Intramolecular mobility and its role in the glass transition temperature of ionic polymers

Dennis G. Peiffer
Exxon Research and Engineering Co., P.O. Box 8, 1600 E. Linden Avenue, Linden, NJ 07036, USA
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The glass transition temperature of ionic polymers is found to depend on the molar ionic cohesive energy, the universal gas constant and a factor (n) that is related to intramolecular interactions. The polyphosphates, polyacrylates and X,Y-ethylene ionenes polymer families are shown to follow the equation interrelating the above-mentioned variables. The significance of n can be understood by deriving various rules of constant specific heat at T_g (ΔC_p). The results of this analysis show that approximately 2/3 of ΔC_p is attributable to intersegmental interactions, while 1/3 of ΔC_p is related to intramolecular forces. Similar relationships were established between the degrees of freedom of the polymer repeat unit and ΔC_p. These rules are shown to be related to Wunderlich's 'bead' concept.

INTRODUCTION

The magnitude of the intermolecular forces and intramolecular barriers to rotation are two of the most prominent factors affecting the behaviour of polymeric materials. Given sufficient information of these two quantities would help in the understanding and prediction of many phenomena observed in these substances. For example, it was recently shown that the change in the specific heat (ΔC_p), in going from the glassy state to the liquid (rubbery) state, at the glass transition temperature (T_g) was dependent on the rotational motion of the units within the repeat unit of the polymer. A rule of constant ΔC_p was derived[1] which is directly related to the basic units of the molecular motion. This motion was defined in terms of a classical torsional oscillation.

The glassy state is generally regarded[3-8] as a rigid liquid in which both the free volume and, for all practical purposes the polymer conformations, become completely frozen at T_g. At or below T_g, the segments of the polymer chain cannot change their mean positions with respect to any other chain. Thus it is observed there is a physical basis for incorporating both intermolecular (hole-equilibrium considerations) and intramolecular (intersegmental interactions) factors in an analysis of T_g.

The above considerations can be extended to include both the intermolecular and intramolecular contributions to ΔC_p in terms of the basic units that comprise the molecular structure of the polymer. The inclusion of the intramolecular factors allows an equation to be derived relating the molecular structure of ionomers to their T_g. The polyphosphates, X,Y-oxyethylene ionenes and polyacrylate ionomer series will be used to show the general applicability of this treatment.

INTRAMOLECULAR AND INTERMOLECULAR CONTRIBUTIONS TO ΔC_p

As stated previously, in the glassy state it is assumed that conformations within the polymer structure and their respective intersegmental interactions are completely frozen in. The influence of these interactions on physical properties is greatly reduced above T_g. Thus Nose[3] proposed that ΔC_p can be expressed separately by the sum of these two factors:

$$\Delta C_p = \Delta C_p^{inter} + \Delta C_p^{intra} \qquad (1)$$

where the superscripts refer to inter- and intra-molecular interactions respectively. Presented in *Table* 1 are the results (calculated on a molar basis) as given by Nose[3] of the appropriate values for equation (1) on several polymers. Included in this Table are the degrees of freedom (n) corresponding to each polymer repeat unit. In general, an increase in ΔC_p^{inter} or ΔC_p^{intra} is observed with an increase in n. This is brought out more clearly in *Figure* 1, in which is found a linear relationship between the specific heat values and n. The equations obtained from this graph are given in the following expressions:

$$\Delta C_p^{inter} = 0.2\ n \qquad (2)$$

$$\Delta C_p^{intra} = 0.1\ n \qquad (3)$$

In both cases, a simple relationship is obtained as is the case in plots of ΔC_p *versus* n. The equation that results

Table 1 Intermolecular and intramolecular contributions to the specific heat change at T_g

Polymer	ΔC_p^{inter} (cal/mol deg)	ΔC_p^{intra} (cal/mol deg)	n
Polystyrene	5.0	2.8	23
Poly(methyl methacrylate)	5.6	3.0	34
Poly(vinyl chloride)	3.0	1.25	16
Poly(vinyl acetate)	5.4	3.2	31
Poly(α-methyl styrene)	5.34	3.63	30[a]

[a] Value estimated from $n = 3.36\ \Delta C_p$

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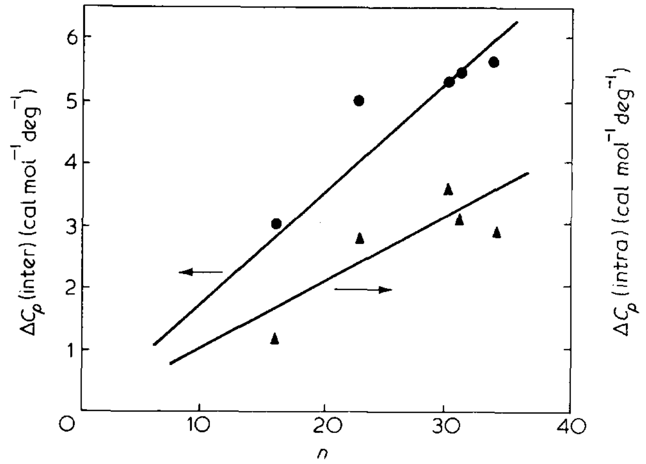

Figure 1 Plot of the intermolecular and intramolecular contribution to the change in the specific heat (ΔC_p) in going from a glass to a liquid *versus* the degrees of freedom

from this analysis is given by[1]:

$$\Delta C_p = 0.3\, n \tag{4}$$

Comparison of the previous equations leads to the conclusion that approximately 2/3 of the specific heat change at T_g is attributed to intermolecular considerations, while 1/3 can be related to intramolecular interactions. This result parallels the finding that the excess enthalpy arising from intersegmental interactions in polystyrene is approximatley 2/3 of the total excess enthalpy[3]. The remaining 1/3 is attributed to the conformational energy of the hindered rotation about chain bonds.

Equations (2), (3) and (4) allow one to relate n to the inter- and intra-molecular contributions to the degrees of freedom:

$$n^{intra} = \frac{n}{3} \tag{5}$$

$$n^{inter} = \frac{2n}{3} \tag{6}$$

The above two equations are essentially identical to that found concerning the ΔC_p values.

The above equations (2) and (3) can be considered as rules of constant ΔC_p similar to that found by Peiffer[1] and Wunderlich[9]. Comparison of Wunderlich's equation with equation (4) shows[1] that the number of rotational degrees of freedom per 'bead' is equal to 9 or:

$$\frac{n}{\text{bead}} = 9 \tag{7}$$

A 'bead' is defined as the smallest unit in the polymer structure capable of independent torsional oscillation[1]. It is shown that a definite relationship exists between n and the number of 'beads'; that is, the degrees of rotational freedom of the 'beads' are responsible for ΔC_p. Combining Wunderlich's equation with equations (2) and (3) lead to the following expressions:

$$\frac{n^{inter}}{\text{bead}} = 6 \tag{8}$$

$$\frac{n^{intra}}{\text{bead}} = 3 \tag{9}$$

These latter two equations show that equation (7) is in reality a composite function of both inter- and intramolecular interactions. Furthermore a definite equality exists between a 'bead' and the various interactions. The number of intermolecular degrees of freedom per 'bead' is 6, while the number of intramolecular degrees of freedom per 'bead' is 3. This conclusion parallels that found in a previous publication[1]: 3 degrees of freedom (n) were approximately equal to 1 classical degree of free rotation, or alternatively, 6 degrees of freedom are equal to 1 classical torsional oscillation. We see, however, that it is inappropriate to used the term free rotation in its normal context, but it should be viewed as a freeing of intersegmental interactions. Thus in comparing equations (8) and (9), it is observed that the number of torsional oscillations per bead is exactly equal to the number of 'freed' inter-bead interactions, which in both cases is one. This conclusion is similar to that reached by Lee and Sewell[6] in which they remarked that the barrier opposing internal rotation is the dominant factor governing the T_g's of polymers, but that its magnitude is regulated to a great extent by cohesive forces.

The calculation of the number of inter- and intramolecular contributions per 'bead' is useful, but the extension to individual molecular groups that comprise most common polymeric materials is of more value. Presented in *Table* 2 are the results of such a calculation. Using equations (5) and (6), both n^{inter} and n^{intra} can be evaluated from known values[10] of n. Dividing n^{inter} by 6 or n^{intra} by 3 will give the approximate numbers of 'beads' in each molecular group. This leads directly to the atomic arrangements that comprise the 'bead'. The data, (as seen in the last column of *Table* 2), show that the molecular groups such as $-CH_2-$, $-CH{=}CH-$, -O- and *p*-phenylene are essentially equivalent to only one 'bead'. These groups act as only one unit due to either structural simplicity ($-CH_2-$, $-CF_2-$) or rigid bonds connecting several groups ($-CH{=}CH-$, *p*-phenylene). Rotation about double bonds is highly improbable due to the high energy required for the process to occur. A similar analysis on more complex

Table 2 Intermolecular and intramolecular contributions to the degrees of freedom of various molecular groups

Molecular group	n^{inter}	n^{intra}	n^a	Number of beads^b
$-CH_2-$	5	3	8	1
$-CH(CH_3)-$	7	4	11	2
$-CF_2-$	5	3	8	1
$-NHCO-$	9	4	13	2
p-phenylene	3	2	5	1
$-CH{=}CH-$	5	3	8	1
$-O-$	4	2	6	1
$-CH(COOCH_3)-$	15	8	23	3
$-COO-$	8	4	12	2
$-NHCOO-$	13	6	19	3
$-CH(C_6H_5)-$	10	5	15	2
$-CH(CH{=}CH_2)-$	7	4	11	2
$-C(CH_3){=}CH-$	7	4	11	2

[a] Data obtained from ref. 10

[b] Due to some scatter in the data, numbers less than one were rounded off the nearest whole number (which is 1). Numbers that ranged from 1 to 2 were approximated to 2 while those greater than 2 were rounded off to 3

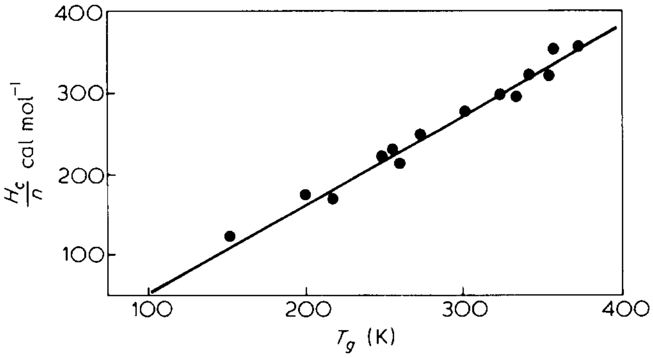

Figure 2 Relationship of the ratio of the molar cohesive energy H_c and the degrees of rotational freedom n with the glass transition temperature of numerous non-ionic polymers. The reader is referred to *Table 1* of ref. 1 for the complete list of the polymers used in this graph

structures leads to the identification of the molecular units comprising the 'beads'.

DISCUSSION

Relationship between H_c/n *and* T_g *for non-ionic polymers*

Figure 2 shows the result of plotting the ration H_c/n (H_c being the molar cohesive energy) *versus* T_g for a number of common non-ionic polymers. As is observed, a linear relationship is found with the slope of the line equal to $0.5R$ (R being the universal gas constant). Similar findings have been noted by Peiffer[1]. One is thus drawn to the conclusion that both the magnitude of the intersegmental forces and the n degrees of freedom significantly affect T_g. A marked change in any of these quantities will shift T_g along the line shown in *Figure* 2.

The relationship found for H_c *versus* T_g for the non-ionic polymers indicate a totally different result. No trend is at all observed due to marked data scatter that a curve fitting attempt would be of no value. A graph of the molar ionic cohesive energy *versus* T_g does, however, produce a straight line.

Cohesive energy and T_g *of ionic polymers*

The total molecular cohesive energy is the sum of all contributions from all intermolecular interactions. However, due to the overwhelming magnitude of the ionic interaction, the total energy can be approximated with the following equality:

$$H_c = H_c^{ionic} \tag{10}$$

H_c^{ionic}, in turn, is derived[2] by assuming that the work needed to completely separate the univalent ionic sites on the polymer chain and all the corresponding q_c-valent counter-ions.

$$H_c^{ionic} = N_A \frac{qe^2}{a} \tag{11}$$

where N_A is Avogadro's number, a is equilibrium distance between the centre of a cation and an anion, and e is the electronic charge.

Eisenberg[11], in his study of the T_g of several families of ionic polymers, noted that in spite of significant structure differences between them, the results were very similar. This led to the conclusion that the T_g of ionic polymers was determined by the magnitude of the cation-anion interaction. At T_g, sufficient energy is placed into the polymer structure as to allow the anion to escape the coordination sphere of the cation. This analysis leads to the conclusion that T_g is directly proportional to q/a (one assumes that the anionic charge is constant for any series of materials). A study[2] of polyphosphate, silicate, acrylate and aliphatic ionene systems confirms the above analysis.

Tables 3 and 4 list the calculated H_c^{ionic} values of the polyphosphates and polyacrylates with their T_g values. The T_g measurements of these polymers were reported by Eisenberg *et al.*[12,13], while the method of estimating the density is given by Tsutsui and Tanaka[2]. The range of q/a values used in this study is from 0.1 to 0.9. In general, one finds that with increasing H_c^{ionic}, a concomitant increase in T_g is observed.

All the H_c^{ionic} data are plotted in *Figure* 3. Included in this Figure are two points pertaining to X,Y-oxyethylene ionenes. More data points could be added, but that was unnecessary since all other points laid along the two parallel lines. The ordinate value for both lines is approximately identical; therefore, equation (12) can be easily obtained:

$$\frac{H_c^{ionic}}{200} = 3\frac{RT_g}{2} - 3^3(25) \tag{12}$$

In essence, equation (12) states H_c^{ionic} is a function of the universal gas constant (R), T_g and a series of constants. The term, $H_c^{ionic}/200$ can be considered as a sort of reduced energy term. The constant, 200, appears because of the lack of knowledge of the absolute n that is attributed to an ion-pair (i.e., an ion-pair 'bead'). All the ionic polymers studied so far have been found to obey this equality. Only minor differences are noted in the constant, $3^3(25)$, and even in these

Table 3 Ionic cohesive energy and T_g of polyphosphates

Counter ion	M (g/mol)	ρ^a (g/cm^3)	CED^a (cal/cm^3)	H_c^{ionic} (cal/mol)	T_g (K)
Li	85.9	2.34	4.52 x 10^3	166 x 10^3	608
Na	102.0	2.53	3.46	139.5	553
Ca	99.1	2.74	7.71	279.0	793
Sr	122.8	3.34	7.13	262.0	758
Ba	147.6	3.95	6.49	242.5	743
Zn	111.7	3.06	8.46	308.8	793
Cd	135.2	3.64	7.51	279.0	723

^{a} Data obtained from ref. 2

Table 4 Ionic cohesive energy and T_g of polyacrylates

Counter ion	M (g/mol)	ρ^a (g/cm^3)	CED^a (cal/cm^3)	H_c^{ionic} (cal/mol)	T_g (K)
Na	94.0	1.97	2.95 x 10^3	140.7 x 10^3	524
K	110.1	2.31	2.55	122.5	467
Cs	203.9	4.27	2.24	107.0	447
50% Na	102.1	2.14	2.75	131.2	492
25% Ca	93.1	1.95	3.67	175.2	560

^{a} Data obtained from ref. 2

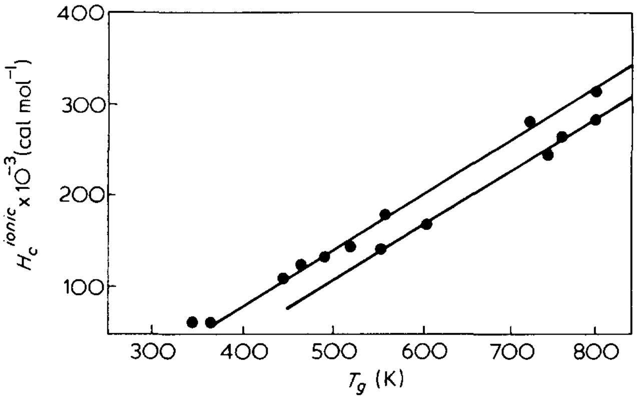

Figure 3 Plot of the ionic cohesive energy of the polyphosphate, X, Y-oxyethylene ionenes (only two ionenes data points shown) and polyacrylate ionomers *versus* their corresponding glass transition temperature

cases, the deviations are not dependent on any particular polymer series. This equation has a parallel form[10] which is used in the prediction of T_g of non-ionic polymers and copolymers. Hayes originally[10] assumed that the basic reason for rotational restrictions at T_g is the lack of sufficient rotational energy to overcome the cohesive forces holding the molecules together. This point has also been elaborated on in previous sections of this work. Hayes further noted that if n could be predicted from the polymer structure (and H_c calculated), one could consistently predict T_g of many polymers. n values, as given by Hayes, were entirely empirical.

$$H_c = n\,\frac{RT_g}{2} - 25n \qquad (13)$$

Recently[1] (and in this paper) n was found to be related to the units comprising a polymer repeat structure, thus eliminating its empirical character. In any event comparison of equation (13) with (12) leads to an interesting conclusion even though the latter two equations describe different polymer systems (non-ionic *versus* ionic interactions).

The coefficients of the $RT_g/2$ term (equation (12)) and the constant, $3^2(25)$, indicates that $n=3$ for all the ionic polymers ($n=6$ applies to the non-ionic polymeric materials[1]). This is, as discussed previously, due to the freeing of intramolecular attractions between the anion and its counterion. Intersegmental forces play little role in determining T_g of these ionic polymers, which is not the case for the non-ionic polymers. The constant, 25, is related to molecular weight and rate effects[10].

CONCLUSION

Eisenberg *et al.*[11], in their studies on ionic polymers, found that the slopes of T_g *versus* q/a graphs were slightly different from each other. These slopes ranged from 625 for polyphosphates to 730 for polyacrylates. Since the slopes were so close to each other, it was assumed that one might be dealing with some type of a general constant for polyanions (or polycations) with fairly small repeat units. This, as has been shown here, turns out to be exactly that case. An equation can be derived that fits the T_g *versus* q/a data of several ionic polymer systems. This expression is based upon the fact that the inter- and intra-molecular interactions could be separated from each other at T_g. Subdividing the specific heat change at T_g into the two above-metioned interactions leads to a series of rather simple equations, that are in essence, rules of constant ΔC_p. These rules relate the degrees of freedom to the various units that comprise the polymer repeat structure. Using this information, one can interpret equation (12).

A reformulation of the equation relating T_g of an ionic polymer to its molecular structure is given in the following expression:

$$T_g = \frac{2N_A e^2}{3CR}\,(q/a) + \frac{12}{R}(25) \qquad (14)$$

We should point out that T_g is expressed in terms that are a function of the ionic groups incorporated in the polymer chain. C is a constant whose value is equal to 200. As shown previously, these groups affect the physical properties of these materials through their intramolecular interactions. It is worth recalling at this point that even though ion pairs form through intramolecular forces; these can, in turn, associate with each other. This has a profound effect on the properties of these materials. Even at low concentrations, these ions act as simple crosslinks in which multiple ion pairs aggregate. The ion pairs are uniformly dispersed throughout the polymer material. Above a certain threshold ion concentration, clusters are formed, giving the material properties that are similar to other phase separated systems. In fact, from physical property measurements, ion clusters (containing as many as several hundred ion pairs) can be viewed as acting as a reinforcing filler.

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