ELSEVIER

Polymer 40 (1999) 329–335

polymer

Positronium–salt interactions and ionic conductivity in poly(2-hydroxyethyl methacrylate) gel electrolytes

R.M. Hodge[a,b,*], P.E.M. Allen[c], D.A. Miller[c], D.R.G. Williams[c], G.P. Simon[b]

[a]*METSS Corporation, 720-G Lakeview Plaza Blvd, Columbus, OH 43085, USA*
[b]*Department of Materials Engineering, Monash University, Clayton, Victoria 3168, Australia*
[c]*Department of Chemical Engineering, The University of Adelaide, North Terrace, Adelaide, South Australia 5005, Australia*

Received 28 July 1997; accepted 26 January 1998

Abstract

The effects of copolymerization of poly(2-hydroxyethyl methacrylate) with oligo-(ethylene glycol) dimethacrylates (OEDs) on the ionic conductivity of the gel electrolyte copolymers was investigated. A series of HEMA–OED cross-linked copolymers were produced with the number of ethylene glycol units varying between zero (uncross-linked) and nine. The conductivity of samples containing distilled and deionized water (DDIW) and 1 M KBr electrolytes was characterized by AC impedance measurements. The relationship between the amount of water/salt solution contained within the gel electrolytes and resultant conductivity is investigated and discussed with reference to the free volume in the system. The free-volume characteristics were probed by positron annihilation lifetime spectroscopy (PALS), and the influence of free volume and the amount of water/solution in the gels on conductivity discussed. The results indicate a positive correlation between the amount of mobile conducting phase and the available free volume in the system, with the amount of conducting phase present matched by a proportionate amount of free volume in the gel. The system showed evidence of orthopositronium (oPs) inhibition in the ion containing samples when compared with the DDIW samples. Slight differences in the oPs pickoff rate recorded in DDIW and KBr solution are attributed to microviscosity differences between the two fluids, rather than oPs quenching. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Gel electrolytes; Ionic conductivity; Positron

1. Introduction

Solid polymer electrolytes posses the ability to solvate a number of ionic salts by coordination and achieve conductivity through a mechanism of ionic conductivity. This ionic conductivity has been discussed in terms of a model whereby ionic transport is facilitated through large amplitude motion of the main chain macromolecules as cation–heteroatom interactions are formed and broken at various sites along the polymer chains. Conductivity in these polymers has been shown to be enhanced by the addition of plasticizers, which enhance molecular motion, however this increase in conductivity is achieved at the expense of mechanical rigidity [1].

Polymer gel electrolytes consist of a polymer–solvent–salt system, in which a low molecular weight solvent solvates the salt ions and acts as the conducting medium. In gel electrolytes, the macromolecular matrix plays an indirect, secondary role in achieving ionic conductivity, by providing a mechanical support framework through which ionic transport is facilitated via the solvent–salt medium. There is an added benefit in gel electrolyte systems in that whilst the solvent–salt mixture acts directly as a charge carrying medium, it further enhances conductivity by plasticizing the polymer matrix and increasing molecular mobility. Polymer electrolytes exhibit superior stiffness and dimensional stability, but are subject to ion pair formation at high ion concentrations, and may contain regions of crystallinity which act as barriers to charge transport through the polymer matrix. Gel electrolyte systems offer mechanical integrity as the polymer matrix supports the conducting phase, which dissociates the charge carriers and plasticizes the polymer network, along with a high degree of homogeneity since no crystals are present in the matrix.

In the present study, we have studied the poly(2-hydroxyethyl methacrylate) (pHEMA)–salt–water gel electrolyte system. This system is capable of absorbing large amounts (40–45 wt%) of water [2], while retaining the essential properties of a solid such as shear and compression moduli.

---

[*] Corresponding author.

PII: S0032-3861(98)00197-9

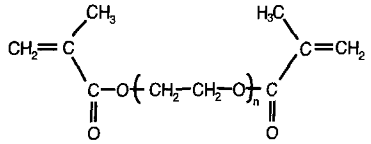

Fig. 1. Generalized structure of oligo-(ethylene glycol) dimethacrylate molecules. Molecule shown ($n = 1$) is EGDMA.

pHEMA is a relatively simple gel in structural terms and its water absorbing characteristics and mechanical properties may be readily controlled by cross-linking with ethylene glycol dimethacrylate (EGDMA). EGDMA is usually found to some degree as an impurity byproduct of the HEMA monomer production process, and its presence decreases the equilibrium water content (EWC)—the maximum amount of water that may be absorbed by the gel—as it is hydrophobic with respect to pHEMA. Additionally, the cross-linking effect of the EGDMA restricts the amount of swelling in the pHEMA, thereby further limiting the EWC of the gels. EGDMA is the first in a series of oligo-ethyleneglycol dimethacrylates (OEDs), which have the general structure represented in Fig. 1, where n represents the number of ethylene glycol repeat units. Altering n regulates the length and flexibility of the cross-links which form in the gels as a result of the presence of the methacrylate functional groups at either end of the EGDMA molecule.

In this investigation, a series of pHEMA gel electrolytes with varying cross-link lengths were prepared and the conductivities of the gels containing distilled and deionized water (DDIW) and aqueous KBr solution were measured. KBr was chosen as the electrolyte in this investigation as it has been shown [3] to have a minimal effect on the EWC of pHEMA, therefore allowing more direct comparison between the DDIW and salt solution samples to be made. The nature of the water/solution phase in the gels was characterized using differential scanning calorimetry (d.s.c.), and the free volume was probed using the positron annihilation lifetime spectroscopy (PALS) technique. PALS has been used previously with some success to investigate ionic conductivity in solid polymer electrolyte systems [4–6]. Forsyth et al. [4] confirmed that the increase in free volume brought about by plasticizer addition in polyether–urethane solid polymer electrolytes was predominantly responsible for observed increases in the ionic conductivity of the systems. In gel electrolytes where the chain mobility plays an important role in determining conductivity, a technique enabling free-volume characteristics of the gel to be assessed would likewise be particularly instructive. The PALS technique is sensitive to areas of reduced electron density in condensed matter, such as voids and vacancies, and free volume in polymers. The localization of the ortho-positronium (oPs) positron species in free-volume cavities, which typically range in size from about 100 to 400 $Å^3$ enables free volume in polymers to be readily probed by the PALS technique. After localizing in free-volume cavities in the polymer, the oPs annihilates by a pickoff process with a lifetime dependent on the free-volume cavity size. PALS provides two parameters useful in assessing variation in free-volume characteristics of the polymer system under investigation. τ_3 is determined by local electron density, with a high local electron density (such as that associated with a relatively small free-volume cavity) yielding a short oPs lifetime. I_3 determines the percentage of annihilation events which occur by the pickoff mechanism and so is useful in determining the relative number of free-volume sites (in which pickoff takes place) in the system.

2. Experimental

2.1. Materials and sample preparation

HEMA was obtained from Mitsubishi Chemicals and contained 50 ppm hydroquinone monomethyl ether as inhibitor. N.m.r. measurements (S. Hagias, private communication, 1995) indicated the presence of 0.3 mol% EGDMA in the HEMA monomer. EGDMA, DiEGDMA ($n = 2$), TEGDMA ($n = 4$) and P400 ($n \approx 9$) were obtained from Polyscience. The peroxide initiator used was *t*-butyl per-2-ethyl hexanote (TBO) and was supplied by Interox (Australia). The KBr salt for solution preparation was an analytical grade obtained from BDH. All chemicals were used as received without further purification.

Polymerization was carried out by a casting process described by Cowperthwaite [8], followed by curing (if applicable) and annealing at 60°C and 110°C, respectively. The OED–HEMA copolymers produced contained 3 mol% OED molecules. The cast samples were slowly cooled to ambient temperature in order to prevent quench-induced fracture. The resultant casts were insoluble in water owing to the presence of the chemical cross links imparted by the various oligo-EGDMA in the monomer. All casts were transparent and approximately 2.0 mm thick.

Samples were soaked in distilled and deionized water (DDIW) or 1 M KBr solutions until the EWC was reached. The EWC is defined by the following:

$$\mathrm{EWC} = \frac{W_w - W_d}{W_d} \times 100\% \quad (1)$$

where W_w and W_d is the weight of the fully saturated and dry polymer, respectively. Before property measurement, surface water/solution was removed from the samples by blotting with soft tissue paper.

2.2. Experimental measurements

Conductivity measurements were performed with a Hewlett Packard HP4284 LCR bridge at 25°C. The measurement cell consisted of two stainless steel disk electrodes mounted on a brass stand whose separation was controlled by a micrometer spindle so as to ensure good electrical contact.

The water/solution environments were measured on a Perkin Elmer DSC II differential scanning calorimeter with the head maintained in a dedicated dry box, purged with helium gas. Samples were placed in sealed pans for measurement, and the heating rate employed was 10°C/min. Water content was calculated from the area under melting endotherms.

PALS data were collected on an automated EG&G Ortec thermally stablilized, fast/fast coincidence system with a ^{22}Na resolution of 250 ps at 22°C. The 35 μCi ^{22}Na positron source was heat sealed between two teflon coated Kapton sheets, with the teflon surfaces facing inwards. Data were analysed using the PFPOSFIT program [9], with the shortest lifetime fixed at 125 ps (corresponding to pPs self annihilation). Three to eight spectra of 30 000 counts were collected for each sample, with collection time varying between 90 min and 7 h, depending on experimental conditions. Errors in the PALS data are population standard deviations. PALS parameters (lifetimes and intensities) were approximately constant within each sample, even after prolonged contact with the source, indicating that no radiation induced damage was evident. 35% of the spectrum of annealed Al was found to originate from the Kapton source with a lifetime of 400 ps and a suitable source correction was therefore applied to remove this intermediate lifetime annihilation from the spectra collected from the gel samples.

3. Results and discussion

The EWC and conductivity characteristics of the various OED–HEMA copolymer samples are shown in Figs 2 and 3, respectively. The EWC and conductivity both initially decrease significantly on copolymerization with EGDMA, followed by a gradual increase in both quantities as n is increased in the OED comonomers. The gradual increase in conductivity for $n > 1$ is almost linear however, whereas the EWC increases more sharply between $n = 1$ and $n = 2$ before appearing to approach a limiting value. The results are more instructive, however when the effects of the structure of the water in the system are taken into account. The different components of water have been calculated previously in this system [10]. Non-freezing water molecules are those involved directly in forming secondary bonding interactions with hydroxyethyl and/or ethylene glycol moities in the polymer network. As a direct result of these interactions, non-freezing water (discrete domains of which typically consist of only one or two water molecules per binding site [10]) does not undergo melting or freezing transitions of the type normally associated with water clusters.

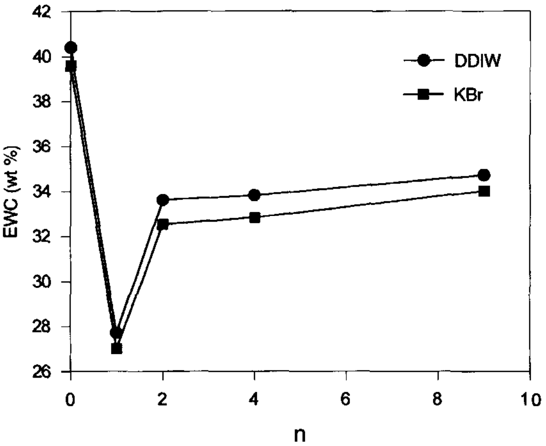

Fig. 2. The variation in EWC with OED species at 25°C for samples containing DDIW and 1 M KBr solution. n is the number of ethylene glycol units in the OED.

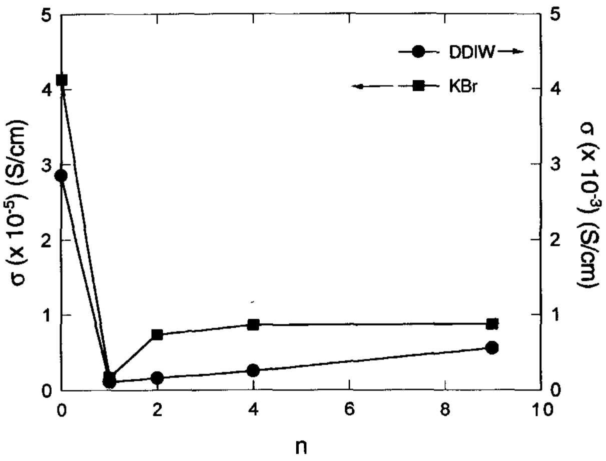

Fig. 3. The variation in conductivity with OED species at full hydration and 25°C for samples containing DDIW and 1 M KBr solution. n is the number of ethylene glycol units in the OED.

Table 1 presents the different components of the water calculated for each of the OED–HEMA copolymers in this investigation. Table 1 reveals that the amount of non-freezing water increases between $n = 2$ and $n = 4$ in conjunction with the increased hydrophilicity of the cross-link species (with respect to EGDMA), but is then observed to decrease as n increases further. This suggests that the increased hydrophilicity of the cross-links is dominated by a corresponding increase in flexibility for higher n, promoting structural conformations of the polymer network which in turn favour increased intra-molecular hydrogen bonding, excluding tightly bound water molecules. The amount of freezing water in the OED–HEMA copolymers was found by Allen et al. [10] to increase monotonically with cross-link length. This is presumably owing to the cross-link molecules maintaining the polymer network in an increasingly open state with increasing cross-link length. In addition to water existing in these polymers in freezable and non-freezing form, within the freezable water category there exists a further two distinct and separate states of water. Interfacial water molecules are not directly associated via secondary bonding to the polar moities within the polymer network. They are, however, subject to influence by the tightly bound non-freezing water

Table 1
Summary of sample characteristics, showing the relative amounts of freezable and non-freezing water in each of the OED–HEMA copolymers

Cross-link agent	n	EWC[a] (wt%)	Total freezable water (g/g_{gel}) [12]	Non-freezing water (g/g_{gel}) [12]	Freezable/non-freezing
—	0	40.4	0.130	0.262	0.496
EGDMA	1	27.7	0.019	0.261	0.073
DiEGDMA	2	33.3	0.022	0.308	0.071
TEGDMA	4	33.8	0.031	0.306	0.101
P400	9	34.7	0.062	0.283	0.219

[a] Indicates measurements made on samples prepared for this work, almost identical EWC values were recorded by Allen et al. [12] during including d.s.c. evaluations of freezable and non-freezing water contents of identical copolymers

domains—with which they are closely associated—and as such behave sufficiently differently to bulk water to be considered as a distinct phase. Free water exists within the polymer network essentially as microscopic aggregations of bulk water, behaving in a manner essentially identical to bulk water. Non-freezing, interfacial and free water can, therefore, be considered to have progressively diminishing strength of interaction with the polymer network, with the microviscosity of each of these phases decreasing accordingly.

A plot of the ratio of freezable water to non-freezing water against n, as shown in Fig. 4 leads to a trend which is strikingly similar to that observed in the conductivity data (Fig. 3). The strong correlation in the form of the two sets of data contained in Fig. 4 indicates that the conductivity appears more closely related to the ratio of freezable water to non-freezing water than to the EWC of the polymer. Since the conductivity characteristics are primarily influenced by the mobility of the carrier phase (in this case, the freezable water contained within the polymer network), it is reasonable to assume that parameters which influence the mobility of the carrier phase will markedly affect the conductivity of the system. The data presented in Fig. 4, therefore, takes account of the influence on the higher mobility freezable phases by the less mobile non-freezing phase. A high ratio of freezable to non-freezing water indicates a highly mobile carrier phase, whereas the opposite is true of a low ratio. This distinction is impossible to deduce if only the EWC is considered.

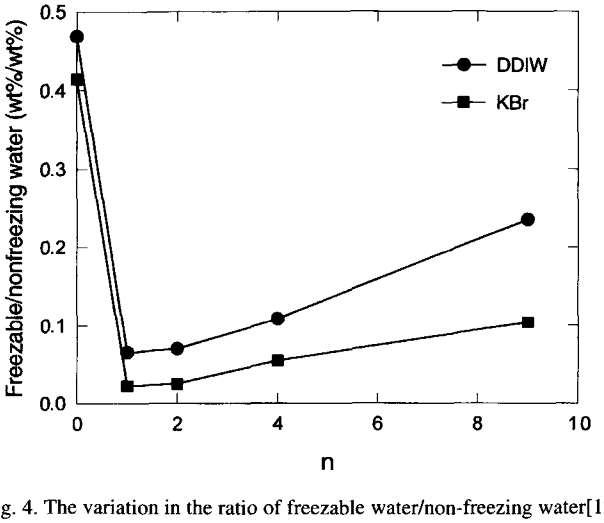

Fig. 4. The variation in the ratio of freezable water/non-freezing water[12] with OED species at full hydration and 25°C for samples containing DDIW and 1 M KBr solution. n is the number of ethylene glycol units in the OED.

Figs 2 and 4 indicate that both the EWC and the ratio of freezable water to non-freezing water in samples containing DDIW is consistently higher than that in the samples containing the salt solution. The decrease in EWC and the freezable/non-freezing water ratio has been attributed previously to an enhancement of hydrophobic inter and intramolecular bonding within the polymer network [11]. Additionally, KBr alters the structure of the occluded water, decreasing the amount of freezing water as the KBr solution concentration is increased. The extra number of charge carrying entities in the KBr salt solution is clearly reflected in the conductivity data in Fig. 3, which shows an approximate 100-fold increase in conductivity in the salt containing samples when compared with the DDIW samples.

In addition to the behaviour of the charge carriers themselves, however, it is also necessary to consider the influence of the water phases on the polymer network itself. Conductivity is a function not only of the number of available charge carriers, but also depends on the mobility of these charge carriers, which is in turn effected by various polymer–water–ion interactions. A high mobility carrier phase is most efficiently conducted through a polymer network when the network is itself in a relatively mobile state.

PALS data were collected from the OED–HEMA copolymer samples in order to assess the influence of water addition on free-volume characteristics of the system. Fig. 5 shows the τ_3 behaviour of the OED–HEMA copolymer system for gels containing DDIW and the KBr salt solution. It has been shown previously in poly(vinyl alcohol) [12] that positron data must be corrected to account for oPs annihilations in water. These annihilations occur by the so-called 'bubble' mechanism [13]—in which contributions to the positron spectrum are made by the water by the oPs entering the liquid, blowing a bubble around itself and subsequently annihilating by pickoff. If free-volume characteristics in the polymer network are to be isolated from those occurring in the system as a whole, the contribution to the spectra from the DDIW and KBr solution must therefore be removed. The data presented in Fig. 5 are corrected to account for these effects using experimentally determined

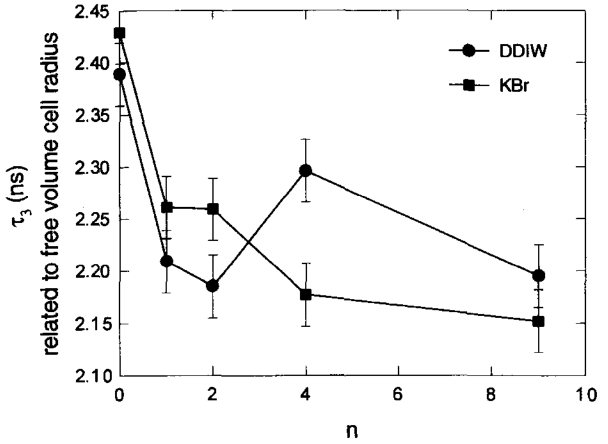

Fig. 5. The variation in oPs lifetime, τ_3 (related to the mean free-volume cell radius) with OED species at full hydration and 25°C for samples containing DDIW and 1 M KBr solution. n is the number of ethylene glycol units in the OED. Error bars are population standard deviation of the data.

values of τ_3 by subtracting the weighted contribution from the freezable water/solution in the manner described elsewhere [12]. The experimentally determined values used in this correction for both DDIW and KBr solution were 1.897 and 1.824 ns, respectively. As previously mentioned, the KBr solution microviscosity is slightly altered with respect to that of DDIW, which would be reflected in a slight change in size of the oPs bubble formed in the KBr liquid prior to annihilation. The small magnitude of the decrease in τ_3 in the KBr solution indicates that it is owing to the increase in viscosity of the solution, rather than oPs quenching arising from oPs—ion interactions. Indeed, it has been recognized previously [14] that reduction of oPs lifetime in liquids owing to the addition of salts can be attributed to increasing solution density and a corresponding increase in oPs pickoff rate.

The τ_3 (related to the free-volume cell radius) of the polymer network in the gel systems is observed to decrease significantly in both the DDIW and KBr electrolyte series on cross-linking. This decrease is the expected result of the introduction of cross-links into the network, which constrict the main chain macromolecules, preventing them from swelling to the same degree observed in the uncross-linked pHEMA samples and, consequently, limiting the size of the free-volume cavities interspersed throughout the gel network. τ_3 continues to decrease as n is increased from one to nine, reflecting a gradual decrease in free-volume cavity size with increasing cross-link length. Again, it is postulated that the increased length of the cross-link molecules is dominated by a corresponding increase in flexibility, which allows the network to pack more efficiently. The exception is the datum at $n = 4$ for the DDIW series, which indicates a sudden increase in free-volume cavity size not observed in the KBr series. It is possible that the KBr solution promotes ion–polymer coordination and/or intra-chain interactions not present in the DDIW series at this cross-link length which act to constrict the network and lower the mean free-volume cavity size.

It is interesting to note that the mean free-volume cavity size is larger in the KBr solution series than in the DDIW series for smaller values of n. It is believed that this is again due to the microviscosity differences between the two liquids, with the KBr solution not able to fill smaller free-volume cavities as well as the lower viscosity DDIW. The remaining unfilled free volume in the polymer probed by the oPs is, therefore, larger in the KBr series than in the DDIW series until the chain flexibility is sufficiently high (at higher n) to allow for the solutions to better fill the available free volume in the network.

Fig. 6 shows the variation in I_3 with cross-link length for the polymers. Once again, the data contained in Fig. 6 has been corrected to account for the contribution from free-volume sites in the polymer only by removing the contribution from annihilation events in the DDIW–KBr solution. Corrections were performed using experimentally obtained values of I_3 for the DDIW and KBr solution of 17.795% and 16.498%, respectively. Changes in oPs annihilation intensity (I_3) are indicative either of decreasing number of oPs annihilation sites, commensurate with a decrease in available free-volume sites in polymers, or to a decrease in the probability of oPs formation. Decreases in the probability of oPs formation arise from oPs inhibition brought about by a competing mechanism of positronium species formation. The introduction of salts into a water swollen polymer complicates an already complex system. For example, inhibition of positronium (Ps) formation by electron scavengers is often reported [15] and quenching of oPs can also occur [16]. Whilst quenching of Ps formation (such as by electron scavengers which combine with electrons in the terminal spur) leads mainly to changes in oPs intensity (I_3), quenching of oPs by reaction may also effect the oPs lifetime (τ_3) [16]. The same processes occur in some polymeric materials, such as chlorinated macromolecules, however the effect tends to be weaker in these materials. It is also

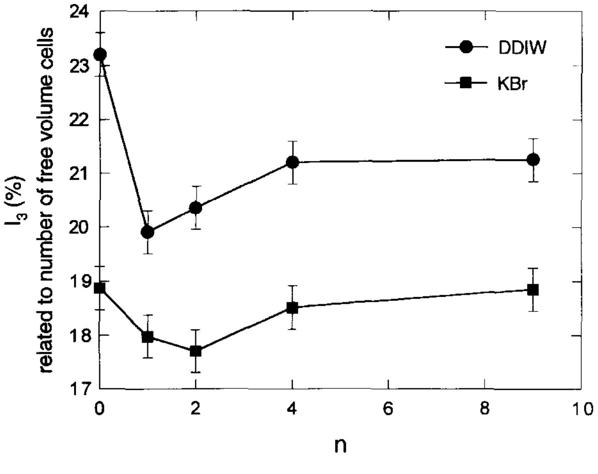

Fig. 6. The variation in oPs pickoff intensity, I_3 (related to the number of free-volume cells in the polymer) with OED species at full hydration and 25°C for samples containing DDIW and 1 M KBr solution. n is the number of ethylene glycol units in the OED. Error bars are population standard deviation of the data.

possible, for example, for the salts to alter the dipole character of polymer side groups and main chains, thereby increasing local negative charge density and promoting chemical inhibition of oPs formation in favour of positron capture by anion species [14]. The magnitude of the inhibition is dependent on anion concentration, following an approximately exponential relationship up to some saturation value [4]. Inhibition is believed to have occurred in these samples given the decrease in I_3 on addition of KBr to the DDIW.

The magnitude of oPs inhibition varies significantly only in samples with different anion concentrations, whereas a series of samples containing consistent anion concentration will be subject to similar influences with respect to oPs formation rate. The KBr sample series tested in this work contained a constant anion concentration (1 M with respect to Br$^-$), and the oPs annihilation intensity is not used in absolute terms in arguments in the present work, but rather presented as an indication of trends occurring within the gel system. Since the relevant variables are internally consistent, the oPs annihilation intensity in the system can, therefore, be discussed in isolation from external effects such as chemical inhibition.

The form of the curves displayed in Fig. 6 is similar to that shown in Fig. 5, with a sharp decrease in I_3, immediately evident with incorporation of cross-links into the polymer network, indicating a sharp decline in the number of free-volume sites probed by the oPs. The relative decrease in available free-volume sites is consistent with the restrictive action imparted on the network by introduction of the short inflexible cross-links. The initial decrease in I_3 is followed by a gradual increase to a limiting value as the length of cross-link molecules is increased. Seemingly, as the length of cross-link molecules increases, more free-volume sites become available to act as sites for oPs annihilation. This is reflected in the increase in I_3 over the intermediate range of cross-link lengths, followed by the annihilation rate intensity reaching an approximately limiting value as the flexibility of the molecules begins to dominate the length, leading to a corresponding increase in packing efficiency.

The data presented in Fig. 7 illustrate changes in the fractional free volume of the system. The oPs pickoff lifetime, τ_3, is dependent on the local electron density in free-volume cavities and therefore proportional to the average free-volume cell radius, whereas I_3 is indicative of the relative number of free-volume cells in the polymer. Variations in the quantity $I_3 \times \tau_3^3$, therefore, provide an approximation of changes in fractional free volume in the system. As a result of this simple calculation, Fig. 7 is a composite of Figs 5 and 6, and indicates that the free volume decreases markedly in the system in response to cross-linking with EGDMA. As n increases, the free volume remains essentially constant in both the DDIW and KBr series, with the exception of the datum for $n = 4$ in the KBr series, which has been discussed previously. The data indicate, therefore, that free volume is maximized in the uncross-linked samples, before decreasing to a limiting value in the cross-linked samples. This similarity in form of Figs 7, 3 and 4 indicates that free volume, conductivity and the relative amount of conducting phase are inter-related quantities.

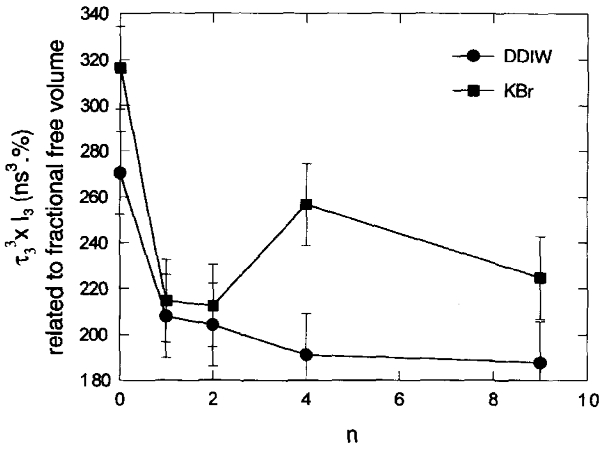

Fig. 7. The variation in $(\tau_3^3) \times I_3$ (related to the amount of fractional free volume) with OED species at full hydration and 25°C for samples containing DDIW and 1 M KBr solution. n is the number of ethylene glycol units in the OED. Error bars are calculated from population standard deviation of the τ_3 and I_3 data.

Ionic conductivity depends to varying degrees on three factors. The amount of conducting phase present is primarily responsible for determining the conductivity of the system. The absolute amount of conducting phase present must, however, be considered with reference to the nature of the conducting phase, the mobility of which plays a significant role in the behaviour of the system. Additionally, the nature of the polymer network remains a determining factor in the conductivity behaviour of the system. The polymer network also plays an important role by determining the continuity of the conductive phase, altering the microscopic viscosity of the water/solution phase as a result of interactions between the water phase and polar moities in the network, and owing to its own flexibility and mobility.

Whether the free volume in the system determines or is determined by the amount of conducting phase is unclear. It is certainly difficult to imagine a system containing large amounts of conducting phase without the pre-existence of free volume into which the water/solution may diffuse, yet it is also clear from investigations by other workers (K.J. Heater, unpublished data; and Refs. [12] and [17]) that free volume increases in hydrophilic polymers as a result of water absorption. It is, thus, probable that the amount of available charge carrying phase and the free volume in the system are inter-dependent. In any case, the data indicate that conductivity in the polymers investigated in the current work is influenced by both molecular variables and the nature and amount of available charge carrying phase.

4. Conclusions

Although the amount of charge carrying phase in the polymer is primarily responsible for determining the ionic conductivity, the role of the polymer network is also important. The experimental data and discussion support the conclusion that a relationship of interdependence exists between the amount of mobile conducting phase present in the gels and the available free volume (and hence molecular mobility) throughout the polymer. The amount of conducting phase present is matched by a proportionate amount of free volume in the gel. Free-volume data in this system collected by PALS indicate oPs inhibition in the KBr solution, presumably as a result of oPs—anion interactions. A slight discrepancy in the oPs pickoff rate in DDIW compared with that in the 1 M KBr solution is ascribed to microviscosity differences between the two fluids and is not believed to arise from oPs quenching.

References

[1] Voice AM, Southall JP, Rogers V, Matthews KH, Davies GR, McIntyre JE, Ward IM. Polymer 1994;35:3363.

[2] Bennett DJ. Ph.D. dissertation, University of Adelaide, Adelaide, Australia, 1991.

[3] Hamilton CJ, Murphy SM, Atherton ND, Tighe BJ. Polymer 1988;29:1879.

[4] Forsyth M, Meakin P, MacFarlane DR, Hill AJ. J Phys Condens Matter 1995;7:7601.

[5] Hung SI, Such K, Wieczorek W, Stevens JR. J Polym Sci B: Polym Phys 1994;32 (16):2733.

[6] Stevens JR, Chung SH, Horoyski P, Jeffrey KR. J Non-Cryst Solids 1994;1207:172–174.

[8] Cowperthwaite GF, Foy JJ, Malloy MA. In: Geblen GG, Koblitz FF, editors, Biomedical and dental applications. New York: Plenum Press, 1981:397.

[9] Puff W. Comput Phys Commun 1983;30:359.

[10] Allen PEM, Bennett DJ, Williams DRG. Eur Polym J 1993;29(2/3): 231.

[11] Refojo M. J Polym Sci Pt A-1 1967;5:3103.

[12] Hodge RM, Bastow TJ, Edward GH, Simon GP, Hill AJ. Macromolecules 1996;29:8137.

[13] Ferrell RA. Phys Rev 1958;110:1355.

[14] Goldanski VI. Atom Energy Rev 1968;6:3.

[15] Bartal LJ, Nicholas JB, Ache HJ. J Phys Chem 1972;76:1124.

[16] Mohamed HFM, Ito Y, El-Sayed AM, Abdel-Hady E. Polymer 1996;37:1529.

[17] Welander M, Maurer FHJ. J Mater Sci Forum 1992;1815:105–110.