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# Syntheses of aminated poly(vinyl chloride)s using methyl piperazine for the development of pH-selective membranes

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Fifty-seven copolymers of poly(vinyl chloride-vinyl methyl piperazine) were prepared from the reaction of poly(vinyl chloride) (PVC) and 1-methyl piperazine (Me-PIP) either with dimethyl sulfoxide (DMSO) or without any aprotic solvent. Reaction temperatures, times and concentrations were varied from 23 to 45°C, from 1 to 35 days, and from 0.125 to 1.0 mol. eq. of Me-PIP, respectively. Nitrogen (N) analyses, electromotive force (EMF) responses and subjective colours were reported. From these measurements the N contents, slopes of the EMF–pH responses, activation energies and time–temperature superposition via the WLF expression were analyzed. The resulting powders had up to 2.0 wt%N, although insolubility was reached in tetrahydrofuran above 1.2 wt%N. After storing at room temperature, the soluble formulations remained soluble for up to two years. With all reaction conditions the degree of amination was directly proportional to the reaction time. In addition to the amination reactions, elimination reactions produced conjugated polyenes as indicated by the changes in colour from white for the homopolymer of PVC to dark brown for the copolymers of PVC having the highest nitrogen contents. With the soluble formulations membranes were cast with o-nitrophenyl octyl ether and potassium tetrakis (p-chlorophenyl) borate as plasticizer and negative sites, respectively. Nernstian behaviour was generally obtained for the membranes that were cast from materials with from 0.3 to 1.2 wt%N. The activation energy (17–20 kcal·mol$^{-1}$ was calculated for the substitution reaction in DMSO. Based on the WLF equation, a time–temperature shift factor was determined. In DMSO the amination reaction was directly proportional to the concentration of Me-PIP. Without any solvent, amination yielded formulations that produced membranes that approximated Nernstian responses. These solventless aminations followed the same reaction rate as the DMSO aminations. © 1997 Elsevier Science Ltd.

**(Keywords: copolymer; methyl piperazine; membranes)**

## INTRODUCTION

During the last decade, extending the lifetime of ion-selective membrane electrodes has been the focus of numerous studies[1–10]. The lifetime of these electrodes is often limited by processing errors and/or material deficiencies[4,5]. A primary reason for short electrode lifetimes is the leaching-out of the liquid components from the ion-selective membranes (plasticizer and ionophore) to the outer surfaces[6,7]. When the ionophore leaches-out, the electrode malfunctions due to the loss of sufficient numbers of charge carriers. When the plasticizer migrates to the surface, the electrode fails because the plasticizer forms a non-conductive surface layer that increases the resistance of the electrode[6,7]. Since the plasticizer is necessary for ion mobility, failure also occurs because of a loss in mobility. Several studies have evaluated the optimal ratio of plasticizer to polymer[8–10], i.e. the amount required for mobility while minimizing the non-conductive surface layer. Reducing the amount of plasticizer should not only favourably affect ion mobility and surface contamination, but also improve biocompatibility.

To restrict the leaching of the ion-selective moiety, extensive research has been conducted on the development of fixed-site proton selective membranes via the halo-substitution of poly(vinyl chloride) (PVC) with basic diamines[1,11–17]. With these reactions the ion conducting moiety is bonded directly to the PVC. Following the initial work by Ma and Meyerhoff with linear mono- and diamines[11,12], over 50 formulations were prepared using methanol (MeOH) as the reaction media and the diamine, piperazine (PIP), by reacting 5 molar equivalence (mol. eq.) of PIP with PVC for 0.2–49 days (d) at 25–64°C[13,14]. Over half of these aminated PVC products (PVC-$NR_2$)* exhibited pH–response curves having slopes that exceeded −50 mV/pH and approached the theoretical Nernstian value of −59.2 mV/pH. Chemical analyses indicated that the nitrogen (N) contents ranged from 0.23 to 1.63 wt%, of which those products with Nernstian slopes had N contents ranging from 0.44 to 0.87 wt%. Subsequently, a patent was issued (US#5,403,895) for this process[18]. Unfortunately, deleterious elimination and crosslinking reactions were competing with the favourable substitution reaction.

Substitution reactions often compete with elimination reactions. With strong bases and secondary halides, such as

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* In previous work on this subject the authors used PVC-$NH_2$ as the symbol for aminated PVC. At the suggestion of one of the reviewers, we will now use PVC-$NR_2$ to indicate the use of a secondary amine rather than a primary amine

PIP and PVC, respectively, elimination is favoured. Polar solvents, lower reaction temperatures and lower nucleophile concentrations favour substitution. Because aprotic solvents do not have hydrogen atoms available for bonding, such polar solvents are now favoured for substitution reactions[19].

In an attempt to drive the reaction towards more substitution and less elimination, a series of reactions was initiated using the highly polar and aprotic solvent, dimethyl sulfoxide (DMSO), at a reduced temperature (23°C) and lower PIP concentrations (0.125, 0.25, 0.5 and 1.0 mol.eq.)[16]. No attempt was made to maintain isothermal conditions. From 12 formulations, eight products yielded membranes with Nernstian responses to pH and nitrogen contents from 0.2 to 0.4 wt%. As with the reactions using MeOH[14], these reaction products became insoluble with time. This was attributed to the crosslinking reaction of the second nitrogen on the piperazine molecules with nearby PVC molecules.

An alternative to PIP was sought in which the basicity of the PIP moiety would be maintained and low nucleophile concentrations could be utilized without adverse substitution reactions via crosslinking. The present work investigates the reaction of a derivative of piperazine on which one of the nitrogens was bonded to a methyl group instead of a hydrogen. Under certain conditions, 1-methyl piperazine (Me-PIP) can provide Nernstian responses with some elimination (as evidenced by a gradual darkening in colour), but without appreciable crosslinking (as evidenced by a loss in solubility).

## EXPERIMENTAL

### *Synthesis—solvent*

As received PVC powder (MW = 110 000, Polysciences) and Me-PIP (Aldrich) in various ratios (0.125, 0.25, 0.5 and 1.0 mol.eq.) were placed in a round bottom flask that contained a Teflon-coated magnetic stirring bar. The aprotic solvent, dimethyl sulfoxide (DMSO, Mallinckrodt), was added in a constant DMSO:PVC ratio of 17.5 ml/g. Under a static argon atmosphere and a constant concentration of 0.5 mol.eq. of Me-PIP, the temperature was variously maintained at 30, 35, 40 and 45°C from 1 to 23 d (*Table 1*, columns 1–3). A small heat tape was used for these 21 batches and regulated via a controller that used a subsurface thermocouple placed into a thermowell in the flask. In addition, 22 batches were prepared using a controlled temperature water bath at 23°C from 2 to 28 d at four concentrations: 0.125, 0.25, 0.5 and 1.0 mol.eq. of Me-PIP (*Table 2*, columns 1–3). When each reaction was complete, each mixture was poured into an excess of HPLC-grade MeOH (Mallinckrodt), and the precipitate sedimented. Using a vacuum, the supernatant was removed. The polymer was first washed with 0.1 M KOH once and then repeatedly washed with deionized water, and the aqueous solution was checked until the pH paper registered neutral. The polymer was washed twice with MeOH and finally filtered through a PTFE vacuum filter. The filtrate was dried overnight under vacuum at room temperature (23°C).

### *Synthesis—no solvent*

Instead of using an aprotic solvent, PVC powder and Me-PIP (1.0 mol.eq.) were combined under an argon atmosphere in a round bottom flask containing a magnetic stirring bar using no solvent. For these 14 batches each flask was placed in a controlled temperature water bath at 23°C for periods that ranged from 1 to 35 d (*Table 3*, columns 1 and 2). After 1 d the Me-PIP was absorbed into the PVC. At the end of the specified reaction time MeOH was added to the reaction flask, and the product was washed as described in the preceding section.

**Table 1** Influence of temperature and time on Me-PIP-modified PVCs reacted in DMSO[a]

| Batch # | Temperature (°C) | Time (d) | Nitrogen (wt%) | – Slope (mV/pH) | pH range | Relative colour |
|---|---|---|---|---|---|---|
| PVC | | | 0.02 | [b] | [b] | White |
| 193 | 45 | 7 | 1.97 | [c] | [c] | Dark Brown |
| 192 | 45 | 5 | 1.23 | [c] | [c] | Dark Brown |
| 195 | 45 | 3 | 0.78 | 54.5 | 6–12 | Brown |
| 203 | 45 | 2 | 0.57 | 27.1 | 4–11 | Brown |
| 181 | 40 | 8 | 1.28 | 54.6 | 6–12 | Brown |
| 187 | 40 | 7 | 1.03 | 52.8 | 6–12 | Brown |
| 163 | 40 | 5 | 0.48 | 55.6[d] | 5–10 | Reddish-Yellow |
| 164 | 40 | 4 | 0.57 | 55.2[d] | 6–10 | Reddish-Yellow |
| 169 | 40 | 3 | 0.36 | 56.2 | 6–10 | Reddish-Yellow |
| 171 | 40 | 2 | 0.34 | 54.5 | 6–10 | Dark Yellow |
| 204 | 40 | 1 | 0.22 | 1.4 | 4–12 | Dark Yellow |
| 194 | 35 | 14 | 1.17 | 56.2[d] | 6–10 | Brown |
| 196 | 35 | 11 | 1.08 | 52.7 | 4–12 | Brown |
| 202 | 35 | 7 | 0.57 | 50.3 | 5–10 | Brown |
| 198 | 35 | 4 | 0.39 | 48.9 | 5–10 | Dark Yellow |
| 178 | 30 | 23 | 1.20 | 54.4 | 5–10 | Brown |
| 175 | 30 | 18 | 1.03 | 50.1 | 4–10 | Light Brown |
| 188 | 30 | 14 | 0.56 | 47.5 | 4–10 | Light Brown |
| 173 | 30 | 10 | 0.47 | 42.6 | 5–10 | Dark Yellow |
| 174 | 30 | 7 | 0.35 | 54.6 | 5–10 | Dark Yellow |
| 210 | 30 | 4 | 0.22 | 0.8 | 4–12 | Dark Yellow |

[a]Reactions run at a constant concentration of 0.5 mol.eq. of Me-PIP [b]Not tested [c]Not soluble in THF [d]Only partially soluble in THF

**Table 2** Influence of time and concentration on Me-PIP-modified PVCs reacted in DMSO[a]

| Batch # | Time (d) | Me-PIP (mol. eq.) | Nitrogen (wt%) | – Slope (mV/pH) | pH range | Relative colour |
|---|---|---|---|---|---|---|
| 166 | 14 | 1.0 | 0.69 | 52.8 | 4–12 | Yellow |
| 165 | 14 | 1.0 | 0.76 | 57.5 | 5–11 | Light Brown |
| 159 | 7 | 1.0 | 0.46 | 52.6 | 5–11 | Light Brown |
| 160 | 7 | 1.0 | 0.46 | 47.6 | 5–11 | Reddish-Yellow |
| 149 | 6 | 1.0 | 0.28 | 41.8 | 4–11 | Yellow |
| 168 | 17 | 0.5 | 0.40 | 51.2 | 5–10 | Dark Yellow |
| 155 | 13 | 0.5 | 0.31 | 53.1 | 4–12 | Dark Yellow |
| 184 | 13 | 0.5 | 0.38 | 45.4 | 4–10 | Dark Yellow |
| 158 | 7 | 0.5 | 0.24 | 33.1 | 5–10 | Yellow |
| 148 | 7 | 0.5 | 0.13 | 14.6 | 4–11 | Yellow |
| 219 | 5 | 0.5 | 0.13 | [b] | [b] | Yellow |
| 129 | 3 | 0.5 | 0.21 | 7.5 | 4–12 | Yellow |
| 205 | 2 | 0.5 | 0.08 | [b] | [b] | Light Yellow |
| 176 | 18 | 0.25 | 0.22 | 38.3 | 4–10 | Dark Yellow |
| 146 | 11 | 0.25 | 0.14 | 8.7 | 5–11 | Yellow |
| 183 | 11 | 0.25 | 0.13 | 7.0 | 4–10 | Yellow |
| 182 | 7 | 0.25 | 0.09 | 1.4 | 4–10 | Yellow |
| 179 | 28 | 0.125 | 0.21 | 30.1 | 4–10 | Dark Yellow |
| 150 | 19 | 0.125 | 0.12 | 7.1 | 4–11 | Yellow |
| 218 | 7 | 0.125 | 0.11 | [b] | [b] | Light Yellow |
| 217 | 5 | 0.125 | 0.03 | [b] | [b] | Light Yellow |
| 209 | 4 | 0.125 | 0.08 | [b] | [b] | Light Yellow |

[a] Reactions run at a constant temperature of 23°C [b] Not tested

**Table 3** Influence of time on Me-PIP-modified PVCs reacted in no solvent[a]

| Batch # | Time (d) | Nitrogen (wt%) | – Slope (mV/pH) | pH range | Relative colour |
|---|---|---|---|---|---|
| 190 | 35 | 1.59 | 57.0[b] | 5–10 | Dark Brown |
| 172 | 28 | 1.30 | 50.4 | 5–12 | Dark Brown |
| 177 | 21 | 0.97 | 50.6 | 5–10 | Brown |
| 180 | 21 | 1.01 | 41.1 | 5–10 | Dark Brown |
| 191 | 17 | 0.81 | 52.1 | 5–10 | Brown |
| 170 | 14 | 0.56 | 46.3 | 5–11 | Dark Yellow |
| 189 | 14 | 0.68 | 42.0 | 5–10 | Light Brown |
| 162 | 12 | 0.54 | 51.8 | 5–11 | Dark Yellow |
| 161 | 7 | 0.40 | 57.1 | 5–11 | Yellow |
| 197 | 7 | 0.26 | 40.2 | 4–10 | Yellow |
| 201 | 7 | 0.55 | 52.5 | 4–10 | Light Yellow |
| 206 | 5 | 0.45 | [c] | [c] | Light Yellow |
| 207 | 2 | 0.26 | [c] | [c] | Light Yellow |
| 208 | 1 | 0.14 | [c] | [c] | Light Yellow |

[a] Reactions run at a constant temperature at 23°C and 1.0 mol.eq. of Me-PIP [b] Only partially soluble in THF [c] Not tested

### *Nitrogen analysis*

Using a Perkin Elmer Elemental Analyzer 2400, the nitrogen content of each sample was determined. After calibration with an organic standard, acetanilide (Perkin Elmer), 2–3 mg of powder was placed in a tared tin holder. Each crimped tin holder was dropped into an oxygen enriched combustion column at 925°C. A flow of 99.998% Helium carried all combustion gases through a reduction column at 640°C. After chromatographic separation, the elemental concentration of nitrogen (wt%) was detectable via thermal conductivity measurements.

### *Electromotive force measurements*

Using a constant ratio of plasticizer:anion sites:aminated polymer of 200:2:100, the o-nitrophenyl octyl ether (o-NPOE, Fluka), potassium tetrakis (p-chlorophenyl) borate (KTpClPB, Fluka)†, and PVC-$NR_2$ were dissolved in 5 ml of chromatographic-grade tetrahydrofuran (THF, Mallinckrodt). Using the general procedure of Craig *et al.*[20], membranes were made, after evaporating the THF in a class 100 clean room. Membrane disks (1 cm in diameter) were attached to PVC tubing. An internal filler solution of TRIS buffer at pH 7 and a Ag/AgCl internal reference were added. After conditioning at least 24 h in TRIS buffer, the electromotive force (EMF) of each electrode was measured

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† KTpClPB not only provided mobile anion sites but also lowered the resistance of the membranes

at room temperature with an Orion pH/mV meter (720A) using an external reference electrode (Orion model 90-02) over a range of pH from 4 to 12. The slope of each EMF–pH response curve was calculated, and the pH range of linearity was recorded.

## RESULTS

The N analyses, EMF–pH slopes, pH ranges of linearity and subjective colour determinations of 57 batches of Me-PIP modified PVC were summarized for all reactions (*Tables 1–3*). Nitrogen contents ranged from a low of 0.03% for batch #217 to a high of 2.0% for batch #193. Each nitrogen content was directly proportional to reaction time regardless of reaction temperature, Me-PIP concentration or presence of a solvent. Membranes from 25 of the batches had EMF/pH slopes greater than −50 mV/pH. Seven of these had slopes ranging from −55.2 to −57.5 mV/pH, which approximates the theoretical Nernstian slope of −59.2 mV/pH. Remarkably, three of these 25 were not completely soluble and contained some gel: batches #163, 164 and 194 (cf. *Table 1*).

On the other hand, batch #159 is an example of an excellent PVC-$NR_2$ (*Figure 1*). This material was formed when 1.0 mol.eq. Me-PIP and PVC reacted in DMSO at 23°C for 7 d to yield a product with 0.46 wt%N (*Table 2*). A membrane formed from this batch showed a slope (−52.6 mV/pH) with little difference from that of a glass electrode and had linearity over the pH range from 5 to 11. In contrast the results for two other batches (#158 and #182), which were also formed from reactions in DMSO at 23°C for 7 d but with different amounts of MePIP (0.5 and 0.25 mol. eq., respectively), did not yield good pH responses. These two batches had nitrogen contents of 0.24 and 0.09 wt% N and slopes of −33.1 and −1.4 mV/pH, respectively (Table 2).

With a constant amount of Me-PIP (0.5 mol.eq.), increasing the temperature from 23 to 45°C in DMSO yielded batches with colours that ranged from light yellow to dark brown (*Tables 1 and 2*). In conjunction with the colour change at a constant reaction time of 7 d the nitrogen content increased from 0.13 wt% for batch #148 to 1.97 wt% for batch #193. With the same reaction time of 7 d but at a constant temperature of 23°C in DMSO and varying concentrations of Me-PIP, the colour of the batches changed from light yellow (batch #218, 0.125 mol.eq.) to light brown (batch #159, 1.0 mol.eq.) [*Table 2*]. Nitrogen content remained relatively constant at 0.11 wt% up to 0.5 mol.eq. Me-PIP, but increased as much as four fold (0.46 wt%) by 1.0 mol.eq. Me-PIP. As presented above (*Figure 1*), the slopes of the EMF–pH response curves increased with this same change in Me-PIP concentration.

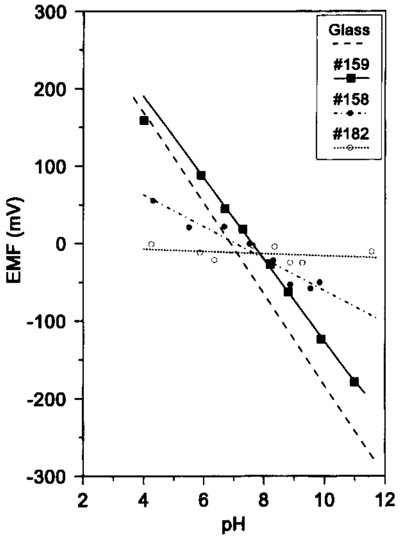

**Figure 1** Potentiometric responses (EMF) of membranes, which were made from three batches of PVC-$NR_2$s, versus pH (cf. inset and Table 2). The response of a glass pH electrode is shown for comparison

For the reactions with no solvent the nitrogen contents increased as the reaction times increased (*Table 3*). For similar reaction times of 7 and 14 d the batches formed in DMSO and the batches formed with no solvent had similar nitrogen contents (*Tables 2 and 3*). The solvent batches yielded membranes with slightly better pH responses. Elimination continues to be a problem with these reactions, as indicated by the shift to dark brown colours with longer reaction times.

## DISCUSSION

### *Elimination and substitution*

As was the case with PIP[14], reactions of PVC and Me-PIP yielded both the desired substitution products (*Figure 2a*) and the undesired elimination products (*Figure 2b*). The presence and relative amount of elimination was monitored by the colour change from white of the unreacted PVC to various shades of yellow and brown. The change to darker colours parallelled the increase in nitrogen content. In the thermal degradation of PVC most models propose a "zipper reaction" in which, following the initial elimination of an "H" and a "Cl" from the PVC backbone, elimination occurs on the adjacent mer and continues until the process is stopped yielding conjugated polyenes of 5 to 25 double bonds[21–23]. The length of the tactic sequence of the PVC partially limits the length of these polyenes. Longer tactic sequences yield longer conjugated chains[24]. These conjugated double bonds form chromophores when six or more occur[25].

We know that some substitution occurs because the nitrogen content increases and the potentiometric response improves. Unlike the earlier PIP reaction products[14], however, the Me-PIP products did not become insoluble in THF when stored in amber bottles for up to two years in the prevailing atmosphere at room temperature. The presence of the methyl group must limit the reactivity of the second N due to steric interferences so that post-reaction crosslinking is not possible.

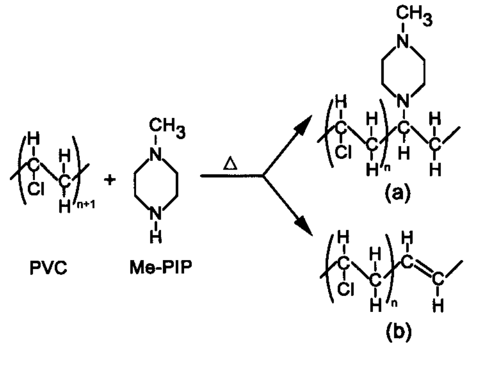

**Figure 2** Possible reactions of 1-methyl piperazine (Me-PIP) and poly(vinyl chloride) (PVC): (a) substitution; (b) elimination. Note that only the changes to the PVC backbone are shown

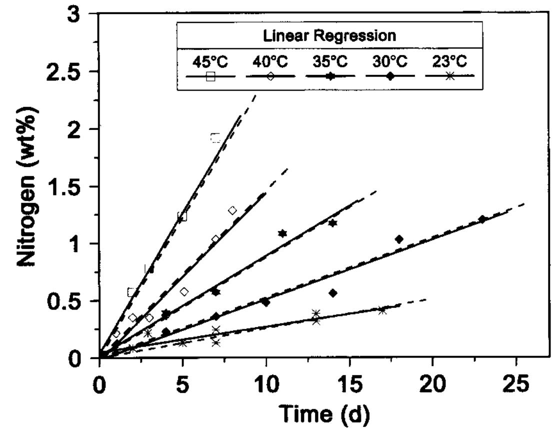

**Figure 3** Influence of wt% nitrogen (N) versus the times of reaction in dimethyl sulfoxide (DMSO) as a function of various temperatures (cf. inset) at a Me-PIP concentration of 0.5 mol.eq. The dashed lines represent the empirical lines generated for the five temperatures tested using equation (1)

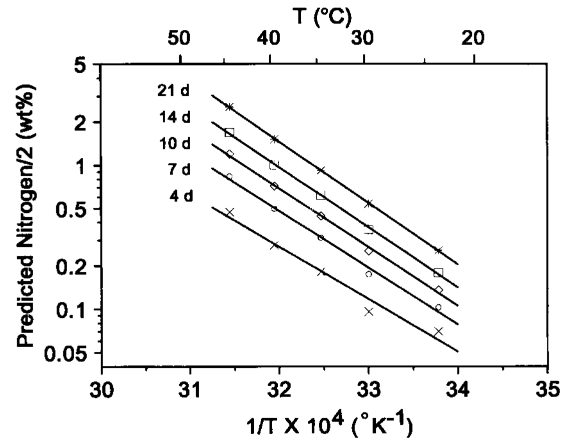

**Figure 5** Arrhenius plots of one-half the wt% N contents versus $1/T$ for the five reaction temperatures that were shown in Figure 3 and were run in DMSO at a Me-PIP concentration of 0.5 mol.eq. The activation energies (*ca.* 17–20 kcal·mol$^{-1}$) were determined for five reaction times

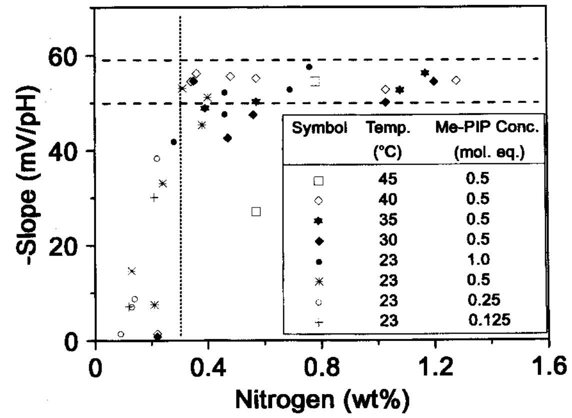

**Figure 4** Relationship of the slopes of the potentiometric responses versus wt% N for all soluble samples (cf. inset, and Tables 1 and 2) prepared in DMSO. The horizontal dashed lines represent the region for "good" pH responses, and the vertical dotted line represents the lower limit of wt% N that was necessary to obtain a "good" pH response. Although not shown, the upper limit of wt% N that was necessary to obtain a "good" pH response occurred at N contents as low as 1.2 wt%

### *Kinetics of reaction*

From linear regressions of the weight percent of N against time at discrete reaction temperatures a family of statistically significant ($p < 0.01$) lines was obtained (solid lines, *Figure 3*). If the slopes of these solid lines are assumed to be proportional to the reaction rates, then these amination reactions do not follow the empirical rule that reaction rates double with each 10°C increase in temperature[26]. To the contrary, there was approximately a three- to four-fold increase in the reaction rates per 10°C. Alternatively, these data can be described by a common empirical equation (dashed line, *Figure 3*),

$$N = 0.0522t(1.8^{((T-303)/5)}) \qquad (1)$$

in which $N$ is the nitrogen content in wt%, $t$ is the time in days and $T$ is the temperature in K. Overall, no differences were noted between these two approaches.

As observed with the PIP reactions in MeOH[14], there appears to be a lower limit of N necessary to obtain a "good" pH response (defined as the region between the two horizontal dashed lines, *Figure 4*). Using the present Me-PIP reactions, this occurs around 0.3 wt% N (vertical dotted line) versus 0.44 wt%N with PIP[14]. Once again, N content alone is not the sole requirement for "good" pH response as indicated for the batches with N greater than 0.3 wt% but less than 0.6 wt%. These six batches showed, for some unexplained reason, slopes below the accepted range of −50 mV/pH.

Insolubility in THF is generally reached at a nitrogen content of about 1.2 wt%. This corresponds to batches from either higher reaction temperatures or longer reaction times. Whether this insolubility is due to the presence of the increased number of Me-PIP substituents on the PVC backbone or the increased number of polyenes in the polymer backbone, as indicated by the darker colours, is not known. However, as stated above, soluble batches maintained their solubility for up to two years. This shelf-life is important for applications of these aminated materials as proton conductors.

Using the regression equations for the solid lines in *Figure 3*, the weight percent N was predicted as a function of temperature for 4, 7, 10, 14 and 21 d. Arrhenius plots of one half the wt%N‡ versus $1/T$ (K$^{-1}$) yielded activation energies that ranged from 17 to 20 kcal·mol$^{-1}$ ($p < 0.01$) [*Figure 5*]. By performing the equivalent calculations using equation (1), an activation energy of 22 kcal·mol$^{-1}$ was determined. By comparison, the theoretical energy of the substitution reaction is −11 kcal·mol$^{-1}$, based on the abstraction of a hydrogen (*ca.* 95 kcal·mol$^{-1}$) and a chlorine (*ca.* 81 kcal·mol$^{-1}$) from the Me-PIP and PVC, respectively, followed by the substitution of the nitrogen in Me-PIP onto the PVC (*ca.* −84 kcal·mol$^{-1}$) and the formation of HCl (*ca.* −103 kcal·mol$^{-1}$)[27]. The present activation energies for the Me-PIP reaction in DMSO agree closely with the range of 17 to 18 kcal·mol$^{-1}$ calculated for our PIP reactions in MeOH[14].

This approximate equivalence of activation energies for reactions, which were previously run in the non-polar MeOH[14] versus the present polar DMSO, seemingly contradicts the principal that increased solvent polarity enhances those reactions in which the transition state involves an increase in the separation of charge[19,28,29]. There should be a separation of charge in the transition state

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‡ One half of the wt% N is used, since only one of the two nitrogens on each Me-PIP is reacting

for a typical bimolecular nucleophilic substitution ($S_{N2}$) like ours in which the bond between the carbon and the incoming nucleophile (the nitrogen electron pair on Me-PIP) is being made at the same time as the carbon-chlorine bond is being broken[30]. The observed differences between the calculated heats of reactions and calculated activation energies, 28–33 kcal·mol$^{-1}$, must be due to the energetic requirements that are necessary to satisfy both the conformational requirements of aligning the free electron pair on the N with the back lobe of the carbon that is bonded to the chlorine[19,28] and the subsequent inversion of the PVC backbone[19,29]. The energy required for these two steps must be the limiting step of this reaction and may explain the similarity of the activation energies for these DMSO reactions and the PIP reactions[14].

In *Figure 5* the lines also appear to manifest slight upward curvatures with apparent discontinuities in their slopes around 30°C. These discontinuities correspond to the temperature at which the PVC begins to dissolve in the DMSO. The upward curvatures suggest the existence of composite reactions, in which two or more parallel reactions are available that have different activation energies[30–32]. If real, such curvatures may represent the change in reactivity due to the increased mobility of the PVC, after dissolution has occurred.

### *Time-temperature superposition*

When PIP was reacted with PVC in MeOH[14], time–temperature superposition was possible using the WLF expression[33],

$$\log a_T = \frac{-C_1(T - T_{ref})}{C_2 + T - T_{ref}} \tag{2}$$

in which $a_T$ is the shift factor, and $C_1$ and $C_2$ are constants. Traditionally, the glass transition temperature ($T_g$) has been used as the $T_{ref}$ in the WLF equation. In the earlier PIP work[14], however, 298K (25°C, the lowest temperature evaluated) was used as $T_{ref}$, and $C_1$ and $C_2$ equalled 8.2 and 89.5, respectively. Using these same values for $C_1$ and $C_2$ but 296K (23°C) as $T_{ref}$, a highly significant correlation ($p < 0.001$) was obtained between nitrogen content and $t/a_T$ (*Figure 6*).

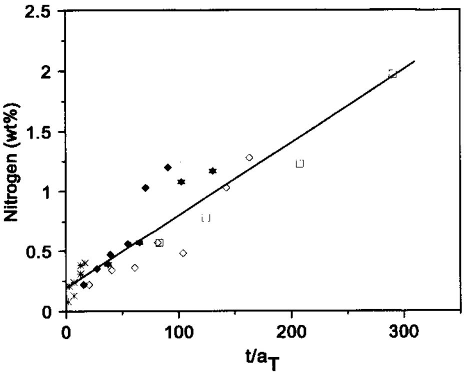

**Figure 6** Time–temperature superposition of reaction parameters, when PVC is aminated in DMSO at a Me-PIP concentration of 0.5 mol.eq. (cf. inset in Figure 3). The curve defines the relation, $N(\text{wt\%}) = 0.193 + 0.00606(t/a_T)$, in which $t$ is the reaction time (d) and $\log a_T = [-8.2\ (T - 296)]/(89.5 + T - 296)$, where $T$ is the temperature (K)

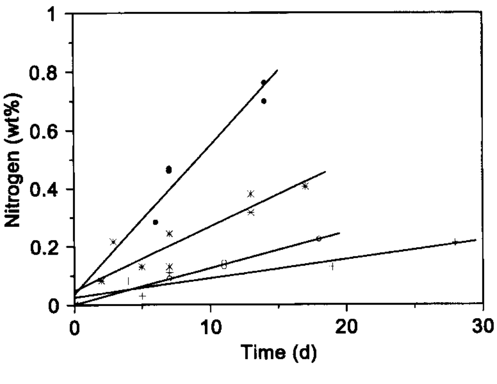

**Figure 7** Influence of wt%N versus the times of reaction as a function of various Me-PIP:PVC ratios (cf. inset in Figure 4) in DMSO at a constant temperature of 23°C

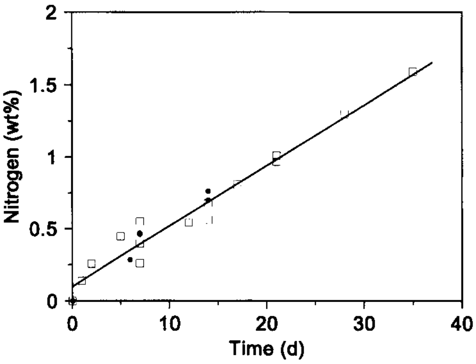

**Figure 8** Influence of wt%N versus the times of reaction with 1.0 mol.eq. Me-PIP at a constant temperature of 23°C and no solvent (line and □). The results are superposed (● as in Figure 4) for comparable reaction conditions that were reacted in DMSO

### *Influence of other parameters*

Plots of wt%N against reaction times, using a constant DMSO:PVC ratio (17.5 ml/g) and temperature (23°C), but with variable Me-PIP:PVC ratios, indicated that the rates of amination increase at a rate equal to the increase in Me-PIP concentration (*Figure 7*). That is, as the relative concentration of Me-PIP was doubled, the rate of amination doubled. This outcome is consistent for an $S_{N2}$ reaction. The change in concentration and the resulting increase in N content also influenced the EMF-pH response (*Table 2*). Specifically, using the same reaction time but a four-fold increase in Me-PIP concentration, a five-fold increase in the wt%N and a 38-fold increase in the pH response were observed (*Figure 1* and *Table 2*).

When reactions were run with no solvent, a highly significant relationship ($p < 0.001$) between wt%N and reaction times was obtained [*Figure 8* (□)]. The Me-PIP was able to react with the PVC particles without the aid of a solvent. When data was superposed on the same plot from the present reactions that were run with 1.0 mol.eq. Me-PIP in DMSO [*Figure 8* (●)], amination was not dependent on the presence of a solvent. Whether this trend would continue at higher reaction temperatures or whether the reactions with no solvent would have the same activation energy as with DMSO is not know. If the similarities persist, the role of the solvent and the mechanism of amination would require further refinement.

## CONCLUSIONS

Methyl piperazine can be used to prepare aminated PVCs with approximately Nernstian behaviour over the pH range of 4 to 12.

A linear relationship exists between the extent of the amination of PVC and the reaction time for both a range of temperatures and a range of concentrations of Me-PIP. For a range of temperatures the data can be expressed by an empirical equation in which all amination reactions are directly proportional to the relative concentrations of Me-PIP and PVC.

A good pH response requires a minimum of 0.3 wt%N. Unfortunately, insolubility occurs in some batches above about 1.2 wt%N.

The substitution of Me-PIP onto PVC in DMSO follows an Arrhenius behaviour having an activation energy of 17–20 kcal·mol$^{-1}$. These activation energies agree with those values calculated for the amination of PVC by piperazine in methanol.

For the amination of DMSO time–temperature superposition is possible, which enables the prediction of comparable amination outcomes.

Unlike previous reactions using piperazine, formulations made with Me-PIP remain soluble in THF for up to two years when stored in amber bottles at room temperature. Specifically, no evidence of post-reaction crosslinking occurs.

Elimination and substitution reactions compete as indicated by the colour change from the white unreacted PVC to shades of yellow and brown for batches reacted at longer times and/or higher temperatures. These chromophores indicate that six or more conjugated bonds are still present.

The amination reaction does not require a solvent to yield materials that approach Nernstian behaviour. The same dependency with respect to reaction time occurs whether DMSO is present or not.

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