# Role of electrostatic forces in the glass transition temperatures of ionic polymers

**T. Tsutsui and T. Tanaka**
*Department of Materials Science and Technology, Faculty of Engineering, Kyushu University 36, Fukuoka, Japan 812*

*(Received 31 January 1977)*

The glass transition temperatures of ionic polymers have been correlated with cohesive energy densities (*CED*). The *CED*s of ionic polymers, such as ionene polymers, polyphosphates, and polyacrylates were calculated under the assumption that they could be approximated to the electrostatic energy of the system. The $T_g$s of ionic polymers could be conveniently expressed by the equation $T_g = K_1(CED)^{1/2}$, in which $K_1$ took a different value for each polymer system. This paper discusses the influence on $T_g$ of the change in both the cohesive energy and the degree of freedom of segmental motion caused by the introduction of ionic characteristics in polymeric chains.

## INTRODUCTION

Intermolecular forces, flexibility of chains, and chain geometry are the three principal variables that govern the glass transition of polymers[1–5]. For ionic polymer systems, the intermolecular forces are predominant; the introduction of ionic structural units in polymers invariably resulted in a drastic increase in $T_g$[6–8]. Eisenberg and his coworkers[9] summarized the $T_g$s of some ionic polymers by use of the parameter $q/a$, the ratio of the counter-ion charge $q$ to the distance between the centres of cations and anions $a$. Their treatment, however, did not fully explain the dependence of $T_g$ on ion concentration, or give a satisfactory rationale for the applicability of $q/a$ to all molecules.

We have recently reported the effect of ion concentration and the sizes of counter-ion on the value of $T_g$ for various ionene polymers, which are among the simplest ion-containing organic polymers[10–13]. However, the interpretation of these data on the basis of molecular structures remains to be discussed.

In this paper, we propose to make use of cohesive energy density (*CED*) as a significant parameter for understanding the $T_g$ of ionic polymers. An approximate method is presented for estimating the cohesive energies of ionic polymers; then the *CED* values of some ionene polymers are calculated, and the $T_g$s of ionene polymers are analysed on the basis of the *CED*. The $T_g$ data of polyphosphates and polyacrylates, reported by Eisenberg and his coworkers, are also used to examine the relation between $T_g$ and *CED* in higher ion-concentration regions than those of ionene polymers. Since *CED* is already known to be one of the most useful quantities in summarizing the $T_g$ data of non-ionic polymers, it provides a convenient means for comparing the $T_g$ values of ionic and non-ionic polymers.

## COHESIVE ENERGY DENSITY OF IONIC POLYMERS

The molecular cohesive energy of ionic polymers is the sum of contributions from several types of interaction:

$$\text{(Total interaction)} = \text{(Ionic interaction)} + \text{(Van der Waals interaction)} + \text{(Hydrogen bond)} + \ldots \quad (1)$$

In a system with high ion concentration:

$$\text{(Ionic interaction)} \gg \text{(Van der Waals interaction)} \quad (2)$$

In a system without hydrogen bonding, the cohesive energy density of the system can be approximated by the ionic interaction:

$$CED \cong CED_{\text{ionic}} \quad (3)$$

The ionic cohesive energy of a skeletal chain carrying a number of univalent ionic sites and the corresponding number of $q_c$-valent counter-ions can be given, in rough approximation, by the work required to removal all the counter-ions from the skeletal chain. The ionic cohesive energy per mole of the skeletal ion, $E_{\text{ionic}}$, is given by:

$$E_{\text{ionic}} = N_A \frac{q_c \cdot e^2}{a} \quad (4)$$

where $N_A$ is Avogadro's number, $e$ is the electronic charge, and $a$ is the equilibrium distance between the centre of an anion and a cation. Using a molecular weight $M$ per skeletal ion and polymer density $\rho$, we can write:

$$CED_{\text{ionic}} = N_A e^2 \frac{\rho}{M} \frac{q_c}{a} \quad (5)$$

We took only the dissociation energy of each ion pair into consideration, and ignored both intrachain and interchain interactions between ion pairs. To allow for these interactions a correction factor, such as the Madelung constants used in the calculation of the lattice energy of ionic crystals[14], may be necessary. Tentatively, however, equation (5) will be used without any corrections; the approximation of equation (3) might be rather ambitious, and over-refinement with-

*Table 1* $T_g$ and cohesive energy density of aliphatic *m,n*-ioenes, $-\![\!-(CH_2)_m-N^+(CH_3)_2X^- -(CH_2)_n-N^+(CH_3)_2X^-]_p-$

| No. | *m,n* | Counter-ion | *M* | $q_c/a$ | $\rho$ (g/cm$^3$) | *CED* (cal/cm$^3$) | $T_g$ (K)* |
|---|---|---|---|---|---|---|---|
| 1 | 6.3 | Br | 187.1 | 0.185 | 1.38 | $4.51 \times 10^2$ | 406 |
| 2 | 6,5 | Br | 201.1 | 0.185 | 1.35 | 4.11 | 400 |
| 3 | 6,8 | Br | 222.2 | 0.185 | 1.32 | 3.64 | 393 |
| 4 | 6,10 | Br | 236.2 | 0.185 | 1.25 | 3.25 | 382 |
| 5 | 12,3 | Br | 229.2 | 0.185 | 1.27 | 3.38 | 376 |
| 6 | 12,4 | Br | 236.2 | 0.185 | 1.25 | 3.28 | 356 |
| 7 | 12,5 | Br | 243.2 | 0.185 | 1.24 | 3.11 | 369 |
| 8 | 12,6 | Br | 250.2 | 0.185 | 1.22 | 2.99 | 366 |
| 9 | 12,8 | Br | 264.3 | 0.185 | 1.20 | 2.78 | 357 |
| 10 | 12,10 | Br | 278.3 | 0.185 | 1.18 | 2.60 | 345 |
| 11 | 6,10 | I | 283.2 | 0.178 | 1.50† | 3.13 | 377 |
| 12 | 6,10 | $C1O_4$ | 255.8 | 0.158 | 1.35† | 2.77 | 343 |
| 13 | 6,10 | $BF_4$ | 243.1 | 0.160 | 1.28† | 2.79 | 341 |

* See reference 12.
† Estimated values; see Appendix

*Table 2* $T_g$ and cohesive energy density of *x,y*-oxyethylene ionenes,

$-\![-(CH_2CH_2O)_{x-1}CH_2CH_2-N^+(CH_3)_2Br^- -(CH_2CH_2O)_{y-1}CH_2CH_2-N^+(CH_3)_2Br^- -]_p-$

| No. | *x,y* | *M* | $q_c/a$ | $\rho$ (g/cm$^3$)* | *CED* (cal/cm$^3$) | $T_g$(K)† |
|---|---|---|---|---|---|---|
| 1 | 2,3 | 218.1 | 0.185 | 1.29 | $3.63 \times 10^2$ | 362 |
| 2 | 2,4 | 240.1 | 0.185 | 1.25 | 3.19 | 344 |
| 3 | 3,3 | 240.1 | 0.185 | 1.25 | 3.19 | 327 |
| 4 | 3,4 | 262.2 | 0.185 | 1.21 | 2.82 | 307 |
| 5 | 4,4 | 284.2 | 0.185 | 1.18 | 2.54 | 295 |
| 6 | 4,5 | 306.2 | 0.185 | 1.16 | 2.32 | 280 |
| 7 | 5,5 | 328.2 | 0.185 | 1.14 | 2.12 | 267 |

* Estimated values; see Appendix
† See reference 11

in the framework of equation (3) might be of little significance.

Before the numerical estimation of *CED*, the validity of equation (3) should be examined. The $CED_{\text{ionic}}$ of ionene polymers ranges between 250 and 450 cal/cm$^3$, as will be shown later. On the other hand, $CED_{\text{van der Waals}}$ of ionene polymers can be roughly estimated by use of Small's method[15]; it is between 50 and 60 cal/cm$^3$. The contribution from van der Waals interactions can be as large as 15% of total cohesive energy. Since the $CED_{\text{ionic}}$ itself is also considered to include an uncertainty of about 10%, the use of $CED_{\text{ionic}}$ to represent total cohesive energy density is justified.

## APPLICATION TO SOME IONIC POLYMER SYSTEMS

### *Ionene polymers*

*Tables 1* and *2* list the calculated *CED* values of aliphatic ionenes and oxyethylene ionenes, with their $T_g$ values[11-13]. The origin and the method of estimation of densities of the polymers are presented in the Appendix. The value of 3.47 Å for the ionic radius of the tetramethylammonium cation, used by Robinson and Stokes[16], was adopted as the ionic radius of the skeletal dimethylammonium cation. Pauling's ionic radii, 1.95 and 2.15 Å, were used for the ionic radii of the Br and I counter-ions. For the $C1O_4$ and $BF_4$ ions, an approximate ionic radius was given by the sum of the van der Waals radii of an outer atom and the Cl–O or F–B bond distance. Although the values of cationic or anionic radii include some inaccuracy, a slight change of these values does not affect the general scope of the calculations.

In *Figure 1*, the $T_g$s of ionene polymers are plotted against the *CED*s. The $T_g$s and *CED*s of several non-ionic polymers as measured by Lee and Sewell[4] are also plotted in the Figure. It appears to be difficult to correlate the $T_g$s of ionene polymers with those of non-ionic polymers. The square root of *CED* was therefore tentatively used in place of *CED* itself (*Figure 2*). As pointed out by Boyer[3], the $T_g$s of the flexible polymers without bulky side chains are located near the straight line with its intercept very close to 0K at $(CED)^{1/2} = 0$. The $T_g$s of ionene polymers, which are representative of flexible polymers without bulky side chains, are found near this line. The selection of abscissa is arbitrary of course, but *Figure 2* may suggest the presence of some similarity of glass transition behaviour between ionene polymers and common non-ionic polymers.

### *Polyphosphates and polyacrylates*

The $T_g$ data on ionic polymers with high ion concentrations are limited. Polyphosphates and polyacrylates are among the few polymer systems available for the investigation of the $T_g$s of such ionic polymers. *Tables 3* and *4* list the calculated *CED* values of these polymers with their $T_g$ values as reported by Eisenberg and his coworkers[17,18]. The densities of the polymers necessary for the calculations of *CED* are mentioned in the Appendix. The oxygen anionic radius of both the polyphosphates and the polyacrylates was taken to be 1.40 Å according to Eisenberg. The ionic

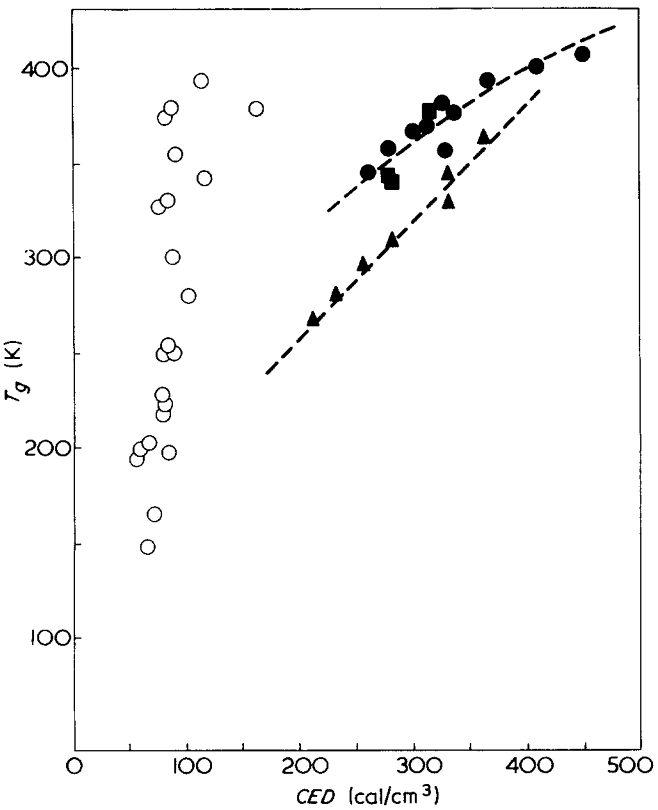

*Figure 1* Plots of $T_g$ (K) vs. *CED* (cal/cm$^3$). ○, Non-ionic polymers[4]; ●, aliphatic ionenes (counter-ion Br); ■, aliphatic ionenes (counter-ions I, C1O$_4$, and BF$_4$); ▲, oxyethylene ionenes

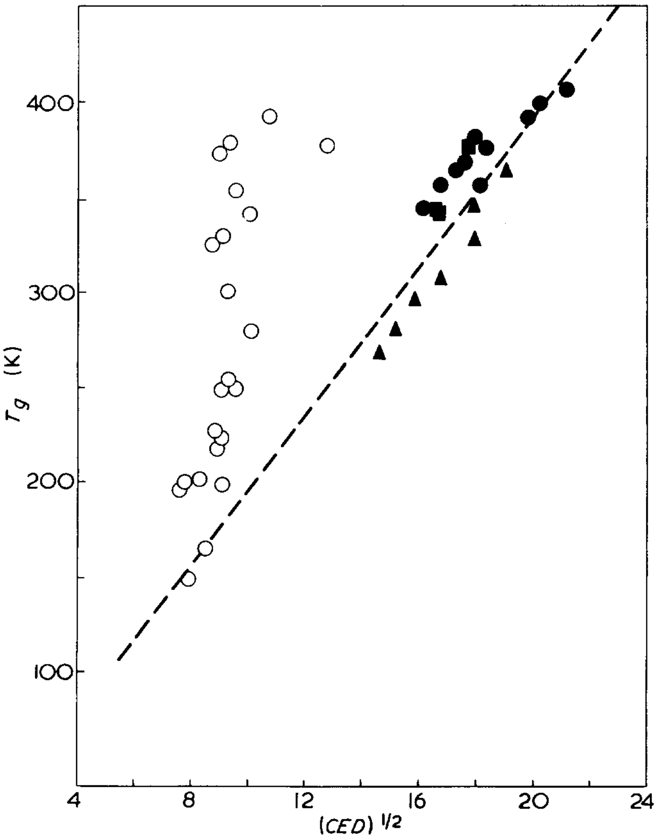

*Figure 2* Plots of $T_g$ vs. $(CED)^{1/2}$. ○, Non-ionic polymers; ●, aliphatic ionenes (counter-ion Br); ■, aliphatic ionenes (counter-ions I, C1O$_4$, and BF$_4$); ▲, oxyethylene ionenes

radii of the cations were Pauling's ionic radii. For copolymeric polyacrylates, the sum of the *CED*s of each component was taken to be the *CED* of the copolymer system. Eisenberg and his coworkers have tentatively determined the average $q_c/a$ of copolymer systems with respect to the number of counter-ions. It seems more reasonable to take the average $q_c/a$ values with respect to the number of skeletal ions from the viewpoint of the ionic cohesive energy of the system.

The plots of $T_g$ against *CED* for polyphosphates and polyacrylates fall on the same straight line. Since the *CED* values used in this paper are proportional to the $q_c/a$ values, the linear relationship between $T_g$ and *CED* is essentially the same as the relation between $T_g$ and $q_c/a$, reported by Eisenberg and his coworkers. They rationalized the linear relationship between $T_g$ and $q_c/a$ by stating that the glass transition takes place around the temperature where the kinetic energy $kT$ becomes comparable with that required for the elimination of counter-ions from the coordination sphere of skeletal ions. Although our treatment was not concerned with the kinetic aspects of the glass transition, the resulting formulation is similar.

## DISCUSSION

### *Empirical relation between* $T_g$ *and* CED

All the $T_g$ data are plotted with logarithmic scales on both axes in *Figure 3*. We have applied the relation $T_g = K_1(CED)^n$ for each of three systems: aliphatic ionenes, oxyethylene ionenes, and the combined system with polyphosphates and polyacrylates. The value of $n$, obtained by the least-squares method procedure between log ($T_g$) and log (*CED*), was 0.33 for aliphatic ionenes, 0.56 for oxyethylene ionenes, and 0.44 for the combined system of polyphosphates and polyacrylates. Since there is scatter among the data, and we used assumed values for the densities of some polymers, we are not tempted to compare the values

*Table 3* $T_g$ and cohesive energy density of polyphosphates

| No. | Counter-ion | $M$ | $q_c/a$ * | $\rho$ (g/cm$^3$) | *CED* (cal/cm$^3$) | $T_g$ * (K) |
|---|---|---|---|---|---|---|
| 1 | Li | 85.9 | 0.50 | 2.34 | 4.52 × 10$^3$ | 608 |
| 2 | Na | 102.0 | 0.42 | 2.53 | 3.46 | 553 |
| 3 | Ca | 99.1 | 0.84 | 2.74† | 7.71 | 793 |
| 4 | Sr | 122.8 | 0.79 | 3.34† | 7.13 | 758 |
| 5 | Ba | 147.6 | 0.73 | 3.95† | 6.49 | 743 |
| 6 | Zn | 111.7 | 0.93 | 3.06† | 8.46 | 793 |
| 7 | Cd | 135.2 | 0.84 | 3.64 | 7.51 | 723 |

* See reference 17
† Estimated values; see Appendix

*Table 4* $T_g$ and cohesive energy density of polyacrylates

| No | Counter-ion | $M$ | $q_c/a$ | $\rho$ (g/cm$^3$) | *CED* (cal/cm$^3$) | $T_g$ (K) |
|---|---|---|---|---|---|---|
| 1 | Na | 94.0 | 0.425 | 1.97 | 2.95 × 10$^3$ | 524 |
| 2 | K | 110.1 | 0.366 | 2.31† | 2.55 | 467 |
| 3 | Cs | 203.9 | 0.323 | 4.27† | 2.24 | 447 |
| 4 | 50% Na | 102.1 | (0.396) | 2.14† | 2.75 | 492 |
| 5 | 25% Ca | 93.1 | (0.484) | 1.95† | 3.67 | 560 |

* See reference 18.
† Estimated values; see Appendex

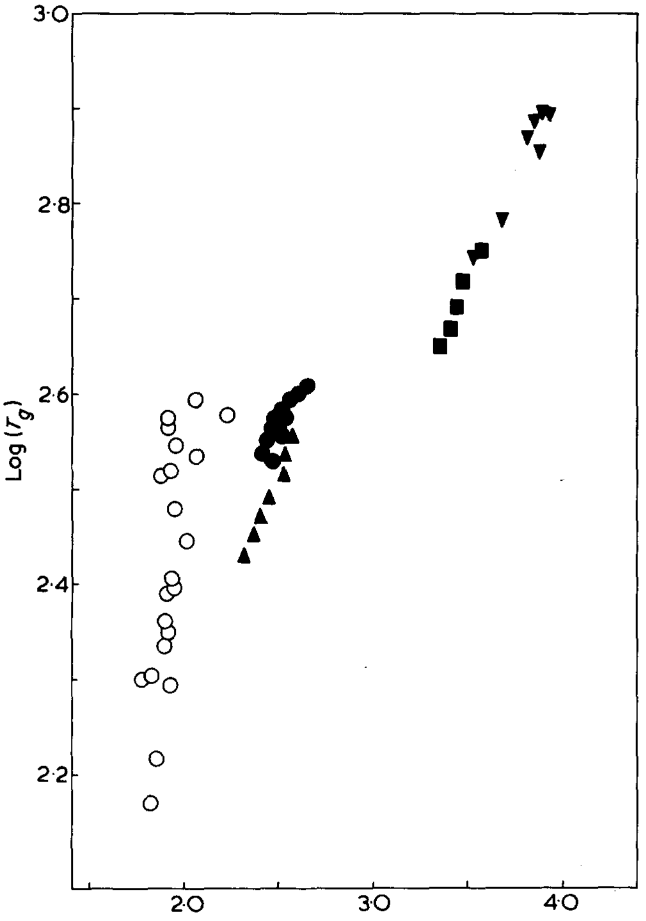

*Figure 3* Plots of log($T_g$) vs. log(*CED*). ○, Non-ionic polymers; ●, aliphatic ionenes; ▲, oxyethylene ionenes; ▼, polyphosphates; ■, polyacrylates

of $n$ between the three systems. Roughly speaking, $n$ is around 0.5 for all systems, and a plot of $T_g$ against $(CED)^{1/2}$ seems to be the most convenient for summarizing the $T_g$ data of ionic polymers. The coefficient $K_1$ may differ among the polymers with different skeletal chains, and in practice it should be evaluated in each polymer system with polymers of similar chemical structure.

*Correlation with the* $q_c/a$ *postulate by Eisenberg*

Eisenberg and his coworkers found empirically that the slope of $T_g$ vs. $q_c/a$ ranged from 625 to 730 in four ionic polymer systems when $a$ was expressed in Angstroms, and speculated that this constancy might reflect some unknown molecular causes. We can now discuss this on the basis of the *CED*. If the presence of a universal relation in $T_g$ and $(CED)^n$ is postulated, we have:

$$T_g = K_1\left(N_A e^2 \frac{\rho}{M}\frac{q_c}{a}\right)^n = K_2\left(\frac{\rho}{M}\right)^n\left(\frac{q_c}{a}\right)^n \qquad (6)$$

Using a molar volume per skeletal ion $V_0$, we rewrite:

$$T_g = K_2\frac{1}{V_0^n}\left(\frac{q_c}{a}\right)^n \qquad (6a)$$

Provided that equation (6a) is valid, and if the molar volume per skeletal ion is reasonably constant for the polymers under consideration, then the universal relation between $T_g$ and $q_c/a$ should hold. Of course, Eisenberg's empirical relation between $T_g$ and $q_c/a$ is apparently different from the postulated relation between $T_g$ and $(q_c/a)^n$, and the intercepts of their plots never cross at 0K. We should point out again that the similarity of molar volume per skeletal ion may be one of the necessary conditions for the existence of a universal relationship between $T_g$ and $q_c/a$.

*Factors affecting* $T_g$ *other than* CED

According to the theory based on the principle of corresponding states of polymer liquids, $T_g$ is expressed as follows[19,20]:

$$T_g = \text{const}\,\frac{E^*}{c} = \text{const}\,(CED)\frac{V^*}{c} \qquad (7)$$

where $E^*$ and $V^*$ are the cohesive energy and the volume of a segmental unit, respectively, and $3c$ corresponds to the external degree of freedom of the segmental unit. Thus $V^*/c$ expresses the volume of the segmental unit whose external degree of freedom is three. The above expression suggests that the effect of the $V^*/c$ term should be taken into consideration in the evaluation of $T_g$ based on *CED*. However, the molecular meaning of the term $V^*/c$ is not clear so that its numerical evaluation is difficult, although a few attempts to evaluate it have been made for non-ionic polymers[20,21]. We will only discuss $V^*/c$ from a qualitative point of view here.

*Figure 3* indicates that the $T_g$ values of the ionic polymers, especially the polyphosphates and polyacrylates, are considerably lower than those expected from their high *CED* values. The reason for this becomes apparent from equation (7) if we assume the presence of large difference of $V^*/c$ between polymers with different ion concentrations. In other words, the external degree of freedom of segments might become larger as the ion concentration increases. Superficially, this explanation seems to contradict the idea that the increase of ionic character forces polymer chains to take extended conformations behave as rigid chains. However, glass transitions are mainly concerned with local segmental motions, including those of counter-ions, and are little influenced by the chain conformation as a whole. The external degree of freedom of segments may increase with the ionic character, if we take into account the degree of freedom of counter-ions which are connected not with covalent bonds but with loose ionic bonds and can migrate in the system. The introduction of ionic forces in polymers produces an increase in cohesive energy density of the system, and results in a large increase of $T_g$. On the other hand, the introduction of ions into the system necessarily brings about a change in the mode of molecular motions of both skeletal chains and their counter-ions, and this effect partially cancels the large increase of $T_g$.

In the work which connected the Gibbs-DiMarzio theory with the free volume theory, Eisenberg and Saito[22] dealt with the $T_g$ data of both non-ionic and ionic polymers (polyphosphates) in the same formulation. They found empirical equality between the hole-formation energy $\Delta\epsilon/k$ ($k$ = Boltzmann's constant) and the chain-stiffness energy $2\alpha/k$. The equality also held for ionic polymers, despite the presence of large difference in $2\alpha/k$ between non-ionic polymers (300–900) and ionic polymers (1200–1800). Their findings support our above interpretation of equation (7); the increase in cohesive energy (in their treatment, hole-formation energy) is necessarily accompanied by a change in the quantity concerned with chain flexibilities.

## ACKNOWLEDGEMENT

The authors wish to thank Dr R. Tanaka, of their Department, for encouraging discussions.

## REFERENCES

1 Kawai, R. *High Polymers Japan,* 1957, **6,** 348
2 Hayes, R. A. *J. Appl. Polym. Sci.* 1961, **5,** 318
3 Boyer, R. F. *Rubber Chem. Technol.* 1963, **36,** 1303
4 Lee, W. A. and Sewell, J. H. *J. Appl. Polym. Sci.* 1968, **12,** 1397
5 Privalko, V. P. and Lipatov, Yu. S. *J. Macromol. Sci. (B)* 1974, **9,** 551
6 Fitzgerald, W. E. and Nielsen, L. E. *Proc. R. Soc. London (A)* 1964, **282,** 137
7 Moacanin, J. and Cuddihy, E. F. *J. Polym. Sci. (C)* 1966, **14,** 313
8 Otocka, E. P. and Kwei, T. K. *Macromolecules* 1968, **1,** 401
9 Eisenberg, A. *Macromolecules* 1971, **4,** 125
10 Tsutsui, T., Sato, T. and Tanaka, T. *Polym. J.* 1972, **5,** 332
11 Tsutsui, T., Tanaka, R. and Tanaka, T. *J. Polym. Sci. (Polym. Phys. Edn)* 1975, **13,** 2091
12 Tsutsui, T., Tanaka, R. and Tanaka, T. *J. Polym. Sci. (Polym. Phys. Edn)* In press
13 Tsutsui, T., Tanaka, R. and Tanaka, T. *J. Polym. Sci. (Polym. Phys. Edn)* In press
14 Sherman, J. *Chem. Rev.* 1932, **11,** 93
15 Small, P. A. *J. Appl. Chem.* 1953, **3,** 71
16 Robinson, R. A. and Stokes, R. H. 'Electrolyte Solutions', 2nd Edn, Butterworth, London 1959, p 124
17 Eisenberg, A., Farb, H. and Cool, L. G. *J. Polym. Sci. (A-2)* 1966, **4,** 855
18 Eisenberg, A., Matsuura, H. and Yokoyama, *J. Polym. Sci. (A-2)* 1971, **9,** 2131
19 Simha, R. and Boyer, R. F. *J. Chem. Phys.* 1962, **37,** 1003
20 Nose, T. *Polym. J.* 1971, **2,** 427
21 Eskin, V. Ye. and Korotkina, O. Z. *Vysokomol. Soedin. (A)* 1974, **16,** 41
22 Eisenberg, A. and Saito, S. *J. Chem. Phys.* 1966, **45,** 1673
23 Kordes, E. and Becker, H. *Z. Anorg. Chem.* 1949, **260,** 185
24 Tsutsui, T., Yokoyama, T. and Tanaka, T. *Kobunshi Ronbunshu,* 1974, **31,** 565
25 Illers, K. H. *Ber. Bunsenges Phys. Chemie* 1966, **70,** 353

## APPENDIX

### *Estimation of densities of ionic polymers*

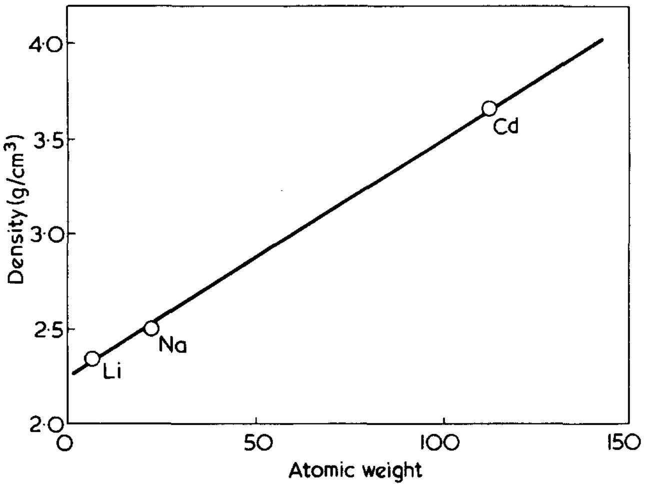

*Figure A1* Relation between the densities of polyphosphates and the atomic weight of their counter cations

*Aliphatic ionenes.* The experimental densities at 25°C were available for aliphatic ionenes with Br as the counter-ion[12]. They were crystalline polymers and the experimental densities must have some difference from amorphous (glassy-state) densities. We used the experimental densities without correction for crystallinity. No density data were available for aliphatic ionenes with I, $ClO_4$, and $BF_4$ as the counter-ions. Thus the densities of these polymers were estimated from those of the same polymers with Br counter-ion under the assumption that the change of molar volume due to an alteration of counter-ion species was small and could be ignored. Correcting only the effect from the change of mass of the counter-ion, we obtain the density of the polymer with molecular weight $M$ per skeletal ion:

$$\rho = \frac{M}{V} \cong \frac{M}{V_0} = \rho_0 \frac{M}{M_0} \qquad \text{(A1)}$$

where $\rho_0$ is the density of the polymer with molecular weight $M_0$, per skeletal ion, and $V_0$ are the molar volumes per skeletal ion of the polymers with density $\rho_0$ and $\rho$, respectively.

*Oxyethylene ionenes.* In this case, there were no available density data. We therefore employed the relationship between the densities and the number of skeletal atoms between cationic nitrogens in aliphatic ionenes to estimate the density of oxyethylene ionenes[12]. The oxygen atoms in the polymeric skeleton were regarded as behaving like methylene groups in aliphatic ionenes.

*Polyphosphates.* Density data for the Li, Na, and Cd salts of polyphosphates were available[23]. Since the plot of density against atomic weight of a counter cation showed a straight line (*Figure A1*), the required densities of the other polymers could be estimated from the plot.

*Polyacrylates.* No density data of poly(metal acrylate) could be found. The density of poly(sodium acrylate) was obtained by extrapolation from the densities of methyl acrylate–sodium acrylate copolymers and that of poly(methyl acrylate)[24,25]. No density data were found for other non-crystalline copolymer systems including a metal acrylate component. Then equation (A1) and the density of poly(sodium acrylate) were used for the estimation of other polyacrylates with counter ions K, Cs, and Ca.