# Syntheses and kinetics of piperazine-modified poly(vinyl chloride)s for use as fixed-site proton carrier membranes

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Analytical-grade piperazine was dissolved in methanol and reacted with commercial-grade poly(vinyl chloride) powders over a range of temperatures from 25 to 64°C and times from 0.17 to 49 days. The products were aminated polymers that also contained conjugated double bonds. Chemical analysis of the resulting powders showed that up to 1.6 wt% N was possible in this solid–liquid heterogeneous reaction, although insolubility of the aminated polymer in tetrahydrofuran was always realized by 0.8 wt% N content. In those polymer formulations that were soluble, membranes were cast from solution using *o*-nitrophenyloctyl ether and potassium tetrakis(*p*-chlorophenyl)borate as the plasticizer and negatively charged sites, respectively. After conditioning, many of these fixed-site proton carrier membranes showed Nernstian pH sensitivity in potentiometric cells, independent of synthesis parameters. The nitrogen content of the aminated PVC and the pH sensitivity of the membrane correlated below a limiting nitrogen content, where Nernstian behaviour was generally observed over a range from 0.4 to 0.8 wt% N content. A three-dimensional plot over the soluble region of the polymer predicted the overall dependence of the reaction parameters, from which an activation energy (17 kcal $\mathrm{mol}^{-1}$) was determined for the substitution process. A time–temperature correspondence was demonstrated that allowed the construction of a master curve of amination in which the shift factor was of the same form as either the Williams–Landel–Ferry equation or a rearranged Doolittle equation. This format was extended to three dimensions, where the pH sensitivity is shown as a function of both the weight percentage N content and the shift factor.

**(Keywords: kinetics; membranes; piperazine-modified PVC)**

## INTRODUCTION

Almost 20 years ago, Reboul[1] showed that ions occur in poly(vinyl chloride)s (PVC) for two reasons. First, ions are *extrinsically* added in the form of catalysts and stabilizers in amounts of up to 4% of PVC[2]. Horvai *et al.*[3] showed their presence, when they characterized the electrical conductivity of dioctyl sebacate-, dibutyl sebacate- and *o*-nitrophenyloctyl ether-plasticized PVCs. Secondly, PVCs are *intrinsically* subject to decomposition by thermal-, oxidative- and photo-initiated processes. The specifics of intrinsic ionic impurities are reported by van den Berg *et al.*[4]. Manifestations of decomposition are seen in the production of hydrochloric acid, chromophores and transient ionic currents until a final stabilized value is obtained[1]. If the aim of the work is to make ion conductive membranes, then neither of the above reasons for achieving ion conductivity are really acceptable because the chemistry of the end-product cannot be controlled with certainty, and indeed may always be in a dynamic state of decomposition.

Although Simon *et al.* doped polymeric membranes with various amino-based proton carriers[5,6], it was not until 1987 that Gurgiolo *et al.*[7] first filed a patent describing the attachment of amine groups onto the backbone of a dehydrohalogenated polymer such as PVC. A year later Ma, Chaniotakis and Meyerhoff[8] fixed aminated sites onto PVC chains. Then in 1990, Ma and Meyerhoff[9] 'aminated PVC' ($NH_2$–PVC) with both mono- and diamines by refluxing in methanol for 3–45 h. The pH response was linear with slopes ranging from 24.0 to 55.1 mV/pH unit over a pH range from 5 to 12, although never were they greater than five pH units in any single membrane. In the same year, Kusy and Whitley began aminating PVC with 1,4-diaminobutane followed by other members of that homologous series as well as with 1,2-diaminopropane, *trans*-1,4-diaminocyclohexane, 1,8-diamino-*p*-menthane and 1,4-bis(3-aminopropyl) piperazine. Two years later in a collaborative effort between the materials science and electrochemistry groups, Kusy and Whitley first aminated PVC powders based upon the strong base of diethylenediamine (piperazine), and then Cosofret *et al.*[10] and Lindner *et al.*[11] measured the electromotive force potentials of a series of

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electrodes prepared from the respective membranes. The details of the syntheses of the aminated PVC materials were withheld pending further experimentation and filing of patents.

The present work investigates some 50 batches of piperazine-modified PVC powders, of which over 40 are soluble in tetrahydrofuran (THF) and suitable for the fabrication of fixed-site proton carrier membranes. After determining the nitrogen content, the soluble batches are cast into membranes and their pH response is measured in appropriate potentiometric cells. Using three-dimensional plots, the kinetics of the amination reaction are detailed, and the activation energy of amination is determined. Using the Williams–Landel–Ferry (WLF) equation, a time–temperature equivalence is established.

## EXPERIMENTAL

### General amination procedure

One part by weight (w/w) of as-received PVC beads ($MW = 110\,000$; Polysciences) was placed in a clean, round-bottomed flask that contained a polytetrafluoroethylene (PTFE)-coated magnetic stirring bar. Seven parts of analytical-grade anhydrous piperazine (PIP; Aldrich)* was poured into that flask, followed by 14 parts of h.p.l.c.-grade methanol (MeOH; Fisher Scientific). A Claisen adapter was connected to the flask. In the straight arm of this adapter a second adapter was attached that had a gas inlet for argon and a centre opening for a thermowell. A Graham condenser, which had a gas trap attached to its top opening, was connected to the curved arm of the Claisen adapter. While the PIP was dissolving, argon purged the system. Temperatures were maintained from 25 to 64°C via a small heat tape. The temperature was regulated via a controller that used a thermocouple, which was placed in the thermowell. Reaction time was measured in days (d), once the solution reached the desired reaction temperature. At the end of the desired time, which ranged from 0.17 to 49 d, the controller was turned off, and excess MeOH was added to the flask to quench the reaction. The solution was carefully decanted through a PTFE filter–funnel combination, leaving the polymer in the flask. The polymer was washed once more with MeOH, and again the supernatant was removed. The polymer was then washed with deionized water twice and then washed with 0.1 M NaOH once. The polymer was washed repeatedly with deionized water, and the pH was checked with pHydrion paper until the pH was neutral. Then the polymer was washed with MeOH twice more prior to being washed out of the flask and into the funnel. The filtrate was washed once with MeOH and finally dried in a vacuum at room temperature overnight.

### Nitrogen analysis

The nitrogen content, which indicated the possible extent of amination, was assayed using the services of Galbraith Laboratories Inc., Knoxville, TN. For most batches, one of three different combustion instruments were used, having a precision of ±0.15 wt%. In a dozen other batches, the Kjeldahl method was used, in which the titration was precise to ±0.05 wt%. A distinction among the two methods and their four instruments is noted later in the 'Results' section.

### Membrane preparation

The basic preparation of solvent polymeric membranes followed the general procedures of Moody *et al.*[13], except without the addition of any ionophore. The $NH_2$–PVC product, potassium tetrakis(*p*-chlorophenyl)borate (KT*p*ClPB; Fluka) and *o*-nitrophenyloctyl ether (*o*-NPOE; Fluka 73732) were dissolved in tetrahydrofuran (THF; Aldrich) in the proportions 100:2:200. The addition of the lipophilic salt, KT*p*ClPB, reduced membrane resistance, anion interference and response time. The highly polar *o*-NPOE was a monodisperse, low-molecular-weight plasticizer[14] that had been shown to provide good electrochemical characteristics in PVC membranes[15]. For every 300 mg of polymer, negatively charged sites and plasticizer, about 3 ml of THF was added as a solvent for membrane casting. Membrane discs that were about 200 μm in thickness were recovered following solvent evaporation of THF for ca. 24 h.

### Conditioning

The membrane discs (0.7 cm in diameter) were incorporated into an electrode body (Philips IS-560 containing an internal electrolyte solution at a pH 7.0 buffer) and were conditioned for at least 24 h in a citrate–borate buffer (pH 7.0) containing lithium as an ionic background.

### Electromotive force measurements

The electromotive force (EMF) of each potentiometric cell was measured at room temperature (22.5±0.5°C) with an Orion pH/mV-Meter (model 720A) using an Ag/AgCl external reference electrode (Orion model 90-02). Readings were taken only after the potential change was less than 0.2 mV min$^{-1}$. The pH of the buffer solutions were made more acidic or basic by the addition of hydrochloric acid or sodium hydroxide, respectively. These pH values were checked and adjusted by means of a hydrogen selective glass electrode (Orion model 91-57).

## RESULTS

The basic parameters of the synthesis (temperature and time) of some 50 PIP-modified batches of PVC are summarized in *Table 1* along with the results of the nitrogen analyses, pH response ranges and slopes. Nitrogen content of the materials ranged from 0.23 to 1.63 wt%. As a consequence of the synthesis, many $NH_2$–PVC batches were rendered insoluble by 0.8 wt% N. After nominally one day of electrode conditioning, the piperazine-based membrane showed some response to hydrogen-ion activity changes in the pH range from 4 to 12. Of these, eight formulations had nearly theoretical pH sensitivity; their slopes ranged from −56.5 to −59.7 mV/pH unit and closely approximated Nernstian behaviour (−59.2 mV/pH). An example of an outstanding $NH_2$–PVC is batch 73 (*Figure 1*). This aminated PVC material was made by reacting the PVC and PIP for 10 d at 35°C. A nitrogen content of 0.72 wt% was assayed. Practically no difference was seen between the potentiometric data

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* Piperazine is prone to absorb moisture and carbon dioxide, forming a carbonated hexahydrate. Being reasonably stable, this form melts at 44°C and boils at 125°C. In contrast, the anhydrous base has a melting point of 104°C and a boiling point of 145°C[12]. Consequently, the extent of hydration can be readily determined by differential thermal analysis or thermogravimetric analysis

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

| Batch | Temperature (°C) | Time (d) | Nitrogen (wt%) | Nitrogen analysis method[b] | pH range | −Slope (mV/pH unit) |
|---|---|---|---|---|---|---|
| 45 | 64 | 0.17 | 0.56 | E7-1 | 5–12 | 54.6 |
| 44 | 64 | 0.33 | 1.07 (ns)[c] | E7-1 | – | – |
| 43 | 64 | 0.60 | 1.63 (ns) | E7-1 | – | – |
| 42 | 64 | 1 | 0.91 (ns) | ME-2 | – | – |
| 80 | 50 | 0.17 | 0.64 | ME-6 | 5–11 | 59.5 |
| 96 | 50 | 0.29 | 0.66 | ME-2 | 4–12 | 59.2 |
| 82 | 50 | 0.33 | 0.57 | ME-6 | 5–11 | 58.6 |
| 79 | 50 | 0.67 | 0.86 | E7-5 | 5–11 | 60.9 |
| 81 | 50 | 0.67 | 0.60 | E7-5 | 5–11 | 59.8 |
| 78 | 50 | 1 | 0.64 | ME-6 | 5–11 | 60.6 |
| 94 | 50 | 3 | 1.05 (ns) | ME-2 | – | – |
| 95 | 50 | 5 | 1.29 (ns) | ME-2 | – | – |
| 106 | 45 | 0.21 | 0.46 | E7-5 | 3–12 | 19.0 |
| 105 | 45 | 0.29 | 0.57 | E7-5 | 3–12 | 21.5 |
| 99 | 45 | 0.63 | 0.58 | ME-2 | 5–12 | 58.2 |
| 48 | 45 | 1 | 0.74 | E7-1 | 4–10 | 54.2 |
| 83 | 45 | 1 | 0.55 | ME-6 | 5–11 | 60.1 |
| 84 | 45 | 2 | 0.73 | ME-6 | 5–11 | 60.8 |
| 85 | 45 | 3 | 0.60 | ME-6 | 5–12 | 61.8 |
| 93 | 45 | 4 | 0.76 | ME-2 | 4–12 | 59.7 |
| 100 | 45 | 6 | 1.22 (ns) | E7-5 | – | – |
| 98 | 40 | 2 | 0.60 | ME-2 | 4–12 | 59.6 |
| 86 | 40 | 3 | 0.62 | ME-6 | 5–11 | 60.7 |
| 88 | 40 | 4 | 0.65 | ME-6 | 5–12 | 61.6 |
| 66 | 40 | 6 | 0.84 | ME-6 | 4–11 | 56.9 |
| 97 | 35 | 4 | 0.50 | ME-2 | 4–12 | 58.2 |
| 47 | 35 | 7 | 0.62 | E7-1 | 4–11 | 58.0 |
| 60 | 35 | 7 | 0.45 | E7-1 | 4–10 | 48.0 |
| 61 | 35 | 7 | 0.83 (ns) | E7-1 | – | – |
| 62 | 35 | 7 | 0.39 | E7-1 | 4–11 | 26.1 |
| 71 | 35 | 7 | 0.50 | E7-5 | 4–12 | 58.8 |
| 65 | 35 | 10 | 0.66 | E7-1 | 5–12 | 57.5 |
| 72 | 35 | 10 | 0.67 | ME-6 | 4–10 | 44.7 |
| 73 | 35 | 10 | 0.72 | ME-6 | 5–12 | 58.9 |
| 102A | 35 | 10 | 0.87 | E7-5 | 5–12 | 58.6 |
| 102B | 35 | 10 | 0.74 | E7-5 | 5–12 | 58.5 |
| 103 | 35 | 10 | 0.80 | E7-5 | 4–12 | 58.7 |
| 92 | 35 | 20 | 0.78 (ns) | ME-2 | – | – |
| 107 | 30 | 4 | 0.31 | E7-5 | 2–6 | 24.0 |
| 101 | 30 | 6 | 0.37 | E7-5 | 3–12 | 19.0 |
| 87 | 30 | 7 | 0.55 | ME-6 | 5–11 | 60.3 |
| 90 | 30 | 10 | 0.58 | ME-2 | 5–12 | 58.1 |
| 89 | 30 | 14 | 0.44 | E7-5 | 4–12 | 57.1 |
| 104 | 30 | 20 | 0.60 | E7-5 | 4–12 | 56.5 |
| 46 | 25 | 11 | 0.23 | E7-1 | 7–12 | 0 |
| 58 | 25 | 14 | 0.30 | E7-1 | 2–6 | 26.1 |
| 59 | 25 | 31 | 0.56 | E7-1 | 4–11 | 57.8 |
| 91 | 25 | 49 | 0.88 (ns) | E7-5 | – | – |

[a] Ratio of reagents MeOH:PIP:PVC = 14:7:1

[b] E7-1 = Kjeldahl titration (±0.05 wt%); ME-2 = Perkin-Elmer 230 CHN combustion (±0.14 wt%); ME-6 = LECO CHN 800 combustion (±0.16 wt%); and E7-5 = LECO FP428 combustion (±0.14 wt%)

[c] ns = not soluble in THF

of a glass electrode and that of the aminated PVC membrane-based electrode over the range of pH from 5 to 12. The outstanding stability of this membrane is discussed elsewhere[16]. For comparison, two other batches (i.e. 60 and 101) are shown that were much less successful with respect to their pH response. The former was only enriched with 0.45 wt% N and had a slope of −48.0 mV/pH; the latter was enriched even less (0.37 wt% N) and consequently its slope was slight (−19.0 mV/pH). Among all of the batches prepared, those judged to be the best were often the ones that had been aminated from 0.6 to 0.8 wt% N such as batches 47, 73 and 103.

## DISCUSSION

### *Elimination and substitution*

The amination of PVC with PIP involves both elimination and substitution (*Figure 2*). We know that elimination occurs because of the colour change that appears with time at temperature from white to shades of yellow (the limit of solubility), orange, brown and finally black. Likewise, we know that substitution occurs because, in addition to a change in solubility and nitrogen content, the potentiometric and adhesive properties change[17].

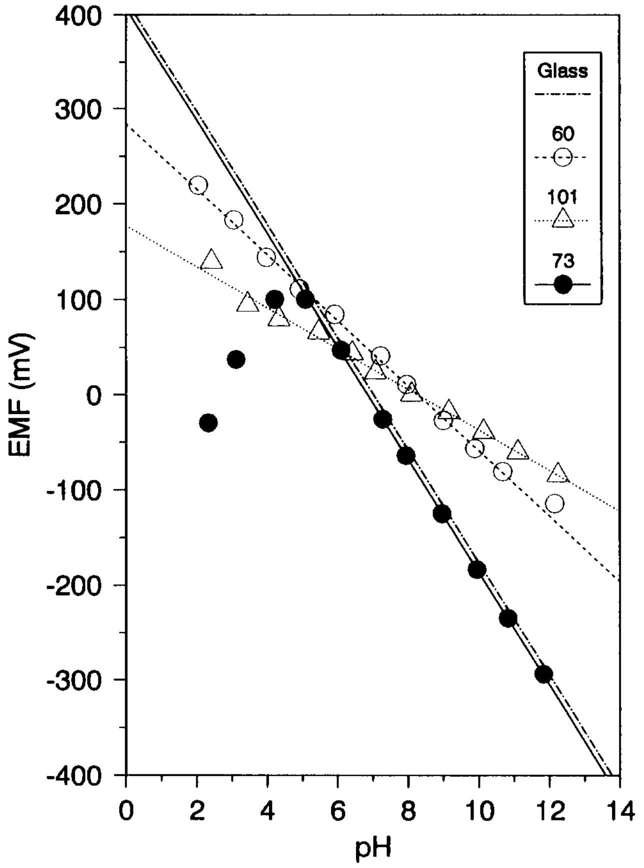

**Figure 1** Potentiometric responses (EMF) of membranes from three batches of $NH_2$-PVCs *versus* pH (cf. *Table 1*). Outcomes from a glass electrode show why batch 73 is so highly regarded

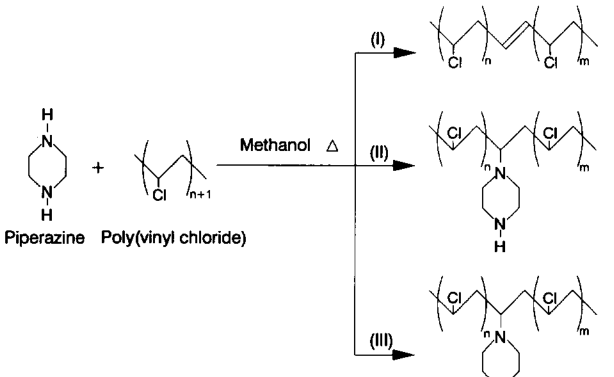

**Figure 2** Possible reactions of piperazine (PIP) and poly(vinyl chloride) (PVC): (I) is an elimination reaction; (II) and (III) illustrate substitution. Note that only the changes to the PVC backbone are shown

In the elimination reaction (*Figure 2*, I), double bonds are formed as piperazine hydrochloride is produced. When six or seven such bonds occur in a row, the conjugation creates a chromophore[18]. In the substitution reaction, the attachment of PIP as a substituent group takes two possible forms, simple substitution (*Figure 2*, II) and/or crosslinking (*Figure 2*, III). Crosslinking can occur intramolecularly by backbiting, but is more likely intermolecularly. Many years ago in Sebrell's patent[12], PIP was actually suggested as an accelerator for the vulcanization of rubber.

### *Kinetics of reaction*

When weight percentage of N is linearly regressed against time and displayed on a semi-lorarithmic plot using reaction temperature as a parameter (*Figure 3*), a statistically significant outcome is observed at five temperatures (see probabilities *p* at the base of the figure). Indeed, even at 30°C the trend suggests a curve that would lie between the 25 and 35°C data. In spite of the fact that insolubility of $NH_2$–PVC occurs by 0.8 wt% N (cf. horizontal broken line in *Figure 3*), many time–temperature schemes appear to yield soluble aminated products.

This last observation is further substantiated when only the data of the soluble $NH_2$–PVCs were plotted as the slope of the EMF–pH response *versus* time for the seven temperatures (*Figure 4*). In this plot some two dozen formulations show a Nernstian behaviour (cf. broken line in *Figure 4*) at reaction times that range from 0.17 to 31 d and at reaction temperatures that range from 25 to 64°C. One could infer, therefore, that no unique time–temperature scheme exists. Moreover, if an optimal scheme exists, it may be beyond the present boundaries of the formulation parameters and the capabilities of the validation methodologies.

After the negative slopes (i.e. the pH sensitivities) of the potentiometric responses *versus* wt% N contents of the 36 soluble batches are plotted, the 11 non-Nernstian batches are linearly regressed, and a positive correlation is found ($p<0.01$ in *Figure 5*). Generally speaking, the synthesized materials are bounded vertically by the nitrogen content and horizontally by the theoretical Nernstian response (cf. broken lines in *Figure 5*). More specifically, the 'window' of useful carrier membranes ranges from 0.44 to 0.87 wt% N and from −54.2 to −61.8 mV/pH (cf. dotted box in *Figure 5*). The limitations of the window have been addressed elsewhere[19], and so it is sufficient to say here that the width of the window is controlled by chemical insolubility at one boundary and insufficient numbers of fixed-site proton carriers at the other.

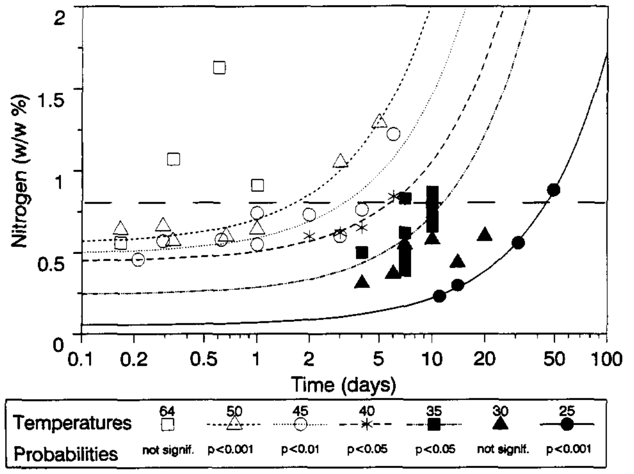

**Figure 3** Influence of wt% N *versus* the time of reaction as a function of various reaction temperatures (see inset at figure base). The value of 0.8 wt% N (the horizontal broken line) represents the solubility limit of these aminated PVCs in THF

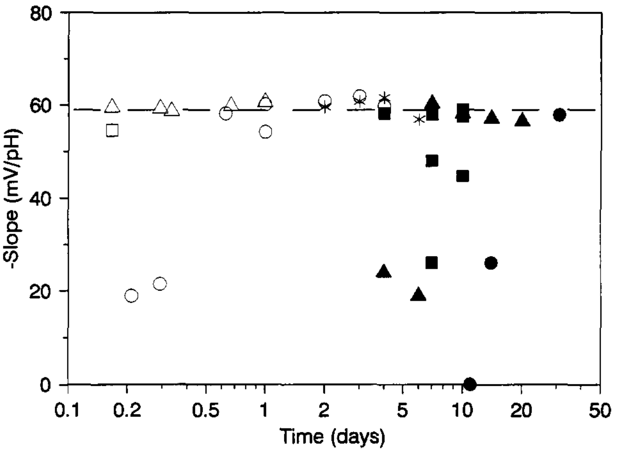

**Figure 4** Slopes of potentiometric responses *versus* time as a function of temperature (see inset in *Figure 3*). The value of −59.2 mV/pH (the broken line) represents theoretical Nernstian behaviour

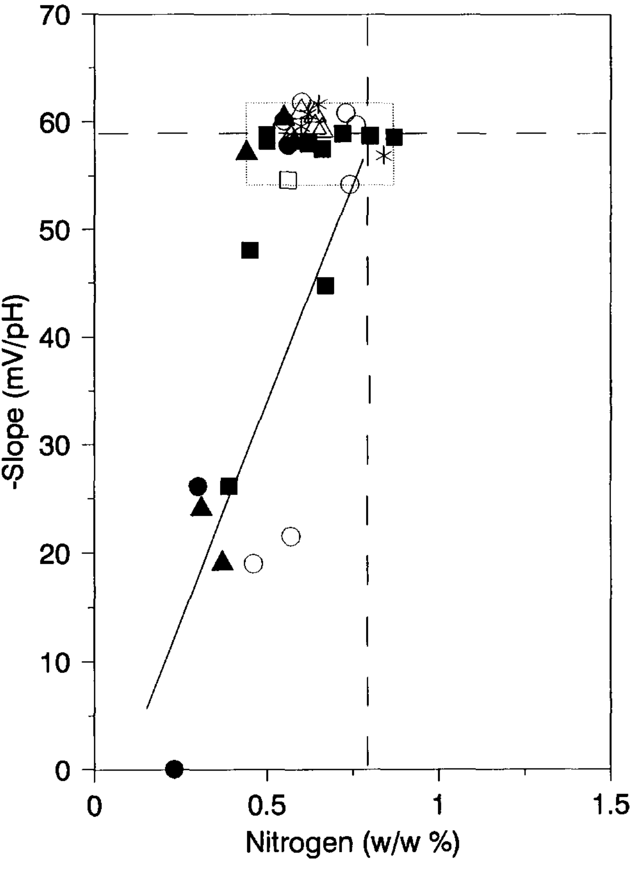

**Figure 5** Relationship of the slopes of the potentiometric responses *versus* wt% N (for temperatures, see inset in *Figure 3*). The two broken lines represent the solubility limit in THF and the theoretical Nernstian response; the dotted box represents the 'window' wherein useful membrane materials may be found. For 11 non-Nernstian batches prepared, the linear regression analysis gave a correlation coefficient of 0.749 for a statistical probability $p<0.01$

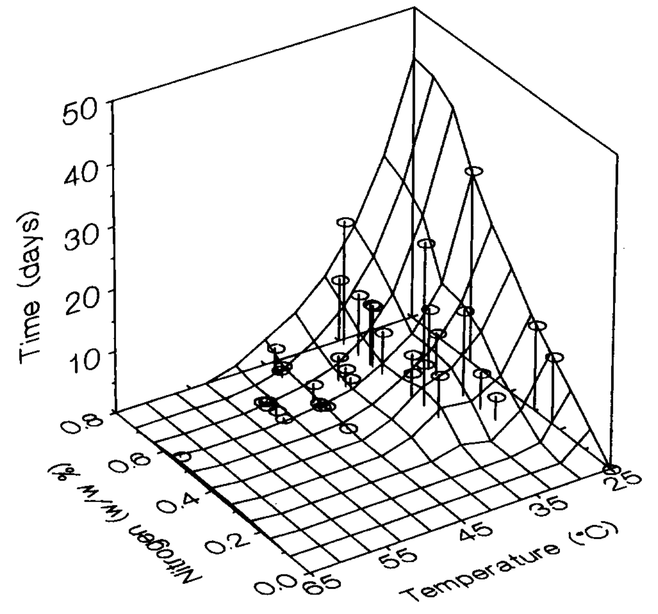

**Figure 6** Topographical map that predicts amination behaviour from the reaction parameters of the soluble $NH_2$-PVC batches that were prepared

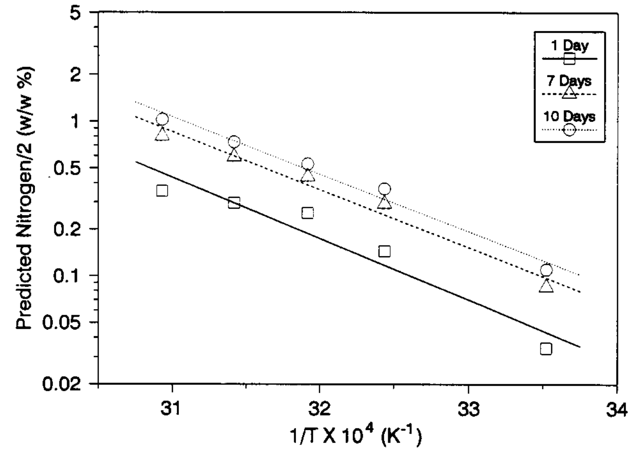

**Figure 7** Arrhenius plot of one-half the wt% N content *versus* $1/T$ for the five statistically significant reaction temperatures (cf. *Figure 3*). The activation energy (ca. $17\,\mathrm{kcal\,mol^{-1}}$) is restricted to the tertiary amines directly involved with substitution, assuming a 1:1 correspondence with elimination and no crosslinking

A topological map of temperature–time–nitrogen content over only the soluble region suggests, as expected, an inverse relationship between temperature and time (*Figure 6*). If the map is used as a model, predictions are possible. For example, for 0.8 wt% N at a reaction temperature of 25°C, amination will require about 43 d; while at a reaction temperature of around 50°C, amination will occur in a few hours.

From such a map, horizontal slices may be taken at several times, and the wt% N may be predicted as a function of temperature (*Figure 7*). When this is done for 1, 7 and 10 d, these Arrhenius plots of one-half the wt% N* *versus* $1/T$ yield activation energies that range from 17 to $18\,\mathrm{kcal\,mol^{-1}}$ ($p<0.01$). In contrast, the calculated reaction energy of the substitution process equals $-11\,\mathrm{kcal\,mol^{-1}}$, based on the abstraction of a chlorine (ca. $81\,\mathrm{kcal\,mol^{-1}}$) and hydrogen (ca. $95\,\mathrm{kcal\,mol^{-1}}$) from the PVC and PIP, respectively, followed by the substitution of the PIP moiety onto the PVC (ca. $-84\,\mathrm{kcal\,mol^{-1}}$) and the formation of HCl ($-103\,\mathrm{kcal\,mol^{-1}}$)[20].

*Time–temperature superposition*

The foregoing plots, and in particular *Figures 3* and *7*, suggest that a time–temperature superposition may be possible with respect to the kinetics of amination. Such master curves have been constructed to reduce stress relaxation or creep data to a common reference temperature. Williams, Landel and Ferry[21] derived the classic 'WLF' expression using the glass transition temperature ($T_g$) as their reference temperature ($T_{ref}$) according to the form:

$$\log a_T = \frac{-C_1(T-T_{ref})}{C_2+T-T_{ref}} \tag{1}$$

in which $a_T$ is the shift factor and $C_1$ and $C_2$ are constants. This expression has become the keystone for predicting, from limited elastic modulus data of a polymer, its global viscoelastic response. Given that the semiempirical Doolittle equation[22] for the viscosity of a liquid can be rearranged into the form of equation (1) (whilst only making the assumption of a linear expansion of free volume about $T_g$) and that the tensile viscosity[23] may be viewed in much the same way as elastic modulus, the general form of equation (1) might have other applications as well.

If, as in the textbook by Aklonis, MacKnight and Shen[23], we assume that the ideas embodied in the WLF equation not only apply just above the $T_g$ but also can be applied at temperatures considerably below $T_g$ (in their text they cite $T_g$ minus 50°C), then we can recast our kinetic data that occur from 16 to 55°C below the $T_g$ of PVC ($T_g = 80$°C by d.s.c. technique). Using our room-temperature reaction (25°C) as the reference temperature, the outcome of this time–temperature superposition is a highly significant correlation ($p<0.001$) between the nitrogen analyses of 46 formulations *versus* time, when a shift based on equation (1) is used in which the constants $C_1 = 8.2$ and $C_2 = 89.5$ are chosen (*Figure 8*).

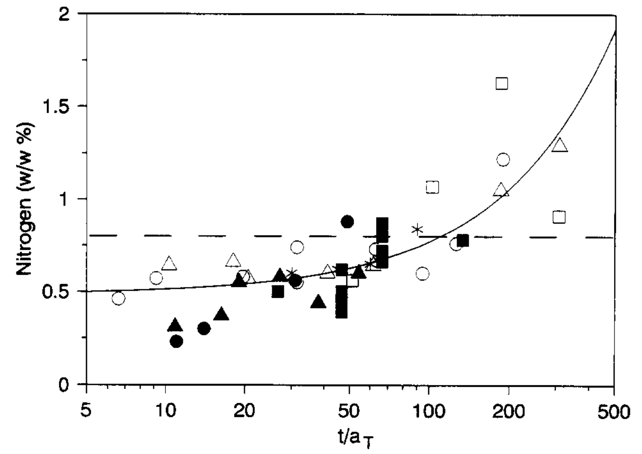

**Figure 8** Time–temperature superposition of reaction parameters, when PVC is aminated (for temperatures, see inset in *Figure 3*). The full curve defines the relation, $\log a_T = [-8.2(T-298)]/(89.5+T-298)$. For 46 batches prepared, the linear regression analysis gave a correlation coefficient of 0.756 for a statistical probability $p<0.001$. The broken line has the same connotation as in *Figures 3* and *5*

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

The culmination of these experiments is to predict, within the region of solubility, the interrelationship of reaction parameters, extent of amination and the potentiometric response. *Figure 9* elucidates this by plotting some three dozen data points and fitting a linear mathematical grid through the data, without any regard to the physical significance of the boundaries. Nonetheless, we begin to see that, in principle, a plethora of formulations exist within the soluble region denoted by $t/a_T < 150$ (cf. *Figure 8*). These will approach Nernstian behaviour ($-59.2$ mV/pH), particularly when $0.55 < \mathrm{N}\,(\mathrm{wt}\%) < 0.79$. If future reactions are carried out in close proximity to the experimental parameters investigated herein, then the same kinetic reaction schemes should be operative and the topographical map of *Figure 9* should be valid.

*Influence of time and temperature*

In these experiments we have primarily investigated time and temperature, but even these parameters have not been fully explored. For example, although we know the possible extent of amination via a nitrogen analysis, how that nitrogen is distributed—as intramolecular pendent groups *versus* intramolecular or intermolecular crosslinks—is not known. This may be crucial with respect to the analytical response. Reducing dehydrochlorination reactions to only those which involve the attachment of PIP moieties should increase the mechanical flexibility and chemical solubility of the final $NH_2$–PVC product. Indeed, generally finding routes by which the substitution to elimination ratio is increased should enhance ion conduction.

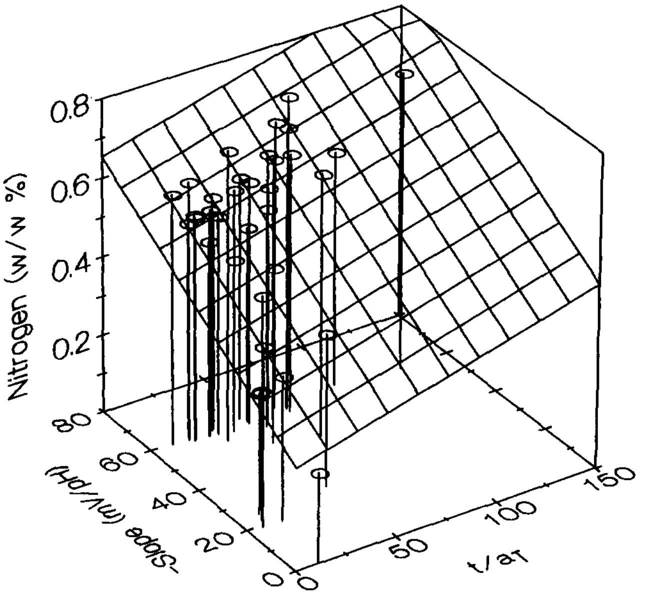

**Figure 9** Topographical map that predicts reaction parameters, extent of amination and slopes of potentiometric response curves from the soluble $NH_2$-PVC batches that were prepared

*Influence of other parameters*

The initial states of reagents, their solvation characteristics and their relative concentrations require further investigation as well.

In the first, the initial states of hydration of the PIP and purity of the PVC are two concerns. Being such a hygroscopic base, any opened PIP jars were always flushed with argon prior to recapping. On the other hand, no special purification or fractionation procedures were carried out to ensure that trace catalysts, stabilizers, or oligomers were removed from the PVC. In the past, PVC purities have been determined from the resistances of membranes that were cast from powders of different suppliers[3,24]. When future formulations are prepared for medical applications, these precautions must be employed.

Solvation of reactants should also contribute to the final product. Presently, PIP dissolves in MeOH, but PVC does not. If the reaction is moderated by the MeOH, does it only occur on the surface of the PVC powders because the MeOH does not wet the powders? Alternatively, does the PIP not only cross the liquid–solid interface but also diffuse and react in the solid state with PVC? In this regard, Sakai *et al.*[25] have shown that 4-vinylpyridine can be homogeneously grafted through a 50 μm thick PTFE film even though the methanol solvent does not wet the PTFE. How future aminated products would differ from the present aminated outcomes if a common solvent for PIP and PVC were used (e.g. 2-butanone) might prove quite interesting as well.

Finally, the relative reagent concentrations may influence the incidence of substitution *versus* elimination. In the general procedure outlined earlier, the reagent ratios of MeOH:PIP:PVC were 14:7:1. For a reaction time of 7 days and a temperature of 35°C, this is represented by batch 47 (cf. *Table 1*). For clarity, the data of batch 47 are merged with the data from three other reagent ratios in which the amount of MeOH was changed from 14 parts to 16, 11 and 5 (*Table 2*), while maintaining the other reagents constant. From *Table 2* we observe that increasing the relative concentration of reactants affects the N content, the colour and the solubility of the product. In the three batches that could be cast

**Table 2** Influence of reagent ratios on the syntheses of PIP-modified PVCs[a] and on the characteristics of fixed-site proton carrier membranes[b]

| Batch | Reagent ratios MeOH:PIP:PVC | Nitrogen (wt%) | Nitrogen analysis method[c] | pH range | –Slope (mV/pH unit) | Colour |
|---|---|---|---|---|---|---|
| 76 | 16:7:1 | 0.53 | ME-6 | 5–12 | 60.8 | Light yellow |
| 47 | 14:7:1 | 0.62 | E7-1 | 4–11 | 58.0 | Yellow |
| 74 | 11:7:1 | 0.77 | ME-6 | 5–12 | 59.4 | Dark yellow |
| 75 | 5:7:1 | 1.24(ns)[d] | ME-6 | – | – | Reddish brown |

[a] All reacted at 35°C for 7 days under argon

[b] $NH_2$-PVC, KTpClPB and *o*-NPOE were first dissolved in THF in the proportions 100:2:200, then cast, and finally recovered after solvent evaporation for ca. 24 h (cf. 'Membrane preparation' in 'Experimental' section)

[c] E7-1 = Kjeldahl titration (±0.05 wt%); and ME-6 = LECO CHN 800 combustion (±0.16 wt%)

[d] ns = not soluble in THF

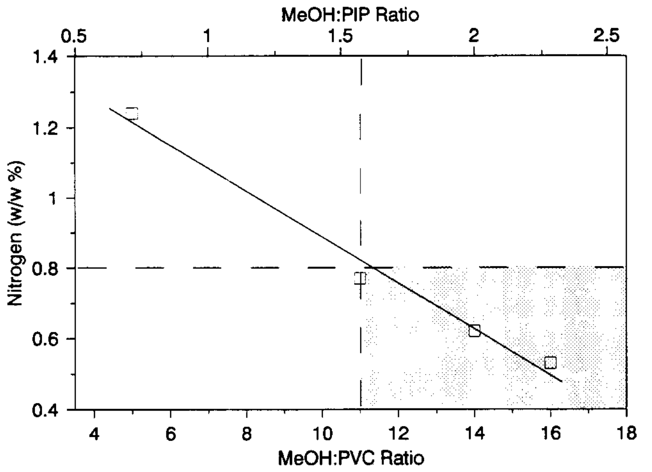

**Figure 10** Influence of wt% N *versus* the MeOH:PVC and MeOH:PIP ratios for four batches of $NH_2$-PVCs (cf. *Table 2*). A linear regression analysis gave a correlation coefficient of 0.992 for a statistical probability $p<0.01$. Assuming the solubility limit (the horizontal broken line) is the same as that suggested by the extensive data of *Table 1* (also shown in *Figures 3, 5* and *8*), we project that only MeOH:PVC and MeOH:PIP ratios of more than about 11:1 and 1.6:1, respectively (the vertical broken line), will yield soluble products (the stippled region)

into membranes, in accordance with the same procedures outlined earlier (cf. 'Membrane preparation' in 'Experimental' section), the pH ranges were similar and the slopes straddled the theoretical Nernstian behaviour. As the relative concentrations of the MeOH:PVC and the MeOH:PIP decrease, the wt% N increases (*Figure 10*) and the colour changes from light yellow to reddish brown (*Table 2*). Consequently, using a concentrated PIP solution is not desirable; to the contrary, one would like to increase the extent of amination without inducing unnecessary chromophores. Thereby, the solubility of the final product would be retained at a higher extent of amination, and the mobility of the final product would not be hampered by an excessive amount of double bonds. In the proposed model of ion conduction[19], the configurational entropy of PVC must be maintained as much as possible so that chain conformation can be maximized. These conformational considerations were, in part, the rationale behind why the small, compact and highly basic molecule of PIP was chosen in the first place.

## CONCLUSIONS

Aminated PVCs can be prepared using the strong base, piperazine. These can be used as electroactive materials in pH sensors, having Nernstian behaviour over a pH range from 4 to 12.

Nernstian behaviour can be attained with membranes cast from aminated PVCs over a range of reaction times and temperatures.

Based upon these batches, a linear relationship exists between the extent of amination of PVC and the slope of the potentiometric response curves of aminated PVC membranes.

A 'window' of useful products may be defined, above which insolubility occurs and below which insufficient numbers of fixed-site proton carriers exist.

The substitution of piperazine onto PVC may be predicted and follows an Arrhenius behaviour having an activation energy that ranged from 17 to 18 kcal $mol^{-1}$.

Time–temperature superposition of the amination is possible and may be used as the basis to predict reaction parameters, the extent of amination and the slopes of potentiometric response curves.

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## REFERENCES

1 Reboul, J.-P. *J. Appl. Phys.* 1975, **46**, 2961
2 Tuczai, E. and Cortolano, F. *Mod. Plast.* 1992, **69** 123
3 Horvai, G., Graf, E., Toth, K., Pungor, E. and Buck, R. P. *Anal. Chem.* 1986, **58**, 2735
4 van den Berg, A., van der Wal, P. D., Ptasinska, M.-S., Sudholter, E. J. R., Reinhoudt, D. N. and Bergveld, P. *Anal. Chem.* 1987, **59**, 2827
5 Erne, D., Ammann, D. and Simon, W. *Chimia* 1979, **33**, 88
6 Ammann, D., Lanter, F., Steiner, R. A., Schulthess, P., Shijo, Y. and Simon, W. *Anal. Chem.* 1981, **53**, 2267
7 Gurgiolo, A. E., Winquist, M. E., Knobel, T. M. and Teeters, D. C. US Pat. 4774294, September 1988
8 Ma, S.-C., Chaniotakis, N. A. and Meyerhoff, M. E. *Anal. Chem.* 1988, **60**, 2293
9 Ma, S.-C. and Meyerhoff, M. E. *Mikrochim. Acta* (*Wien*) 1990, **I**, 197
10 Cosofret, V. V., Lindner, E., Buck, R. P., Kusy, R. P. and Whitley, J. Q. *J. Electroanal. Chem.* 1993, **345** 169
11 Lindner, E., Cosofret, V. V., Kusy, R. P., Buck, R. P., Rosatzin, Th., Schaller, U., Simon, W., Jeney, J., Toth, K. and Pungor, E. *Talanta* 1993, **40**, 957
12 Sebrell, L. B. US Pat. 1616994, February 1927
13 Moody, G. J., Oke, R. B. and Thomas, J. D. R. *Analyst* 1970, **95**, 910
14 Simon, M. A. and Kusy, R. P. *Polymer* 1993, **34**, 5106
15 Cosofret, V. V., Nahir, T. M., Lindner, E. and Buck, R. P. *J. Electroanal. Chem.* 1992, **327**, 137
16 Cosofret, V. V., Lindner, E., Buck, R. P., Kusy, R. P. and Whitley, J. Q. *Electroanalysis* 1993, **5**, 725
17 Lindner, E., Cosofret, V. V., Ufer, S., Kusy, R. P., Buck, R. P., Ash, R. B. and Nagle, H. T. *J. Chem. Soc., Faraday Trans.* 1993, **89**, 361
18 Marvel, C. S., Sample, J. H. and Roy, M. F. *J. Am. Chem. Soc.* 1939, **61**, 3241
19 Kusy, R. P., Whitley, J. Q., Buck, R. P., Cosofret, V. V. and Lindner, E. *J. Mater. Sci. Lett.* in press
20 Weast, R. C. (Ed.) 'CRC Handbook of Chemistry and Physics', CRC Press, Boca Raton, FL, 1984, pp. F182–90
21 Williams, M. L., Landel, R. F. and Ferry, J. D. *J. Am. Chem. Soc.* 1955, **77**, 3701
22 Doolittle, A. K. *J. Appl. Phys.* 1951, **22**, 1471
23 Aklonis, J. J., MacKnight, W. J. and Shen, M. 'Introduction to Polymer Viscoelasticity', Wiley-Interscience, New York, 1972, p. 55
24 Lindner, E., Graf, E., Niegreisz, Zs., Toth, K., Pungor, E. and Buck, R. P. *Anal. Chem.* 1988, **60**, 295
25 Sakai, Y., Sadaoka, Y. and Matsuguchi, M. *J. Electrochem. Soc.* 1989, **136**, 171