Review

Glass Transitions in Ionic Polymers

A. Eisenberg

McGill University, Montreal, Canada. *Received June 30, 1970*

I. Introduction

The effect of ions on the physical properties of polymers is profound. In this paper, a review will be presented of the effect of the incorporation of ions on the glass transition temperature, in both organic and inorganic polymers. The phenomena encountered in inorganic materials have been reviewed before,[1] so they will be treated here only briefly, and only insofar as they relate to the organics.

In addition to the obvious technical importance of the subject, it is interesting to compare the effects in organic and inorganic polymers; while inorganic ionic polymers in the solid state have been known for a long time—the silica based window glass type of materials, for instance, have been investigated quite extensively—no *a priori* statements can be made about the effect of ions on properties of organic polymers. The dielectric constants of the materials, the solubilities of salts in them, etc., are so drastically different that no reliance can be placed on simple extrapolations, and experimental approaches are essential.

The presentation will be divided into three parts. The first will concern itself with the effects of incorporating relatively few ionic groups into the polymer, either by a process of copolymerization or by dissolving salts of low lattice energies into polar polymers. The second part will review the phenomena encountered in completely ionizable polyacids and their salts, specifically those based on the polyphosphate, silicate, and acrylate systems. Finally, the glass transition relations found in the aliphatic ionenes will be described.

It should be stressed that the field of ionic polymers is growing very rapidly at this time. This review should, therefore, be regarded as a beginning effort in the field, rather than as definitive study of a highly explored area.

II. Effects of Ions at Low Concentrations

Several studies have been performed to explore the effect of relatively low ion concentrations. Moacanin and Cuddihy[2] studied the internal friction in poly(propylene glycol) with added lithium perchlorate and took the maximum of the damping peak as the glass transition. $LiClO_3$, because of its low lattice energy, dissolves in the polyether, and changes a number of its properties, among them the glass transition. They observed that initially the T_g of the solution rises linearly from *ca.* −70° at 0 wt % salt to *ca.* −20° at 16 wt %, which corresponds to *ca.* 9.4 formula weights of the salt/100 formula weights of repeat units. Beyond that concentration the effect of the salt is stronger, *i.e.*, the curves rise even more sharply, reaching 40° at *ca.* 24 wt % salt. This study indicates that as a result of the strong ion–dipole interactions present in the solution, the average segmental mobility is lowered and the glass transition temperature raised over what it would be in the absence of the salt, the increase being linear with concentration.

Fitzgerald and Nielsen[3] studied the dynamic mechanical properties of sodium salts of styrene–methacrylic acid copolymers of three concentrations of the salt, *i.e.*, 2, 10, and 40 mol %. They observed that the maximum in the logarithmic decrement increased from *ca.* 120° for the 2% sample to 145° for 10% to 185° for the 40% sample. Judging from these three points alone, it seems that the relationship is nonlinear; the trend, however, is quite clear and parallels the one found by Moacanin and Cuddihy.

Otocka and Eirich,[4] in their extensive studies of butadiene containing ionic copolymers, investigated the glass transitions of three series of samples containing various concentrations of ionic groups. The first comprised the butadiene–lithium methacrylate system, the second the butadiene–methyl(2-methyl-5-vinyl)-pyridinium iodide, and the third was an equimolar mixture of the first two, with the lithium iodide which is formed in the process of mixing left in the polymer. The authors found that the glass transition increased linearly with concentration of ionic groups, the effect being strongest for the pyridinium salt, weakest for the lithium salt, and intermediate for the mixture. Quantitatively, the T_g's of samples containing *ca.* 1.2 mequiv of the ionic material/g of polymer (equivalent to *ca.* 6.5 mol %) would be −32, −45, and −55° for the pyridinium salt, the mixture, and the Li salt, respectively. The T_g for the homopolymer extrapolates in all cases to *ca.* −90°. It is of interest to note that in a study of the viscoelastic properties of quaternary pyridinium salt the authors found a temperature (in all cases far above T_g) below which the ions seemed to act as relatively stable cross-links. This indicates that T_g itself is due not to the onset of mobility of ionic groups, but to the other segments, suggesting that the ions probably act as cross-links and increase T_g by that mechanism.

The dynamic–mechanical properties of ethylene–metal methacrylate copolymers have been investigated

---

(1) A. Eisenberg, *Advan. Polym. Sci.*, **5,** 59 (1967).

(2) J. Moacanin and E. F. Cuddihy, *J. Polym. Sci., Part C*, **14,** 313 (1966).

(3) W. E. Fitzgerald and L. E. Nielsen, *Proc. Roy. Soc., Ser. A*, **282,** 137 (1964).

(4) E. P. Otocka and F. R. Eirich, *J. Polym. Sci., Part A-2*, **6,** 921 (1968).

TABLE I
dT_g/dc FOR VARIOUS IONIC POLYMERS

Polymer–ionic material (range)	dT_g/dc, deg/mol %
Styrene–sodium methacrylate (2–10 mol %)	3.1
Butadiene–lithium methacrylate (0–8 mol %)	5.4
Polypropylene glycol–lithium perchlorate (0–10 mol %)	5.5
Ethylene–sodium methacrylate (0–3 mol %)	5.7
Butadiene–methyl(2-methyl-5-vinyl)pyridinium iodide (0–8 mol %)	8.9
Ethylene–magnesium methacrylate (0–2 mol %)	9.7

in several laboratories,[5,6] the metal being most frequently sodium, although others have also been studied. Otocka and Kwei,[6] in their study of the sodium and magnesium salts, ascribe the loss maximum in dynamic mechanical tests which occurs between 0 and $-20°$ (the β peak) to the glass transition for these materials. They find that the temperature at which the maximum occurs shifts to higher temperatures with increasing salt content, and that the system obeys the copolymerization equation

$$T_g = n_1T_{g_1} + n_2T_{g_2}$$

where n_1 and n_2 are the mole fractions and T_{g_1} and T_{g_2} the glass transitions of the two homopolymers. They take the T_g of polyethylene as *ca.* $-20°$, and estimate that of poly(sodium acrylate) and poly(magnesium acrylate) as 230 and 400°, respectively. If this assignment of the β peak as the glass transition is correct, then one can calculate dT_g/dc for both materials in the region of low salt content. The results are 5.7 and 9.7 deg/mol %, respectively.

In this light, it is of interest to compare the effectiveness of the various ions in the materials discussed so far in raising the glass transition. Expressing the effectiveness in all cases as the slope of the T_g *vs.* c plot (c in mol %), we find that the effect increases as shown in Table I.

There are only six materials listed here, so no meaningful correlations can be made. It seems, however, that the efficiency increases as the glass transition temperature of the host material decreases. At this time it is impossible to distinguish whether this supports cross-linking by the ionic species as a mechanism for raising the glass transition, because the success of Otocka and Kwei in applying a copolymerization approach to copolymers of ethylene with sodium or magnesium methacrylate makes an explanation in terms of a copolymerization effect also feasible. Perhaps we are dealing with a superposition of two effects of the type encountered in the cross-linking of organic polymers.[7] It is also feasible that clustering of the ions,[8] particularly at moderately high ionic concentrations, decreases segmental mobility sufficiently to have an appreciable effect on the glass transition.

III. Completely Ionizable Homopolymers

A. Counterion Effect. The effect of the nature of the counterion on the glass transition temperature of completely ionizable homopolymers has been investigated to date for three systems, the polyphosphates,[9] the silicates,[10] and polyacrylates.[11] In spite of the drastic differences in the structures of these polymers, the results are surprisingly similar.

The polyphosphates were studied most extensively,[9] with several homopolymers and counterion copolymers included in the study. The homopolymers included the nonionic $(HPO_3)_x$, the glass transition of which was $-10°$, and, among others, the lithium, sodium, and calcium polyphosphates, with glass transitions of 335, 285, and 520°, respectively. The counterion copolymer systems included sodium–lathanum, sodium–calcium, sodium–potassium, and the partly ionic $NaPO_3$–HPO_3 system. Altogether, *ca.* 50 materials were included in the study.

An attempt to rationalize the data started with the premise that the glass transition in these systems was determined by the strength of the anion–cation interaction, *i.e.*, that this was the factor which limited segmental mobility. At T_g, kT is just large enough to allow the anion to leave the coordination sphere of the cation (or *vice versa*) at a rate which allows volume equilibration to be achieved with reasonable relaxation times. Thus, kT_g must be proportional to the electrostatic work (W_{el}) of removing an anion from the coordination sphere of a cation, *i.e.*

$$T_g \propto W_{el} \propto \int F_{el}da$$

where F_{el} is the electrostatic interaction, a the internuclear distance between anion and cation, and the limits of integration are the distance of closest approach and infinity. Since F equals the product of the charges divided by the square of the distance between them, upon integration one finds that $T_g \propto q_aq_c/a$, where q is the charge and subscripts a and c refer to anion and cation; since the anion charge is constant for any series of materials, the simplest relationship is

$$T_g \propto (q/a)$$

where q is the cation charge and a is now the internuclear distance between anion and cation at closest approach. Thus, if T_g is plotted against the ratio of q (in units of 1 electron) over a (in ångströms), a straight line is obtained which is given by

$$T_g = 625(q/a) - 12$$

For counterion copolymers, the number average (q/a) value was chosen.

The silicates at a composition of $Na_2O:SiO_2 \approx 1$ represent another predominantly linear polymer system which is quite easy to investigate. Here, however, only one counterion copolymer system was investigated,[10] *i.e.*, Na_2SiO_3–$CaSiO_3$; the results, again, were very

---

(5) W. J. MacKnight, L. W. McKenna, and B. E. Read, *J. Appl. Phys.*, **38**, 4208 (1967).

(6) E. P. Otocka and T. K. Kwei, *Macromolecules*, **1**, 401 (1968).

(7) T. G Fox and S. Loshaek, *J. Polym. Sci.*, **15**, 371 (1955).

(8) A. Eisenberg, *Macromolecules*, **3**, 147 (1970).

(9) A. Eisenberg, H. Farb, and L. G. Cool, *J. Polym. Sci., Part A-2*, **4**, 855 (1966).

(10) A. Eisenberg and K. Takahashi, *J. Non-Cryst. Solids*, in press.

(11) A. Eisenberg, H. Matsuura, and T. Yokoyama, to be published.

similar to those obtained for the polyphosphates. The expression for T_g as a function of q/a was

$$T_g = 635(q/a) + 132$$

indicating that the slope is identical within experimental error.

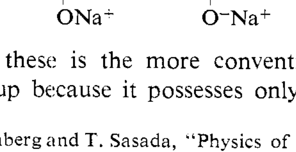
Most recently, several polyacrylate salts were studied,[11] including sodium, potassium, and the sodium–calcium counterion copolymer system. Here, however, the study is much more difficult, because the salts cannot be dried completely without serious decomposition. It was, therefore, necessary to plasticize a particular polymer to various extents, measure the T_g values as a function of composition, and extrapolate to zero plasticizer content. Both water and formamide were used as plasticizers to avoid a problem which will be described more fully below in connection with the ionenes, and the extrapolated results for the two plasticizers were identical. Again T_g was found to be linearly related to q/a, in this case the equation being

$$T_g = 730(q/a) - 67$$

The slope is again close to that for the phosphates or silicates, indicating that one might be dealing with some type of a general constant for polyanions with relatively small repeat units. The results of a q/a study of the ionenes, which also seem to indicate a linear relation between T_g and q/a, will be described in section IV.

It should be pointed out that while in the polyphosphate case the partly neutralized HPO_3–$NaPO_3$ system does fit onto the T_g *vs.* q/a plot, this is not the case for the acrylate system. The extrapolated value for PAA from the T_g *vs.* q/a plot of the metal acrylates would be −67°, while the actual value is *ca.* +105°. This substantial difference is probably due to the fact that in PAA we are dealing with a material in which the acid groups are capable of forming a high concentration of highly structured, rigid hydrogen-bonded dimers, or even higher "polymers," which lower the segmental mobility of the polymer appreciably. Hydrogen bonding exists in the phosphoric acid case also, but there the acid hydrogen can interact with more than just one oxygen per repeat unit. Highly structured dimers are probably not formed, and segmental mobility is not decreased as strongly as it is in the acrylates.

B. Molecular Weight Effect. The effect of the molecular weight on the glass transition of ionic polymers was studied for only one system, sodium polyphosphate;[12] however, two different types of terminal groups were investigated. By utilizing different synthetic routes, it is possible to prepare polymers which possess as an end group either



$$\sim\!\sim\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle ONa^+}{|}}{OPOH}} \quad \text{or} \quad \sim\!\sim\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-Na^+}{|}}{OPO^-Na^+}}$$

The first of these is the more conventional type of terminal group because it possesses only one ion just like a normal repeat unit; by contrast, the second possesses two ions.

It was found that polymers possessing the first type of end group, *i.e.*, the hydroxyl terminated polymers, exhibited a perfectly normal increase in T_g with molecular weight; a plot of T_g *vs.* the reciprocal number average degree of polymerization yielded a straight line which could be fitted by any of several theoretical approaches. One of those tried was the simplest copolymerization equation,[13] the middles being regarded as one comonomer and the ends the other. The equation is

$$1/T_g = f_1/T_{g_1} + f_2/T_{g_2}$$

where f was taken as the mole fraction. An excellent fit was achieved with $T_{g_1} = 299°$ for middles and $T_{g_2} = -150°$ for chain ends. Another equation that was applied was[14]

$$T_g(\infty) - T_g = 2\rho N\theta/\alpha P = K/P$$

where $T_g(\infty)$ is the glass transition temperature of the infinite polymer, ρ the density, N Avogadro's number, θ the excess free volume per chain end, α the free volume expansion coefficient, and P the degree of polymerization. Again excellent fit was obtained with $\theta = 27$ Å^3. The volume of a chain repeat unit ($NaPO_3$) is *ca.* 70 Å^3, which makes the ratio of these two values 0.40. By comparison, the value for polystyrene is $40/170 \approx 0.23$. Finally it was found that the Gibbs–DiMarzio equation was obeyed, *i.e.*, the molecular weight dependence of the glass transition could be predicted from only a knowledge of the glass transition of the polymer of any one molecular weight and the difference of the cubic expansion coefficients above and below the glass transition for that polymer. A choice of either 4 or 8 as the coordination number yielded an equally good fit.

By contrast to the above, the polymers possessing the second type of terminal group, *i.e.*, those with two ions per chain end exhibit a most unusual behavior: over a range of degrees of polymerization from *ca.* 150 down to the tetramer the glass transition changes by only 8°, from 285 to 277°. The Gibbs–DiMarzio theory is, of course, completely inapplicable, the more phenomenological theories, however, do apply. With $T_{g_1} = 284°$ and $T_{g_2} = 260°$, the copolymerization equation yields a very good fit, as does also the free volume based equation relating T_g to degree of polymerization. In the latter case, however, θ equals 0.5 Å^3, very much less than for the hydroxyl terminated material. This is perhaps an indication of the cross-linking character of the diionic terminal group.

The discrepancy in the T_{g_1} values in the copolymerization approach for the two materials (299 *vs.* 284°) is noteworthy. Since T_{g_1} refers to the chain middles, one should expect that the two values should be identical. The discrepancy is caused by the impossibility, resulting from the synthetic methods employed, of excluding all the hydroxyl groups from the diionically terminated polymer. The residual hydroxyl groups lower the glass transition temperature by *ca.* 15°, and since the

---

(12) A. Eisenberg and T. Sasada, "Physics of Non-Crystalline Solids," J. A. Prins, Ed., North Holland Publishing Co., Amsterdam, 1966, pp 99–116.

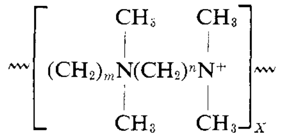
(13) T. G. Fox, *Bull. Amer. Phys. Soc.*, **1**, 123 (1956).

(14) F. Bueche, "Physical Properties of Polymers," Wiley, New York, N. Y., 1962.

molecular weight for the diionically terminated polymer is determined from the stoichiometry, a plot of T_g *vs.* $1/\overline{P}_n$ extrapolates to a $T_g(\infty)$ which is 15° lower than the value for the hydroxyl terminated material, in which $\overline{P}_n$ was determined from the intrinsic viscosity.

IV. Polymers Containing Quaternary Ammonium Ions in the Backbone. The Ionenes[15]

The only other series of ionic polymers, the glass transition of which have been investigated extensively, are the ionenes. These polymers consist of short methylene sequences separated by dimethylammonium ions along the backbone. The structure of a typical ionene is



$$\sim\left[(CH_2)_m\overset{CH_3}{\underset{CH_3}{N}}(CH_2)^n\overset{CH_3}{\underset{CH_3}{N^+}}\right]_X\sim$$

where m and n can vary from 2 to 16. The glass transition relations found for these materials[16] do not conform with any of those found for the polymers described before, so they are described separately.

Because of their regularity, the ionenes are highly crystalline, so a direct determination of their glass transition is impossible. It is, therefore, necessary to determine the T_g values of any one polymer with several different concentrations of diluent and to extrapolate to zero diluent concentration using some reasonable equation. The one chosen here was[17]

$$T_g = w_1T_{g_1} + w_2T_{g_2} - Kw_1w_2$$

where w is the weight fraction, T_{g_1} and T_{g_2} the glass transition temperatures of the polymer and diluent, and K a constant. The solvents used in the study included water, glycerine, and formamide, for which the glass transition temperatures are either known or can be determined by extrapolation. For example, the water–glycerine system has been studied extensively, and the T_g of water has been calculated to be −146°.[18] Thus since T_{g_2} is known, T_{g_1} and K are regarded as calculable parameters and obtained from a plot of $(T_g - T_{g_2})/w_1$ *vs.* w_2 from the slope and intercept respectively. It should be pointed out that Angell and Sare[19] obtained an extrapolated value of −134° for the T_g of water. That value was published after the completion of the study of the glass transition of the ionenes, and thus was not used in the extrapolation calculations. However, a difference of 12° for the T_g of water will not introduce an appreciable error in the extrapolated glass transition temperature of the ionenes since the majority of the points used in the extrapolation lie at low water contents.

Using glycerine as a plasticizer, the accessible concentration range of 0–80% diluent, and the effect of spacing of the ions seems minor. Thus, the 6,4-ionene bromide (m = 6, n = 4) and the 6,5-ionene bromide both have an extrapolated transition of −88°, while that of the 6,8-ionene bromide is *ca.* −82°. Using water as a plasticizer, the accessible concentration range is 5–50% polymer, but the extrapolated glass transitions come out to be very much higher. For example, the value for the 6,8-ionene is −4°, in contrast to the −82° obtained with glycerine. The effect of spacing, however, is also quite small. A tabulation of T_g *vs.* composition is given in Table II for the 6 series and the 4 series, indicating a slight increase in T_g as the concentration of ions along the backbone increases.

TABLE II
GLASS TRANSITIONS OF THE IONENE BROMIDES

$m - n$	6 − 3	6 − 5	6 − 8	6 − 10	6 − 12	6 − 16
T_g, °C	+3	−3	−4	−8	−3	−14
$m - n$	4 − 3	4 − 5	4 − 8	4 − 10	4 − 12	
T_g, °C	−6	−7	−6	−7	−15	

TABLE III
VARIATION OF GLASS TRANSITIONS OF 6,8-IONENES WITH PLASTICIZER COMPOSITION

% glycerine in plasticizer	100	80	60	40	0
T_{g1}, °C	−82	−76	−57	−31	−4

Since water and glycerine give such drastically different T_g values, several water–glycerine mixtures were used as plasticizers for the 6,8-ionene. The results are shown in Table III, which correlates the glass transitions extrapolated to zero plasticizer concentration with the composition of the plasticizer.

It should be added that formamide, the dielectric constant of which is 109 at room temperature (*i.e.*, larger than water) gives a T_g of *ca.* 0°, whereas ethylene glycol, which has a room temperature dielectric constant of 38, gives a value of *ca.* −80°, *i.e.*, very close to that of glycerine. It is highly probable that a conformational transition of the polymer chain occurs in a dielectric constant range corresponding to that encountered in glycerine–water mixtures, and that this conformational effect influences the glass transition profoundly. So far, this effect on the glass transition has not been observed in any other polymer system, but it should be recalled that no other ionic polymer–diluent system has been studied as extensively as that of 6,8-ionene with water and glycerine with respect to the glass transition properties.

An attempt was also made to see whether the q/a relation was encountered in the ionenes. Owing to the very small range of ion concentrations accessible here, the uncertainty was very much greater than in any of the above systems: however for the 6.8 series, a plot of T_g *vs.* q/a can be represented as a straight line given by the relation

$$T_g = 695(q/a) - 23$$

"a" was taken as 5 Å from crystal structure studies of tetramethylammonium bromide, and the extreme, *i.e.*, the completely ionized polymer, was assumed to be $(N(CH_3)_2{}^+)_X$. The above finding seems to confirm the generality of the q/a relation.

Acknowledgment. The partial support of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

---

(15) A. Rembaum, W. Baumgartner, and A. Eisenberg, *Polym. Lett.*, **6**, 159 (1968).

(16) A. Eisenberg, H. Matsuura, and T. Yokoyama, to be published.

(17) E. Jenckel and R. Heusch, *Kolloid-Z. Z. Polym.*, **130**, 89 (1953).

(18) I. Yannas, *Science*, **160**, 298 (1968).

(19) Angell and Sare, *ibid.*, **168**, 280 (1970).