

Molecular Stiffness and Thermal Properties of Polymers

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Synopsis

Because it merely reflects rotational hindrance, the parameter σ alone does not convey a measure of chain stiffness. Stiffness can arise from short links joined by rigid joints, or from long, stiff links with flexible joints. Flexibility results from the absence of rigid joints and stiff, long links. The slope of the product $\sigma\Delta T$ versus T_R indicates stiffness; the higher the slope, the stiffer the chain. The polymers whose thermal data are presented in this paper are divisible into two major groups. Those whose $d(\sigma\Delta T)/dT_R = 1.37$ are flexible, and those whose $d(\sigma\Delta T)/dT_R = 3.44$ are stiff. The indication is that there exists a direct relationship between the polymer expansivity above T_g and the stiffness parameter of the chain.

INTRODUCTION

It is now well established, through small-angle neutron scattering¹⁻⁴ and persistence length determinations,⁵ that the unperturbed dimensions of macromolecules in solution under θ conditions are retained with no substantial change in the solid amorphous state of the polymer. The unperturbed dimensions of a macromolecule, i.e., pervaded volume or end-to-end distance per repeat unit, depend on the overall stiffness of the chain; the stiffer the chain, the larger the dimensions would be. The chain stiffness is dictated, in turn, by several interrelated parameters such as rotational freedom around chain bonds, angular restrictions along the chain, interference by pendent groups or atoms, and hindered flexibility due to rigid structures within the chain.

A measure of rotational freedom derives⁶ from a comparison of the experimentally determined unperturbed end-to-end distance per repeat unit, $(\langle r^2 \rangle_0/nl^2)^{1/2}$, with an end-to-end distance per repeat unit calculated theoretically assuming free rotation of the chain elements, $(\langle r^2 \rangle_{of}/nl^2)^{1/2}$, where r is the end-to-end distance, $\langle r^2 \rangle_0$ and $\langle r^2 \rangle_{of}$ are root-mean-square unperturbed and freely rotating end-to-end distances, n is the number of repeat units, and l is the length of each such unit.

The characteristic ratio

$$(\langle r^2 \rangle_0/\langle r^2 \rangle_{of})^{1/2} = \sigma \quad (1)$$

describes the restrictions on chain rotation; the larger the σ value, the more hindered is the rotation.

TABLE I
 Polymer Characteristics

No.	Polymer	T_g , °K	$\alpha_L \times 10^4$	$\alpha_G \times 10^4$	$\Delta\alpha \times 10^4$ ^a	ΔT , °K	T_R , °K	$\Delta\alpha \cdot T_g$	$\Delta\alpha \cdot \Delta T$	σ^a	$\sigma \cdot \Delta T$, °K
1	Poly(methyl acrylate)	275			3.80	306	584	.1055	.1165	2.05(8)	627
2	Poly(ethyl acrylate)	251			3.30	399	650	.0828	.1320	2.1(9)	840
3	Poly(<i>n</i> -butyl acrylate)	217			3.40	413	630	.0739	.1405	1.8(9)	744
4	Poly(morpholide acrylate)	418			2.40	501	919	.1002	.1205	2.42(8)	1212
5	Poly(piperolide acrylate)	381			2.50	494	875	.0952	.1235	2.30(8)	1136
6	Poly(methyl methacrylate)	378			3.15	377	755	.1190	.118	2.08(8)	784
7	Poly(iso-methyl methacrylate)	320	5.83	2.34	3.49(10)	326	646	.1117	.1138	2.14(11)	698
8	Poly(ethyl methacrylate)	338			2.88	420	758	.0970	.121	1.96(8)	823
9	Poly(<i>n</i> -butyl methacrylate)	300			2.58	530	830	.0770	.136	1.98(8)	1049
10	Poly(<i>n</i> -hexyl methacrylate)	268			2.40	625	893	.0643	.150	2.25(8)	1406
11	Poly(<i>n</i> -octyl methacrylate)	253			2.35	665	918	.0595	.156	2.19(8)	1456
12	Poly(<i>n</i> -dodecyl methacrylate)	208			3.00	510	718	.0624	.153	2.59(8)	1320
13	Poly(cyclohexyl methacrylate)	380	5.91	2.93	2.98(12)	379	759	.1132	.1129	2.15(13)	815
14	Polystyrene	373			3.565	295	668	.146	.105	2.22(8)	655
15	iso-Polystyrene	360			3.3(14)	334	694	.1188	.1102	2.3(15)	768
16	Poly(<i>p</i> -bromostyrene)	391			3.38(16)	309	700	.1322	.1044	2.3(17)	711
17	Poly(α -methylstyrene)	445			3.00	343	788	.1335	.1030	2.30(8)	789
18	Poly(<i>o</i> -methylstyrene)	403			2.71	422	825	.109	.114	2.27(18)	960
19	Poly(<i>p</i> -chlorostyrene)	383			2.9(16)	393	776	.1111	.1140	2.18(8)	857
20	Polyethylene	188			5.10	242	430	.0955	.1235	1.63(8)	394
21	Polypropylene	256			4.18	276	532	.107	.115	1.85(18)	511
22	iso-Polypropylene	298		1.97	2.69(19)	499	797	.0802	.1342	1.93(20)	963
23	Poly-1-butene	249			4.25	274	523	.106	.116	1.82(8)	502
24	Polyisobutene	198			3.92	348	546	.0778	.136	1.80(8)	626
25	Polyisobutylene	200			4.175	320	520	.0835	.1335	1.80(8)	576
26	Polybutadiene	180			4.40	305	485	.079	.134	1.45(8)	442
27	iso-Polypentene-1	273	6.65	3.66	2.99(21) ^b	445	718	.0816	.1331	2.13(13)	948
28	Natural rubber	201			4.48	285	486	.090	.1275	1.71(22)	487
29	Poly- <i>cis</i> -isoprene	203			4.26	304	507	.0866	.1290	1.74(13)	492
30	Poly- <i>trans</i> -isoprene	205			4.87	247	452	1.000	.120	1.46(22)	361
31	Poly(4-methylpentene-1)	302			3.78	298	600	.1145	.112	2.2(18)	656
32	Polychloroprene	233			4.3	279	512	1.00	.120	1.40(8)	391

33	Poly(oxymethylene)	190	4.75	265	455	.090	.1255	1.9(13)	503
34	Poly(ethylene oxide)	206	5.95(11)	182	388	.1226	.1083	1.63(11)	298
35	Poly(propylene oxide)	198	6.0(11)	267	465	.1020	.119	1.59(8)	398
36	Poly(tetramethylene oxide)	187	6.4(11)	172	359	.1197	.1101	1.68(11)	289
37	Poly(2,6-dimethyl-1,4-phenylene oxide)	480 ^a	3.95	220	700	.190	.087	1.0(23)	220
38	Poly(2,6-diphenyl-1,4-phenylene oxide)	493	5.65	128	621	.2785	.0724	1.1(23)	141
39	Poly(vinyl methyl ether)	251	4.29	269	520	.1077	.1150	2.23(13)	600
40	Poly(vinyl alcohol)	358	7.20	318	676	3.78	1.088	2.04(8)	649
41	Poly(vinyl acetate)	305	4.30	244	549	3.42(24)	1.312	2.12(8)	517
42	Poly(vinyl chloride)	357	4.19	233	590	4.30	.098	2.37(11)	552
43	Poly(chlorotrifluoroethylene)	325	3.84	280	605	4.19	1.245	2.03(8)	568
44	Poly(vinylidene fluoride)	318(25)	2.83(24)	447	765	.0900	1.265	1.66(26)	742
45	Poly-ε-caprolactam	290	4.04	275	565	.117	.111	1.63(8)	448
46	Poly(hexamethylenedipamide)	323	3.46	326	649	.112	.113	1.63(8)	531
47	Poly(hexamethylenesbacamide)	323	4.30	237	560	.139	.102	1.7(27)	403
48	Poly(N,N-dimethylacrylamide)	362	3.0	378	740	.1085	.113	2.17(8)	820
49	Polyacrylamide	426	1.56	945	1371	.0665	1.475	2.72(8)	2560
50	Polyacrylonitrile	378	1.8	810	1188	.0680	1.46	2.37(8)	1920
51	Poly(ethyl adipate)	216	6.1(11)	172	388	.1318	.1049	1.68(11)	289
52	Poly(ethylene terephthalate)	340	3.48	318	658	.118	.1105	1.4(28)	445
53	Polycarbonate of bisphenol A	420	3.10	340	760	.130	.105	1.8(29)	612
54	Poly(γ-benzyl-L-glutamate)	285	2.7	507	792	.0770	.1365	2.32(8)	1175
55	Poly(oxy-1,4-phenylsulfonyl-1,4-phenylene isopropylidene-1,4-phenylene)	462	7.3	91	552	.337	.0665	1.03(30)	94
56	Poly(dimethylsiloxane)	150	5.5	240	390	.0825	.132	1.35(13)	324
57	Cellulose acetate	430	1.60	223	653	.069	.0358	1.61(13)	359
58	Cellulose tributyrate	365	5.6	535	900	.0876	1.284	1.79(13)	958
59	Cellulose nitrate	440	5.30	148	588	.233	.0785	1.77(13)	262
60	Cellulose tricaproate	223	5.5	1053	1276	.0401	.1895	2.65(8)	2790
61	Cellulose tricaprillate	204	9.9	172	376	.1265	.1066	2.35(8)	404

^a Numbers in parentheses are reference numbers. All unreferenced thermal expansion and T_g data are taken from ref. 7.

^b Calculated from dilatometer data in this reference.

^c These values are expansivities and are estimated to be about 10% smaller than the correct coefficients of expansion.

DISCUSSION

The glass transition temperature T_g is the temperature at which long-range segmental mobility sets in. At this temperature, sufficient free volume exists in the system and enough kinetic energy is possessed by an average segment so that segmental mobility through the formation and filling of effective holes ensues.⁷ Long-range segmental mobility is expected to be related to the characteristic ratio σ and, therefore, one may expect a dependence of T_g on σ . A plot of the σ values of the polymers in Table I against T_g reveals no such dependence. The bulk of the data points fill a block covering the range of $1.6 < \sigma < 2.35$ and $185^\circ < T_g < 445^\circ\text{K}$.

A characteristic temperature of polymers, T_R , was recently described^{7,32} as the temperature at which the number of nonbonded nearest neighbors (NN) of each segment is one less than at T_g . The T_R is also defined as the temperature at which the extrapolated strength of a polymer reaches zero and becomes independent of the loading rate.³³ The temperature value of T_R is determined by the combined effect of two variables: the amount of free volume present in the polymer at T_g and the rate of expansion above T_g . Numerically, T_R is calculated^{32,34} from T_g and $\Delta\alpha$, the difference between α_L and α_G the coefficients of expansion above and below T_g . Plots of σ against T_R and σ against $\Delta T = T_R - T_g$ fail to reveal any relationship between σ and these temperatures. On the contrary, the wide temperature range associated with each σ , and vice versa, in the three plots $\sigma - T_g$, $\sigma - T_R$, and $\sigma - \Delta T$ indicate that no simple σ -temperature relationship exists. A plot of ΔT versus T_R of the polymers in the table reveals a very broad scatter of the data points and no obvious dependence of one temperature on the other.

When the product $\sigma\Delta T$ is plotted against T_R , as in Figure 1, two linear relationships between $\sigma\Delta T$ and T_R emerge. Since no relationship between σ and T_R or ΔT and T_R was observed, the existence of a relationship between $\sigma\Delta T$ and T_R is most intriguing. In light of the experimental difficulties in obtaining accurate $\Delta\alpha$ and σ values, and because such data were obtained in various laboratories from different samples, the correlations between $\sigma\Delta T$ and T_R seem to be significant and the fit of all but one (number 12) of the points remarkable. The numbers of the polymers in Figure 1 corresponds to their enumeration in Table I.

Since $\Delta T (= T_R - T_g)$ reflects the ease of expansion above T_g and σ , the rotational hindrance, the rate of change of their product with T_R , $d(\sigma\Delta T)/dT_R$, may be construed to reflect the overall chain rigidity. We shall call it the stiffness parameter. The lower slope line in Figure 1,

$$\sigma\Delta T = 1.37(T_R - 175) \quad (2)$$

belongs to the flexible polymers. These are characterized by average σ values and relatively short links between flexible joints. The stiffness parameter associated with this line is

$$d(\sigma\Delta T)/dT_R = 1.37; T_R \geq 175^\circ\text{K} \quad (3)$$

The steeper slope line,

$$\sigma\Delta T = 3.44(T_R - 535) \quad (4)$$

is associated with relatively rigid polymers. Its stiffness parameter is

$$d(\sigma\Delta T)/dT_R = 3.44; T_R \geq 535^\circ\text{K} \tag{5}$$

Polymers such as the polyamides may be considered of intermediate stiffness, leading to an intermediate stiffness parameter; but, as of now, there is insufficient data available concerning this point.

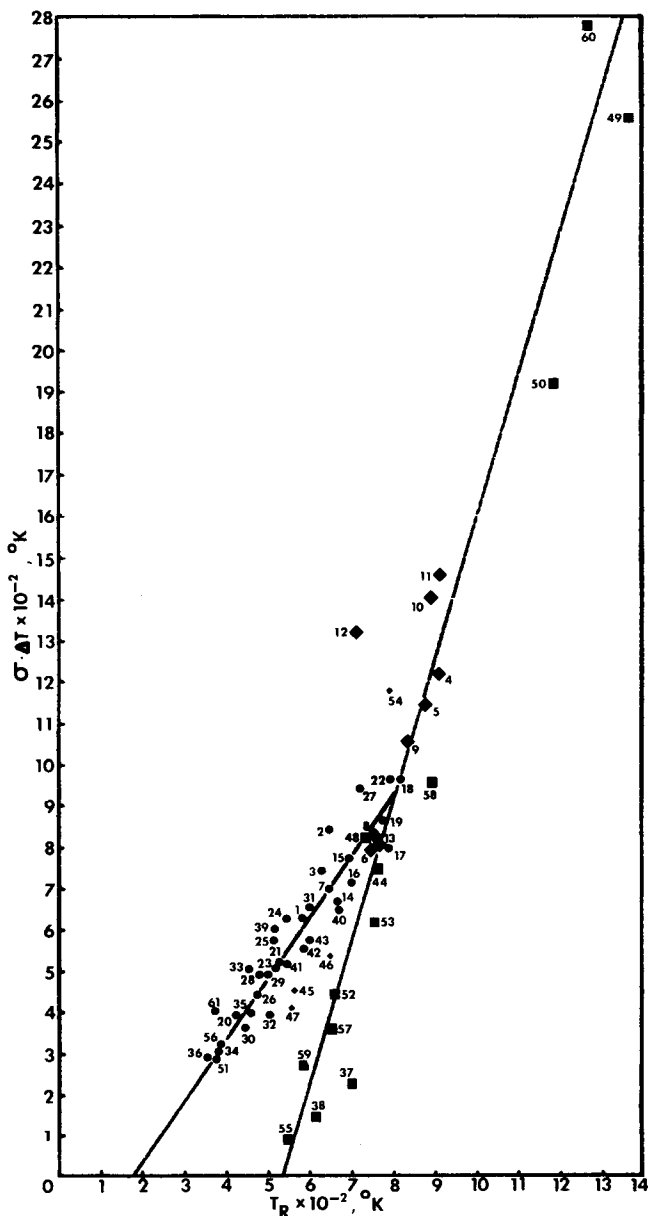


Fig. 1. $\sigma\Delta T-T_R$ relationship: (●) flexible polymers, (■) rigid polymers, (◊) methacrylates and acrylates rigidized because of large pendant groups; (◆) semicrystalline polyamides.

Equations (2) and (4) can be recast in another form, revealing a dependence of T_R on both T_g and σ :

$$T_R(\sigma - 1.37) = \sigma T_g - (1.37)(175) \quad (6)$$

replaces eq. (2) and

$$T_R(\sigma - 3.44) = \sigma T_g - (3.44)(535) \quad (7)$$

replaces eq. (4). It is evident that the functional dependence of T_R on T_g and σ is the same for all polymers but that numerically the relationship depends on the rigidity, or flexibility, characteristics of the individual polymers. Close approximations can be derived from the values associated with the lines in Figure 1, keeping in mind that the latter are only averages of many polymers.

The rigid polymers, described by eq. (5), can be cast into two classes:

a. Polymers with long and stiff links between very flexible joints. These appear only in the range of $\sigma\Delta T < 950^\circ\text{K}$. Examples are polycarbonate (53 in Table I), poly(phenylene oxides) (37 and 38) and polysulfone (55). These polymers are all tough at temperatures far below T_g .

b. Polymers with short links between rigid joints. The latter are made stiff either because of bulky pendent groups or because of the effects of polar pendent groups. The polymers in this category appear in the range of $\sigma\Delta T > 950^\circ\text{K}$ and examples are polyacrylonitrile (50 in Table I), polyacrylamide (49), poly(morpholide acrylate) (4) and poly(*n*-octyl methacrylate) (11). These polymers are considerably more brittle below T_g than those whose $\sigma\Delta T < 950^\circ\text{K}$.

In a previous paper,⁷ it was demonstrated that the rate of change of fractional free volume ($\Delta\alpha\cdot\Delta T$) in the ΔT interval is typical of homologous polymer families. The rate, defined as $d(\Delta\alpha\cdot\Delta T)/d(\Delta T - T_g)$, is about 1.65×10^{-4} for flexible polymers such as the polyolefins, 1.35×10^{-4} for the poly(vinyl ethers), about 1×10^{-4} for the stiffer methacrylates, and 0.8×10^{-4} for such stiff polymers as polyacrylonitrile and polyacrylamide. Upon comparison, one observes that the data points for the line $\sigma\Delta T = 1.37(T_R - 175)$ in Figure 1 are for polymers whose $d(\Delta\alpha\cdot\Delta T)/d(\Delta T - T_g) > 1.3 \times 10^{-4}$, and the points on the line $\sigma\Delta T = 3.44(T_R - 535)$ are for polymers whose $d(\Delta\alpha\cdot\Delta T)/d(\Delta T - T_g) < 1.3 \times 10^{-4}$. The interval around 1.3×10^{-4} covers the polyamides which are intermediate in the $\sigma\Delta T$ - T_R relationship, too.

The above observations indicate that an inverse, and possibly complex, relationship exists between the ease of expansion of a polymer above T_g and the stiffness parameter: the stiffer the polymeric chain, the harder the expansion of the polymeric bulk. It is also evident that further experimental and theoretical work is required to elucidate the mutual relations between such parameters as σ , $\sigma\Delta T$, $d(\sigma\Delta T)/dT_R$, $\Delta\alpha$, T_g , ΔT , and T_R .

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