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Glass Transition Temperature Calculations for Styrene Derivatives Using the Energy, Volume, and Mass Model

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ABSTRACT: We have previously described an original model called the EVM (energy, volume, and mass) model, which uses only three descriptors, the energy of a polymer segment conformation using molecular mechanics and molecular dynamics, its volume (the occupied space by the atoms as well the unoccupied space between them), and the repeat unit molar mass, to calculate successfully the glass transition temperatures (T_g) of aliphatic acrylate and methacrylate polymers. We report here the application of this model to a series of various polystyrenes. The EVM model allows correct description of the substituent position effect on the ring as well as on the backbone, for various alkyl group and halides. The estimated T_g values with the EVM model are in excellent agreement with literature values. We compare this model with two other methods (Bicerano's model and Porter's approach) and find better or comparable correlations.

Introduction

The glass transition temperature (T_g) is of special interest in the development of new amorphous polymers because many properties of technological importance show a significant change in magnitude, or in temperature dependence, at this temperature.

Recent developments in computers allow calculation of T_g completely from molecular dynamics[1−5] or Monte Carlo simulations.[6] However, the large amount of computation time required has limited these approaches to simple polymers such as polyethylene, polystyrene, or poly(vinyl chloride). This approach, therefore, has not allowed extensive investigation of the effects of substituent variations in a family of polymers.

An alternative approach is to derive a quantitative structure−property relationship (QSPR) between the T_g and appropriate descriptors. Van Krevelen[7,8] showed through the group additivity property (GAP) the usefulness of QSPR to predict a broad range of polymer physical properties (such as refractive index, C_p, T_g, and density). The GAP approach, however, requires the existence of property increments for each desired structure. By combining the GAP approach with molecular modeling, Hopfinger et al. have shown that determination of an unknown increment is possible for new structures using molecular mechanics calculations (torsional angle unit theory).[9−11] Recently, Bicerano[12] used connectivity indices as fundamental descriptors of molecular structure for the repeat unit of a given polymer to bypass the unknown increments problem for new polymers. With the above descriptors, a neural network model was developed recently.[13] The problem with this approach is that even though the method gives good results, it does not provide information on what really affects T_g at the molecular level; i.e., it works as a black box.[13] However, it is not clear that even in-depth analysis of the results will provide such information. More recently, Porter[14] developed a new methodology: group interaction modeling or GIM. This model is an extension of both van Krevelen's and Bicerano's work, using concepts from both although based on a more fundamental framework of polymer physics.

Most of these methods were intended to be universal, i.e., using one equation and one set of data for all possible polymers. As suggested by Hopfinger (ref 11, p 30), however, setting up a designer equation (i.e., one equation for one polymer family) gives more accurate predictions than developing a universal equation for diverse polymer structures. Family specific equations can provide better information and are also useful for developing and testing new models. We previously developed a designer equation for acrylate and methacrylate[15−18] where T_g is represented as an energy density function. This model, called the EVM (energy, volume, mass) model, provides information that allows better understanding of polymer behavior and of the factors determining T_g within a given polymer family. In the present paper, we present an extension of the EVM model to various styrene derivatives. This polymer family is particularly interesting since more substitution positions are available than with the acrylates (as illustrated in Figure 1) and small changes in the structure (position, size, and/or nature of substituents) dramatically affect T_g. We demonstrate that the EVM model can uniquely describe such effects, which are not well reproduced with models such as those of Bicerano or Porter. This work also demonstrates the capacity of the EVM model for predicting the T_g's of a given class of polymers.

Model Development

The EVM model defines T_g as a function of three descriptors: the conformational energy of a polymer

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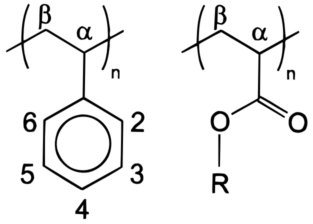


Figure 1. Difference in substitution position between styrene and acrylate polymers.

segment, the amount of volume occupied by this polymer (by the atoms themselves as well as by the space between them, called the total space around a standard deviation volume (TSSV)[17]), and the molecular weight of the polymer segment normalized by the number of repeat units in the polymer segment.

In this approach, we assume that the glass transition can be explained by a physical change from a glassy material to a less ordered rubbery state, which typically does not involve large scale atomic motions. Movement of atoms requires energy and either a place for the movement to occur (free volume), or cooperativity in segment motion. This definition can be quantified by the energy/volume ratio where the higher the ratio is, the higher the T_g. As we have shown, the mass term M_w must also be taken into consideration,[17,18] and the T_g can be described using eq 1. The energy term used

$$T_g = F\left(\frac{\text{energy} \times M_w}{\text{TSSV}}\right) \qquad (1)$$

in eq 1 is derived from an atomistic simulation (see Computational Methods), and it has been separated into two terms. The first one is the van der Waals energy, E_{vdw}, which is the sum of the attractive and repulsive van der Waals intramolecular interactions. It represents the long-range interactions within a polymer segment (side group/side group and side group/backbone). For this term, we assume that these interactions are similar to the intermolecular interactions that can exist between two side groups of two different polymer chains. In the present work, a single polymer segment is considered for the calculation, and studies with multiple chains are in progress. The second term is the internal energy, E_{int}. Characteristic of the short-range interactions (from 1−2 to 1−4 interactions), it represents the sum of the bond valence, angles, and torsional angle deformations. The volume term, TSSV, takes into account the space occupied by the atoms, as well as some of the free space between atoms, both of which have an influence on the T_g. As previously shown, eq 1[17] becomes eq 2:[18] It has not been necessary to add an

$$T_g = A + B\left(\frac{E_{vdw}M_w}{\text{TSSV}}\right) + C\left(\frac{E_{int}M_w}{\text{TSSV}}\right) \qquad (2)$$

electrostatic term to eq 2 because we assume that such effects within a polymer family are constant and are implicitly taken into account in the *A*, *B*, and *C* parameters.

Computational Methods

Computational results were obtained using software programs from MSI of San Diego; polymer building was performed with Polymerizer 8.0, while molecular mechanics and molecular dynamics calculations were carried out with the Discover 95.0 program. The force field used is the extensible systematic force field[19] (ESFF) provided with Discover 95.0 using the default potential types. For treatment of nonbonded interactions, the cell multipole method[20−22] (CMM) was used with the number of cells equal to the 26 immediate neighbors and with a distance-dependent dielectric value. The CMM provides a more rigorous and efficient treatment of nonbonded interactions for nonperiodic systems than the application of a typical cutoff limit.[19] We have previously shown that the force field used, with or without the nonbonded treatment, seems to not have an effect on the EVM approach, with respect to deriving a new set of *A*, *B*, and *C* values.[17,18,23]

After the initial monomer structure was constructed and minimized, a corresponding homopolymer segment with 20 repeat units was built with a probability of meso diad equal to 0.5 (atactic structure). The starting conformation of the backbone dihedral angles was set to *cis*−*trans*−*cis* (Polymerizer 8.0). Before application of molecular dynamics (MD), the polymer segment was relaxed by classical molecular mechanics calculations (MM). Backbone atom positions were fixed and bond lengths constrained for all the atoms during dynamics simulations using the RATTLE option, which is the velocity version of the SHAKE algorithm.[19,24] The NVT ensemble (constant temperature and volume) and direct velocity scaling were used during simulations at a temperature of 900 K for 1000 steps (1 fs/step). This high temperature was used to rapidly randomize conformations of the substituents.[17,18] After the MD simulation, the structure was relaxed again by unfixing the backbone and removing the bond length constraints. It should be pointed out that the geometry optimization sequence used is not an MM/MD sequence applied to a polymer segment to find the most stable conformation; it is only a fast and efficient way to get a reasonably stable geometry of the polymer segment. As shown earlier,[17] larger polymer segments or longer dynamics times do not affect the results.

For the computation of the volume term, we developed a method that takes into account the space occupied by the atoms (van der Waals volume), as well as a portion of the free space between atoms, both of which have an influence on the T_g. This volume can be described by a cylinder that surrounds the polymer segment. The polymer backbone is fixed during the MD sequence to avoid being bent by the high-temperature MD. The volume of this cylinder (termed TSSV for total space around a standard deviation volume for a polymer segment)[17,18] is represented by eq 3,

$$\text{TSSV} = \pi \prod_{a=x,y,z} \sigma_a = \pi \prod_{a=x,y,z} \sqrt{\frac{1}{N-1}\sum_N (a)^2} \qquad (3)$$

where *N* is the number of atoms in the optimized polymer segment and σ_a is the standard deviation along the *a* direction (*x*, *y*, or *z*).

After the reference of the polymer segment (i.e., the atoms) is moved to its center of gravity (nonweighted system) and the *x*, *y*, and *z* axes are aligned with respect to the principal axis of the polymer segment, the standard deviation along each direction *x*, *y*, and *z* is computed (σ_x, σ_y, σ_z).

The use of the standard deviation instead of the range eliminates end effects along the *x* axis and gives better

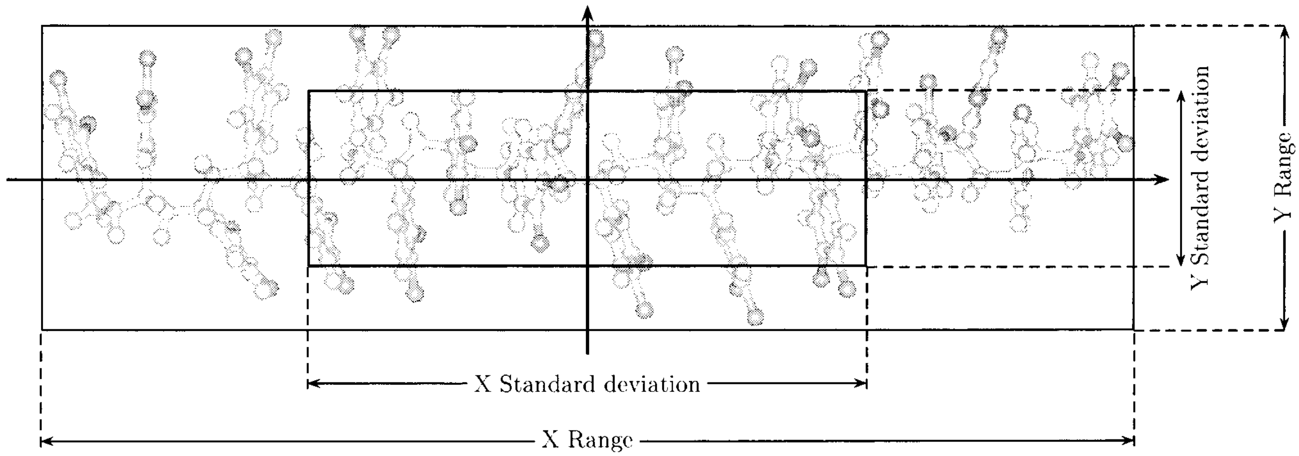


Figure 2. Illustration of the range and standard deviation along the *X* and *Y* axes for poly(3,4-dichlorostyrene); only heavy atoms are represented.

Table 1. Polymers and Experimental T_g Values (in K) Used to Set up the Constants *A*, *B*, and *C* for Equation 2[a]

			predicted[b]		
	names	experimental	EVM	Synthia	GIM[c]
1	poly(4-*sec*-butylstyrene)	**359**[31]	370	344	360
2	poly(3-methylstyrene)	**370**[31]	375	373	354
3	poly(styrene)	**373**[8,28]	371	382	372
4	poly(4-carbonylmethoxystyrene)	**386**[31]	391	376	396
5	poly(4-*tert*-butylstyrene)	**399**[29]/402[14]	394	369	398
6	poly(2,4,5-trimethylstyrene)	**409**[31]	404	361	NA
7	poly(4-phenylstyrene)	**411**[25]/431[14]	412	409	441
8	poly(2,6-dichlorostyrene	**440**[31]	448	406	NA
9	poly(2,4,6-trimethylstyrene)	**435**[31]	426	361	NA
10	poly(α-methylstyrene)	409[14]/441[8,14]/**453**[28]	463	411	404

[a] For multiple entries the bold values were used. [b] Predicted T_g values were obtained by using EVM (eq 4), Synthia, and GIM models. [c] NA: not available.

Table 2. Experimental and Predicted T_g's (K) of Additional Aliphatic Mono- and Disubstituted Styrenes

			predicted		
	names	experimental	EVM	Synthia	GIM[a]
11	poly(2-methylstyrene)	408[26]/409[31]	407	373	404
12	poly(4-methylstyrene)	366[26]/373[29]/374[31]/380[8]	369	373	354
13	poly(4-ethylstyrene)	300[31]/351[31]/359[31]	360	351	NA
14	poly(2,4-dimethylstyrene)	385[26]	388	366	404
15	poly(3,4-dimethylstyrene)	380[26]/384[26,31]	378	366	404
16	poly(2,5-dimethylstyrene)	405[25]/416[25,26]	407	366	404
17	poly(3,5-dimethylstyrene)	377[31]	373	366	404

[a] NA: not available.

information on how the molecule fits within the cylinder, as shown in Figure 2).

All the sequences (MM/MD sequence and TSSV calculation) are done sequentially in Discover 95.0 for all the polymers. The command file is available upon request.

Results and Discussion

Molecules reported in Table 1 were used to set up *A*, *B*, and *C* for eq 2 using multiple variable linear regression. Analysis of variance (ANOVA) was used to validate the model. Equation 2 became

$$T_g = 325.312 + 0.991\left(\frac{E_{vdw}M_w}{TSSV}\right) + 0.771\left(\frac{E_{int}M_w}{TSSV}\right) \quad (4)$$

The correlation coefficient (r) was 0.987 (r^2 was 0.974), and the standard deviation in 5.6 K. Deviations for *A*, *B*, and *C* were, respectively, 5.783, 0.212, and 0.116. ANOVA gave an *F* value of 131.80, which means that the dependent variable T_g can be reliably predicted from a linear combination of the independent variables $(E_{vdw}M_w)$/TSSV and $(E_{int}M_w)$/TSSV.

Tables 1 and 2 for the poly(aliphatic mono- and disubstituted styrenes) and Table 3 for the poly(halogenated styrenes) contain predicted T_g values obtained with eq 2 along with those calculated using Synthia (from MSI, based on the Bicerano's model[12]) and the GIM method (Porter's model[14]) as benchmarks. Two points should be noted. First, the T_g equations used in the two latter methods were established using a large number of polymers (i.e., encompassing with different families) and are more universal equations rather than designer equations. Second, in many cases more than one experimental T_g value is reported for many polymers in the literature. Variations are due to different experimental conditions, various measurement techniques, and different polymer sample preparations. Figures 3 and 4 report the predicted T_g values for the three models and the closest experimental T_g to this

Table 3. Experimental and Predicted T_g's (K) of Halogenated Styrene Derivatives Plus the 4-Methoxy Polymer

	names	experimental T_g (K)	predicted EVM	predicted Synthia	predicted GIM[a]
18	poly(2-chlorostyrene)	392^{26}	405	395	403
19	poly(3-chlorostyrene)	363^{26}	385	395	403
20	poly(4-chlorostyrene)	$383^{31}/389^{12}/401^{29}/406^{27}$	387	395	403
21	poly(2,4-dichlorostyrene)	$406^{12}/408^{26}/416^{29}$	412	406	427
22	poly(2,5-dichlorostyrene)	$379^{26}/401^{31}$	388	406	427
23	poly(3,4-dichlorostyrene)	401^{26}	397	406	427
24	poly(4-fluorostyrene)	$379^{26}/384^{27}/386^{31}$	385	388	352
25	poly(2,5-difluorostyrene)	391^{31}	392	393	NA
26	poly(4-bromostyrene)	$391^{31}/414^{28}/417^{26,29}$	402	395	425
27	poly(α,β,β-trifluorostyrene)	475^{32}	464	404	475
28	poly(2,3,4,5,6-pentafluorostyrene)	378^{32}	431	406	NA
29	poly(4-methoxystyrene)	$362^{14}/386^{28}$	387	372	356

[a] NA: not available.

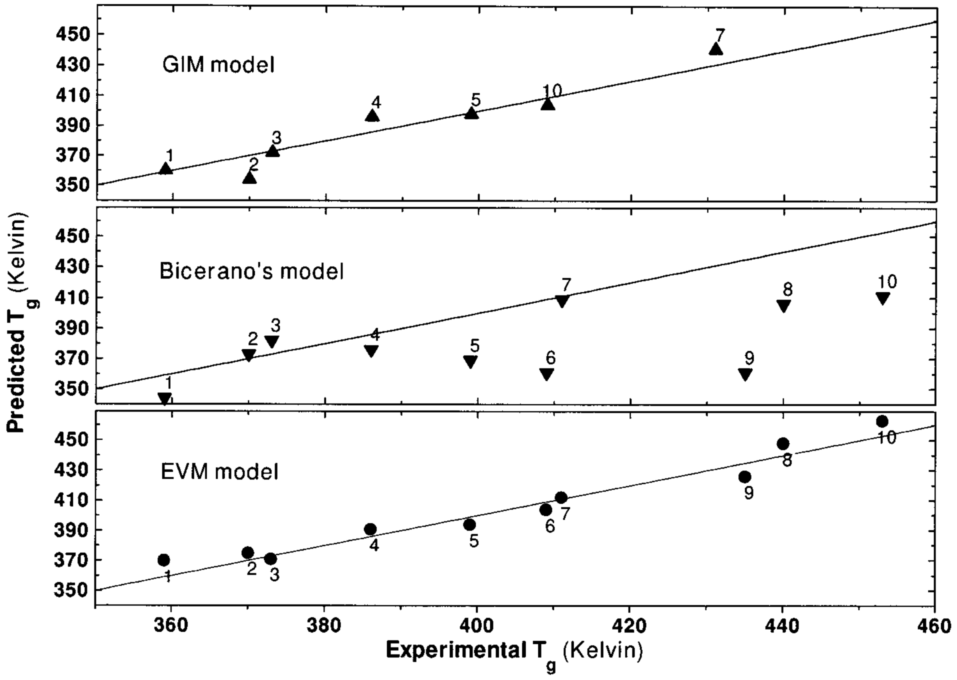


Figure 3. Comparison of the predicted T_g's obtained with EVM, GIM, and Synthia vs experimental T_g's (in Kelvin) for molecules 1–10 in Table 1.

value found in the literature. To improve the agreement with a predicted T_g value using a specific model, the most suitable reference T_g value was selected among the experimental values available.

The EVM model is able to reproduce qualitatively and quantitatively the effect on T_g of even small changes in the structure. For example, comparing the T_g of polystyrene with poly(2-methylstyrene), poly(3-methylstyrene), and poly(4-methylstyrene), one observes experimentally that for *ortho* substitution, the T_g increases dramatically (over 30 K) whereas with *meta* and *para* substitution, the changes in T_g were not significant (ΔT_g = 5 K)[25,26] (see Tables 1 and 2). This *ortho* effect is readily understood as one steric hindrance that makes backbone motion more difficult,[25] as illustrated in Figure 5. The EVM model is uniquely able to quantify what happens at the molecular level with such structural changes. Due to larger interactions between the methyl group and the backbone, higher energies are calculated for the *ortho* derivative (E_{vdw} = 86.67 kcal/mol and E_{int} = 113.65 kcal/mol) (Figure 5a) compared to those of the *meta* (Figure 5b) and *para* derivatives (E_{vdw} = 70.13 kcal/mol, E_{int} = 82.00 kcal/mol and E_{vdw} = 71.88 kcal/mol, E_{int} = 83.36 kcal/mol, respectively). The steric hindrance is clearly reflected in both energy terms and, when combined with a lower volume for the *ortho* derivative (TSSV = 252.7 Å^3) than for the *meta* and the *para* derivatives (TSSV = 319.7 and 368.4 Å^3, respectively), allowed more accurate calculation of the variation in T_g. These observations are in good agreement with those of Barb[25] and Dunham.[26] When two or three methyl groups are present on the ring, position effects gave similar results. One or two methyls in the *ortho* positions increased the T_g, whereas *para* or *meta* substitution decreased it (monomethylated derivatives **11** and **12**, dimethylated derivatives **14**, **15**, **16** and **17**, and trimethylated derivatives **6** and **9**).

Synthia and GIM (Tables 1 and 2) show their limitations regarding such effects. The position on the ring of a substituent seems to not be taken into account accurately, and the same values for all poly(methylstyrenes) (373 K), poly(dimethylstyrenes) (366 K), and poly(trimethylstyrenes) (361 K) were obtained using Synthia. While GIM gives different values for the poly(methylstyrenes), it gives the same value for the various poly(dimethylstyrene)s (404 K) (Tables 1 and 2). These preliminary results obtained with the EVM model emphasize particularly the ability to take into account

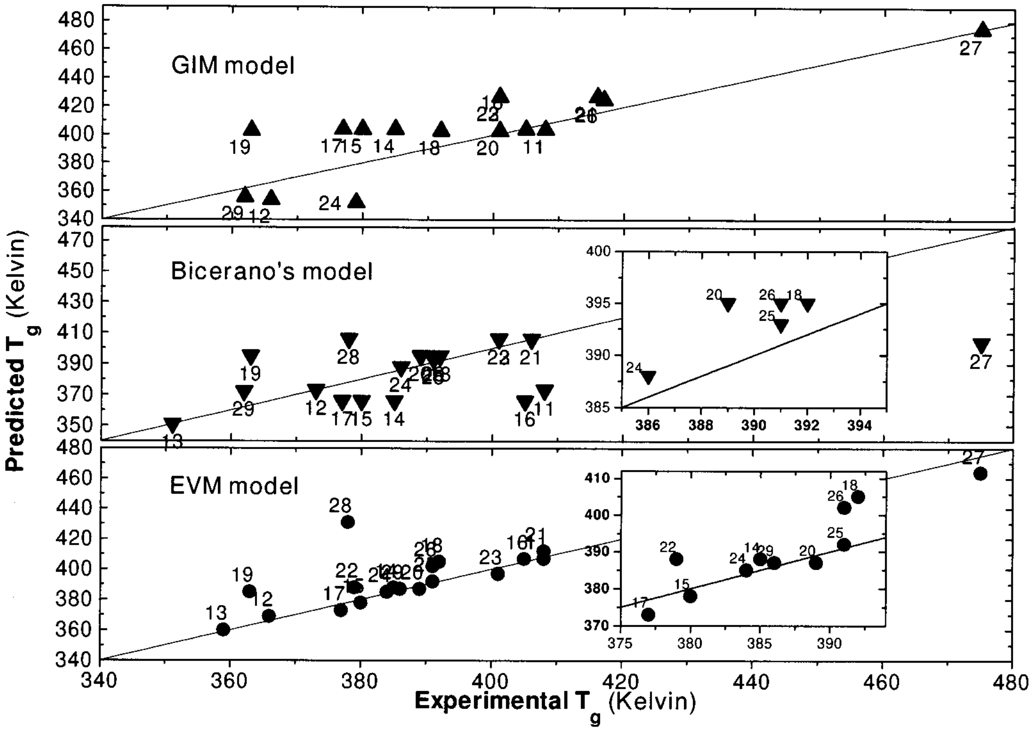
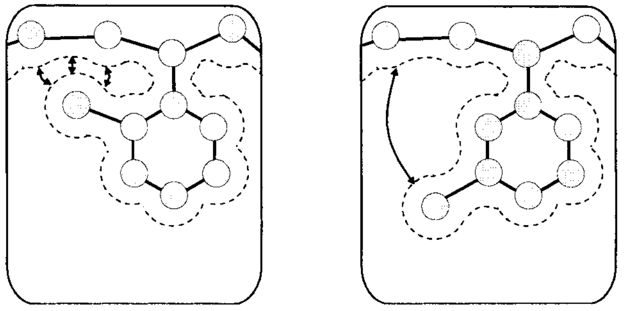


Figure 4. Comparison of the predicted T_g's obtained with EVM, GIM, and Synthia vs experimental T_g's (in Kelvin); molecules 11–29 from Tables 2 and 3.



(a) *Ortho* effect (b) *Meta* effect

Figure 5. Representation of the possible interactions between the methyl group in the *ortho* position (a) and in the *meta* position (b) with the polymer backbone.

effects of the ring substitution position. This was further confirmed with a series of halogenated styrene polymers and poly(4-methoxystyrene). Again, the EVM model was able to reproduce qualitatively and quantitatively the effect on the T_g of the nature, position, and number of halogens (Table 3). For example, the model predicted both trend and values for the poly(chlorostyrene)s but with larger deviation compared to the aliphatic compounds. Excellent results were obtained with the chloride derivatives with respect to experimental values[26] (compounds 18–23, Table 3).

For styrene polymers with various substituents in the *para* position, the T_g values were correctly predicted. For example, on going from brominated to fluorinated derivatives, the EVM model predicted a T_g decrease consistent with literature data.[27–29] A test on the methoxy derivative (molecule 29, Table 3) also gave good results ($\Delta T_g = 1$ K). This is interesting since the basis data set does not contain this kind of ether derivative. However, a single example of such a substituent effect is not sufficient at this stage of our work to confirm the more general utility of the model. Another interesting point involves the influence of backbone modification. Examples are shown with poly(α-methylstyrene) (molecule 10, Table 1) and poly(α,α,β-trifluorostyrene) (molecule 27, Table 3). Deviations between predicted T_g's and experiment were only 10 and 11 K, respectively. This confirms that the model can also be used to study effects of backbone modification.[15–18]

Finally, a very large deviation was obtained ($\Delta T_g = 58$ K) for the poly(2,3,4,5,6-pentafluorostyrene) (molecule 28) for EVM prediction. This may be due to greater electronic effects than in the other styrenes. We have indeed assumed that the electronic effect is constant within a family; as a result, the predicted temperature is overestimated in the present case.

Statistical Comparison

After the interpretation of the model's predictions was looked at in detail, a statistical discussion seems necessary since, until now, the EVM model has been compared with Bicerano's model (Synthia) and Porter's (GIM) using absolute values of deviation between predicted and experimental values. Consideration of the variance allows a more reliable comparison between the various models. In a first step, Bartlett's test[30] was used to investigate the global significance of the variances of the three models, assuming normally distributed populations. As the constants *A*, *B*, and *C* of the EVM equation have been calculated using T_g values of Table 1, the latter have not been taken into consideration because they would bias the EVM model variance. Accordingly, we considered exclusively the data reported in Tables 2 and 3. Many more polymers and their T_g's were used to establish the Bicerano and Porter models,[12,14] rendering them more general, but less likely to give as good fits for the specific families evaluated here. It should be emphasized also that this variance comparison is done only on the basis of the dependent variable (i.e., experimental T_g's) and the estimated

Table 4. Results of the Hartley Test

	$S_{\max}{}^2/S_{\min}{}^2$	critical value of $F_{\max}(0.05)$	null hypothesis H_0[a]
EVM vs Synthia	4.18	2.95−3.54	rejected
Synthia vs GIM	2.59	2.95−3.54	not rejected
EVM vs GIM	1.61	2.95−3.54	not rejected

[a] Are the variances equal ?

variable (predicted T_g obtained using the models), and not on the independent variables (i.e., for EVM ($E_{\mathrm{vdW}}M_{\mathrm{w}}$)/TSSV and ($E_{\mathrm{int}}M_{\mathrm{w}}$)/TSSV or θ and E_{coh}/N for GIM (ref 14, p 276) and δ and N_{T_g}/N for Synthia (ref 12, p 148)). The three estimates of the variance calculated here were $S_{\mathrm{EVM}}{}^2 = 191$ for EVM model, $S_{\mathrm{GIM}}{}^2 = 308$ for GIM, and $S_{\mathrm{SYN}}{}^2 = 798$ for Synthia. After the overall variance S^2 was calculated (eq 5), as well as the two values needed for the statistics test, B and C (eqs 6 and 7); B will approximate a χ^2 distribution with $(K - 1)$

$$S^2 = \frac{\sum_{j=1}^{K}(n_j - 1)S_j{}^2}{\sum_{j=1}^{K}(n_j - 1)} \qquad (5)$$

$$B = \frac{2.30259}{\mathrm{C}}[\Sigma(n_j - 3)\log S^2 - \Sigma(n_j - 1)\log S_j{}^2] \qquad (6)$$

$$C = 1 + \frac{1}{3(K+1)}\left[\Sigma\frac{1}{(n_j - 1)} - \frac{1}{\Sigma(n_j - 1)}\right] \qquad (7)$$

degrees of freedom. The null hypothesis H_0 of equal variances is rejected if B is larger than the critical value obtained from a table (Table 13, ref 30). We found $S^2 = 439.67$, $B = 9.495$, and $C = 1.013$. The critical value for the $\chi^2{}_2(0.05)$ was 7.38 (Table 5, ref 30). The null hypothesis H_0 of equal variances was therefore rejected, and the three models must be considered as not comparable.

We therefore needed to compare the models two by two, to find out which model gives the best estimates. We used Hartley's test[30] to investigate the significance of variance differences between pairs of models. Assuming the sample sizes were (approximately) equal, we have applied this test to the three models under investigation. The Hartley test relies on the calculation of $F_{\max} = S_{\max}{}^2/S_{\min}{}^2$, where $S_{\max}{}^2$ is the largest of the model variances and $S_{\min}{}^2$ is the smallest. Critical values of $F_{\max}$ were obtained from ref 30 (Table 13); if the $F_{\max}$ exceeds this critical value, the null hypothesis of equal variances should be rejected. The best model is the one with the lowest variance. Examination of the results (Table 4) shows that on a statistical point of view, the three models are relatively equivalent. Nevertheless EVM is better than Synthia in this polystyrene polymers family.

Conclusions

The EVM model and corresponding QSPR equation originally developed for aliphatic acrylate and methacrylate polymer T_g values has been successfully applied to polystyrene derivatives. The constants A, B, and C which are different on going from one polymer family to another, were recalculated from a small set of polystyrene molecules, and used to make predictions on different sets of polymers. Within a given polymer family, some effects (such as the electronic effects of the styrene ring) are constant from one structure to the other and are included in the constants. A unique feature of the EVM model is the ability to correctly quantify the effects of substituent position on the phenyl ring that have a high impact on the T_g. Thus, by taking into account the variation of molecular geometry, conformational energy, and volume surrounding the polymer backbone, the EVM model allows an accurate evaluation of the T_g variations within specific polymer families (linear and non-cross-linked polymers).

Further extensions of our approach to other polymer families are underway, and we hope to build a true universal QSPR equation based on this model. If the model can be applied in the present form to other vinyl-like polymers, it would be necessary to redefine our energy density function to be invariant with the backbone length. If the backbone length for the styrenes and the acrylates is defined by the same backbone sequence, $-(CH_2CH_2)-$, it would be different in other families like the polycarbonates or the polyamides, which often include a styrene ring in the backbone.

One major problem of such work is the large variation in experimental T_g values reported in the litterature. Deciding which values to use for the initial correlation and the evaluation set is difficult; we believe that it is necessary to develop a reliable database of values based on carefully synthesized, purified, and characterized samples. A method based on D-optimal design[33−35] and uniform design[36,37] has been developed to define how many polymers (and which one) are required for such a database.[38,39]

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