

# Effect of ion association on the properties of ionomers obtained from methyl methacrylate–methacrylic acid copolymer

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(Received 14 April 1989; revised 19 October 1989; accepted 27 November 1989)

The solution behaviour of Na, Ba, Zn and Al ionomers of methyl methacrylate–methacrylic acid copolymer (P(MMA–MAA)) with different ion contents has been studied by viscosity and dipole moment measurements. Two solvents with different character are chosen for viscosity measurements: dioxane ( $\epsilon=2.22$ ) and acetone ( $\epsilon=20.7$ ). The expected polyelectrolyte behaviour of the ionomers in acetone is reflected by the viscometric measurements. Mean squared dipole moment  $\langle\mu^2\rangle$  values are calculated over a temperature range of 20–100°C in dioxane. Effects of neutralization, cation size and cation charge are discussed for each ionomer.

(Keywords: ionomers; copolymer; dipole moment)

## INTRODUCTION

Dipole moment studies of ionomer solutions are rather recent and seem to give comparative information about the structures of the ion clusters prepared in this work. An increase in the ion content increases the mean squared dipole moment  $\langle\mu^2\rangle$ , showing that more dipoles are produced by a larger quantity of cations. The size and the charge of the cation also affects  $\langle\mu^2\rangle$ . This effect is especially observable in Ba ionomers.

The observed increase in  $\langle\mu^2\rangle$  might be due to increase in the thermal motion of the dipoles or decrease in the size of the ionic clusters.

The viscometric behaviour of all ionomer solutions in both dioxane and acetone is in good agreement with literature<sup>1,2</sup>.

## EXPERIMENTAL

Anionic methyl methacrylate–methacrylic acid copolymer (P(MMA–MAA)) was a Rhom Pharma product, where the ratio of carboxyl groups to ester groups was 1:2 (i.e. 33.3% MAA). Its number-average molecular weight was 135 000. After determining the acid content of the copolymer, Na ionomers were prepared by NaOH, Ba by Ba(OH)<sub>2</sub>, Zn by Zn(CH<sub>3</sub>COO)<sub>2</sub> and Al by Al(OH)<sub>3</sub>, with the appropriate degrees of neutralization. Solvents were Merck products and they were used directly without further purification.

Viscosity measurements were obtained with an Ubbelohde viscometer in a constant-temperature water bath at 20°C.

A General Radio Co. type 1620-A capacitance-measuring assembly was used to measure capacitances at 10 kHz frequency. The solutions were confined in a Balsbaugh Laboratories model 350-G three-terminal cell of two coaxial cylinders, which require about 50 ml of solution. The three-terminal cell was mounted in a plastic

vessel and immersed in a thermostat. Solvent evaporation was completely eliminated and the temperature of the cell was controlled to  $\pm 0.1^\circ\text{C}$ . Solutions were prepared by weighing both components and the thermal expansions of all solutions were assumed to be the same as that of the pure solvent.

Refractive index increments were obtained with standard Brice-Phoenix equipment.

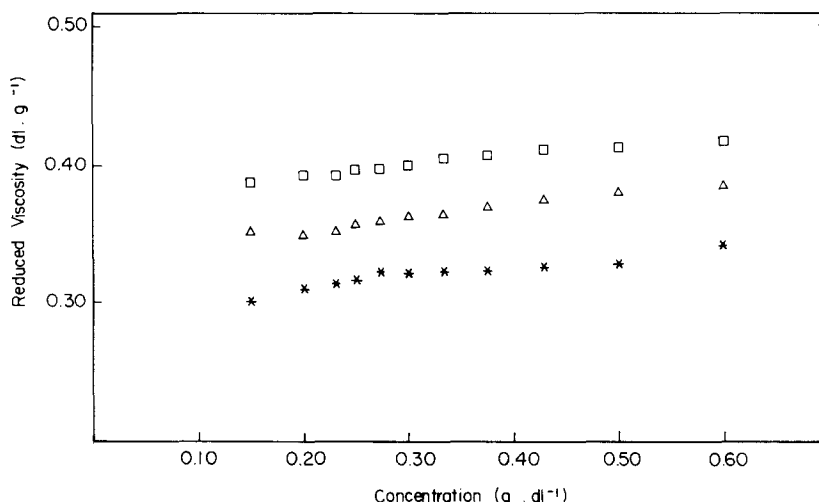
## RESULTS AND DISCUSSION

Dilute-solution behaviour of carboxylated ionomers has been studied extensively by different methods<sup>3</sup>. The results of viscometric measurements on the copolymer and each ionomer prepared in our laboratory in polar and non-polar solvents are in good agreement with the literature. The results of viscosity measurements are given in Figures 1 and 2 for Ba ionomers in dioxane and acetone as an example. The expected polyelectrolyte behaviour, inter- and intramolecular interactions are all observed<sup>4,5</sup>.

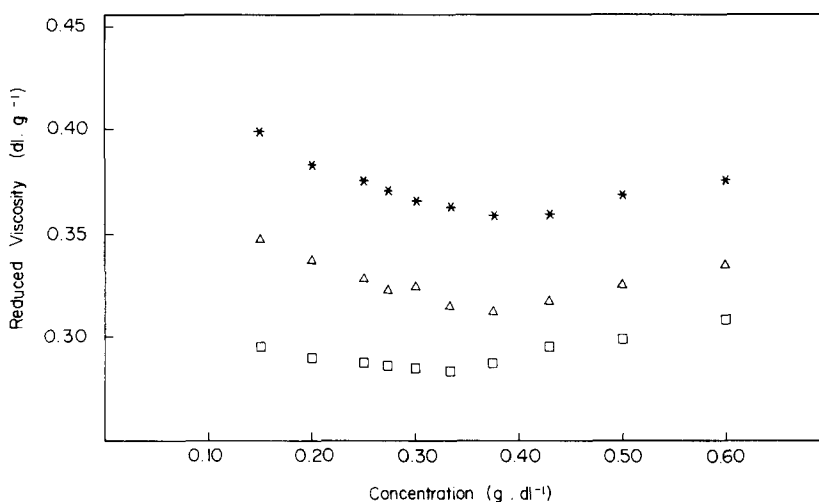
The main objective of this work was to approach the problem by means of  $\langle\mu^2\rangle$ . It is well known that the dipole moment of a macromolecule in solution is the vectorial sum of the dipoles located along the chain<sup>6</sup>. When cations and carboxylate anions are present, cluster association of the ions will take place and this will affect the net mean squared dipole moment of the chain. A non-polar medium was deliberately chosen (dioxane,  $\epsilon=2.24$ , b.p. = 110°C) since according to Marina *et al.*<sup>7</sup> and Forsman *et al.*<sup>8</sup> a medium with a low dielectric constant imitates, to a certain extent, the environment of the ionomer in bulk; non-polar solvents solvate ionic species very weakly and formation of ionic associated species is established to a maximum extent. The mean squared dipole moments per repeat unit of the polymer chain were calculated by the Guggenheim–Smith equation<sup>9,10</sup>:

$$\frac{\langle\mu^2\rangle}{x} = \frac{27kTM_0}{4\pi N_A} \left( \frac{d\epsilon/dc}{(\epsilon_1 + 2)^2} - \frac{2n_1(dn/dc)}{(n_1^2 + 2)^2} \right)$$

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**Figure 1** Reduced viscosity vs. concentration curves at 20°C in dioxane: (□) 5% neutralized Ba<sup>2+</sup>; (△) 15% neutralized Ba<sup>2+</sup>; (\*) 30% neutralized Ba<sup>2+</sup>



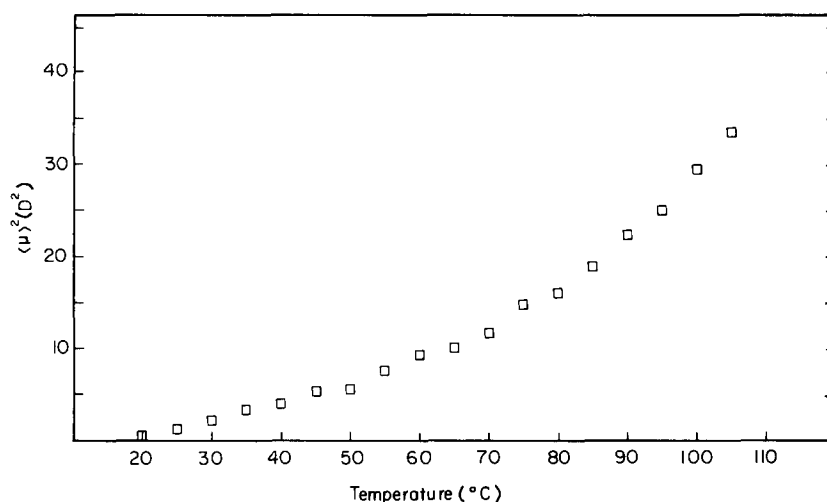
**Figure 2** Reduced viscosity vs. concentration curves at 20°C in acetone: (□) 5% neutralized Ba<sup>2+</sup>; (△) 15% neutralized Ba<sup>2+</sup>; (\*) 30% neutralized Ba<sup>2+</sup>

where  $M_0$  is the molecular weight of the repeat unit calculated by taking into account the percentage neutralization and the type of cation [ $M_0 = MC + (\% \text{ neutralization} \times M^{n+} - \% \text{ neutralization} \times H)$ ],  $MC$  is the molecular weight of the repeat unit of the copolymer (274 g mol<sup>-1</sup>),  $M^{n+}$  is the atomic weight of the cation (g mol<sup>-1</sup>) and  $H = 1$  g mol<sup>-1</sup>,  $N_A$  is Avogadro's number,  $k$  is Boltzmann's constant,  $T$  is absolute temperature,  $\epsilon$  is static dielectric constant,  $n$  is refractive index, and subscript '1' refers to values for pure solvent.

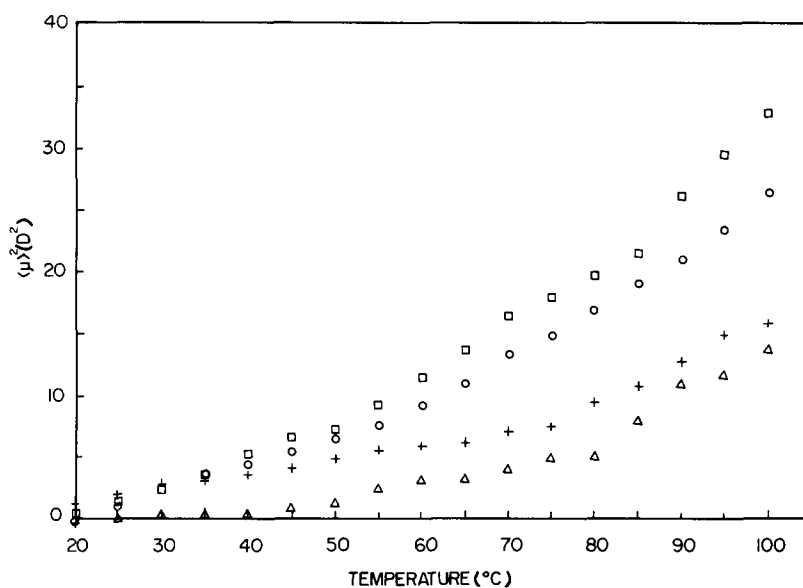
Figure 3 shows  $\langle \mu^2 \rangle$  versus temperature for the MMA-MAA copolymer in dioxane. The hydrocarbon backbone consists of pendant -COOH and -COOCH<sub>3</sub> groups with dipole moments of 1.7 D and 1.4 D, respectively<sup>11</sup>. The observed lower  $\langle \mu^2 \rangle$  values near room temperature confirm the dimerization of the carboxyl groups through H bonding<sup>12,13</sup>. These dimers are expected to be dielectrically inactive.

The increase of  $\langle \mu^2 \rangle$  due to free carboxyl groups is expected since dimers are progressively dissociated with increasing temperature, thus tending to make the dipoles active in capacitance measurements.

Results obtained in dioxane with 5% neutralized Na, Zn, Ba and Al ionomers can be seen in Figure 4. At first sight, the experimental plots show that  $\langle \mu^2 \rangle$  increases when the temperature increases. The highest increase is observed for Na neutralized ionomers. The dipole moment of -COO<sup>-</sup>Na<sup>+</sup> is 6.0 D, which is higher than the dipole moments of -COOH and -COOCH<sub>3</sub> groups<sup>11</sup>, and this fact is well reflected in  $\langle \mu^2 \rangle$  values when they are compared with  $\langle \mu^2 \rangle$  of the copolymer (Figure 3). The  $d \ln \langle \mu^2 \rangle / dT$  values are all positive but take different values in different temperature ranges. There are many  $d \ln \langle \mu^2 \rangle / dT$  values calculated for different polymers in different solvents and different temperature ranges. For example, Baysal *et al.*<sup>14</sup> determined  $d \ln \langle \mu^2 \rangle / dT$  for poly(*p*-chlorostyrene) (PPCS) as  $-8 \times 10^{-3} \text{ } ^\circ\text{C}^{-1}$ ; Saiz *et al.*<sup>15</sup> obtained  $-3 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$  for atactic PPCS and  $-2.4 \times 10^{-3} \text{ } ^\circ\text{C}^{-1}$  for syndiotactic PPCS chains; Tonelli *et al.*<sup>16</sup> calculated the temperature coefficients as  $5 \times 10^{-3} \text{ } ^\circ\text{C}^{-1}$  (PPCS in *p*-dioxane),  $4 \times 10^{-3} \text{ } ^\circ\text{C}^{-1}$  (poly(*p*-bromostyrene) (PPBS) in *p*-dioxane) and  $6 \times 10^{-3} \text{ } ^\circ\text{C}^{-1}$  (PPBS in CCl<sub>4</sub>); Work *et al.*<sup>17</sup> as  $9 \times 10^{-3} \text{ } ^\circ\text{C}^{-1}$ ; Kotera *et al.*<sup>18</sup> as  $2 \times 10^{-3} \text{ } ^\circ\text{C}^{-1}$ ; and Burshtein and



**Figure 3** Mean squared dipole moment vs. temperature curves for P(MMA-MAA) in dioxane



**Figure 4** Mean squared dipole moment vs. temperature curves for 5% neutralized ionomers of P(MMA-MAA) in dioxane: (□) Na<sup>+</sup>; (○) Zn<sup>2+</sup>; (+) Ba<sup>2+</sup>; (△) Al<sup>3+</sup>

Stepanova<sup>19</sup> as  $-3 \times 10^{-3} \text{ } ^\circ\text{C}^{-1}$ . A portion of scattering was attributed to differences in tacticity among the PPCS samples studied. The measurements in these studies were done at two temperatures widely separated from each other, such as 20 and 50°C.

The temperature coefficients for 5% neutralized samples and the copolymer are given in Table 1. There are two temperature coefficients for Na and Zn neutralized samples. The change in  $d \ln \langle \mu^2 \rangle / dT$  values occurs at about 65°C for Na and Zn neutralized samples. The values are higher for lower temperatures and lower for higher temperatures. For Ba and Al neutralized samples there are three temperature coefficients, which show a short plateau region at 45–70°C. The existence of positive temperature coefficients observed in dioxane suggests the possible influence of specific solvent–segment interactions and population of *trans* and *gauche* states in the polymer molecule. Chain expansion, as indicated by increasing temperature, is not a consequence of long-range excluded-volume effects. The dipole moments of most polar polymers are expected to be exclusively sensitive to

**Table 1** Values of  $d \ln \langle \mu^2 \rangle / dT$  for 5% neutralized samples

Temp. range (°C)	Sample	$d \ln \langle \mu^2 \rangle / dT$
30–50	Copoly.	$4.9305 \times 10^{-2}$
50–100	Copoly.	$2.974 \times 10^{-2}$
30–50	Na	$5.775 \times 10^{-2}$
80–100	Na	$2.504 \times 10^{-2}$
30–50	Zn	$4.984 \times 10^{-2}$
80–100	Zn	$2.125 \times 10^{-2}$
20–35	Ba	$6.327 \times 10^{-2}$
40–75	Ba	$2.177 \times 10^{-2}$
75–100	Ba	$3.03 \times 10^{-2}$
30–50	Al	$7.00 \times 10^{-2}$
55–75	Al	$3.23 \times 10^{-2}$
75–100	Al	$4.12 \times 10^{-2}$

short-range intramolecular interactions or conformations and not to excluded-volume effects. The positive temperature coefficient may also imply that the antiparallel arrangement of neighbouring  $-\text{COO}^- \text{M}^+$  units is breaking up upon increase of temperature<sup>20–23</sup>.

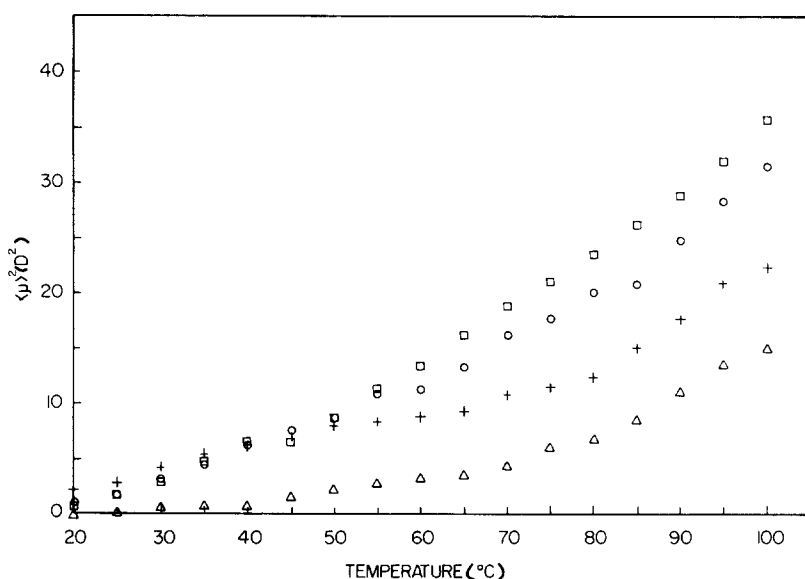


Figure 5 Mean squared dipole moment vs. temperature curves for 15% neutralized ionomers of P(MMA-MAA) in dioxane: ( $\square$ )  $\text{Na}^+$ ; ( $\circ$ )  $\text{Zn}^{2+}$ ; (+)  $\text{Ba}^{2+}$ ; ( $\triangle$ )  $\text{Al}^{3+}$

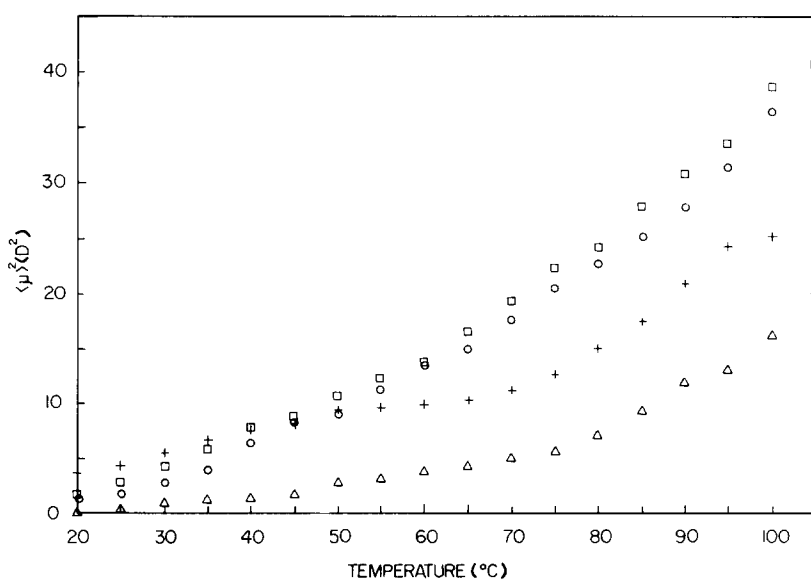


Figure 6 Mean squared dipole moment vs. temperature curves for 25% neutralized ionomers of P(MMA-MAA) in dioxane: ( $\square$ )  $\text{Na}^+$ ; ( $\circ$ )  $\text{Zn}^{2+}$ ; (+)  $\text{Ba}^{2+}$ ; ( $\triangle$ )  $\text{Al}^{3+}$

Zn and Ba neutralized ionomers are expected to form doublets where the effective dipole moment is decreased compared with singlets. Owing to solvent and temperature effects, the conformation of the chain changes and higher  $\langle \mu^2 \rangle$  result at higher temperatures. Al neutralized ionomer has the lowest  $\langle \mu^2 \rangle$  values, and it is expected to make triplets, thus decreasing the net effective dipole of the chain.

Figures 5 and 6 show  $\langle \mu^2 \rangle$  vs. temperature curves in dioxane for the ionomers obtained from MMA-MAA copolymer by 15% neutralizations and 25% neutralizations, respectively, of Na, Zn, Ba and Al.

The trends of the curves seem similar except for slight increase in  $\langle \mu^2 \rangle$  values with increase in degrees of neutralization. The 15% neutralized Na, Zn and Ba ionomers behave similarly up to 50°C and follow their general trends beyond that temperature (Figure 5). An important remark on Figure 6 is that 25% neutralized Na and Zn samples behave similarly in dioxane in the

temperature range 20–105°C, which may be explained by the covalent character of  $\text{Zn}^{2+}$  compared with the ionic characters of  $\text{Na}^+$ ,  $\text{Ba}^{2+}$  and  $\text{Al}^{3+}$ .

## CONCLUSIONS

Niezette *et al.*<sup>4</sup> have studied the viscometric behaviour of n-butyl methacrylate ionomers in tetrahydrofuran ( $\epsilon=7.4$ ) and in toluene ( $\epsilon=2.4$ ). In both solvents, the viscosities decrease with increasing number of ionic groups and the lowest values are obtained in toluene, which confirmed that macromolecular coils contract when ionic and/or acid groups are present in the chains<sup>4</sup>. The contraction is associated with the impairment of the thermodynamic quality of the solvents. Dioxane solvates ionic species weakly and the hydrophobic environment tends to promote the formation of stable ionic associations, which can act as intramolecular aggregates, leading to a reduction in effective dipoles. Yet, increasing

temperature has the reverse effect and unravelling of the macrocoils takes place, which increases the effective dipoles. The unravelling of polymer chains, which results from the dissociation of salt groups, tends to increase with the degree of neutralization. As a result,  $\langle\mu^2\rangle$  values of ionomers depend on solvent medium, type of cation, degree of neutralization and temperature.

#### ACKNOWLEDGEMENTS

This work is partially supported by Middle East Technical University, Ankara, Turkey, under Research Project AFP-86-01-03-01, and Turkish National Technical Research Council (TBTAK); this support is gratefully acknowledged.

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