

Correlation between the Glass Transition Temperatures and Repeating Unit Structure for High Molecular Weight Polymers

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A set of five-parameter descriptors, $\Sigma MV_{\text{ter}}(R_{\text{ter}})$, L_F , ΔX_{SB} , ΣPEI , and Q_{\pm} , are developed to express the chain stiffness (or mobility) and the intermolecular forces of polymers. Investigated results show a good correlation ($R = 0.9517$, $R^2 = 0.9056$, $s = 20.86$ K) between the glass transition temperatures (T_g s) and the five parameters for a diverse set of 88 polymers. The descriptors are easy to calculate directly from the repeating unit structure and have clear physical meanings. This approach provides a new insight for Quantitative Structure–Property Relationship (QSPR) correlation of glass transition temperatures of high molecular weight polymers.

1. INTRODUCTION

Glass transition temperature, T_g , is also known as glass temperature or glass–rubber transition temperature.¹ The glass transition is perhaps the most important single parameter which one needs to know before one can decide on the application of the many noncrystalline polymers that are now available.² Even if in the design of the polymer molecule, it is also necessary to predict the glass transition temperature of the designed polymer for evaluating its application. For the available polymers, their glass transition temperatures can be determined experimentally, but they cannot be done for those being designed. Additionally, T_g is not a precise point² and is more difficult to determine experimentally than the boiling or melting point because the transition takes place over a comparatively wide range of temperatures. Therefore it is known to heavily depend on both the method and the duration of an experiment.³ For this reason, the discrepancy between reported values in the literature can be quite high.¹ Thus, we can say that a quantitative structure–property relationship (QSPR) analysis of T_g would be of large theoretical and applied utility. A good QSPR equation can help us to understand the effect of the repeating unit structure on the T_g s of polymers and guide us to design the polymer molecule. It is also used to predict the T_g s of polymers and to judge the accuracy of T_g determined experimentally for specific polymer.

There have been numerous attempts to predict T_g s for polymers by various approaches. According to the view of Katritzky et al.,¹ these methods can be roughly divided into two kinds of empirical method and theoretical estimation. Empirical methods were based on the correlation with other physical or chemical properties of polymers, such as the group additive property (GAP) theory for predicting T_g .⁴ GAP approaches can sometimes give relatively good predictive

correlations, but a serious limitation is that these methods are only applicable for polymers containing chemical structural groups previously investigated. Theoretical estimations are based on the molecular descriptors of a repeating unit in polymers instead of based on the group-containing or GAP theory to predict the T_g s, such as the topological method based on the monomer structure.⁵ Recently Camelio et al.⁶ correlated the T_g values of some 50 acrylates and methylacrylates with their “backbone flexibility” and got a relatively good correlation with R^2 of 0.83. In this approach, all necessary parameters were calculated with molecular mechanics. Katritzky et al.⁷ used the Comprehensive Descriptors for Structural and Statistical Analysis (CODESSA) program to develop a four-parameter model with R^2 of 0.928 for a set of T_g values of 22 linear, medium molecular weight polymers and copolymers. After this work, Katritzky et al.¹ further chose 88 un-cross-linked homopolymers including polyethylenes, polyacrylates, polymethylacrylates, polystyrenes, polyethers, and polyoxides as the data set. They developed a five-parameter correlation of molar glass transition temperatures (T_g/M) for the above polymers covering a relatively wide range of T_g s and representing an extensive variety of chemical groups with the CODESSA program. This important progress shows that it is possible to perform a QSPR analysis of the T_g values for a large set of polymers with diverse chemical structures only from the molecular structure descriptors. In this work we propose a new QSPR model of the T_g values with a set of simple repeating unit structure descriptors.

2. PREPARATION OF MOLECULAR DESCRIPTORS

It is impossible to calculate descriptors directly for entire molecule because all the polymers possessed high molecular weights.¹ As we know, if the molecular weight is high enough, the terminal groups hold only a very small proportion in a polymer and its effect on the T_g can be ignored. The 88 polymers in Katritzky et al.'s work¹ have relatively wide representation, and all the polymers in the set considered have molecular weights of $>50\,000$.⁸ Therefore, we also

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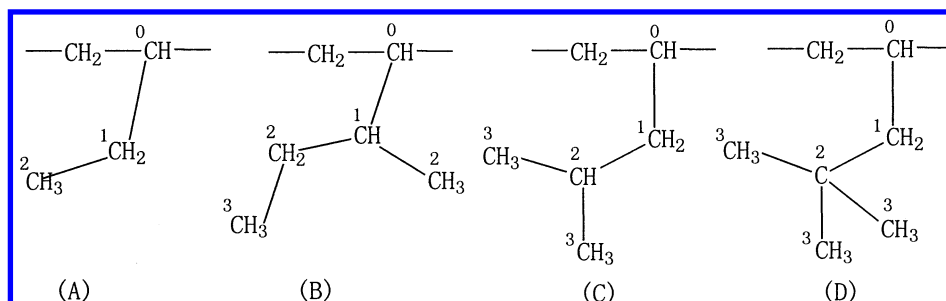


Figure 1. The repeating unit structures for some polyethylenes. The digit above the carbon atom in the side chain is a serial number far from the backbone chain of polymer.

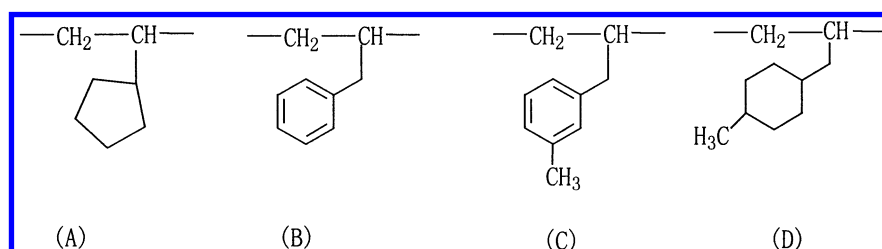


Figure 2. The repeating unit structures for some polyethylenes with the side chain containing a ring.

chose these polymers as model compounds. Here we only focus on their repeating unit structures to calculate the molecular descriptors and use these descriptors to correlate the T_g s of polymers. Generally, the major factors affecting the T_g s of polymers are the chain stiffness (or mobility) and the intermolecular forces.² The mobility of polymer chains is primarily affected by the barrier of rotation around backbone carbon-carbon bonds. This, in turn, is determined primarily by the size of the substituent group on the carbon atoms. For the polymers with structure $-(CH_2-CHR)_n-$, the larger the substituent R, the higher the glass transition temperature, and the longer the side chain, the lower the glass transition temperature. The intermolecular forces include the hydrogen bond between the backbone chains, polarities of repeating units, and substituent groups. Thus, this paper abstracts the repeating unit molecular descriptors from the chain stiffness and intermolecular forces.

To simplify the procedure of abstracting molecular descriptors, we start with the nonpolar polyethylenes. Know from the structure $-(CH_2-CHR)_n-$, when the substituent group R is alkyl (that is, its sp^3 hybrid orbital connects the backbone carbon), that the polymer chains are nonpolar. Their T_g s are determined primarily by the size and the length of the substituent groups R. The following fact was found by our careful analysis: it is the size of the terminal group (R_{ter}) in the substituent group R (or side chain) instead of the total size of the substituent group R that affects the T_g s of polyethylenes. Therefore, we take the volume of the terminal group (MV_{ter}) in the substituent group R and the free length (L_F) of side chain as parameters to correlate the T_g s of polyethylenes.

The values of MV_{ter} and L_F are calculated as below.

First, we define the nonfree rotation terminal part of the side chain as the terminal group (whose volume is expressed by the symbol MV_{ter}) and the bond count of the free rotation part of side chain as the free length (L_F). For example, for polyethylenes (A), (B), (C), and (D) of Figure 1, their lengths of the side chain are 2, 3, 3, and 3 bonds (ignore hydrogen atom), respectively. In polymer (A), the bond $^2C-^1C$ can rotate freely around the bond $^1C-^0C$ and so do the $^3C-^2C$

around the $^2C-^1C$ in the (B). But in polymer (C), if one of the two bonds $^3C-^2C$ rotates around the bond $^2C-^1C$, another bond $^3C-^2C$ also rotates around the bond $^2C-^1C$, that is, two bonds $^3C-^2C$ rotate around the bond $^2C-^1C$ simultaneously. For the polymer (D), the three bonds $^3C-^2C$ rotate around the bond $^2C-^1C$ simultaneously. Thus we say that the nonfree rotation terminal parts of the side chains or the terminal groups are $-CH_3$, $-CH_3$, $-CH(CH_3)_2$, and $-C(CH_3)_3$, respectively, for (A), (B), (C), and (D) in Figure 1. From the length discrepancy between the side chain and its terminal group, we can get the free length (L_F) of side chain, 1, 2, 1, and 1 for (A), (B), (C), and (D), respectively.

For the polyethylenes with the side chain containing ring, (A), (B), (C), and (D) of Figure 2, their terminal groups are cyclopentyl, phenyl, methyl-phenyl, and methyl-cyclohexyl, and the free lengths (L_F) of their side chain are 0, 1, 1, and 1, respectively.

Second, we calculate the volume (MV_{ter}) (unit: 10^{-24} cm^3) of terminal group (R_{ter}) in side chain R using the MSS program packages in SYBYL 6.6 of Tripos Inc. Here we calculate the molecular volume (MV) of ethane (H_3C-CH_3), $MV(\text{ethane}) = 204.0 \times 10^{-24} \text{ cm}^3$ first, take its 1/2 as the $MV_{ter}(\text{Me})$ (that is $102.0 \times 10^{-24} \text{ cm}^3$) of methyl group. Then we use eq 1 to compute the $MV_{ter}(R_{ter})$ of other terminal groups (R_{ter}), after obtaining the molecular volume $MV(H_3C-R_{ter})$ of H_3C-R_{ter} :

$$MV_{ter}(R_{ter}) = MV(H_3C-R_{ter}) - MV_{ter}(\text{Me}) \quad (1)$$

Further, we find that the polymer $-(CH_2-CR^1R^2)_n-$ with two equal side groups (that is $R^1=R^2$) has lower T_g than the polymer with two different side groups (that is $R^1 \neq R^2$). For example, the T_g (199 K) of poly(1,1-dimethylethylene) $-(CH_2-CMe_2)_n-$ is lower than T_g (228 K) of poly(ethyl-ethylene) $-(CH_2-CHEt)_n-$. We think that the backbone chain of symmetric substituted polymer rotates more freely than that of unsymmetrical substituted polymer, which results in a lower T_g for the former than the latter. Therefore, this paper uses the sum volume of two terminal groups in the two side chains to express the influence on the T_g for the

Table 1. $\Sigma MV_{\text{ter}}(R_{\text{ter}})$, L_F , and T_g Values of Some Polyethylenes

no.	name	$-(\text{CH}_2-\text{CR}^1\text{R}^2)_n-$		R_{ter}^1 MV_{ter}^a	R_{ter}^2 MV_{ter}^a	$\Sigma MV_{\text{ter}}(R_{\text{ter}})$	L_F	$T_{g,\text{exp}}/K^b$ $T_{g,\text{calc}}/K^c$
		R ¹	R ²					
1	poly(ethylene)	H	H	H 0	H 0	0	0	195 193
2	poly(ethylethylene)	H	Et	H 0	Me 102.0	102.0	1	228 237
3	poly(butylethylene)	H	Bu	H 0	Me 102.0	102.0	3	220 216
4	poly(cyclopentyl ethylene)	H	cyclopentyl	H 0	cyclopentyl 282.2	282.2	0	348 345
5	poly(cyclohexyl ethylene)	H	cyclohexyl	H 0	cyclohexyl 310.5	310.5	0	363 360
6	poly(propylene)	H	Me	H 0	Me 102.2	102.0	0	233 248
7	poly(pentene)	H	Pr	H 0	Me 102.0	102.0	2	220 227
8	poly(1,1-dimethylethylene)	Me	Me	Me 102.0	Me 102.0	0	0	199 193
9	poly(heptene)	H	-(CH ₂) ₄ Me	H 0	Me 102.0	102.0	4	220 206
10	poly(3-methyl-1-butene)	H	i-Pr	H 0	i-Pr 211.3	211.3	0	323 306
11	poly(5-methyl-1-hexene)	H	-(CH ₂) ₂ CHMe ₂	H 0	i-Pr 211.3	211.3	2	259 285
12	poly(4-methyl-1-pentene)	H	i-Bu	H 0	i-Pr 211.3	211.3	1	302 296
13	poly(3-cyclopentyl-1-propene)	H	-CH ₂ -cyclopentyl	H 0	cyclopentyl 282.2	282.2	1	333 334
14	poly(3-phenyl-1-propene)	H	-CH ₂ -phenyl	H 0	phenyl 275.2	275.2	1	333 330
15	poly(3-cyclohexyl-1-propene)	H	-CH ₂ -cyclohexyl	H 0	cyclohexyl 310.5	310.5	1	348 349

^a Unit: 10⁻²⁴ cm³. ^b Taken from ref 1. ^c Calculated by eq 4.

unsymmetrical substituted polymer and the margin volume of two terminal groups in the two side chains to express the influence on the T_g for the symmetric substituted polymer. That is for the unsymmetrical substituted polymer

$$\Sigma MV_{\text{ter}}(R_{\text{ter}}) = MV_{\text{ter}}(R_{\text{ter}}^1) + MV_{\text{ter}}(R_{\text{ter}}^2) \quad (2)$$

and for the symmetric substituted polymer

$$\Sigma MV_{\text{ter}}(R_{\text{ter}}) = MV_{\text{ter}}(R_{\text{ter}}^1) - MV_{\text{ter}}(R_{\text{ter}}^2) = 0 \quad (3)$$

The values of $\Sigma MV_{\text{ter}}(R_{\text{ter}})$ and L_F for some polyethylenes are listed in Table 1.

Correlating the T_g s to the parameters $\Sigma MV_{\text{ter}}(R_{\text{ter}})$ and L_F for polyethylenes in Table 1, we get the following regression analysis equation:

$$T_g(K) = 192.62(\pm 6.85) + 0.53831(\pm 0.0294)\Sigma MV_{\text{ter}}(R_{\text{ter}}) - 10.459(\pm 2.587)L_F \quad (4)$$

$$R = 0.9845, R^2 = 0.9693, s = 11.72, F = 189.20, n = 15$$

Equation 4 and Table 1 show that the T_g s of polyethylenes can be estimated well by the volume $\Sigma MV_{\text{ter}}(R_{\text{ter}})$ of terminal group in side chain R and the free length (L_F) of side chain. The term of $\Sigma MV_{\text{ter}}(R_{\text{ter}})$ heightens the T_g of polymer, and the L_F drops the T_g of polymer. So we can take the parameters, $\Sigma MV_{\text{ter}}(R_{\text{ter}})$ and L_F as repeating unit molecular

descriptors for quantitative structure–property relationship (QSPR) correlation of glass transition temperatures of polymers.

In the case of the repeating unit having polarity, the factors affecting the T_g s of polymers are the chain stiffness (or mobility) and the intermolecular forces. Only two parameters $\Sigma MV_{\text{ter}}(R_{\text{ter}})$ and L_F are not enough to quantify the T_g s of polymers (for the entire T_g s data set of 88 polymers,¹ the correlation between T_g s and the two parameters $\Sigma MV_{\text{ter}}(R_{\text{ter}})$ and L_F is $R = 0.8090$, $s = 39.20$), and the intermolecular forces must be accounted as well. Taking polymer $-(\text{CH}_2-\text{CYZ})_n-$, for example, the polarity of repeating unit $-\text{CH}_2-\text{CYZ}-$ results mainly from the following factors: (a) electronegativity discrepancies (i) between Y and Z and (ii) between CH₂ and CYZ and (b) the polarizability effects of side groups Y and Z. Additionally, if there is an OH or NH group in side groups Y and Z, the hydrogen bond will be formed between the main chains of polymer. When the $-\text{C}\equiv\text{N}$ group exists in the side groups, there is also an additional electrostatic attraction between the main chains of polymer. Both hydrogen bond and electrostatic attraction will enhance the intermolecular force between the backbones of polymer $-(\text{CH}_2-\text{CYZ})_n-$. Here, we develop three parameters, the substituted backbone electronegativity discrepancy ΔX_{SB} , the polarizability effect ΣPEI of side group, and the hydrogen bond (or electrostatic attract) Q_{\pm} between the main chains to describe the intermolecular forces of the polymer.

The ΔX_{SB} of repeating unit $-\text{CH}_2-\text{CYZ}-$ is calculated by the following steps: (a) the group electronegativities X_Y

Table 2. Δ PEI Values of the i th Essential Unit in Alkyl Substituent¹⁰

N_i	Δ PEI	N_i	Δ PEI	N_i	Δ PEI	N_i	Δ PEI
1	1.000 000	6	0.009 052	11	0.002 375	16	0.001 073
2	0.140 526	7	0.006 388	12	0.001 972	17	0.000 945
3	0.048 132	8	0.004 748	13	0.001 628	18	0.000 838
4	0.023 503	9	0.003 666	14	0.001 421	19	0.000 749
5	0.013 800	10	0.002 196	15	0.001 229	20	0.000 673

and X_Z are computed by Bratsch's electronegativity equalization method⁹ (harmonic mean, with Pauling electronegativity units) for side groups Y and Z, respectively. And then their absolute electronegativity discrepancy ($\Delta X_{YZ} = |X_Y - X_Z|$) is obtained. (b) The group electronegativities X_{CH_2} and X_{CYZ} are computed with the same method for groups CH_2 and CYZ , respectively, and then their absolute discrepancy ($\Delta X_{RU} = |X_{CH_2} - X_{CYZ}|$) is obtained. (c) Finally, the substituted backbone electronegativity discrepancy ΔX_{SB} is calculated by eq 5:

$$\Delta X_{SB} = [\Delta X_{YZ} \Delta X_{RU}]^{(1/2)} \quad (5)$$

According to our previous work,¹⁰ the stabilizing energy caused by polarizability effect for a substituent R interacting with a point charge q is expressed as

$$E_{(R)} = \frac{-q^2}{2Dl^4} \sum \frac{\alpha_i}{\left[N_i \frac{1 + \cos\theta}{1 - \cos\theta} - \frac{2\cos\theta(1 - \cos^{N_i}\theta)}{(1 - \cos\theta)^2} \right]^2} \quad (6)$$

where α_i is the polarizability of the i th essential unit in the substituent R, D is the effective dielectric constant, l is the length of C—C bond, N_i is the carbon atom number from the point charge (q) to the i th essential unit, and θ is the supplementary angle of bond angle $\angle CCC$ (that is, $\theta = 180^\circ - 109.5^\circ = 70.5^\circ$ for the sp^3 hybridization).

For the alkyl substituent, α_i is approximately equal to a constant and eq 6 was defined as¹⁰

$$E_{(R)} = K \sum \frac{1}{\left[N_i \frac{1 + \cos\theta}{1 - \cos\theta} - \frac{2\cos\theta(1 - \cos^{N_i}\theta)}{(1 - \cos\theta)^2} \right]^2} = K \sum \Delta PEI = K(PEI) \quad (7)$$

Here $K = -q^2\alpha_i/(2Dl^4)$. PEI is called the Polarizability Effect Index (PEI).¹⁰ The PEI value of an alkyl substituent is the term of $\sum(1/[]^2)$ in eq 7. $\Delta PEI = 1/[]^2$ is the PEI increments of the i th essential unit. Some ΔPEI values are relisted in Table 2.

When the substituent group R_{YZ} contains other atoms besides carbon and hydrogen, α_i is no longer a constant and eq 7 will not work well. It needs to be modified. Here, we use eq 8 evaluating the stabilizing energy caused by the polarizability effect for a substituent R_{YZ} :

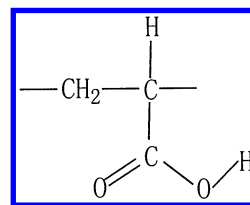
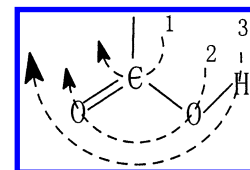
$$E_{(R_{YZ})} = K_m \sum \alpha_i(\Delta PEI) \quad (8)$$

where $K_m = -q^2/(2Dl^4)$. α_i is the polarizability (unit: 10^{-24} cm³)¹¹ of the i th atom in substituent R_{YZ} . Some atomic α_i values are listed in Table 3.

Table 3. α_i Values and the Pauling Electronegativities (X_P) of Some Atoms

atom	H	C	N	O	F	Cl	Br	I	S	P
α_i^a	0.6668	1.76	1.10	0.802	0.557	2.18	3.05	5.34	2.90	3.63
X_P^b	2.20	2.55	3.04	3.44	3.98	3.16	2.96	2.66	2.58	2.19

^a Taken from ref 11, unit: 10^{-24} cm³. ^b Taken from ref 12.

**Figure 3.** The repeating unit of poly(acrylic acid).**Figure 4.** The tiers of atoms in the side group CO_2H (The digit above the dotted line indicates a atom serial number far from the backbone chain of polymer).

Because K_m is a constant, this work only calculates the term $\sum \alpha_i(\Delta PEI)$ of eq 8. Then take the sum of $\sum \alpha_i(\Delta PEI)$ for all side groups of a repeating unit in a polymer as the polarizability effect $\sum PEI$, that is

$$\sum PEI = \sum (\sum \alpha_i(\Delta PEI)) \quad (9)$$

If the side group is only a hydrogen, its $\sum \alpha_i(\Delta PEI)$ is ignored.

The calculation of hydrogen bond or electrostatic attract descriptor Q_{\pm} , take XH ($X = O$ or N) for example, is divided into two steps. At first, compute the group electronegativity (X_{XH}) of XH and part charges on X (q_X) and H (q_H), respectively, with Bratsch's electronegativity equalization method.⁹ Then calculate the Q_{\pm} with eq 10:

$$Q_{\pm} = q_X q_H \quad (10)$$

Here we take poly(acrylic acid) (Figure 3 shows its repeating unit) as the calculating example. In accordance with presume, the side group Y is CO_2H and Z is H. The Pauling electronegativities (X_P) of some atoms are listed in Table 3.

The electronegativity of the side group CO_2H is $X_Y = X_{CO_2H} = 4/(1/2.55 + 2/3.44 + 1/2.20) = 2.8009$. The electronegativity of hydrogen $X_Z = X_H = 2.20$. Then the $\Delta X_{YZ} = |X_{CO_2H} - X_H| = |2.8009 - 2.20| = 0.6009$.

The electronegativity of CYZ is $X_{CYZ} = 3/(1/2.55 + 1/2.20 + 1/2.8009) = 2.4923$. The electronegativity of CH_2 is $X_{CH_2} = 3/(1/2.55 + 2/2.20) = 2.3055$. Then the $\Delta X_{RU} = |X_{CH_2} - X_{CYZ}| = |2.3055 - 2.4923| = 0.1868$.

Thus, according to eq 5, we obtain $\Delta X_{SB} = [0.6009 \times 0.1868]^{(1/2)} = 0.3350$.

The $\sum \alpha_i(\Delta PEI)$ of side group CO_2H is calculated as follows: First, set up the tier for each atom as shown in Figure 4. So the C, O, and H atoms are in the first, second, and third tier, in other words, their N_i (in eq 7 and Table 2) are 1, 2, and 3, respectively. Second, combine Tables 2 and 3 to calculate its $\sum \alpha_i(\Delta PEI) = 1.76 \times 1 + 2(0.802 \times 0.1405)$

Table 4. Parameters $\Sigma MV_{\text{ter}}(R_{\text{ter}})$, L_F , ΔX_{SB} , ΣPEI , Q_{\pm} , and T_g s for Some Polymers

no. ^a	name	$\Sigma MV_{\text{ter}}(R_{\text{ter}})$	L_F	ΔX_{SB}	ΔPEI	Q_{\pm}	$T_g(K)_{\text{exp}}^b$	$T_g(K)_{\text{calc}}^c$ $T_g(K)_{\text{LOO}}^c$	$\Delta 1^d$ $\Delta 2^d$
1	poly(ethylene)	0.0	0	0.0000	0.0000	0	195	204 205	−9 −10
2	poly(ethylethylene)	102.0	1	0.0000	2.2909	0	228	256 256	−28 −28
3	poly(butylethylene)	102.0	3	0.0000	2.4438	0	220	239 240	−19 −20
4	poly(cyclopentylethylene)	282.2	0	0.0000	2.7085	0	348	339 338	9 10
5	poly(cyclohexylethylene)	310.5	0	0.0000	2.7683	0	363	350 349	13 14
6	poly(acrylic acid)	139.2	0	0.3350	2.0174	−0.0483	379	380 380	−1 −1
7	poly(methyl acrylate)	102.0	2	0.2096	2.1170	0	281	274 274	7 7
8	poly(ethyl acrylate)	102.0	3	0.1634	2.1703	0	251	259 259	−8 −8
9	poly(<i>sec</i> -butyl acrylate)	102.0	3	0.1245	2.2567	0	253	255 255	−2 −2
10	poly(vinyl alcohol)	77.9	0	0.2737	0.8957	−0.0483	358	337 331	21 27
11	poly(vinyl chloride)	93.2	0	0.5126	2.1800	0	348	331 330	17 18
12	poly(acrylonitrile)	106.0	0	0.3209	1.9146	−0.0692 ^f	378	388 398	−10 −20
13	poly(vinyl acetate)	166.4	1	0.2096	1.2195	0	301	300 300	1 1
14	poly(styrene)	275.2	0	0.1050	2.5699	0	373	349 348	24 25
15	poly(2-chrolostyrene)	307.8	0	0.1466	2.6427	0	392	368 367	24 25
16	poly(3-chrolostyrene)	315.7	0	0.1466	2.6055	0	363	371 371	−8 −8
17	poly(4-chrolostyrene)	309.0	0	0.1466	2.5908	0	389	368 367	21 22
18	poly(2-methylstyrene)	323.3	0	0.0958	2.6695	0	409	368 365	41 44
19	poly(3-methylstyrene)	327.1	0	0.0958	2.6232	0	374	369 368	5 6
20	poly(4-methylstyrene)	319.6	0	0.0958	2.6030	0	374	366 365	8 9
21	poly(4-fluorostyrene)	290.4	0	0.1669	2.5684	0	379	364 363	15 16
22	poly(propylene)	102.0	0	0.0000	2.0411	0	233	262 263	−29 −30
23	poly(1-pentene)	102.0	2	0.0000	2.3905	0	220	247 248	−27 −28
24	poly(ethoxyethylene)	102.0	2	0.1117	1.2451	0	254	253 252	1 2
25	poly(<i>tert</i> -butyl acrylate)	258.1	2	0.1245	2.2769	0	315	325 325	−10 −10
26	poly(<i>n</i> -butyl acrylate)	102.0	5	0.1245	2.2261	0	219	236 237	−17 −18
27	poly(vinyl hexyl ether)	102.0	6	0.0821	1.3705	0	209	214 214	−5 −5
28	poly(1,1-dimethylethylene)	0.0	0	0.0000	4.0821	0	199	241 249	−42 −50
29	poly(1,1-dichloroethylene)	0.0	0	0.0000	4.3600	0	256	243 240	13 16
30	poly(1,1-difluoroethylene)	0.0	0	0.0000	1.1140	0	233	214 213	19 20
31	poly(<i>a</i> -methylstyrene)	377.2	0	0.0956	4.6110	0	409	406 406	3 3
32	poly(methyl methylacrylate)	211.3	2	0.2084	4.1581	0	378	335 333	43 45
33	poly(ethyl methylacrylate)	211.3	3	0.1595	4.2114	0	324	320 320	4 4
34	poly(isopropyl methylacrylate)	258.1	2	0.1336	4.2647	0	327	344 345	−17 −18
35	poly(ethyl chloroacrylate)	195.2	3	0.5175	4.3503	0	366	364 364	2 2
36	poly(2-chloroethyl methylacrylate)	195.2	4	0.2108	4.2323	0	365	312 310	53 55
37	poly(<i>tert</i> -butyl methylacrylate)	408.0	2	0.1174	4.3180	0	380	401 402	−21 −22

Table 4 (Continued)

no. ^a	name	$\sum MV_{\text{ter}}(R_{\text{ter}})$	L_F	ΔX_{SB}	ΔPEI	Q_{\pm}	$T_g(K)_{\text{exp}}^b$	$T_g(K)_{\text{calc}}^c$ $T_g(K)_{\text{LOO}}^c$	$\Delta 1^d$ $\Delta 2^d$
75	poly[<i>p</i> -(<i>n</i> -butyl)styrene]	102.0	3	0.0828	2.6546	0	279	252	27
76	poly(<i>n</i> -butyl methacrylate)	211.3	5	0.1174	4.2671	0	293	252 297	27 -4
77	poly(2-methoxyethyl methacrylate)	211.3	5	0.1648	2.2008	0	293	297 285	-4 8
78	poly(3,3,3-trifluoropropylene)	68.8	1	0.6643	1.9948	0	300	284 332	9 -32
79	poly(4-methyl-1-pentene)	211.3	1	0.0000	2.4901	0	302	336 300	-36 2
80	poly(vinyl chloroacetate)	93.2	3	0.2831	1.2551	0	304	300 264	2 40
81	poly(<i>n</i> -propyl methacrylate)	211.3	4	0.1336	4.2445	0	306	263 308	41 -2
82	poly(3-cyclopentyl-1-propene)	282.2	1	0.0000	2.5469	0	333	308 328	-2 5
83	poly(3-phenyl-1-propene)	275.2	1	0.0000	2.5267	0	333	328 325	5 8
84	poly(<i>n</i> -propyl <i>a</i> -chloroacrylate)	195.2	4	0.5210	4.3834	0	344	325 356	8 -12
85	poly(<i>sec</i> -butyl <i>a</i> -chloroacrylate)	195.2	4	0.5228	4.4367	0	347	357 357	-13 -10
86	poly(3-cyclohexyl-1-propene)	310.5	1	0.0000	2.5832	0	348	358 340	-11 8
87	poly(vinyl acetal)	310.5 ^e	1	0.1810	2.0150	0	355	339 360	9 -5
88	poly(vinyl formal)	310.5 ^e	0	0.2589	1.9154	0	378	360 378	-5 0
								378	0

^a The number is the same order as the polymers of Table 1 in ref 1. ^b Taken from ref 1. ^c $T_g(K)_{\text{calc}}$ is calculated by eq 11, $T_g(K)_{\text{LOO}}$ is predicted by the Leave-One-Out method. ^d $\Delta 1 = T_g(K)_{\text{exp}} - T_g(K)_{\text{calc}}$, $\Delta 2 = T_g(K)_{\text{exp}} - T_g(K)_{\text{LOO}}$. ^e Take cyclohexyl as its terminal group because of a backbone containing hexatomic ring. ^f Calculated by the charges q_C and q_N on group $-\text{C}\equiv\text{N}$.

Table 5. Interrelations of $\sum MV_{\text{ter}}(R_{\text{ter}})$, L_F , ΔX_{SB} , $\sum \text{PEI}$, and Q_{\pm}

	$\sum MV_{\text{ter}}(R_{\text{ter}})$	L_F	ΔX_{SB}	$\sum \text{PEI}$	Q_{\pm}
$\sum MV_{\text{ter}}(R_{\text{ter}})$	1				
L_F	-0.08787	1			
ΔX_{SB}	-0.04591	-0.01058	1		
$\sum \text{PEI}$	0.53043	0.19117	0.12952	1	
Q_{\pm}	0.07982	0.13895	-0.13951	0.07320	1

+ 0.6668 × 0.0481 = 2.0174. For the repeating unit of poly(acrylic acid), its polarizability effect $\sum \text{PEI} = 2.0174$ (from eq 9) because of no other side groups but for group CO_2H .

In the side group CO_2H , there is an O–H bond. It will result in a hydrogen bond between the backbone chains of the poly(acrylic acid). Based on the Bratsch's electronegativity equalization method,⁹ the electronegativity of OH is $2/(1/2.20 + 1/3.44) = 2.6837$, $q_O = (2.6837 - 3.44)/3.44 = -0.2199$, $q_H = (2.6837 - 2.20)/2.20 = +0.2199$. Thus its Q_{\pm} is obtained by eq 10: $Q_{\pm} = q_O q_H = (-0.2199) \cdot (+0.2199) = -0.0483$.

By now, we have introduced all five parameters, $\sum MV_{\text{ter}}(R_{\text{ter}})$, L_F , ΔX_{SB} , $\sum \text{PEI}$, and Q_{\pm} . These parameters of some polymers are listed in Table 4, and their interrelations are also studied (see Table 5). Results of Table 5 show that the five parameters are independent of each other. Therefore this paper employs the above parameters as the repeating unit descriptors for high molecular weight polymers.

3. RESULTS AND DISCUSSION

Taking the same T_g s data of 88 polymers as Katritzky et al.¹ we carry out the correlation between the T_g s and the five parameters $\sum MV_{\text{ter}}(R_{\text{ter}})$, L_F , ΔX_{SB} , $\sum \text{PEI}$, and Q_{\pm} and get

Table 6. The *t*-Test of Parameters $\sum MV_{\text{ter}}(R_{\text{ter}})$, L_F , ΔX_{SB} , $\sum \text{PEI}$, and Q_{\pm} in Eq 11

descriptor	intercept	$\sum MV_{\text{ter}}(R_{\text{ter}})$	L_F	ΔX_{SB}	$\sum \text{PEI}$	Q_{\pm}
<i>t</i> test	36.55	15.38	-9.91	11.26	4.12	-5.41

the following regression equation:

$$T_g(K) = 203.97(\pm 5.58) + 0.39(\pm 0.03) \sum MV_{\text{ter}}(R_{\text{ter}}) - 8.93(\pm 0.90) L_F + 138.82(\pm 12.33) \Delta X_{\text{SB}} + 9.01(\pm 2.18) \sum \text{PEI} - 1174.41(\pm 216.89) Q_{\pm} \quad (11)$$

$$R = 0.9517, R^2 = 0.9056, s = 20.86, F = 157.41, n = 88$$

Equation 11 shows a good correlation between the T_g s and the parameters, $\sum MV_{\text{ter}}(R_{\text{ter}})$, L_F , ΔX_{SB} , $\sum \text{PEI}$, and Q_{\pm} . The standard deviation is 20.86 K, and the absolute average error between the experimental and calculated T_g values is only 15.30 K for the 88 polymers in Table 4. Figure 4(a) shows the plot of calculated T_g s versus experimental T_g s. Katritzky et al.¹ even developed a five-parameter correlation equation of molar glass transition temperature (T_g/M) with CODESSA program for the same data set of 88 polymers and got a good correlation equation. The standard error 32.9 K was estimated for T_g from predicted T_g/M values. This paper obtained a smaller standard deviation than that obtained by Katritzky et al.¹ Additionally, the *t*-test (see Table 6) indicates that the five parameters all are significant descriptors in the QSPR model (eq 11).

To test the reliability of eq 11, we further finished the multiple linear regressions and predicted the T_g s values with

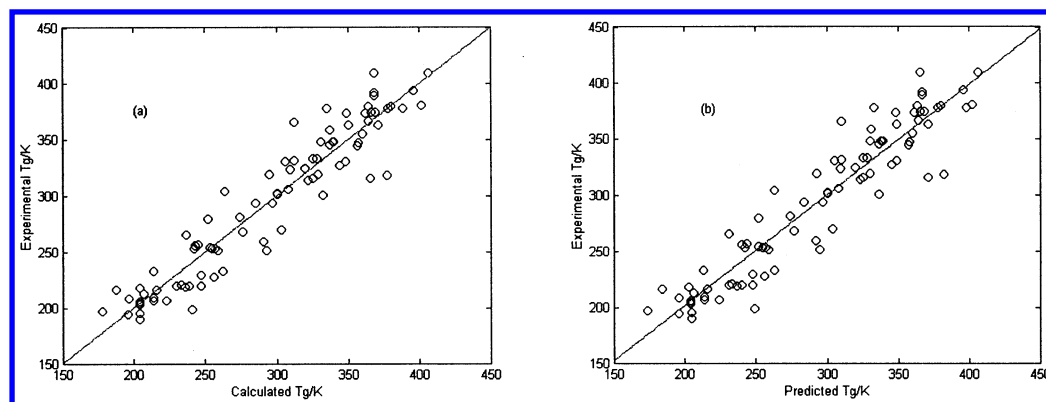


Figure 5. (a) Plot of experimental $T_g(K)_{\text{exp}}$ versus $T_g(K)_{\text{calc}}$ calculated by eq 11. (b) Plot of experimental $T_g(K)_{\text{exp}}$ versus $T_g(K)_{\text{LOO}}$ predicted by the Leave-One-Out method.

the Leave-One-Out (LOO) method for the same 88 T_g s data set in Table 4, using the MSS program packages in SYBYL 6.6 of Tripos Inc. The predicted $T_g(K)_{\text{LOO}}$ values are very close to the calculated $T_g(K)_{\text{calc}}$ values (see Table 4). As compared with the $T_g(K)_{\text{calc}}$ calculated by eq 11, the plot of $T_g(K)_{\text{exp}}$ versus $T_g(K)_{\text{LOO}}$ is also shown in Figure 5(b). The values of $T_g(K)_{\text{calc}}$ and $T_g(K)_{\text{LOO}}$ in Table 4 and the plots of Figure 5 confirm the eq 11 reliable.

Seen from eq 11, the $\sum MV_{\text{ter}}(R_{\text{ter}})$ increases the T_g s of polymers, which can be understood that the volume of the terminal group increase will result in an increase of the rotational barrier of backbone chain. In the solid state, one polymer chain is tightly surrounded by other polymer chains, the terminal group of the side chain is closer to the neighbor polymer chains, so the terminal group with a larger volume will resist more heavily the free-rotation of its backbone chain. This explanation is somewhat different from Mark's² explanation, who considered "for flexible alkyl side chains, it is only the first unit of side chain, which is attached rigidly to the main chain, that increases the glass transition temperature". Seen from Table 1, the nos. 2, 12, 13, and 15 of polymers all have the same first unit CH_2 of the side chain, but they have different T_g s, 228, 302, 333, and 348(K). While their terminal group volumes increase in the order of $\text{Me} < i\text{-Bu} < \text{cyclopentyl} < \text{cyclohexyl}$, which corresponds to their T_g s change. For the free length of side chain L_F , it drops the T_g s of polymers. As pointed out by Mark² the effect of a flexible alkyl side chain in a main chain on the T_g of polymer is like the addition of low molecular weight materials to the polymers, which depresses the glass transition temperature. Of course, it should be more reasonable for the length of the side chain replaced by the free length. For example, nos. 20 and 83 in Table 4 have the same length of side chain, $-\text{CH}_2\text{Ph}$ and $p\text{-PhMe}$, but their T_g s are 333 and 374(K), respectively. The reason for this phenomenon can be mainly due to the different free lengths 1 and 0 for $-\text{CH}_2\text{Ph}$ and $p\text{-PhMe}$. Thus the stiffness of the polymer chain can be described by the $\sum MV_{\text{ter}}(R_{\text{ter}})$ and L_F together. The parameters, ΔX_{SB} , $\sum \text{PEI}$, and Q_{\pm} all increase the T_g s of polymers. The larger ΔX_{SB} indicates a larger polarity of the repeating unit, the larger $\sum \text{PEI}$ value represents a larger charge-induced dipole of the side group, and the more negative Q_{\pm} stands for a stronger hydrogen bond or

electrostatic attract between the main chains of a polymer. The parameters, ΔX_{SB} , $\sum \text{PEI}$, and Q_{\pm} together express the intermolecular forces of polymers.

The descriptors developed by this paper are easy to calculate directly from the repeating unit structure and have clear physical meanings. This approach provides a new insight for Quantitative Structure–Property Relationship (QSPR) correlation of glass transition temperatures of high molecular weight polymers.

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