Application of chemical graph theory for the estimation of polymer dielectric properties

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Chemical graph theory has been used to estimate the polarizability and dielectric constant of 20 polymers. The compounds examined included aliphatic, chlorinated and aromatic polymers, as well as polyethers and polycarbonates. The dielectric properties of these polymers were estimated based on the chemical composition of the repeat unit, with one phantom carbon atom attached to each end of the repeat unit, using a variation of the index proposed by Randic. The calculated values were found to be within ±2.5% of the experimentally determined polarizabilities.

(Keywords: chemical graph theory; dielectric constant; polarizability, group additivity)

INTRODUCTION

In many instances the pattern of interconnections between the atoms of a molecule are found to correlate strongly with its physical properties. A partial list of properties which have been found to correlate with molecular topology include[1–3] heat of vaporization, molar refraction, molar volume, refractive index, boiling point, specific gravity and viscoelasticity.

The dielectric constant of an insulator is defined as the ratio of capacities of a parallel plate condenser measured with and without the dielectric material placed between the plates. When a voltage is applied across the condenser, polarization proceeds by dipole orientation (normal permittivity) and by ionic conduction. If the electrodes are blocking, or if the dielectric is heterogeneous, ions will accumulate at the electrode or at interfaces within the dielectric, forming a charged layer. This charged layer will be quantitatively similar to that established by dipole orientation. Both group additivity and chemical graph theory will be unable to estimate the polarizability (dielectric constant) of a material if the permittivity is controlled by mobile ions. Chemical graph theory and group additivity can, however, estimate the permittivity and dielectric constant of polymers whose dielectric properties are dominated by dipole orientation effects.

The ability to estimate accurately the dielectric properties of a polymer is of value in the development of new materials for printed circuit boards and flex circuits and as interlevel dielectrics for integrated circuit packaging applications. A recently described interpolation routine, which utilizes an experimentally derived database and group contribution theory, is capable of predicting (and optimizing) the dielectric constant (and other properties) of polymers for printed circuit boards[4]. However, this procedure has no provision for the estimation of property values of polymers made up of groups not included in the original database. It is the purpose of this investigation to devise a complementary extrapolation routine and to extend our ability to estimate polymer property values to new groups (including groups not yet developed).

Chemical graph theory is based on the supposition that the topology (connectivity) of a molecule is correlated to many of its intrinsic physical properties. A property that is independent of state and is based on the intrinsic nature of the isolated molecule is said to be a molecular property. Molecular properties include polarizability, molar refraction, heat of formation, molar magnetic susceptibility, etc. Properties that depend on the state of aggregation, such as the dielectric constant, ε', and the index of refraction are referred to as molar or bulk properties. Chemical graph theory has been shown to be very successful in providing an estimate of the intrinsic properties of both organic and inorganic compounds when used in conjunction with a regression analysis of the structure–property relationships of similar compounds[5,6]. However, relatively little work has been performed in applying chemical graph theory to the estimation of intrinsic polymer properties based on the chemical structure of the repeat unit.

In many instances a bulk property can be expressed in terms of an intrinsic property, as is the case with the dielectric constant and the molecular polarizability. With the aid of the Clausius–Mossotti equation the dielectric constant, ε', can be calculated if the polarizability, P, and the molar volume, V_m, are known:

$$\frac{\varepsilon'-1}{\varepsilon'+2}=\frac{P}{V_m} \tag{1}$$

Upon rearrangement equation (1) becomes

$$\varepsilon'=\frac{1+2P/V_m}{1-P/V_m} \tag{2}$$

In its simplest form, chemical graph theory assumes that the polymer is amorphous and that all non-hydrogen

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atoms in the polymer are identical, and ignores the influence of hydrogen atoms on the physical properties of a molecule. Although numerous indices have been developed[1,3], most are not well suited for dealing with compounds composed of more than one element (in this instance all hydrogen atoms are ignored). In its simplest form chemical graph theory assumes that all atoms of a molecule are the same (once all of the hydrogen atoms have been removed). However, the assumption that all atoms in a molecule are identical (in other words there are no heteroatoms) can cause severe problems. For instance, the polarizability of polystyrene is 31.96 cm^3 mol^{-1}, while the polarizability of poly(vinyl pyridine), which would be identical to polystyrene if all atoms were carbon, is 41.99 cm^3 mol^{-1} (Reference 7). To differentiate atom types, the concept of 'valence' is introduced into the chemical graph theory formalism. In chemical graph theory, valence (not to be confused with the chemical valence of an atom) is used to take into account the differences in physical properties that occur as a result of the introduction of a heteroatom into a chemical structure.

In chemical graph theory, the tools used in making property predictions are known as indices. They are algorithms for representing the structure of a molecule in terms of a set of characteristic numbers. In chemical graph theory these indices do not, in general, uniquely identify a chemical structure. As a result, indices of the same type are often highly correlated with one another. In this case, only the most significant indices (both statistically, and in providing the greater physical insight) are used. In general, the most significant indices were those of the lowest order.

While numerous indices have been developed[1,3], most deal with how atoms are connected to one another, and are unable to differentiate between different elements in a molecule (they are unable to differentiate among heteroatoms in a molecular structure). The indices which were used in this study are a variation on Randic's χ indices[7], ${}^m\chi_t$, where t denotes the type of subgraph, and m denotes the subgraph order, the number of edges (bonds) in the corresponding subgraph. Using Randic's χ index, as modified by Kier and Hall[3], heteroatoms can easily be taken into account. Four types of subgraphs can be identified: path-labelled ${}^m\chi_p$; cluster-labelled ${}^m\chi_c$; path/cluster-labelled ${}^m\chi_{p/c}$; and chain-labelled ${}^m\chi_{ch}$.

The connectivity indices ${}^m\chi_t$ are evaluated as the sum of terms over all distinct connected subgraphs, ${}^mS_j$, of a molecule and are given by:

$$ {}^m\chi_t = \sum_{j=1}^{n_m} {}^mS_j \tag{3}$$

where n_m is the number of type t subgraphs of order m, and ${}^mS_j$ is given by the product of the reciprocal square root of the vertex (atom) valences, δ_i^v:

$$ {}^mS_j = \prod_{i=1}^{m+1} (\delta_i^v)_j^{-1/2} \tag{4}$$

Here j denotes the particular set of edges (non-hydrogen bonds) that constitutes the subgraph and δ_i^v for carbon is given by

$$ \delta_C^v = 4 - h \tag{5}$$

where h is the number of hydrogen atoms attached to the carbon atom (alternatively, δ_C^v can be viewed as the difference between the number of valence electrons, Z^v, and the number of hydrogen atoms). In many instances reasonable values of δ_i^v for heteroatoms can be obtained from the expression:

$$ \delta_i^v = Z^v - h \tag{6}$$

In general, empirically derived values for δ_i^v are found to result in a higher correlation with the polymer polarizability.

As will be shown in a following section, the two χ indices which display the greatest statistical significance in predicting the dielectric constants of polymers are the zero-order path, ${}^0\chi_p$, and the fourth-order path/cluster, ${}^4\chi_{p/c}$.

As an example of how to calculate the zero-order path, ${}^0\chi_p$, and the fourth-order path/cluster, ${}^4\chi_{p/c}$, indices, consider the molecule isopentane (*Figure 1*). The first step is to draw the hydrogen-suppressed diagram of isopentane as shown in *Figure 1*.

The atoms in *Figure 1* have been arbitrarily numbered for future reference. Using the nomenclature described above, and the δ_i^v values from *Table 1*, the zero-order path term, ${}^0\chi_p$ is given by:

$$ {}^0\chi_p = \sum_{i=1}^{n_0} (\delta_i^v)^{-1/2} \tag{7a}$$

$$ {}^0\chi_p = \overset{(1)}{\frac{1}{\sqrt{1}}} + \overset{(2)}{\frac{1}{\sqrt{3}}} + \overset{(3)}{\frac{1}{\sqrt{1}}} + \overset{(4)}{\frac{1}{\sqrt{2}}} + \overset{(5)}{\frac{1}{\sqrt{1}}} = 4.28 \tag{7b}$$

where the numbers in brackets above the equation refer to the atom numbers in *Figure 1*.

A path/cluster is composed of a third- or fourth-order cluster and a first or higher-order path. In *Figure 1*, atoms 1, 2, 3, 4, and 5 form the only fourth-order path/cluster in the molecule, with ${}^4\chi_{p/c}$ given by:

$$ {}^4\chi_{p/c} = \sum_{s=1}^{n_4} (\delta_i^v\delta_j^v\delta_k^v\delta_l^v\delta_m^v)_s^{-1/2} \tag{8a}$$

$$ {}^0\chi_{p/c} = \overset{(1)}{\frac{1}{\sqrt{1}}} \times \overset{(2)}{\frac{1}{\sqrt{3}}} \times \overset{(3)}{\frac{1}{\sqrt{1}}} \times \overset{(4)}{\frac{1}{\sqrt{2}}} \times \overset{(5)}{\frac{1}{\sqrt{1}}} = 0.4082 \tag{8b}$$

where δ_i^v, δ_j^v, δ_k^v, δ_l^v, and δ_m^v are the valences of atoms i, j, k, l and m, respectively, and n_4 is the number of fourth-order path/cluster subgraphs.

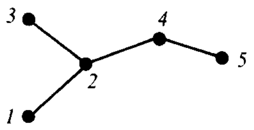


Figure 1 Isopentane

Table 1 Heteroatom δ^v values

Chemical unit	δ_i^v
$-(\mathrm{CH_3})$	1.0
$-(\mathrm{CH_2})-$	2.0
$-\overset{\vert}{(\mathrm{CH})}-$	3.0
Aromatic carbon	3.0
Cl–	0.37
–O–, –OH; sp^3 oxygen	0.75
=O	1.5

Table 2 Comparison of predicted and measured polarizabilities and dielectric constants, based on equation (10)

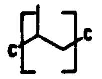
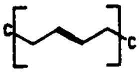
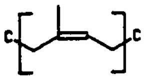
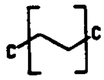
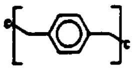
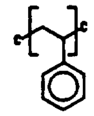
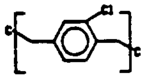
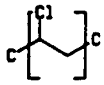
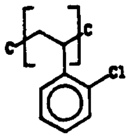
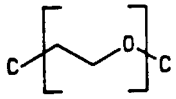
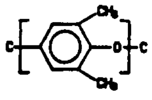
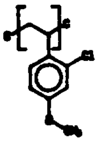
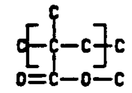
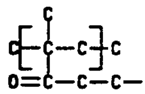
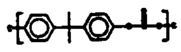
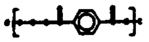
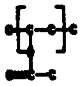
Repeat unit		P_{pred}	P_{expt}	$V_m{}^{14}$ ($cm^3 mol^{-1}$)	ε_{pred}	ε_{expt}	Ref.
1		14.9	11.6/13.6	46.3	2.4	2.0/2.25	8, 10, 14
2		19.25	18.64	55.67	2.58	2.51	12
3		24.4	23.35	74.48	2.46	2.37	12
4		45.5	46.9	140.0	2.44	2.51	9
5		46.3	45.59	138.0	2.51	2.48	9
6		10.7	9.84/9.95	32.9	2.44	2.28/2.3	8, 10, 14
7		32.8	34.12	96.16	2.55	2.65	12
8		31.4	31.88	94.0	2.50	2.54	9, 14
9		41.7	42.94	109.0	2.86	2.95	8
10		18.7	17.49	42.71	3.34	3.08	8, 14
11		41.55	40.92	125.0	2.49	2.46	8
12		40.6	39.97	125.0	2.44	2.41	8
13		19.2	20.07	37.77	4.10	4.4	7
14		40.23	39.1/39.37	113.2	2.65	2.58/2.6	8
15		44.76	49.95	122.0	2.74	3.08	9
16		30.0	25.18/32.9	72.39	3.12	2.6/3.5	7, 8, 11, 12, 14
17		34.6	32.89/40.0	90.09	2.87	2.7/3.4	14
18		79.8	78.75/81.4	211.7	2.82	2.8/2.9	8, 10

Table 2

Repeat unit	P_{pred}	P_{expt}	$V_m{}^{14}$ ($cm^3 mol^{-1}$)	$\varepsilon_{\mathrm{pred}}$	$\varepsilon_{\mathrm{expt}}$	Ref.
19 	64.5	60.9	144.0	3.43	3.2	8, 12
20 	30.77	30.94	72.2	3.23	3.25	14

PROCEDURE AND RESULTS

As a result of the large size of most polymers (which may have a molecular weight in the hundred thousand range) it is computationally impossible to calculate the exact indices of a polymer. To circumvent this problem it is generally assumed that the intrinsic properties of a polymer are identical to those of the repeat unit. Therefore, one needs only calculate the intrinsic property of interest for the repeat unit.

To develop a general expression for the polarizability of a polymer, the first eight aliphatic polymers from *Table 2* were used as the basis from which to generate an expression which relates the ${}^m\chi_t$ indices to the observed polarizabilities. This expression can then be used to estimate the polarizability of other aliphatic polymers. To model the repeat unit more realistically, end effects must be taken into account. This turns out to be difficult. However, in the series of polymers examined in this study the terminal atoms at the end of each repeat unit are always connected to another carbon atom, so a simple correction would be to introduce a 'phantom carbon' at each end of the repeat unit. *Table 2* shows the polymer repeat unit structures with the two phantom carbon atoms.

Using the first eight repeat units in *Table 2*, the indices ${}^0\chi_p$–${}^6\chi_p$, ${}^3\chi_c$–${}^6\chi_c$, ${}^4\chi_{p/c}$–${}^6\chi_{p/c}$ and ${}^6\chi_{ch}$ were calculated. These indices, and the experimentally determined polarizabilities, were then used in a multivariable linear regression analysis. Of the fifteen indices, only two exhibited significant correlation with the polarizability data, those being ${}^0\chi_p$ and ${}^4\chi_{p/c}$. The expression for the polarizability of an aliphatic polymer in terms of ${}^0\chi_p$ and ${}^4\chi_{p/c}$ is given by:

$$P = 8.86\,{}^0\chi_p - 8.85\,{}^4\chi_{p/c} - 21.49 \tag{9}$$

By calculating the ${}^0\chi_p$ and ${}^4\chi_{p/c}$ indices for any aliphatic polymer, equation (9) can be used to estimate the polarizability of any aliphatic polymer based on the structure of its repeat unit.

To take heteroatoms into account, the value of δ_i^v for each heteroatom must be determined. An empirical determination of the δ_i^vs was found to give the best results, although non-empirical methods have been suggested[3,8]. *Table 1* lists the empirically derived δ_i^v values used in this study. An initial estimate for the δ_i^v values was obtained by starting with a polymer of known polarizability having a single heteroatom, and calculating ${}^0\chi_p$ and ${}^4\chi_{p/c}$ while varying δ_i^v. These indices were then substituted into equation (9) until a value of δ_i^v was obtained which resulted in the best match between the experimentally measured polarizability and that obtained from equation (9).

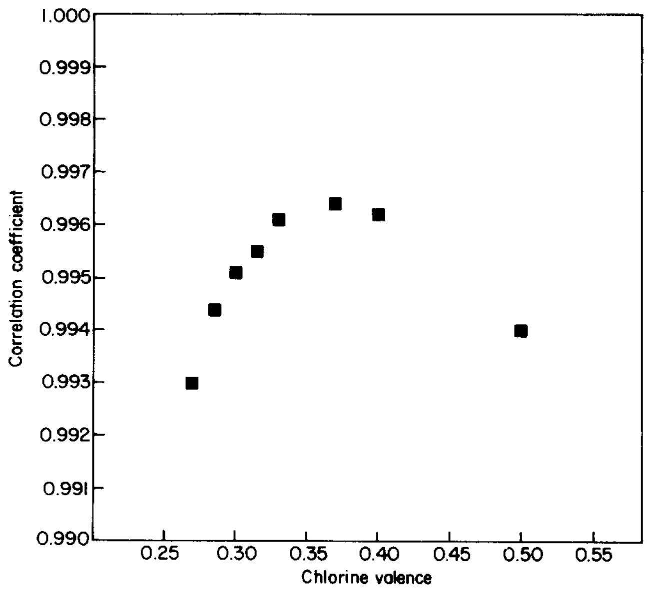


Figure 2 Optimization of the δ_{Cl}^v value

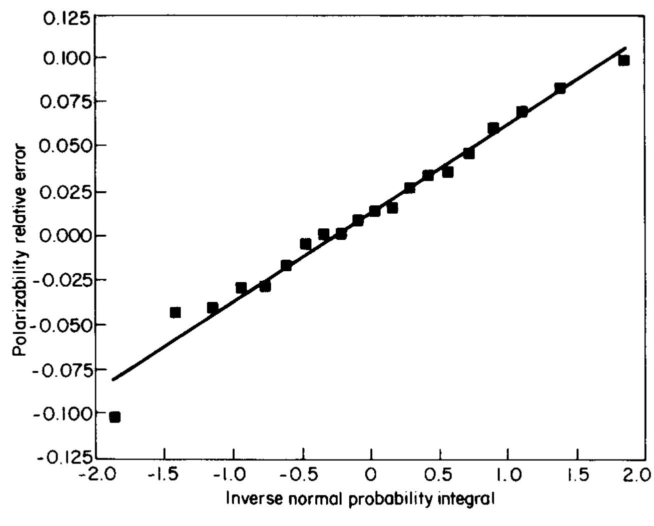


Figure 3 Normal probability plot of the relative error between the experimentally measured and predicted polarizability, obtained from *Table 2*, and the inverse normal probability integral

To improve the model further, other macromolecules (with known polarizabilities) which contain the same heteroatoms were introduced into the data set. The valence values (which were obtained by the procedure described above) were varied slightly until the highest correlation coefficient (r^2) was obtained. For example, *Figure 2* shows a plot of δ_{Cl}^v *versus* r^2, using polymers 1–8 (aliphatic) and 9–12 (chlorinated) from *Table 2*. As can be seen, the highest correlation coefficient was obtained when $\delta^{v}_{Cl}=0.37$.

This procedure was repeated for the polymers in *Table 2* which contained ether and carbonyl units, resulting in the following expression for the polarizability, with an r^2 of 0.9887:

$$P=7.385\,{}^{0}\chi_{p}-4.715\,{}^{4}\chi_{p/c}-14.47 \qquad (10)$$

Table 2 lists the experimentally measured polarizabilities and the polarizabilities calculated by using equation (10). When a normal distribution plot is made of the relative error in the polarizability *versus* the inverse normal probability integral, as shown in *Figure 3*, it is evident that all of the polymers belong to the same parent distribution, with $\sigma=\pm 2.5\%$. This error is well within the experimental error ($\pm 5\%$) associated with polarizability measurements. In this study, all of the polymers which were examined were amorphous, or, as in the case of polyethylene and poly(ethylene terephthalate), the experimentally determined polarizability values were extrapolated to the amorphous polymer.

Knowing the polarizability of a polymer, and its molar volume (as tabulated from Reference 7), the dielectric constant of the polymer can be determined with the aid of equation (2). Shown in *Table 2* is a comparison of the experimentally measured dielectric constants, and the dielectric constants calculated from chemical graph theory (using equation (10)). The calulated dielectric values shown in *Table 2* have a standard deviation of ± 0.13 from the experimentally measured value.

Based on the form of equation (10), several interesting conclusions can be drawn in designing a polymer with specific dielectric properties. For instance, to design a polymer with a low dielectric constant:

(1) The δ_i^{v} of the constituent atoms should be high.

(2) The ratio of the number of atoms in the repeat unit to its molar volume should be small.

(3) Atoms with high valence numbers (>4, such as tetra- and hexavalent sulphur) should be incorporated in the repeat unit.

(4) Hydrogen should be incorporated into the polymer to as large an extent as possible.

CONCLUSIONS

Calculations based on chemical graph theory have been shown to be capable of estimating the polarizability and dielectric constant of a wide variety of polymers. In general the calculated values are within 2.5% of those measured experimentally. As a natural consequence of the regression analysis used to correlate the chemical graph theory indices to physical properties, insight into the influence of structural units on physical and chemical properties becomes evident. An extension of this theory to co- and terpolymers is straightforward. In addition, it may be possible to estimate other physical properties of polymers (and other materials), such as coefficients of expansion, moduli, gas permeability, viscoelastic properties, refractive index and molar volume by the application of chemical graph theory.

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