A New Group Contribution Scheme To Estimate the Glass Transition Temperature for Polymers and Diluents

2 AUTHORS, INCLUDING:

F. Alberto Ruiz-Treviño
Universidad Iberoamericana Ciudad de México

31 PUBLICATIONS   **379** CITATIONS

CORRELATIONS

A New Group Contribution Scheme To Estimate the Glass Transition Temperature for Polymers and Diluents

C. Camacho-Zuñiga and F. A. Ruiz-Treviño*

Departamento de Ingenierías, Universidad Iberoamericana, Prol. Paseo de la Reforma 880, Lomas de Santa Fe, México D.F. 01210, México

A simple group contribution scheme is presented to predict the glass transition temperature, T_g, of pure polymers and pure diluents, also called additives, once their chemical structures have been defined. This method considers that the glass transition of any polymer can be calculated from the contribution of the groups that make up the main and side chains of the repeating unit, while the T_g of any diluent can be estimated from the contribution values reported here as if the groups present in the diluent were part of the side chain of a polymer with no "main backbone". The 66 contribution values reported are intended for very small groups and may be used to predict the glass transition temperature of linear polymers in their most atactic forms, polymers having side-chain groups, or diluents based on the elements C, N, O, H, S, P, Si, and halogens. Phenyl and naphthalene rings are also included. Compared to Bicerano's method, the proposed method is as effective as his; however, it has the advantage of considering neither solubility parameter nor structural factors. In addition, it may be used to predict the T_g's of pure diluents.

Introduction

The glass transition temperature, T_g, is an important property for pure polymers and pure diluents. Its value sets the temperature during the processing of polymers, polymer blends, and polymer−diluent mixtures. It also conditions their uses because it defines mechanical,[1,2] volumetric,[3] gas permeation,[4] and other important properties.[5−7]

The experimental determination of T_g's for these systems is easy once the materials have been synthesized, mixed, and processed. However, when the goal is to select the minimum set of structures to be used for a specific purpose, the discrimination procedure among the huge variety of possibilities is simplified if a useful scheme to predict T_g is available at our desks.

The estimation of T_g is not an easy task because its value depends on variables such as chain stiffness, interchain and intrachain mobility, conformational factors (tacticity), and morphological factors (mainly crystallinity), among other important influences.[5−7] In the case of polymers, current literature[5−14] reports methods to predict the T_g's of pure polymers that can be amorphous or elastomeric at room temperature. Some methods rely on "universal equations" or equations of state,[12,13] whereas others rely on group contributions.[7,8] Universal equations usually contain parameters that are difficult to evaluate, while the most successful group contribution schemes have been developed only for a particular family of polymers or, in the best case, they contain

contributions made up of big molecular groups.[7] To date, one of the most reliable methods is that proposed by Bicerano,[5] consisting in of a correlation equation to predict glass transition temperature. It considers some "structural parameters"—which can be evaluated from the polymer's chemical structure—related to chain stiffness, and the solubility parameter, related to the cohesive forces.

In the case of pure diluents, to the best of our knowledge, there are no methods reported to estimate their glass transition temperature. In fact, there have not been attempts to study a general correlation that can predict both the glass transition of pure polymers and pure diluents. Thus, in this work, a new scheme is being presented that may be used to evaluate the T_g's of these materials once their chemical structures have been proposed. It is based on the assumption that the structural groups in the diluent or in the polymer repeating unit provide weighed additive contributions to the T_g, which depend on their position.

Method

It is proposed that the T_g of any polymer or any diluent can be calculated from their chemical structure according to

$$T_g = \frac{1}{M}\left[\sum_i (T_g M)_i + \sum_j (T_g M)_j\right] \qquad (1)$$

where T_g and M are the glass transition temperature and the molecular weight of the repeating unit in the case of polymers or of the whole molecular structure in the case of diluents. In eq 1, it has been assumed that

* To whom correspondence should be addressed. Telephone: (52) 55 5950 4074. Fax: (52) 55 5950 4279. E-mail: alberto.ruiz@uia.mx.

Table 1. Group Contribution Values To Predict the Glass Transition Temperature for Pure Polymers and Pure Diluents[a]

group	M_i (g/gmol)	$T_{gi}M_i$ in the main chain	(g/gmol)[b] in side chains	group	M_i (g/gmol)	$T_{gi}M_i$ in the main chain	(g/gmol)[b] in side chains
>C<	12.0	44020	26377	benzene (1,2-disubst.)	76.1	11489	31798
(m)—C=C—(m)	12.0	14403		benzene (1,3-disubst.)	76.1	17218	26811
—CH—	13.0	20600 n / 17770 c	13033	triazine	81.1	-12643	
—CH=	13.0	2120		benzene (1,4-disubst.)	76.1	34975	29109
—CH₂—	14.0	2427 n / -949 c	2635	benzene (p)(m)(m)-trisubst.	75.1	53573	45454
—CH₃	15.0		-12600 n / -13818 c / -7690 s	benzene trisubst.	75.1	48328	
—C(CH₃)₂—	42.1	17506		benzene (trimethyl)	75.1		46937
—CH(CH₃)₂	43.1		-5259	benzene tetrasubst.	74.1	86311	46652
—C(CH₃)₃	57.1		8673	benzene tetrasubst.	74.1	90843	
—C(=O)—	28.0	19606 n / 24233 c	7420	naphthalene	127.2		42359
—O—	16.0	-7948 n / -1286 c	2264	naphthalene	126.2		51577
—S(=O)₂—	64.1	50499		fused ring	126.2	63386	
—S—	32.1	-5548		fused ring	126.2	94642	
—P(=O)—	47.0		12017	naphthalene	126.2	60515	
—CF₂—	50.0	11875	28267	naphthalene	126.2	69329	
—CF₃	69.0		21560	fused ring	125.2		73607
—F	19.0		-7209	phthalide-type	132.1	105576	
—Cl	35.5		-1655	fluorene	164.2	131731	
—Br	79.9		22625	thioxanthone-type	192.2	151882	
imide —N(C=O)₂—	145.1	83586		bisphenol-type	274.4	157986	
—CN	26.0		-4768				
—NH—	15.0	10455	-3458				
—OH	17.0		-4475				
—Si—	28.1	34112					
cyclopentane	69.1		10738				
cyclohexane	83.2		16892				
cycloheptane	77.1		18552				
dimethylcyclohexane	82.1	44907					

[a] For the T_g's of diluents, the values are those located in the column labeled "in side chains". [b] n = nonconjugated or attached to a nonconjugated atom; c = one- or two-sided conjugation with an aromatic ring (beside one or between two aromatic rings) or attached to an atom with these characteristics; s = at the end of a side chain; (m) = attached to the main backbone; (p) = attached to the main backbone only in PI and PEI.

the contribution of each chemical group present in the structure of a polymer depends also on its position. So, the product $(T_gM)_i$ is the contribution of every group located in the main chain, whereas $(T_gM)_j$ is the contribution of every group located in the side groups or chains.

In the case of diluents, it has been assumed that the groups that make up their chemical structure have a contribution equal to the one shown by the same groups but located in the side chain of a polymer structure. In other words, it is assumed that any diluent can be considered as a branched polymer with no "main backbone" so that $\sum_i(T_gM)_i$ is equal to zero.

Every contribution reported here was evaluated by multiple linear regression applying eq 1 to a data set of 308 polymers and 25 low molecular weight diluents using the glass transition temperatures reported in the literature. Restrictions in the structural or composition factors, such as symmetry, tacticity, polarity, etc., were not taken into account, and the experimental T_g value for each polymer corresponds to a very high molecular weight.

Results and Discussion

Table 1 reports the group contribution values to predict the T_g's of pure polymers or pure diluents. It contains two different values for each group, which are used depending on their position in the polymer repeating unit ("in the main chain" or "in side chains"). The values to estimate the T_g's of pure diluents are those placed in the column labeled "in side chains". During the process to select the best fitting, it was noted that best results are obtained when the contribution of each group that makes up the chemical structure of a diluent is considered in the vector formed by the contribution of the groups labeled as "in side chains". Thus, at least from the point of view of the T_g estimation, this result suggests that the chemical structure of any diluent can be envisioned as the side-chain structure of a polymer that does not have a "main backbone".

There are two worthwhile observations to be noted in Table 1. The first one is related to the size of the groups. In contrast to Van Krevelen's scheme,[7] the values reported in this work are for very small groups; thus, the number of T_g's to be predicted is more flexible than that in the mentioned scheme. The second one is related to the type or composition of the groups. There are 48 groups based on C, N, O, H, S, P, Si, and halogens, including phenyls and naphthalenes, which are the basis of a huge variety of polymers and diluents typically found in industry and academia.

Figure 1 shows a plot of predicted versus experimental T_g's for all of the amorphous and elastomeric polymers as well as the diluents that were used to obtain the contributions. The analyzed interval of T_g's goes from 100 up to 700 K. Its correlation coefficient is well satisfactory, $R^2 = 0.9968$, and, interestingly, a great number of polymers and diluents fall on the interval $T_g \pm 20$ K. Also note that the T_g's of pure diluents can be predicted reasonably well when its chemical structure is considered as the side chain of a polymer that does not have a "main chain".

From all of the polymers and diluents used to get the contributions, 61% of them falls in the interval $T_g \pm 20$ K, which may be considered as an acceptable value because of the fact that experimental T_g depends on the method of measurement (dilatometry, differential scan-
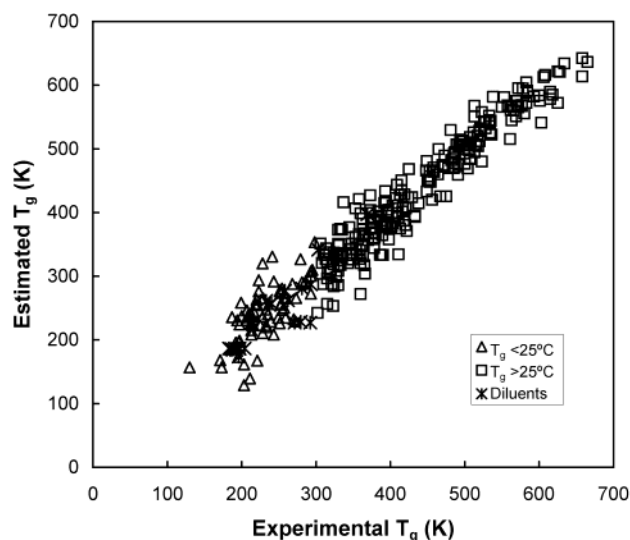
Figure 1. Predicted versus experimental glass transition temperature for elastomeric and amorphous polymers and diluents, as obtained by the proposed method. Correlation coefficient $R^2 = 0.9968$.

Table 2. Name and the Experimental and Estimated Glass Transition Temperatures for Some Common Polymers

	T_g (K)	
polymer	exptl	estimated
Teflon	200	237
polyisoprene	203	129
poly(ϵ-caprolactone)	213	208
polypropylene	233	248
poly(vinylidene fluoride)	233	223
poly(ethylene sebacate)	243	208
perfluoropolymer 1[a]	260	265
poly(methyl acrylate)	281	291
poly(n-propyl methacrylate)	308	321
poly(7-aminoheptanoic acid)	330	351
poly(ethylene terephthalate)	345	377
poly(vinyl chloride)	347	342
poly(vinyl alcohol)	358	421
polystyrene	373	399
polyacrylonitrile	378	344
poly(phenylmethylsilane)	390	333
poly(ethylene-2,6-naphthalenedicarboxylate)	397	404
poly[methane bis(4-phenyl)carbonate]	420	380
poly(bisphenol A isophthalate) BPA/IA	456	420
polysulfone	459	464
poly(etherimide) 2[a]	482	482
poly(ether sulfone)	498	513
fluorene bisphenol polysulfone	550	566
polyimide[b]	577	567
polyphenolphthalein 1[a]	593	582

[a] As reported by ref 5. [b] As reported by ref 15.

ning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), etc.). In the case of DSC or DMTA, T_g is a rate-dependent phenomenon, and many values have been measured at different rates (5, 10, or 20 °C/min). In addition, researchers and laboratories report either the onset or the medium value of T_g, causing larger discrepancies in its reported values.

Table 2 summarizes the name and the experimental and estimated T_g's for some well-known polymers that were used in this work to set the group contribution values reported in Table 1. The estimated values are in excellent agreement with those values reported in the common literature.

In the same way, Table 3 shows the name and the experimental and estimated T_g's for all of the diluents

Table 3. Name and the Experimental and Estimated Glass Transition Temperatures for the Diluents Used To Evaluate the Group Contribution Values Reported in Table 1

additive	M (g/gmol)	T_g (K) exptl	T_g (K) estimated
dioctyl phthalate[a]	391	183	186
di-*n*-octyl phthalate[b]	391	186	186
diethyl phthalate[b]	222	188	185
di(2-ethylhexyl) phthalate[b]	391	191	186
dimethyl phthalate[a]	194	193	184
diisodecyl phthalate[b]	447	196	174
diundecyl phthalate[a]	475	197	186
ditridecyl phthalate[a]	531	204	187
tricresyl phosphate[c]	368	212	225
triphenyl phosphate[a]	326	213	228
dibenzyl succinate[b]	298	215	225
m-phenylene dibenzoate[a]	318	233	262
glycetyl tribenzoate[a]	404	237	255
dicyclohexyl phthalate[b]	330	240	257
diphenyl phthalate[b]	318	258	277
phenyl naphthylamine[c]	219	262	262
neopentyl glycol phenyl phosphate[a]	226	271	227
ethylene glycol dibenzoate[a]	270	279	228
tetraxylyl hydroquinone diphosphate[a]	687	281	281
tetramethyl bisphenol A[c]	284	292	227
tetra *tert*-butyl bisphenol A	453	293	287
tetrabromo bisphenol A[c]	544	303	342
naphthol AS BI[c]	372	328	328
1,1'-bi-2-naphthol[c]	286	329	329
fluorene bisphenol[c]	350	369	397

[a] Reference 1. [b] Reference 2. [c] Reference 3.

Table 4. Name and the Experimental and Estimated Glass Transition Temperatures for Some Polymers That Were Not Used To Evaluate the Group Contribution Values Reported in Table 1, Showing the Prediction Ability of the Proposed Scheme

polymer	T_g (K) exptl	T_g (K) estimated
PEK 5a[a]	409	382
m-TPEEK[b]	421	434
m-TPEEKK[b]	432	463
PEK 7a[a]	432	473
6F-PDE[c]	446	460
3F-CPES[d]	447	470
m-TPES[e]	451	481
PEK 9[a]	473	574
PEI m−m[f]	502	489
PEI TMA-tert[f]	517	516
PEI m-tert[f]	520	496
PEI TMA-m[f]	530	509

[a] Reference 16. [b] Reference 19. [c] Reference 20. [d] Reference 17. [e] Reference 18. [f] Reference 21.

analyzed in this work. As in the previous case, the method proposed here can estimate the T_g's of pure diluents with an excellent agreement with those values reported in the common literature. In fact, the group contribution values reported in Table 1 have predicted the T_g's of 72% of the diluents used in the database with an error of less than 20 K.

To test the prediction ability of the proposed group contribution scheme, some polymers recently reported in the literature and not included in the original database were tested. Table 4 presents the name and the experimental and estimated T_g's of the results, showing there is an excellent agreement between these two values.

Finally, Figure 2 shows the values of T_g for some glassy and elastomeric polymers as predicted by this work and by the correlation reported by Bicerano.
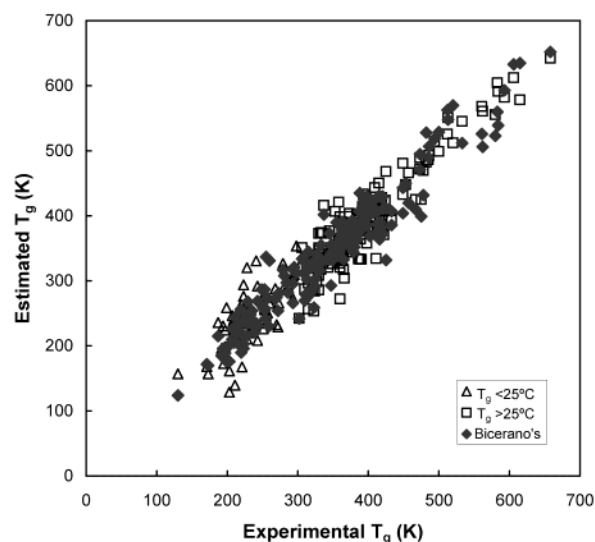
Figure 2. Estimated versus experimental T_g for some polymers, as obtained by the proposed method and the one published by Bicerano's. No diluents were used in this comparison because Bicerano's method does not apply to them.

Interestingly, the values predicted by this work compete favorably with those predicted by Bicerano's correlation. In fact, inside the interval $T_g \pm 20$ K, Bicerano's correlation can predict the T_g's of at least 59.9% of the polymers used to compare both methods, whereas the proposed method can predict at least 57.4%.

It should be noted that Bicerano's correlation includes the solubility parameter and a universal intercept value different from zero to improve the prediction of T_g, while the proposed method here does not consider either of these conditions; thus, it is simpler to use than Bicerano's. From the prediction point of view, there are no elements to discriminate one method against the other one. Nevertheless, it is interesting to say that the present technique contains no rules and that it can predict the T_g's of pure diluents, as was shown in Table 3.

Conclusions

A simple general group contribution method to estimate the glass transition temperature for pure polymers and pure diluents is presented in this work. A total of 66 contribution values for 48 of the most representative groups, based on C, N, O, H, S, P, Si, and halogens and phenyl and naphthalene rings, are reported, and their values depend only on their position in the polymer repeating unit. For pure diluents, the values to be used are those reported in the column labeled as "in side chains".

When the method reported in this work is compared to the well-known Bicerano's correlation, from the prediction point of view there is no way to discriminate one method against the other one because both of them have reasonably good prediction ability. However, the scheme proposed here to estimate the glass transition of pure polymers and pure diluents contains no rules, thus simplifying the selection of new chemical structures to be synthesized.

Acknowledgment

Supporting Information Available: Polymer chemical structures, molecular weights, and experimental and estimated glass transition temperatures for polymers used to get the group contribution values reported in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Kambour, R. P.; Kelly, J. M.; McKinley, B. J. Modulus and Yield Resistance of Glassy Blends Containing Diluents Manifesting Varying Degrees of Mobility: Polyphenylene/Ether/Polystyrene/Diluent Mixtures. *J. Polym. Sci., Part B: Polym. Phys.* **1989**, *27*, 1979.

(2) Garfield, L. J.; Petrie, S. E. Viscosity and Glass-Transition Behavior of Polymer−Diluent Systems. *J. Phys. Chem.* **1964**, *68*, 1750.

(3) Ruiz-Treviño, F. A.; Paul, D. R. A Quantitative Model for the Specific Volume of Polymer−Diluent Mixtures in the Glassy State. *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 1037.

(4) Eichler, S.; Miltz, J. Prediction of Gas Permeability of Nylon From Glass-Transition Temperature. *J. Appl. Polym. Sci.* **1993**, *50*, 2095.

(5) Bicerano, J. *Prediction of Polymer Properties*; Marcel Dekker Inc.: New York, 1996.

(6) García-Domenech, R.; de Julián-Ortiz, J. V. Prediction of Indices of Refraction and Glass Transition Temperatures of Linear Polymers by Using Graph Theoretical Indices. *J. Phys. Chem. B* **2002**, *106*, 1501.

(7) Van Krevelen, D. W. Properties of Polymers. *Their Correlation with Chemical Structure; Their Numerical Estimation and Prediction from Additive Group Contributions*; Elsevier: Amsterdam, The Netherlands, 1990.

(8) Boudouris, D.; Constantinou, L.; Panayiotou, C. Prediction of Volumetric Behavior and Glass Transition Temperature of Polymers: A Group Contribution Approach. *Fluid Phase Equilib.* **2000**, *167*, 1.

(9) Camelio, P.; Cypcar, C. C.; Lazzeri, V.; Waegell, B. A Novel Approach Toward the Prediction of the Glass Transition Temperature: Application of the EVM Model, a Designer QSPR Equation for the Prediction of Acrylate and Methacrylate Polymers. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 2579.

(10) Gao, H.; Harmon, J. P. An Empirical Correlation Between Glass Transition Temperatures and Structural Parameters for Polymers with Linear and Branched Alkyl Substituents. *J. Appl. Polym. Sci.* **1997**, *64*, 507.

(11) Sumpter, B. G.; Noid, D. W. On the Use of Computational Neural Networks for the Prediction of Polymer Properties. *J. Therm. Anal.* **1996**, *46*, 833.

(12) Matsuoka, S.; Quan, X. A Model for Intermolecular Cooperativity in Conformational Relaxations near the Glass Transition. *Macromolecules* **1991**, *24*, 2770.

(13) Hopfinger, A. J.; Koehler, M. G.; Pearlstein, R. A. Molecular Modeling of Polymers. IV. Estimation of Glass Transition Temperatures. *J. Polym. Sci., Part B: Polym. Phys.* **1988**, *26*, 2007.

(14) Hayes, R. A. The Relationship Between Glass Temperature, Molar Cohesion, and Polymer Structure. *J. Appl. Polym. Sci.* **1961**, *5*, 318.

(15) Husk, R. G.; Cassidy, P. E.; Gebert, K. L. *Macromolecules* **1988**, *21*, 1234.

(16) Back, J. B.; Tan, L. S. Synthesis of Poly(ether ketones) and a Poly(ether sulfone) using Polyphosphoric acid/P_2O_5 as Polymerization Medium. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2002**, *43* (1), 533.

(17) Hu, W.; Liu, B.; Jiang, Z.; Zhang, W.; Wu, Z. Trifluoromethylated Aromatic Poly(ether sulfones)s. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2002**, *43* (1), 557.

(18) Hu, W.; Liu, B.; Rao, X.; Jiang, Z.; Zhang, W.; Wu, Z. Preparation of Aromatic Poly(ether nitrile) and Poly(ether sulfone) with (3-methyl)phenyl Pendant Groups. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2002**, *43* (1), 640.

(19) Liu, B.; Hu, W.; Jin, Y.; Chen, C.; Jiang, Z.; Zhang, W.; Wu, Z. Synthesis and Characterization of Novel Soluble Poly(aryl ehter ketones)s. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2001**, *42* (2), 377.

(20) Liu, B.; Chen, C.; Zhao, X.; Jiang, Z.; Zhang, W.; Wu, Z. Synthesis and Characterization of Fluorinated Polyether Containing Biphenyl. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2001**, *42* (2), 470.

(21) Liaw, D. J.; Hsu, C. Y.; Chen, I. W.; Liaw, B. Y. Synthesis of Soluble Poly(ether imide)s Derived from Various New Bis(ether anhydride)s. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2001**, *42* (1), 596.