Effect of ionic concentration and counterion on properties of poly(vinyloxyacetic acid)

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Poly(vinyloxyacetic acid) and its metal salts show polyelectrolyte behaviour in water. The order of counterion binding to this polymer is $K^+ > Na^+ > Li^+ > Ca^{2+}$. The glass transition temperature (T_g) of poly(vinyloxyacetic acid) with low ionic content and that of its metal salts are the same as that of poly(vinyl alcohol) whereas poly(vinyloxyacetic acid) with high ionic content shows an increased T_g.

(Keywords: poly(vinyloxyacetic acid); ionomers; solution properties; thermal properties; polyelectrolyte behaviour)

INTRODUCTION

Ionomers[1–3] have been developed in order to take advantage of their strong coulombic interactions. Properties such as solution[4–21], glass transition temperature[22,23] (T_g), melt viscosity[23,24], mechanical, transparency, and oil resistance are varied by the incorporation of ionic groups into the polymer chain by copolymerization or grafting. Ionomers are used as thickening agents and as membranes such as surlyn, nafion[18], etc. Fuoss and Cathers[25] found that the reduced viscosity of the diluted ionomeric solution increases with decreasing concentration. This is because of aggregation behaviour in non-polar solvents and polyelectrolyte behaviour in polar solvents[12,19,26]. This behaviour can be detected by viscometry, light scattering[17,19,20] and neutron scattering[15] studies. There are several factors that influence solution properties of the ionomers such as molecular weight, ionic content, counterion binding, polarity of the solvent, etc. Reduced viscosity increases with increasing molecular weight and ionic content[12] whereas it decreases with increasing counterion binding[19]. In general, the T_g increases while incorporating bulky and polar groups whereas it decreases with increasing side chain length of the polymers. Poly(vinyloxyacetic acid) (PVOAA) is a well known biodegradable polyelectrolyte[27] consisting of flexible $-O-CH_2-$ linkages and rigid $-COOH$ groups. It is interesting to see the effect of long flexible side chains on solution properties, the T_g and counterion binding. In this paper, the effect of ionic concentration and counterions on the solution and thermal properties of PVOAA are reported.

EXPERIMENTAL

Poly(vinyl alcohol) (PVA) ($M_w = 14\,000$), chloroacetic acid, and sodium hydroxide were used as received.

Measurements. The Fourier transform infra-red (*FT*i.r.) spectrum of PVOAA-I was recorded as a thin film on a Nicolet 20 DXB model *FT*i.r. spectrophotometer. The ^1H n.m.r. spectrum of PVOAA-I was recorded in D_2O on a Bruker 90 MHz ^1H n.m.r. instrument. The viscosity measurements were carried out in double-distilled water using an Ubbelohde viscometer at 30°C. D.s.c. was carried out with a Dupont 910 differential scanning calorimeter over the temperature range 30–360°C at a heating rate of 20°C min^{-1} in N_2 atmosphere.

PVOAA was prepared by using the reported method[26] with different ionic contents; the compositions of PVOAA-I, -II, -III and -IV are given in *Table 1*. The basic aqueous solutions of PVA and chloroacetic acid were mixed together with vigorous stirring and the mixtures were then allowed to stand overnight. The basic solutions obtained were neutralized by adding dilute HCl, reprecipitated from acetone and dried in vacuum.

*FT*i.r.: 2946 and 2880 (C–H str.), 1600 and 1330 (COO^- str.), 1445 (CH_2 bending), 1090 cm^{-1} (C–O– str. of ether).

^1H n.m.r.: 4.8 ($-CH_2-$), 4.1 ($-CH-$), 1.8 ppm ($-O-CH_2-$).

Metal ionomers (PVOAA-M) were prepared from PVOAA by adding excess aqueous metal (Li^+, Na^+, K^+, Ca^{2+}) hydroxide, and reprecipitating from acetone followed by drying *in vacuo*.

RESULTS AND DISCUSSION

Figure 1 shows the reduced viscosity plotted against concentration for PVOAA in water for various ionic contents. The reduced viscosity increases with decreasing polymer concentration, because of the polyelectrolyte behaviour of the system. At constant polymer concentration, the reduced viscosity is directly proportional to the ionic content. As the ionic content increases, repulsive forces between fixed ions ($-COOH$) also increase. This increase in repulsive forces, increases the hydrodynamic volume and the end-to-end distance of the PVOAA. The Fuoss plot for PVOAA in water for various ionic contents was obtained by using the Fuoss equation and the

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Table 1 Composition of PVOAA samples

Code	PVA[a] (M)	$ClCH_2COOH$ (M)	PVA:$ClCH_2COOH$ mole ratio	NaOH (M)
PVOAA-I	0.1136	0.1136	1.0:1.0	0.2272
PVOAA-II	0.1136	0.0909	1.0:0.8	0.1818
PVOAA-III	0.1136	0.0682	1.0:0.6	0.1364
PVOAA-IV	0.1136	0.0227	1.0:0.2	0.0454

[a] Based on the molecular weight of vinyl alcohol

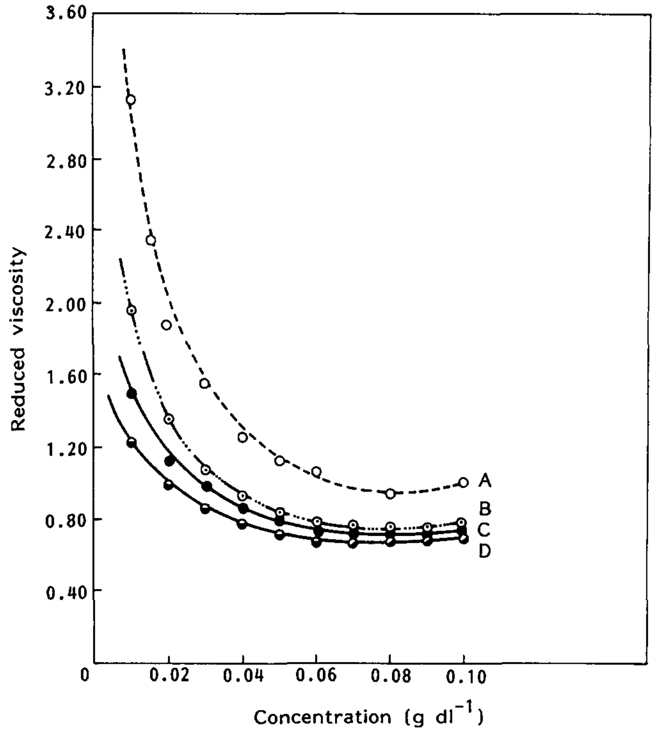

Figure 1 Reduced viscosity *versus* concentration for PVOAA in water for various ionic contents: (A) PVOAA-I; (B) PVOAA-II; (C) PVOAA-III; (D) PVOAA-IV

Table 2 *A* and *B* values from the Fuoss plot for PVOAA in water for various ionic contents

PVOAA	*A* $(g/dl)^{-1}$	*B* $(g/dl)^{-1/2}$
I	−0.77	−3.54
II	11.11	55.56
III	5.00	24.04
IV	2.63	12.65

corresponding *A* and *B* values are given in *Table 2*. The values of *A* and *B* are directly proportional to the ionic content (except PVOAA-I). The *A* values show that the extent to which the polymer coil can spread out increases with increasing ionic content. The values of *B* show that the electrostatic forces decrease with decreasing ionic content. The negative values of *A* (−0.77) and *B* (−3.54) for PVOAA-I show that the Fuoss plot is not applicable to high ionic content ionomers.

Figure 2 shows the reduced viscosities of PVOAA-M in water for various counterions. All PVOAA-M show polyelectrolyte behaviour and the reduced viscosity increases in the order $Li^+ > Na^+ > K^+ > Ca^{2+}$. *Table 3* shows the *A* and *B* values of PVOAA-I-M in water for various counterions. The *A* value is the same for all counterions, as there is no change in molecular weight and ionic content of acid ionomer in the preparation of PVOAA-M. The *B* value changes in the order: $Li^+ < Na^+ < K^+ < Ca^{2+}$. This is due to the Debye–Hückel type electrostatic interaction between fixed ions and counterions[25]. So, counterion binding increases in the order: $Li^+ < Na^+ < K^+ < Ca^{2+}$. Hara *et al.*[19], however have reported the reversed order of counterion binding to the –COOH system. It is known that coulombic interaction and site binding are the two factors that affect counterion binding. If we consider coulombic

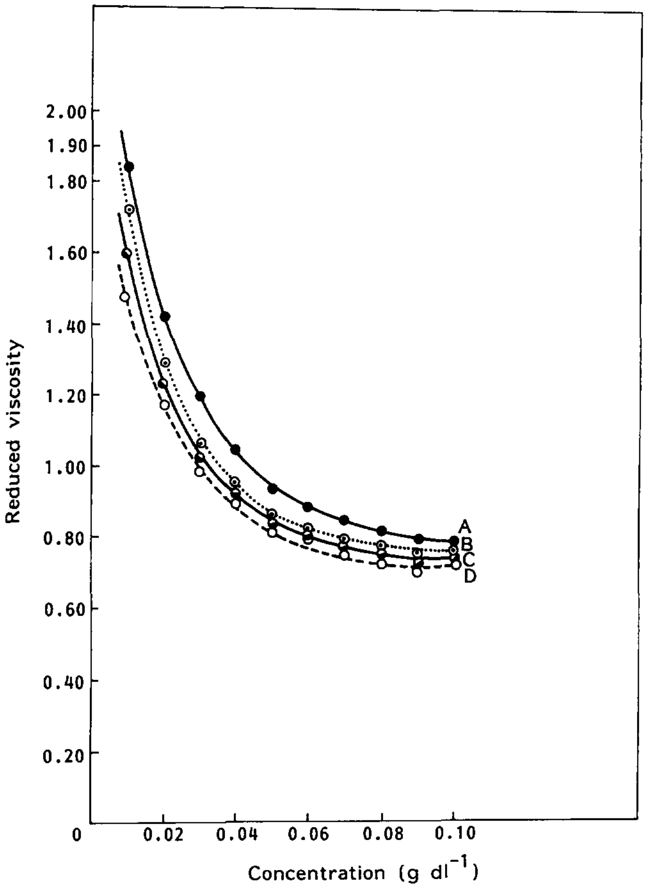

Figure 2 Reduced viscosity *versus* concentration for PVOAA-I-M in water for various counterions: (A) Li; (B) Na; (C) K; (D) Ca

Table 3 *A* and *B* values from the Fuoss plot for PVOAA-I in water for various counterions

Counterion	*B* $(g/dl)^{-1/2}$	*A* $(g/dl)^{-1}$
Li^+	35.09	8.33
Na^+	38.33	8.33
K^+	39.86	8.33
Ca^{2+}	43.16	8.33

interaction, counterions of high charge and small hydrated radius (K^+) would be expected to displace ions of lower charge density from the polyion atmosphere (i.e. the order of counterion binding should be $K^+ > Na^+ > Li^+$). In site binding, it is thought that counterion binding is accompanied by partial desolvation of the hydrated cations as a charged site replaces one or more water ligands of the bound counterion and the desolvated alkali metal ions would be expected to bind in the sequence: $Li^+ > Na^+ > K^+$. According to Hara *et al.*[19], coulombic interaction takes predominance in the $-SO_3H$ system while site binding is predominant in the -COOH system. According to Strauss and Leung[28], flexible ionomers appear to follow the sequence $K^+ > Na^+ > Li^+$, due to the binding of cations to specific $-SO_3^-$ sites. So, the presence of flexible ionic groups ($-SO_3H$) follows coulombic interaction predominantly whereas rigid ionic groups (-COOH) follow site binding predominantly. In PVOAA, the long side chain imparts flexibility and the ionic groups (-COOH) impart rigidity. The results show that flexibility plays a major role so that coulombic interaction take place predominantly and hence the counterion binding is in the order: $K^+ > Na^+ > Li^+$.

D.s.c. scans of PVOAA with different ionic content and PVOAA-III with various counterions are shown in *Figures 3* and *4*, respectively. Except for PVOAA-I, the T_gs for the ionomers are the same. The increase in T_g of PVOAA-I of ~3°C, is due to the presence of a high amount of polar groups and also because of ion quadrupolar crosslinking. The effect of polar groups on T_g in low ionic content ionomers is cancelled by the presence of long side chains. As reported earlier, it was found that the T_g does not change upon neutralization of PVOAA by metal hydroxides[29].

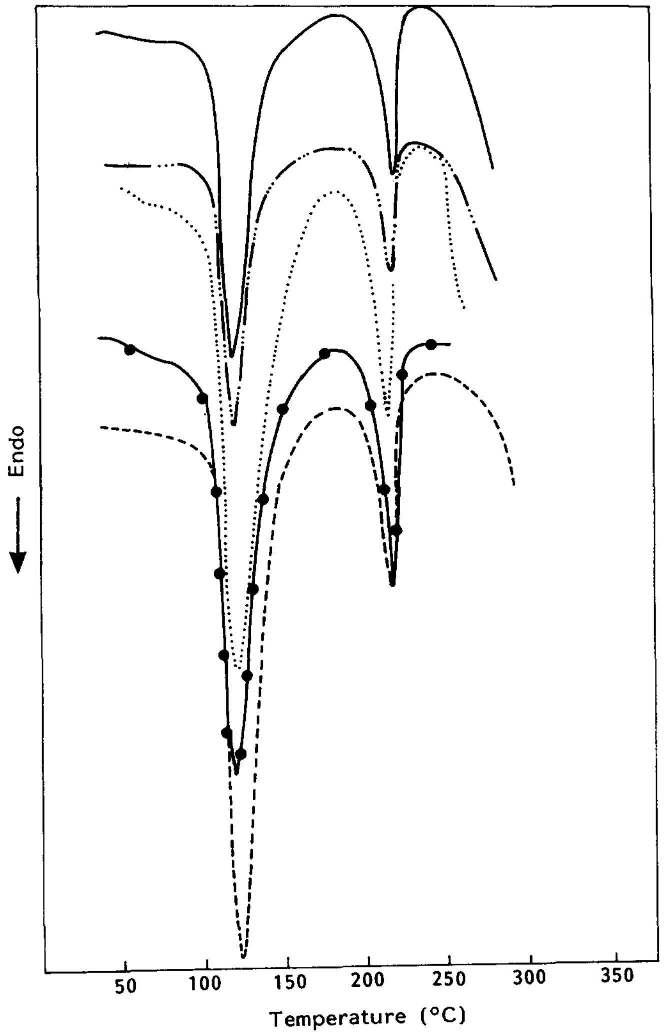

Figure 3 D.s.c. scans of PVA (···), PVOAA-I (---), PVOAA-II (-···), PVOAA-III (——) and PVOAA-IV (-●-)

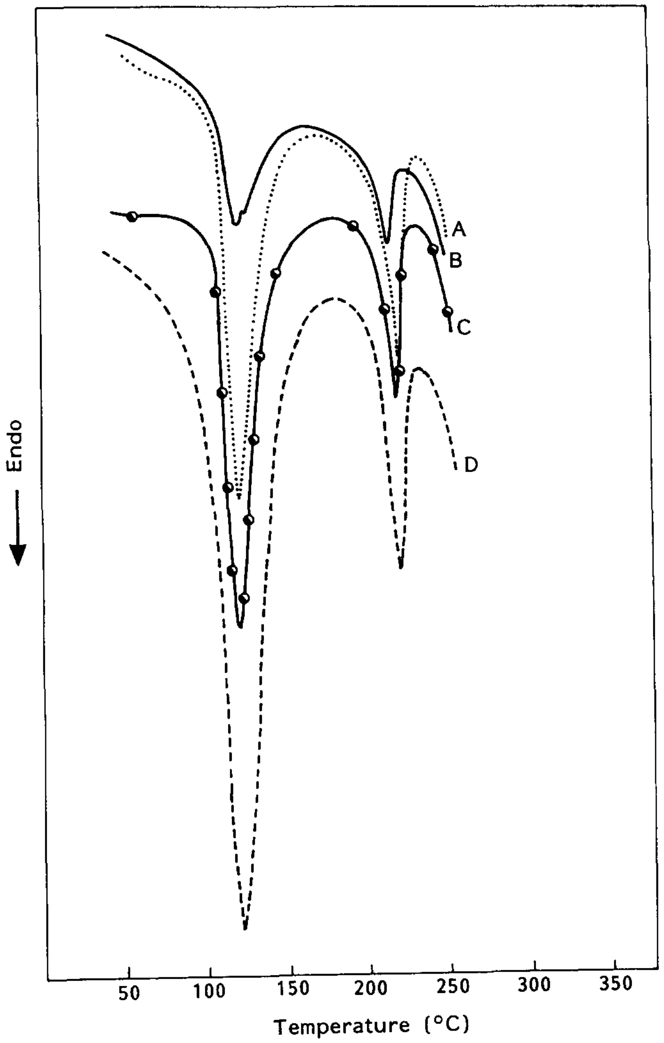

Figure 4 D.s.c. scans of PVOAA-III-M ionomers. M: (A) Na; (B) Li; (C) K; (D) Ca

CONCLUSIONS

The effect of ionic content and counterion on PVOAA was studied. Although PVOAA consists of -COOH groups and a long side chain, the counterion binding is similar to that observed for the $-SO_3H$ system. Long side chain length and polar groups play a major role on the T_g. It is possible to develop ionomers with long flexible side chains and it may be of interest to study not only the application of ionomers in industry but also to have a basic understanding of the effect of ionic content and counterion effect on the T_g and solution properties.

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