

Method for Separating Intramolecular and Intermolecular Interactions which Influence Polymer Glass Temperatures

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Synopsis

It is shown that the glass temperature (T_g) for homopolymers of the type $-\text{CH}_2-\text{CXY}-$ can be expressed by a simple additive equation involving two terms: (1) a parameter E which is directly related to the molar cohesion energy and (2) a parameter E_s^* which is a measure of restricted rotation about valence bonds. E_s^* , at least for a large number of polymers, is related to the Mark-Houwink K_g value (as measured in θ solvents at T_g) via anti-log $E_s^* \propto 1/K_g^{2/3}$. It is also shown that for homologous series [e.g., poly(*n*-alkyl methacrylates)], there is a constant relationship between E and anti-log E_s^* . The T_g values for copolymers may be estimated by a simple weighted (via mole fraction) summation of the E and E_s^* values of the components. When used in this form, a linear variation between T_g and composition is assumed, which may not be strictly correct but still yields useful approximations.

Introduction

Numerous expressions for predicting T_g of homopolymers and copolymers as well as for relating T_g to structure have appeared in the literature.¹⁻⁷ Much of this work was summarized a few years ago by Boyer.¹ Some of the better-known expressions include eqs. (1) and (2)^{2,3} for symmetrical and asymmetrical polymers, respectively,

$$T_m = 2T_g \quad (1)$$

$$T_m = 1.4T_g \quad (2)$$

where T_m is melting point,

$$T_g = \{ [a\Delta H' + k_1(\text{CED})] / (\Delta S_0 - k_2\epsilon/kT) \} + b \quad (3)$$

where a , ΔH , k_1 , k_2 , b , and ΔS_0 are characteristic constants for a system; ϵ is a complex function^{1,4} describing the energy difference between *trans* and *gauche* conformations; CED is cohesive energy density; k is the Boltzmann constant; and T is temperature. Also

$$T_g = v_1T_{g1} + v_2T_{g2} + \dots + v_nT_{gn} \quad (4)$$

where v_1 and v_2 are volume fractions of components 1 and 2 with T_{g1} and T_{g2} , respectively, and

$$\frac{1}{T_g} = \frac{w_1}{T_{g_1}} + \frac{w_2}{T_{g_2}} + \dots + \frac{w_n}{T_{g_n}} \quad (5)$$

where w_1 and w_2 are weight fractions of components 1 and 2 with T_{g_1} and T_{g_2} , respectively.⁶

More complicated expressions have been given by Wood.⁷

In this paper, a method is presented for expressing T_g as a simple additive function containing contributions from intra- and intermolecular interactions which are determined by and emphasize polymer structures.

Homopolymers

It is known in organic chemistry⁸ that the overall effect of structure on the free energy of activation (or the logarithm of a rate constant) may be approximated by a linear combination of the separate contributions of polar, resonance, and steric factors. For example, a series of organic reactions which have the same types of transition states which are influenced by both polar and steric factors may often be correlated by an expression such as

$$\log (k/k_0) = \rho\sigma + S \quad (6)$$

where k_0 is the rate constant for a reference reactant; k is the rate constant for the reaction in question; ρ is a constant for the given reaction series (the sensitivity or response of the series to changes in σ); σ is the polar substituent constant; and S is the steric substituent constant.

While the changes in polymer molecules which occur at T_g are not those associated with the formation of an activated complex or transition state, they are of sufficient magnitude to suggest that there does occur an abrupt change in the free energy of the system. Furthermore, the chemical factors which influence T_g (the temperature or energy necessary to cause these changes) should be common to many polymers. In this work, it was assumed that two factors especially would be of importance: (1) sufficient energy would be needed to disrupt—or at least greatly diminish—intermolecular interactions, and (2) beyond this, there would be needed extra energy to allow for rotation about single bonds, i.e., to allow segmental motion. The assumption of the motion of segments—via rotation about valence bonds follows from the fact that T_g versus molecular weight is an asymptotic function. If whole molecules had to move freely, there would be a much stronger dependence of T_g on molecular weight. The preceding constitutes a statement of the major assumptions used as well as a description of the model upon which they were based.

Hence, on the basis of the considerations above and by analogy with eq. (6), one may write

$$\log T_g = b \sum_i N_i E_i + \sum_i N_i E_{s_i}^* + C \quad (7)$$

where T_g is the glass temperature (absolute) for the polymer or copolymer in question; b is a constant; N_i is the mole fraction of constituent i ; E_i

is the intermolecular interaction parameter for constituent i ; $E_{s_i}^*$ the intramolecular interaction parameter (steric factor) for constituent i ; and C is a constant (actually $\log T_g$).

For E , the molar cohesive energy was chosen, mainly because (for model systems at least) it is defined⁹ as the energy necessary to disrupt intermolecular contacts and it is easily computable with reasonable accuracy.⁹ The value of E_s^* was calculated from known values of T_g and E for homopolymers via eq. (7). The value of C was taken as 2.394, which is the logarithm of 248°K. (the glass temperature of polyethylene¹⁰). A value of 1×10^{-5} for b was found best to fit the data. Table I lists E and E_s^* values for a number of monomer-polymer systems.

Copolymers

Since it is assumed [eq. (7)] that E and E_s^* for a copolymer will vary linearly with changes in composition, their calculation is relatively simple

TABLE I
 E and E_s^* Values of Various Systems

Monomer	T_g , °C. ^a	E	E_s^*
Ethylene	-25 ^b	2,157	-0.02157
Propylene	-15	3,070	-0.0127
Methyl vinyl ether	-15	3,562	-0.0176
<i>tert</i> -Butyl vinyl ether	88	5,384	0.1102
Vinyl chloride	87	4,104	0.1229
Vinylidene chloride	-17	3,060	-0.0166
Acrylonitrile	96	7,245	0.1015
Methacrylonitrile	120	7,424	0.1258
Vinyl acetate	29	6,428	0.0217
Methyl acrylate	3	6,900	-0.022
Ethyl acrylate	-22	7,930	-0.063
<i>o</i> -Methylstyrene	120	9,043	0.1096
α -Methylstyrene	185	9,057	0.1714
α -Vinyl naphthalene	162	12,289	0.1217
Styrene	101	8,150	0.0965
<i>p</i> -Methylstyrene	101	9,360	0.0860
<i>p-n</i> -Butylstyrene	6	12,820	-0.0762
<i>p-n</i> -Hexylstyrene	-27	16,300	-0.166
<i>p-n</i> -Octylstyrene	-45	17,400	-0.210
<i>p-n</i> -Nonylstyrene	-53	18,700	-0.239
<i>p-n</i> -Decylstyrene	-65	20,200	-0.278
Methyl methacrylate	105	7,206	0.1119
Ethyl methacrylate	65	8,020	0.055
<i>n</i> -Propyl methacrylate	35	9,450	-0.0005
<i>n</i> -Butyl methacrylate	21	10,490	-0.0309
<i>n</i> -Hexyl methacrylate	-5	12,400	-0.090
<i>n</i> -Octyl methacrylate	-20	15,580	-0.147
<i>n</i> -Decyl methacrylate	-65	16,880	-0.245

^a Most T_g data from Nielsen.¹¹

^b Data of Magill et al.¹⁰

and rapid. Thus, for a two-component polymer where N_1 is the mole fraction of component 1, $E_2 < E_1$ and $E_{s_2}^* < E_{s_1}^*$, one obtains

$$E = (E_1 - E_2)N_1 + E_2 \quad (8)$$

$$E_s^* = (E_{s_1}^* - E_{s_2}^*)N_1 + E_{s_2}^* \quad (9)$$

The use of eq. (7) to calculate T_g for some copolymers is illustrated in Table II along with literature values and those computed by eq. (5) for comparison. When the variation in measured T_g values is considered, especially as a function of the method of measurement (the literature values¹² in Table II were obtained from refractive index measurements, for example, whereas the T_g values used to obtain E and E_s^* were mainly based on volume expansions), the agreement among the methods is quite satisfactory.

TABLE II
Calculated and Experimental T_g Values for Some Copolymers

M_1	M_1	W_1	M_2	M_2	W_2	$T_g, ^\circ\text{C.}$		
						Calc. from eq. (7)	Lit. ^a	Calc. from eq. (5)
Styrene	0.156	0.18	Methyl acrylate	0.844	0.82	12	22	17
Styrene	0.45	0.5	Methyl acrylate	0.55	0.5	43	49	45
Styrene	0.652	0.7	Methyl acrylate	0.348	0.3	63	65	75
Styrene	0.49	0.5	Ethyl acrylate	0.51	0.5	31	30	25
Styrene	0.743	0.75	Ethyl acrylate	0.257	0.25	63	57	49
Vinyl chloride	0.258	0.2	Vinyl acetate	0.242	0.8	43	36	39
Vinyl chloride	0.578	0.5	Vinyl acetate	0.422	0.5	62	48	57
Vinyl chloride	0.848	0.8	Vinyl acetate	0.152	0.2	77	62	74
Methyl meth- acrylate	0.222	0.25	Methyl acrylate	0.778	0.75	24	37	14
Methyl meth- acrylate	0.461	0.5	Methyl acrylate	0.539	0.5	46	71	47
Methyl meth- acrylate	0.718	0.75	Methyl acrylate	0.282	0.25	78	88	73
Acrylonitrile	0.289	0.2	Methyl acrylate	0.711	0.8	27	25	9
Acrylonitrile	0.619	0.5	Methyl acrylate	0.381	0.5	57	56	43

^a Data of Illers.¹²

Discussion

In principle, a relationship such as eq. (7) is very flexible, in that one might arbitrarily weight one parameter more heavily than the other in order to magnify its effect and adjust the other accordingly. In this respect, it is of some value to point out the origin of the 1×10^{-5} value used for the constant b . This constant was derived from the polyethylene data where, since C was taken as $\log T_{g_0}$ or $\log T_g$ for polyethylene, E and E_s^* values had to cancel one another. Since C was then fixed at 2.394, it was

necessary to choose b of such magnitude that the $\log T_g$ term would respond properly to changes in E and E_s^* so that C would ordinarily (for the polymers considered here) be the largest component of the sum on the right-hand side of eq. (7). The quantity $b = 1 \times 10^{-5}$ fits these requirements very well.

The parameter E [eq. (7), Table I] is relatively simple to visualize and its computation takes into account both van der Waals and polar interactions. On the other hand, while E_s^* is also easy to obtain, it must in fact represent an average value for a large number of complex interactions (if it is to be considered a real measure of anything at all). In principle, it was assumed that E_s^* would be a measure of short-range interactions which restrict rotation of the main polymer chain. It was further assumed that T_g would be related to E_s^* , as, other things being equal, a higher energy (temperature) would be necessary to overcome rotational barriers for polymers containing components of high E_s^* than those with low E_s^* . This concept then assumes that E_s^* is a relative measure of the maximum in a rotational energy barrier diagram. This seems to be at least qualitatively correct. Thus, the E_s^* values in Table I (especially the top half) generally increase in the direction that one would predict for increasing or decreasing ease of rotation as a function of the nature of X and Y in $-\text{CH}_2-\text{CXY}-$.

In an attempt to establish that E_s^* was related to (or a measure of) restricted rotation as a function of structure, the relationships¹³ of eqs. (10) and (11) were considered for θ solvents at T_θ :

$$[\eta]_\theta = \Phi(\bar{h}^2)^{3/2}M \quad (10)$$

$$[\eta]_\theta = K_\theta M^{1/2} \quad (11)$$

where $[\eta]_\theta$ is the intrinsic viscosity; Φ is a universal constant for polymers; (\bar{h}^2) is the root-mean-square end-to-end distance of the chain; K_θ is a constant; and M is molecular weight.

Elimination of $[\eta]_\theta$ from eqs. (10) and (11) gives

$$K_\theta M^{1/2}/\Phi = (\bar{h}^2)^{3/2} \quad (12)$$

which can be rearranged to

$$(\bar{h}^2) = K_\theta^{2/3}(M/\theta^{2/3}) \quad (13)$$

For polymers of sufficiently high molecular weight, T_g is only slightly sensitive to molecular weight. Therefore, for all of the polymers listed in Table I, it is possible to choose the same value of M for each of them so that T_g is virtually not a function of the degree of polymerization. With this assumption, eq. (13) predicts that (\bar{h}^2) will be proportional to $K_\theta^{2/3}$. Since (\bar{h}^2) is strongly influenced by restricted rotation, i.e., (\bar{h}^2) increases as restrictions to rotation in the polymer backbone increase, a relationship between $K_\theta^{2/3}$ and E_s^* would be anticipated, since they both are measures of the same type of interaction. In Table III, it is shown that $K_\theta^{2/3}$ and E_s^* vary in the same direction.

TABLE III
 K_θ Values for Some Homopolymers^a

Polymer	$K \times 10^4$	$(K \times 10^4)^{2/3}$	$(10/K \times 10^4)^{2/3}$	E_s^*
Poly(methyl methacrylate)	5.92	3.27	3.06	0.1119
Poly(ethyl methacrylate)	4.75	2.82	3.55	0.055
Poly(butyl methacrylate)	3.73	2.41	4.15	-0.0309
Poly(hexyl methacrylate)	3.54 ^b	2.32	4.32	-0.090
Poly(octyl methacrylate)	3.35	2.04	4.9	-0.147
Poly(α -methylstyrene)	7.68	3.90	2.57	0.1714
Polystyrene	8.44	4.14	2.42	0.0965
Poly(vinyl acetate)	8.5	4.16	2.40	0.0217
Poly(methyl acrylate)	5.4	3.1	3.23	-0.022
Poly(ethyl acrylate)	4.75 ^c	2.82	3.55	-0.063
Poly(vinyl chloride)	15.6	6.25	1.6	0.1229

^a Values from J. Brandrup and E. H. Immergut.¹⁴

^b Extrapolated value obtained by plotting K_θ vs. alkyl chain length. This plot was linear for this series for the region butyl through octyl.

^c Estimated from data taken in methyl alcohol at 30°C. These are not θ conditions (α in $[\eta]_\theta = K_\theta M^\alpha$ was 0.55, $K = 4.88$).

A plot of antilog E_s^* versus $(1/K_\theta \times 10^4)^{2/3} + f$, where $f = 0$ for $-\text{CH}_2-\text{CCH}_2\text{X}-$ and $f = 0.9$ for $-\text{CH}_2-\text{CHX}-$ (Fig. 1), was linear. For the eleven polymers for which data were obtained, only two of them [poly(vinyl chloride) and poly(vinyl acetate)] were obviously not on the line. It is not clear at this time why they should deviate. It is interesting, however, to observe that these points are the basis of a line parallel to the main one. The need for a shift factor ($f = 0.9$) along the $1/K_\theta \times 10^4$ axis is not unexpected and reflects either the steric difference between a proton and α -methyl group and/or a fundamental difference in stereoregularity of the α -methyl species.¹⁵

The relationship between E_s^* and K_θ indicates that common factors influence them both and that E_s^* does turn out to be a measure of restricted rotation. The use of one of these parameters to predict the value of the other is inherent in the relationship. It should be pointed out that such relationships between fundamental bulk and solution properties are of considerable interest.

At first glance (Table 1), the E_s^* data for the *p-n*-alkylstyrenes, *n*-alkyl methacrylates, and *n*-alkyl acrylates seem to be contrary to the concept of E_s^* , i.e., E_s^* decreases as the size of the alkyl group increases for these homologs. However (Table III and Fig. 1) this is in complete accord with $K_\theta^{2/3}$ [and, hence, via eq. (13), with (\bar{h}^2)] for the same polymers. An inspection of scale models of polymer segments containing these groups shows that there is really no significant difference, for example, between an ethyl and hexyl group as far as the more favored *trans* and *gauche* conformations are concerned for polymers such as the poly(*n*-alkyl methacrylates). Yet, the regular variation (decrease) of $K_\theta^{2/3}$ and E_s^* with increases in the sizes of the alkyl groups indicates that, on the average, the polymers containing

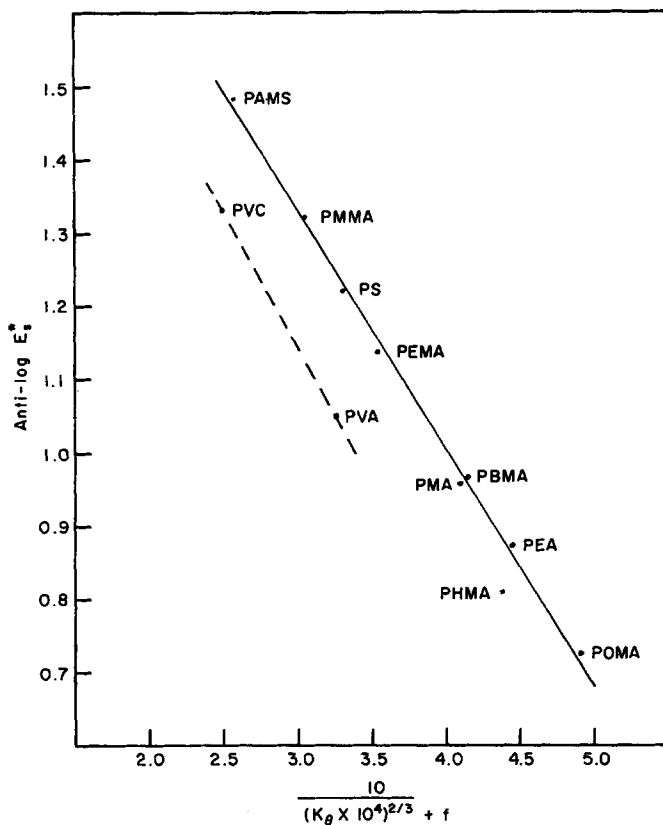


Fig. 1. Plot of antilog E_s^* vs. $[10/(K_g \times 10^4)^{2/3}] + f$.

the higher alkyl groups are able to exist in more unstable conformations than those with lower alkyl groups, or, in the limit, are able to rotate more freely. This means that the rotational barrier is lower for a polymer such as poly(*n*-octyl methacrylate) than for poly(ethyl methacrylate). This suggests that van der Waals interactions between the alkyl groups (when the polymer backbone is rotated to bring substituent groups into the *cis* conformation) increases with increasing size of the alkyl group and that this attraction helps to lower the barrier to rotation. Since boiling points of model homologous systems, e.g., *n*-alkyl chlorides, reflect this interaction, a relationship between E_s^* and boiling point would be anticipated. In fact, a plot of antilog E_s^* versus boiling point is essentially linear (Fig. 2).

The homologous series in Table I, i.e., *p-n*-alkystyrenes, *n*-alkyl methacrylates, and *n*-alkyl acrylates, are of special interest. The steady decrease in E_s^* (discussed above) and increase in E with increasing size of the alkyl groups suggested that there might be a regular relationship between the two parameters. As shown in Table IV, $(E) \times (\text{antilog } E_s^*)$ for given families is essentially constant with no apparent systematic deviations. This is a

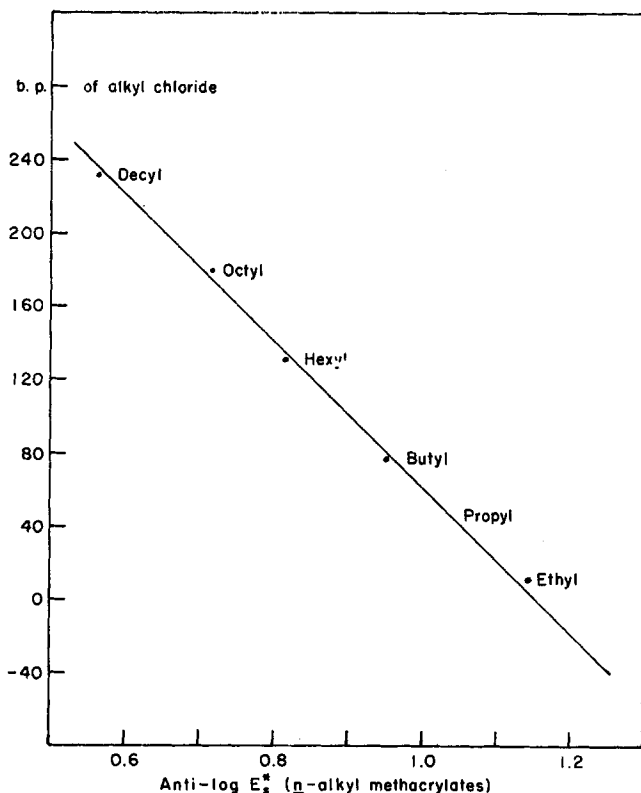


Fig. 2. Plot of antilog E_s^* vs. boiling point of n -alkyl chlorides.

useful correlation in that it also allows rapid, fairly reliable estimates of T_g to be made for a member of a polymer family on the basis of data for only a few members of that family.

Equation (7) is only approximate for copolymers because it predicts a linear relationship between T_g and composition, whereas, in fact, in certain cases the relationship may be either curved or exhibit maxima or minima.¹² Nonetheless, eq. (7) still will yield sufficiently accurate predictions of T_g for copolymers (Table II) to be very useful.

For those systems which exhibit serious departures from linearity in a T_g -composition plot, the E_s^* term in eq. (7) may be oversimplified. As discussed previously, E_s^* probably is an average representation of a complex series of interactions, and eq. (7) predicts that for a copolymer the overall effect would be given by a simple weighted average of E_s^* values for the individual components. If one considers the conformational (or rotational) characteristics of segments such as $-\text{CH}_2-\text{CHX}-\text{CH}_2-\text{CHX}$, $-\text{CH}_2-\text{CHY}-\text{CH}_2-\text{CHY}-$, and $-\text{CH}_2-\text{CHY}-\text{CH}_2-\text{CHX}-$, it seems reasonable that the assumption E_s^* (copolymer) = $\sum_i N_i E_{s_i}^*$ will

be more closely approximated if X and Y are more nearly similar in size and polarity.

TABLE IV
 Antilog $E_s^* \times E$ for Some Homologous Series

Polymer	E	E_s^*	Anti-log E_s^*	$E \times$ antilog E_s^*	Avg. for series
Polystyrene	8,150	0.0965	1.25	10,190	11,120
Poly(<i>n</i> -methylstyrene)	9,360	0.0860	1.22	11,420	
Poly(<i>n</i> -butylstyrene)	12,820	-0.0762	0.924	11,850	
Poly(<i>n</i> -hexylstyrene)	16,300	-0.166	0.75	12,225	
Poly(<i>n</i> -octylstyrene)	17,400	-0.210	0.617	10,735	
Poly(<i>n</i> -nonylstyrene)	18,700	-0.239	0.576	10,770	
Poly(<i>n</i> -decylstyrene)	20,200	-0.278	0.527	10,650	9,830
Poly(methyl methacrylate)	7,210	0.1119	1.311	9,450	
Poly(ethyl methacrylate)	9,020	0.055	1.135	9,100	
Poly(<i>n</i> -propyl methacrylate)	9,450	-0.0005	1.00	9,450	
Poly(<i>n</i> -butyl methacrylate)	10,490	-0.0309	0.954	10,000	
Poly(<i>n</i> -hexyl methacrylate)	12,400	-0.090	0.812	10,070	
Poly(<i>n</i> -octyl methacrylate)	15,580	-0.147	0.714	11,120	6,710
Poly(<i>n</i> -decyl methacrylate)	16,880	-0.245	0.569	9,600	
Poly(methyl acrylate)	6,900	-0.022	0.95	6,560	
Poly(ethyl acrylate)	7,930	-0.063	0.865	6,860	

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Résumé

La température de transition vitreuse T_g d'homopolymères du type $-\text{CH}_2-\text{CXY}-$ peut être exprimée par une simple équation additive comprenant deux termes: (1) un paramètre E qui est directement relié à l'énergie de cohésion molaire et (2) un paramètre E_s^* qui est une mesure de la rotation limitée autour des liens de valence. En outre, E_s^* , au moins pour un grand nombre de polymères est lié à la valeur K_θ de Mark-Houwink (telle que mesurée dans un solvant θ à la température T_θ) dans la relation antilog $E_s^* \propto 1/K_\theta^{2/3}$. On montre également que pour une série homologue (par exemple, les polyméthacrylates de *n*-alcyle), il y a un rapport constant entre E et anti-log E_s^* . Des

valeurs T_g pour les copolymères peuvent être estimées par une sommation simple en poids (via la fraction molaire) des valeurs de E et de E_s^* des composants. Utilisée sous cette forme, une variation linéaire entre T_g et la composition est admise (qui peut ne pas être strictement correcte) mais fournit toutefois un approximation très utile.

Zusammenfassung

Die Glasstemperatur (T_g) von Homopolymeren vom Typ $-\text{CH}_2-\text{CXY}-$ kann durch eine einfache additive Gleichung mit zwei Termen dargestellt werden: (1) einen Parameter E , der in direkter Beziehung zur molaren Kohäsionsenergie steht, und (2) einen Parameter E_s^* , der ein Mass für die behinderte Rotation um Valenzbindungen bildet. Es stellt sich heraus, dass E_s^* , zumindest für eine grosse Zahl von Polymeren, mit dem in θ -Lösungsmitteln bei T_g gemessenen Mark-Houwink K_θ -Wert durch die Beziehung $\text{anti-log } E_s^* \sim 1/K_\theta^{1/2}$ verknüpft ist. Weiters wird gezeigt, dass für homologe Reihen [z.B. Poly-(*n*-alkyl)methacrylate] eine konstante Beziehung zwischen E und $\text{anti-log } E_s^*$ besteht. Die T_g -Werte für Copolymere können durch eine einfache gewichtsmässige (über die Molenbrüche) Summierung der E und E_s^* -Werte der Komponenten bestimmt werden. Bei der Anwendung in dieser Form wird eine lineare Abhängigkeit des T_g von der Zusammensetzung angenommen, was vielleicht nicht völlig korrekt ist, aber doch eine brauchbare Lösung liefert.

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