boundary effect theory utilized in this work.

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Molecular Parameters of Polymers Obtained from the Gibbs–DiMarzio Theory of Glass Formation

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ABSTRACT: A numerical method of calculation of molecular parameters of the two-state Gibbs–DiMarzio (GD) model of glass formation using data on 15 polymers is presented. Experimental values of the glass transition temperature T_g, the change in the isobaric heat capacity ΔC_p, the change in the temperature volume expansion coefficient $\Delta\alpha$, and the hypothetical equilibrium transition temperature T_2 (obtained from viscoelastic data) were used to calculate the GD parameters: flex energy ϵ, hole energy E_h, and coordination number z. It was found that the energies ϵ and E_h increase with T_g of the polymer approximately linearly and do not differ too much from each other. The coordination number z first decreases with increasing T_g and then assumes a value of $z \approx 4.9$, thus supporting the favored theoretical value $z = 4$. The fractional free volume at T_2, $V_0(T_2)$, increases slightly with increasing T_g, while $V_0(T_g)$ increases less markedly, thus indicating that the free-volume concept of glass transition and the condition that configurational entropy equals zero at T_2 can both be valid simultaneously. The configurational entropy $S_c(T_g)$ and also the product $T_gS_c(T_g)$ decrease with increasing T_g. Theory predicts a rise in $\Delta\alpha(T)$ and a drop in $\Delta C_p(T)$ with increasing temperature, in accordance with the experiment. The Prigogine–Defay ratio determined by a combination of experimental and calculated thermodynamic quantitites at T_g is higher than unity for all polymers, which suggests that the glass transition is a freezing-in process controlled by more than one order parameter.

Much attention has been devoted in the literature to theoretical and experimental problems of transition of the polymeric liquid into amorphous glass. This process is a kinetic one, as indicated by the dependence on the rate of cooling of both the glass transition temperature T_g and the state of glass thus obtained. The Gibbs–DiMarzio statistical-mechanical theory (GD)[2-4] describes a case of hypothetical, infinitely slow cooling, during which a second-order transition should occur between the equilibrium liquid and equilibrium glass at a temperature T_2 situated approximately 50 K below the usually measured T_g. Oels and Rehage[5] criticize this concept and argue that glass transition is a freezing-in process and remains such also at T_2. Nose[6] chose a procedure which was somewhat different from GD and described glass transition on the basis of the hole theory of liquids. Tanaka[7] suggested an alternative partition function in order to demonstrate the effect of polymer conformations on the glass transition temperature.

The GD theory takes into account specific features of polymers, thus allowing one to express thermodynamic quantities as a function of the limited number of molecular parameters, namely, of flex energy ϵ, hole energy E_h, coordination number z, degree of polymerization x, and number of rotatable groups per monomer unit n_r. Due to its compact form and comparatively simple mathematical relations, the GD theory is suited for comparison with experimental data. So far, comparisons have always been carried out by the use of simplified assumptions. Usually, it was assumed that T_g equals T_2 and $z = 4$, and the calculations were performed with the following experimental data being known: (i) the change in the temperature volume expansion coefficient $\Delta\alpha$ (ref 3 and 8–10), (ii) the dependence of T_g on the molecular weight (ref 11–14), and (iii) changes in the heat capacity at constant pressure ΔC_p and the isothermal compressibility of the polymer $\Delta\beta$ (ref 15).

The assumptions just outlined allow one to reduce the number of looked-for parameters of the theory usually to one or two, that is, flex energy ϵ and hole energy E_h. Conclusions following from these comparisons were then affected by initial assumptions: for instance, the fractional free volume at T_g, V_{0g}, yielded a universal value $V_{0g} \approx 0.036$, and it was found that $\epsilon/k = E_h/k$ (ref 8). In another analysis[16] the assumed validity of the Simha–Boyer empirical relation $\Delta\alpha T_g$ = constant and $T_g \approx T_2 + 30$–50 K gave $V_{0g} = 0.025$, E_h/kT_2 in the range 5–6, and ϵ/kT_2 in the range 2.1–4, depending on z (in the range $z = 4$–12). The dependence of T_2 on z, on the type of lattice, and on the flex energy ϵ in the case of one infinite molecule was investigated by Gordon et al.,[17] who came to the conclusion that Huggins' lattice model of the polymer solution approximates the number of possible arrangements of the molecule on the lattice more adequately than does the

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Flory–Huggins model. One of the consequences of assumptions $z = 4$ and $T_2 = T_g$ is the fact that for a number of polymers given in ref 8 the ΔC_p values calculated from the GD theory reach 75% of the experimental ΔC_p on the average.

In this paper the GD theory is compared with experimental data on 15 polymers without limiting assumptions, and the moleular parameters z, ϵ, and E_h are calculated with the use of the known values of ΔC_p, $\Delta\alpha$, T_g, and T_2.

Gibbs–DiMarzio Theory

In the statistical-mechanical GD theory,[2-4] the polymer chain is divided into segments, or "rotatable" groups of atoms, each of which occupies one site of the lattice. The number of possible arrangements of n_x polymer molecules with x segments and n_0 empty sites was determined by the theory of polymer solutions. Each way of filling up the lattice is weighted by the total energy of the system, composed of inter- and intramolecular contributions. The intermolecular energy of the system is given by the number of segment–segment contacts and represents cohesion energy. The intramolecular contribution is based on an assumption that the rotational potential of each rotatable group involves one minimum having zero energy and (z − 2) minima having energy ϵ. z is at the same time the coordination number of the lattice.

These assumptions allowed DiMarzio et al.[4] to construct the isobaric–isothermal partition function of the system of polymer molecules and to obtain the Gibbs free energy as a function of two internal parameters, V_0 and f. For the configurational entropy of the system $S_c(T)$ related to one mole of monomer units for $T > T_2$ it follows that

$$S_c(T) = n_r R\left\{-\frac{V_0}{V_x}\ln S_0 + \frac{z-2}{2V_x}\ln\frac{V_0}{S_0} - \frac{\ln S_x}{x} + \frac{1}{x}\ln([(z/2-1)x+1](z-1)) + \frac{x-3}{x}\left[\frac{f\epsilon}{kT} - \ln(1-f)\right]\right\} \quad (1)$$

In eq 1, k is the Boltzmann constant, R is the gas constant, T is the absolute temperature, n_r is the number of rotatable groups per monomer unit, $V_0 = n_0/(xn_x + n_0)$, $V_x = 1 - V_0$, $S_0 = zn_0/([(z-2)x+2]n_x + zn_0)$ and $S_x = 1 - S_0$. The dependence of the internal parameter $V_0(T)$ is given by the implicit equation

$$\ln(V_0^{z/2-1}/S_0^{z/2}) - E_h S_x^2/kT = 0 \quad (2)$$

in which E_h is the hole energy. Another internal parameter, the fraction of all bonds situated in a position with higher energy, f, depends on temperature explicitly

$$f = [(z-2)\exp(-\epsilon/kT)]/[1 + (z-2)\exp(-\epsilon/kT)] \quad (3)$$

T_2 is defined as a temperature at which the number of possible configurations of polymer molecules decreases and the configurational entropy in eq 1, $S_c(T_2) \equiv 0$. The internal parameters V_0 and f do not vary with temperature below T_2, i.e., for $T \le T_2$, $V_0(T) \equiv V_0(T_2)$ and $f(T) \equiv f(T_2)$.

For the difference $\Delta\alpha(T)$ between the temperature volume expansion coefficients of the equilibrium liquid $\alpha_l(T)$ and the glass α_g it follows

$$\Delta\alpha(T) \equiv \alpha_l(T) - \alpha_g(T_2) = \frac{V_0 E_h S_x^2/kT^2}{zS_x/2 - 2E_h S_x^2 S_0/kT - (z-2)V_x/2} \quad (4)$$

Similarly, the change in heat capacity $\Delta C_p(T)$ at constant pressure related to 1 mol of monomer units is given by

$$\Delta C_p(T) = n_r R\{\Delta\alpha E_h S_x^2/V_x k + (\epsilon/kT)^2 f(1-f)\} \quad (5)$$

The change in the molar heat capacity at constant volume $\Delta C_v(T)$ has the form

$$\Delta C_v(T) = n_r R(\epsilon/kT)^2 f(1-f) \quad (6)$$

For the isothermal compressibility $\beta_l(T)$ of the liquid it holds

$$\beta_l(T) = \frac{V_0 C/kT}{zS_x/2 - 2E_h S_x^2 S_0/kT - (z/2-1)V_x} \quad (7)$$

where C is the volume of the unit cell of the lattice, $C = V/(xn_x + n_0)$ (V is the total volume). For the isothermal compressibility of glass β_g it holds that

$$\beta_g = \beta_l(T_2)\Delta C_v(T_2)/\Delta C_p(T_2) \quad (8)$$

The difference in compressibilities in eq 7 and 8 may be expressed by an alternative relation

$$\Delta\beta(T) = T_2 V_2[\Delta\alpha(T_2)]^2/\Delta C_p(T_2) \quad (9)$$

Results

Relations 4–6 and 9 hold for differences in the thermodynamic quantitites of the liquid at T ($>T_2$) and of glass formed at T_2. Experimentally available, however, are values of the $\Delta\alpha$, ΔC_p, and $\Delta\beta$ at T_g; their utilization in eq 4–6 and 9 requires that the parameters f and n_0 should freeze at T_g and do not change for $T \le T_g$ any more, i.e., $n_0(T) \equiv n_0(T_g)$ and $f(T) \boxminus f(T_g)$.

For a quantitative solution of the GD model three molecular parameters, z, E_h, and ϵ, are needed, which means that the calculation calls for three experimental quantities. Those quantities readily available in the literature are two, namely, ΔC_p and $\Delta\alpha$ measured at T_g. The values of $\Delta\beta$ are known only for a few polymers or are subjected to a comparatively large experimental error. In our calculations the third quantity was T_2, which, though not experimentally available, can be estimated either from calorimetric or from viscosity or viscoelastic measurements. For physical reasons $T_{2,\text{cal}}$ and $T_{2,\text{vis}}$ ought to be identical, and this really is so in most cases.[18] On the other hand, however, Miller[19] believes that these temperatures may differ for polymers possessing a bulky side group. The extrapolation method[20] of obtaining $T_{2,\text{cal}}$ of an amorphous material by means of its crystalline modification is not convincing. For this reason, our calculations were performed with the use of $T_{2,\text{vis}}$. The method of calculation of $T_{2,\text{vis}}$ from reported viscoelastic data on many polymeric systems and based on the theory of Adam and Gibbs[21] has been described in detail elsewhere.[22]

The system of two equations, namely, eq 1 at T_2 in the form $S_c(T_2) = 0$ and eq 5 at T_g, was numerically solved for an unknown z and ϵ with the use of Rosenbrock's minimization method.[23] The values of V_{02} (for T_2) and V_{0g} (for T_g) needed for the solution were calculated together with the unknown E_h by solving simultaneously eq 2 and 4. Hence, calculation of the molecular parameters z, ϵ, and E_h required the knowledge of experimental values of $\Delta\alpha$, ΔC_p, T_g, and T_2. The hole energy E_h was regarded as temperature independent. The number of rotatable groups in the monomer unit, n_r, was that of bonds about which rotation is possible with the exclusion of bonds of end atoms and of rotationally symmetrical groups. This n_r differs in some cases from n_r reported by O'Reilly.[15] Since all 15 polymers (input data given in Table I) had a high molecular weight, the limit $x \to \infty$ was used in eq 1–9.

The calculated molecular parameters z, ϵ/k, and E_h/k are given in Table II. The internal parameters V_0 and f determined at T_g and T_2 are tabulated in Table III. For

Table I
Experimental Data Used as Input Data for the Calculation of Parameters of the Gibbs-DiMarzio Model

polymer	abbreviation	T_g,[a] K	T_2,[a] K	ΔC_p, J/(K mol)	$\Delta\alpha 10^4$, K^{-1}	$V_g 10^3$, m^3/kg	n_r
poly(dimethylsiloxane)	PDMS	150	81	22.3[b]	5.52[h]	0.905[h]	2
polybutadiene	PBD	180	112	33.4[c]	4.4[i]	1.025[s]	3
natural rubber	NR	200	143	31.3[d]	3.75[j]	1.040[j]	3
polyisobutylene	PIB	205	128	22.6[d]	3.75[h]	1.078[h]	2
poly(2-hydroxyethoxyethyl methacrylate)	PHEOEMA	283	231	62.7[e]	2.7[p]	0.789[p]	9
selenium	SE	303[k]	259[k]	14.7[c]	2.88	0.23	1
poly(vinyl acetate)	PVAC	305	257	41.8[d]	4.26[l]	0.844[l]	4
poly(ethyl methacrylate)	PEMA	335	267	29.6[e]	2.95[m]	0.900[m]	5
poly(ethylene terephthalate)	PET	340	277	64.5[d]	3.51[n]	0.771[n]	6
poly(vinyl chloride)	PVC	350	296	18.6[d]	2.93[o]	0.733[o]	2
poly(2-hydroxyethyl methacrylate)	PHEMA	370	322	36.4[e]	2.2[p]	0.793[p]	6
polystyrene	PS	373	325	33.5[f]	3.12[f]	0.9725[f]	3
poly(methyl methacrylate)	PMMA	388	305	34.2[d]	3.1[r]	0.864[r]	4
polycarbonate of bisphenol A	PCA	416	366	63.5[d]	3.9[n]	0.89[q]	6
poly(α-methylstyrene)	PαMS	445	395	37.5[g]	3.98[g]	0.9584[g]	3

[a] T_g and T_2 values were taken from ref 22. [b] R. F. Boyer, *J. Macromol. Sci., Phys.*, **7**, 487 (1973). [c] B. Wunderlich, *J. Phys. Chem.*, 64, 1052 (1960). [d] B. Wunderlich and L. D. Jones, *J. Macromol. Sci., Phys.*, 3, 67 (1969). [e] J. Biroš, private communication. [f] S. Ichihara, A. Komatsu, Y. Tsujida, T. Nose, and T. Hata, *Polym. J.*, 2, 530 (1971). [g] S. Ichihara, A. Komatsu, and T. Hata, *Polym. J.*, 2, 650 (1971). [h] S. C. Sharma, L. Mandelkern, and F. C. Stehling, *J. Polym. Sci., Polym. Lett. Ed.*, **10**, 345 (1972). [i] S. M. Aharoni, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **14**, 334 (1973). [j] N. Bekkedahl, *J. Res. Natl. Bur. Stand.*, **13**, 411 (1934). [k] A. Eisenberg and L. Teter, *J. Am. Chem. Soc.*, **87**, 2108 (1965). [l] A. J. Kovacs, *J. Polym. Sci.*, **30**, 131 (1958). [m] S. S. Rogers and L. Mandelkern, *J. Phys. Chem.*, **61**, 985 (1957). [n] K. H. Hellwege, J. Hennig, and W. Knappe, *Kolloid Z. Z. Polym.*, **186**, 29 (1962). [o] K. H. Hellwege, W. Knappe, and P. Lehmann, *Kolloid Z. Z. Polym.*, **183**, 110 (1962). [p] M. Ilavský and J. Hasa, *Collect. Czech. Chem. Commun.*, **33**, 2142 (1968). [q] Reference 13. [r] J. C. Wittman and A. J. Kovacs, *J. Polym. Sci., Part C*, **16**, 4443 (1969). [s] V. E. Lucas, P. H. Johnson, L. B. Wakefield, and B. L. Johnson, *Ind. Eng. Chem.*, **41**, 1629 (1949).

Table II
Molecular Parameters of Polymers Calculated with the Use of the GD Theory

polymer	z	ϵ/k, K	ϵ/k,[a] K	ϵ/k,[b] K	E_h/k, K	E_h/k,[a] K	E_h/k,[c] K	E_h/k,[d] K
PDMS	13.5	321	326	250	420	388	494	
PBD	9.19	383	421		507	446	554	327
NR	6.84	426	438	462	567	496	647	468
PIB	9.33	441	439	455	584	521	619	503
PHEOEMA	4.29	508			767			
Se	8.00	854			819			
PVAC	5.35	694	683	532	695	698	852	
PEMA	3.82	529	737		820	852	963	
PET	5.72	772	775	667	803		1000	
PVC	4.97	751	795	595	867	838	941	554
PHEMA	3.76	631			965			
PS	5.66	907	839	842	889	876	1041	755
PMMA	4.82	753	851	660	904	881	1024	
PCA	5.08	984	950	764	871		933	
PαMS	5.90	1172		950	905		1162	

[a] ϵ/k and E_h/k values from ref 8. [b] ϵ/k values from ref 15. [c] Average E_h/k values from: ref 25; W. Wrasidlo, *Adv. Polym. Sci.*, 13, 1 (1974); R. Becker, *Plaste. Kautsch.*, 25, 1 (1978). [d] E_h/k values from ref 26.

Table III
Internal Parameters of Polymers Calculated with the Use of the GD Theory

polymer	V_{02}	V_{0g}	V_{0g}[a]	f_2	f_g
PDMS	0.00194	0.0249	0.0250	0.180	0.575
PBD	0.00367	0.0236	0.0335	0.190	0.461
NR	0.00624	0.0221	0.0255	0.197	0.366
PIB	0.00354	0.0227	0.0290	0.190	0.461
PHEOEMA	0.0110	0.0224		0.203	0.275
SE	0.0156	0.0256		0.182	0.264
PVAC	0.0243	0.0416	0.0365	0.183	0.256
PEMA	0.0138	0.0298	0.0276	0.200	0.272
PET	0.0197	0.0379		0.186	0.278
PVC	0.0184	0.0317	0.0340	0.191	0.258
PHEMA	0.0149	0.0239		0.199	0.242
PS	0.0237	0.0368	0.0345	0.183	0.243
PMMA	0.0173	0.0378	0.0355	0.192	0.288
PCA	0.0361	0.0528		0.173	0.225
PαMS	0.0418	0.0590		0.167	0.219

[a] Values from ref 8.

comparison, both tables also contain data obtained under various simplifying conditions mentioned in the introduction. The comparison shows that the value least sensitive to the method of calculation is hole energy E_h/k. The parameter ϵ/k already exhibits major differences: while values obtained by O'Reilly[15] are usually lower than ours (probably owing to the assumption $z = 4$), those given by Eisenberg and Saito[8] are higher in most cases than our values (probably as a result of the assumption $S_c(T_g) = 0$). The largest differences between our values and those determined earlier may be seen for the free volume V_{0g}, which however may be due not only to the simplifying assumptions but in some cases also to the small differences between the input data of $\Delta\alpha$.

The stability of calculation, i.e., the effect of the experimental scatter in input quantitites on the magnitude of calculated parameters, was tested on data for polystyrene by gradually changing the value of a single input

Table IV
Stability of Calculation with Respect to the Scatter in the Input Data (Calculated for Polystyrene)

change in input data	change in calculated data, %						
	z	ϵ/k, K	E_h/k, K	V_{02}	V_{0g}	f_2	f_g
$T_g \pm 10$ K	±1.5		±1.7	∓5.5	±3.0		±5.7
$T_2 \pm 10$ K	∓2.4	±2.5		±10.0		∓1.1	∓7.0
$\Delta C_p \pm 10\%$	±10.0	±6.0				±1.1	
$\Delta\alpha \pm 10\%$	±1.3		±3.6	∓12.0	∓11.0	±1.6	±1.2

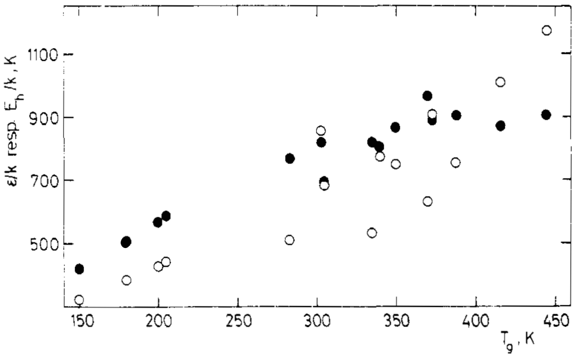

Figure 1. Dependence of molecular parameters of the GD theory, the flex energy of the chain (○) and the hole formation energy (●) on the glass transition temperature T_g of different polymers.

quantity each time (T_g and T_2 by ±10 K, ΔC_p and $\Delta\alpha$ by ±10%). It follows from Table IV that the most sensitive output parameter is the volume V_0 (to $\Delta\alpha$) and that together with f_g it also depends on T_2. It can be seen, in spite of this, that both the output values of molecular parameters z, ϵ/k, and E_h/k and the internal parameters V_0 and f are sufficiently stable to scatter in the input data.

Discussion

A. Molecular and Internal Parameters of the GD Theory. Although many polymers have several rotational degrees of freedom with different energetic minima, the present form of the GD model employs flex energy ϵ/k, which may be regarded as the average difference of minima. A quantitative comparison of ϵ/k with experimental results obtained by the spectral method (energy difference between the gauche and trans minimum) leads to agreement within an order of magnitude. For instance, the ϵ/k of liquid n-alkanes lies within the interval 250–400 K (cf. ref 24); with respect to our results, this interval includes polymers with a low T_g (PDMS, PIB, NR, PBD, cf. Table II). With increasing T_g the ϵ/k values increase as expected, in accordance with the results of Eisenberg and Saito.[8]

Interaction between chemically not bound segments is characterized in the GD theory by the so-called hole energy E_h, which corresponds to the formation of an empty site in the quasi-lattice without interruption of any chemical bond. The hole formation energy appears in a number of theoretical approaches to glass transition, such as the free volume theory of Kanig[25] and the theory of Hirai and Eyring.[26] The E_h/k values provided by these approaches are summarized in Table II. Even though E_h/k calculated with the use of Kanig's theory lies systematically above E_h/k calculated by us and E_h/k of the theory of Hirai and Eyring lies below our values, the differences are not large and cannot be regarded as very important. The increase in the hole formation energy with T_g (Figure 1) is similar to the increase in ϵ, but the agreement between ϵ and E_h is not as perfect as in the case of Eisenberg and Saito[8] (the E_h values are somewhat higher than ϵ).

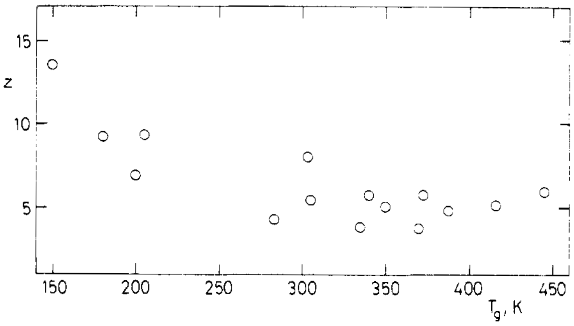

Figure 2. Coordination numbers calculated with the use of the GD theory as a function of the glass transition temperature T_g of different polymers.

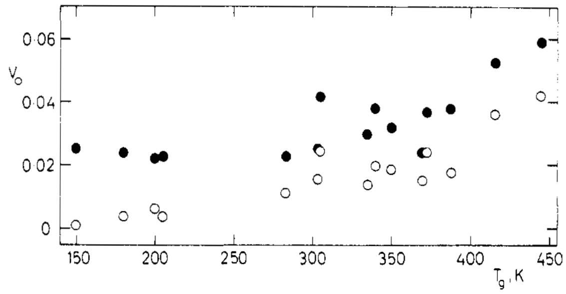

Figure 3. Dependence of free volume V_{0g} at T_g (●) and V_{02} at T_2 (○) on the glass transition temperature T_g of different polymers.

For polymers with $T_g > 250$ K (with the exception of Se), the coordination numbers (Figure 2) are nearly constant, having an average value of 4.9, in agreement with the value of 4 expected for the case of a threefold rotational potential. Four polymers with $T_g < 250$ K reach higher z values, which can be understood rather from the viewpoint of the closest packing of spheres (e.g., for the cubic face-centered system $z = 12$). For selenium is it possible to compare the number of the closest neighbors of amorphous selenium calculated from the GD theory and of crystalline selenium. Se crystallizes in the trigonal system and has six nearest neighbors and three next-nearest neighbors which are situated only a little further away than the first six. Hence, $z = 8$ found for polymeric Se is in good agreement with the structural order of crystalline Se.

With the exception of PαMS and PCA the fractional free volume V_{0g} (Figure 3) differs only a little for different polymers (increasing slightly with T_g), which seems to justify the concept of glass transition as an iso-free-volume process. The average $V_{0g} = 0.029$ agrees comparatively well with the value 0.025 following from the free-volume interpretation of the Williams–Landel–Ferry equation.[27] On the other hand, the V_{02} increases with increasing T_g, thus indicating the dependence of V_{02} on the polymer structure. Opposite dependences on T_g are exhibited by the other internal parameter, namely, the bond fraction f in the higher energy position. At T_2, f_2 remains almost constant with the mean value 0.189; this fact indicates universal topological conditions reflected in the same degree of chain coiling at T_2. On the contrary, the decrease in values f_g with the increasing T_g of polymers is due to an increase in flex energy ϵ and thus to an increase in chain rigidity.

B. Thermodynamic Functions. The form of eq 5 predicts a rise in $\Delta C_p(T)$ with decreasing temperature and therefore $\Delta C_{p2} \equiv \Delta C_p(T_2)$ (Table V) are higher than experimental $\Delta C_p \equiv \Delta C_{pg}$ values (Tables I). Such a prediction is in agreement with the experience that the dependence of C_p on T exhibits a higher slope in the glassy than in the liquid state.[28] For the temperature dependence of ΔC_p, Angell and Sichina[29] suggested the empirical relation

$$\Delta C_p(T) = \text{constant}/T \qquad (10)$$

Table V
Specific Heat and Configurational Entropy of Polymers

polymer	ΔC_{Vg},[a] J/(mol K)	ΔC_{Vg},[b] J/(mol K)	ΔC_{p2},[c] J/(mol K)	$\Delta C_{pg}T_g/T_2$,[d] J/(mol K)	S_{cg},[e] J/(mol K)	$\Delta C_{pg}\ln(T_g/T_2)$,[d] J/(mol K)	$\Delta C_{pg}[(T_g/T_2)-1]$,[d] J/(mol K)	T_gS_{cg}, J/(mol K)
PDMS	18.8	18.0	39.34	41.30	20.9	13.7	19.00	3135
PBD	28.1		46.92	53.68	20.1	15.8	20.28	3618
NR	26.3	24.0	37.70	43.78	11.9	10.5	12.48	2380
PIB	19.1	12.3	31.59	36.20	13.5	10.6	13.60	2768
PHEOEMA	48.1		68.53	76.81	13.3	12.7	14.11	3764
SE	12.8		14.87	17.20	2.34	2.31	2.50	709
PVAC	32.8	19.0	43.33	49.61	7.38	7.16	7.81	2254
PEMA	20.5		32.30	37.14	7.03	6.72	7.54	2358
PET	51.6	43.1	68.23	79.17	13.8	13.2	14.67	4692
PVC	14.7	9.4	19.49	21.99	3.8	3.12	3.39	1113
PHEMA	26.6		38.13	41.83	5.18	5.06	5.43	1917
PS	27.1	25.0	34.29	38.45	4.75	4.67	4.95	1772
PMMA	25.7	19.0	37.30	43.51	8.65	8.23	9.31	3356
PCA	48.7	15.2	64.22	72.17	8.21	8.13	8.67	3412
PαMS	29.6	24.0	37.38	42.25	4.50	4.47	4.75	2003

[a] ΔC_{Vg} calculated with the use of eq 6. [b] ΔC_{Vg} from ref 13. [c] ΔC_{pg} calculated from eq 5. [d] ΔC_{pg} is the experimentally measured ΔC_p value. [e] S_{cg} calculated with the use of eq 1.

Table VI
Calculated and Experimental Isothermal Compressibilities of Polymers

polymer	$\Delta\alpha(T_2)10^4$, K	$\beta_l(T_g)10^5$,[a] MPa	$\beta_{l(\text{exptl})}10^5$, MPa	$\beta_g(T_g)10^5$,[b] MPa	$\beta_{g(\text{exptl})}10^5$, MPa	$(T_2V_2\alpha_{l_2}^2/C_{pl_2})10^5$,[c] MPa	r_g[d]
PDMS	1.27	82	60[g]	9.5		0.22	5.30
PBD	1.55	36		7.2		0.32	4.99
NR	1.86	39	51[j]	12.3		0.92	4.20
PIB	1.32	50	40[h]	10		0.41	5.20
PHEOEMA	1.81	19		8.7		1.5	2.28
SE	2.18	23		14		1.3	2.90
PVAC	3.32	45	50[i]	23	29[i]	4.7	2.28 (2.18)
PEMA	1.88	33		12.6		3.0	2.02
PET	2.46	44		21		3.1	2.58
PVC	2.17	35	44[j]	18	24[i]	2.8	2.30 (2.71)
PHEMA	1.67	19		9.6		2.4	1.85
PS	2.46	58	61[e]	32	32[e]	5.7	2.37 (2.64)
PMMA	2.01	38	58[j]	15	30[e]	2.9	2.44 (2.97)
PCA	3.15	91	55[f]	49	30[f]	11.9	1.96 (1.16)
PαMS	3.28	100	64[e]	57	32[e]	12.6	2.02 (1.51)

[a] β_l values calculated with the use of eq 7. [b] β_g values calculated with the use of eq 8. [c] $T_2V_2\alpha_{l_2}^2/C_{pl_2}$ values calculated with the use of eq 9. [d] r_g values calculated with the use of eq 12; numbers in brackets calculated with $\Delta\beta_{g,\text{exptl}}$. [e] A. Quach and R. Simha, *J. Appl. Phys.*, **42**, 4592 (1971). [f] Reference 13. [g] S. Beret and J. M. Prausnitz, *Macromolecules*, 8, 536 (1975). [h] H. Singh and A. W. Nolle, *J. Appl. Phys.*, **30**, 337 (1959). [i] J. E. McKinney and M. Goldstein, *J. Res. Natl. Bur. Stand., Sect. A*, **78**, 331 (1974). [j] P. Heydemann and H. D. Guicking, *Kolloid-Z.*, **193**, 16 (1963).

which gives $\Delta C_{p2} = \Delta C_{pg}T_g/T_2$. Comparison of ΔC_{p2} values from eq 10 with the values of the GD theory (Table V) allows us to conclude that eq 10 predicts a stronger dependence of ΔC_p on temperature than eq 5. Table V also gives ΔC_{Vg} values (for T_g) calculated from eq 6 together with ΔC_{Vg} calculated earlier by O'Reilly.[15] The differences in both columns are a consequence of O'Reilly's assumption that $z = 4$.

In some cases the configurational entropy at T_g, S_{cg}, was regarded as a quantity controlling glass transition, either directly, i.e., S_{cg} = constant (iso-entropical process[30]), or indirectly, through a constant value of relaxation time at T_g, τ_g, which is expressed by means of the product[21] T_gS_{cg} ($\sim 1/\ln \tau_g$). Comparison between the S_{cg} and T_gS_{cg} of different polymers (Table V), along with V_{0g} (Table III), shows that the free volume at T_g fulfills with the best approximation the condition of constant value. Table V also gives the entropy values

$$S_{cg} \equiv \int_{T_2}^{T_g} (\Delta C_p/T)\,\mathrm{d}T \qquad (11)$$

assuming on the one hand that ΔC_p = constant and on the other the validity of eq 10. By comparing these values with S_{cg} of the GD model, one can see that while ΔC_p = constant leads to agreement between S_{cg} for polymers with a high T_g, eq 10 provides agreement between S_{cg}'s for polymers with a low T_g.

The excess temperature volume expansion $\Delta\alpha_2$ calculated from eq 4 at T_2 decreases with decreasing temperature T_g (Table VI). For low T_g's (PDMS, PBD, PIB), the values of $\Delta\alpha_2$ are much lower than the experimental $\Delta\alpha$ (Table I). The product α_2T_2 for different polymers varies more than ten times; for this reason, the Simha-Boyer relation for T_g is not valid at T_2.

C. Prigogine-Defay Ratio. Equation 9 means that the Prigogine-Defay ratio[31]

$$r = \Delta C_p\Delta\beta/TV(\Delta\alpha)^2 \qquad (12)$$

at T_2 is unity. On the other hand, however, according to the parameter concept of glass transition,[32-34] in the case of more than one parameter (two in the GD theory, i.e., f and n_0) it should hold $r > 1$. This controversy has been discussed in the literature especially from the viewpoint of behavior of the order parameters below the $T_2(P)$ line.[35,36] The equilibrium GD theory can formally be employed also in calculations of r_g at T_g. At this temperature, the order parameters freeze in, and they do not minimize the Gibbs free energy of glass; the transition is no longer an equilibrium one and can be regarded as a freezing-in transition. This view is also corroborated by the Prigogine–Defay r_g ratios as given in Table VI. In all cases $r_g > 1$, especially for polymers with a lower T_g. This agrees well with findings described by other authors[30,37] and supports the view that glass transition is a freezing-in process controlled by more than one independent order parameter.

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Molecular Interpretation of the Glass Transition Temperature of Polymer–Diluent Systems

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ABSTRACT: An explicit expression based on both classical and statistical thermodynamics has been derived for predicting the glass transition temperature of polymer–diluent mixtures. The result is expressed in terms of the molecular weight, size, and concentration of the diluent, the number of lattice sites, the monomer molecular weight, and the transition isobaric specific heat increment. The prediction of the theory is in good agreement with published experimental data and, therefore, can be used for molecular engineering.

The depression of the glass transition temperature (T_g) by plasticizers and its composition dependence in compatible polymer blends have been known for some time.[1,2] There has, however, been strong interest recently[3-7] in deriving predictive expressions for T_g in terms of fundamental compositional parameters. Empirical equations based on data fitting, relations from the free volume hypothesis and from the point of view of classical thermodynamics, have been reported.[3-11] However, there has been no effort to interpretate T_g by using statistical mechanics since the work of DiMarzio and Gibbs.[12] Their work does not predict T_g explicitly, and the present work complements and extends their development by deriving an explicit expression for T_g of polymer–diluent systems.

In the study of an order–disorder transition, the Bragg–Williams approximation[13] has been known for its simplicity and success in displaying essential features of the phenomenon. In this paper, the method is adopted in the determination of the configurational partition function. The glass transition temperature is related to nondimensional parameters which are a function of the molecular weight and concentration of diluent, number of lattice sites, monomer molecular weight, and transition isobaric heat capacity increment of the polymer. The theoretical equation is then compared with published experimental data.

Derivation

The glassy state represents a situation of frozen-in disorder which is in a state of quasiequilibrium, and the glass transition has been explained by using both equilibrium thermodynamics and kinetic theories. Theoretical treatments of the glass transition have been either purely equilibrium[14,15] or purely kinetic[16] in nature. In this paper, our approach to the problem is an equilibrium one. First, we consider the discontinuity conditions which occur at the glass transition temperature. A relation expressing the glass transition temperature (T_g) of a polymer–diluent

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