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A GRAPH-STRUCTURAL METHOD FOR PREDICTION OF POLYMER PROPERTIES

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Abstract - Group contribution methods have been widely used for the estimation and prediction of properties of a great variety of chemical compounds and mixtures of compounds. In this paper, the glass transition temperature of polymers is evaluated by a second-order group contribution method previously developed by Ourique and Silva Telles (1997). From a total of 1018 polymers in the data base, 923 are selected as the training set to which group and interacting group contributions are assigned. The remaining 95 polymers are used as the validation set. Results are compared to the ones obtained by application method of Van Krevelen method's to the same data base.

*Keywords***:** Glass transition temperature, graph-structural method, property estimation.

INTRODUCTION

Prediction of the physical and chemical properties of pure substances and mixtures is a modern problem that frequently arises in the chemical process industries. These properties are essential for modeling, simulating and controlling chemical plants, as well as for designing new chemical specialties. Many researchers are involved in the development of methods for predicting properties of organic, inorganic and biochemical compounds. Most of them are first-order group contribution methods (Joback and Reid, 1987; Reid et al.; 1987), although some second-order group contribution methods have also been considered (Gani et al., 1991).

In the polymer industry is also required reliable and robust methods for estimating the development of properties of polymers. The early work in this area can be credited to Van Krevelen (1990), who extended the group contribution approach to prediction of polymer properties.

This paper aims to extend the second-order group contribution technique proposed by Ourique and Silva Telles (1998) to prediction of polymer properties. The value of a monomer property is to be obtained by adding the contributions assigned to individual groups and pairs of groups. We apply the proposed technique to the estimation of the glass transition temperature of polymers, yet it can be applied to a large set of polymer properties.

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SELECTION OF FUNCTIONAL GROUPS FOR DESCRIPTION OF STRUCTURE

The main task in any group contribution strategy is the choice of the representation set from which all molecular structures will be generated. The selection of these groups must take into account three basic assumptions. First, the molecular structure of any desired substance should be assembled by combining the functional groups contained in the presentation set. Second, there must be a quantitative value associated with the prediction of every property for each functional group in the representation set. Third, the representation set as well as its property values must remain constant while compounds are assembled.

According to these assumptions, the total value of a property can be accurately calculated by adding all group contributions, provided these contributions can be precisely assigned (first-order group contribution methods). The contribution of a group to a given property, however, varies within different classes of compounds reducing the accuracy of group contribution techniques. The inclusion of more assembling units which can be considered a set of single units and their group contribution the sum of these single units can be seen as an attempt to overcome these limitations.

Table 1 shows the functional groups that are used in this work for estimating glass transition temperature (Tg) for polymers, which are very similar to the ones adopted by Joback and Reid (1987). Functional groups are labeled as primary, secondary, tertiary and quaternary according to the number of attachments they can establish with other groups. Groups with one or more double bonds are labeled as unsaturated groups used for building cyclic structures are labeled as ring groups and groups that constitute aromatic structures are labeled as aromatic groups.

Table 1: Functional groups used for estimation of the glass transition temperature for polymers.

Primary groups	-CH3-, -F, -Cl, -Br, -OH, -COOH, -CN, -NO$_2$
Secondary groups	-CH2-, -O-, -eO- (esther), -CO-, -CS-, -S-, -COO-, -NH-
Tertiary groups	>CH-, >N-
Quaternary groups	>C<, >Si<
Ring, aromatic and unsaturated groups	-CH=,=C<,>aC=, -aC=, -cCH2-, >cCH-,>cC<

Table 2: Functional groups used for estimation of the glass transition temperature in Van Krevelen's method - all them secondary groups.

Secondary groups	-CH2-, -CH(CH$_3$)-, -CH(i-propyl)-, -CH(t-butyl)-, -CH(c-pentyl)-, -CH(c-hexyl)-, -CH(ϕ)-, -CH(ϕCH$_3$)-, -CH(OH)-, -CH(OCH$_3$)-, -CH(OCOCH$_3$)-, -CH(COOCH$_3$)-, -CH(CN)-, -CHF-, -CHCl-, -C((CH$_3$)$_2$)-, -(CH$_3$)C(ϕ)-, -(CH$_3$)C(COOCH$_3$)-, -CF$_2$-, -CClF-, -CCl$_2$-, -CH=CH-, -CH=C(CH$_3$)-, -CH=CCl-, -C≡C-, -CO-, -orto ϕ-, -para ϕ-, -3,5 dimethyl-, -3,5 diphenyl , -(ϕϕϕ)- , -(ϕϕ)-, -O-, -S-, -Si(CH$_3$)$_2$-, -OCOO-, -OOCNH-, -COO-, -NHCONH-, -CONH-, -COOCO-, -SO$_2$-, -ϕ-ϕ-, -ϕCH$_2$ϕ-, -ϕC(CH$_3$)$_2$ϕ-, -ϕ-O-ϕ-, -ϕ-S-ϕ-, -ϕ-CO-ϕ-, -ϕ-SO$_2$-ϕ-

where

c - group in cyclic chain

ϕ - benzene ring

- (ortho, meta, para) ϕ - benzene ring substituted in these positions

$\phi\phi$ - naphtalene ring

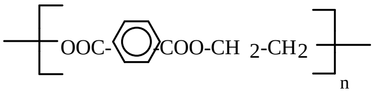
$\phi\phi\phi$ - antracene ring

Examples of Functional Group Assignment for Some Polymers

In order to illustrate how functional groups are assigned, we provide two examples of these assignments for some polymers.

Example 1,

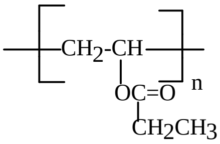
Polyethylene terephtalate:



- Group assignment: 2 $-CH_2-$; 2 -COO-; 4 -aCH=; 2 >aC= .

Example 2,

Polyethylene propionate:



$$\left[-CH_2-\underset{\substack{| \\ OC=O \\ | \\ CH_2CH_3}}{CH}- \right]_n$$

- Group assignment: $-CH_3$; 2 $-CH_2-$; -eO-; -CO-; >CH- .

METHODOLOGY

Van Krevelen (1990) proposed that polymer properties be calculated by the purely group additive relationship,

$$F = \sum_{i=1}^{N_c} n_i F_i , \tag{1}$$

where F_i defines the identity and contribution of a functional group i and n_i corresponds to its frequency in the molecule.

Values for the groups presented in Table 2 are available in Van Krevelen (1990), and for estimation of Tg calculated as stated in equation 1.

In this work, polymer properties are estimated by a second-order group contribution method, according to the following expression:

$$F = \sum_{i=1}^{N_c} n_i F_i + \sum_{j=1}^{S_c} m_j G_j , \tag{2}$$

in which F is the property to be estimated N_c denotes the total number of functional groups in the polymer structure and S_c represents the number of pairs of these groups F_i corresponds to the contribution of group i to property F and G_j is the contribution of pair j to property F and n_i and m_j represent the frequencies of groups and pairs of groups, respectively.

Considering that a whole set of NP properties is to be calculated for a single molecule, this expression can be put into an equivalent matrix form:

$$F = X \cdot A , \tag{3}$$

in which F is an NS x NP matrix with estimated values for NP properties of NS substances X is an NS x (N_c+S_c) matrix containing the number of occurrences for each group and for each pair in the desired molecules and A is an (N_c+S_c) x NP matrix with group and pair contributions for a whole set of NP properties.

Application of the proposed formulation requires that matrix A be known. Also, each molecular structure of each polymer must be depicted in terms of functional groups and pairs of groups, allowing matrix X in Eq. 3 to be assigned. In order to specify matrix A, one must choose a set of polymers whose molecular structures contain all functional groups and pairs of groups used for further molecular representation. On the other hand, the number of times a group or a pair appears in this data set will determine the reliability of its contribution for every estimated property. For all these reasons, the choice of a well-balanced data set is essential for the success of the proposed method.

We have thus constructed a data base with several important properties for 923 polymers. This data set is then used to determine group and pair contributions to each one of these properties, as described below.

From Eq. 3, one can see that matrix A, which contains values for group and pair contributions, is the unknown. Matrix X contains frequencies for groups and pairs of groups in each polymer structure. Since matrix A is not-square, solution of Eq. 3 for A can be obtained with

$$A = X^{*}F, \tag{4}$$

in which X* is the Moore-Penrose pseudo-inverse matrix, defined as the matrix that minimizes the quadratic deviation,

$$\left|R(X)\right|^{2} = (X \cdot A - F) \cdot (X \cdot A - F) \tag{5}$$

which is equivalent to

$$\left|R(X)\right|^{2} = A^{T}AX \cdot X - 2A^{T}F \cdot X + F \cdot F \tag{6}$$

The minimum value is obtained by

$$\frac{\partial \left|R(X)\right|^{2}}{\partial X} = 0 = 2A^{T}AX - 2A^{T}F \tag{7}$$

from which X is determined as follows:

$$X = \left(A^{T} \cdot A\right)^{-1} A^{T}F, \tag{8}$$

with

$$\left(A^{T}.A\right)^{-1} A^{T} = A^{*} \tag{9}$$

RESULTS

Group and pair contributions obtained by application of the procedure described in the previous section for the set of 923 polymers listed in Brandup and Immergut (1989) are employed for estimation of the glass transition temperature (Tg) of another 95 polymers. Table 3 contains the results for this verification set.

Table 3: Glass transition temperature for 95 polymers. Values estimated by the proposed method, experimental values and Van Krevelen's method.

Method Polymer	Tg (K) Exp.	Tg (K) Calc.	Error (%)	Tg (K) Van Krevelen	Error (%)
Poly-1 butyl 1 butenylene	192	209	9	202	5
Polydecyl ethylene	237	245	3	200	16
Polydodecylethylene	241	234	3	248	3
Polyheptylethylene	226	261	15	224	1
Poly(2-chlorophenyl acrylate)	326	341	5	-	-
Poly(5-cyano-3-tiapentyl acrylate)	223	237	6	-	-
Poly(ciclohexyl acrylate)	292	309	6	-	-
Poly(hexadecyl acrylate)	308	184	40	295	4
Poly(hexyl acrylate)	216	237	10	225	4
Sindiotatic poly(isopropyl acrylate)	277.5	320	15	298	7
Isotatic poly(isopropyl acrylate)	262	286	9	298	14
Poly(4 metoxycarbonyl phenyl acrylate)	340	360	6	334	2
Poly(3-methyl butyl acrylate)	228	266	17	261	14
Poly(1,3-dimethyl butyl acrylate)	258	283	10	277	7
Poly(nonyl acrylate)	215	221	3	205	5
Poly(octyl acrylate)	208	227	9	211	1
Poly(2-octyl acrylate)	228	250	9	195	14
Poly(4-tiapentyl acrylate)	208	208	0	243	17
Poly(m-tolyl acrylate)	298	326	10	314	5
Poly(2-tert-butylamino ethyl metacrylate)	306	411	34	292	5
Isotatic poly(ethyl metacrylate)	285	281	1	338	19
Poly(1H,1H,7H-dodecafluoroheptyl metacrylate)	286	386	35	252	12
Poly(4-metoxycarbonyl phenyl metacrylate)	379	385	2	362	4
Poly(3,3-dimethyl butyl metacrylate)	318	289	9	270	15
Poly(cyclohexyl chlorocrylate)	387	369	5	-	-
Poly(isopropyl chloroacrylate)	363	349	4	290	20

Continuation Table 3

Method Polymer	Tg (K) Exp.	Tg (K) Calc.	Error (%)	Tg (K) Van Krevelen	Error (%)
Poly(methyl chloroacrylate)	413	349	16	337	18
Poly(methyl fluoroacrylate)	404	430	6	324	20
Poly(methyl fluorometacrylate)	357	363	2	402	13
Poly(isopropoxyethylene)	270	298	10	262	3
Poly(benzoyloxyethylene)	344	342	1	346	1
Poly(3-bromo benzoyloxyethylene)	331	367	11	-	-
Poly(4-methyl benzoyloxy)ethylene	343	349	2	342	0
Poly(4-benzoylstyrene)	371	418	13	419	13
Poly(4-butylrylstyrene)	347	322	7	332	4
Poly(4-carboxystyrene)	386	444	15	400	4
Poly(4-chloro-3-fluorostyrene)	395	338	14	385	3
Poly(3-ethylstyrene)	303	340	12	282	7
Poly(4-ethylstyrene)	325.5	338	4	342	5
Poly(2,5-difluorostyrene)	374	334	11	-	-
Poly[4-(1-hydroxy-1-methylbutyl)styrene]	403	406	1	-	-
Poly(2-isopropoxy carbonyl styrene)	419	386	8	-	-
Poly(2-dimethyl aminocarbonyl styrene)	463	394	15	-	-
Poly[4-(2-dimethyl aminoetoxycarbonyl) styrene]	373	352	6	-	-
Poly(2,5-dimethyl styrene)	416	348	16	-	-
Poly(3,5-dimethyl styrene)	377	376	0	-	-
Poly(4-octyl styrene)	228	306	34	221	3
Poly(2-phenylamino carbonyl styrene)	464	459	1	-	-
Poly(l-naphtyl ethylene)	432	264	39	-	-
Poly(2-chloro-1,4-phenyleneethylene)	343	329	4	407	19
Poly(2-cyano-1,4-phenyleneethylene)	363	367	1	-	-
Poly(1,4-phenylene-1-phenylethylene)	428	398	7	409	4
Poly(oxy-tert-butylethylene)	308	306	1	-	-
Poly(oxy-2-hydroxy trimethyleneoxy-1,4-phenylene)	333	313	6	336	1
Poly(oxy-2-hydroxytrimethyleneoxy-1,4-phenylene-l-ethyl-1,4-cyclohexylene-1.4-phenylene)	413	399	3	-	-
Poly(oxytetramethylene)	189	198	5	205	8
Poly(oxy- 1,1-dimethylethylene)	264	218	17	261	1
Poly(oxy-1,4-phenylene-2,2-dicyanotrimethylene-l,4-phenylene)	420	530	26	-	-
Poly(oxy-1,4-phenylene hexafluoro-2,2-propylidene-1,4-phenylene oxy-1,4-phenylene carbonyl-l,4-phenylene]	448	535	19	-	-
Poly(oxycarbonyloxy-2-chloro-1,4-phenylene cyclohexylidene-3-chloro-1,4-phenylene)	447.5	471	5	400	11
Poly(oxycarbonyloxy-1,4-phenyleneethylidene-1,4-phenylene)	403	409	1	408	1
Poly(oxycarbonyloxy-1,4-phenylene-4,4-heptylidene-1.4-phenylene)	421	411	2	380	10
Poly(oxycarbonyloxy-1,4-phenylenemethylene-1,4-phenylene)	435	341	22	376	14
Poly(oxycarbonyloxy-1,4-phenylenecarbonyloxycarbonyl-1,4-phenylene)	318	388	22	352	11
Poly(oxyadipoyloxydecamethylene)	217	205	6	221	2
Poly(oxyadipoyloxy-2.6-dimethyl-1,4-phenylene isopropylidene-3.5-dimethyl 1,4-phenylene)	366	401	9	386	5
Poly(oxyadipoyloxy-1,4-phenyleneisopropylidene-1,4-phenylene)	341	325	5	363	6
Poly[di(oxyethylene)oxy oxalyl]	265	212	20	249	6
Poly[di(oxyethylene)oxy pentylmalonyl]	226	198	12	223	1

Continuation Table 3

Method Polymer	Tg (K) Exp.	Tg (K) Calc.	Error (%)	Tg (K) Van Krevelen	Error (%)
Poly(oxy-5-ethyl-1,3-phenyleneoxylsoftaloyl)	395	326	17	-	-
Poly(oxyisoftaloyloxy-4,4'-biphenylylene)	510	412	19	400	22
Poly(oxyisoftaloyloxy-1,4-phenyleneisopropylidene-1,4-phenylene)	462	395	15	400	13
Poly di(oxy- 1,4-phenylene)oxyisoftaloyl	446	363	19	366	18
Poly[oxy-1,3-phenyleneoxy-5-(pentadecafluoroheptyl) isoftaloyl]	374	329	12	-	-
Poly(oxypimeloyloxy-2,6-diphenyl-1,4-phenylenemethylene-3,5-diphenyl-1,4-phenylene)	384	617	61	441	15
Poly(oxycarbonyl-1,4-phenylenetiotetramethylenetio-1,4-phenylenecarbonyl)	335	309	8	307	8
Poly(oxyethyleneoxycarbonylimino-1,4-phenylene trimethylene-1,4-phenyleneiminocarbonyl)	347	359	3	382	10
Poly(oxy-2,2-diethyltrimethyleneoxycarbonylimino-4-methyl-1,3-phenyleneiminocarbonyl)	213	400	88	-	-
Poly(oxy-2,2,3,3-tetrafluorotetramethyleneoxycarbonyl-iminohexamethyleneiminocarbonyl)	282	277	2	322	14
Poly(oxynonamethyleneoxycarbonyl-iminohexametileneiminocarbonyl)	331	286	14	335	1
Poly(oxyhexamethyleneoxycarbonyl-imino-4-methyl-1,3-phenyleneiminocarbonyl)	305	304	0	347	14
Poly(oxymethylpentafluorphenyl-sylylene)	248	197	21	-	-
Poly[oxy(methyl)-3,3,3-trifluoropropylsylylene-ethyldodecafluorohexamethylene-ethylene(methyl)-3,3,3-trifluoropropylsylylene]	249	249	0	-	-
Poly[oxy(methyl)-3,3,3-trifluoropropylsylylene-3,3,4,4-tetrafluoro hexa methylene (methyl)-3,3,3-trifluoropropylsylylene]	246	196	20	-	-
Poly[oxytri(dimethylsylyleneoxy)-(methyl)phenyl sylylene-1,3-phenylene (methyl)phenylsylylene]	231	274	19	-	-
Poly(tetratioethylene)	249	224	10	239	4
Poly(tio-1-ethylethylene)	218	343	57	239	10
Poly(tiotrimethylene)	228	253	11	217	5
Poly(tio-1,4-phenylene)	370	305	18	347	6
Poly(oxycarbonylneopentylene-sulfonylneopentylene)	323	254	21	293	9
Poly(oxy-1,4-phenylene sulfonyl-1,4-phenylene oxy-1,4-phenylene methylene-1,4-phenylene)	453	438	3	444	2
Polysulfonylneopentylene	386	406	5	346	10
Nylon 6,8 [Poly(iminohexamethylene iminosuberoyl)]	330	309	6	325	2
Nylon 7 - [Poly(imino-1-oxoheptamethylene)]	325	266	18	321	1
Nylon 8 - [Poly(imino-1-oxooctamethylene)]	323	264	18	319	1

Figure 1 shows the distribution of percentage of error between experimental values and calculated values. Figure 2 shows the distribution of percentage of error between Van Krevelen estimations for Tg and the experimental values.

Figures 3 and 4 show percentage of errors by range of values for the proposed method and for of Van Krevelen's method.

The best results are obtained for the set of polyvinyl esthers (mean error of 5%). The worst results are obtained for poly(oxy-2,2-diethyltrimethyleneoxycarbonylimino-4-methyl-1,3-phenyleneiminocarbonyl) with 88% error; poly (oxypimeloyloxy-2,6- diphenyl-1,4-phenylenemethylene-3,5-diphenyl-1,4-phenylene) with 61% error and poly(tio-1-ethylethylene) with 57%. Van Krevelen's method can not be applied to the estimation of Tg for 26 compounds of the validation set, because of the absence of some groups in Van Krevelen's set of group contribution.

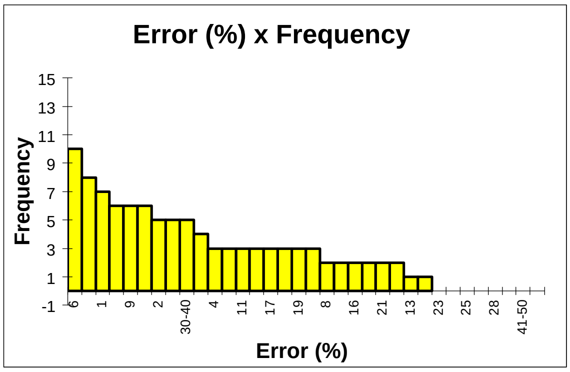


Figure 1: Distribution of percentage of error between experimental values and calculated values

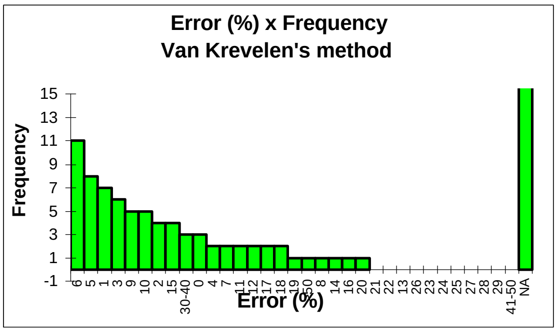


Figure 2: Distribution of percentage of error between Van Krevelen estimations for Tg and the experimental values

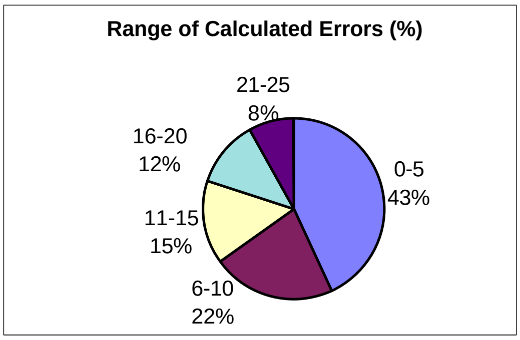


Figure 3: Percentage of errors by range of values for the proposed method

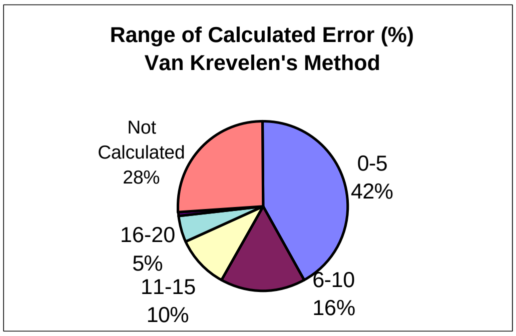


Figure 4: Percentage of errors by range of values for the method of Van Krevelen

CONCLUSIONS

The proposed method (second order method) for estimation of the glass transition temperature of polymers is shown to be generic, simple and numerically reliable. Results are quite satisfactory, specially when compared to the ones obtained by Van Krevelen's method. Despite the fact that for some polymers calculated values of Tg are very poor, it should be observed that the number of groups and pairs used for molecular description is relatively small compared to that of Van Krevelen. Also, the equation for estimation of Tg is linear in the parameters (groups and pair contributions) and has no correction terms. This is a desirable feature for application in reverse problems.

Better results could be obtained if functional groups of greater complexity were adopted for molecular description. However, the number of groups and pairs would also have to be larger.

Finally, we state that the proposed method compares very favorably to Van Krevelen's method, since it provides better results, uses fewer functional groups and has a simple calculation procedure with no correction terms.

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