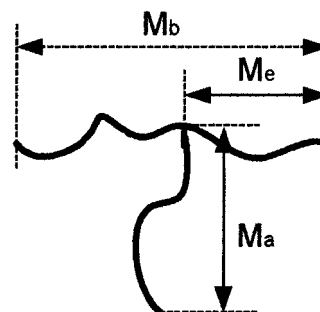
Polymer	Structural variable			g'	Rheological property			
	$M_b \times 10^{-3}$ (backbone)	$M_a \times 10^{-3}$ (arm)	$M_c \times 10^{-3}$ (end)		E_a (kcal/mol)	η_0 (Pa · s)	λ (s)	α
Linear PE								
1	101	0	0	0.92	7.26	2.24×10^3	9.15×10^{-4}	1.31
2	134	0	0	0.98	6.68	6.58×10^3	3.68×10^{-3}	1.41
3	135	0	0	1.00	7.07	6.89×10^3	3.90×10^{-3}	1.42
4	151	0	0	1.00	6.89	1.01×10^4	4.93×10^{-3}	1.39
5	167	0	0	1.05	7.13	2.85×10^4	1.38×10^{-2}	1.19
6	244	0	0	1.00	7.04	4.93×10^4	3.00×10^{-2}	1.14
3-Arm star PE								
7	100	5	50	1.04	14.3	9.25×10^5	1.83×10^0	0.908
8	100	25	50	0.84	16.3	2.28×10^6	3.09×10^1	0.813
9	100	50	50	0.72	17.0	5.90×10^6	3.71×10^1	0.834
10	100	40	40	0.83	16.8	6.42×10^6	6.23×10^1	0.829
11	100	15	50	0.82	13.1	9.28×10^6	9.89×10^1	0.848
12	100	15	50	0.82	14.9	1.68×10^7	1.58×10^2	0.852
13	130	65	65	0.76	18.1	3.90×10^8	2.63×10^3	0.860

rect relation between the Wiener index, the mean square radius of gyration, and zero-shear viscosity. In the present study, the topological descriptors were applied to the modeling of some rheological properties from an available set of monodisperse polyethylene (PE) samples. This is part of a more general approach, searching for specific combinations of topological and complexity parameters that would determine optimal ranges of rheological and mechanical polymer properties for industrial purposes. Such an approach might be regarded as a methodology for optimizing the design of branched polyolefins proceeding from predictions based on topology–property models. The experience accumulated from series of monodisperse species could help in the search for topology–property relationships to describe broad-distribution commercial polyolefins. They can also form the basis for structure interpretation and prediction, once the relevant topological and complexity descriptors are identified and applied.

EXPERIMENTAL

Training set

The training set consisted of experimental data for 13 monodisperse PEs: six linear and seven starlike structures. They were treated both in two separate subsets of linear and star polymers, given their different molecular dynamics, and in a joint set because mixtures of linear and star polyolefins are common in industrial practice. The star-type PE was regarded to be composed of a backbone (b) and a single arm (a); the position of the latter on the backbone is determined by the length of the shorter chain (c).



These model polymers have precisely controlled branching structures. They were prepared by Hadjichristidis et al.¹¹ through the hydrogenation of anionically synthesized polybutadienes. The synthetic method does not allow for side reactions that would change molecular weight and structure. The number of branches per molecule was determined by use of ¹³C- and ¹H-NMR, and by size exclusion chromatography (SEC), whereas molecular weights were measured by membrane osmometry, vapor phase osmometry, light scattering, and SEC.¹¹ The structural information on the model polymers examined by us is detailed in Table I. The molecular weight of the polymers is in the range of 100,000 to 250,000 Da.

Table I also presents the rheological properties modeled in this study. Included here are zero-shear viscosity η_0 , the branching index g' (the ratio of intrinsic viscosity of the branched polymer and that of the linear polymer of the same molecular weight), and the activation energy of viscous flow E_a , used as an indication of the processability of polymer melts. Graessley³⁸ related an increase in E_a to the presence of branching in PEs. (It should be mentioned that the difference in the activation energy is unique to some PEs, and the relation with the topological parameters

found in our study cannot be extended beyond this class of polymers.) The other two rheological parameters examined are the characteristic time λ and the power law index α from the Cross equation³⁹:

$$|\eta^*(\omega)| = \frac{\eta_0}{1 + (\lambda\omega)^\alpha} \quad (1)$$

which describes the dependency of the absolute value of complex viscosity $|\eta^*(\omega)|$ on angular frequency ω (rad/s). The oscillatory shear rheology data were obtained, as described in the study by Hadjichristidis et al.,¹¹ using a Rheometrics (Amherst, MA) RMS-800 instrument. In each case a single sample was run through a melt temperature range of 150 to 300°C, with master curves fit to a reference temperature of 190°C.⁴⁰ The activation energy of viscous flow E_a was determined proceeding from the time-temperature superposition principle and by assuming Arrhenius-type behavior:

$$a_T = \frac{\lambda(T)}{\lambda(T_0)} = Be \frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \quad (2)$$

The quality of the data was evaluated using standard statistical criteria. The overall conclusion was that the training set is limited with respect to the number of monodisperse polymers and the ranges of the properties under examination. Nevertheless, a positive assessment of the data set was inferred from the fact that the coupling between the zero-shear viscosity η_0 and the λ parameter was well reflected by their intercorrelation with $r = 0.96$. The activation energy E_a was also shown to correlate well with η_0 ($r = 0.93$) and λ ($r = 0.90$).

The descriptors of polymer branching

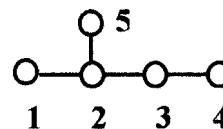
From a chemical point of view graphs are structural formulas in which the atomic symbols are replaced by points called *vertices*. Bonds are preserved as lines connecting the vertices and are called *edges*. Graphs thus preserve the useful information contained in structural formulae and, in addition, they provide the opportunity to use the powerful mathematical formalism of graph theory. The topological structure of a molecule is quantified by using the so-called *topological index*, a number that is uniquely derived from the respective graph. A molecular graph is a hydrogen-depleted (or, rather, hydrogen-implied) one.

Different kinds of polymer graphs can be constructed, depending on whether a vertex stands for a single nonhydrogen atom or for a selected group of atoms. In this study, we make use of graphs, each vertex in which stands for a carbon atom in the respective PE macromolecule. The Wiener number W

and the complexity index K were selected as topological descriptors on the basis of earlier extensive studies on molecular branching,^{20–22,28,41} and the successful use of the Wiener number in structure–property modeling.⁴²

The Wiener³⁰ number W counts the total number of bonds that separate all pairs of atoms along the shortest path between them. In a set of isomeric molecules the largest Wiener number is obtained for the linear structure, whereas the smallest one characterizes the most branched starlike structure. More generally, at a given number of nonhydrogen atoms the Wiener number decreases with the increase in the number of branches and their length, as well as with decreasing spacing (branch–branch distance), and with more central branch positioning.^{20,21} However, W increases rapidly with molecular size, which is another component of molecular complexity. Because of the opposing trends of increasing with size and decreasing with complexity, the Wiener number is a very useful tool for analyzing *isomeric* compounds. For nonisomeric species it is used in combination with other topological variables or is subjected to different modifications. In this study, it was also used after being normalized by dividing by: (1) the total number of carbon atoms n : $W' = W/n$; (2) the total number of distances in the graph $n(n - 1)/2$: $W'' = 2W/n(n - 1)$; and (3) the Wiener number W_{lin} of the unbranched PE having the same molecular weight: W/W_{lin} .

The topological complexity index K is defined as the sum of all substructures into which the overall molecular structure could be decomposed.^{31–35} In terms of graph theory, K is the total number of subgraphs in the molecular graph. This descriptor increases very rapidly with both the size of the molecule and the extent of its branching. For polymers it has to be used either in a logarithmic form ($\log K$) or normalized by dividing by the value K_{lin} it has for the linear structure with the same molecular weight (K/K_{lin}). The calculation of W and K is illustrated below for an asymmetric star graph having five vertices.



Distances 1: 1–2, 2–3, 2–5, 3–4

Distances 2: 1–3, 1–5, 2–4, 3–5

Distances 3: 1–4, 4–5

The Wiener number $W = (4 \times 1) + (4 \times 2) + (2 \times 3) = 18$

Normalized Wiener number:

$$W' = 18/5 = 3.6, \quad W'' = (2 \times 18)/(5 \times 4)$$

$$= 1.8, \quad W/W_{\text{lin}} = 18/20 = 0.9$$

TABLE II
Parameters Used in the Modeling of the Training Set of 13 Monodisperse Linear and 3-Arm Star Polyethylenes

No.	log MW	S	W ($\times 10^{-10}$)	W ⁿ	W/W _{lin}	log K	K/K _{lin} ($\times 10^2$)
1	5.004	0	62.57	2405	1	7.415	100
2	5.127	0	14.61	3191	1	7.661	100
3	5.130	0	14.94	3214	1	7.667	100
4	5.179	0	20.91	3595	1	7.765	100
5	5.223	0	28.28	3976	1	7.852	100
6	5.387	0	88.22	5809	1	8.182	100
7	5.021	0.292	6.570	2336	0.934	9.661	163
8	5.097	0.864	9.578	2404	0.808	10.36	573
9	5.176	1	15.93	2775	0.778	10.66	794
10	5.146	0.945	13.16	2632	0.789	10.54	700
11	5.061	0.666	7.863	2331	0.851	10.14	406
12	5.061	0.666	7.863	2331	0.851	10.14	406
13	5.290	1	35.02	3611	0.778	11.00	1033

Subgraphs:

1. vertices: 5 (1, 2, 3, 4, 5)
2. edges: 4 (1-2, 2-3, 3-4, 2-5)
3. two-edge subgraphs: 4 (1-2-3, 2-3-4, 1-2-5, 5-2-3)
4. three-edge subgraphs: 3 (1-2-3-4, 5-2-3-4, 1-2-3-5)
5. four-edge subgraph: 1 (the entire graph)

Complexity index:

$$K = 5 + 4 + 4 + 3 + 1 = 17,$$

$$K/K_{lin} = 17/15 = 1.133$$

A third topological index, the starness *S*, was introduced by us elsewhere³⁶ as a measure for the similarity of an asymmetrical star to the symmetrical one. *S* ranges from zero for linear polymers to one for a symmetrical star. In the singly branched PE the starness is defined as the product of the length of the three arms *A*, *B*, and *C*, expressed by the number of bonds (graph edges) e_A , e_B , and e_C in each arm, and normalized by dividing it by the total number of edges *E*. Alternatively, one may use the respective molecular weights M_A , M_B , M_C , and *M*, which for PEs are expressed by the number of atoms *n* by the relation $M = 14n + 2$, where $n = E + 1$ and $E = e_A + e_B + e_C$.

$$S = \frac{27e_Ae_Be_C}{E^3} = \frac{27(M_A - 16)(M_B - 16)(M_C - 16)}{(M - 48)^3} \tag{3}$$

For the graph shown above, $e_A = e_B = 1$, $e_C = 2$, $E = 4$, and $S = (27 \times 1 \times 1 \times 2)/4^3 = 0.843$ or 84.3% of 3-starness.

The calculations of the Wiener number and the complexity index of the model linear and star polymers

were performed using eqs. (4) to (7). The formula for the Wiener number of linear structures was given by Wiener in terms of the number of carbon atoms *n*.³⁰ The formulae for complexity index and starness index, as well as for those for the Wiener number of asymmetrical starlike graphs, were derived in the first part of this study. For polymer calculations, the number of atoms was replaced in eqs. (4) to (7) by the PE molecular weight $M = 14n + 2$, and those of the star polymers' three arms M_A , M_B , M_C :

$$W_{lin} = \frac{1}{6} n(n + 1)(n - 1) = \frac{M^3 - 6M^2 - 184M + 384}{16,464} \tag{4}$$

$$K_{lin} = \frac{n(n + 1)}{2} = \frac{M^2 + 10M - 24}{392} \tag{5}$$

$$W_{3\text{-arm star}} = \frac{n(n - 1)(n + 1)}{6} - n_A n_B n_C$$

$$= \frac{1}{16,464} [(M - 2)(M - 16)(M + 12) - 6(M_A - 2)(M_B - 2)(M_C - 2)] \tag{6}$$

$$K_{3\text{-arm star}} = n_A n_B n_C$$

$$+ \frac{n_A(n_A - 1) + n_B(n_B - 1) + n_C(n_C - 1)}{2}$$

$$+ \frac{(M_A - 2)(M_B - 2)(M_C - 2) + 7(M_A^2 + M_B^2 + M_C^2 - 126(M_A + M_B + M_C) + 672)}{2744} \tag{7}$$

These topological indices were applied to the study of 13 model polymers as far as their rheological perfor-

TABLE III
Comparison of the Correlation Coefficients of the Single-Variable Topological Descriptor/Rheological Property Models of the Examined Monodisperse Polyethylenes

Index	g'	E_a	$\log \eta_0$	$\log \lambda$	α
$\log K$	0.81	0.98^a	0.97	0.98	0.95
K/K_{lin}	0.89	0.89	0.87	0.87	0.76
W/W_{lin}	0.90	0.96	0.92	0.94	0.89
S	0.90	0.93	0.85	0.94	0.89
M_e	0.75	0.96	0.95	0.96	0.93
M_a	0.85	0.86	0.83	0.82	0.70
M_b	0.52	0.58	0.39	0.45	0.44
W''	0.38	0.49	0.32	0.38	0.39
W'	0.24	0.30	0.13	0.24	0.25
W	0.22	0.28	0.09	0.15	0.13
MW	0.07	0.14	0.05	0.02	0.07
$\log MW(a)^b$	0.64	0.14	0.96	0.97	0.67
$\log MW(b)$	0.63	0.84	0.79	0.62	0.26

^a The highest correlation coefficient for each property is given in bold.

^b (a) and (b) refer to the two subsets of linear and branched polyethylene, respectively.

mance is concerned. The calculated values of the topological parameters are given in Table II.

RESULTS AND DISCUSSION

Single-variable correlations

The multiple regression analysis was performed with the package OASIS.^{43,44} The option used selects the model with the best statistics (highest correlation coefficient r , lowest standard deviation s , and largest Fischer ratio F , the latter being a measure for the statistical significance of the regression) after testing all statistically significant variable combinations.

The single-variable models were studied in detail (Table III), with the purpose of evaluating the relative importance of the examined structural descriptors. Several of these simplest models were obtained with statistics high enough to allow their application for practical purposes. High correlation coefficients were obtained with some of the topological descriptors (e.g., 0.89 to 0.96 for the W/W_{lin} models and 0.85 to 0.94 for the models with the index of starness S).

The best results, shown in eqs. (8)–(12) were obtained with the complexity index K , with correlation coefficients reaching 0.96–0.98 for activation energy E_a , zero-shear viscosity η_0 and the parameters λ and α of the Cross equation,³⁹ and 0.90 for the branching index g' . The correlation obtained is high, particularly when taking into account the accuracy of the data in the training set. The normalized complexity index K/K_{lin} also performed well, with $r = 0.87$ –0.90.

$$g' = -0.106 (\pm 0.015) \ln \left(\frac{K}{K_{\text{lin}}} \right) + 1.49 (\pm 0.08) \quad (8)$$

$$n = 13, \quad r = 0.902, \quad s = 0.05, \quad F = 48$$

$$E_a = 0.183 (\pm 0.010) (\log K)^2 - 3.92 (\pm 0.87) \quad (9)$$

$$n = 13, \quad r = 0.985, \quad s = 0.86, \quad F = 352$$

$$\log \eta_0 = 1.151 (\pm 0.093) \log K - 4.93 (\pm 0.86) \quad (10)$$

$$n = 13, \quad r = 0.966, \quad s = 0.45, \quad F = 155$$

$$\log \lambda = 0.0866 (\pm 0.0052) (\log K)^2 - 7.48 (\pm 0.46) \quad (11)$$

$$n = 13, \quad r = 0.981, \quad s = 0.46, \quad F = 281$$

$$\alpha = -1.568 (\pm 0.141) \ln(\log K) + 4.52 (\pm 0.31) \quad (12)$$

$$n = 13, \quad r = 0.958, \quad s = 0.075, \quad F = 124$$

The molecular weight–type variables did not perform so well. An extremely low correlation (0.02 to 0.14) was obtained with the total molecular weight for the examined rheological properties. This result supports the observations that branching is much more significant than molecular weight for the rheological properties of PEs. Another factor contributing to these unrealistically low values is the grouping together of linear and branched monodisperse PEs because their rheology depends on molecular weight in a drastically different way. Separating the training set into two subsets of six linear and seven branched PEs produced considerably stronger property dependency on molecular weight, although it is still weaker than that of the topological branching parameters $\log K$, W/W_{lin} , K/K_{lin} , and S .

$$\log \eta_0 = 3.66 (\pm 0.50) \log MW - 14.91 (\pm 2.60) \quad (13)$$

$$n = 6, \quad r = 0.964, \quad s = 0.14, \quad F = 53$$

$$\log \lambda = 4.00 (\pm 0.46) \log MW + 22.97 (\pm 2.40) \quad (14)$$

$$n = 6, \quad r = 0.974, \quad s = 0.13, \quad F = 74$$

The respective correlation coefficients for the branched PEs are 0.79 for $\log \eta_0$ and 0.62 for $\log \lambda$. The slope 3.66 (± 0.50) of eq. (13) coincides, within the error limit, to the well-known exponent of 3.4 in the intrinsic viscosity dependency on molecular weight. Similarly, the slope of 7.18 (± 2.50) in eq. (15) for $\log \eta_0$ of the subset of branched PEs

$$\log \eta_0 = 7.18 (\pm 2.50) \log MW - 29.83 (\pm 12.81) \quad (15)$$

$$n = 7, \quad r = 0.789, \quad s = 0.56, \quad F = 8.2$$

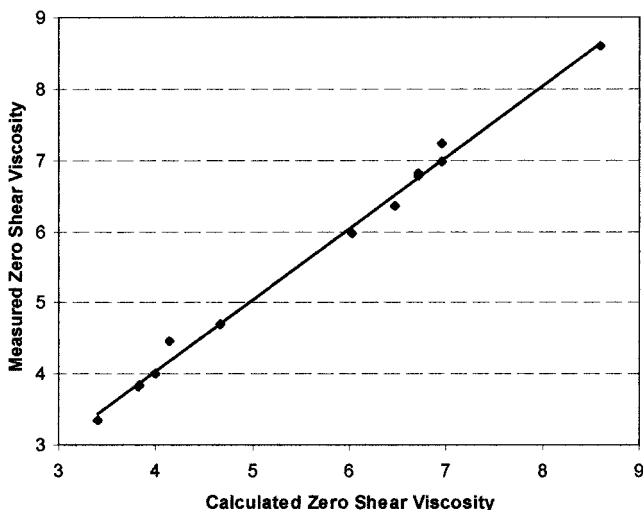


Figure 1 Experimental versus calculated [eq. (18)] values of zero-shear viscosity of the set of six linear and seven 3-arm star monodisperse polyethylenes.

is within the error limit to the experimental values. The large uncertainty ranges for the two MW exponents in eqs. (13) and (15) for the viscosity of linear and branched PEs (± 0.50 and ± 2.50 , respectively) result from the very small subsets of six linear and seven branched polymers in our training set.

It was also of interest to compare the performance of the topological indices against the theoretical models showing that viscosity of star-branched molecules depends exponentially on the molecular weight of the shortest arm M_b . As shown below in the mathematically equivalent log-log form for the zero-shear viscosity, the complexity index K provides a higher correlation than M_b . The result is further improved in the next section by use of a combination of topological descriptors.

$$\log \eta_0 = 1.38 (\pm 0.74) \log M_b + 0.92 (\pm 3.26) \quad (16)$$

$$n = 7, \quad r = 0.639, \quad s = 0.70, \quad F = 3.4$$

$$\log \eta_0 = 1.43 (\pm 0.58) \log K - 7.82 (\pm 5.99) \quad (17)$$

$$n = 7, \quad r = 0.741, \quad s = 0.61, \quad F = 6.1$$

Two- and three-variable correlations

Combining two or three structural parameters improved the structure-property models and increased their statistical significance, as measured by the Fischer ratio F . The correlation coefficients for three of the examined five properties reached or exceeded 0.99. More important, the standard deviations of the calculated properties, particularly those of the zero-shear viscosity and the Cross parameter λ , were reasonably small, thus allowing the use of the models for predic-

tive purposes. The best two- or three-variable models for each of the examined properties are presented below and illustrated in Figures 1 and 2. In all cases these are nonlinear models in which logarithmic and even double logarithmic functions are used, given the very strong dependency of the topological descriptors on polymer branching.

$$\log \eta_0 = 12.9 (\pm 1.0) \ln(\log K) + 5.65 (\pm 0.61) \ln\left(\frac{K}{K_{lin}}\right) + 52.1 (\pm 5.6) \ln\left(\frac{W}{W_{lin}}\right) - 48.46 (\pm 3.64) \quad (18)$$

$$n = 13, \quad r = 0.997, \quad s = 0.15, \quad F = 470$$

$$\log \lambda = 15.6 (\pm 1.68) \ln(\log K) + 5.16 (\pm 1.04) \ln\left(\frac{K}{K_{lin}}\right) + 46.1 (\pm 9.4) \ln\left(\frac{W}{W_{lin}}\right) - 58.02 (\pm 6.18) \quad (19)$$

$$n = 13, \quad r = 0.995, \quad s = 0.26, \quad F = 298$$

$$E_a = -0.0555 (\pm 0.0084) \frac{K}{K_{lin}} - 0.0610 (\pm 0.0074) W'' - 1.45 (\pm 0.18) MW + 12.60 (\pm 0.79) \quad (20)$$

$$n = 13, \quad r = 0.992, \quad s = 0.70, \quad F = 179$$

$$\alpha = -0.218 (\pm 0.019) \log K - 0.0044 (\pm 0.0014) M_b + 0.488 (\pm 0.152) \log W - 1.84 (\pm 1.43) \quad (21)$$

$$n = 13, \quad r = 0.979, \quad s = 0.06, \quad F = 68$$

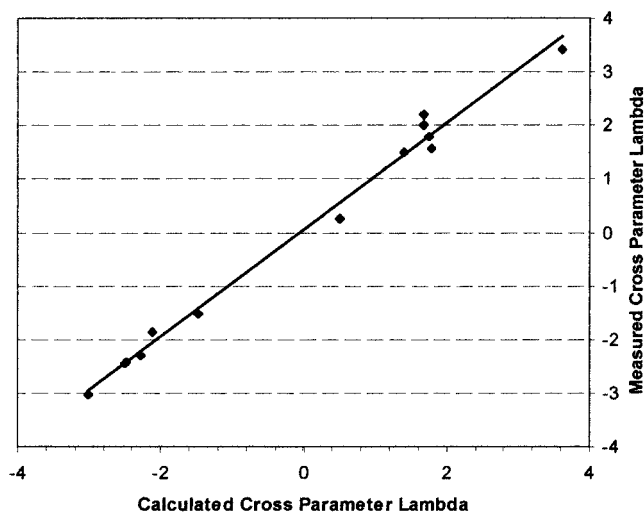


Figure 2 Experimental versus calculated [eq. (19)] values of the Cross equation's characteristic time lambda of the set of six linear and seven 3-arm star monodisperse polyethylenes.

TABLE IV
Predicted Rheological Properties of Some Not Yet Synthesized Monodisperse 3-Arm Star Polyethylenes^a

No.	M_b	M_s	M_a	MW	g'	E_a (kcal/mol)	η_0 (Pa · s)	λ (s)	α
1	80	40	40	120	0.79	15.8	1.0×10^7	67.6	0.87
2	80	40	25	105	0.82	15.1	5.9×10^6	29	0.84
3	80	40	10	90	0.87	13.9	2.1×10^6	6.0	0.85
4	80	30	30	110	0.81	15.2	6.7×10^6	36	0.86
5	80	30	10	90	0.92	13.8	1.9×10^6	5.4	0.85
6	80	20	20	100	0.89	14.2	3.3×10^6	12	0.87
7	100	50	35	135	0.78	16.0	1.5×10^7	120	0.83
8	100	40	30	130	0.80	15.6	1.2×10^7	84	0.83
9	100	40	20	120	0.84	14.9	7.3×10^6	41	0.83
10	100	40	10	110	0.85	13.8	3.3×10^6	12	0.85
11	100	25	25	125	0.86	14.6	7.1×10^6	39	0.86
12	100	25	10	110	0.97	13.5	2.5×10^6	7.9	0.88
13	130	50	50	180	0.75	17.0	3.7×10^7	550	0.80
14	130	50	35	165	0.78	16.2	2.5×10^7	280	0.79
15	130	50	20	150	0.84	15.0	1.3×10^7	100	0.80

^a η_0 , λ , E_a , α , and g' were calculated by eqs. (10), (11), (18), (19), and (20), respectively.

$$g' = 0.582 (\pm 0.247) \ln(\log K) - 0.199 (\pm 0.040) \ln\left(\frac{K}{K_{\text{lin}}}\right) + 0.71 (\pm 0.34) \quad (22)$$

$$n = 13, \quad r = 0.945, \quad s = 0.04, \quad F = 41$$

The obtained models have good predictive power. We used the models to calculate the rheological properties of 15 as yet unsynthesized monodisperse 3-arm star PEs with molecular weights ranging from 90,000 to 180,000. The estimates made are presented in Table IV.

Additional data analysis was carried out to compare the performance of the selected topological descriptors against that of the molecular weight of each of the star arms (parameters included in the dynamic theory of stars' viscoelasticity) in reproducing the zero-shear viscosity of the branched molecules. As shown below, the replacement of molecular weights with the generalized topological parameters resulted in a fourfold decrease in the standard deviation:

$$\log \eta_0 = -4.84 \log M1 + 8.66 \log M2 + 0.602 \log M3 - 12.66 \quad (23)$$

$$n = 7, \quad r = 0.898, \quad s = 0.52, \quad F = 4.1$$

$$\log \eta_0 = 17.67 \log K + 37.20(W/W_{\text{lin}}) - 0.0175(K/K_{\text{lin}}) - 196.60 \quad (24)$$

$$n = 7, \quad r = 0.994, \quad s = 0.13, \quad F = 78$$

Neural network models

An additional substantial improvement of the model statistics resulted from applying the neural network program "Neural Works Predict."⁴⁵ The program methodology provides an efficient optimization of the structure-property models but does not produce models in a classical analytical form. Rather, the application produces each model as a code. In Table V, we compare the statistics of the best linear and nonlinear models, as produced by the OASIS programs, with those of the neural network models.

As seen from Table V, the neural network models show very high correlation, which in all cases is better than that of the MRA linear and nonlinear models. Four of the correlation coefficients are within the range of 0.9993–0.9997. Particularly impressive is the decrease in the standard deviation, which for g' is even 10-fold; for $\log \lambda$, more than fourfold; and for E_a and $\log \eta_0$, more than twofold. All these results were obtained with the standard Neural Nets version after an exhaustive testing of the optional parameters of the

TABLE V
Comparative Statistics of the Best Structure-Property Neural-Network and Multiple-Regression-Analysis Models of Linear and 3-Arm Star Monodisperse Polyethylenes

Property	Neural network models		MRA models (OASIS)	
	r	s	r	s
g'	0.9994	0.004	0.945	0.04
E_a	0.9970	0.348	0.992	0.70
$\log \eta_0$	0.9993	0.062	0.997	0.15
$\log \lambda$	0.9997	0.056	0.995	0.26
α	0.9996	0.058	0.979	0.059

program. One may thus expect to improve the predictive potential of the polymer structure–property models by the use of the neural net technique.

CONCLUSIONS

Two topological descriptors of polymer structure, the Wiener number W and the complexity index K , were selected for this study on the basis of their high sensitivity to intimate details of molecular architecture. They were shown to correlate very well with the melt rheological properties of linear and branched monodisperse PEs: the zero-shear viscosity, the activation energy, the Cross equation parameters λ and α , and the branching ratio g' . The single-variable linear and nonlinear regression models derived are characterized by correlation coefficients r ranging from 0.95 to 0.98, whereas the models including two or three variables have $r > 0.99$, and the standard deviations in both cases are reasonably small. The models were additionally improved by applying the neural network method. An important result of this study is the statistical confirmation of the views that molecular weight has much less effect on the rheology of polyethylene melts than does long-chain branching.

The practical implication of the models derived lies in their predictive power as far as the rheological properties of monodisperse linear and 3-arm star polymers are concerned, as exemplified in Table IV. More generally, this study shows that topological descriptors of polymer structure can provide highly significant structure–rheology relationships with a good predictive potential. Given the generality of the topological approach, one may expect this conclusion to be extended to comblike and hyperbranched structures, as well as to random distribution polyolefins, which will be the subject of future studies. (Formulas for the Wiener index and the complexity index K for these highly branched polymers were derived in our recent publications.^{36,37}) Thus, the present study might be regarded as part of a methodology for optimizing the design of branched polyolefins proceeding from predictions based on topology–property models. Such a methodology offers universal *tools*—topology/complexity descriptors—to be applied to polymers of different chemistry and to identify common structural patterns. Indeed, the regression models derived are not universal. They are specific for the class of polymers for which they are derived, and no *quantitative* predictions can be made beyond this class.

The high correlations obtained with the rheological properties of polyolefins raise the question about a possible link of the topological formalism used and polymer dynamics, which determines these properties. This conclusion is supported by the favorable comparison of the statistics of our models with those based on the molecular weights of each of the star

arms, regarded by molecular dynamics models as crucial parameters. During the last few years, significant progress has been made in the description of the dynamics of branched polymers. It was realized that inner segments of the branched chains could relax only after the relaxation of the outer segments. The key parameters describing this hierarchy of relaxation, called priority and seniority, are also topological in nature.^{46,47} Then, the high-correlation models obtained in our study could indicate a possible link of the Wiener index and complexity index with priority/seniority parameters. The Wiener index shows certain similarity with these parameters in characterizing structural patterns in polyolefins. Thus, at a given molecular weight, and excluding linear and star polymers for which all chain priorities are the same, the Wiener index and chain priority/seniority of statistical polymers have their highest values for comb macromolecules having unbranched branches, and both decrease in hyperbranched species with the increase in the extent of branching. Work on the quantitative relation between these important topological descriptors of polymer structure is in progress.⁴⁸

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References

1. Roovers, J. *Macromolecules* 1991, 24, 5895.
2. Fetters, L. J.; Kiss, A. D.; Pearson, D. S.; Quack, G. F.; Vitus, F. J. *Macromolecules* 1993, 26, 647.
3. Graessley, W. W. In: *Physical Properties of Polymers*, 2nd ed.; Mark, J. E.; Eisenberg, A.; Graessley, W. W., Eds.; American Chemical Society: New York, 1993; pp. 97–143.
4. Yurasova, T. A.; McLeish, T. C. B.; Semenov, A. N. *Macromolecules* 1994, 27, 7205.
5. McLeish, T. C. B. *Phys World* 1995, 3, 32.
6. Vlassopoulos, D.; Pakula, T.; Fytas, G.; Roovers, J.; Karatasos, K.; Hadjichristidis, N. *Europhys Lett* 1997, 39, 617.
7. Gell, C. B.; Graessley, W. W.; Evstratiadis, V.; Pitsikalis, M.; Hadjichristidis, N. *J Polym Sci B* 1997, 35, 1943.
8. Pakula, T.; Vlassopoulos, D.; Fytas, G.; Roovers, J. *Macromolecules* 1998, 31, 8931.
9. Mishra, M. K.; Kobayashi, S., Eds. *Star and Hyperbranched Polymers*; Marcel Dekker: New York, 1999.
10. McLeish, T. In: *Mathematical Chemistry: Chemical Topology*; Bonchev, D.; Rouvray, D. H., Eds.; Gordon & Breach: Reading, UK, 1999; Vol. 5, pp. 265–315.
11. Hadjichristidis, N.; Xenidou, M.; Iatrou, H.; Pitsikalis, M.; Poulos, Y.; Avgeropoulos, A.; Sioula, S.; Paraskeva, S.; Velis, G.; Lohse, D. J.; Schulz, D. N.; Fetters, L. J.; Wright, P. J.; Mendelson, R. A.; Garcia-Franco, C. A.; Sun, T.; Ruff, C. *Macromolecules* 2000, 33, 2424.
12. Randall, J. C. *J Macromol Sci Rev C* 1989, 29, 201.
13. McCord, E. F.; Shaw, W. H.; Hutchinson, R. A. *Macromolecules* 1997, 30, 246.
14. Binder, K., Ed. *Monte Carlo and Molecular Dynamics Simulations in Polymer Science*; Johannes Gutenberg-Universität: Mainz, 1995.

15. Hawker, C. J.; Lee, R.; Fréchet, J. M. J. *J Am Chem Soc* 1991, 113, 4583.
16. Hölter, D.; Burgath, A.; Frey, H. *Acta Polym* 1997, 48, 30; Hölter, D.; Frey, H. *Acta Polym* 1997, 48, 298.
17. Widmann, A. H.; Davies, G. R. *Comput Theor Polym Sci* 1998, 8, 191.
18. Harary, F. *Graph Theory*; Addison-Wesley: Reading, MA, 1969.
19. Trinajstić, N. *Chemical Graph Theory*, 2nd ed; CRC Press: Boca Raton, FL, 1992.
20. Bonchev, D.; Trinajstić, N. *J Chem Phys* 1977, 67, 4517.
21. Ruch, E.; Gutman, I. *J Combinatorics* 1979, 4, 285.
22. Bonchev, D. *J Mol Struct* 1995, 336, 137.
23. Bonchev, D.; Mekenyan, O. *Z Naturforsch* 1980, 35a, 739.
24. Mekenyan, O.; Dimitrov, S.; Bonchev, D. *Eur Polym J* 1983, 12, 1185.
25. Bonchev, D.; Mekenyan, O.; Kamenska, V. *J Math Chem* 1992, 11, 107.
26. Bicerano, J. *Prediction of Polymer Properties*, 2nd ed.; Marcel Dekker: New York, 1996.
27. Duidea, M. V.; Katona, G. *Adv Dendritic Macromol* 1999, 4, 135.
28. Balaban, T.-S.; Balaban, A. T.; Bonchev, D. *J Mol Struct* 2001, 535, 81.
29. Nikolaić, S.; Trinajstić, N.; Tolić, I. M.; Rucker, G.; Rucker, C. In: *Mathematical Chemistry Series, Vol. 7, Molecular Complexity*; Bonchev, D.; Rouvray, D. H., Eds.; Gordon & Breach: Reading, UK, to appear.
30. Wiener, H. *J Am Chem Soc* 1947, 69, 17; *J Phys Chem* 1948, 52, 1082.
31. Bertz, S. H.; Herndon, W. C. In: *Artificial Intelligence Applications in Chemistry*, Pierce, T. H.; Hohne, B. A., Eds.; ACS Symposium Series 306; American Chemical Society: Washington, DC, 1986; pp. 169–175.
32. Bertz, S. H.; Sommer, T. *J. Chem Commun* 1997, 2409.
33. Bonchev, D. *SAR QSAR Environ Res* 1997, 7, 23.
34. Bonchev, D. In: *Topological Indices and Related Descriptors in QSAR and QSPR*; Devillers, J.; Balaban, A. T., Eds.; Gordon & Breach: Reading, UK, 1999; pp. 361–401.
35. Bonchev, D. *J Chem Inf Comput Sci* 2000, 40, 934.
36. Bonchev, D.; Dekmezian, A. H.; Markel, E. *J Chem Inf Comput Sci* 2001, 41, 1274.
37. Bonchev, D.; Markel, E.; Dekmezian, A. H. *Polymer* 2002, 43, 203.
38. Graessley, W. W. *Acc Chem Res* 1977, 10, 332.
39. Cross, M. M. *J Colloid Sci* 1965, 20, 417.
40. Lohse, D. J.; Xenidou, M.; Schulz, D. N.; Milner, S. T.; Fetters, L. J.; Wright, P. J.; Hadjichristidis, N.; Iatrou, H.; Pitsikalis, M.; Poulos, Y.; Avgeropoulos, A.; Sioula, S.; Paraskeva, S.; Velis, G.; Mendelson, R. A.; Carcia-Franco, C. A.; Lyon, M. K.; Sun, T.; Ruff, C. J. *ACS Polym Prepr* 2000, 80, 123.
41. Randić, M. *Acta Chim Slovenica* 1997, 44, 57.
42. *MATCH (Communications in Mathematical Chemistry and in Computer Chemistry)*, Vol. 35, Fifty Years of the Wiener Number; Kerber, A., Ed.; 1997.
43. Mekenyan, O.; Karabunarliev, S.; Bonchev, D. *J Math Chem* 1990, 4, 207.
44. Mekenyan, O.; Karabunarliev, S.; Bonchev, D. *Comput Chem* 1990, 14, 193.
45. NeuralWare. NeuralWare Inc.: Pittsburgh, PA, 1997.
46. Bick, D. K.; McLeish, T. C. B. *Phys Rev Lett* 1996, 76, 2587.
47. McLeish, T.; Milner, S. *Adv Polym Sci* 1999, 143, 195.
48. Bonchev, D.; Dekmezian, A. H.; Jiang, P., to appear.