Application of connectivity indices in polymer chemistry

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Abstract

A method for the calculation of connectivity indices of polymers was presented as useful tool for prediction of important properties of polymers. The proposed method makes it possible to correlate the chemical structure of molecules with large amount of information about their physical features.

Keywords: polymers, prediction of properties

Introduction

The structural formula of polymer contains coded within it properties. It is important to elucidate in detail how these properties depend on the molecular structure. The chemistry of the 21st century is focused on studies concerning mathematical relationships between chemical structure of polymers and their observable properties. The quantitative structure-property relationship (QSPR) methodology appears to be an essential tool in polymer chemistry. Structural descriptors describe numerically the structure of the molecule. The descriptors can be obtained on the basis of graphs of molecules consisting of vertices (i.e. atoms) and edges (i.e. bonds). Approach for prediction of molecular properties of polymers uses connectivity indices such as zeroth- and first-order which were described in the work of Bicerano [1-7].

Experimental Procedure

A molecular graph is constructed by representing each atom of a molecule by a vertex and bonds between atoms by edges. The degree of each vertex equals the valence of the corresponding atom. For example, propane and cyclopropane are represented by graphs shown in Fig. 1.

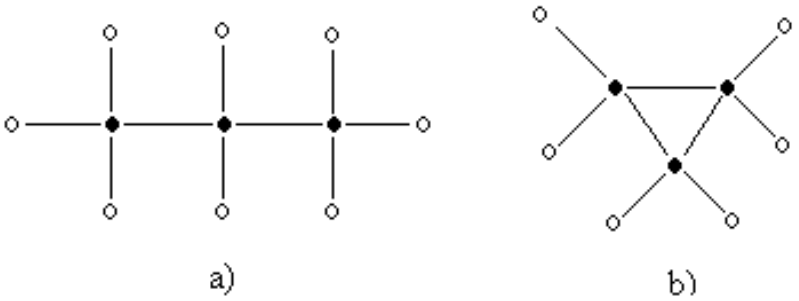

Fig.1. Molecular graphs of hydrogencarbons: a) propane, b) cyclopropane

Properties of substances depend on their chemical composition as well as the shape of their molecules, thus there are correlations of descriptors of molecular shape to certain properties of

substances. Molecular graphs are *hydrogen suppressed graphs*, i.e. vertices of the graph correspond to non-hydrogen atoms.

The Randić branching index R is defined as $R = \sum_{edges} \sqrt{\frac{1}{m \cdot n}}$, where for any edge in the summation term, *m* and *n* stand for degrees of adjacent vertices joined by that edge.

Results and Discussion

It is possible to use molecular graphs to construct descriptors of molecular shape and size that correlate to properties of substances. The hydrogen suppressed molecular graph of 2-methylbutane is shown below (Fig. 2).

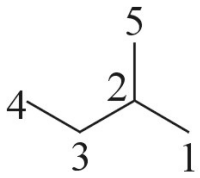

Fig.2. Hydrogen suppressed molecular graph of 2-methylbutane

The Randić index of 2-methylbutane is $R = \sqrt{\frac{1}{1 \cdot 3}} + \sqrt{\frac{1}{3 \cdot 2}} + \sqrt{\frac{1}{2 \cdot 1}} + \sqrt{\frac{1}{1 \cdot 3}} \approx 2{,}270$.

The first bond (between atoms 1 and 2) connects vertices of the first and of third degree, the second of third (2) and second (3) degree etc. There are four edges, and two ways of choosing two non adjacent edges (Fig.3).

Fig.3. Two ways of choosing two non adjacent bonds in 2-methylbutane

In the case of polymers, graphs describe the bond pattering between monomers. The vertices and edges consist of a data structure that stores important informations. Connectivity indices are based on path fragments of a molecular graph. First, it should be assigned δ-values to each atom (vertex degrees being the number of adjacent vertices) according to formula $\delta^{v} = \frac{Z^{v} - N_H}{Z - Z^{v} - 1}$, where Z^{v} is the number of valence electrons around an atom, Z is the total number of electrons around an atom, and N_H is the number of hydrogens bonded to an atom. In the next step, it should be calculated zeroth- and first-order indices: $0_{\chi} = \sum_{atoms} \frac{1}{\sqrt{\delta_i}}$, $1_{\chi} = \sum_{bonds} \frac{1}{\sqrt{\delta_i \delta_j}}$, where i and j are indices of the endpoint atoms of a bond. χ increases as the molecule size increases. In this case, the path finding algorithm is needed. In order to create the predictive model, numerical descriptors of structure are related to physical and chemical properties of polymeric materials.

Conclusions

The main goal of chemistry and technology of polymers is synthesis of molecules having defined properties. The use of topological and connectivity indices as structural descriptors is important in proper and optimal polymer design. The combinatorial design approach appears to be a useful platform for numerical experimentation in the design of polymeric materials.

References

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