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Dependence of T_g (K) on the Product of the Cohesive Energy Density (CED) and Chain Stiffness Parameter C_∞

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ABSTRACT: A selected group of standard atactic polymers with CC, CO, diene, and SiO backbones and some crystalline polymers for which an amorphous phase T_g is known have T_g's which increase with the product of cohesive energy density (CED) times the characteristic ratio (C_∞), falling on either of two straight lines of positive slope, intersecting at $T_g = 118$ K. The principal difference between polymers on the two lines concerns their low-frequency mechanical relaxation spectra: upper line polymers tend to have a relatively strong $T_\beta \sim 0.75T_g$ but weak or missing $T_\gamma < T_\beta$; those on the lower line show a weak or missing T_β and a strong T_γ arising from side-group motion about the C–R bond. This motion appears to generate extra free volume in the glassy state for the lower-line polymers compared to those in the upper line. All polymers follow the conventions $\Delta\alpha T_g = 0.113$ and $\alpha_l T_g = 0.164$. Polymers with longer side chains, i.e., poly(n-butyl methacrylate), poly(ethyl acrylate), and polybutene-1, no longer lie on their respective lines. Many prior studies may have failed through inclusion of polymers of diverse structural types, i.e., in-chain rings, cellulosics, long side chains, etc., in addition to the basic standard polymers selected herein and generally included in some earlier studies. CED × C_∞ may be thought of as the product of a persistence length times an intermolecular force.

Introduction

Polymer scientists have long sought to understand the dependence of T_g on polymer structure, i.e., chemical factors such as cohesive energy density (CED)[1] and energy of hole formation, ϵ_h,[2,3] and/or physical factors such as chain stiffness σ[4] and flex energy.[5] We have reviewed CED and σ factors on prior occasions,[6,7] the latter being primarily concerned with employing correct values of T_g for the amorphous phase of semicrystalline polymers, notably polyethylene (PE) and poly(tetrafluoroethylene) (PTFE).

Then a more recent consideration of the T_g–CED studies led us to the tentative conclusion that (a) inclusion of too many polymers of diverse structural type, especially the homologous series of poly(alkyl acrylates), methacrylates, and poly(alkyl vinyl ethers), was responsible for much of the observed scatter and (b) a product of C_∞ × CED might be a better parameter than either alone.

Hence, a small set of relatively basic polymer types with CC, CO, diene, and SiO backbones was chosen. These are assembled in Table I which lists T_g, CED, and C_∞ values, the latter being the characteristic ratio of Flory[9] recommended to us by Stockmayer[10] as more meaningful than the σ values of Kurata and Stockmayer.[11] Also listed is the product C_∞ × $\mathrm{CED_R}$ where CED is the ratio CED_x/CED(PE).

Values of T_g, σ, C_∞, and CED were located where possible in several editions of the *Polymer Handbook*.[12] CED values were also taken from Van Krevelen; both numerical values were from Table 7.5 and Table 7.4 which permitted the calculation of CED from group values.[13] Incidentally, we found a rather exact linear correlation between σ^2 and C_∞ which proved useful on a few occasions when only σ or C_∞ values were available.

These data were evaluated as T_g–CED, T_g–σ, σ^2, and T_g–C_∞ hand plots (not shown). The first one still exhibited unsatisfactory scatter, while the σ^2 and C_∞ plots were both relatively linear. It then occurred to us that since T_g was a function of both CED and σ^2 or C_∞ a combined function of (CED,σ) was indicated. For scaling reasons, the following equation was finally chosen:

$$T_g = K(C_\infty \times \mathrm{CED_R}) \qquad (1)$$

where $\mathrm{CED_R}$ is the ratio of CED_x for any polymer to that of a standard polymer arbitrarily chosen as amorphous PE. This relation left the argument as a small dimensionless parameter ranging from 1 to 20 for most common polymers.

Figure 1 shows the computer-drawn least-squares lines for the data of Table I. Unexpectedly, the data required a two-line fit with no points in between. The equations of those lines are as follows:

top line (7 points)

$$T_g\ (\mathrm{K}) = 93.8 + 20.9X \qquad (2)$$

$$R^2 = 0.879$$

$$\text{standard error in } T_g(\text{calc}) = \pm 25.5\ \mathrm{K}$$

(The point for atactic poly(methyl methacrylate) (at-PMMA) is plotted but not used in regression analysis.)

lower line (4 points)

$$T_g\ (\mathrm{K}) = 38.1 + 18.7X \qquad (3)$$

$$R^2 = 0.953$$

$$\text{standard error in } T_g(\text{calc}) = \pm 20.0\ \mathrm{K}$$

The correlation coefficients are reasonably good even with the small number of data points. Naturally a rationale for the existence of two lines was desirable, to be followed by the selection of additional polymer types which might be expected to fit one or the other line. Early consideration was given to a natural tendency for tactic sequences in atactic polymers because an atactic form of poly(vinyl acetate) (PVAc) was not known. However, since T_g is affected only in disubstituted polymers such as PMMA, this approach was quickly dropped.

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Table I
Preselected Simple Polymers and Their Properties

no.	polymer[a]	T_g (K)	CED[b] (cal/cm^3)	C_∞[c]	C_∞(CED)$_R$[d]	locus in Figures 1 and 3[e]
1	PDMS	150[f]	54	7.8	6.94	L
2	*cis*-PBD	171[f]	73	5.15	6.18	L
3	PE	195[c]	61	5.3	5.3	U
4	PIB	195[f]	64	5.80	6.09	U
5	PEO	165[f]	63	3.8	3.8	U
6	*cis*-PI	203[f]	72	5.0	5.9	U
7	at-PP	260[f]	69	6.2	7.0	U
8	PMA[h]	273[f]	95	8.4	13.0	L
9	PnBMA	294[f]	77	8.6	10.8	U
10	PVAc	303[f]	92	9.0	13.6	L
11	at-PS	373[f]	87	8.4	12.0	U
12	at-PMMA	380[f]	87	6.9	9.8	U

[a] Arranged in order of increasing T_g. [b] Cohesive energy density in calories per cubic centimeter. Multiply by 4.18 to obtain joules per milliliters. [c] Characteristic ratio of Flory, dimensionless.[9] [d] (CED)$_R$ is the cohesive energy density relative to that of PE (CED = 61 cal/cm^3) as a means of obtaining small dimensionless numbers. [e] L signifies that the polymer falls on the lower line of Figure 4 and U that the polymer falls on the upper lines of Figures 1 and 3. These loci were found experimentally and were not predicted. [f] Molecular weights are not known but are believed to be well above the oligomeric range because of the high values of T_g.

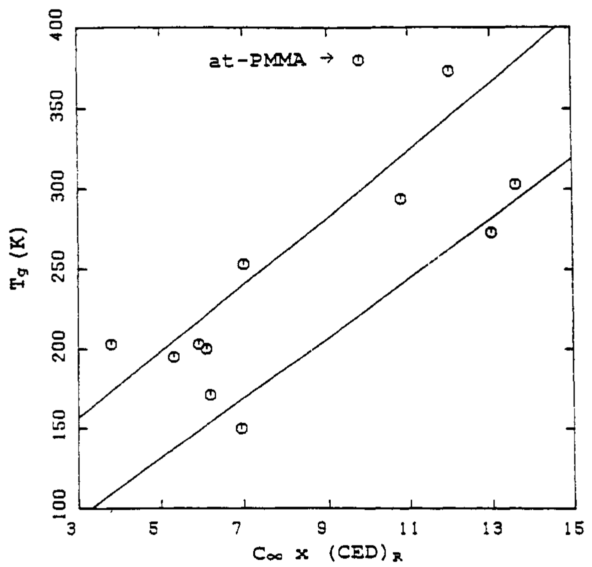

Figure 1. Linear least-squares lines showing T_g vs $C_\infty \times$ CED$_R$ for the polymers in Table I.

A tentative hypothesis based on our extensive background[6] in observing the mechanical and/or dielectric relaxation "spectra" of atactic polymers, i.e., tan δ or G'' or J'' vs T or tan δ or ϵ'' vs T plots suggested the following:

(A) Polymers in the top line have a relatively strong T_β at $0.75T_g$ but a missing or weak $T_\gamma < T_\beta$, both considered to arise from motion about the chain axis.

(B) Conversely, polymers on the bottom line, strongly influenced by results on polymethacrylate (PMA) and PVAc, were considered to have a weak or missing T_β and a relatively strong T_γ arising from side-group motion about an axis to the chain backbone.

One early concern involved the role of CH_3 which is attached to the main chain as in polypropylene (PP) and polyisobutylene (PIB) and the α-CH_3 side group in PMMA. They are also attached to ester groups as in PMMA and to ether groups. Their frequency of rotation from polymer to polymer varies over 6 orders of magnitude, at a fixed temperature from poly(dimethylsiloxane) (PDMS) to the α group in PMMA.[14] PDMS has a rotational frequency of 10^{16} Hz at T_g.[15] CH_3 groups exist in polymers in both lines. CH_3 rotation is the only side-group motion available to PDMS, PPO, and poly(methyl vinyl ether) (PMVE). The presence of PVDC on the lower line seems anomalous since it lacks CH_3 and $T < T_g$ motion.

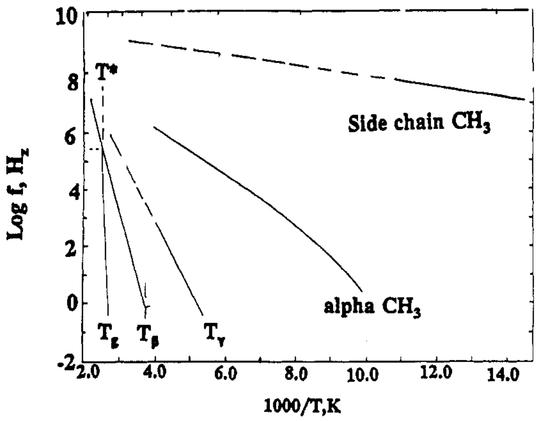

Figure 2. Schematic relaxation map showing low-frequency (1–10-Hz) loss, tan δ vs 1000/T (K). This is a composite of the actual data on several polymers, such as at-PS and at-PMMA, based on Figures 8.8 and 10.35 of McCrum et al.[16]

Table II
Postselected Simple Polymers Based on Table I and Figure 2

no.	polymer[a]	T_g (K)	CED[b] (cal/cm^3)	C_∞[c]	$C_\infty \times$ CED$_R$[d]	predicted locus[e]	actual locus[e]
13	*trans*-PI	266	72.0	7.2	8.5	U	U
14	*trans*-PBD	215	73.0	5.8	6.94	U	U
15	PVME	242	62	9.95	9.95	L	L
16	PVDCl	255	102	8.10	13.0	?	L
17	PEA	256	88	10.9	15.7	L	L
18	iso-PMMA	323[f]				?	L
19	PVC	353	93	6.70	10.2	U	U
20	PAN	374[g]	162	9.70	25.9	?	
21	PtBS	414	60	13.4	13.3	U	U
22	PαMS	433	80	10.5	13.8	U	U
23	PMAN	377	105	11.5	19.9	L	L
24	PΦMSi	247	95.5	8.35	13.1	L	L
25	PPO	198	74.1	5.05	7.07	L	L

[a] Does not follow increasing T_g. [b] Same as Table I. [c] Same as Table I. [d] Same as Table I. [e] Based on Table I and Figure 2. [f] It was decided that tactic PMMAs followed a different set of rules for T_g. iso-PMMA falls exactly on the lower line. There is also uncertainty about CED values. [g] Concern about crystallinity and uncertainty about T_g.

We then reviewed the extensive survey of world literature presented by McCrum et al.,[16] a smaller survey by McCall, who also emphasized NMR results,[17] the torsion pendulum data of Schmieder and Wolf,[18] which listed the 1–10 Hz loci of T_β and T_γ for numerous polymers, the extensive thermal expansion data of Simha et al. for poly(alkyl methacrylates)[20] and poly(alkyl vinyl ethers),[21] an extensive tabulation of polymer parameters by Wrasidlo,[2] and specific references from the current literature, especially those cited in refs 16 and 17. All of these sources confirmed our tentative hypothesis which can be better appreciated by consideration of the schematic drawings of Figure 2.

For polymers lacking a T_β, literature sources frequently label T_γ as T_β. For our purposes, it is important to specify that T_β (K) $\sim 0.75T_g$ at $f \sim 1$ Hz and $1.2T_g$ at the intersection of T_β with T_g. T_γ is polymer specific, does not intersect the T_g locus, and has, instead, a frequency above $\sim 10^6$ at T^*. $T_\gamma \ll 0.75T_g$.

This relaxation map represents at-PMMA if the T_γ locus is removed; it represents at-PS if the two loci for CH_3 groups are removed. It might represent poly(α-methyl,

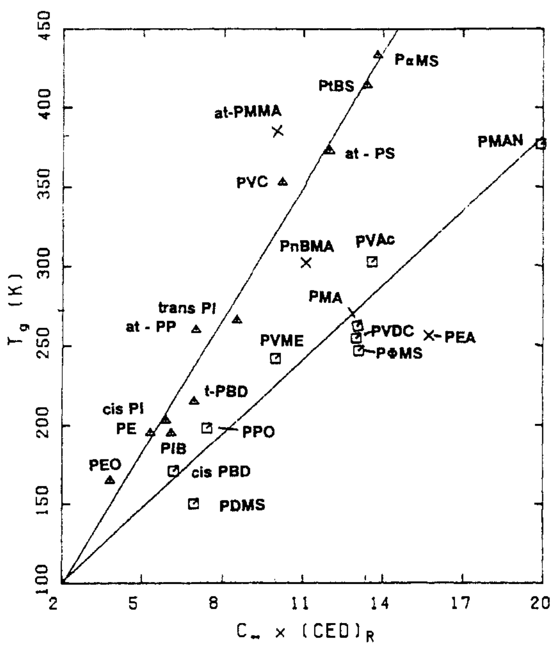

Figure 3. Linear least-squares lines for the combined sets of polymers in Tables I and II.

ring methoxy)polystyrene, for which pertinent parameters have not been located.

Having provided an initial justification for our hypothesis, additional polymers were now selected with the expectation that they would fall either on the top line, i.e., PS derivatives and poly(n-butyl methacrylate) (PnBMA) or on the bottom line, i.e., PPO, PMVE, and poly(ethyl acrylate) (PEA). This group of additional polymers is collected in Table II. The last column predicts L and U line loci. The results from Tables I and II are plotted in Figure 3. Linear least-squares regression lines are as follows:

upper line (11 points)

$$T_g = 43.1 + 27.96X \tag{4}$$

$$R^2 = 0.973$$

$$\text{SEY calc} = 16.5 \text{ K}$$

(Points for PMMA and PnBMA are shown but not included in the calculation.)

lower line (9 points)

$$T_g \text{ (K)} = 69.5 + 15.6X \tag{5}$$

$$R^2 = 0.919$$

$$\text{SEY calc} = 21.4 \text{ K}$$

(The point for poly(ethyl acrylate) was not included in the calculation.) Each line gained additional points much as anticipated. The R^2 coefficient was improved in both cases. PMAN is an example for which no spectrum was located by us. Thermally stimulated (electrical) current (TSC) traces[27] were obtained which indicated the presence of two low-temperature events, a T_β as shown in Figure 4 and T_γ. This point fell on the lower line and determined its high-temperature terminus. A CH_3 group frequency by NMR was not located for PMAN; T_g at 371 K was found but is not shown.

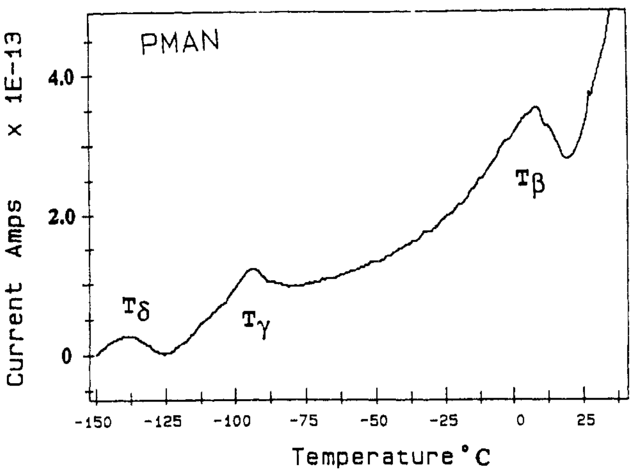

Figure 4. Thermally stimulated electrical discharge (TSC) trace[19] showing several glassy state relaxations to which we assign the designations T_β and T_γ based on the conventions of Figure 2. Effective frequency ~ 1 Hz. T_g at 377 K (not shown) has a peak intensity of 3×10^{-10} A.

The approximately parallel original lines of Figure 1 now diverge—the top line increasing in slope and the bottom line decreasing over the corresponding Figure 1 lines. The increase in the slope for the upper line was influenced by use of several PS derivatives; the decrease for the lower line arose largely from PMAN. An intersection falling just below the point for PDMS, i.e., at $T_g \sim 118$ K, prompted a search for such a polymer, possibly poly(diethylsiloxane) for which a C_∞ value was not found.

Discussion of Results

Having shown a two-locus empirical correlation between T_g and $\text{CED}_R \times C_\infty$, a molecular interpretation is now in order. We propose the following:

As shown in Figure 2, organic polymers exhibit a series of loss peaks below T_g. Linear thermal expansion data reveal a small number of step increases in the coefficient of expansion for the glassy state.[14,15] There is a one to one correspondence along the temperature scale for these two phenomena in any given polymer, assuming low-frequency loss data. Thermal expansion data signify a step increase in free volume in the glassy state associated with the onset of motion.

This can be seen in the combined linear thermal expansivity data and mechanical loss data of Simha and collaborators for a series of poly(alkyl methacrylates)[20] and poly(alkyl vinyl ethers).[21] A one to one correspondence between dynamic mechanical loss peaks and step increases in thermal expansion in the glassy state was found. A comparison of Figure 7 of ref 20, torsion pendulum loss plots, and the corresponding expansion data for the same polymers in Figure 2 of ref 20 are illustrative, as in the multiple loss peak data of Figure 7 with the expansivity data of Figure 2, both for poly(vinyl n-butyl ether) both in ref 21. Dielectric loss data are also cited in Figure 1 of ref 21.

This one to one correspondence between loss data and thermal expansivity at T_g has long been known for T_g. Systematic studies on the glassy state by Simha et al.[20,21] extend these results well below T_g, usually to liquid-N_2 temperature.

Newer thermal expansion data on several key polymers such as at-PS, at-PMMA, and poly(vinyl chloride) (PVC) from 113 to ~473 K have been presented by Greiner and Schwarzl.[22] These authors indicate loci for mechanical loss data. Their results include data for the top-line polymers of Figures 1 and 2 and none for the bottom-line polymers.

Table III
Values of $\Delta\alpha$ (10^{-4}) for Upper and Lower Line Polymers of Figure 3

authors	PS	PMMA	PVA	PMA	PMVE
		A. Measured			
S/B[a]	3.0	3.75(2)	3.9	3.9	
S/M/S[b]	3.09	3.09	4.38	3.59	
Wrasidlo[c]	3.35(2)	2.96(4)	3.76(2)	2.9	4.29
S/S/A[d]					4.30
Illers[e]			4.49	4.49	
ave	3.20	3.30	3.95	3.72	4.295
$\Delta\alpha T_g$	0.119	0.125	0.119	0.103	0.104
		B. Calculated			
$\Delta\alpha = 0.113/T_g$	3.03	2.99	3.73	4.06	4.67

[a] Simha and Boyer.[23] [b] Sharma, Mandelkern, and Stehling.[25] [c] Reference 2. [d] Schell, Simha, and Aklonis.[21] [e] K. H. Illers from refractive index–temperature. See Figures 14 and 15 of *Kolloid Z. Z. Polym.* **1963**, *190*, 16.

Thermal expansivity data and free-volume considerations just discussed invoke a reexamination of the Simha–Boyer relations for conditions at T_g[23]

$$\Delta\alpha T_g = 0.113 \tag{6}$$

$$\alpha_l T_g = 0.164 \tag{7}$$

where $\Delta\alpha = \alpha_l - \alpha_g$, the difference in expansion coefficients across T_g for the liquid and glassy state, respectively. Examination of this paper suggests that eqs 5 and 6 hold reasonably well for polymers on both the upper and lower lines. Since T_g is lower for the lower line, $\Delta\alpha$ must be higher for polymers on the bottom line. Data collected in Table III support this deduction.

The original Simha–Boyer equation[23] has been criticized on several occasions, first by Kanig[24] and later by Sharma et al.[25] Kanig[24] applies the hole theory to the T_g of polymers and derives a free-volume parameter, Φ^*, which has an average value of 0.0235 for 11 polymers. However, Φ^* is not a constant but varies from polymer to polymer. This is consistent with the WLF value which has been extensively verified by melt viscosity and other means.[24] Kanig[24] conclues that his free volume, Φ^*, is the free volume available for transport of polymers. He states that the Simha–Boyer $\Delta\alpha T_g$ is a total free volume, a point subsequently proposed independently by Litt.[26]

Sharma, Mandelkern, and Stehling (S/M/S)[25] generally criticize the Simha–Boyer conclusions. A rebuttal has been given elsewhere.[27] Sharma et al.[25] to give values of $\Delta\alpha T_g$ reasonably consistent with Simha–Boyer values but also covering additional polymers not listed in ref 23. In fact, the average for six polymers also found in our Tables I and II is 0.120 ± 0.10 from their Table I.[25]

Both Kanig[24] and S/M/S[25] included data on long-side-chain polymers. These were excluded by Simha–Boyer[23] because their large values of α_g lend to understandably low values of $\Delta\alpha T_g$. The $\alpha_l T_g$ relationship still holds. Thus, the original Simha–Boyer result of eq 6 was known from the beginning to apply only to polymers free of long side groups. The departure of PnBMA and PEA from the upper and lower lines of Figure 2 should have been anticipated by us had we been aware of $\Delta\alpha T_g = 0.113$ for Tables I and II before their selection.

One basic question which arises is as follows: if there exist two distinct classes of polymers, why have they not been revealed in prior studies? The simple answer is that they may be present as such but are obscured by the inclusion of too many diverse polymer types. A Lee–Sewell plot of T_g–CED[1] using their tabulated values of T_g and CED but only the selected polymers of Tables I and II some of which also occur in the Lee and Sewell Table I do suggest two distant lines. Their Table I lacks data on the crucial PDMS but includes PMAN and the low- and high-temperature termini of the lower line. PIB, PS, and PMMA define the low- and high-temperature termini of the upper line. The approximate slopes are 6.7 for the upper line and 4.8 for the lower line (not treated by linear least squares). This simple pattern is obscured by the proliferation of data points in Figure 1 of ref 1.

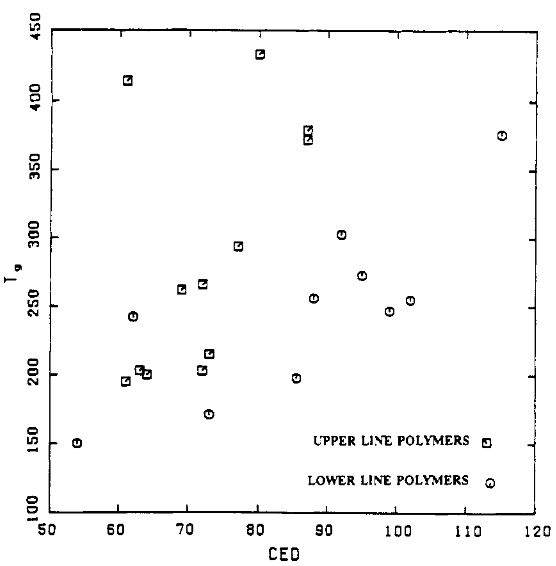

Figure 5. Simple plot of T_g vs CED based on T_g from Tables I and II, with polymers following a scatter pattern as indicated and with some bottom-line polymers (⊙) and some top-line polymers (▣) no longer having their Figure 3 loci. This emphasizes the value of using the two parameters CED and C_∞.

Our original thesis condemned T_g–CED studies for including too many diverse types of polymers which then led to a scatter diagram. Having now a "homogeneous set" of polymers, it was pertinent to ask how this group of polymers behaved in a T_g–CED plot.

Figure 5 shows the T_g–CED plot which still yields a scatter diagram even when using only the simply basic polymers of Tables I and II. Some lower-line polymers from Tables I and II actually fall near the upper line. No upper-line polymers fall in with the lower-line group, and at the same time some appear abnormally high. Hence, our second parameter, C_∞, as in Figure 3, clearly simplifies the pattern not only into two well-defined lines but also into two groups of polymers each with a common significant relaxation behavior.

Our Figures 2 and 3 may be considered to represent a combined effect of a persistence length, a_p, times an intermolecular force. Flory, for example, defines a persistence length a_p as

$$a_p = (l/2)(C_\infty + 1) \tag{8}$$

where l is the bond length. Hence, our product of CED × C_∞ may be considered as a persistence length times an intermolecular force binding polymer chains in the glassy state.

Monte Carlo computer studies were conducted by Kolinski et al.[28] on a number of chains containing 12 or 24 beads packed at volume fractions of 0.5 and 0.75 on a diamond lattice. A necessary condition for local order is chain stiffness, taken as the energetic preference of trans over gauche states. No correlations were found between different ordered regions, implying the absence of long-range order. Introduction of an attractive interaction between nonbonded nearest-neighbor pairs of beads produces an isotropic to anisotropic phase transition with increasing temperature, "which is probably first order". We are concerned here with a second-order event, i.e., T_g, where stiffness, $\sim C_\infty$ leads to local order with CED holding chains together as a segment–segment interaction. We became aware of the Kolinski et al. publications only after the above relationship was reached.

Summary and Conclusions

This study differs from prior related ones in the literature first by preselecting for consideration a small number of basic organic polymer types free from long side groups and second by employing the product of the two factors, CED and C_∞, both of which had been used independently in prior literature.

Several unexpected results emerged:

(1) T_g fell on either of two straight lines, which seemed to relate to differences in the dynamic mechanical loss spectra of polymers on the two lines. This difference could be related in terms of an increase in α_g, the coefficient of expansion of the glassy state, caused by the presence or absence of a strong $T_\gamma < T_\beta < T_g$ relaxation process on lower-line polymers; at the same time $\Delta\alpha = \alpha_l - \alpha_g$ is larger for lower-line polymers.

(2) Polymers on both lines meet the criteria of Simha–Boyer for T_g as an iso-free volume state, namely, $\Delta\alpha T_g$ = constant.

(3) Tentatively, it appears that one can predict from dynamic mechanical or dielectric loss data on which of two lines a given polymer might be found.

While the initial set of polymers in Table I met two qualitative requirements, i.e., addition polymers of simple structure free from long side chains, and increased glassy state expansion, it now appears that we can add a numerical criterion, namely

$$\Delta\alpha T_g = \text{constant} \tag{6}$$

This needs to be tested on yet other polymers such as highly polar ones, i.e., PVOH, PVNH$_2$, and still others including in-chain sulfides and polymers with rings in their chains. In fact, this criterion already excludes poly(alkyl acrylates), methacrylates, vinyl ethers all above CH$_3$ and poly(α-olefins) above polypropylene.

General

We have conducted a preliminary test of other T_g–structure relations in the literature. Some do show evidence for a double line when confined to our group of polymers. These results will be published later.

Acknowledgment. We appreciate greatly the several computerized linear least-squares equations and figures prepared by Dr. Robert L. Miller of MMI at our request. He also made valuable suggestions about data interpretation on several occasions. Miss Anne Barolo of MMI provided the TSC trace on PMAN. Preparation of this manuscript was provided by Mrs. Sara Macartney of MMI using an IBM computer. Comments or questions by various members of the audience following a seminar lecture at MMI on Oct 25, 1990, helped us to refine our concepts. Significant contributions by each of two reviewers then led to the present revised manuscript.

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Registry No. *cis*-PBD, 9003-17-2; PE, 9002-88-4; PIB, 9003-27-4; PEO, 25322-68-3; *cis*-PI, 9003-31-0; at-PP, 9003-07-0; PMA, 25087-26-7; PnBMA, 9003-63-8; PVAc, 9003-20-7; at-PS, 9003-53-6; at-PMMA, 9011-14-7; PVME, 9003-09-2; PVDCl, 9002-85-1; PEA, 9003-32-1; iso-PMMA, 25188-98-1; PVC, 9002-86-2; PAN, 25014-41-9; PtBS, 26009-55-2; PαMS, 25014-31-7; PMAN, 25067-61-2; PΦMSi, 76188-55-1; PΦMSi (SRU), 31324-77-3; PPO, 25322-69-4.