Preparation of inner salt polymers from vinylimidazolium sulphobetaines

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(Received 31 March 1977)

The preparation and properties of ampholytic polymers has been a relatively unexplored area. In this work are discussed the syntheses of monomeric vinylimidazolium sulphobetaines, a class of aromatic inner salt monomers, their free radical polymerizations, and the properties of the resulting polymeric inner salts. Several of the ampholytic polymers prepared were shown to have hydrogel characteristics.

INTRODUCTION

The preparation of cationic polyelectrolytes has been an area of increasing interest because of the various commercial applications of these materials[1]. In general, cationic polyelectrolytes are normally derived either from the free radical (homo- or co-) polymerization of a cationic vinyl monomer or from the quaternization of a preformed, neutral, nucleophilic polymer. The cationic vinyl monomers normally studied are those derived from quaternary (meth)acrylates and quaternary (meth)acrylamides. In the latter two types of monomers, the positive charge is far removed from the double bond to facilitate free radical polymerization.

Our research in the area of cationic vinyl monomers and polymers has involved those derived from the vinylpyridine and vinylimidazole families. Both of these quaternary monomer systems have the positive charge on an aromatic ring in resonance with the double bond. Whereas a majority of our work in vinylpyridinium systems has been in the area of spontaneous polymerization[2], the research on vinylimidazolium systems has involved more easily controllable free radical homopolymerization and copolymerization[3–10]. For the latter monomeric salts, it was possible to produce polymers which ranged in aqueous solution properties from typical polyelectrolytes to polysoaps, depending on the hydrophilic/hydrophobic character of the polyion. In regard to their copolymerization behaviour it was noted that, as expected, there was a change in the *e* value of the Afrey–Price *Q*–*e* scheme from that of a negative *e* for the unquaternized monomers to that of the positive *e* for the quaternized salts[7].

In conjunction with our investigations on the syntheses and aqueous solubility studies of vinylimidazolium salts, it was of interest to prepare zwitterionic sulphobetaine monomers derived from the ring-opening of a sultone by nucleophilic vinylimidazole, followed by their free radical polymerization to the corresponding poly(vinylimidazolium sulphobetaines). Although monomeric and polymeric vinylimidazolium betaines and sulphobetaines have been reported in the patent literature, the isolation and characterization of these compounds was usually not undertaken[11,12]. Whereas the preparation of other aromatic betaine and sulphobetaine polymers have been reported, based principally on poly-2- and 4-vinylpyridine[13,14], a majority of these ampholytic polymers appear to be derived from aliphatic, nucleophilic monomers such as the dialkylaminoethyl acrylates and methacrylates[15]. One major difficulty with the aliphatic (sulpho)betaines of the latter type is that they are susceptible to hydrolysis of the ester linkage, thus ultimately generating a polyanion with concomittant destruction of the zwitterionic nature of the polymer. This, of course, is not possible with aromatic (sulpho)betaines in which there are no readily hydrolysable groups present in the inner salt structures. Furthermore, the sulphobetaine structure was considered to be of more interest in this study than that of the normal betaine structure because the anionic sulphonate group is more difficult to protonate than the anionic caboxylate group and would maintain an inner salt structure over a wider pH range. In the latter case, if protonation of the carboxylate group were to occur, it would be expected that the resulting polymer would behave as a polycation instead of a polymeric inner salt.

In this investigation are reported the syntheses and polymerizations of several vinylimidazolium sulphobetaines as well as a study of the hydration properties of the resulting zwitterionic polymers which, in some cases. display hydrogel character.

EXPERIMENTAL

Monomer preparations

1-Vinyl-3-(3-sulphopropyl)imidazolium hydroxide inner salt (I). To 35.0 g (0.287 mol) of 1,3-propanesultone in 500 ml of dry ethyl acetate was added 25.0 g (0.265 mol) of freshly distilled 1-vinylimidazole at 25°C. After reaction under slight reflux and constant stirring for 7 days, a finely divided white precipitate was obtained. Upon filtering, thorough washing with dry ethyl acetate, and vacuum drying a crude product was obtained in 94.3% yield. Final recrystallization from absolute ethanol yielded the product in the form of white prisms, which were quite hygroscopic, m.p. 189.5°–190.4°C. Analysis calculated for $C_8H_{12}N_2SO_3$: C, 44.43%; H, 5.59%; N, 12.95%. Found: C, 44.33%; H, 5.52%; N, 12.8%.

1-Vinyl-2-methyl-3-(3-sulphopropyl)imidazolium hydroxide inner salt (II). To 35.0 g (0.287 mol) of 1,3-propanesultone in 500 ml of dry ethyl acetate was added 25.0 g (0.231 mol) of freshly distilled 1-vinyl-2-methylimidazole at 25°C. After reaction at room temperature and constant stirring for 7 days, a white precipitate was obtained. Upon filtering, thorough washing with dry ethyl acetate, and vacuum drying the product was obtained in 77.8% yield. Final recrystallization from absolute ethanol yielded hygroscopic prisms, m.p. 240.7°–242.1°C. Analyses calculated for $C_9H_{14}N_2SO_3$: C, 46.94%; H, 6.13%; N, 12.16%. Found: C, 46.96%; H, 6.20%; N, 11.76%.

1-Vinyl-3-(4-sulphobutyl)imidazolium hydroxide inner salt (III). To 5.0 g (0.0367 mol) of 1,4-butanesultone in 50 ml of dry ethyl acetate was added 3.0 g (0.0213 mol) of freshly distilled 1-vinylimidazole at 25°C. The reaction mixture was allowed to react under slight reflux for 14 days, after which the white precipitate was filtered and washed thoroughly with dry ethyl acetate. After vacuum drying, the product was recrystallized from absolute ethanol and obtained in 85.6% yield, m.p. 226.5°–227.5°C. Analysis calculated for $C_6H_{14}N_2SO_3$: C, 46.94%; H, 6.13%; N, 12.16%. Found, C, 47.08%; H, 5.96%; N, 11.89%.

1-Vinyl-2-methyl-3-(4-sulphobutyl)imidazolium hydroxide inner salt (IV). To 5.0 g (0.0367 mol) of 1,4-butanesultone in 50 ml of dry ethyl acetate was added 3.3 g (0.035 mol) of freshly distilled 1-vinyl-2-methylimidazole at 25°C. The reaction mixture was then allowed to react under slight reflux for 14 days, after which the white precipitate that was obtained was filtered and thoroughly washed with dry ethyl acetate. Drying and recrystallization from absolute ethanol yielded the product in 35.1% yield, m.p. 247.5°–248.5°C. Analysis calculated for $C_{10}H_{16}N_2SO_3$: C, 49.16%; H, 6.60%; N, 11.47%. Found: C, 49.46%; H, 6.55%; N, 11.27%.

1-Vinyl-3-(2-sulphobenzyl)imidazolium hydroxide inner salt (V). To 2.55 g (0.015 mol) of α-hydroxy-*o*-toluenesulphonic acid-γ-sultone in 100 ml of dry ethyl acetate was added 1.22 g (0.013 mol) of freshly distilled 1-vinylimidazole at 25°C. After reaction under slight reflux and constant stirring for 7 days, an off-white precipitate was obtained. Upon filtering, thorough washing with dry ethyl acetate, and vacuum drying a crude product was obtained in 80.7% yield. Final recrystallization from absolute ethanol yielded off-white needles, m.p. 223 9°–225.4°C. Analysis calculated for $C_{12}H_{12}SO_3$: C, 54.33%; H, 4.58%; N, 10.59%. Found: C, 54.68%; H, 4.54%; N, 10.61%.

1,4-Butanediyl-3,3'-bis-1-vinylimidazolium diiodide (VI). This crosslinking agent was prepared as previously reported[5], m.p. 160.0°–160.5°C.

Polymer Preparations

Poly[1-vinyl-3-(3-sulphopropyl)imidazolium hydroxide inner salt] (VII). Into a 25 ml polymerization tube was introduced 1.0 g (0.0046 mol) of I and 0.013 g (1 mol %) of 4,4'-azobis-4-cyanovaleric acid (ACVA). To this, 20 ml of distilled water was added, yielding a 0.23 M aqueous solution of monomeric salt. The contents of the tube were then flushed with nitrogen and sealed *in vacuo* after utilization of the freeze–thaw technique. The tube was then placed in a constant temperature bath at 60°C for 24 h. The resulting heterogeneous mixture was then turned homogeneous by addition of 50 ml of 1.0 M KBr solution and exhaustively dialysed against deionized water. The resulting water-insoluble polymer was amber coloured and rubbery when wet. After vacuum drying at 110°C, the dried, brittle polymer was obtained in 72.3% yield. Analysis calculated for $C_8H_{12}N_2SO_3$: C, 44.43%; H, 5.59%; N, 12.95%. Found: C, 44.04%; H, 5.79%; N, 12.72%.

Poly[1-vinyl-2-methyl-3-(3-sulphopropyl)imidazolium hydroxide inner salt] (VIII). This polymer was prepared by the same procedure as that for VII, except for the utilization of 1.152 g (0.0050 mol) of II, 0.0070 g (1 mol %) of ACVA, and 25 ml of distilled water, yielding a 0.20 M aqueous solution of the monomeric salt. The resulting polymer was again obtained from a heterogeneous mixture with the exception that it was opaque and white in colour. The yield of the polymer was 82.5% after vacuum drying. Analysis calculated for $C_9H_{14}N_2SO_3$: C, 46.94%; H, 6.13%; N, 12.16%. Found: C, 46.30%; H, 6.42%; N, 11.85%.

Poly[1-vinyl-3-(4-sulphobutyl)imidazolium hydroxide inner salt] (IX). Using the same technique as described for VII, 1.324 g (0.00575 mol) of III in 25 ml of distilled water containing 0.0612 g (1 mol %) of ACVA were polymerized at 60°C for 24 h. The resulting heterogeneous polymerization mixture was made homogeneous by addition of 50 ml of 1.0 M KBr solution and dialysed against deionized water. Final extraction until negative to silver nitrate and vacuum drying yielded an amber coloured polymer in 75.6% yield. Analysis calculated for $C_9H_{14}N_2SO_3$: C, 46.94%; H, 6.13%; N, 12.16%. Found: C, 45.55%; H, 6.03%; N, 11.46%.

Poly[1-vinyl-2-methyl-3-(4-sulphobutyl)imidazolium hydroxide inner salt] (X). To 1.405 g (0.00575 mol) of IV in 25 ml of distilled water was added 0.0162 g (1 mol %) of ACVA. The polymerization mixture was prepared as previously described and allowed to polymerize at 60°C for 24 h. The resulting heterogeneous mixture was made homogeneous by addition of 50 ml of 1.0 M KBr solution and then dialysed against deionized water. The polymer was white in colour and was obtained in 50.0% yield after vacuum drying. Analysis calculated for $C_{10}H_{16}N_2SO_3$: C, 49.16%; H, 6.60%; N, 11.47%. Found: C, 47.78%; H, 6.56%; N, 10.75%.

Poly[1-vinyl-3-(2-sulphobenzyl)imidazolium hydroxide inner salts] (XI). The same conditions as in the previous cases, with the exception of 0.275 g (0.001 mol) of V, 0.003 g (1 mol %) of ACVA, and 4 ml of 0.50 M aqueous KCl solution, were used to prepare XI. The resulting polymer was obtained from a heterogeneous mixture, in spite of the use of the added KCl solution, and it did not possess the hydrogel character exhibited by the previous polymers. The polymer was obtained in 50.5% yield and was insoluble in a saturated aqueous solution of KI. The polymer was soluble in concentrated sulphuric acid. Analysis calculated for $C_{12}H_{12}N_2SO_3$: C, 54.53%; H, 4.58%; N, 10.59%. Found: C, 52.36%; H, 4,82%; N, 10.15%.

Crosslinking reactions

Crosslinked VII. To a polymerization tube was added 2.0 g (0.009 mol) of I, incremental amounts of 1 to 5 mol % of VI, 0.026 g (1 mol %) of ACVA, and 10 ml of distilled water. The resulting polymerization mixture was treated under the same conditions as VII. The polymer was obtained in the form of a porous sponge and was extracted with a 1.0 M aqueous KBr solution to dissolve any homopolymer that may have been produced as well as to dissolve any residual monomer. The completely crosslinked material was repeatedly extracted using distilled water and finally dried to give the end product in 42.0, 60.0, 66.8, 68.6 and 71.2% yields for the respective amount of crosslinking agent used.

Viscosity studies

Polymer samples VII and VIII were dissolved in 0.50 M KCl solutions to yield an approximately 0.01 M stock solu-

Table 1 N.m.r. spectral data of monomeric imidazolium inner salts in D_2O

	2[a]			Vinyl[c]			Alkyl					Coupling constants (Hz)			
Monomer	H	CH_3	4,5[b]	A	B	C	$N-CH_2$	$-CH_2-$	$-CH_2CH_2-$	$-CH_2SO_3$	Aromatic	J_{45}	J_{AB}	J_{AC}	J_{BC}
I	9.20	–	7.93, 7.76	7.27	5.91	5.52	4.52*t*	2.44*m*	–	3.04*t*	–	0	15	9	3
II	–	2.77	7.80, 7.62	7.22	5.83	5.56	4.41*t*	2.33m	–	3.01*t*	–	2	15	9	2
III	9.08	–	7.80, 7.62	7.16	5.81	5.44	4.31*t*	–	1.92*m*	2.97*t*	–	0	16	9	3
IV	–	2.71	7.74, 7.54	7.17	5.78	5.52	4.25*t*	–	1.96*m*	2.97*t*	–	2	15	9	2
V	9.20	–	7.79, 7.63	7.16	5.83	5.46	–	5.92	–	–	7.7–8.0	0	16	9	3

[a] All peaks in singlets; [b] all peaks in doublets; [c] all peaks in doublets of doublets.

tion. Viscosities were then determined with an Ubbelohde No. 1 viscometer at 25.0° + 0.02°C, taking thorough precautions to keep all solutions dust free. Polymer samples VII and VIII had intrinsic viscosities of 0.22 and 0.68 dl/g, respectively.

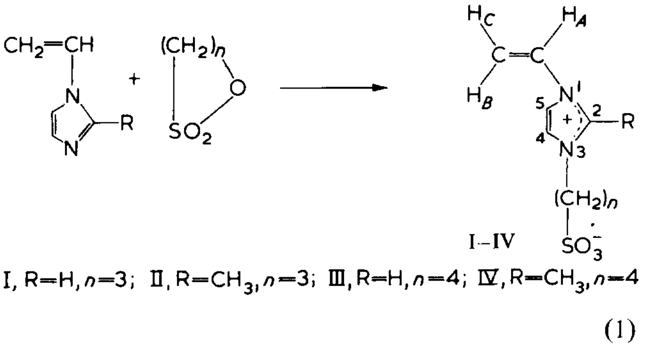
Hydration studies

Polymer samples VII, VIII, IX and X and crosslinked VII were allowed to equilibrate in distilled water at the temperature of interest for 5 days, patted dry with bibulous paper, and weighed to yield the wet weight. Each sample was then dried in a vacuum oven at 100°C for 24 h and then allowed to come to room temperature under vacuum. Weight of the samples then gave the dry weight, which allowed calculation of the amount of water absorbed.

RESULTS AND DISCUSSION

Monomer preparations

In this work, it was of interest to prepare several vinylimidazolium sulphobetaine inner salts of different chemical structures. The preparation of two of these monomeric salts was readily achieved by the quaternization of 1-vinylimidazole and 1-vinyl-2-methylimidazole with 1,3-propanesultone in ethyl acetate (reaction 1, $n = 3$) according to the procedures given in the Experimental section. These reactions result in the quaternization of the respective vinylimidazole at the 3-position as verified by their n.m.r. spectra (*Table 1*) in relation to those of related vinylimidazolium salts[5]. It was found that both 1-vinyl-3-(3-sulphopropyl)imidazolium hydroxide inner salt (I) and 1-vinyl-2-methyl-3-(3-sulphopropylimidazolium hydroxide inner salt (II) were obtained in high yield upon reaction at room temperature for one week.



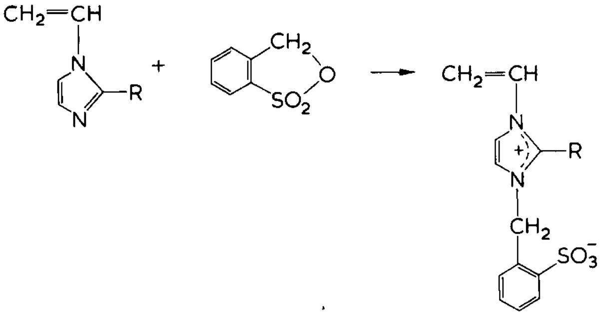
I, R=H, n=3; II, R=CH_3, n=3; III, R=H, n=4; IV, R=CH_3, n=4

(1)

When the quaternization reaction was performed under reflux, the monomeric salts were again obtained in high yield, although a small amount of polymer formation occurred which could be removed upon recrystallization of the monomeric inner salt. For both monomers, recrystallization from absolute ethanol yielded hygroscopic white prisms.

The quaternization of the vinylimidazole monomers with 1,4-butanesultone yielded the monomeric inner salts III and IV, respectively (reaction 1, $n = 4$). The reaction conditions were similar to the conditions for the previous two inner salts; however, refluxing of the reaction mixtures was necessary to achieve similar yields for the same period of reaction time. Recrystallization of the products from absolute ethanol yielded white needles, which appeared to be less hygroscopic than their sulphopropyl analogues.

Another monomeric inner salt of interest was that obtained by the quaternization of 1-vinylimidazole with α-hydroxy-*o*-toluenesulphonic acid-γ-sultone (reaction 2). The utilization of this aromatic five-membered sultone as a quaternization agent has apparently not been reported in the literature. This reaction appeared to proceed less rapidly than those utilizing 1,3-propanesultone and the resulting product, 1-vinyl-3-(2-sulphobenzyl)imidazolium hydroxide inner salt (V), was recrystallized from absolute ethanol, yielding off-white needles. It should be noted that V is more hydrophobic than either I or II and that it has an *o*-toluenesulphonate linkage at the imidazolium 3-position which could exhibit strong counterion binding to cationic groups[16].



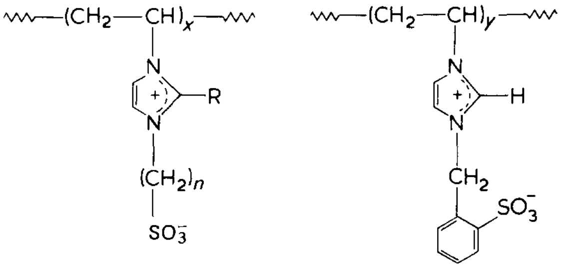
(V) R=H (2)

Of further interest in this work were the preparation and properties of crosslinked poly(vinylimidazolium sulphobetaines). In order to ensure effective copolymerization and yet maintain an overall polyvinylimidazolium backbone, it was decided to employ 1,4-butanediyl-3,3′-bis-1-vinylimidazolium diiodide (VI), a monomer which as been previously reported as a crosslinking agent with other vinylimidazolium salts[5]. Although this monomer is in fact a true salt, it was expected to copolymerize with the inner salts, since most vinylimidazolium salts appear to have similar $Q-e$ values under similar experimental conditions[6].

Polymerization reactions

The polymerization of vinylimidazolium salts having either iodide or methylsulphate counterions through their free radical initiation, in either water or alcohol solution, has been previously reported[5]. For these salts it was found that the persulphate initiating system was ineffective for the iodide salts in that iodine appeared to be released and no noticeable polymerization occurred; consequently, these polymerizations were initiated at 60°C with the water soluble azo initiator 4,4′-azobis-4-cyanovaleric acid (ACVA).

In a similar fashion, for the inner salts I–V it was initially decided to employ ACVA as the initiator in aqueous solutions at 60°C. Each of these solutions had to be carefully degassed in order for polymerization to occur. For the polymerization of I, II, III and IV to form VII, VIII, IX and X, respectively, it was found that the polymeric inner salts coacervated from the aqueous solutions as the polymerizations progressed. These polymers were purified by dissolution of the resulting rubber gels into aqueous salt solution of sufficiently high molarity, followed by exhaustive dialysis against distilled water. During this time the polymers again precipitated. Polymer VII and IX were found to be rubbery when wet, translucent, and amber in colour, while polymers VIII and X were opaque, white and less rubbery when wet. These polymers readily dissolved in salt solutions in which the ions are considered to have strong cation and/or anion site binding ability. Consequently, using a 0.50 M aqueous potassium chloride solution at 25°C as an example, intrinsic viscosity values of 0.22 and 0.68 dl/g were determined for VII and VIII, respectively.



VII–X (XI)

VII, $R=H, n=3$; VIII, $R=CH_3, n=3$; IX, $R=H, n=4$, X, $R=CH_3, n=3$

Presumably, other salt concentrations and solutions utilizing different salts would yield different results, as this has been indicated for other polymeric inner salts[17–21].

In order to ascertain if a clear, colourless hydrogel could be obtained for VII it was decided to conduct the polymerization in 0.50 M potassium chloride solution under analogous conditions to those previously employed since it was expected that the polymer would not precipitate during polymerization. In this case, the solution remained homogeneous; however, after dialysis against distilled water, an opaque, white material was obtained. The intrinsic viscosity of this polymer was 0.31 dl/g under the conditions given above. Another effort was made to prepare a clear, colourless hydrogel through polymerization at a lower temperature (25°C), using the redox initiating system of sodium bisulphite and potassium persulphate in aqueous solution. Again, the resulting polymer was opaque and white.

For the polymerization of the more hydrophobic monomer inner salt V to XI, it was again decided to conduct the polymerization in aqueous 0.50 M potassium chloride solution in order to facilitate solubilization. However, this polymer precipitated in spite of the added electrolyte and it was noted that it was also insoluble in saturated potassium iodide solution which would be a solvent of greater anion counterion binding ability. This may indicate a high degree of counterion binding of the imidazolium ring with the strongly bound *o*-toluenesulphonate group in the presence of competitive iodide anions. In all of these studies the resulting polymer (XI) did not possess any hydrogel character.

It should be noted that the four polymeric inner salts VII–X had the very unusual feature of being water-insoluble in the absence of added electrolyte, and soluble in the presence of certain added electrolytes. None of the polymers prepared in this study were soluble in polar organic solvents, although this was possible for the monomers. In strong acid solution, however, solubilization of all polymers occurred readily, most likely as a result of the protonation of the pendant sulphonate group. The general insolubility in water is most likely a result of strong intramolecular and/or intermolecular attraction between the imidazolium and sulphonate groups. These results appear to be analogous to those of a scrambled salt polyelectrolyte complex consisting of 'ionic crosslinks' between two polyions of opposite charges[22].

Since the above polymers were ionically and not covalently crosslinked, it was of interest to ascertain the effect of crosslinking on the polymerization reaction. Using increments of 1 to 5 mol % of 1,4-butane-diyl-3,3′-bis-1-vinylimidazolium diiodide VI with monomer I in aqueous solution, the crosslinked plugs were thoroughly extracted with distilled water, washed several times with salt solution to extract any homopolymer, and again treated with distilled water until a negative silver nitrate test was obtained. The crosslinked polymers were always obtained in the form of hydrated, amber coloured plugs. When dried and then rehydrated, the polymers became opaque and were easily broken into pieces. This brittleness was more apparent in the presence of aqueous salt solutions in which more rapid and greater swelling occurred. None of these crosslinked polymers gave any indication of producing a covalently crosslinked, clear, rubbery hydrogel as was thought possible.

Hydration studies

The procedure employed for the hydration studies was similar to that generally used in the study of hydrogels[23]. The material to be studied is polymerized to yield a suitable physical form, such as a film, and then allowed to equilibrate in distilled water at a certain temperature. This is followed by blotting the polymer with bibulous paper to remove any surface water, weighing, vacuum drying, and final weighing of the dried material. However, due to the physical nature of the poly(vinylimidazolium sulphobetaines), it was difficult to prepare the polymer in the form of thin films to facilitate equilibration, drying, and measurement of dimensions. In most cases the samples under study spread in water and formed somewhat thick films, which did not keep their form upon being patted dry. To ascertain the applicability and consistency of the procedure used, samples were measured up to five times with varying amounts of swelling time, ranging from 3 to 14 days. In all cases, the water content of each sample agreed to within 1%. For the crosslinked materials, which did not exist in the form of films at any time, the procedure showed the same consistency as before.

The first stage of the hydration studies involved the investigation of the effect of initial dilution of the monomer solution on the amount of water absorbed by the polymer. This was prompted by an earlier report on the polymerization of 2-hydroxyethyl methacrylate in water solution, which illustrated the equilibrium water content of the hydrogel depended on the initial dilution of the monomer solution

Table 2 Effect of temperature and monomer concentration on the equilibrium water of hydration

Monomer concentration (M)	Equilibrium water of hydration (wt %)		
	25°C	35°C	45°C
0.10	38.1	–	–
0.20	40.9	41.2	40.6
0.30	40.4	40.5	39.3
0.40	40.5	40.5	40.8
0.50	40.4	40.5	40.2

Table 3 Effect of crosslinking agent on the equilibrium water of hydration

Crosslinking agent (%)	Equilibrium water of hydration (wt %)
1.0	43.4
2.0	49.5
3.0	50.0
4.0	51.5
5.0	53.1

as well as the temperature[23]. Using VII as an example in the monomer concentration range of 0.10 to 0.50 M, such an effect was not observed (*Table 2*). Furthermore, upon increasing the temperature of these polymerizations (*Table 2*), the equilibrium water of hydration remained essentially constant. This, again, is quite different from the behaviour of the neutral hydrogels, which show a definite change in the equilibrium water of hydration upon temperature change[23]. Furthermore, for certain neutral hydrogels in water it has been reported that opacity can develop at high molecular weight and/or at high equilibrium water of hydration[24]. Since polymer VIII behaves very similarly to polymer VII, it is quite conceivable that the apparent higher molecular weight of VIII, as reflected by its higher intrinsic viscosity, is related to its opacity relative to the transparency of VII with the additional possibility that it is slightly more hydrophobic due to the presence of an additional methyl group in the 2-position.

The second stage of the hydration studies concerned the crosslinking of the poly [1-vinyl-3-(3-sulphopropyl)imidazolium hydroxide inner salt] and its effect on the equilibrium water of hydration. Somewhat surprisingly, a definite increase in the water of hydration with increasing crosslinking is observed, as shown in *Table 3.* For an overall neutral material, the opposite effect was anticipated. However, consideration of the chemical nature of the crosslinking agent indicates that, upon crosslinking, a small amount of cationic sites have been introduced, which may cause the network to behave similarly to a crosslinked, cationic polyelectrolyte, known to swell upon equilibration in aqueous solution, but not necessarily known to increase in swelling with increasing crosslinking density[25]

It is apparent that the poly(vinylimidazolium sulphobetaines) display very unusual solubility behaviour, especially in the presence of added salt. This is clearly indicated by their insolubility in water and their ability to dissolve in the presence of certain aqueous salt solutions. Further studies will be reported in the near future on the elucidation of the properties of these polymeric inner salts.

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