

## Computing Polymer Properties Using Correlations

Correlative methods allow the prediction of a wide range of polymer properties. Cohesive energy densities, glass transition temperatures, molecular volumes, densities, and many additional properties may be estimated using techniques based on the chemical structure of constitutional repeat units and predefined correlations. When employed in the study of systems which resemble training set materials, correlative methods are of value in the development of novel materials, providing rapidly acquired property information which may be used in targeting specific characteristics. Here we describe the topology based methodology for polymeric property prediction developed and pioneered by Jozef Bicerano of Dow Chemical and made available in the MedeA® environment. The basis for the correlations employed is described and typical results for molar volumes and glass transition temperatures are illustrated.

*Keywords: polymer, glass transition temperature,  $T_g$ , topological indices, empirical correlation*

### Polymer Properties

The importance of polymeric systems has led to interest in the relationships between polymer structure and properties. Understanding such relationship allows for the design and optimization of materials targeting specific property characteristics. Much effort has therefore been dedicated to the development of methods which can reliably predict polymer properties [1]. Atomistic simulation methods [2] are particularly capable and successful, and when coupled with reliable forcefield [3] descriptions, are able to describe the properties of a wide range of polymeric systems with accuracies comparable to those obtained experimentally [4].

However, the unique character of polymers, where systems with long relaxation times predominate, and the large number of possible structural and copolymer blends which must be considered, mean that empirical correlative property prediction methods also play an important role in polymer research. A range of such methods has been described and these are summarized in the literature [5].

In this application note we describe and review the topologically based polymer property prediction scheme developed by Jozef Bicerano and described in his book, *Prediction of Polymer Properties*[6]. This capability is available in the

MedeA® environment and may be employed to evaluate a wide range of polymer properties.

In contrast to other empirical polymer property prediction schemes, which employ group based correlations, Bicerano's method is based on topological connectivity indices, originally developed by Kier and Hall [7-9], and employed in quantitative structure activity relationship (QSAR) based analysis of pharmaceutically active compounds. Bicerano has augmented correlations based on connectivity indices with correction terms relating to key features contained within constituent repeat units.

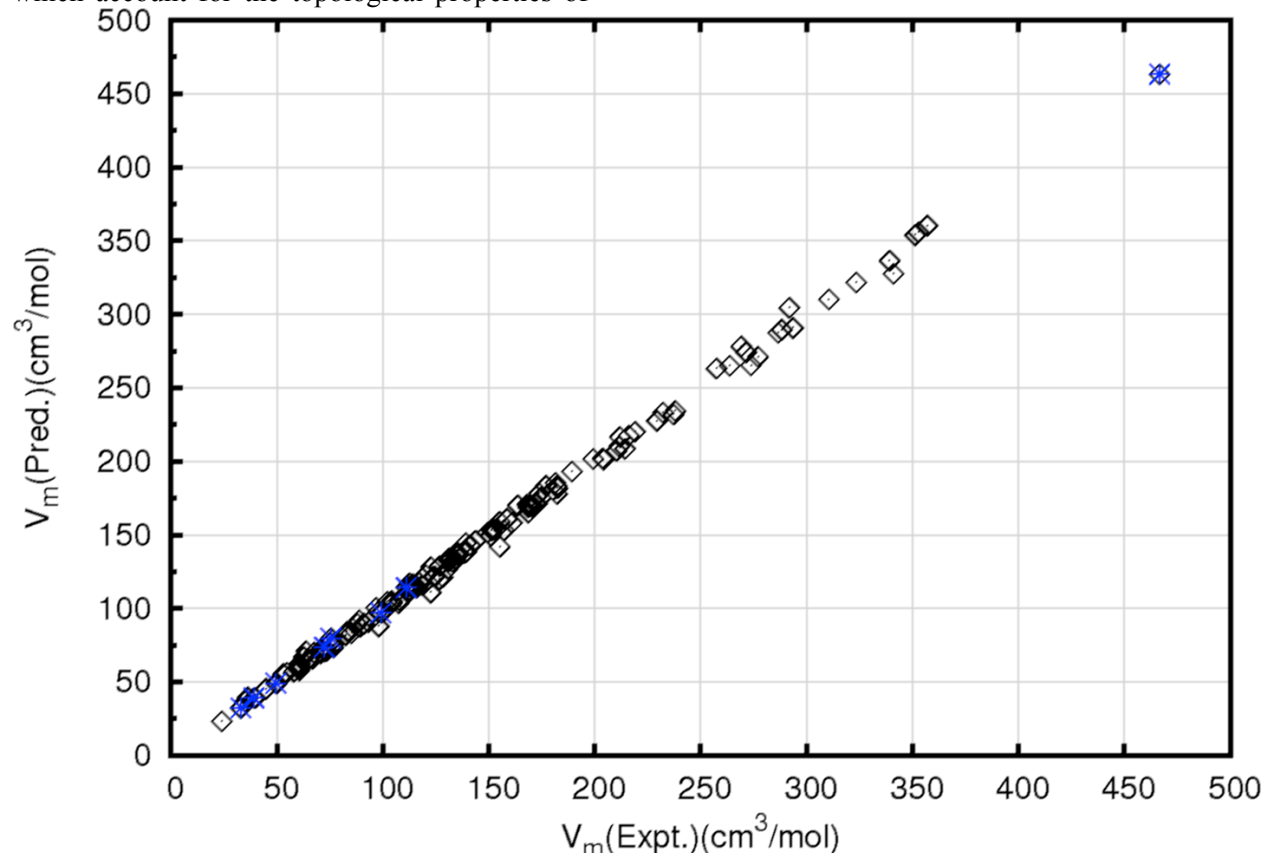
The strength of Bicerano's approach is that the reliance on non-group based descriptors implies that predictions for polymers not part of the training set, composed of groups which have not yet been encountered, will generally be reliable.

### Topological Indices

As discussed by Kier and Hall [7], flexible descriptors of molecular properties can be extracted from the hydrogen-suppressed connectivity graph of a given compound. Here atoms represent the vertices in the connectivity graph, and bonds represent connecting edges between vertices. The resulting graph is then analyzed in terms of its topological properties.

Kier and Hall developed connectivity indices which account for the topological properties of

the graph and account for vertices,



**Figure 1.** Comparison of experimental and predicted molar volumes,  $V_m$ , for 152 polymers as reported by Bicerano [6] (black open symbols). MedeA® Polymer Property value results are shown (blue crosses) for a selection of systems.

edges, and higher order constructs within that graph. For example, a simple topological index,  ${}^0\chi$ , may be obtained by counting heavy atoms connected by a single edge to each vertex, and for the complete structure by forming the sum of the reciprocal of the square root of this count over all vertices. Summed in this way, a single real number,  ${}^0\chi$ , represents a measure of the level of heavy atom branching for any chemical system. The more heavily branched a given repeat unit, the lower its  ${}^0\chi$  index.

A similar vertex level descriptor may be obtained by counting not nearest vertex neighbors but nearest neighbor valence electrons at each vertex. This descriptor, dubbed  ${}^0\chi^v$ ,

contains information relating to the bonding content of the system in a single descriptor.

This summation approach may be extended to include similar sums over edges (bonds), and as such samples the heavy atom connectedness and valence electron counts. Such topological descriptors, called  ${}^1\chi$  and  ${}^1\chi^v$ , succinctly represent information about the bonding and electronic character of repeat units.

Kier and Hall showed that the resulting topological indices provide valuable descriptors for a range of physical properties [9]. Bicerano recognized that such descriptors provide a route to reliable predictions of properties for polymers with different chemistries, and Bicerano's

*Prediction of Polymer Properties* provides extensive details of the resulting prediction scheme for polymer systems developed at the Dow Chemical Company [6]. Here repeat units are treated as being infinitely bonded through the connection of head and tail atoms, and the  ${}^0\chi$ ,  ${}^0\chi^v$ ,  ${}^1\chi$ , and  ${}^1\chi^v$  topological indices computed for the resulting (essentially infinite) polymer system. Bicerano provides information on the correlation of these descriptors with empirical polymer property data, and augments the resulting correlations using counts of specific entities in repeat units.

The resulting set of correlations and descriptor types provides an extensive database of information which may be used to predict polymer properties.

### An Example Correlation

An illustration of the form of correlation proposed by Bicerano is shown in Equation 1:

$$V = 3.64277 \cdot {}^0\chi + 9.798697 \cdot {}^0\chi^v - 8.542819 \cdot {}^1\chi + 21.693912 \cdot {}^1\chi^v + 0.978655 \cdot N_{MV} \quad (1)$$

Here the molar volume,  $V$ , of the polymer is given as a function of vertex and edge  $\chi$  descriptors, with suitably fitted correlation coefficients. Equation (1) also contains a correction term,  $N_{MV}$ . This term is based on a count of key structural features known to significantly affect polymer volume. For example,  $N_{MV}$  contains counts of double bonded carbon atoms, ring structures, and bulky halogen atoms.

The resulting correlation between experimental and predicted molar volumes obtained by Bicerano for a set of 152 polymers is shown in Figure 1.

Each of the correlations described by Bicerano has been carefully designed and such property correlations may be employed in predicting additional quantities. For example, correlations for the molecular volume of a given polymer may be combined with cohesive energies from

an additional correlation, yielding cohesive energy densities, and then solubility parameters. Solubility parameters may in turn be combined with additional correction terms to produce correlations capable of describing glass transition temperatures. The correction terms employed in the estimation of glass transition temperatures are extensive, including for example, counts of the presence of *meta*-, *ortho*-, and *para*- ring systems on the polymer backbone. Property predictions which rely on several correlations, such as those for glass transition temperatures, will not in general be in as good agreement with experiment as properties which rely on only one correlation. Nevertheless, the speeds of prediction, and the flexibility of its practical application, are valuable in repeat unit selection and design, particularly when employed with careful validation.

### An Additional Example Correlation

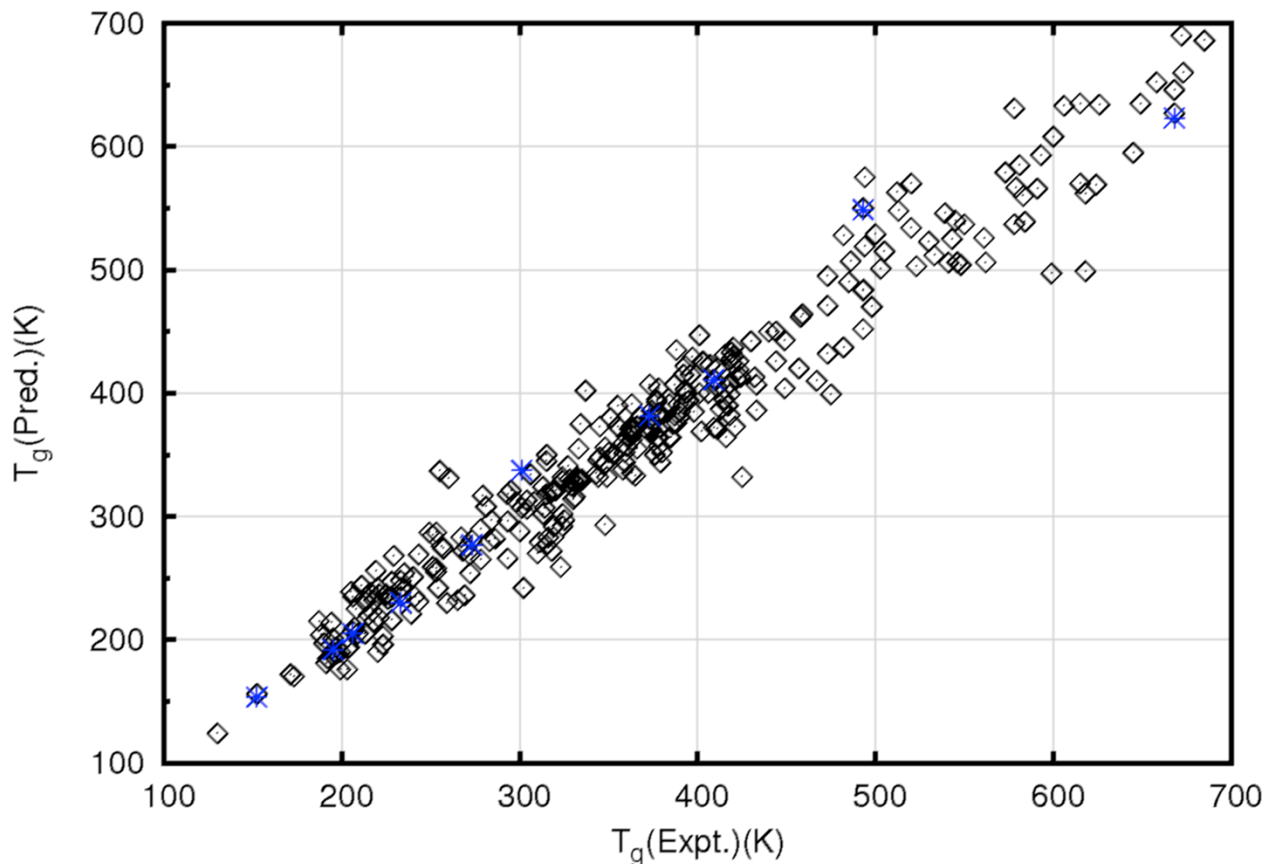
An illustration of the comparison obtained for 320 polymer systems and the correlation model for glass transition temperatures, using data from Bicerano's *Prediction of Polymer Properties* is provided in Figure 2. The agreement between experimental and calculated values shows some spread, (the standard deviation of 24.6K is reported by Bicerano). However, the level of agreement achieved is sufficient to provide general guidance as to the likely behavior of putative systems.

### Computing Polymer Properties using Correlative Methods with Medea®

The Polymer Properties stage available in Medea® flowcharts takes as input a polymer repeat unit, containing head, tail, and backbone atoms. Such a unit may be readily constructed using the Medea® Molecular Editor. Once constructed, a Flowchart containing a Polymer Properties stage will analyze the topology of the repeat unit, compute its  $\chi$  descriptors and

correction terms and report computed polymer properties. The properties provided currently include:

- $V_w$ , van der Waals volume
- $V$ , the molar volume
- $d$ , the amorphous density



**Figure 2.** Comparison of experimental and predicted glass transition temperatures for 320 polymers as reported by Bicerano [6] (black open symbols). Selected MedeA® Polymer Property values are shown in blue crosses.

- $E_{coh1}$  and  $E_{coh2}$ , cohesive energy densities
- Solubility parameters (based on both  $E_{coh1}$  and  $E_{coh2}$ )
- $C_p$ , the heat capacity
- $P_s$ , the molar parachor
- $T_g$ , the glass transition temperature

The use of MedeA® Flowcharts in providing access to Polymer Properties allows for efficient

reporting and storage of computed property reports, using the MedeA® Job Server architecture, and supports the computation of properties for collections of potential polymers.

### Designer Correlations

The Polymer Property stage reports a wide range of molecular descriptors, enabling the development of designer correlations employing custom stages. Additional support for the

development of designer correlations will be added in future releases.

## Summary

The MedeA® environment Polymer Property Prediction stage provides a robust implementation of the topology based correlative methods described by Bicerano [6], for rapid calculation of a wide variety of materials properties. The method provides polymer properties rapidly based on the topology and chemistry of constituent repeat units and provides a complementary capability to the atomistic simulation capabilities provided by the Polymer Builder, Materials Builder, PCFF+, and the MedeA® LAMMPS modules.

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