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

*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 $j$: $d_{ij} = 1, 2, 3, \ldots, d_{\text{max}}$. 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 $W$: