NOTE

Dependence of Glass Transition Temperature on Chain Flexibility and Intermolecular Interactions in Polymers

INTRODUCTION

The glass transition temperature of bulk polymer, T_g, is accessible by various computational schemes. Most of these approaches hinge on the basic assumption that each of the structural units in a repeat unit contributes additively to the overall T_g.[1-3] Although these algorithms are indeed useful for predictive purposes, they neglect the physical characteristics of the systems. In contrast, Aharoni has shown that T_g is directly related to the polymer thermal expansion coefficients as well as the steric hindrance parameter, σ.[4] Moreover, it has been demonstrated that T_g is a linear function of the product of the cohesive energy density of polymer, B, and the chain cross-sectional area recently.[5] All these analytical expressions are developed empirically. This note reports new correlations between T_g and other chain parameters.

It is well known that T_g depends crucially upon two important factors, viz., chain flexibility and intermolecular interactions in polymers. The former factor may be measured by the characteristic ratio, C_∞, generally defined by[6]

$$C_\infty = \lim_{n \to \infty} \overline{r_0^2}/n\overline{l^2} \tag{1}$$

where $\overline{r_0^2}$ is the mean-square end-to-end distance of a polymer in the unperturbed state, n is the number of backbone bonds with the mean-square bond length l^2. It also serves as an estimate of the effects of short-range interactions. In any case, the long-range interaction effects virtually vanish for solid polymers. Practically, the intensity of the foregoing intermolecular interactions is quantified by the intensive variable B computed by

$$B = \delta^2 \tag{2}$$

where δ is the solubility parameter of the polymer. Intuitively, one can write

$$T_g \propto C_\infty^\alpha \tag{3}$$

and

$$T_g \propto B^\beta \tag{4}$$

where α and β are positive exponents to be determined empirically. On the basis of these prevailing concepts, the following analysis is in order.

RESULTS AND DISCUSSION

Table I exhibits the literature values of C_∞, T_g, and B for a collection of polymers covering a wide spectrum of chemical structures and stereoregularities. These data result in $\alpha = 1/2$ and $\beta = 3/2$. Figure 1 is constructed accordingly by plotting $C_\infty^{1/2}/T_g$ against $B^{-3/2}$. Clearly, the polymers listed in Table I divide into two groups, which may be appropriately termed as weak and tough polymers for the reason apparent from the following remarks. The first group which exhibits relatively weak interactions with $B \leq 380$ J/mL, indeed follows the straight line passing through the origin, whereas, the second one does not obey proportionality (4) at all. In fact, T_g is directly proportional to $C_\infty^{1/2}$, and practically independent of B for adequately strong intermolecular forces in the sense $B > 380$ J/mL. Mathematically, we have

$$C_\infty^{1/2}/T_g = 59/B^{3/2} \ (\text{J}^{3/2} \ \text{mL}^{-3/2} \ \text{K}^{-1}),$$

$$B \leq 380 \ \text{J/mL} \tag{5}$$

and

$$C_\infty^{1/2}/T_g = 8.0 \times 10^{-3} \ (\text{K}^{-1}), \quad B > 380 \ \text{J/mL} \tag{6}$$

for the weak and tough polymers, respectively. The standard error of estimate of y on x is found to be 0.85×10^{-3} K^{-1}, which corresponds to 9% error in y, where $y = C_\infty^{1/2}/T_g$ and $x = B^{-3/2}$. Considering the diversity of polymers, the large sample population, and the sizable experimental uncertainties involved, the foregoing correlations are indeed justifiable. For example, the most scattered point in Figure 1 due to poly(methyl acrylate) (polymer 22 in Table I) registers a δ value approximately 9% higher than the predicted one. The average observed uncertainty in δ is believed to be around 10%. This implies that the substantial discrepancy encountered in this par-

Table I Characteristic Parameters of Polymers

No.	Polymer	$C_\infty{}^a$	$T_g{}^b$ (K)	B^c (J/mL)
1	Polyacrylamide	14.8	438	1296[d]
2	Poly(acrylic acid)	6.7	379	415[e]
3	Polyacrylonitrile	9.7	378	655
4	*Cis*-polybutadiene	4.9	171	274
5	Poly(*n*-butyl methacrylate)	7.9	300	320
6	Poly(ε-caprolactam)	5.3	313	506
7	Polychloroprene, 85% *trans*	5.6	233	310
8	Poly(4-chlorostyrene)	11.1	383	331[e]
9	Poly(decamethylene adipate)	3.6	217	331[e]
10	Poly(*N,N*-dimethyl acrylamide)	9.2	362	1326[d]
11	Poly(2,6-dimethyl-1,4-phenylene oxide)	3.6 (18.0)[g]	485[f]	361
12	Polydimethylsiloxane	6.0	146	222
13	Poly(ethyl methacrylate)	7.7	338	335
14	Polyethylene	7.0	188	256
15	Poly(ethylene oxide)	3.8	206	372[e]
16	Poly(ethylene terephthalate)	3.2 (8.0)	340	392
17	Poly(hexamethylene adipamide)	6.1	323	773
18	Poly(*n*-hexyl methacrylate)	10.1	268	310
19	Polyisobutene	6.5	198	259
20	Polyisoprene			
	(a) *Cis*	5.5	206[h]	279
	(b) *Trans*	6.4	203[h]	276
21	Poly(4,4'-isoproylidene diphenoxy di(4-phenylene) sulfone)	2.0 (16.0)	462	412
22	Poly(methyl acrylate)	8.0	282	392
23	Poly(methyl methacrylate)			
	(a) Atactic	8.7	378	357
	(b) Isotactic	9.3	311	357
24	Poly(4-methyl styrene)	11.4	374	346[e]
25	Poly(*n*-octyl methacrylate)	9.6	253	296
26	Poly(1-pentene)	9.2	233	274[e]
27	Poly(2,2-propane bis(4-phenyl) carbonate)	2.4 (12.0)	418	412
28	Polypropylene			
	(a) Atactic	6.7	267[h]	361
	(b) Isotactic	5.2	255[h]	361
	(c) Syndiotactic	6.3	269[h]	361
29	Poly(propylene oxide)	4.9	200	317[e]
30	Poly(propylene sulfide), isotactic	4.0	226	342[e]
31	Polystyrene	10.0	373	331
32	Polytetrafluoroethylene	24.0	160	161
33	Poly(tetramethylene oxide)	4.8	187	299
34	Poly(vinyl acetate)	8.9	305	369
35	Poly(vinyl alcohol)	8.3	358	666
36	Poly(*N*-vinyl carbozole)	16.2	481	467[i]
37	Poly(vinyl chloride)	6.7	357	392
38	Poly(vinyl pyrrolidone)	9.9	359	592[i]

[a] Data obtained from (a) Aharoni[10] (b) M. Kurata, Y. Tsunashima, M. Iwama, and K. Kamada, in *Polymer Handbook,* 2nd ed., J. Brandrup and E. H. Immergut, Eds., Wiley-Interscience, New York, 1975, pp. IV 34–60, and (c) Flory,[6] pp. 40–43.

[b] Data obtained from (a) Aharoni,[4] (b) van Krevelen and Hoftyzer,[1] pp. 574–581, and (c) W. A. Lee and R. A. Rutherford, cited in *Polymer Handbook,* Wiley-Interscience, New York, 1975, pp. III 139–192.

[c] B is estimated by $B = \delta^2$, where δ is the solubility parameter whose values are tabulated in (a) H. Barrell, cited in *Polymer Handbook,* Wiley-Interscience, New York, 1975 pp. IV 337–359 and (b) van Krevelen and Hoftyzer.[1]

[d] K. Nakazato and K. Suzuki, *Macromolecules,* **23,** 1800 (1990).

[e] Estimated by means of the addition of group contributions after van Krevelen and Hoftyzer,[1] Chap. 7.

[f] T. K. Kwei and H. L. Frisch, *Macromolecules,* **11,** 1267 (1978).

[g] Values in parentheses refer to C'_∞ introduced in the text.

[h] D. R. Burfield, *J. Chem. Educ.,* **64,** 875 (1987).

[i] Estimated by means of the addition of group contributions outlined in R. F. Fedors, *Polym. Eng. Sci.,* **14,** 147 (1974).
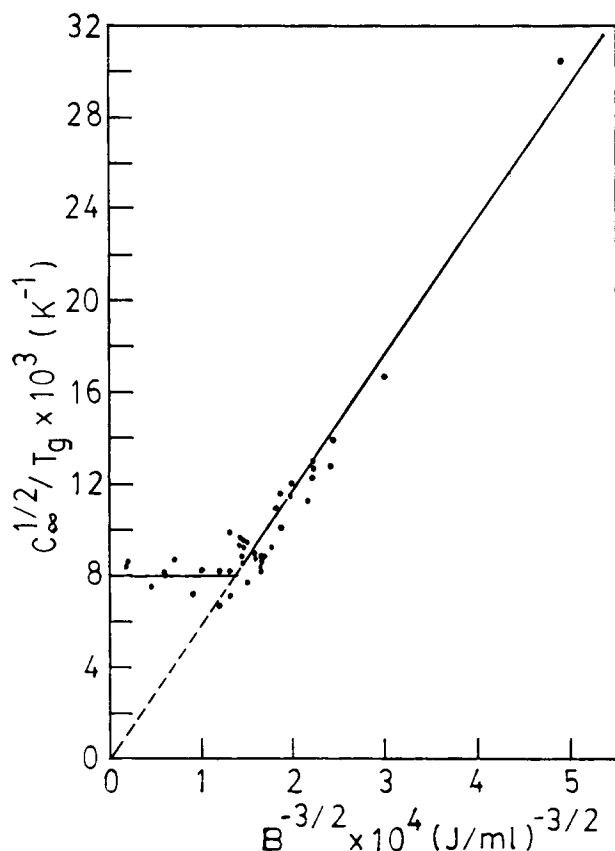
Figure 1 Plot of $C_\infty^{1/2}/T_g$ against $B^{-3/2}$ for the various polymers listed in Table I.

ticular case may be attributed to uncertainty in the δ determination.

Perhaps, the most distinct polymers studied in this work are those listed in Table I as polymers 11, 16, 21, and 27 representing an aromatic polyether, polyester, polysulfone, and polycarbonate, respectively. A common feature of these systems is that they all contain phenylene rings connected by flexible ether and/or sulfide links in the main chains that result in remarkably small C_∞. However, their T_g's are unusually high in the sense that the corresponding $C_\infty^{1/2}/T_g$ ratios are consistently and considerably lower than the expected value of 8.0×10^{-3} K^{-1}. In order to overcome this adverse situation, the foregoing aromatic polymers are assumed to be convertible to their hypothetical aliphatic counterparts having the equivalent T_g and B, but a new characteristic ratio designated by C'_∞, following a practical scheme. Here, we propose empirically

$$C'_\infty = pN_1 C_\infty/(rN_2 + sN_3) \qquad (7)$$

where p is the chain stiffness enhancing factor per skeletal phenylene structure, r and s are the chain stiffness de-

pressing factors for the chain atoms —O— and —S— respectively, and N_1 is the number of skeletal phenylene units in a repeat unit containing N_2 ether and N_3 sulfide links. Tentative assignments for the factors p, r, and s are respectively equal to 5, 1, and $\frac{1}{2}$. The values of C'_∞ obtained by eq. (7) are included in Table I, and in good agreement with eq. (6) as shown in Figure 1. Other deviant polymers are the derivatives of cellulose which, on the other hand, exhibit unexpectedly high C_∞ not listed in Table I. Attempts to deal with this particular series of polymers likewise, have, however, been hindered by the dearth of relevant information.

Some workers have resorted to the parameter σ to describe the chain flexibility instead.[7,8] It is defined by

$$\sigma = (\overline{r_0^2}/\overline{r_f^2})^{1/2} \qquad (8)$$

where $\overline{r_f^2}$ is the mean-square end-to-end distance of a model freely rotating chain. Early study has reported that T_g is a linear function of σ.[9] However, detailed investigation has outright rejected such a T_g–σ correlation.[4] The present analysis prefers C_∞ to σ for the same purpose, as the former considers the effects of restrictions on not only the chain rotation but also the bond angles. This means that the parameter C_∞ is less ambiguous than σ, particularly when diverse polymers containing distinct linkages are compared.

It has been established that

$$N_c = 10C_\infty^2 \qquad (9)$$

where N_c is the number of chain atoms between entanglements.[10] Combining eqs. (5) and (9) yields

$$N_c = 1.2 \times 10^8 T_g^4/B^6 \quad (\text{J}^6/\text{mL}^6 \text{ K}^4) \qquad (10)$$

which offers a new method to predict N_c. However, eq. (10) must be applied with caution, as eq. (9) is by no means in the exact form and valid only for selective flexible (or weak) polymers.

In conclusion, we have found that T_g is related to C_∞ and B by simple power laws expressed by eqs. (5) and (6). A total of 42 polymers has been examined and classified into two major groups, according to the strength of the intermolecular attractions. The present findings indeed contribute positively towards the better understanding of glass transition behavior. However, their theoretical origins have yet to be explored.

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