Glass transition temperature and critical properties

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In a preceding paper it was shown that for high molecular weight polymers, the volume of the repeating unit at T_g is proportional to the total free space defined as V_c-V_0 where V_c is the volume of the repeating unit at the critical temperature and V_0 is the volume of the repeating unit at absolute zero. Here it will be demonstrated that this proportionality is also true for a host of low molecular weight liquids. In addition, an empirical method of estimating T_c for a high molecular weight polymer is proposed which provides values of T_c which are consistent with those for low molecular weight liquids.

INTRODUCTION

In a preceding paper,[1] it was shown that the volume of the repeating unit of a polymer at the glass transition temperature, V_g, is proportional to the total free space defined as V_c-V_0 where V_c is the hypothetical volume of the repeating unit at the critical temperature and V_0 is the hypothetical volume at absolute zero. Both of these volumes are estimated from a knowledge of the chemical structure and tables of additive atomic and group contribution,[1,2] and involves the assumption that a given atom or group of atoms makes a fixed contribution to the volume of the liquid. Specially, it was shown that:

$$\frac{V_g}{V_c - V_0} = K \qquad (1)$$

where K had the value 0.369 with a standard deviation of 0.0178 for 28 polymers[3] with glass transition temperatures ranging from 140 to 480 K. We would now like to report that equation (1) is also applicable to simple, low molecular weight liquids and in addition to define a new quantity, the hypothetical critical temperature of a polymer.

RESULTS AND DISCUSSION

In calculating the value of K, Sugden's atomic and group contributions[2] were used to estimate V_0 and the atomic and group contributions from ref 1 were used to estimate V_c. For many liquids, the value of V_g (or the density at T_g) was not reported. Accordingly, in these instances we estimated V_g using Sugden's equation which is given by:[3]

$$V = \frac{V_0}{(1 - T/T_c)^{0.3}} \qquad (2)$$

By substituting T_g for T and estimating V_0 from the additive contributions we were able to estimate V_g. Equation (2) is similar to the Goldhammer equation,[4] but Sugden[3] has shown that equation (2) provides a better fit to temperature-density (or volume) data than the Goldhammer equation.

For high molecular weight polymers, there are no established methods for estimating the critical temperature or for that matter, that a T_c even exists. On the other hand, concepts like the energy of vaporization have been applied to polymers in order to define the very useful solubility parameter which can be used in conjunction with suitable theory to predict events such as solubility and surface tension.[5] The energy of vaporization of a polymer has never been directly measured; its value is estimated indirectly using measurements of equilibrium swelling or intrinsic viscosity in a variety of solvents for example.[5]

If we differentiate equation (2) with respect to temperature, the following equation applicable to the liquid at T_g is obtained:

$$\frac{0.3\,V_0}{\beta_1 T_g M} = \frac{(1 - T_r)^{1.3}}{T_r} \qquad (3)$$

where β_1 is the slope of the specific volume-temperature response of the liquid at T_g, M is the molecular weight of the liquid, V_0 is the molar volume at $T = 0$ and T_r is the ratio T_g/T_c. For high molecular weight polymers, both M and V_0 can be taken equal to the molecular weight and molar volume of the repeating unit, respectively. The quantity on the left hand side of equation (3) can be calculated if the experimental values of β_1 and T_g are available and hence estimates of $T_r = T_g/T_c$ can be obtained. It is convenient to do this graphically by assigning values to T_r and calculating the appropriate values of $0.3\,V_0/\beta_1 T_g M$ and plotting the results. When values of $0.3\,V_0/\beta_1 T_g M$ are obtained using direct experimental data, these together with the plot will provide ready values for T_r.

We have taken the β_1 and T_g data for a variety of polymers published by Sharma, Mandelkern and Stehling[6] and have estimated both T_r and T_c in this manner and the results are given in *Table 1.* The T_c values for these polymers range from a low value of 645 K for polypropylene to a high value of 1129 K for poly(2-hydroxyl propyl methacrylate).

Although it may seem strange to consider critical temperatures of high molecular weight polymers, there is strong empirical evidence that T_c remains finite in the limit of infinite molecular weight. Based on theoretical considerations of Kurata and Isida,[6] Kreglewski[7] and Zowlinski and

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Table 1 Selected properties of various polymers

Polymer	T_g(K)	$\beta_1 \times 10^4$ (cm^3/deg.)	T_r	T_c(K)	γ calc. (dyne/cm)	γ expt. (dyne/cm)
Polyethylene	140	5.31	0.185	757	32.2	31
Natural rubber	201	6.02	0.270	744	29.4	
Polyisobutylene	202	6.00	0.263	768	29.4	33.6
Poly(methyl acrylate)	282	5.60	0.385	733	37.1	41
Poly(vinyl acetate)	302	5.98	0.414	730	37.0	36
Poly(4-methyl pentene-1)	302	7.61	0.390	774	28.9	
Polystyrene	373	5.50	0.412	905	37.9	33
Poly(methyl methacrylate)	378	4.6	0.394	959	40.1	39
Poly(ethyl methacrylate)	337	5.40	0.394	853	37.1	33
Poly(propyl methacrylate)	308	5.80	0.384	802	35.3	
Poly(n-butyl methacrylate)	291	6.00	0.374	778	34.3	32
Poly(n-hexyl methacrylate)	268	6.80	0.374	718	31.9	
Poly(n-octyl methacrylate)	253	6.0	0.333	760	33.3	
Poly(n-dodecyl methacrylate)	208	6.8	0.312	667	29.6	
Poly(sec-butyl methacrylate)	330	5.55	0.384	869	35.4	
Poly(iso-butyl methacrylate)	327	5.85	0.393	832	34.4	
Poly(tert-buryl methacrylate)	355	6.30	0.427	831	31.4	
Poly(methyl vinyl ether)	251	6.45	0.360	697	32.2	29
Poly(ethyl vinyl ether)	240	7.26	0.366	656	30.0	
Poly(isopropyl vinyl ether)	261	6.69	0.360	725	30.3	
Poly(n-butyl vinyl ether)	217	7.26	0.336	646	29.1	
Poly(isobutyl vinyl ether)	251	6.78	0.352	713	30.0	
Poly(sec-butyl vinyl ether)	241	6.36	0.330	730	30.6	
Poly(n-hexyl vinyl ether)	199	6.66	0.296	672	29.9	
Poly(2-hydroxyl ethyl methacrylate)	359	3.78	0.330	1088	46.5	
Poly(2-hydroxyl propyl methacrylate)	346	3.60	0.309	1129	46.3	
Poly(2-methoxyl ethyl methacrylate)	293	4.95	0.341	859	46.4	
Poly(trifluoro chloro ethylene)	325	2.51	0.347	937	44.6	31
Poly(propylene)	258	9.40	0.400	645	2.54	29
Poly(α-methyl styrene)	453	5.40	0.442	1025	41.9	
Poly(ethylene terephthalate)	337	4.50	0.400	843	47.3	43
Poly(2,6-dimethyl, 1,4-phenylene oxide)	480	5.13	0.456	1053	44.4	
Poly(piperlide acrylate)	381	4.50	0.393	970	47.9	
Poly(morpholide acrylate)	418	4.40	0.449	931	40.4	
Polybutadiene	188	7.80	0.302	623	27.1	32

Kreglewski[8] found that the T_c dependence on molecular weight of n-alkanes could be well described by an equation of the form:

$$\log(961 - T_c) = 2.95597 - 0.090570\, m^{2/3} \qquad (4)$$

Here m is the number of carbon atoms in the alkane. When $m \to \infty$, equation (4) indicates that a limiting T_c of 961 K is reached, i.e. 961 K is the T_c value of high molecular weight polyethylene. Kreglewski[7] also observed that the same limiting $T_c = 961$ K is also applicable to n-alkyl derivatives such as the 1-mono-olefins, n-alkyl cyclohexanes and the n-alkylbenzenes. Although the form of equation (4) was found to not be applicable to branched alkanes or alkyl derivatives in general, we can still reasonably expect the existence of a limiting T_c for high molecular weight liquids.

In order to determine how T_c depends on the molecular weight of polymeric liquids, we have taken the data of both Fox and Flory[9] and Ueberreiter and Kanig[10] for the dependence of T_g on M for fractionated polystyrene samples. The relevant data are tabulated in *Table 2*. The data of Fox and Flory show a slight increase in T_c at low molecular weight which levels out at a molecular weight of about 3000 g/mol. The data of Ueberreiter and Kanig show a definite increase in T_c at low molecular weight and a levelling-off at a molecular weight of also about 3000 g/mol. Thus, this data is consistent with the behaviour observed with the low molecular weight n-alkanes. It is interesting to note that the lowest molecular weight material used by Ueberreiter and Kanig was stated to be the dimer of polystyrene; for this material, T_c as estimated from T_g and β_1 data is 625 K. While there are apparently no experimental data for T_c for styrene dimer, the experimentally observed

T_c for ethylbenzene is 617 K.[11]

For the polymeric materials listed in *Table 1,* the value of T_r ranges from a low of 0.185 for polyethylene, to a high of 0.456 for poly (2,6-dimethyl-1,4-phenylene oxide); however, most values tend to cluster in the range 0.3-0.4. The average value is 0.363 with a standard deviation of 0.0565. If we use this average value to represent all polymers, then from equation (3), it can be shown that:

$$\alpha_1 T_g = \frac{0.3}{T_c/T_g(1 - T_g/T_c)} = 0.171 \qquad (5)$$

where α_1 is $(1/V)(\partial V/\partial T)$. A similar relationship with a numerical value of 0.164 was proposed by Simha and Boyer.[12] This agreement indicates that equation (2), and therefore equation (3) is consistent with experimental data. Also shown in the Table are calculated and experimentally measured values of the surface tension; the calculation was carried out as follows. The surface tension, γ, can be estimated by the use of atomic and group contributions to the parachor $[P]$, as pointed out by Sugden,[13] i.e.:

$$\gamma = \frac{[P]^4}{V} \qquad (6)$$

Table 2 Dependence of T_g on M for polystyrene

$M \times 10^{-3}$ (g/mol)	T_g(K)	$\beta_1 \times 10^4$ (cm^3/deg.)	T_r	T_c(K)
Data of Fox and Flory[24]				
1.675	313	5.3	0.365	857
2.085	326	5.5	0.382	853
2.60	335	6.0	0.406	825
3.04	338	5.5	0.390	867
3.59	348	5.1	0.380	916
4.98	351	5.5	0.398	882
6.65	350	5.6	0.400	875
13.3	359	5.7	0.411	873
19.3	362	5.7	0.413	877
85.0	373	5.0	0.390	956
Data of Ueberreiter and Kanig[25]				
0.21	195	7.5	0.312	625
0.32	233	6.53	0.329	708
0.34	228	6.56	0.327	697
0.43	248	6.24	0.337	736
0.72	292	6.05	0.370	789
0.84	284	5.81	0.357	796
1.25	311	5.66	0.374	831
2.60	336	5.64	0.392	857
4.68	353	5.68	0.404	874
8.42	360	5.58	0.417	863
14.5	360	5.52	0.404	891
25.2	369	5.49	0.409	902
30.4	362	5.55	0.407	889
31.10	364	5.69	0.414	879
41.6	370	5.41	0.406	911
93.6	371	5.47	0.410	904

Using equation (1) to estimate the volume we have:

$$\gamma = \frac{[P]^4}{V_0}(1 - T_r)^{1.2} \qquad (7)$$

which contains two quantities $[P]$ and V_0 whose values can be estimated from additive atomic and group contributions as well as the critical temperature. Using the T_c values estimated from T_g and β_1 values as well as the appropriate values of $[P]$ (ref 14) and V_0 the values of γ shown in *Table 2* have been calculated. Also shown are values of γ obtained experimentally and as may be seen, the calculated and experimental values are reasonably close. Thus, using T_c of a polymer in conjunction with equations which are known to apply to low molecular weight liquids, reasonable values of γ are calculable.

Finally, we may note that T_R appears to be a function of T_g for both low molecular weight liquids and polymers as well. *Figure 1* shows T_R as a function of T_g for all the entries in *Table 1,* as well as for low molecular weight liquids not reported here. As may be seen, there is a rough correlation between these two parameters for both high and low molecular weight liquids. We should note that the behaviour of the low molecular weight liquids where T_c was obtained from measured data or estimated using a reliable method and that of the high molecular weight polymers where T_c was estimated indirectly all fall roughly on a common curve. This implies that our estimates of T_c for high molecular weight polymers are consistent with T_c values for low molecular weight liquids which have been measured experimentally.

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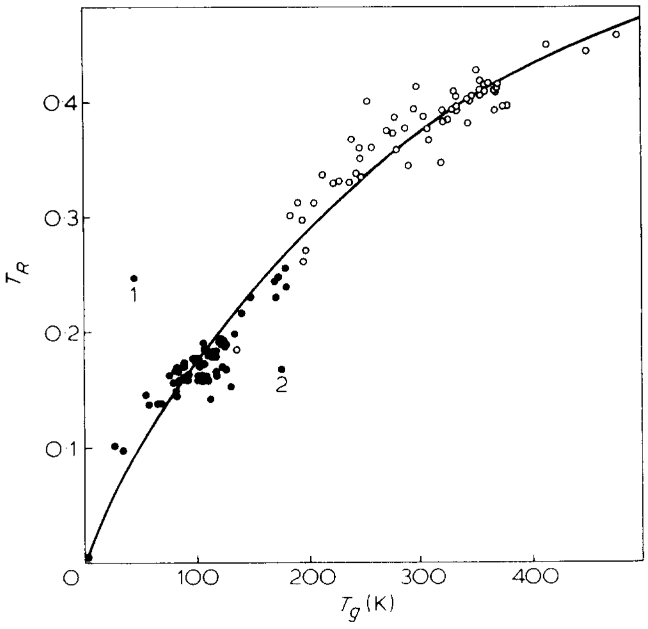

Figure 1 Dependence of T_r on T_g for both low molecular weight liquids (filled circles) and for high molecular weight polymers (open circles). Point number 1 is methane and point number 2 is n-tetrahexacontane

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