

# On the Chain Cross-Sectional Area and Motion of Macromolecular Chains

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## Synopsis

This paper attempts to relate the chain cross-sectional area to the glass transition temperature of a polymer and to discuss the effect of the chain cross-sectional area in view of the motion of molecular chains. It has been found that the definite relationship between glass transition temperature and cross-sectional area can be obtained only when taking account of intermolecular interaction of polymer chains. It is considered that the chain cross-sectional area will characterize the chain flexibility of a polymer since the glass transition temperature is related both to intermolecular interaction and chain flexibility of a polymer. The concept of the structural parameter cross-sectional area per chain, first introduced by Vincent<sup>1</sup> and used by Boyer and Miller,<sup>2-5</sup> is useful in empirically correlating properties and structures of polymers. The glass transition temperature is a basic parameter of bulk polymers and is characteristic of their intermolecular interactions and chain flexibility. This paper attempts to relate chain cross-sectional areas to glass transition temperatures of polymers and to discuss the effect of the chain cross-sectional area in view of the motion of molecular chains.

## ANALYSIS OF EXPERIMENTAL DATA

The chain cross-sectional area can be calculated from crystal lattice parameters for crystalline polymers and estimated for amorphous polymers and copolymers from the lattice parameters of crystalline homopolymers. The relation used is

$$A = V/n_1 \cdot c \quad (1)$$

where  $V = (\mathbf{a} \times \mathbf{b}) \cdot \mathbf{c}$  is the volume of the unit cell calculated from vectors of unit cell parameters,  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$ ,  $n_1$  is the number of polymer chains per unit cell, and  $c$  is the fiber periodic distance. The published values of glass transition temperatures and chain cross-sectional areas calculated from crystal lattice parameters for a number of polymers with various chemical structures are listed in Table I.

In the logarithmic plot (Fig. 1) of the values of glass transition temperatures vs. chain cross-sectional areas listed in Table I, it is noted that three straight lines, with a common origin, satisfy the following relation:

$$\log T_g = 2.18 + (\log A + 0.79) \cdot C \quad (2)$$

The slopes of the lines a, b, and c in Figure 1,  $C_a$ ,  $C_b$ , and  $C_c$ , are 3.44, 0.50, and 0.29, respectively.

Since the polymers of series (a) in Table I have the conformation of extended chains in crystalline state and mostly have polar groups, these

TABLE I  
Glass Transition Temperatures and Cross-Sectional Areas of Polymers

No.	Polymer	Area <sup>6</sup> A (nm <sup>2</sup> )	Glass temp T <sub>g</sub> (K) <sup>7</sup>	Helic type <sup>6</sup>
(a)				
1	Poly(tetramethylene oxide)	0.176	187	1/1
2	Polyethylene	0.182	200 <sup>8</sup>	1/1
3	Poly(ethylene adipate)	0.198	216	1/1
4	Poly(hexamethylene adipamide)	0.199	317	1/1
5	Poly( $\epsilon$ -caprolactam)	0.203	313	1/1
6	Poly(8-amino caprylic acid)	0.203	323	1/1
7	Poly(hexamethylene sebacamide)	0.203	323	1/1
8	Poly(7-amino enanthic acid)	0.203	325	1/1
9	Poly(11-amino undecanoic acid)	0.205	316	1/1
10	Poly(vinyl alcohol)	0.216	358	1/1
(b)				
11	Poly( <i>cis</i> -1,4-butadiene)	0.207	165	—
12	Poly(propylene oxide)	0.245	198	2/1
13	Poly( <i>cis</i> -1,4-isoprene)	0.280	200	—
14	Poly(vinylidene chloride)	0.352	254	—
15	Polypropylene	0.378	260	3/1
16	Polybutene-1	0.452	249	3/1
17	Poly(methyl acrylate)	0.593	304	—
18	Poly(vinyl acetate)	0.593	302	—
19	Poly(methyl methacrylate)	0.638	353	5/1
20	Polystyrene	0.698	373	3/1
21	Poly(vinyl isobutyrate)	0.723	329	—
22	Poly(3-methyl-butene-1)	0.742	326	4/1
23	Polyhexene-1	0.780	337	7/2
24	Poly( <i>tert</i> -butyl acrylate)	0.953	380	3/1
(c)				
25	Polytetrafluoroethylene	0.296	160	—
26	Polyisobutylene	0.434	203	8/3
27	Polypentene(II)	0.748	233	4/1
28	Poly( <i>sec</i> -butyl acrylate)	0.931	251	3/1

polymers have stronger intermolecular interactions than those of series (b) and (c). In spite of the fact that polymers of series (b) and (c) in Table I both have helical conformation in crystalline state, the larger side groups weaken intermolecular interactions of the polymers of series (c). This proposition coincides with the fact that the steepness of the slopes of lines b and c in Figure 1 are less than that of line a and with that of line c the least. In other words, the slopes of the lines in Figure 1 represent different types of intermolecular interactions for different polymer serieses in Table I. This is not unexpected on view of previous findings in the literature.<sup>4,9</sup>

## DISCUSSION

Since the differences among the polymers in series (a)–(c) in Table I lie in their difference in intermolecular interactions, an account of this factor should make the disparity in lines a–c in Figure 1 disappear. Molar cohesive energy or cohesive energy density of polymers is commonly used to characterize intermolecular interactions in polymers. Various equations relat-

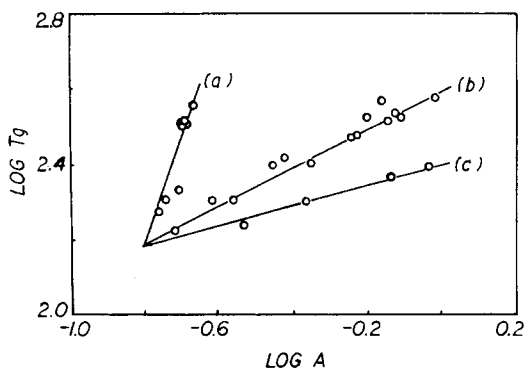


Fig. 1. Logarithmic plot of glass transition temperature vs. cross-sectional area of polymers.

ing glass transition temperature of a polymer to its molar cohesive energy or cohesive energy density have been established. For example, the suggestion by Hayes<sup>11</sup> is

$$T_g = H_c/n + 25 \quad (3)$$

and that by Kreibich and Bartzler<sup>12</sup> is

$$T_g = 0.0145 (E_{\text{col}}/\sum_i a_i) + 120, \quad (4)$$

where  $H_c$  and  $E_{\text{col}}$  are molar cohesive energy,  $n$  is the integer reflecting effective degree of rotational freedom per repeating unit, and  $\sum_i a_i$  is the total number of rotational structural factor per repeating unit. It is not difficult to find that both  $H_c/n$  and  $E_{\text{col}}/\sum_i a_i$  in eqs. (3) and (4), respectively, are the contribution of repeating units of molecular chains to molar cohesive energy. For example, the effective degree of rotational freedom,  $n$ , in eq. (3) is calculated with the repeating unit of polymer as a basic unit, so  $H_c/n$  is the contribution of the effective degree of rotational freedom from a repeating unit.

If the formula relating glass transition temperature to chain cross-sectional area is assumed to be,

$$T_g = (E \cdot A) \cdot b + a \quad (5)$$

where  $E$  is the cohesive energy density of polymer, then according to the definition of cross-sectional area by Vincent,<sup>1</sup> eq. (5) may be written as

$$T_g = (E_c \cdot M_0/\rho \cdot c) \cdot b + a \quad (6)$$

where  $M_0$  is the molecular weight of repeating unit,  $\rho$  is the density of the polymer, and the meaning of  $c$  is the same as that in eq. (1). It is noted again that dimension  $E_c \cdot M_0/\rho \cdot c$  is also a contribution of the length of the

TABLE II  
Cohesive Energy Density  $E_c$ , Cross-Sectional Area  $A$ , and Glass Temperature  $T_g$  of Polymers

No.	Polymer	$E_c^a$ (cal/cm <sup>3</sup> )	$A^6$ (nm <sup>2</sup> )	$E_c \cdot A$	$T_g^7$ (K)
1	Poly(tetramethylene oxide)	97.3 <sup>b</sup>	0.176	17.1	187
2	Polyethylene	68.9	0.182	12.5	200 <sup>6</sup>
3	Poly(hexamethylene adipate)	127.5 <sup>b</sup>	0.198	25.2	216
4	Poly(hexamethylene sebacamide)	196.0	0.199	39.0	317
5	Poly(8-amino caprylic acid)	210.3	0.203	42.7	323
6	Poly(vinyl alcohol)	310.3 <sup>c</sup>	0.216	67.0	358
7	Poly( <i>cis</i> -1,4-butadiene)	65.6	0.207	13.6	165
8	Poly(propylene oxide)	80.1 <sup>10</sup>	0.245	19.6	198
9	Poly( <i>cis</i> -1,4-isoprene)	68.9	0.280	19.3	200
10	Poly(vinylidene chloride)	98.0	0.352	34.5	254
11	Polypropylene	86.5	0.378	32.7	260
12	Polybutene-1	74.2 <sup>b</sup>	0.452	33.6	249
13	Poly(methyl acrylate)	94.1 <sup>10</sup>	0.593	55.8	304
14	Poly(vinyl acetate)	77.4	0.593	45.9	302
15	Poly(methyl methacrylate)	84.6	0.638	54.0	353
16	Polystyrene	81.0	0.698	56.5	373
17	Poly(3-methyl-butene-1)	67.5 <sup>b</sup>	0.742	50.1	326
18	Polyhexene-1	62.8 <sup>b</sup>	0.780	49.0	357
19	Polytetrafluoroethylene	38.4	0.296	11.4	160
20	Polyisobutene	62.4	0.434	27.1	203

<sup>a</sup> Obtained from data of solubility parameters of polymers in ref. 7.

<sup>b</sup> Calculated according to Ref. 13.

<sup>c</sup> Calculated according to Ref. 14.

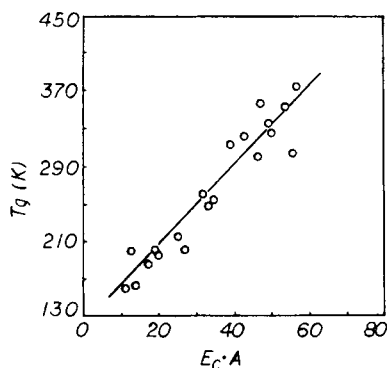
repeating unit to the molar cohesive energy. Thus, eq. (5) is established. From values of cohesive energy density  $E_c$ , cross-sectional area  $A$ , and glass transition temperature  $T_g$  in the literature (Table II), a straight line is found in the plot of  $T_g$  vs.  $E_c \cdot A$  with values of 4.33 for its slope and 116 for its intercept (Fig. 2).

Since the polymers satisfying eq. (5) are from different groups in Table I, it is reasonable to say that taking account of intermolecular interactions combines the three lines in Figure 1 into one line as shown in Figure 2.

The values of glass transition temperatures and cohesive energy densities of 1,2-polybutadienes with various content of 1,2 units were measured experimentally in this laboratory, and the chain cross-sectional areas of these samples were then obtained from eq. (5) (Table III). Obviously, 1,2-polybutadienes as an elastomer are similar to poly(*cis*-1,4-butadiene) and poly(*cis*-1,4-isoprene) chemically and physically. Since the latter two are members of series (b) in Table I, values of glass transition temperatures of several 1,2-polybutadienes are calculated with their chain cross-sectional areas from eq. (2), where  $C$  is taken as 0.50. A comparison of the experimental  $T_g$  values with the calculated ones is satisfactory (Table III). Thus eq. (5) seems reliable for estimating  $T_g$  of polymers from their  $E_c$  and  $A$  and vice versa.

The steric factor in internal rotation of the chains of 1,2-polybutadienes (Table III),  $\sigma$ , was obtained through eq. (7) from their cross-sectional area<sup>4</sup>:

$$\log \sigma = 0.38 + 0.22 \log A \quad (7)$$

Fig. 2. Relation of  $T_g$  to  $E_c \cdot A$  of polymers.

The values of  $\sigma$  and experimental  $T_g$  values satisfy eq. (8):

$$T_g = B \cdot (\sigma - d) \quad (8)$$

where  $B = 233$  and  $d = 0.93$ .

It was reported<sup>9</sup> that energy of rotational isomerization, characteristic of flexibility of macromolecular chains, could be given by

$$\epsilon = C' \cdot B \cdot k \cdot (\sigma - d) \quad (9)$$

where  $k$  is the Boltzmann factor and parameter  $C' = \epsilon/k \cdot T_g$ . Unfortunately, parameter  $C'$  is a variable quantity and then eq. (9) could not give directly the energy of rotational isomerization. According to our previous work,<sup>15</sup> the parameter  $C'$  is expressed as

$$C' = -\ln\left(\frac{\Delta\alpha \cdot T_g}{1 - \Delta\alpha \cdot T_g}\right) \quad (10)$$

where  $\Delta\alpha$  is the difference in coefficients of volume expansion of a polymer in glassy state and liquid state, respectively. Combination of eqs. (8)–(10) give the energy of rotational isomerization of 1,2-polybutadienes as listed

TABLE III  
Cross-Sectional Area and Energy of Rotational Isomerization of 1,2-Polybutadienes

Content of 1,2 unit	$E_c$ (cal/cm <sup>3</sup> )	$T_g$ (K)		$A^c$ (nm <sup>2</sup> )	$\sigma^d$	$\Delta\alpha$ $\times 10^4$	$\epsilon$ (kcal/mol)		
		a	b				This work	Ref. 15	Ref. 15
30%	74.0	188	178	0.22	1.73	4.77	0.86	0.87	0.82
50%	72.3	209	205	0.30	1.84	4.21	0.99	0.97	0.91
66%	72.3	221	218	0.34	1.87	3.75	1.05	1.06	0.96
90%	72.3	249	245	0.43	1.99	3.31	1.18	1.19	1.08

<sup>a</sup> Experimental values.

<sup>b</sup> Obtained from eq. (2) with values of  $A$  in Table III.

<sup>c</sup> Obtained from eq. (5) with experimental values of  $E_c$  and  $T_g$  in Table III.

<sup>d</sup> Obtained from eq. (7) with values of  $A$  in Table III.

<sup>e</sup> Obtained from eqs. (8)–(10).

in Table III. These  $\epsilon$  values coincide with the other two groups of values reported in our previous paper.<sup>15</sup>

It is seen in Table III that increasing in the content of 1,2 units makes internal rotation of the chains of 1,2-polybutadienes more difficult and their chain cross-sectional areas larger; therefore, the chain cross-sectional area does relate to the internal rotation of polymers and hence to the flexibility of the chains.

Since cohesive energy density and chain cross-sectional area characterize intermolecular interactions and chain flexibility respectively, it should be reasonable to estimate glass transition temperature of polymers, at least the polymers discussed, by eq. (5), because the glass transition temperature of a polymer depends on both intermolecular interactions and chain flexibility.

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