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W.M. Davis and J.P. Szabo.

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Research
Establishment
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A COMPARISON OF METHODS FOR CALCULATING THE GLASS TRANSITION TEMPERATURE OF POLYMERS

W.M. Davis — J.P. Szabo

July 1998

Approved by: R.M. Morchat
Head / Dockyard Laboratory (Atlantic)

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**Defence
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**Centre de
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Abstract

Three methods of calculating the glass transition temperature (T_g) of polymers on the basis of their chemical structure have been tested in this study. These methods were the connectivity index method, Van Krevelen's group contribution method, and the newly developed Group Interaction Modelling (GIM) method. The methods were applied to one set of polymers containing a variety of structural groups, and to a set of polyurethanes. In addition, a modified Van Krevelen approach was used on a set of 14 polyurethanes containing 9 structural groups. The results of the calculations were compared to experimental T_g values, and sources of error specific to each method were explored.

Résumé

Nous avons étudié, au cours de cette étude, trois méthodes permettant de calculer la température de transition vitreuse (T_g) des polymères, à partir de leur structure chimique. Il s'agit de la méthode de l'indice de connectivité, de la méthode de la contribution de groupes de Van Krevelen et de la méthode nouvellement mise au point de la modélisation d'interaction de groupes (MIG). Ces méthodes ont été appliquées à un ensemble de polymères contenant divers groupes structuraux, ainsi qu'à un ensemble de polyuréthanes. De plus, nous avons utilisé une approche de Van Krevelen sur un ensemble de 14 polyuréthanes contenant 9 groupes structuraux. Nous avons comparé les résultats des calculs avec les valeurs de T_g obtenues expérimentalement, et nous avons cherché à déterminer les sources d'erreur spécifiques à chaque méthode.

DREA TM/98/220

**A Comparison of Methods for Calculating the Glass Transition Temperature of
Polymers**

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EXECUTIVE SUMMARY

Background

The dynamic mechanical properties of polymers are both temperature and frequency dependent, with the Young's modulus changing by 3 orders of magnitude in the region of the glass transition temperature, T_g . The glass transition temperature of a polymer may be measured using a variety of experimental methods, including differential scanning calorimetry, or it may be calculated on the basis of its chemical structure. The purpose of this work was to compare several methods for calculating T_g , and was part of a larger TTCP study of polymer modelling. The methods included Van Krevelen's group contribution approach, Group Interaction Modelling (GIM), and a commercial software package, SciPolymer, which implements Bicerano's connectivity index theory.

Principal Results

For a general set of polymers containing a variety of structural groups, previously published GIM results were closest to experimental data. Our implementation of GIM gave results that were much more in error, due to our use of the SciPolymer cohesive energy parameter. The SciPolymer approach to calculating T_g resulted in errors (average deviation from the true value) of 27-29 degrees. The Van Krevelen group contribution method gave more accurate T_g 's for a set of polyurethanes (error = 15 degrees) than for the general group (error = 40 degrees). A modified Van Krevelen approach was also used on a set of 14 polyurethanes. Self consistent group contribution coefficients were derived for 9 structural groups and were used to calculate T_g . This modified method resulted in much lower errors (3 degrees) than the general Van Krevelen method (16 degrees).

Significance of the Results

All the methods reviewed here, with the exception of the modified Van Krevelen method, gave errors greater than 14 degrees. The modified Van Krevelen method, while being more accurate, may only be applicable to polymers that are very similar to those for which the analysis has been conducted.

Future Plans

Limitations of the modified Van Krevelen method will be explored in future TTCP work.

Table of Contents

	Page Number
Abstract	ii
Executive Summary	iii
Table of Contents	iv
1. Introduction	1
2. Discussion of Methods	1
a. SciPolymer	1
b. Group Interaction Modelling (GIM) Based Methods	1
c. Van Krevelen's Method	3
d. Modified Van Krevelen's Method for Polyurethanes	3
3. Results and Discussion	3
4. Summary	5
5. Acknowledgements	6
6. References	17

1. Introduction

The control and reduction of vibration in industrial and military structures depends on the high loss properties of polymeric materials, which form key components of vibration isolation mounts, free layer and constrained layer damping treatments, and acoustic absorbers. The effectiveness of these sound damping treatments depends on the dynamic mechanical properties of the polymer at the temperature and frequency range it is used. Analytical expressions have been derived which relate the behaviour of simple systems to the material properties of the polymeric component^{1,2}, and finite element methods may be applied to more complex structures. In addition, software packages have been written which implement some of these methods.^{3,4,5} While the physics of these systems has received a lot of attention and study, only recently have methods been developed which relate the *chemical structure* of the polymer to its dynamic mechanical properties.^{2,5,6,7,8} Of particular importance is the glass transition, a region of temperature and frequency for which a polymer is most effective in converting mechanical and acoustic energy into heat. The purpose of this paper is to compare several methods of calculating the glass transition temperature (T_g) for a set of polyurethanes.

2 Discussion of Methods

The methods discussed below include a commercial software package, a set of relatively new techniques called Group Interaction Modelling (GIM), and the group contribution method described by Van Krevelen.

a. SciPolymer

SciPolymer³ is a commercial software package that implements the connectivity index method developed by Bicerano in his monograph.⁴ This method of calculating the glass transition temperature is denoted T_{gs} . The method correlates the glass transition temperature with 12 structural parameters calculated using Bicerano's selection rules leading to the following equation:

$$NT_{gs} = 15x_1 - 4x_2 + 23x_3 + 12x_4 - 8x_5 - 4x_6 - 8x_7 + 5x_8 + 11x_9 + 8x_{10} - 11x_{11} - 4x_{12}$$

where x_1 to x_{12} are the aforementioned structural parameters and N is the number of chain backbone atoms in the monomer unit. In this study, each monomer unit was first built in the Alchemy 2000⁵ software package, and then imported into SciPolymer.

b. Group Interaction Modelling (GIM) Based Methods

Many computational techniques are available to study the structure and properties of polymers⁶, which range from fundamental *ab initio* techniques to purely empirical structure property correlations. Unfortunately, the vast majority of these techniques only give a limited number of observable values from the input of the polymer structure. As well, the accuracy of these methods usually fall short of that required to assess the value of making structural changes. Group Interaction Modelling, developed by David Porter⁷,

overcomes some of the limitations of previous methods in that a wide range of thermal and mechanical properties may be predicted from the polymer structure. The characteristics of the groups of atoms in the characteristic monomer unit of the polymer are important and define the chemical identity of the polymer. Each parameter in the GIM method is a physical property, which is a function of the group chemical composition. The GIM method defines the physical properties of a polymer as a function of six variables listed in Table 1. Using these six parameters and the equations presented in Reference 7, it is possible to calculate many different polymer properties. For this paper, however, we will concentrate on the GIM methods of calculating the glass transition temperature, using equation 3.2.9 in Porter's book⁷

$$T_g = 0.224\theta_1 + 0.0513 \frac{E_{\text{coh}}}{N}$$

where E_{coh} is the cohesive energy, N is the number of degrees of freedom of the mer unit, and θ_1 is the reference temperature. For each polymer, the cohesive energy was calculated in SciPolymer,³ while N is calculated using selection rules laid out in the text.⁷ GIM uses two different methods to calculate the reference temperature θ_1 . The elucidation of the value for θ_1 has been done by Porter and the reader is referred to his book for a more detailed discussion. The two methods used to calculate θ_1 derive from the two possible conformations of polymer chains. The chain can be either mainly *trans* or mainly *gauche*. Ideally, the fractions of *trans* and *gauche* conformers should be calculated by rotational transition state theory in order to obtain an average value for θ_1 . However, most polymers tend to be either mainly *trans* or mainly *gauche*. As such, only one value of the reference temperature need be calculated. Most polymers adopt a mainly *trans* conformation, except for aliphatic polyoxides and a few other classes⁷. The guidelines given in Reference 7 were used to determine which polymers were considered as *trans* or *gauche*. As shown in Porter's book,⁷ the reference temperature can be calculated using the following two equations, depending on whether the conformer is *trans* (θ_{1t}) or *gauche* (θ_{1g}):

$$\theta_{1t} = 550\sqrt{14/M_{av}} \qquad \theta_{1g} = 316\sqrt{14/M_{av}}$$

where M_{av} is the average value of the masses associated with each atom of the chain backbone. For example, polyvinyl chloride with $M=62.5$ and two chain carbon atoms per mer unit would have a value of $M_{av} = 31.3$.

In our calculations for the glass transition temperature using GIM, we have used either the θ_{1t} or θ_{1g} value, except for the polyurethanes where an average of the two values was used. The latter reflects a mainly *gauche* polyoxide soft segment, and a mainly *trans* hard segment in a 1:1 molar ratio for the polyurethanes.

c. Van Krevelen's Method

The predictive method outlined by Van Krevelen in his book⁸ has also been employed for our dataset of polymers. In this method, the glass transition temperature is taken to be additive with respect to a group specific parameter Y_{gi} and the total molecular weight of the monomer unit M according to the following equation:

$$T_g = \sum_i Y_{gi} / M$$

Y_{gi} 's were taken from Reference 2, which contains a database that was derived from a large group of polymers. It was not possible to calculate the glass transition temperature for every polymer in Tables 2 and 3 because of the limited number of structural groups that are listed in the Van Krevelen's book².

d. Modified Van Krevelen's Method for Polyurethanes

A group of 14 polyurethanes^{9,10} with 9 structural groups were subjected to group contribution analysis. A least squares fitting procedure was used to derive group contribution coefficients specific to these 9 structural groups from the limited dataset of polyurethanes.

3. Results and Discussion

In order to ascertain the best method to use to calculate T_g over a wide range of polymer structures, a set of well-known and experimentally well-characterized polymers were first studied using the four methods. The polymers chosen include polyalkenes, sulfur based polymers, halogenated polymers, and other polymers containing a variety of structural groups. The results of these calculations are presented in Table 2 along with the GIM results taken from Reference 7. The error associated with each method was calculated according to the equation below and is summarized at the bottom of Table 2.

$$Error = \frac{\sum |T_g (calc) - T_g (exp)|}{n}$$

In the equation above, $T_g (calc)$ is the calculated T_g , $T_g (exp)$ is the experimental T_g , and n is the number of polymers in the data set. Note that the GIM results from Reference 7 agree much better with experiment than the GIM results from this work. The primary reason for this is that different values of E_{coh} were used. We have used $E_{coh2}(calc)$ values from SciPolymer³ (denoted in the software as "Van Krevelen-type cohesive energy calculated by SciPolymer"), which are always smaller than those of Reference 7. As a result, our GIM T_g 's tend to be too low.

The SciPolymer method for this general group of polymers had an error of 27 degrees associated with it, compared to 40 degrees for the Van Krevelen method, 19 degrees for

GIM (book) and 50 degrees for GIM (this work). The results of Table 2 are plotted as a scatter diagram in Figure 1.

The three methods described above were then applied to the group of polyurethanes^{9,10}. The results of the calculations are listed in Table 3 and shown as the scatter diagram in Figure 2. Note that the table includes an average GIM glass transition temperature which results from taking the average of the *trans* and *gauche* reference temperatures. The correlation of the calculated values with experiment was better for these polyurethanes than for the general set of polymers discussed above. The best method in this case was the Van Krevelen method with a average deviation of 15 degrees from experiment for this set of polyurethanes. The SciPolymer based method had an average deviation of 29 degrees from experiment. The GIM calculation, based on taking the average of the *trans* and *gauche* reference temperature and using the SciPolymer E_{coh} values, lead to a average deviation of 26 degrees from experiment.

A general problem for all methods is that the effects of phase mixing, crystallinity, and crosslinking have not been accounted for in these calculations, although GIM has a capability for including these effects. Another possible source of error with the SciPolymer and GIM based approaches is the assumption that the cohesive energy is independent of temperature. In reality, the cohesive energy varies as a skewed Gaussian about the glass transition temperature¹¹.

The Van Krevelen method makes no use of the internal connectivity in the monomer unit. This method is only concerned with the chemical species present in the monomer unit and not how they are connected together. In addition, the same value of the glass transition temperature will be obtained regardless of whether the polymer adopts a mainly *trans* or mainly *gauche* conformation. The internal database in SciPolymer is conspicuously devoid of polyurethanes which causes some concern as to whether the urethane linkage will be treated properly. The Van Krevelen method may give better results than the SciPolymer method for the polyurethanes simply because the urethane group is treated explicitly. It is somewhat surprising, however, that the Van Krevelen method gives much poorer predictions for the more general set of polymers. Perhaps a larger set of polymers need to be included in the calculation of the additive parameter Y_{gi} .

Despite the problems outlined above, it appears that methods for predicting the glass transition temperature of polymers based on additivity or group contribution methods show some promise. It has recently been shown^{10,12} that additivity methods applied to a group of polyurethanes can accurately predict the glass transition temperature to within 2 degrees. In that study, the Van Krevelen approach was applied to a specific set of polyurethanes to derive a self-consistent set of Y_{gi} coefficients for the four specific structural groups found in the polyurethanes studied. It may be that the derived coefficients should not be universally applied but must take on different values for different classes of polymers.

To further test this approach we selected a set of 14 polyurethanes containing 9 structural groups for which there was published T_g data. Table 4 lists the polymers, the number of

structural groups per monomer (N_i), the molecular weights of each group (M_i) and the total molecular weight (M). Adapting the Van Krevelen approach to this problem, we assumed that

$$T_g = \frac{\sum_i N_i M_i T_{gi}}{M}$$

where T_{gi} is a coefficient specific to each group. Least squares methods were used to derive self consistent coefficients using the above equation and the known glass transition temperatures for these polyurethanes. The results of this analysis are listed in Table 5. As shown in Table 6 and Figure 3, using coefficients more specific to polyurethanes produced better results than the general Van Krevelen approach, where the results of many different polymers are used to calculate the coefficients. The errors for this data set were 3 degrees and 16 degrees for the modified and general Van Krevelen methods, respectively.

Note that the derived group coefficient in Table 5 for urethane is zero. This is due to the fact that the urethane and phenyl groups are essentially invariant to each other, that is, they occur in the same ratio in all the polymers in this dataset with the exception of one. If we combined the urethane and phenyl groups into a single group and repeated the analysis, the weighting function would no longer be "rank deficient" and there would be no zero coefficients. A closer examination of Table 5 shows that some of the derived group coefficients are negative. This problem may be attributed to the relative ratios of the structural groups in the polymer set, which Fedderly *et al*¹² have shown must contribute to a "well conditioned" weighting function matrix. The problem may be overcome by careful selection of the structural groups and polymers in the dataset being analyzed, and by carrying out an error analysis similar to that presented in Reference 12, to ensure that each group is well represented.

4. Summary

A comparison of several computational methods for calculating the glass transition temperature of polymers from chemical structure was carried out. For a general set of polymers containing a variety of structural groups, previously published GIM results were closest to experimental data. Our implementation of GIM gave results that were much more in error, due to our use of the SciPolymer cohesive energy parameter. The SciPolymer approach to calculating T_g resulted in errors (average deviation from the true value) of 27-29 degrees. The Van Krevelen group contribution method gave more accurate T_g 's for a set of polyurethanes (error = 15 degrees) than for the general group (error = 40 degrees). A modified Van Krevelen approach was also used on a set of 14 polyurethanes. Self consistent group contribution coefficients were derived for 9 structural groups and were used to calculate T_g . This modified method resulted in much lower errors (3 degrees) than the general Van Krevelen method (16 degrees).

5. Acknowledgements

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Table 1: Description of GIM model parameters.

Parameter	Description	Units
M	Molecular weight of mer unit	g/mol
V_w	Van der Waals volume of mer unit	cc/mol
E_{coh}	Cohesive energy	J/mol
N	Skeletal modes of vibration of polymer glass up to T_g	mer unit ⁻¹
θ_1	Reference temperature of skeletal modes	K
L	Length of a mer unit in the chain axis	M or Å

Table 2: Calculated glass transition temperatures for selected polymers using the three methods.

Chemical Name	Sci Polymer [K]	GIM* This Work [K]	GIM Book [‡] [K]	Van Krevelen [K]	Tg (exp) [K]	Ref.
Poly1-butene	213	215[t]	219		228	13
Poly1-hexene	196	242[t]	225		223	7
Poly1-octene	187	245[t]			208	13
Poly3-methyl-1-butene	263	231[t]	270		323	7
Poly4-methyl-1-pentene	246	215[t]	269		302	7
Poly5-methyl-1-hexene	234	205[t]	267		259	7
Poly6-methyl-1-heptene	225	197[t]	267		239	7
Nylon 11,rislan	277	308[t]		230	319	13
Nylon 66	330	358[t]	344	252	318	13
Nylon 610	302	331[t]	320	240	323	13
Kodel poly(cyclohexane-1,4-dimethylene terephthalate)	379	313[t]		324	365	13
Dacron poly(ethylene terephthalate)	370	310[t]		322	342	13
Lexan polycarbonate	416	346[t]		369	423	13
Polyethylene oxide	205	191[g]		213	206	13
Polyphenylene sulfide	362	490[t]	374	347	358	13
Polydimethylsiloxane	154	140[g]		148	150	13
Polydiphenylether sulfone	484	493[g]		443	503	13
Udel polysulfone	462	454[t]		409	463	13
Polyacrylamide	366	439[t]			438	13
Polyacrylic acid	344	379[t]	366		379	13
Polyacrylonitrile	363	322[t]	355	377	358	13
Neoprene (cis)	239	239[t]	236	233	253	13
Polyvinyl alcohol	333	468[t]	380	357	372	13
Polyvinylfluoride	274	216[t]	269	328	253	13
Polyvinylchloride	293	232[t]	333	354	348	13
Polyvinylbromide	289	233[t]	284		373	13
Polyvinylidenechloride	279	200[g]	281	255	280	13
Polyvinylidene fluoride	241	149[g]	278	206	286	13
Error (Average deviation)	27	50	19	40		

* the glass transition temperature that corresponds to the conformation of the polymer using GIM is listed in this column. The conformation is denoted by a t for trans and a g for gauche.

[‡]Taken from Reference 7.

Table 3: Calculated glass transition temperatures for polyurethanes using the three methods.

Chemical Name	Sci Polymer [K]	GIM trans [K]	GIM gauche [K]	GIM average [K]	Van Krevelen [K]	Tg (exp) [K]	Ref.
peg100-hdi	279	235	186	211	259	290	10
peg200-hdi	261	237	188	212	248	258	10
bdo14-mdi	406	316	265	291	330	343	10
peg1000-mdi	264	256	205	231	246	234	10
peg1000-hdi	223	241	190	215	224	223	10
ptmg650-mdi	278	261	209	235	252	242	10
ptmg650-hdi	225	239	188	214	222	214	10
ptmg1000-mdi	256	254	202	229	239	223	10
ptmg1000-hdi	217	240	189	214	217	213	10
ptmg1400-mdi	244	251	200	225	231	213	10
ptmg1400-hdi	213	240	189	215	214	202	10
peg600-hdi	230	249	199	224	230	232	10
1ptmg1000/3mdi/2dmpd	307	267	216	242	270	279	9
1ptmg1000/3mdi/2depd	303	270	220	245		275	9
1ptmg1000/3mdi/2bdo13	311	269	218	244	273	273	9
1ptmg1000/3mdi/2empd	314	268	218	243		282	9
1ptmg1000/3mdi/2bepd	300	273	224	248		284	9
1ptmg1000/3mdi/1bdo14	320	290	238	264	271	225	9
1ptmg1430/3mdi/1bdo14	298	278	227	253	259	216	9
1ptmg650/3h12mdi/1bdo14	315	275	224	250	270	286	9
Error (Average deviation)	29	26	43	26	15		

ptmg=poly(tetramethylene ether) glycol
 peg=poly(ethylene oxide)glycol
 mdi=4,4'-diphenylmethane diisocyanate
 h12mdi=4,4'-dicyclohexylmethane diisocyanate
 hdi=hexamethylene diisocyanate
 tdi=2,4-toluene diisocyanate
 bdo13=1,3-butanediol
 bdo14=1,4-butanediol
 dmpd=2,2-dimethyl-1,3-propanediol
 depd=2,2-diethyl-1,3-propanediol
 empd=2-ethyl-2-methyl-1,3-propanediol
 bmpd=2-butyl-2-ethyl-1,3-propanediol

Table 4: Number of structural groups per monomer unit for the polymer used to calculate the group contribution coefficients.

Monomer	MW										
		-CH ₂ -	-O-	phenyl	cyclohexane	urethane	DMPD	EMPD	BEPD	DEPD	
		14	16	76	82	59	43	56	98	70	
ptmg2000/3mdi/2dmpd	2999	119	27	6	0	6	2	0	0	0	
ptmg2000/4mdi/3dmpd	3354	122	27	8	0	8	3	0	0	0	
ptmg2000/6mdi/5dmpd	4065	128	27	12	0	12	5	0	0	0	
ptmg1000/3mdi/2dmpd	1989	63	13	6	0	6	2	0	0	0	
ptmg1000/3mdi/2depd	2043	63	13	6	0	6	0	0	0	2	
ptmg2000/3mdi/2depd	3053	119	27	6	0	6	0	0	0	2	
ptmg1000/3mdi/2bdo13	1931	65	13	6	0	6	0	0	0	0	
ptmg1000/3mdi/2empd	2015	63	13	6	0	6	0	2	0	0	
ptmg2000/3mdi/2empd	3025	119	27	6	0	6	0	2	0	0	
ptmg1000/3mdi/2bepd	2099	63	13	6	0	6	0	0	2	0	
ptmg2000/3mdi/2bepd	3109	119	27	6	0	6	0	0	2	0	
ptmg650/3h12mdi/2bdo	1635	47	8	0	6	6	0	0	0	0	
ptmg1000/3mdi/2bdo	1959	67	13	6	0	6	0	0	0	0	
ptmg1430/3mdi/2bdo	2392	91	19	6	0	6	0	0	0	0	

ptmg=poly(tetramethylene ether) glycol
mdi=4,4'-diphenylmethane diisocyanate
h12mdi=4,4'-dicyclohexylmethane diisocyanate
bdo=1,4-butanediol
bdo13=1,3-butanediol
dmpd=2,2-dimethyl-1,3-propanediol
depd=2,2-diethyl-1,3-propanediol
empd=2-ethyl-2-methyl-1,3-propanediol
bepd=2-butyl-2-ethyl-1,3-propanediol

Table 5: Least squares coefficients derived from the polyurethanes listed in Table 4.

Group	T _{gi} Coefficient
-CH ₂ -	-2872
-O-	10759
Phenyl	1990
Cyclohexane	1997
Urethane (OCONH)	0
C(CH ₃) ₂	-763
C(CH ₃)(CH ₃ CH ₂)	-356
C(CH ₃ CH ₂)(CH ₃ CH ₂ CH ₂ CH ₂)	-69
C(CH ₃ CH ₂) ₂	-329

Table 6: Results for the glass transition temperature of selected polyurethanes using the modified Van Krevelen method.

Chemical Name	Van Krevelen's Method [K]	Modified Van Krevelen [K]	Tg exp [K]*
ptmg1000/3mdi/2 13bdo	273	273	273
ptmg1000/3mdi/2bdo	225	229	225
ptmg1000/3mdi/2bepd		283	284
ptmg1000/3mdi/2depd		274	275
ptmg1000/3mdi/2dmpd	270	269	279
ptmg1000/3mdi/2empd		281	282
ptmg1430/3mdi/2bdo	259	215	216
ptmg2000/3mdi/2bepd		241	239
ptmg2000/3mdi/2depd		235	234
ptmg2000/3mdi/2dmpd	254	230	233
ptmg2000/3mdi/2empd		239	238
ptmg2000/4mdi/3dmpd	270	250	252
ptmg2000/6mdi/5dmpd	293	286	275
ptmg650/3h12mdi/2bdo	270	286	286
Error (Average deviation)	16	3	

* All of the experimental numbers are taken from Reference 9.

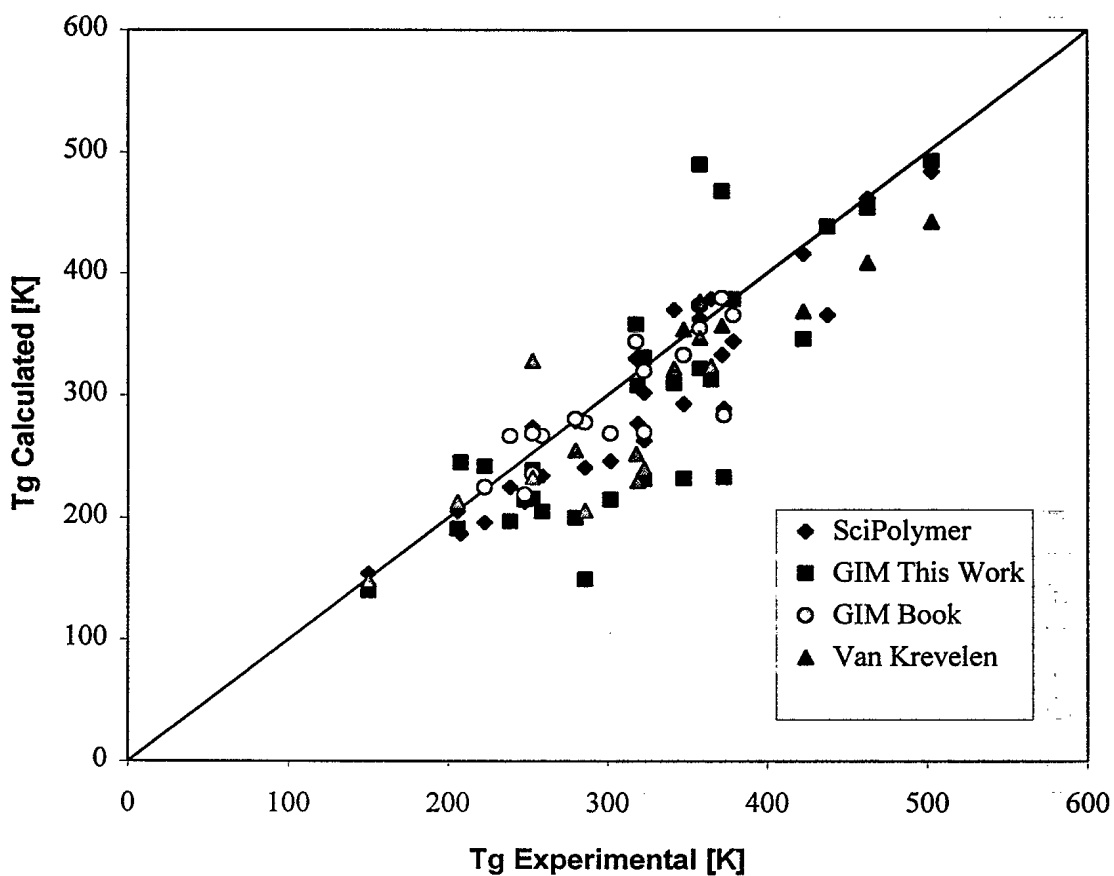


Figure 1: Scatter diagram comparing the four calculated values of T_g with the experimentally measured values for the polymers listed in Table 2.

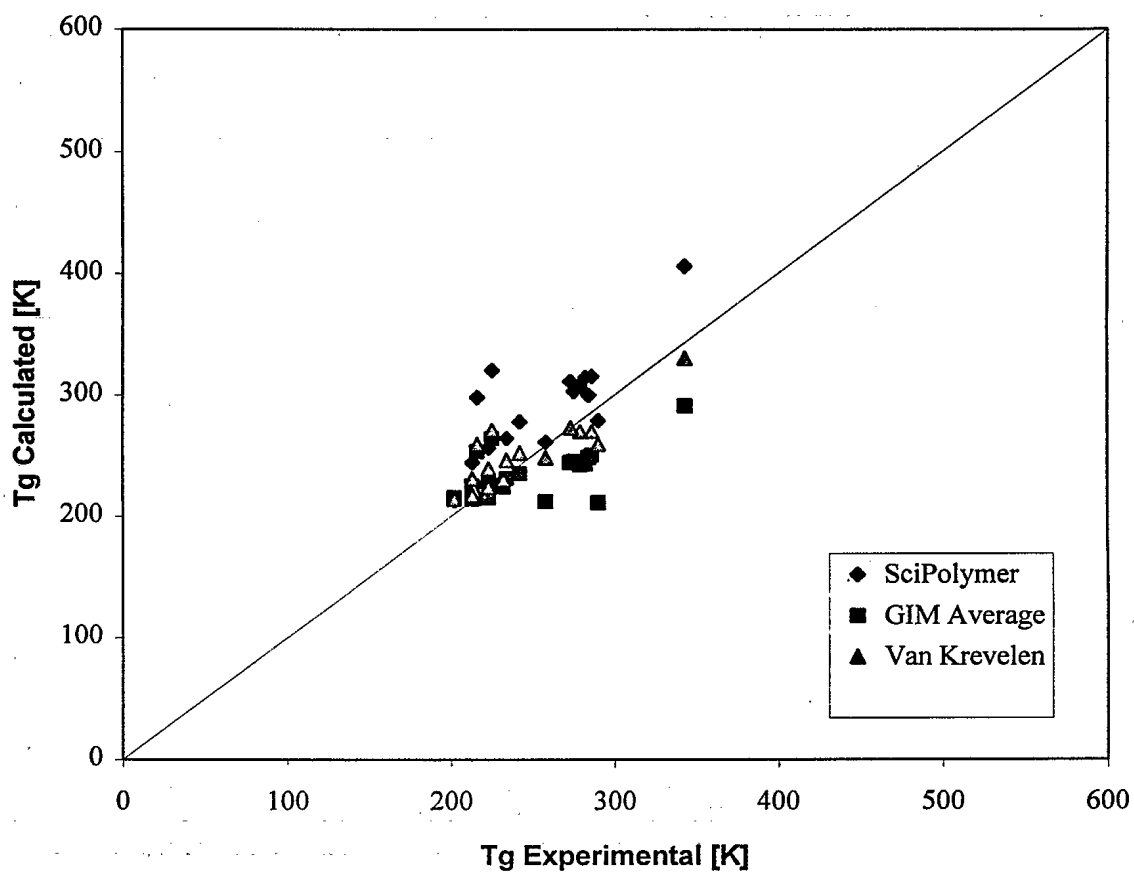


Figure 2: Scatter diagram comparing the three calculated values of T_g with the experimentally measured values for the polymers listed in Table 3.

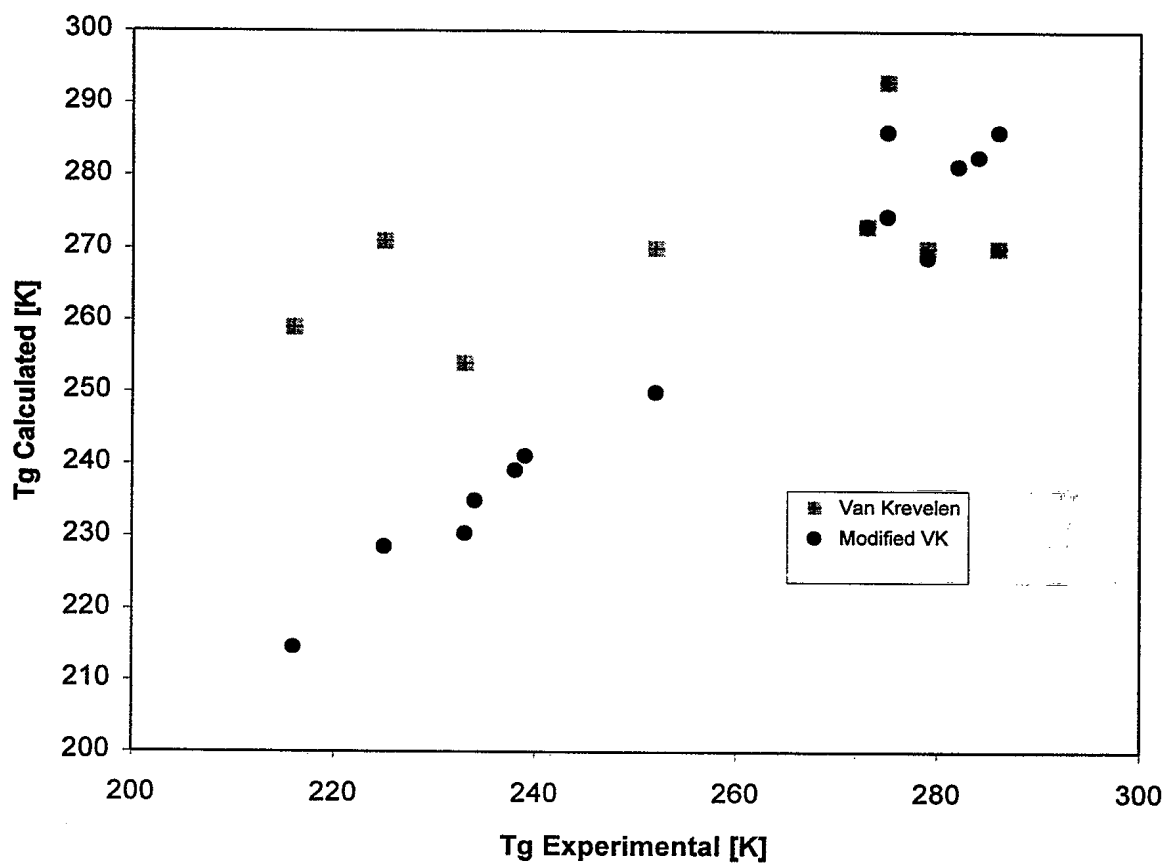


Figure 3: Scatter diagram comparing the calculated T_g using the (a) modified and (b) general Van Krevelen methods for the polymers listed in Table 6.

Appendix A: GIM parameters for the dataset of polymers listed in Table 2.

Chemical Name	E_{coh} [J/mol]	N	θ_{1t} [K]	θ_{1g} [K]
Poly(1-butene)	17527	7	389	223
Poly(1-hexene)	26600	8	317	182
Poly(1-octene)	35673	10	275	158
Poly(3-methyl-1-butene)	20909	7	348	200
Poly(4-methyl-1-pentene)	25292	9	317	182
Poly(5-methyl-1-hexene)	29829	11	294	169
Poly(6-methyl-1-heptene)	34365	13	275	158
Nylon 11,rislan	88995	24	527	303
Nylon 66	132627	28	512	294
Nylon 610	150772	36	520	298
Kodel	79718	21	527	303
Dacron	57031	15	514	296
Lexan	80730	18	516	297
Poly(ethylene oxide)	14285	6	537	308
Poly(phenylene sulfide)	36361	5	523	301
Poly(dimethylsiloxane)	16059	8	288	165
Poly(diphenylether sulfone)	100076	12	505	290
Udel polysulfone	171302	26	518	294
Polyacrylamide	49379	7	345	198
Poly(acrylic acid)	35357	6	343	197
Polyacrylonitrile	27185	6	399	229
Neoprene (cis)	27526	10	438	251
Poly(vinyl alcohol)	43299	6	438	252
Polyvinylfluoride	9329	4	429	247
Polyvinylchloride	17433	6	368	212
Polyvinylbromide	19823	6	281	162
Polyvinylidene fluoride	7981	4	364	209
Polyvinylidenechloride	25250	8	296	170

Appendix B: GIM parameters for the polyurethanes studied in the paper.

Chemical Name	$E_{\text{coh}}[\text{J/mol}]$	N	$\theta_{\text{it}}[\text{K}]$	$\theta_{\text{lg}}[\text{K}]$	$\theta_{\text{avg}}[\text{K}]$
peg100-hdi	79938	34	512	294	403
peg200-hdi	108507	46	518	298	408
bdo-mdi	107254	28	535	307	421
peg1000-mdi	398158	150	536	308	422
peg1000-hdi	365630	154	531	305	418
ptmg650-mdi	294114	108	539	310	425
ptmg650-hdi	261585	112	533	306	420
ptmg1000-mdi	410901	158	540	310	425
ptmg1000-hdi	378372	162	536	308	422
ptmg1400-mdi	527688	208	541	311	426
ptmg1400-hdi	495159	212	537	309	423
peg600-hdi	254482	100	528	303	416
1ptmg1000/3mdi/2dmpd	629167	218	531	305	418
1ptmg1000/3mdi/2depd	649515	218	523	301	412
1ptmg1000/3mdi/213bdo	622780	214	534	307	421
1ptmg1000/3mdi/2empd	639341	218	527	303	415
1ptmg1000/3mdi/2bepd	667660	218	516	297	406
1ptmg1000/3mdi/114bdo	665081	202	538	309	424
1ptmg1430/3mdi/114bdo	805225	262	539	310	424
1ptmg650/3h12mdi/114bdo	517323	170	531	305	418

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Three methods of calculating the glass transition temperature (T_g) of polymers on the basis of their chemical structure have been tested in this study. These methods were the connectivity index method, Van Krevelen's group contribution method, and the newly developed Group Interaction Modelling (GIM) method. The methods were applied to one set of polymers containing a variety of structural groups, and to a set of polyurethanes. In addition, a modified Van Krevelen approach was used on a set of 14 polyurethanes containing 9 structural groups. The results of the calculations were compared to experimental T_g values, and sources of error specific to each method were explored

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