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A TOPOLOGICAL APPROACH TO THE MODELLING OF POLYMER PROPERTIES (THE TEMPO METHOD)*

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Abstract

The topological extrapolation method for the modelling of polymer properties (TEMPO) is outlined. It is based on the topological description of the polymer elementary units by means of the normalised Wiener number represented as a polynomial in degree 3 with respect to the number of atoms. The properties of the infinite polymers are evaluated by making use of a specific extrapolating technique applied to regression models derived for the respective polymerhomologous series. The inherent topological background of the TEMPO approach makes its predictions more reliable than the known Padé approximation. The method is extensively applied to the calculation of π-electron energies and energy gaps of various conjugated polymers, as well as to the assessment of the melting point, density, refractive index, and specific rotation of some industrially produced polymers.

1. Introduction

Contemporary theoretical chemistry has to answer a major challenge: how to derive molecular properties from molecular structure. This problem is not only of academic interest, it is closely concerned with the design of new compounds with valuable properties such as drugs, organic semiconductors, conductors, or even superconductors, organic magnets, special polymers, etc. Quantum chemistry, albeit of essential importance, so far cannot answer all questions. Related to this, different quantitative structure–property relationships have been proposed, mainly on an empirical basis. In a later stage of development, the interest of scientists was to a great extent centered on those molecular properties in which topological structure is a dominant factor [5–15].

Polymer science also follows closely these trends. Thus, polymer properties are frequently assessed by group additivity methods [16]. According to them, some properties can be determined as a sum over all the individual contributions of atoms, bonds and atomic groups in the structure. The graph-theoretical background

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*Part V. See refs. [1–4] for the first four parts of this series.

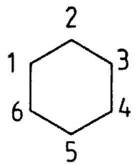
of the additivity schemes has been first revealed by Smolenski [17, 18], who associated the "weight" of the different atoms, bonds, and atomic groups with the number of the respective subgraphs of the graph representing a chemical structure. These topological ideas have been developed further by Gordon, Kennedy, and Essam [19–22], who provided an algorithm based on a combination of all subgraphs.

Although the additive schemes are very popular in polymer science, they have some pitfalls. In fact, what Smolenski, Gordon and others did makes the theory exact, but in practice applications are impractical. On the other hand, the contribution of some atomic groups may vary within a certain range depending on the type of polymer. In dealing with polymers having more complicated atomic groups (e.g. long side-chains in the monomer unit), the contribution of such a group differs from that of the sum of its constituents. This prompted the search for other approaches. Semiempirical structure–property relationships have been reported in which different polymer properties, and first of all the melting point , were found to correlate with such parameters as the number of carbon atoms [23,24] or heteroatoms [25], etc.

A more general approach to such structure–property studies could be based on molecular topology, as described by graph theory [26]. Such a method was developed by the present authors [1–4], proceeding from a particular topological index, the so-called Wiener number [27,28]. The latter is a very convenient measure of molecular compactness, as well as of the branching [29,30] and cyclicity [31–33] of a molecular skeleton, and it was widely applied to the modelling of various molecular properties [34–43]. It will be shown in this paper that after some modifications, the Wiener topological index is in a state to reflect quite satisfactorily various polymer properties, as well. Included here are also the electronic properties of the polymers containing conjugated π-electron systems for which a number of quantum-chemical [44,47] or graph-theoretical [48–52] methods have been devised.

2. The Wiener number

Molecular topology proceeds basically from the atom–atom connectedness or, otherwise, from neighborhood relationships. The latter are expressed by the adjacency matrix of the molecular graph G, $A(G)$. Its entries are either $a_{ij} = 1$ for i, j-neighboring atoms or $a_{ij} = 0$, otherwise. Another matrix of considerable interest is the distance matrix of the graph $D(G)$. It is also a square $N \times N$ matrix, symmetrical with respect to the main diagonal, N being the total number of atoms. The distance d_{ij} between a pair of atoms i and j equals the number of bonds (or graph edges) along the shortest path connecting i and j: $d_{ij} = 1, 2, 3, \ldots, d_{\max}$. The half-sum of the distance matrix elements specifies the total distance of the graph known as the Wiener number W. As an example, the adjacency and distance matrices of a benzene molecule are shown, together with the calculation of W:



$$A(G) = \begin{array}{c|cccccc} \text{atoms} & 1 & 2 & 3 & 4 & 5 & 6 \\ \hline 1 & 0 & 1 & 0 & 0 & 0 & 1 \\ 2 & 1 & 0 & 1 & 0 & 0 & 0 \\ 3 & 0 & 1 & 0 & 1 & 0 & 0 \\ 4 & 0 & 0 & 1 & 0 & 1 & 0 \\ 5 & 0 & 0 & 0 & 1 & 0 & 1 \\ 6 & 1 & 0 & 0 & 0 & 1 & 0 \end{array}; \quad D(G) = \begin{array}{c|cccccc} & 1 & 2 & 3 & 4 & 5 & 6 \\ \hline 1 & 0 & 1 & 2 & 3 & 2 & 1 \\ 2 & 1 & 0 & 1 & 2 & 3 & 2 \\ 3 & 2 & 1 & 0 & 1 & 2 & 3 \\ 4 & 3 & 2 & 1 & 0 & 1 & 2 \\ 5 & 2 & 3 & 2 & 1 & 0 & 1 \\ 6 & 1 & 2 & 3 & 2 & 1 & 0 \end{array},$$

$$W(G) = \tfrac{1}{2} \sum_{i,j=1}^{N} d_{ij} = 6 \cdot 1 + 6 \cdot 2 + 3 \cdot 3 = 27.$$

The Wiener number mirrors such major features of molecular topology like branching and cyclicity of the molecular skeleton.

3. The TEMPO method

The topological extrapolation modelling of polymers (TEMPO) is based on the Wiener number and includes the following stages:

(1) Representing the Wiener index of each polymerhomologous series as a polynomial in degree 3 with respect to the total number of atoms N.

(2) Normalizing the Wiener index by dividing it by another polynomial in degree 3 so as to arrive at a finite value for infinite polymers. Calculation of the Wiener index $\overset{\approx}{W}_\infty$ normalized for $N \to \infty$.

(3) Representing the polymer property X under consideration as a regression model, the single variable in which is the normalized Wiener number of the respective polymerhomologous series: $X = f(\overset{\approx}{W})$. Calculation of the bound value this property has for an infinite polymer X_∞.

(4) Searching for a general dependence between the bound values of the property modelled and the Wiener number of a series of polymers $X_\infty = f(\overset{\approx}{W}_\infty)$. Predictions of the property values for other polymers proceeding from their topology $(\overset{\approx}{W}_\infty)$ only.

In resolving the first problem, one may present the Wiener index of a polymer having n elementary units as follows:

$$W_n = nW'_{11} + (n-1)W'_{12} + (n-2)W'_{13} + \ldots + 1W'_{1n} + k, \tag{1}$$

where W'_{11} is the Wiener index for the elementary unit, while W'_{1i} is the sum of all distances between the 1st and ith elementary units and k is a correcting term having different values depending on the ways of attaching the elementary units. Then, all W_{1i} may be expressed by means of W'_{12}, the closed form of which depends on the specific topology of elementary unit linkages.

In the case of corona-fused benzenoid elementary units attached to each other by a single cata-fusion site (fig. 1), the whole structure being of D_{2h} symmetry, $k = 1$ and

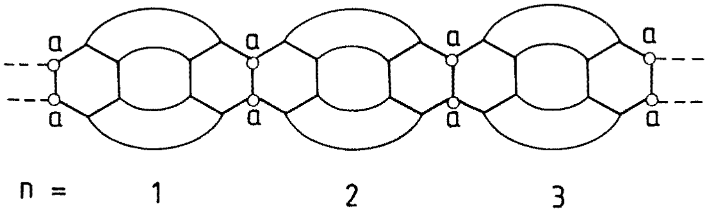


Fig. 1. Scheme of a corona-fused benzenoid polymer whose elementary units are linked by a single cata-fusion site **a**–**a**.

$$W'_{1i} = W'_{12} + (n-2)L, \tag{2}$$

where L depends on both the number of atoms in the elementary unit N'_1 and the shortest distance between the first and third such units $D_{13}^{\min}$:

$$L = D_{13}^{\min} N_1'^{2}. \tag{3}$$

On the other hand, W'_{12} may also be expressed explicitly by taking into consideration the symmetry with respect to the linear polymer main axis x:

$$W'_{12} = N'_1(4d'_{\mathrm{a}} - N'_1)/2. \tag{4}$$

Here, d'_{a} is the distance number (the sum of the distances to all vertices in the unit) of one of the two vertices which constitute the fusion site for a pair of elementary units (see fig. 1).

After substituting eq. (2) into eq. (1), one arrives at the following result:

$$W_n = \tfrac{1}{6}\,[Ln^3 + 3(W'_{12} - L)n^2 + (6W_{11} - 3W'_{12} + 2L - 6)n + 6]. \tag{5}$$

Equation (5) can also be expressed as a function of the total number of atoms N instead of the number of elementary units n by replacing $n = (N-2)/N'_1$.

The second stage of the TEMPO method includes the Wiener number normalizing by dividing it by both the total number of graph distances (H) and edges (B):

$$\overset{\approx}{W} = FW = W/HB = 2W/N(N-1)B. \tag{6}$$

The Wiener number thus normalized represents the mean topological distance per bond in the structure under consideration. On the other hand, the total number of bonds B may be determined from the well-known equation for the number of graph cycles (the cyclomatric number) ν,

$$B = N + \nu - 1, \tag{7}$$

where ν is additive for any polymer composed of n fused elementary units:

$$\nu = n\nu_1 = \frac{N-2}{N_1'}\nu_1. \tag{8}$$

One thus obtains for B

$$B = [(N-1)(N_1' + \nu_1) - \nu_1]/N_1'. \tag{9}$$

Therefore, the normalized Wiener number is a ratio of two polynomials in degree 3, i.e. at $N \to \infty$ it will be a finite number,

$$\overset{\approx}{W}_\infty = \lim_{N\to\infty} \overset{\approx}{W} \neq \infty. \tag{10}$$

One may resume that the first two TEMPO stages provide the topological description of the polymer of interest, a description which is then used to predict the polymer properties. A number of the polymer properties (physicochemical, electronic, optical, etc.) can be calculated by this method, proceeding from the numerical values of these properties (experimental or calculable ones) for the initial members of the respective polymerhomologous series. As will be discussed further, the number n of such data, necessary for a reliable calculation, varies for the different polymers, depending strongly on the elementary unit size as well as on the irregularity introduced by the initial member(s) of each series. The least-squares fitting of the property X and the normalized Wiener number W is expressed by linear or quadratic functions. The quality of the fit is characterized by the correlation coefficient r and standard deviation s. Significance t-test is always made for the regression coefficient of the quadratic term at a 95% level. Then, by substituting the $\overset{\approx}{W}_\infty$ value into the equation $X = f(W)$ thus found, one obtains the X_∞ bound value which property X has for an infinite polymer.

4. An illustration

The procedure is illustrated below by the infinite polycoronene chain (fig. 2).

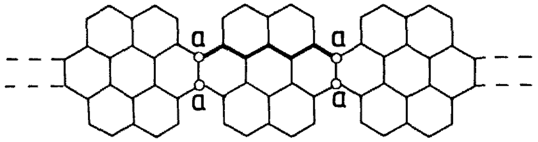


Fig. 2. The graph of an infinite polycoronene polymer for which $D_{13}^{\min} = 6$ (the black zig-zag line), the number of atoms in the elementary unit is $N_1' = 22$, and the distance number of the fusion point a (specified for one elementary unit) is $d_a' = 93$.

Proceeding from the intermediate results $W'_{11} = 1001$, $L = 2904$, $W'_{12)} = 3850$, and $B = (29N - 36)/22$, one obtains

$$W_n = 484n^3 + 473n^2 + 44n + 1 \tag{11}$$

or

$$W_N = (22N^3 + 341N^2 - 660N + 264)/484, \tag{12}$$

$$F = 44/(29N^3 - 65N^2 + 36N), \tag{13}$$

and

$$\overset{\approx}{W}_\infty = \lim_{N\to\infty} \frac{22N^3 + 341N^2 - 660N + 264}{11(29N^3 - 65N^2 + 36N)} = 0.068966. \tag{14}$$

For the specific HMO π-electronic energy E_π (π-electronic energy per electron) and HOMO–LUMO energy gap ΔE_π of the series, one obtains

$$E_\pi = 1.5194 - 0.6523\overset{\approx}{W}, \tag{15}$$

$$n = 10, \quad r = 1.000, \quad s = 0.00004,$$

while for the HOMO–LUMO gap, the regression is

$$\Delta E_\pi = 0.9009 - 10.9359\overset{\approx}{W} + 111.712\overset{\approx}{W}^2, \tag{16}$$

$$n = 9(2 - 10), \quad r = 0.9998, \quad s = 0.0012.$$

Hence,

$$E_\infty = 1.474; \quad \Delta E_\infty = 0.678 \text{ (in } \beta \text{ units).}$$

4.1. ELECTRONIC π-ENERGIES

4.1.1. Acyclic, peri- and catafused, and bridged conjugated polymers

In this section, we summarize all the results obtained so far by the TEMPO method for the specific π-electronic energies and energy gaps of infinite polymers. They are all open chain polymers, regarded as quasi-monodimensional crystals. Included here are mainly benzenoid polymers (cata-, peri-, and corona-fused), as well as a few alternant and non-alternant non-benzenoid or mixed benzenoid systems.

The 25 polymeric systems included in the initial TEMPO studies [1–3] and reevaluated for the present study are shown in fig. 3. Their π-electronic energies were estimated within the HMO-approximation [1], as well as by the PPP-method [2] for polymers 8, 12, 14–20, and 24. In addition, the influence of some structural modifications of polymers 8, 12, 14–17, 19–21, and 24 on their electronic properties has also been studied [3]. More specifically, the latter case deals with the attachment

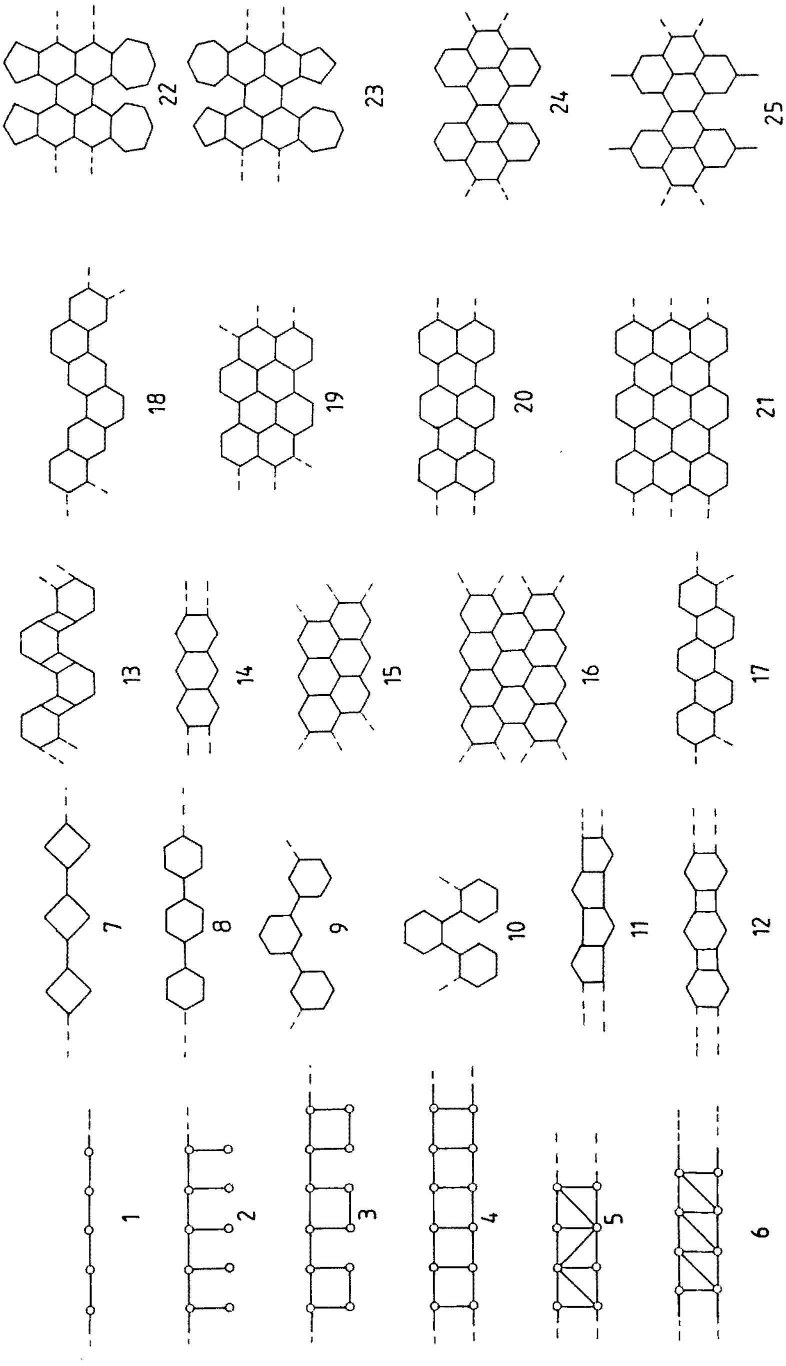


Fig. 3. Twenty-five polymers representing quasi-monodimensional systems with delocalized π-electrons.

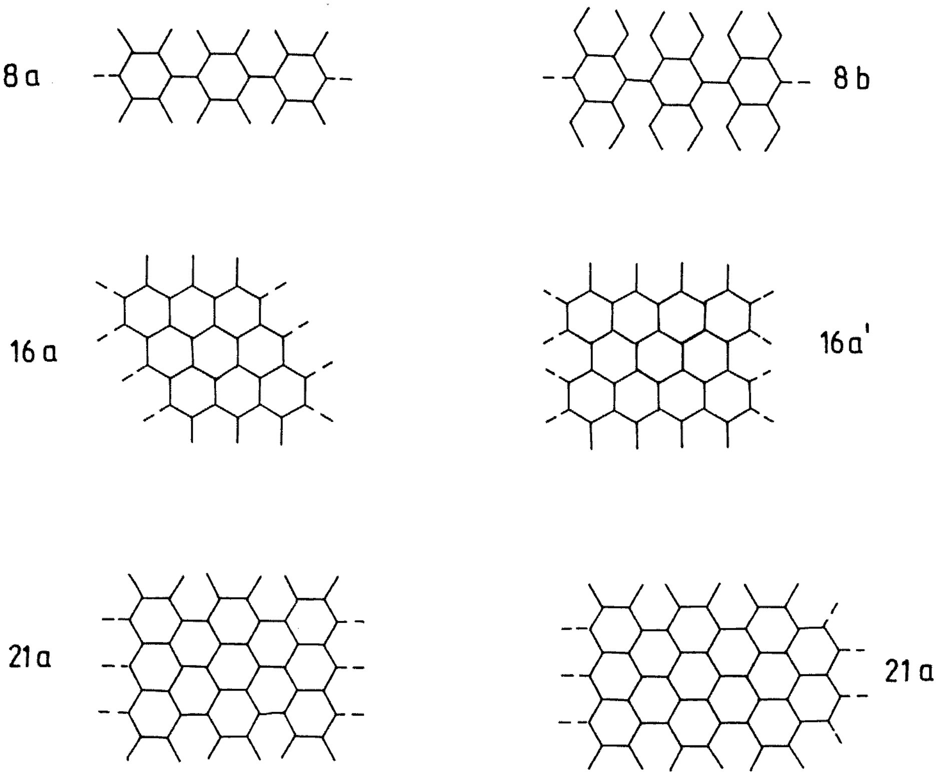


Fig. 4. Two structural modifications of polymers 8, 12, 14–17, 19–21, and 24 from fig. 3, including the attachment of acyclic conjugated branches with (a) one atom, (b) two atoms, illustrated by polymer 8. Two different attachment types are shown for polymers 16 and 21.

of acyclic conjugated branches with one and two atoms, as dispayed in fig. 4. The two different attachment modes of polymers 16 and 21 are also shown.

The polymers derived for the Wiener number vary from very simple to rather complicated ones:

$$\text{polymer } 7\text{:} \quad W = N^3/8, \tag{17}$$

$$\text{polymer } 8\text{:} \quad W = (2N^3 + 9N)/18, \tag{18}$$

$$\text{polymer } 12\text{:} \quad W = (N^3 + 3N^2)/12, \tag{19}$$

$$\text{polymer } 7\text{b:} \quad W = (88N^3 + 1719N^2 + 149990N - 2876112)/290. \tag{20}$$

The normalized Wiener index values for the infinite polymers under study are given in the first three columns of table 1. As seen, this topological index displays a fair discrimination, although some degeneracy of its values takes place. The latter does not affect calculated electronic energies (tables 1 and 2) since they are determined by different regression equations.

Table 1

Wiener numbers and specific π-electron energies of the 25 infinite polymers from fig. 3.

No.[a]	$\overset{\approx}{W}_\infty$	$\overset{\approx}{W}_\infty$ (a)[b]	$\overset{\approx}{W}_\infty$ (b)[b]	$\bar{E}_\infty$ (HMO)[c]	$\bar{E}_\infty$ [c,d]	$\bar{E}_\infty$ (PPP)[e]
1	0.3333			1.268	1.274	
2	0.1667			1.216	1.216	
3	0.1333			1.316		
4	0.1111			1.435		
5	0.0833			1.636		
6	0.0833			1.581		
7	0.2000			1.225		
8	0.1905	0.1212	0.0889	1.397	1.398	48.78
9	0.1429			1.396		
10	0.0952			1.400	1.399	
11	0.1250			1.416		
12	0.1250	NBMO	0.0833	1.412		50.90
13	0.1250			1.425		
14	0.1333	0.0952	0.0740	1.402		51.74
15	0.0833	0.0583	0.0556	1.452	1.455	64.94
16	0.0606	0.0455	0.0784	1.477	1.483	70.60
17	0.1333	0.0952	0.0740	1.434	1.437	49.73
18	0.1333			1.427	1.429	53.01
19	0.0833	0.0666	0.0556	1.476	1.484	61.02
20	0.1026	0.0784	0.0634	1.454	1.461	60.03
21	0.0702	0.0580	0.0493	1.482	1.496	
22	0.0580			1.426		
23	0.0580			1.426		
24	0.0741	0.0666	0.0606	1.457		62.01
25	0.0667			1.378		

[a] According to fig. 3. [b] According to fig. 4. [c] In β-units. [d] Ref. [49]. [e] In eV.

Some examples of the correlations between the normalized Wiener index and the specific π-electronic energy as calculated in β-units within the Hückel or PPP molecular orbital approximation are given below:

polymer 15: $E_{\mathrm{HMO}} = 1.502 - 0.606\overset{\approx}{W}$, (21)

$n = 6,\ r = 0.999,\ s = 4.3 \times 10^{-4}$;

polymer 25: $E_{\mathrm{HMO}} = 1.419 - 0.7225\overset{\approx}{W} + 1.603\overset{\approx}{W}^2$, (22)

$n = 6,\ r = 0.9999,\ s = 2.3 \times 10^{-4}$;

polymer 19: $E_{\mathrm{PPP}} = 138.38 - 1163.5\overset{\approx}{W} + 2819.7\overset{\approx}{W}^2$, (23)

$n = 7,\ r = 0.9826,\ s = 1.8$.

In general, the correlation coefficient is close to 1: in twenty-one out of twenty-five HMO cases, it is either 0.999 or 1.000. The standard deviation in thirteen cases does not exceed 5×10^{-4} and only in six cases is it slightly greater than 10^{-3}. This high accuracy is achieved in six cases with a simple linear function, and in nineteen others with a quadratic function. Even the simplest linear function provides a correlation coefficient close to 0.99 and a standard deviation not greater than 3×10^{-3}. Similarly, the ten equations obtained for the PPP-electronic energy (two linear and eight quadratic ones) have a correlation coefficient within the 0.973–1.000 range and a standard deviation 1.5–3.3. All these evidence that the normalized Wiener number is a topological index very appropriate for the calculation of the π-electronic energy of conjugated polymers.

Table 1 also contains the calculated bound values of the infinite polymers' specific HMO-electronic energy, which are within the 1.22–1.64 β-units range. In eleven cases, they are compared to the energy calculated from the explicit HMO-formulae of Tyutyulkov and Polansky [49], deduced by the finite differences method. The coincidence obtained is very high ($\Delta \leq 0.012$), which may be regarded as an evidence for the reliability of the two different approaches. On the other hand, the PPP-specific electronic energies provide generally a polymer ordering similar to that of the HMO-energies, polymer 8 being the least stable, while polymer 16 is the most stable one.

Applying the fourth stage of the TEMPO procedure, a general dependence was obtained between the specific HMO-electron energies and the normalized Wiener indices of twelve infinite polymers (nos. 4, 12–21, and 24). These are fused non-branched benzenoid and non-benzenoid systems containing six- and four-membered rings. Indeed, one could hardly expect to arrive at an equation comprising all twenty-five polymers under consideration, due to the great difference in their topology (acyclic, fused-, bridged-, and branched polycyclic systems with 3-, 4-, 5-, 6-, and 7-membered rings). The linear dependence obtained shows that the specific π-electronic energy increases with the decrease in the normalized Wiener number of the infinite polymers:

$$E_\infty(\mathrm{HMO}) = 1.531 - 0.843\,\overset{\approx}{W}_\infty\,, \tag{24}$$

$$n = 12,\ r = 0.899,\ s = 0.012.$$

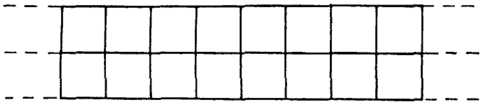
The trend thus found is similar to the previous finding [44] that the π-electronic energy of fused polycyclic molecules increases with the increase in the cyclicity, i.e. with the decrease in the Wiener number. The same trend was found also for the PPP-electronic energies of ten polymers (given in the last column of table 1), although the dependence is more complicated: a quadratic one with a negative $\overset{\approx}{W}_\infty$ term:

$$E_\infty(\mathrm{PPP}) = 97.53 - 588.0\,\overset{\approx}{W}_\infty + 1718\,\overset{\approx}{W}{}_\infty^2\,, \tag{25}$$

$$n = 10,\ r = 0.910,\ s = 3.7.$$

One should also mention here the capability of the Wiener number to produce approximately the same specific π-electron energies for polymers having similar structure. Thus, $\tilde{\tilde{W}}_\infty = 0.0580$ for both polymers 22 and 23, for both of which $E_\infty(\mathrm{HMO}) = 1.426$. Similarly, $\tilde{\tilde{W}}_\infty = 0.0833$ for the pair of polymers 5 and 6, which have $E_\infty(\mathrm{HMO}) = 1.636$ and 1.581, respectively.

Equations (24) and (25) reveal good possibilities for calculating the specific π-electronic energy of other conjugated polymers, proceeding from their topology only, i.e. from the $\tilde{\tilde{W}}_\infty$ values. As an illustration, we calculated the E_∞ values of four additional polycyclic polymers:



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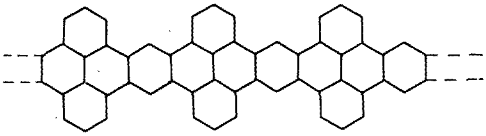

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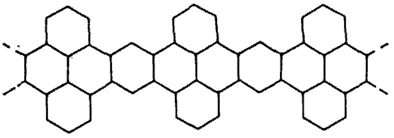
structure 26: $\tilde{\tilde{W}}_\infty = 0.0667$, $E_\infty(\mathrm{HMO}) = 1.475$,
structure 27: $\tilde{\tilde{W}}_\infty = 0.0870$, $E_\infty(\mathrm{HMO}) = 1.458$,



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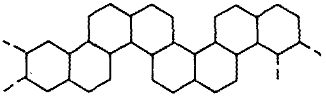

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structure 28: $E_\infty(\mathrm{PPP}) = 59.43$ eV,
structure 29: $E_\infty(\mathrm{PPP}) = 55.91$ eV.

Other conjugated polymers with a similar structure may be treated in this manner. Equations (24) and (25) thus provide a fast prediction of the π-electron energy of this important class of polymers.

4.1.2. Coronoid polymers

In addition to the conjugated polymers containing cata- and peri-fused benzene cycles, some polymers were studied the elementar units of which contain corona-fused benzene rings (fig. 5). The interest toward these polymers increased sharply during the last five years (see, for example, ref. [53]). They were selected so as to

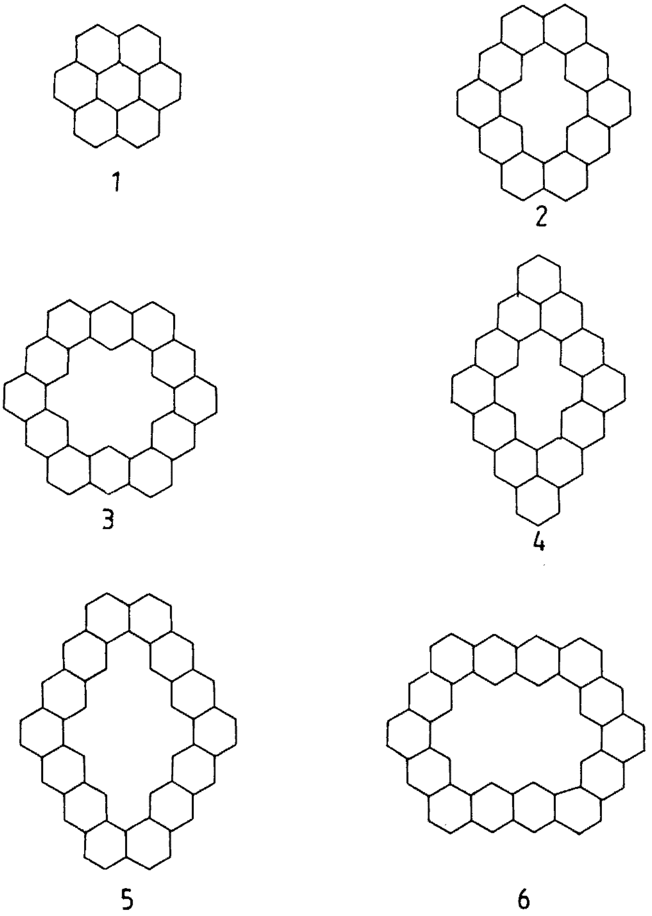


Fig. 5. Corona-fused benzenoids regarded as elementary units of six conjugated polymers.

examine the possible importance for electronic energy of different structural patterns, such as the different size and shape of the internal macrocycle, the addition of benzene cycles peri-fused at the outer periphery of the elementary units, etc.

Aiming at more precise extrapolations, oligomers with 1 to 10 elementary units were taken into consideration for each series. Additional information on the matter was obtained by omitting the first or the last member in each of the series.

The intermediate results obtained in the first part of the applied procedure are shown in table 2. The Wiener number W and the normalizing factor F were presented as polynomials in degree 3 of the total number of atoms N or the number of elementary units n. The last column contains the Wiener number normalized for infinite polymers ($N \to \infty$). Due to the similarity in the monomer unit structure, these numbers are close to each other or even, for polymers 5 and 6, they are the same.

Table 2

Wiener topological index W and its normalizing factor F as polynomial functions of the number of atoms N and that of the elementary units n, as well as the normalized Wiener number value $\tilde{\tilde{W}}_\infty$ for the infinite polymers of fig. 5.

No.[c]	The Wiener number W[a,b] and the normalizing factor F[b]	W_∞
1	$484n^3+473n^2+44n+1$ $(22N^3+341N^2-660N+264)/484$ $44/(29N^3-65N^2+36N)$	0.068966
2	$(7220n^3+3363n^2+1660n+3)/3$ $(190N^3+2223N^2+51908N-109896)/4332$ $76/(49N^3-109N^2+60N)$	0.068027
3	$4232n^3+1725n^2+960n+1$ $(92N^3+1173N^2+38364N-80040)/2116$ $92/(59N^3-131N^2+72N)$	0.067797
4	$(9680n^3+5808n^2+2236n+3)/3$ $(5N^3+102N^3+1768N-3852)/132$ $88/(57N^3-127N^2+70N)$	0.058480
5	$6804n^3+2079n^2+1958n+1$ $(14N^3+147N^2+10992N-22360)/324$ $108/(69N^3-153N^2+84N)$	0.067633
6	$6804n^3+2511n^2+1542n+1$ $(14N^3+195N^2+8304N-17176)/324$ $108/(69N^3-153N^2+84N)$	

[a] n is the number of elementary units.
[b] N is the total number of atoms.
[c] According to fig. 5.

Table 3

Specific π-electronic energy E_π(HMO) of the six coronoid polymer-homologous series of fig. 5 as a linear function of the normalized Wiener index $\tilde{\tilde{W}}$, as well as the energy values for infinite polymers E_∞.

No.[a]	Specific π-electron energy	r	s	E_∞
1	$1.5194-0.6523\tilde{\tilde{W}}$	1.0000	0.00004	1.474
2	$1.4862-0.5397\tilde{\tilde{W}}$	0.9963	0.00051	1.449
3	$1.4770-0.4702\tilde{\tilde{W}}$	0.9957	0.00046	1.445
4	$1.4678-0.4300\tilde{\tilde{W}}$	0.9977	0.00035	1.443
5	$1.4650-0.4117\tilde{\tilde{W}}$	0.9919	0.00053	1.437
6	$1.4678-0.4120\tilde{\tilde{W}}$	0.9951	0.00041	1.440

[a] According to fig. 5.

Table 3 contains the calculated HMO-energies per electron, E_π, of the six coronoid polymers presented as linear functions of the normalized Wiener number, As seen, the correlation is very high ($r = 0.992-1.000$) and the standard deviation is very small ($s \leq 0.00053$). The regression may be improved even further by omitting the first member of the series, thus increasing r to $0.997-1.000$ and diminishing the standard deviation to $s \leq 0.0002$. The extrapolated E_∞ values remain practically the same.

Inspection of all E_∞ values shows that they are within the 1.437–1.474 range, which is an indication of their high stability. The six infinite polymers may be ordered according to their specific π-electronic energy as follows:

$$1 > 2 > 3 > 4 > 6 > 5.$$

Some trends are traced within this inequality sequence. The latter, however, decreases with the increase in the distance between the elementary unit junction points $\Delta_{13}^{\min}$ (e.g. series 1-2-3-5).

The very high accuracy of the equations in table 3 results from the high degree to which the Wiener number describes the topology of polymerhomologues.

4.2. HOMO–LUMO GAP

4.2.1. *Acyclic, cata- and peri-fused, and bridged conjugated polymers*

The second electronic characteristic studied was the π-electronic energy gap which is related to the conductivity of polymers. The calculated HMO [1,3] and PPP [2] energy gaps of twenty-four conjugated polymers from fig. 3 and their structural modifications shown in fig.4 are collected in table 4. Structure 11 is not included since the lack of benzene rings in this 5-membered ring system alters strongly the energy of the highest occupied molecular orbital, which results in a very low correlation with the normalized Wiener index ($r = 0.187$). In the remaining twenty-four cases, the correlation is high, the correlation coefficient being in fourteen cases equal to 0.999 or 1.000, while in the remaining ten cases it is within the 0.982 to 0.998 range. In eleven cases, the standard deviation is less than 5×10^{-3}. In five cases only it is greater than 2×10^{-2}, due to the large relative but not absolute deviation from the zero gap. These results were obtained by making use of fifteen quadratic and nine linear $\Delta E/\overline{W}$ equations.

As seen in table 4, in half of the twenty-four polymers a zero HMO energy gap was found: these are cases 1, 4, 6, 7, 12, 14, 15, 16, 21, 22, and 23. The cases with a HMO energy gap $\Delta E_\infty \leq 0.017$ are also included since this numerical value is within the error limits of the current procedure. In five out of the seven cases, the zero predicted gaps gaps are in accord with the results of Tyutyulkov and Polansky [49] (the remaining five series have not been examined by these authors). In comparing the polymers with non-zero gaps, a good agreement was found for numbers 2, 10, 17, 18, where $\Delta \leq 0.012$ β-units. For four other cases, the disagreement

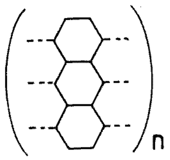
Table 4

Energy gaps of the twenty-four infinite polymers from fig. 3 and their structural modifications given in fig. 4.

No.[a]	ΔE_∞(HMO)[b]	ΔE_∞[b,c]	ΔE_∞(PPP)[d]	ΔE_∞[b,e]	ΔE_∞[b,c]
1	0.006				
2	0.823	0.828			
3	0.385				
4	0.017	0			
5	0.805				
6	0.004				
7	0.007				
8	0.772	0.828	5.40	0.514	0.518
9	1.274				
10	0.893	0.890			
12	0	0	3.42	NBMO	0
13	0.581	0.494			
14	0	0	2.24	0.376	0
15	0	0	0.80	0.182	0
16	0	0	0.52	0.089/0.090	0/0
17	0.752	0.764	5.41	0.030	0.408
18	0.693	0.695	5.09		
19	0.613	0.494	4.64	0	0.533
20	0.098	0	2.84	0	0.045
21	0	0.469		0/0.031	0/0.109
22	0				
23	0				
24	0.600		4.53	0.145	0.599
25	0.149				

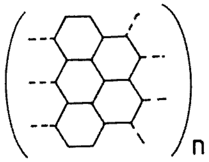
[a] According to fig. 3.
[b] In β units.
[c] Ref. [49].
[d] In eV.
[e] According to fig. 4.

between the two methods is significantly larger: no. 8, $\Delta = 0.056$; no. 13, $\Delta = 0.087$; no. 19, $\Delta = 0.119$. This discrepancy can be explained by the different symmetry of the infinite polymers, which are taken in our study to be open chain polymers, while in ref. [49] the respective cyclopolymers are taken under consideration. A drastic disagreement between the two calculations was found for polymer 21, where an energy gap of 0.47 was reported instead of the TEMPO zero gap. In order to check the symmetry reasonings for this strong disagreement, we re-examined polymer 21 with an open chain having C_{2v}-symmetry like that of the cyclopolymer:



D_{2h}

an open chain polymer
(our study)



C_{2v}

a cyclopolymer
(ref. [49])

Surprisingly, the energy gap thus calculated for polymer 21 was $\Delta E_\infty = 0.226$, which is approximately half the value for the cyclopolymer of the same symmetry. These results may be regarded as an evidence for the non-zero gap of the polymer with C_{2v}-symmetry.

The energy gaps of the examined conjugated polymers are always greater when calculated by the PPP method [2] than those determined by the Hückel method [1], a result anticipated by other authors [49]. Comparison of columns 1 and 3 in table 4 also reveals a certain correspondence between the two types of calculations. Thus, the polymers with zero HMO-gaps have smaller PPP-gaps than those with a non-zero Hückel forbidden zone. Polymers 15 and 16 were found to have rather small gaps, which is an indication for a possible enhanced conductivity.

The influence which the addition of acyclic conjugated branches has on the HMO-energy gaps of some of the twenty-five polymers was also studied. Again, a high correlation was found between the ΔE_∞ and $\tilde{\tilde{W}}_\infty$ values, the correlation coefficient being with very few exceptions 0.999 or 1.000. The standard deviation is also in most cases less than 0.01. Some illustrative examples are given below:

polymer 12b:
$$\Delta E_\infty = -0.9201 + 9.919\tilde{\tilde{W}}, \qquad n = 7,\ r = 0.9997,\ s = 0.0078; \tag{26}$$

polymer 14a:
$$\Delta E_\infty = -0.3409 + 0.02435\tilde{\tilde{W}} + 3.587\tilde{\tilde{W}}^2, \qquad n = 9,\ r = 0.9999,\ s = 0.0012. \tag{27}$$

The results obtained upon the structural modifications examined reveal two major trends: (i) The monocarbon branch addition to an alternant hydrocarbon with a non-zero gap reduces the latter. The attachment of a second atom at each branch enhances the gap again. Typical examples are polymers 17 and 19, having a gap of 0.752 and 0.613, respectively. The methylene branch additions reduce these gaps to zero, while the ethylene ones result in non-zero gaps of 0.408 and 0.533, respectively. (ii) The monocarbon branch addition to a zero-gap polymer produces a non-zero gap, while the subsequent lengthening of the branches with a second carbon atom reduces the gap to zero again. Polymers 14 and 15 exemplify this trend, their gaps being enhanced upon the first modification to 0.376 and 0.182, respectively, and then returning again to zero value upon the second modification. One should mention, however, that the two structure alterations have a minor effect on the zero gaps of polymers 20 and 21.

4.2.2. *Coronoid polymers*

The dependence of the HOMO–LUMO energy gap on the normalized Wiener index was studied in more detail in the case of corona-fused benzenoid polymers (fig. 5). Both linear and quadratic functions were examined for the polymerhomologous series having all ten members each, or having nine members due to the omission of the first or last member. The last case (with $n = 1-9$) produces a correlation with exactly the same correlation coefficients and standard deviations of the series having ten members. The predicted values of ΔE_∞ also change marginally ($\Delta = 0-0.003$ for both the linear and quadratic function). One may thus come to the conclusion that less than ten elementary units suffice for reliable ΔE_∞ predictions, the reason being the large size of each such unit.

For two systems (numbers 4 and 5), the ΔE_∞ prognoses were found to be practically independent of the type of function (linear or quadratic) and the correlation sample ($n = 1-10$, $1-9$ or $2-10$) with $\Delta(\Delta E_\infty) \leq 0.002$. For two other series (numbers 2 and 6), $\Delta(\Delta E_\infty) = 0.004$. The largest difference in the predicted values is displayed by series number 1.

All three linear-type prognoses proved to be very close to each other. In dealing with the $n = 1-10$ sample, the quadratic function improves the correlation as compared to the linear one, leading to correlation coefficients within the 0.9993–0.9999 range and the standard deviation being 0.0002–0.0012 for 5 series, while being 0.0050 for the remaining series 1. Omitting the first member in each series ($n = 2-10$) results in a further improvement of the correlation; the best correlation coefficients increasing to 0.9997 and the largest standard deviation being 0.0012.

The predicted energy gaps do not change essentially as compared to the $n = 1-10$ sample ($\Delta \leq 0.003$), but the deviation is higher for series 1 ($\Delta = 0.018$). Our analysis thus indicates that the $\Delta E/\overset{\approx}{W}_\infty$ correlation is best manifested by the quadratic function for the same samples containing all 1–10 members in each series or even better for the sample with $n = 2-10$. These two types of correlations are given in table 5 for the six coronoid polymerhomologous series examined.

None of the six polymerhomologous series of corona-benzenoids examined was found to have a zero gap for the infinite polymer. The ordering of the latter according to the ΔE_∞ values is the following:

$$\begin{array}{lccccccccccc} \text{no.} & 3 & \geq & 1 & > & 6 & > & 2 & > & 5 & > & 4 \\ \Delta E_\infty & 0.69 & & 0.68 & & 0.62 & & 0.57 & & 0.43 & & 0.12. \end{array}$$

Some conclusions result from the inspection of this sequence. Two trends were traced which diminish the HOMO–LUMO separation. The first one is related

Table 5

Energy gaps of the six corona-benzenoid polymerhomologous series given in fig. 5 as quadratic functions of the normalized Wiener index $\tilde{\tilde{W}}$, as well as the gaps for the infinite polymers ΔE_∞.

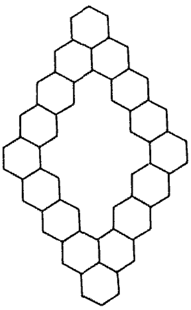
No.[a]	Energy gap[b]	r	s	ΔE_∞
1	$0.1817 + 6.2943\tilde{\tilde{W}} + 9.3035\tilde{\tilde{W}}^2$	0.9993	0.0050	0.660
	$0.9009 - 10.9359\tilde{\tilde{W}} + 111.712\tilde{\tilde{W}}^2$	0.9998	0.0012	0.678
2	$0.2228 + 4.9895\tilde{\tilde{W}} + 1.4040\tilde{\tilde{W}}^2$	0.9998	0.0012	0.569
	$0.6017 - 4.9416\tilde{\tilde{W}} + 66.235\tilde{\tilde{W}}^2$	0.9998	0.0004	0.572
3	$0.6415 - 2.4980\tilde{\tilde{W}} + 46.728\tilde{\tilde{W}}^2$	0.9999	0.0007	0.687
	$0.8976 - 9.2904\tilde{\tilde{W}} + 91.638\tilde{\tilde{W}}^2$	0.9998	0.0004	0.689
4	$0.0670 + 1.0239\tilde{\tilde{W}} - 2.6336\tilde{\tilde{W}}^2$	0.9997	0.0002	0.118
	$0.1085 - 0.2011\tilde{\tilde{W}} + 6.3395\tilde{\tilde{W}}^2$	0.9998	0.0001	0.119
5	$0.1325 + 4.4804\tilde{\tilde{W}} - 2.4373\tilde{\tilde{W}}^2$	0.9999	0.0007	0.424
	degenerate matrix			
6	$0.3182 + 6.1341\tilde{\tilde{W}} - 25.016\tilde{\tilde{W}}^2$	0.9995	0.0006	0.619
	$0.5800 - 0.8639\tilde{\tilde{W}} + 21.628\tilde{\tilde{W}}^2$	0.9997	0.0002	0.620

[a] According to fig. 5.

[b] First row: $n = 1-10$, second row: $n = 2-10$.

to the elongation of the fragments containing linearly fused rings, as is the case with polymers 3 and 6 as well as with 2 and 5. The presence of benzene rings that are peri-fused in the middle of the outer periphery of the structure is strongly favorable for smaller gaps (polymers 4 as compared to polymer 2).

Proceeding from the two favorable structural patterns thus revealed, one may expect that their combination could produce polymers with a very small gap. Such a polymer could be polymer 7 shown below:



7

The normalized Wiener number of this polymer is:

$$\tilde{\tilde{W}} = \frac{14N^3 + 273N^2 + 11208N - 23260}{3(77N^3 - 171N^2 + 94N)}, \tag{28}$$

where $\tilde{\tilde{W}}_\infty = 14/(3\cdot 77) = 0.060606$.

The linear and quadratic regression models derived for the HMO energy gap of the first ten members of this polymerhomologous series are

$$\Delta E_\infty = 0.0473 + 0.2063\tilde{\tilde{W}}, \tag{29}$$

$$n = 10,\ r = 0.9957,\ s = 0.0002;$$

$$\Delta E_\infty = 0.0335 + 0.5661\tilde{\tilde{W}} - 2.2812\tilde{\tilde{W}}^2, \tag{30}$$

$$n = 10,\ r = 0.9997,\ s = 0.00005.$$

As anticipated, proceeding from the favorable trends diminishing the energy gap of the corona-fused benzenoid polymers, both models predict the gap of the infinite polymer 7 to be as small as 0.06.

Concluding this section, one may resume that the TEMPO approach based on the topological index of Wiener, conveniently normalized for infinite polymers, provides a reliable description of the polymer electronic properties. As was well exemplified, this method provides the design of new polymers with low energy gaps, high π-electronic energies, etc. From this, one proceeds with both a qualitative analysis of the major structural trends and generalized equations (like eqs. (24), (25)) for series of polymers with similar structure in which the π-electronic energy or energy gap is calculated from the monomer topology only. Other physical or chemical properties could be treated in the same manner, as shown in the following section.

4.3. PHYSICO-CHEMICAL PROPERTIES OF POLYMERS

In this section, different thermal, volume, and optical properties such as melting point T_m, density d_4^{20}, refractive index n_4^{20}, and specific rotation d_D^{20} of polymers are treated by the TEMPO approach. Nine polymerhomologous series were taken under consideration, viz. alkanes, oligoesters, oligoamides, olygooxy-methylenes, oligoimines, oligopeptides, halogenated alkanes, and olygooxy-ethylenes [4]. The respective polymers are shown in fig. 6, listed in the following order: (1) polyethylene, (2) cyclic polyethylene, (3) polyethyleneimine, (4) polyoxyethylene, (5) polyoxymethylene, (6) polycapramide, (7) polytetrafluoroethylene, (8) poly-L-proline, and (9) polyethyleneterephthalate. Molecular graphs of these polymers are given in fig. 6 in several modifications – with and without hydrogen atoms, as well as without terminal groups or fluorine atoms.

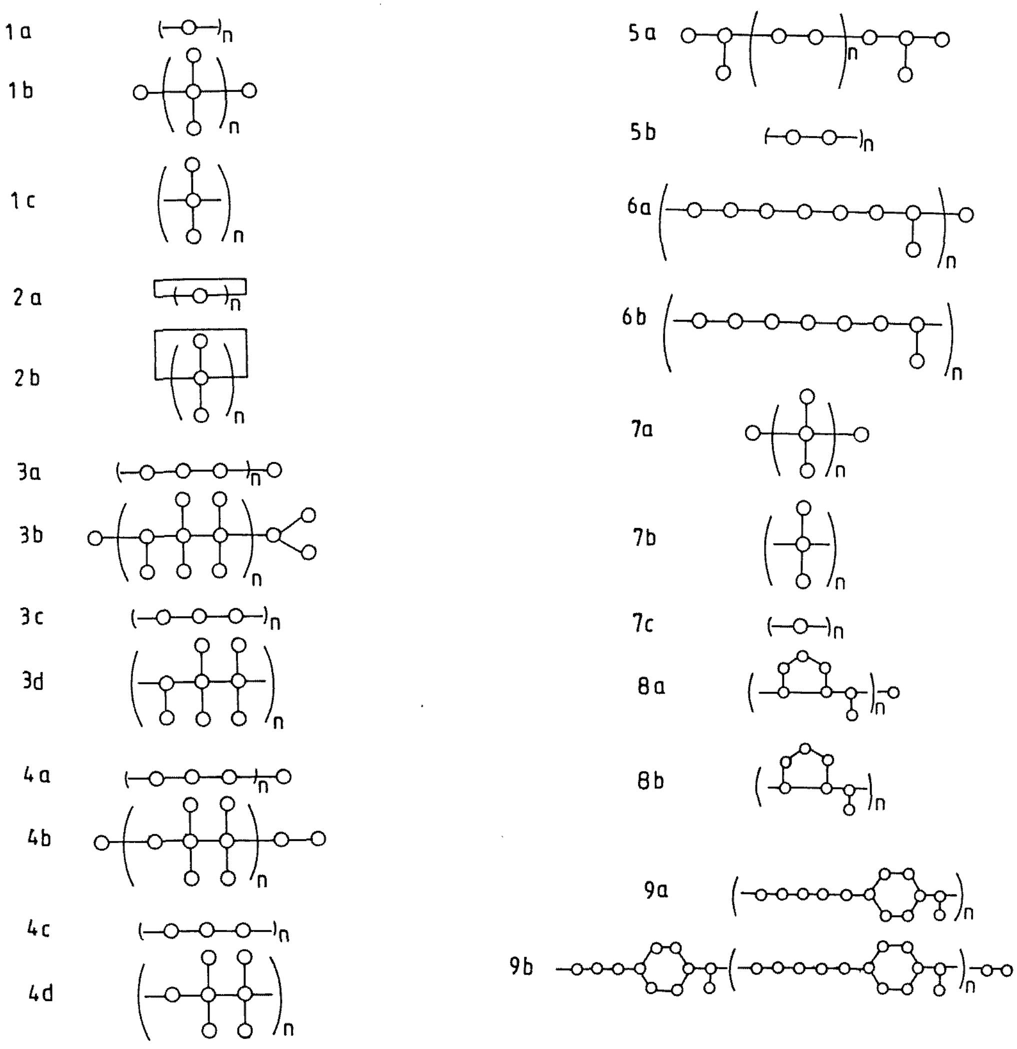


Fig. 6. Molecular graphs of the nine polymers under study and their modifications accounting for the H atom and neglecting the terminal groups. Structure 7c does not contain fluorine atoms.

The following $\overset{\approx}{W}_\infty$-values were obtained: 0.083333 for cases 2b, 2c; 0.11111 for 1b, 1c, 7a, 7b; 0.125 for 3b, 3d, 8a, 8b; 0.14286 for 4b, 4d; 0.22222 for 8c, 8d; 0.25 for 2a; 0.29167 for 6s, 6b; 0.33333 for 1a, 3a, 3c, 4a, 4c, 5a, 7c. Some examples of the correlations derived for the polymer properties under study and the normalized Wiener index $\overset{\approx}{W}$ are given below (for more details, see ref. [4]):

polymer 9a: $$T_m = 1463 - 5318\overset{\approx}{W}, \tag{31}$$

$$n = 10\ (1-10),\quad r = 0.9944,\quad s = 3.3;$$

polymer 3a: $$n_D^{20} = 1.7904 - 1.0556\overset{\approx}{\bar{W}} + 0.8088\overset{\approx}{\bar{W}}^2, \quad n = 6\ (1-9),\ r = 0.9998,\ s = 0.0005; \tag{32}$$

polymer 1b: $$d_4^{20} = 1.1298 - 2.513\overset{\approx}{\bar{W}}, \quad n = 12\ (5-16),\ r = 1.0000,\ s = 0.001; \tag{33}$$

polymer 8a: $$\alpha_D^{20} = -1916 + 14066\overset{\approx}{\bar{W}} + 26981\overset{\approx}{\bar{W}}^2, \quad n = 27\ (1-40),\ r = 0.9975,\ s = 8.8. \tag{34}$$

In table 6, the calculated values of the polymer properties under study are compared with the experimental ones, as well as with those obtained by the additive group method and Padé extrapolation procedure. Three different factors affecting the calculated property values were studied.

An optimized correlation sample is obtained in most cases by excluding the initial members of each series because their properties usually deviate strongly from the general trend. The calculation of the polytetrafluoroethylene melting point is a typical example. The TEMPO method produces a melting temperature within the 350–464 °C range when all data are used. However, it is within the 312–367 °C range, i.e. much closer to the experimental range of 327–342 °C, when the first two points are omitted. Similarly, the polyoxyethylene melting point is 48 °C when all points are used, whereas it increases to 57 °C upon eliminating the first four points, thus approaching the experimental values which are within the 60–76 °C range.

Careful examination of table 6 also indicates that incorporating H atoms in the molecular graph (the latter is usually hydrogen depleted) improves the results only for polymers with a very simple structure whose elementary units contain one or two carbon (or other non-hydrogen) atoms. Such is the case for polyethylene. In dealing with the other polymers where several atoms heavier than hydrogen (C, N, O) constitute the elementary units, the hydrogen atom effect is suppressed and may be neglected.

Elimination of the fluorine atoms in polytetrafluoroethylene, however, resulted in a melting point value which is lower than the experimental one by 80 °C, while the deviation is only 20 °C when these atoms are taken into account. Perhaps one may conclude that no other atom heavier than H could be neglected in describing polymer topology.

Neglection of the terminal groups (indicated by an asterisk in table 6) would simplify the calculations provided it does not significantly affect their accuracy. We observed practically no change of the refractive indices of polyethyleneimine and polyoxyethylene, where the terminal groups are hydrogen atoms ($\Delta n_D^{20} \leq 0.0002$). Similarly, the change in the specific rotation of poly-L-proline is not really significant ($\Delta\alpha \approx 1.5\%$). In the case of melting points, $\Delta T_m \approx 1-2\%$ for polyoxyethylene, polycapramide and polyethyleneterephthalate. For polyethylene and polytetrafluoroethylene, the deviation is very high ($\Delta T_m = 22$ °C, or 22.5% and 55 °C, or 15%,

Table 6

Experimental and calcualted values for some polymeric properties of the polymers under study.

Polymer[a]	Property	Experimental values[b]		GAM[c]	Padé[d]	TEMPO[e,f]
1	T_m (°C)	137–146	[54]	141		21.3
		141	[16]			60.6
		110–135	[55]			115.0^{H}
		104–133	[3]		115.8	$\underline{123.1}^{H}$
		105–130	[56]			95.4^{H*}
1	d_4^{20}	0.855–0.970	[54]	0.8833–0.9981		0.8419
		0.855–1.000	[16]			0.8454
		0.918–0.968	[55]			0.8505^{H}
		0.918–0.955	[56]		0.8555	$\underline{0.8506}^{H}$
						0.8473^{*}
						0.8495^{H*}
2	T_m (°C)	–		–		82.50
						$\underline{69.6}^{H}$
3	n_D^{20}	–		1.5228		1.528
						$\underline{1.528}^{H}$
						1.526^{*}
						1.528^{H*}
4	T_m (°C)	62–76	[54]	140		48.1
		62–72	[16]		191.1	55.5
		60	[3]			$\underline{56.9}^{H}$
		66–68	[55]			55.9^{H*}
4	n_D^{20}	1.4563	[54]	1.478	1.470	1.475
		1.51–1.54	[54]			
		(high molecular)				$\underline{1.475}^{H}$
		1.458–1.467	[55]			1.474^{*}
						1.475^{H*}
5	T_m (°C)	178–200	[54]	187		214.8
		198	[16]		50.5	$\underline{231.0}$
		185	[3]			70.4^{*}
		173–180	[55]			103.4^{*}
		173–178	[56]			
6	T_m (°C)	214–250	[54]	207		217.2
		214–233	[16]		230.7	$\underline{214.3}$
		215	[3]			215.9^{*}
		210–225	[55]			
		215–220	[56]			
7	T_m (°C)	327–342	[54]	300		171.0
		327	[3]			350.5
		327	[55]		55.3	$\underline{366.7}$
		327	[56]			312.1^{*}
						257.9^{**}

. . . continued

Table 6 (continued)

Polymer[a]	Property	Experimental values[b]		GAM[c]	Padé[d]	TEMPO[e,f]
8	T_m (°C)	–		–		357.8
						359.0
						223.2*
						353.5*
8	α_D^{22}	−540	[54]	–		−559.3
						−570.6
					−512.0	−579.3*
9	T_m (°C)	250–265	[54]	203	1193.6	281.3
		265–284	[16]			277.5*
		256	[3]			
		255–265	[55]			
		257	[56]			

[a] The numbering of polymers is given in fig. 6.

[b] References used.

[c] Method of additive groups [16].

[d] Padé approximation [57].

[e] Topological extrapolation method (the values, obtained by the best version of the method, are underlined).

[f] H-molecular graphs including hydrogen atoms. *Molecular graphs without terminal groups. **A molecular graph without fluorine atoms.

respectively). Although more polymers should be examined in order to arrive at definite conclusions, our preliminary conclusion is that terminal groups should not be neglected when using the TEMPO procedure.

The best TEMPO values of the polymer properties under investigation are underlined in the last column of table 6. They are obtained by taking into account the terminal groups, neglecting the initial members of the polymerhomologous series and, in some case, by accounting for hydrogen atoms. As seen in table 6, these best values are very close to the experimental ones. Thus, for the melting points of polymers 1, 4, 5, 6, 7, and 9, the deviation from the nearer bound of the experimentally determined range is (in °C and %): −6.9, −11.9, +33.2, 0, +24.7, −2.7; and 5.3, 19.8, 16.6, 0, 7.2, 1, respectively. The deviations are small for the other properties, as well. They are 0.5%, 1.0% and 3.6% for the density of polyethylene, the refractive index of polyoxyethylene and the specific rotation of poly-L-proline, respectively.

Table 6 reveals that the TEMPO and group additive method provide comparable results, particularly in estimating the refractive index. In two cases (polymers 4 and 9), the TEMPO values are much closer than group additive method values to the experimental ones: 55.5 °C versus 140 °C versus 62–76 °C (polymer 4) and 281.3 °C versus 203 °C versus 250–265 °C (polymer 9), respectively. One should, however, bear in mind the advantage of the group addition method in providing theoretical estimates in cases where experimental data are not available.

It was of considerable importance to compare the predictions of polymer properties made by our topological extrapolation method with those of the well-known Padé approximation. The Padé values calculcated by us are also given in table 6. In the few cases dealing with density, refractive index and specific rotation, the two methods provide comparable results. In dealing with melting points, however, similar results were obtained for polyethylene and polycapramide only. The Padé melting points of polyoxyethylene, polyoxymethylene, polytetrafluoroethylene and polyethyleneterephthalate are, however, very poor, the deviations from the nearer melting point being +115 °C, −128 °C, −272 °C, and even +929 °C, respectively.

The reasons for these unrealistic Padé approximations are the following. Within this method, a certain quantity is presented by a McLaurin series of some parameter (e.g. the degree of polymerization). In dealing with polymer properties, however, the exact functions are not known and the coefficients in the McLaurin series must be determined empiricially by least-squares fitting. The Padé polynomials thus obtained from the failures of this method or, more specifically, small variations of the experimental data, can sometimes significantly change the coefficients, thus producing absurd extrapolations. A second reason is that the optimal degree of the Padé polynomial (diagonal elements of the Padé table) cannot be uniquely determined. As a result, the reliability of the Padé extrapolations is poor.

The TEMPO method describes polymer properties in such a manner which mathematically is equivalent to the Padé approximants. The major advantage of our approach is, however, in a much lesser extent to which the curve fitting is used, due to the derivation of exact (uniquely determined) Wiener number polynomials reflecting polymer topology. Thus, the TEMPO correlation equations for the polymer properties (linear or quadratic functions of the Wiener topological index) are equivalent to polynomials in degree 3 or 6, with the degree of polymerization as a variable. Within the Padé approach, obtaining the latter type of polynomials would require fourteen empirical coefficients.

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