

# Synthesis and homopolymerization studies of vinylimidazolium salts

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The preparations and characterizations of several monomeric vinylimidazolium salts are presented from the quaternizations of 1-vinylimidazole and 2-methyl-1-vinylimidazole with *n*-alkyl iodides and with dimethyl sulphate. Although vinylimidazolium salts have been reported in the patent literature, many of these salts were not isolated and characterized prior to their polymerization. From the reactions of 1-vinylimidazole with *n*-alkyl iodides, a homologous series of 3-*n*-alkyl-1-vinylimidazolium iodides were prepared in which the longer chain derivatives appeared to form micelles in aqueous solution. Dicationic cross-linking agents were also prepared through similar quaternization reactions. All the cationic vinyl monomers were homopolymerized in aqueous solution by free radical initiation. The solution behaviour of the resulting polyions indicated that the longer side-chain polyions had polysoap properties.

## INTRODUCTION

The free radical polymerization of cationic vinyl monomers has been an area of increased interest in recent years<sup>1,2</sup>. Although many such monomers have been synthesized, most of these have contained the positive charge far removed from the double bond. Very few studies have been concerned with monomers in which the positive charge was adjacent to the vinyl group, since these monomers can be difficult to polymerize. However, it has been found that when the cationic site is on an aromatic ring which is adjacent to a double bond, homo- and co-polymerization appears possible. This is illustrated by the free radical polymerizations of various vinylpyridinium<sup>3-7</sup> salts.

In this work are presented the preparation, characterization and polymerization of a variety of quaternary iodide and methylsulphate salts from 1-vinylimidazole and 2-methyl-1-vinylimidazole. Although mention has been made in the patent literature on the free radical polymerization of vinylimidazolium salts<sup>8</sup>, in many cases these quaternary monomers do not appear to have been isolated and characterized.

## EXPERIMENTAL

### *Monomer preparations*

**3-Methyl-1-vinylimidazolium iodide (Ia).** To 9.41 g (0.10 mol) of freshly distilled 1-vinylimidazole was added 85.20 g (0.60 mol) of reagent grade methyl iodide in 100 ml of dry ethyl acetate at  $-10^{\circ}\text{C}$ . The reaction mixture was stirred for 1 h and then brought to room

temperature overnight, during which time off-white crystals formed. The mixture was cooled and filtered, and the monomeric salt was washed three times with anhydrous diethyl ether, followed by three recrystallizations from *n*-propanol giving a 56% yield of off-white needles, m.p.  $77.5-78.0^{\circ}\text{C}$  (lit.  $85-86^{\circ}\text{C}$ )<sup>9</sup>.

Calculated for  $\text{C}_6\text{H}_9\text{N}_2\text{I}$ : C, 30.53%; H, 3.84%; N, 11.87%; I, 53.76%. Found: C, 30.44%; H, 3.79%; N, 11.82%; I, 53.77%.

**3-*n*-Propyl-1-vinylimidazolium iodide (Ib).** This monomer was prepared by a similar procedure to that for Ia except that stirring was conducted for 1 h at room temperature using 19.4 g (0.12 mol) of *n*-propyl iodide. After stirring, the solution was left overnight and an oily product separated. The oil was removed by decantation and triturated with diethyl ether. After a second trituration, solid formed. The quaternary salt was recrystallized from *n*-propanol giving a 58.9% yield with m.p.  $68.0-68.5^{\circ}\text{C}$ .

Calculated for  $\text{C}_8\text{H}_{13}\text{N}_2\text{I}$ : C, 36.38%; H, 4.97%; N, 10.60%; I, 48.05%. Found: C, 36.32%; H, 5.14%; N, 10.28%; I, 48.35%.

**3-*n*-Hexyl-1-vinylimidazolium iodide (Ic).** To 10.60 g (0.050 mol) of *n*-hexyl iodide in 25 ml of dry ethyl acetate at room temperature was added with stirring 2.35 g (0.025 mol) of 1-vinylimidazole. Stirring was continued for 8 h, during which time a light yellow oil separated. The product, which remained as an oil after several triturations with diethyl ether, was obtained in 10.5% yield.

Calculated for  $\text{C}_{11}\text{H}_{19}\text{N}_2\text{I}$ : C, 43.15%; H, 6.26%; N, 9.15%; I, 41.45%. Found: C, 42.44%; H, 6.48%; N, 9.44%; I, 41.74%.

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*3-n-Heptyl-1-vinylimidazolium iodide (Id)*. This monomer was prepared by a procedure similar to that for Ic except that the same molar amount of n-heptyl iodide was used. The reaction was stirred for 48 h, after which time the oily layer which formed was separated by decantation. After repeated triturations with diethyl ether, the product remained as an oil and was obtained in 17.5% yield.

Calculated for  $C_{12}H_{21}N_2I$ : C, 45.01%; H, 6.61%; N, 8.75%; I, 39.63%. Found: C, 44.82%; H, 6.80%; N, 8.77%; I, 39.77%.

*3-n-Dodecyl-1-vinylimidazolium iodide (Ie)*. To 3.55 g (0.012 mol) of n-dodecyl iodide in 100 ml of dry ethyl acetate was added 1.00 g (0.0106 mol) of 1-vinylimidazole. After stirring the mixture for 48 h at room temperature, the solution was cooled to 0°C, and crystallization of the quaternary salt rapidly occurred. The crystals were filtered, washed with diethyl ether and recrystallized three times from ethyl acetate giving 2.02 g (51.0% yield) of off-white needles, m.p. 50.3–51.8°C.

Calculated for  $C_{17}H_{31}N_2I$ : C, 52.30%; H, 8.01%; N, 7.18%; I, 32.24%. Found: C, 52.04%; H, 8.46%; N, 7.08%; I, 32.15%.

*3-n-Hexadecyl-1-vinylimidazolium iodide (If)*. This monomer was prepared by the same procedure as that for Ie except for the utilization of 4.23 g (0.012 mol) of n-hexadecyl iodide. After three recrystallizations from ethyl acetate, off-white needles formed in 30% yield, m.p. 68.0–68.5°C.

Calculated for  $C_{21}H_{39}N_2I$ : C, 56.50%; H, 8.81%; N, 6.27%; I, 28.42%. Found: C, 56.62%; H, 9.08%; N, 6.14%; I, 28.45%.

*2,3-Dimethyl-1-vinylimidazolium iodide (II)*. Using the same conditions as that for Ia with the exception of conducting the entire reaction at room temperature, it was found that crystals formed rapidly. After washing the off-white crystals with diethyl ether followed by three recrystallizations from n-propanol, a 59.2% yield was obtained with m.p. 149.2–151.0°C.

Calculated for  $C_7H_{11}N_2I$ : C, 33.62%; H, 4.43%; N, 11.20%; I, 50.75%. Found: C, 33.80%; H, 4.43%; N, 11.18%; I, 50.64%.

*1,4-Butanediyl-3,3'-bis-1-vinylimidazolium diiodide (IIIa)*. To a solution of 3.10 g (0.010 mol) of 1,4-diiodobutane in 20 ml of dry ethyl acetate was added 1.47 g (0.012 mol) of 1-vinylimidazole. After standing at room temperature for two weeks, the mixture was filtered and a crystalline product was obtained. The crystals were washed with ethyl acetate and then diethyl ether, followed by vacuum drying. The dicationic monomer was dissolved in 50 ml of water, 25 ml of acetone were added and the solution was concentrated *in vacuo* until crystals formed. The solution was stored in a refrigerator until crystallization was complete and the product was then filtered giving a 39.2% yield, m.p. 159.0–161.0°C.

Calculated for  $C_{14}H_{20}N_4I_2$ : C, 33.75%; H, 4.05%; N, 11.25%; I, 50.95%. Found: C, 33.70%; H, 4.01%; N, 11.31%; I, 50.75%.

*1,4-Butanediyl-3,3'-bis-2-methyl-1-vinylimidazolium diiodide (IIIb)*. To a solution of 3.10 g (0.010 mol) of 1,4-diiodobutane in 100 ml of dry ethyl acetate at room

temperature was added 4.33 g (0.040 mol) of 2-methyl-1-vinylimidazole. A precipitate began to form within a few minutes. The solution was then stored overnight at 0°C and the product was then filtered and washed with ethyl acetate. After recrystallization in acetone–water by the procedure given for IIIa, a 53.3% yield of 2-methyl-3-(4-iodobutyl)-1-vinylimidazolium iodide, m.p. 141.0–144.0°C, was obtained. The incompletely quaternized product (1.72 g, 0.0042 mol) was dissolved in 20 ml of methanol and heated at 65°C for 3 h with 3.0 g (0.028 mol) of 2-methyl-1-vinylimidazole. The solution was cooled and poured into excess ethyl acetate to precipitate the dicationic salt. The final product was filtered, washed with diethyl ether and dried giving a 51% yield, m.p. 271.0–273.0°C.

Calculated for  $C_{16}H_{24}N_4I_2$ : C, 36.52%; H, 4.60%; N, 10.65%; I, 48.23%. Found: C, 35.70%; H, 4.54%; N, 10.56%; I, 48.18%.

*3-Methyl-1-vinylimidazolium methylsulphate (IVa)*. To 15.14 g (0.12 mol) of freshly distilled dimethyl sulphate in 60 ml of dry ethyl acetate at –10°C was added 9.41 g (0.1 mol) of 1-vinylimidazole. A precipitate began to form within 10 min. After standing at 0°C for 4 h, the product was filtered, washed with ethyl acetate and then recrystallized from n-butanol. The white crystals were filtered, washed with diethyl ether and dried *in vacuo* at room temperature giving a 66.5% yield, m.p. 66.6–67.9°C. This product was found to be very hygroscopic.

Calculated for  $C_7H_{12}N_2SO_4$ : C, 38.17%; H, 5.49%; N, 12.72%; S, 14.56%. Found: C, 37.63%; H, 5.62%; N, 12.41%; S, 14.30%.

*2,3-Dimethyl-1-vinylimidazolium methylsulphate (IVb)*. To 18.92 g (0.15 mol) of dimethyl sulphate in 60 ml of dry ethyl acetate at –10°C was added 10.81 g (0.10 mol) of freshly distilled 2-methyl-1-vinylimidazole. A precipitate was noted within 5 min. After standing at 0°C for 4 h, the monomeric salt was filtered, washed with ethyl acetate and recrystallized from n-propanol. After filtration, white hygroscopic crystals were obtained which were washed with diethyl ether and vacuum dried at room temperature giving a 42.2% yield with a m.p. of 65.0–66.2°C.

Calculated for  $C_8H_{14}N_2SO_4$ : C, 41.01%; H, 6.02%; N, 11.96%; S, 13.69%. Found: C, 40.89%; H, 5.91%; N, 11.96%; S, 13.57%.

#### Homopolymerization reactions

All homopolymerization reactions were conducted by the following procedure. To a heavy walled polymerization tube was added 10 ml of a 0.45 M aqueous solution of a monomeric salt (Ia–If, II, IVa, IVb) which contained 1 mol% of 4,4'-azobiscyanovaleic acid. The contents of the tube was flushed with nitrogen and sealed *in vacuo* after utilization of the freeze–thaw technique. The tubes were then placed in a constant temperature bath thermostated at 60°C for 20 h. In the cases of the completely water soluble, short chain length polymers (Va, Vb, VI, VIIa, VIIb), the polymeric salt solutions were exhaustively dialysed against de-ionized water and the products were obtained by lyophilization. The intermediate chain length polymers (Vc and Vd) were completely water insoluble and these products were dissolved in ethanol

and dialysed against ethanol-water and then water. Polymers Vc and Vd were then obtained in powder form by filtration. In the formation of the long side-chain polymers (Ve and Vf), the solutions turned opaque during the reaction and approximately 30% water insoluble polymer formed with the remainder existing in an emulsified solution. This solution was dialysed against de-ionized water and then isolated in aqueous solution. The percentage yields and elemental analyses of all polymers are given below.

*Poly(3-methyl-1-vinylimidazolium iodide) (Va)* obtained in 60.4% yield after lyophilization.

Calculated for  $C_6H_9N_2I$ : C, 30.53%; H, 3.84%; N, 11.87%; I, 53.76%. Found: C, 30.52%; H, 3.96%; N, 11.65%; I, 53.69%.

*Poly(3-n-propyl-1-vinylimidazolium iodide) (Vb)* obtained in 58.9% yield after lyophilization.

Calculated for  $C_8H_{13}N_2I$ : C, 36.38%; H, 4.97%; N, 10.60%. Found: C, 36.30%; H, 5.09%; N, 10.50%.

*Poly(3-n-hexyl-1-vinylimidazolium iodide) (Vc)* obtained in 65.0% yield after filtration.

Calculated for  $C_{11}H_{19}N_2I$ : C, 43.15%; H, 6.26%; N, 9.15%; I, 41.45%. Found: C, 43.21%; H, 6.27%; N, 9.54%; I, 40.74%.

*Poly(3-n-heptyl-1-vinylimidazolium iodide) (Vd)* obtained in 59.8% yield after filtration.

Calculated for  $C_{12}H_{21}N_2I$ : C, 45.01%; H, 6.61%; N, 8.75%; I, 39.63%. Found: C, 45.29%; H, 6.66%; N, 9.60%; I, 38.29%.

*Poly(3-n-dodecyl-1-vinylimidazolium iodide) (Ve)* obtained in a total yield of 63.1% (including water-soluble and water-insoluble polymer).

Calculated for  $C_{17}H_{31}N_2I$ : C, 52.30%; H, 8.01%; N, 7.18%; I, 32.24%. Found: C, 52.04%; H, 8.46%; N, 7.08%; I, 32.51%.

*Poly(3-n-hexadecyl-1-vinylimidazolium iodide) (Vf)* obtained in a total yield of 64.7% (including water-soluble and water-insoluble polymer).

Calculated for  $C_{21}H_{39}N_2I$ : C, 56.50%; H, 8.81%; N, 6.27%; I, 28.42%. Found: C, 56.32%; H, 8.62%; N, 6.37%; I, 28.58%.

*Poly(2,3-dimethyl-1-vinylimidazolium iodide) (VI)* obtained in 53.2% yield after lyophilization.

Calculated for  $C_7H_{11}N_2I$ : C, 33.62%; H, 4.43%; N, 11.20%; I, 50.75%. Found: C, 33.42%; H, 4.62%; N, 11.01%; I, 50.70%.

*Poly(3-methyl-1-vinylimidazolium methylsulphate) (VIIa)* obtained in 43.9% yield after lyophilization.

Calculated for  $C_7H_{12}N_2SO_4$ : C, 38.17%; H, 5.49%; N, 12.72%; S, 14.6%. Found: C, 38.12%; H, 5.41%; N, 12.67%; S, 14.54%.

*Poly(2,3-dimethyl-1-vinylimidazolium methylsulphate) (VIIb)* obtained in 67.6% yield after lyophilization.

Calculated for  $C_8H_{14}N_2SO_4$ : C, 41.01%; H, 6.02%; N, 11.96%. Found: C, 41.15%; H, 6.07%; N, 12.08%.

### Crosslinking reactions

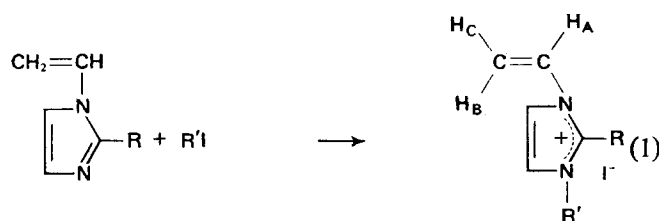
Copolymerization reactions of 1,4-butanediyl-3,3'-bis-1-vinylimidazolium diiodide (IIIa) with 3-methyl-1-vinylimidazolium iodide (Ia) and of 1,4-butanediyl-3,3'-bis-2-methyl-1-vinylimidazolium diiodide (IIIb) with 2,3-dimethylimidazolium iodide (II) were conducted in a similar manner to that of the homopolymerization reactions. Each solution contained a total monomer concentration of 0.45 M in 10 ml of water of which the crosslinking agent (IIIa or IIIb) amounted to 5 mol% of the monocationic salt (Ia or II). After copolymerization at 60°C for 24 h with 1 mol% 4,4'-azobiscyanovaleric acid, the products were obtained as soft gels which were exhaustively dialysed against water followed by lyophilization. The dried sample was then twice slurried in water and centrifuged to separate the soluble and insoluble portions. The reaction between Ia and IIIa gave a 68.5% yield of which 31.3% was water insoluble whereas the reaction between II and IIIb gave an 80.5% yield of which 53.5% was water insoluble.

## RESULTS AND DISCUSSION

### Monomer preparations

In this work, it was of interest to prepare a homologous series of quaternary vinylimidazolium salts in which the linear alkyl moiety could be increased in chain length. Such a series of monomeric salts could have varied hydrophilic-hydrophobic character such that they could function as 'normal' organic salts with the short alkyl moieties or as detergents with the long alkyl moieties. In a similar fashion, the progression in alkyl chain length would also be expected to effect markedly the solution behaviour of the resulting polycations.

The preparation of a homologous series of vinylimidazolium salts was readily achieved by the quaternization of 1-vinylimidazole (reaction 1, R=H) with a series of n-alkyl iodides in ethyl acetate as solvent according to the procedures given in the experimental section. This reaction results in quaternization of the 3-position of 1-vinylimidazole to give the corresponding 3-n-alkyl-1-vinylimidazolium iodide (Ia-If).



Ia: R = H, R' = CH<sub>3</sub>

Ib: R = H, R' = (CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>

Ic: R = H, R' = (CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>

Id: R = H, R' = (CH<sub>2</sub>)<sub>6</sub>CH<sub>3</sub>

Ie: R = H, R' = (CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub>

If: R = H, R' = (CH<sub>2</sub>)<sub>15</sub>CH<sub>3</sub>

II: R = R' = CH<sub>3</sub>

From the reactions of 1-vinylimidazole with methyl iodide, n-propyl iodide, n-dodecyl iodide and n-hexadecyl iodide, the cationic monomers of 3-methyl(Ia)-, 3-n-propyl(Ib)-, 3-n-dodecyl(Ie)- and 3-n-hexadecyl(If)-1-vinylimidazolium iodide were all obtained in the crystalline form as off-white needles. Upon standing,

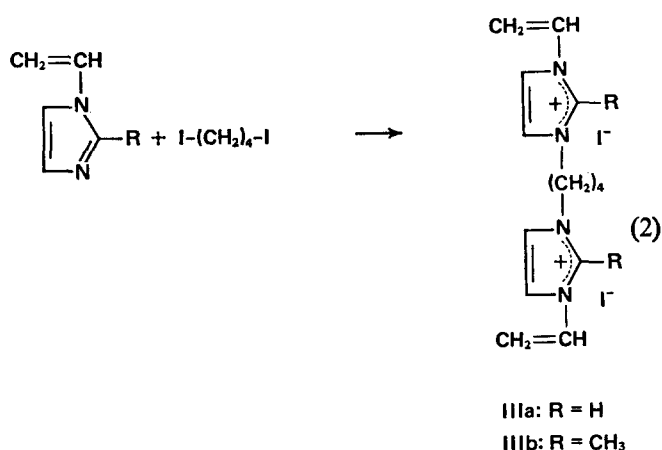
these needles had a tendency to yellow. Although it was possible to obtain crystals of the shortest and longest chain quaternary salts, this was not possible for the intermediate length salts 3-n-hexyl(Ic)- and 3-n-heptyl(Id)-1-vinylimidazolium iodide which remained as oils. In spite of the fact that the elemental analysis of the former compound was slightly in error, a verification of the purity of reagents used in the formation of both Ic and Id by gas chromatography indicated that impurities were not the cause of their non-crystallization behaviour. This characteristic is not unexpected, since intermediate chain length hydrocarbons can cause a phase change from a liquid to an oil or solid. For the shortest alkyl-substituted salt (Ia) it was found that this salt is very hygroscopic and difficult to handle. Furthermore, in the formation of this salt, it is possible to form an oil which can be difficult to crystallize. Recently, Shostakovskii *et al.*<sup>9</sup> prepared this salt and other vinylimidazolium and vinylbenzimidazolium salts for infra-red and ultra-violet spectral studies. Although these authors reported a melting point of 85–86°C in comparison to that which we obtained of 77.5–78.0°C, a detailed description of their preparation was not given.

The solubilities of the cationic monomers Ia–If in water were rather interesting. For the short chain length alkyl-substituted salts (Ia and Ib), it was found that they were readily soluble in water. For the intermediate chain length alkylated monomers (Ic and Id), these appeared to be less water soluble than compounds Ia and Ib, in accord with their greater hydrophobic character. For the long chain length alkyl substituents (Ie and If), it was found that these monomers behaved as detergents in aqueous solution with considerable frothing being noted. The monomer If appeared to be slightly less soluble than Ie. The solubility of the series of monomers in water thus illustrates a distinct change in solution behaviour depending on the length of the quaternary side-chain. The short chain monomers behave as typical water-soluble salts whereas the intermediate chain monomers are less water soluble because of their increased hydrophobic character, and the long chain monomers appear to form micelles in aqueous solution because of their highly hydrophobic character. Transitions in solution behaviour of this type often occur with ionic organic molecules where a hydrophobic moiety can be increased in chain length<sup>10</sup>.

For the monomer 2-methyl-1-vinylimidazole, the only quaternization reaction with an alkyl iodide that was studied was that with methyl iodide (reaction 1, R = R' = CH<sub>3</sub>). It was found that 2,3-dimethyl-1-vinylimidazolium iodide (II) formed very rapidly in comparison to the slower quaternization of 1-vinylimidazole with methyl iodide (reaction 1, Ia). On the basis of stereochemical considerations, this was surprising to note because the more hindered 2-methyl isomer would be expected to quaternize at a slower rate than the less hindered, unsubstituted isomer.

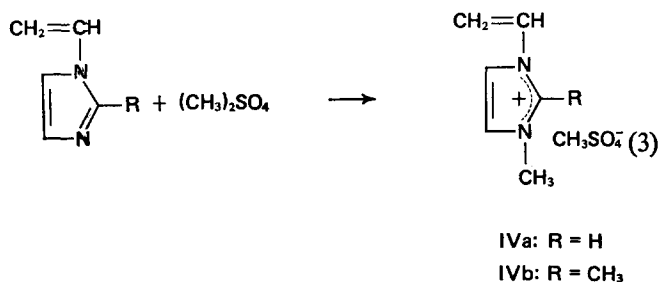
In conjunction with the quaternization of 1-vinylimidazole and 2-methyl-1-vinylimidazole by alkyl iodides, it was also of interest to prepare dicationic monomers that could be used as crosslinking agents. This was effected by the reaction of the nucleophilic vinyl monomers with the alkyl diiodide, 1,4-diiodobutane, in ethyl acetate (reaction 2). In this case it was found that the reaction with 1-vinylimidazole easily gave the dimeric product 1,4-butanediyl-3,3'-bis-1-vinylimidazolium diiodide

(IIIa). However, the reaction with 2-methyl-1-vinylimidazole initially gave the monoquaternized product 2-methyl-3-(4-iodobutyl)-1-vinylimidazolium iodide which underwent complete quaternization upon heating with excess 2-methyl-1-vinylimidazole to 1,4-butanediyl-3,3'-bis-2-methyl-1-vinylimidazolium diiodide (IIIb).



Previously, the only dicationic vinyl monomers that appear to have been reported and characterized have been those prepared from the diquaternization of amino acrylates and methacrylates<sup>2</sup>.

In further studies of the quaternization of 1-vinylimidazole and 2-methyl-1-vinylimidazole, it was also of interest to characterize the salts prepared from the reactions with dimethyl sulphate, since these monomers have been reported in the patent literature but apparently have not been isolated and structurally verified<sup>2, 9</sup>. Employing similar quaternization procedures as with the alkyl iodides, it was found that the quaternizations with dimethyl sulphate (reaction 3) occurred within minutes in cold ethyl acetate solution. As was expected, these quaternization reactions were considerably more rapid than the corresponding preparation of the iodide salts. Furthermore, it was again noted that 2-methyl-1-vinylimidazole appeared to quaternize more rapidly than its unsubstituted isomer.



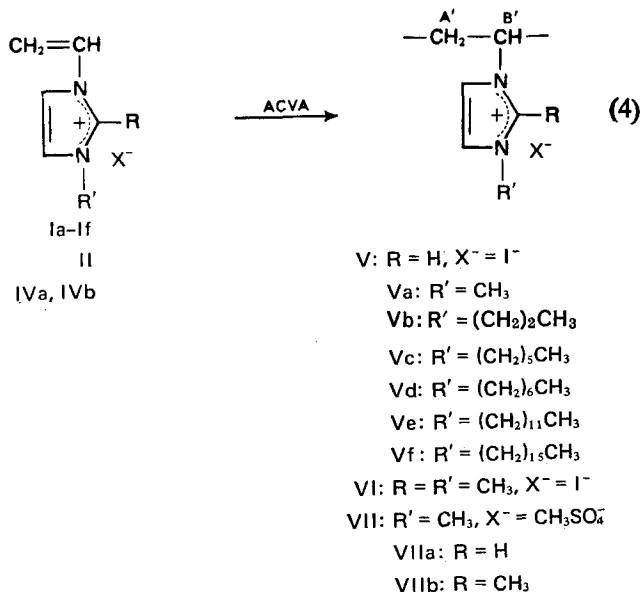
The monomers 3-methyl(IVa)- and 2,3-dimethyl(IVb)-1-vinylimidazolium methylsulphate were found to be extremely hygroscopic, and utilization of anhydrous conditions was needed in their characterization.

#### Polymerization reactions

It was previously indicated that several polyvinylimidazolium salts have been reported in the patent literature in which a variety of vinylimidazoles were quaternized and then free radically homo- or co-polymerized. Alternative preparations of polyvinylimidazolium salts have

also employed the initial formation of a neutral (nucleophilic) polyvinylimidazole, followed by treatment with an alkylating agent<sup>2</sup>. In the latter approach, it can be difficult to achieve complete quaternization.

In our experiments, we have found that the monomeric salts I, II and IV could be homopolymerized in water using the free radical initiator 4,4'-azobiscyanovaleric acid (ACVA, reaction 4) to their corresponding polyvinylimidazolium salts V-VII.



Each of the homopolymerization reactions were done under the same conditions. The solubilities of the resulting polymeric solutions were found to be related to the length of the alkyl chain. For the homologous alkyl iodide series Va-Vf, the short side-chain polyions of poly(3-methyl-1-vinylimidazolium iodide)(Va) and poly(3-n-propyl-1-vinylimidazolium iodide) (Vb) were found to be very soluble in water. The intermediate side-chain polyions of poly(3-n-hexyl-1-vinylimidazolium iodide) (Vc) and poly(3-n-heptyl-1-vinylimidazolium iodide) (Vd) were completely insoluble in water. On the other hand, the long side-chain polyions poly(3-n-dodecyl-1-vinylimidazolium iodide) (Ve) and poly(3-n-hexadecyl-1-vinylimidazolium iodide) (Vf) gave opaque solutions which frothed easily. From these solutions, it was indicated that the short side-chain polymers Va and Vb behaved as normal polyions whereas the long side-chain polyions Ve and Vf were sufficiently hydrophobic to cause micellarization of the macromolecules in aqueous solution such that polysoaps resulted. The intermediate side-chain length polyions Vc and Vd were apparently not sufficiently hydrophobic to cause the formation of polymeric micelles through the hydrophobic intramolecular or intermolecular interactions of the pendant groups. Transitions in solubility behaviour of this type have been reported by Strauss *et al.* on their studies of poly(4-vinylpyridine) which was first quaternized to a small degree with n-dodecyl bromide followed by greater quaternization with ethyl bromide<sup>11, 12</sup>.

In these polymerization reactions, it was noted that when the polysoap solutions were exhaustively dialysed and then lyophilized, the resulting dried solid was insoluble in water, even upon heating. Solubilization could then be effected only through the utilization of organic solutes. It is conceivable that this insolubility could be

caused by extensive intermolecular hydrophobic interactions between the long chain pendant groups such that the ionic charges would be buried in the interior and not near the surface as would occur in micellar solutions. A similar water insolubility of a dried anionic polysoap has been previously reported by Sinha and Medalia<sup>13</sup>.

The other short side-chain polyions, poly(2,3-dimethyl-1-vinylimidazolium iodide) (VI), poly(3-methyl-1-vinylimidazolium methylsulphate) (VIIa) and poly(2,3-dimethyl-1-vinylimidazolium methylsulphate) (VIIb) were also found to be very water soluble. Since the short side-chain monomers and their corresponding homopolymers were all highly water soluble, it was decided to test the crosslinking ability of the difunctional monomers IIIa and IIIb with the simplest monomeric salts, Ia and II, respectively. Using a 5 mol% solution of either crosslinking agent with Ia or II according to the conditions described for the homopolymerizations, followed by several washings with hot water to remove any uncrosslinked polymer, it was found that crosslinked hydrophilic gels resulted. A considerable amount of mechanical loss of crosslinked polymer was obtained by the rigorous purification technique because of the small size of the gel particles that were obtained.

#### N.m.r. measurements

N.m.r. spectra of imidazolium salts have been previously reported in the literature<sup>14-17</sup>. Although our preliminary investigation of the n.m.r. spectra of vinylimidazolium salts Ia and II was conducted in D<sub>2</sub>O<sup>1</sup>, as were most of the salts that have been reported in the literature, it was found that this solvent could not be used effectively for the various monomers and polymers because of their wide range in solubility behaviour. It was found, however, the DMSO-d<sub>6</sub> could be used for the greatest number of compounds, with only the 2,3-dimethyl-substituted iodide polymer (VI) being insoluble at ambient temperature.

The spectral data for the monomeric and polymeric salts prepared in this investigation are given in Tables 1 and 2, respectively. In both Tables, the substituent positions on the imidazolium ring are given by numbers 1-5 according to the numbering system shown in reaction (1). In the case of the monomeric salts, the vinyl hydrogens on the 1-position are denoted by A, B and C for positions *gem*, *cis* and *trans* to the imidazolium ring. In the case of the polyions, the chain-backbones are denoted by A' and B' (reaction 4) for the methylene and methine hydrogens of the 1-position.

In Table 1, it is seen that there is good agreement in chemical shift values for positions 1-5 of the monomers of the homologous series (Va-Vf). For each salt, the hydrogen of the 2-position is furthest downfield. In comparison to neutral (unquaternized) imidazole, the 2-hydrogen of each monomeric salt is shifted furthest downfield, apparently because of the cationic character of the 1- and 3-nitrogens. The chemical shifts and coupling constants for the vinyl hydrogens are in accord with those of other cationic, monomeric salts<sup>18, 19</sup>. Similar agreement in chemical shift data is also noted for the 2,3-dimethyl-substituted iodide (II), the dicationic crosslinking agents (IIa, IIb) and the methylsulphate salts (IVa, IVb). Relative to our previous spectral study of monomeric salts Ia and II in D<sub>2</sub>O<sup>1</sup>, it is found that DMSO-d<sub>6</sub> causes a significant shift downfield for all peak positions.

Table 1 N.m.r. spectra data of monomeric imidazolium salts in DMSO-d<sub>6</sub>

Mono- mer	Chemical shift, $\delta$ (ppm) from TMS													
	2a		4, 5b	Vinylc			Alkyl			Counter- ion	Coupling (Hz)			
	H	CH <sub>3</sub>		A	B	C	N-CH <sub>2</sub> -	-CH <sub>2</sub> -	-CH <sub>3</sub>		J <sub>45</sub>	J <sub>AB</sub>	J <sub>AC</sub>	J <sub>BC</sub>
Ia	9.92	—	8.34, 8.14	7.48	6.11	5.53	—	—	3.82s	—	1	16	9	2
Ib	9.93	—	8.46, 8.20	7.49	6.16	5.55	4.40t	2.35-0.95m	0.90t	—	1	16	9	1.5
Ic	9.95	—	8.34, 8.17	7.44	6.09	5.50	4.36t	2.20-1.15m	0.89t	—	1	16	9	2
Id	9.96	—	8.40, 8.14	7.51	6.15	5.52	4.44t	2.30-1.05m	0.86t	—	1	16	9	2.5
Ie	9.90	—	8.39, 8.15	7.46	6.10	5.48	4.37t	2.30-1.05m	0.89t	—	1	16	9	2
If	9.80	—	8.36, 8.10	7.42	6.05	5.47	4.32t	2.25-1.05m	0.86t	—	1	16	9	2
II	—	2.81	8.20, 7.89	7.58	5.96	5.45	—	—	3.92s	—	2	16	9	2.5
IIIa	9.82	—	8.37, 8.13	7.44	6.02	5.49	4.36t	1.91t	—	—	1	16	9	2
IIIb	—	2.89	8.29, 8.04	7.47	6.06	5.53	4.40t	1.91t	—	—	1	16	9	2
IVa	9.38	—	8.13, 7.88	7.26	5.93	5.45	—	—	3.92s	3.45s	2	16	9	2.5
IVb	—	2.71	8.08, 7.73	7.29	5.86	5.37	—	—	3.86s	3.44s	2	16	9	2.5

a All peaks in singlets

b All peaks in doublets

c All peaks in doublets of doublets

Table 2 N.m.r. spectral data of polymeric imidazolium salts in DMSO-d<sub>6</sub>

Polymer	Chemical shift, $\delta$ (ppm) from TMS								
	2		4, 5	Backbone		Alkyl			Counter-ion
	H	CH <sub>3</sub>		A'	B'	N-CH <sub>2</sub> -	-CH <sub>2</sub> -	-CH <sub>3</sub>	
Va	9.64	—	7.70	4.20	1.70	—	—	3.85	—
Vb	9.62	—	7.70	4.10	1.89	4.10	1.89	0.92	—
Vc	9.61	—	7.83	4.23	1.34	4.23	1.34	0.89	—
Vd	9.64	—	7.71	4.20	1.27	4.20	1.27	0.88	—
Ve	9.60	—	7.70	4.20	1.28	4.20	1.28	0.92	—
Vf	9.70	—	7.95	4.23	1.29	4.20	1.29	0.86	—
VIIa	9.06	—	7.70	3.02	1.77	—	—	3.45	3.45
VIIb	—	2.30	7.70	3.65	1.74	—	—	3.65	3.65

a All peaks are very broad

For the n.m.r. spectra of the polyions (Table 2), it was again found that good agreement occurred with all chemical shift data. Although the peak positions were rather broad, it can be seen that relative to the monomers in DMSO-d<sub>6</sub>, there are significant upfield shifts for positions 2, 4 and 5. This shift is most likely related to the conversion of the double bond of the monomer to the single bond of the chain-backbone. From these data, it is also apparent that the free radical polymerization of the cationic monomers proceeds through a normal vinyl addition in that there is no alteration of the imidazolium ring. In addition, in none of the spectra of the polymers was any monomer indicated. This is particularly important in the solubility properties of the polysoaps, since it indicates that their solubility in aqueous solution is most likely caused by the micellarization of the polymer chains and not by surrounding monomeric detergent molecules.

## CONCLUSION

This study has illustrated the preparations of a variety of homopolymers of vinylimidazolium salts. In the near future we hope to report further studies on the micellar character of the monomers and polymers as well as on the copolymerization behaviour of the monomeric salts.

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