

## Thermal investigation of PVC copolymers for fixed-site proton carrier membranes <sup>☆</sup>

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### Abstract

Poly(vinyl chloride)s were post-polymerization copolymerized using the strong organic base, piperazine. These aminated products were immobilized and cast as fixed-site proton carrier membranes, and the pH responses were evaluated in appropriate potentiometric cells. Unfortunately, all batches were not of uniform quality and required the measurement of subtle differences in chemistry, which many conventional methods could not distinguish. By making thermal measurements via differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), both the glass transition temperatures ( $T_g$ ) and the thermal stabilities of different batches were characterized, although not always differentiated. By using the thermally stimulated current (TSC) technique, however, the global relaxation processes of eight batches of poly(vinyl chloride) copolymers could be differentiated, after each powder was polarized, quenched, and reheated. The results of the depolarization current peaks showed that the number of dipoles and/or their associated mobilities differed in otherwise comparable batches and that the best products corresponded to those that displayed pH Nernstian behavior.

*Keywords:* Copolymer; DSC; EMF; pH; PVC; TGA; TSC

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## 1. Introduction

Aminated poly(vinyl chloride)s (PVC-NH<sub>2</sub>) represent a new approach to conventional mobile site pH electrodes [1–5]. Ma and Meyerhoff [4] were the first to attach mono- and diamines as substituent groups to PVC using post-polymerization copolymerization. Later, Kusy's and Buck's groups [3] synthesized and analyzed eight homologues of diaminoalkanes and several cyclic diamines: *trans*-1,4-diaminocyclohexane, 1,8-diamino-*p*-menthane, 1,4-bis(3-aminopropyl) piperazine, and piperazine. Among those formulations, the piperazine-derivatized PVC copolymers were most promising as proton carrier membrane materials, showing a near-Nernstian response over a pH range from 4 to 12 whether no additional ionophore, or mobile site ionophores, such as ETH 5294 or TDDA were present [3]. Thereby the immobilized amine sites replaced or enhanced mobile proton carriers, reduced electrical resistivities, improved adhesive properties on substrates, permitted the attachment of bioreagents, and eliminated ionophore leaching [4].

One major problem that is associated with the amination reaction is the inability quickly to assess not only whether a new formulation exceeds previous expectations but also whether a new formulation has been successfully reproduced. Previously, elemental nitrogen analyses were used to determine the immobilized amine content [3,5]. Apparently a "window" exists in the vicinity of 0.7–0.8 wt/wt% nitrogen within which Nernstian behavior was observed. Soon, however, this assay was recognized to be a necessary but not sufficient condition for success. For example, the amine assay took no account of inter- or intra-molecular crosslinking that would inefficiently tie up nitrogen and reduce the polymeric chain mobility, which is so essential. Consequently, other conventional methods were investigated, with little success; namely chlorine elemental analysis, X-ray photoelectron spectroscopy, nuclear magnetic spectroscopy (solid state and liquid state (<sup>1</sup>H, <sup>13</sup>C, and <sup>14</sup>N)), and infrared spectroscopy.

The present paper reports recent efforts to supplement conventional methods of nitrogen analyses and EMF measurements with differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and thermally stimulated current (TSC) spectroscopy to measure the glass transition temperatures (*T<sub>g</sub>*), the thermal stability, and the inherent conductivity of different PVC-NH<sub>2</sub> batches, respectively. The last method (TSC) has been used to study the influence of molecular orientation in polymers and the subsequent distribution of local order [6]. Thereby, a functional versus a non-functional aminated material can be discriminated without rigorously preparing membrane electrodes for subsequent electrochemical measurements.

## 2. Experimental

### 2.1. Syntheses

Sixteen batches of PVC-NH<sub>2</sub> were copolymerized using a post-polymerization reaction and evaluated alongside neat PVC powder (Polysciences, MW = 110 000). Except for the neat polymer, i.e., batch 0, each batch was formulated by first

Table 1  
 Synthesis conditions of PVC-NH<sub>2</sub> and the electrochemical and thermal analyses performed

Batch #	Temperature in °C	Time in days	EMF	DSC	TGA	TSC
42 <sup>a</sup>	64	1.0		+		
43 <sup>a</sup>	64	0.60		+	+	+
44 <sup>a</sup>	64	0.33		+		
45 <sup>a</sup>	64	0.17	+	+		
48 <sup>a</sup>	45	1.0	+	+		
73 <sup>a</sup>	35	10	+			+
102A <sup>b</sup>	35	10	+			+
102B <sup>c</sup>	35	10	+			+
103 <sup>a</sup>	35	10	+			+
47 <sup>a</sup>	35	7.0	+	+	+	+
60 <sup>a</sup>	35	7.0	+	+	+	+
61 <sup>a</sup>	35	7.0	+	+	+	
62 <sup>a</sup>	35	7.0	+	+	+	
46 <sup>a</sup>	25	11.0	+	+		
58 <sup>a</sup>	25	14.0	+	+		
59 <sup>a</sup>	25	31.0	+	+	+	
0				+	+	

<sup>a</sup> Reaction quenched with methanol, deionized water, and 0.1 M NaOH in deionized water. <sup>b</sup> Reaction quenched with methanol, 2000 ppm hydrofluosilicic acid in HPLC water, and 0.1 M NaOH in HPLC water. <sup>c</sup> Reaction quenched with methanol, HPLC water, and 0.1 M NaOH in HPLC water.

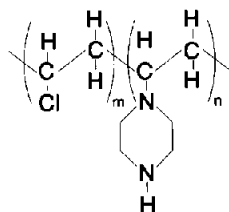


Fig. 1. Chemical formula of PVC-NH<sub>2</sub> copolymers formed by the post-polymerization reactions of piperazine with PVC.

placing PVC powder (approx. 100  $\mu\text{m}$  in diameter) in the reaction flask and by dissolving preweighed amounts of piperazine (PIP) in methanol (MeOH) under a blanket of argon. In all cases the ratio of reagents, MeOH : PIP : PVC, was 14 : 7 : 1 (all wt/wt%). The reaction temperature was established (Table 1, column 2), and the start of the reaction was noted. After the designated time (Table 1, column 3), the heat was turned off, and excess MeOH was added to quench any unreacted PIP. After repeated washings with MeOH, deionized water, and an NaOH solution (except for formulations 102A and 102B, see Table 1), the now PVC-NH<sub>2</sub> was dried under vacuum overnight. The final product was a copolymer in which  $m \geq 100$  and  $n \approx 1$  (Fig. 1).

## 2.2. Nitrogen analyses

All recovered powders were submitted to an independent laboratory (Galbraith, Knoxville, TN) for nitrogen analysis by either Kjeldahl or combustion techniques. These methods had precisions of  $\pm 0.05$  wt/wt% and  $\pm 0.16$  wt/wt%, respectively.

## 2.3. EMF measurements

Some batches were also fabricated into membrane electrodes (Table 1, column 4). First, membranes were cast from a 200:2:100 mixture of plasticizer (*o*-nitrophenyl-octyl ether, *o*-NPOE, Fluka), negative sites (potassium tetrakis *p*-chlorophenyl borate, KTpCIPB, Fluka), and PVC-NH<sub>2</sub> copolymer that had been dissolved in tetrahydrofuran (THF). Then, disks (0.7 cm in diameter and 200  $\mu$ m thick) were cut from these membranes, incorporated into an electrode body (Philips IS-560 containing an internal electrolyte solution of pH 7.0 TRIS buffer), and conditioned for at least 24 h in a citrate-borate buffer (pH 7.0). Using an Orion pH/mV Meter (Model 720A), the electromotive force (EMF) of each potentiometric cell (membrane electrode, Ag/AgCl external double junction reference electrode (Orion Model 90-02)) was measured at room temperature (RT =  $22.5 \pm 0.5^\circ\text{C}$ ). From the responses in a series of buffers (pH 2.0–12.0), the pH range and the slope of the EMF versus pH plot were determined and compared with a standard glass electrode (Orion model 91-57).

## 2.4. DSC measurements

Using a Du Pont DSC Model 990 thermal analyzer, about  $10.0 \pm 0.5$  mg of the neat PVC and the PVC-NH<sub>2</sub> powders (Table 1, column 5) were serially placed in standard aluminum pans under a blanket of nitrogen gas and initially heated from 20 to  $140^\circ\text{C}$  at a rate of  $10^\circ\text{C min}^{-1}$ . After quenching with liquid nitrogen to  $-20^\circ\text{C}$ , second and third runs were heated to  $140^\circ\text{C}$  under the aforementioned conditions. At the end of the third run after quenching to RT, the color of each powder was immediately examined and compared with the initial colors, which had been ranked by three observers. The  $T_g$  values were recorded by the extrapolated onset and the mid-point value methods in which the intersections of the tangents to the baselines, which were parallel to one another, and the tangent to the downslope curve defined the extrapolated onset and the mid-point value of each run (Fig. 2).

## 2.5. TGA measurements

Using a Du Pont TGA Model 950, 10.0–11.6 mg of select powders (Table 1, column 6) were placed in a quartz pan and heated in air from 20 to  $700^\circ\text{C}$  at a rate of  $10^\circ\text{C min}^{-1}$ . In the low temperature region, the weight losses were measured as a function of an expanded temperature scale (Fig. 3, the AB and A'B' lines) up to about  $180^\circ\text{C}$ . Thereafter, the sensitivity was reduced five-fold and the decomposition curve detailed up to  $700^\circ\text{C}$  (Fig. 3, the BC and B'C' lines). By drawing tangents

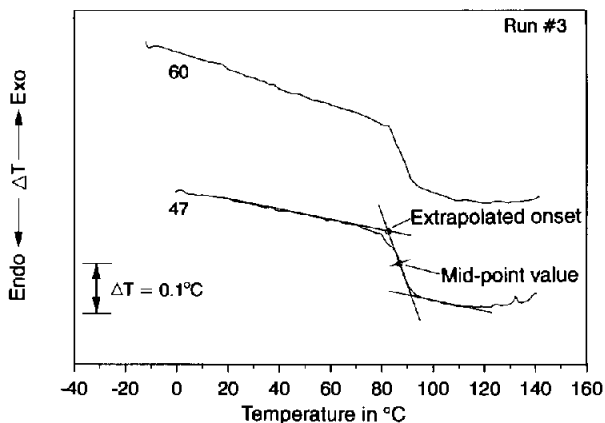


Fig. 2. DSC plots for PVC-NH<sub>2</sub> batch 47 and its complimentary lot, batch 60 (see Table 1). Also shown are the definitions of the  $T_g$  measurements via the extrapolated onset and mid-point value constructions (see Table 3).

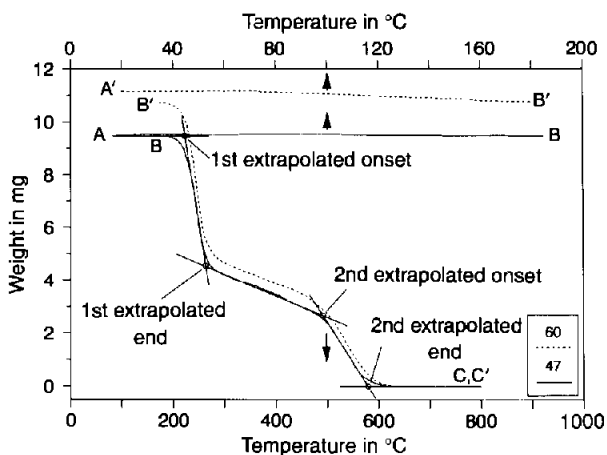


Fig. 3. TGA plots for PVC-NH<sub>2</sub> batch 47 and its complimentary lot, batch 60 (see Table 1). Also shown are the definitions of the extrapolated onsets and extrapolated ends for the first and second downslopes of the decomposition curves (see Table 4).

to the two major downslope regions and their attendant plateau regions, the “1st extrapolated onset”, the “1st extrapolated end”, the “2nd extrapolated onset”, and the “2nd extrapolated end” could be identified (Fig. 3). The “temperature at which half mass loss occurred” was noted in addition to relative changes between each specimen and a working electrode standard (batch 47). These represented the summation of the absolute temperature differences of the five highlighted values ( $\Delta T_1$ ) and the net sum of the temperature differences between each batch and the chosen standard ( $\Delta T_2$ ).

### 2.6. TSC measurements

A few milligrams of seven powders (Table 1, column 7) were placed between the two electrodes of a Solomat TSC/RMA Model 91000 spectrometer. Each sample was poled at 100°C for 2 min under a static electric field of 50 V mm<sup>-1</sup> to align any dipoles. Thereafter, each was quenched to -100°C in 1 min, and the field was removed. Samples were heated to 100°C at 7°C min<sup>-1</sup>, and the depolarization current generated by the relaxation of the oriented dipoles was recorded versus temperature. Details of the instrumentation and the methodology can be found in Ref. [7] and the references cited therein.

### 3. Results

The conventional assays of wt/wt% nitrogen and the EMF measurements, the pH range and slope being determined from the latter, are summarized in Table 2 for three basic time-temperature schemes (Table 1, columns 1–3). The nitrogen analyses range from 0 wt/wt% for neat PVC to 1.63 wt/wt% for batch 43 (Table 2, column 2). The linear pH responses of membrane electrodes based on PVC-NH<sub>2</sub> extend up to 8 orders of H<sup>+</sup> concentration. The largest linear range from pH 4 to 12 was obtained for batch #103 (Table 2, column 3). Ideal Nernstian behavior

Table 2  
Nitrogen analyses and EMF measurements of PVC-NH<sub>2</sub>

Batch #	Nitrogen in wt/wt%	pH range	-Slope in mV/pH
42 <sup>a</sup>	0.91	—	—
43 <sup>a</sup>	1.63 <sup>b</sup>	—	—
44 <sup>a</sup>	1.07 <sup>b</sup>	—	—
45	0.56 <sup>b</sup>	5–12	54.6
48	0.74 <sup>b</sup>	4–10	54.2
73	0.72	5–12	58.9
102A	0.87	5–12	58.6
102B	0.74	5–12	58.5
103	0.80	4–12	58.7
47	0.62 <sup>b</sup>	4–11	58.0
60	0.45 <sup>b</sup>	4–10	48.0
61 <sup>a</sup>	0.83 <sup>b</sup>	—	—
62	0.39 <sup>b</sup>	4–11	26.1
46	0.23 <sup>b</sup>	7–12	0
58	0.30 <sup>b</sup>	2–6	26.1
59	0.56 <sup>b</sup>	4–11	57.8

<sup>a</sup> Electrode membranes were not prepared from this batch because the material was insoluble in THF.  
<sup>b</sup> Kjeldahl titration ( $\pm 0.05$  wt/wt%); all others measured by combustion ( $\pm 0.16$  wt/wt%).

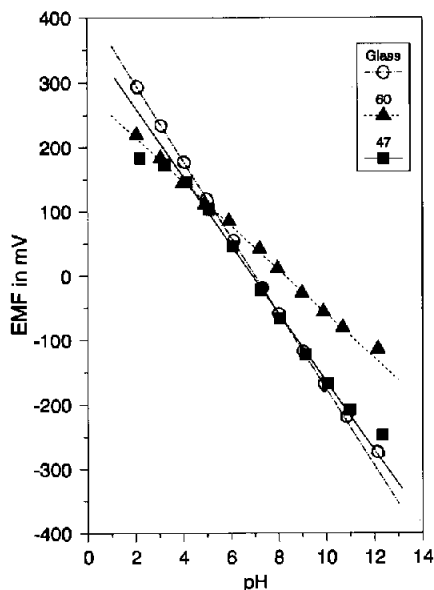


Fig. 4. EMF plots for PVC-NH<sub>2</sub> batch 47 and its complimentary lot, batch 60 (see Table 1). The glass electrode response is provided for comparison. From plots such as these, the pH range and negative slope were obtained (see Table 2).

( $-59.2$  mV/pH) is most closely approached by five batches: 47, 73, 102A, 102B, and 103 (Table 2, column 4). Although batch 60 was formulated identically to batch 47 (Table 1), its pH sensitivity is less ( $-48.0$  versus  $-58.0$  mV/pH; Table 2). Fig. 4 shows how the overall data of these two PVC-NH<sub>2</sub> batches compare along with the corresponding ideal glass electrode data.

The  $T_g$  values were determined for thirteen samples (Table 1, column 5) and ranged from  $80.0$  to  $90.0^\circ\text{C}$  in the case of run #3 (Table 3, onset method). After three DSC runs, the initial colors changed from shades of white, yellow, and orange to colors that also included tans and browns. Such changes signaled an increase in the number of conjugated double bonds [8] from an as yet unspecified reaction.

The TGA scans of seven representative batches (Table 1, column 6) showed that, like the neat PVC, the aminated batches had two downslope regions separated by a gentler sloped, plateau-like region. Following PVC-NH<sub>2</sub> syntheses, the onset and end of this first region occurred at about  $215$  and  $255^\circ\text{C}$ , respectively; similar, the onset and end of the second region occurred at about  $480$  and  $580^\circ\text{C}$ , respectively (see Table 4, columns 3–6). The temperature at which half mass loss occurred was fairly uniform and averaged  $260^\circ\text{C}$  (Table 4, column 7). From the summations of the differences, which were carried out without prejudice towards the intrinsic importance of each of the benchmarks chosen, gross differences could be observed. For example, the neat material was markedly distinct from the PVC-NH<sub>2</sub> batches, and the insoluble batch 43, which was most aminated (Table 2, column 2), was distinct from all other PVC-NH<sub>2</sub> batches (Table 4, columns 8 and 9).

Table 3  
Glass transitions ( $T_g$ ) of PVC–NH<sub>2</sub> in nitrogen via DSC measurements

Batch #	Initial color	Extrapolated onset method in °C			Mid-point value method in °C		
		Run #1	Run #2	Run #3	Run #1	Run #2	Run #3
0	White	78.5	80.0	80.0	85.0	85.0	84.5
46	V.lt. yellow	77.5	79.5	80.5	82.0	84.5	85.0
58	Lt. yellow	77.0	80.0	80.5	82.0	84.5	85.0
59	Yellow	74.5	79.5	81.5	80.0	84.5	86.0
62	Yellow	81.0	82.0	83.0	87.5	86.5	88.0
60	Yellow	77.0	80.0	82.5	83.0	85.0	87.5
47	Yellow	78.0	80.5	82.0	83.0	85.5	87.5
48	Yellow	77.0	81.0	83.0	81.0	86.0	88.0
45	Dk yellow	81.5	84.5	85.0	85.5	89.5	90.5
61	Dk. yellow	80.0	86.5	86.5	84.0	91.0	92.0
42	Dk. yellow	81.5	86.5	86.5	85.0	91.0	93.0
44	Dk. yellow	80.5	85.5	87.0	84.5	91.0	93.5
43	Orange	88.0	90.5	90.0	92.0	101.0	103.0

Table 4  
Thermal stability of PVC–NH<sub>2</sub> in air via TGA measurements

Batch #	Initial mass in mg	1st onset in °C	1st end in °C	2nd onset in °C	2nd end in °C	$T$ at half mass loss in °C	$\Delta T_1$ in °C <sup>a</sup>	$\Delta T_2$ in °C <sup>a</sup>
43	11.32	195	235	470	575	260	75	–75
47	9.97	220	260	490	575	265	0	0
60	11.36	220	265	485	585	260	25	+5
61	11.08	220	250	475	570	255	40	–40
62	11.24	210	250	470	575	250	55	–55
59	10.91	225	270	490	595	265	35	+35
0	11.64	255	295	480	605	290	135	+115

<sup>a</sup> Based on batch 47.

Measures of the depolarization current (Table 1, column 7) show markedly distinct behavior. In Fig. 5, the neat PVC has a depolarization current that coincides with the  $T_g$  obtained on the same product by DSC (80.0°C) (Table 3, column 5) and more recently by DMA (77.1°C) [9]. The other three samples represent PVC–NH<sub>2</sub> batches that were processed at the same time–temperature schedule of 10 days at 35°C. Batches 102A and 102B represent a split formulation that differs only in the details of quenching the reaction and washing the resultant products (Table 1), whereas, batch 103 uses the standard aforementioned quenching and washing reagents and procedures.



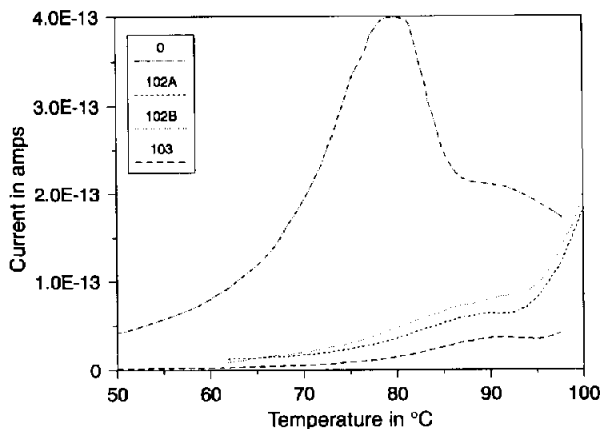


Fig. 5. TSC plots for PVC-NH<sub>2</sub> batches 0, 102A, 102B, and 103 (see Table 1). Note the increase in current as the  $T_g$  of the neat PVC is attained and the relative poor performance of batches 102A, 102B, and 103.

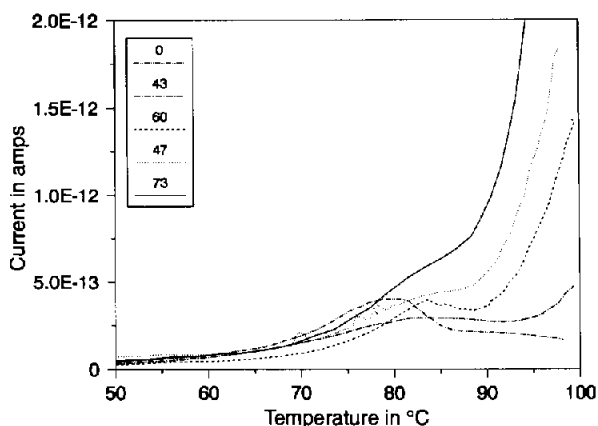


Fig. 6. TSC plots for PVC-NH<sub>2</sub> batches 0, 43, 60, 47, and 73 (see Table 1). Note on this less sensitive scale the relative position of the neat PVC and the increase in current as the electrochemical potentials of the membranes improve (see Table 2) from batch 43 (insoluble), to batch 60 (poor), 47 (good), and 73 (best).

Amidst the backdrop of the neat PVC, Fig. 6 provides further evidence that TSC can unravel the subtleties of the different PVC-NH<sub>2</sub> batches. Among the four batches featured, batch 73 appears the best, followed by 47, 60, and 43. This ranking coincides exactly with the electrochemical measurements [5] that show batch 73 is the best, followed by batch 47. Batch 60 does not show Nernstian behavior, and batch 43 is insoluble in THF (Table 2).

#### 4. Discussion

Experience has shown that about 0.7–0.8 wt/wt% nitrogen content is required to produce a viable PVC–NH<sub>2</sub> copolymer which is ultimately suitable for electrode preparation (Table 2, column 2) [5,10]. Although this is a necessary condition, unfortunately it is not sufficient. Direct copolymerization can involve side reactions such as crosslinking, back-biting, and grafting. These unfavorable chemical reactions can hamper processing, waste aminated sites, reduce molecular segment mobility, and interfere with fixed-site transport. As a consequence, a nitrogen assay tells the polymer chemist only that conditions may be favorable and that further assays would be worthwhile.

The pH range and the slope provide further evidence that a candidate batch may be functionally useful by equilibrating membrane electrodes in different pHs and measuring the EMFs (see Table 2, columns 3 and 4). When these measurements were made, all four batches, which were reacted at 35°C for 10 days (Table 1, columns 2 and 3), approximated the glass electrode over a broad range of pH (Table 2, columns 3 and 4) and appeared similar to batch 47 in Fig. 4. In contrast, when four batches were synthesized at a reaction temperature of 35°C for 7 days (Table 1, columns 2 and 3), the pH range and slope of the EMF–pH response varied considerably (Table 2). Batch 62 lacked sufficient amination and hence had a poor slope; batch 61 was overly aminated to the extent that insolubility occurred. Batch 60 came close to working (Table 2) but fell somewhat short of batch 47 (Fig. 4). Nonetheless, these last two batches provide the basis upon which discriminatory characteristics of assays, such as thermal analyses (Table 1, columns 5–7) would be judged.

When batches 47 and 60 were compared by DSC, the runs appeared quite similar (Fig. 2). Whether the extrapolated onset or the mid-point value method was used for determining  $T_g$ , the results for the three runs were  $\pm 0.5^\circ\text{C}$  of one another (Table 3). Consistent with the other PVC–NH<sub>2</sub> batches, both these batches darkened from their initial yellow hue to a light tan following three runs. No such color change was noted after exposing the neat PVC to the same thermal history, thereby inferring that the conjugation was not a result of ordinary thermal degradation via dehydrohalogenation but rather was associated with a post-amination reaction.

When these two batches were thermally decomposed *in air* by TGA (Fig. 3), gross degradation did not occur until the 1st onset was reached at 220°C. Table 4 shows how similar the scans were at strategic breaks in the thermograms. Using batch 47 as the basis, batch 60 was most comparable to its complementary lot, batch 47, in which  $\Delta T_1 = 25^\circ\text{C}$  and  $\Delta T_2 = +5^\circ\text{C}$ . Considering that this comparison represents the two samples with the greatest mass difference among the PVC–NH<sub>2</sub> batches, the small variations in their  $\Delta T_1$  and  $\Delta T_2$  suggest that only gross differences are reflected by TGA measurements.

Although DSC and TGA were generally useful, only TSC could distinguish PVC–NH<sub>2</sub> powders from the neat PVC powder and one batch from another, including presumably identical lots. Fig. 5 shows that, when there are only subtle

differences in formulation chemistry (as in the quenching conditions of batches 102A and 102B, see Table 1, footnotes), the outcomes can be reproduced. When separate batches are made (as in batches 102 and 103, see Fig. 5 and Table 1), batch 103 follows the same trend as batch 102, although its measured current is always lower for a given temperature. When one copolymer functions as a membrane electrode slightly better than the other (as in batch 73 versus 47, Fig. 6 and Table 1), the onset and rise of the depolarization current occur more quickly. However, when the two seemingly identical batches are formulated and one functions satisfactorily while the other does not (as in batch 47 versus 60, Fig. 6 and Table 1), a further decrease in the depolarization current is noted. The nitrogen analysis would suggest that this is due to a total reduction in aminated sites (Table 2, column 2). At the other extreme, however, is batch 43 (Fig. 6 and Table 1). This PVC-NH<sub>2</sub> has at least twice as many aminated sites as the 0.7–0.8 wt/wt% benchmark cited earlier. Because this copolymer is insoluble in THF, this batch cannot be processed and tested by conventional electrochemical means. Nonetheless, the TSC spectrum indicates that the likelihood of batch 43 (more than any other batch shown in Fig. 6) being used in a membrane electrode is moot, because its depolarization current is relatively broad and shallow. Apparently unfavorable chemical reactions have impeded charge transport in this highly aminated batch, as the  $T_g$  soars to the highest value observed (Table 3).

The mobility that is measured here via the depolarization current is only that of the fixed site carrier. In order to make PVC-based membrane electrodes, the PVC-NH<sub>2</sub> requires (among other ingredients) a plasticizer to facilitate chain motion. In the present EMF measurements, *o*-NPOE was used to accomplish that objective by lowering the  $T_g$  of batch 47 from +82.0°C in the unplasticized state (DSC measurements via run #3 and the extrapolated onset method, Table 3) to -56.0°C in the plasticized state (dynamic mechanical measurements at 1.1 Hz, Ref. [9])<sup>1</sup>. Based on the recent observation that the  $T_g$  must only be reduced below RT to provide satisfactory mobility and attain slopes from EMF measurements that approach ideal Nernstian behavior [9], the tacit assumption is made that any mobility in this rather restricted state can only be enhanced by later plasticization to temperatures below RT. Therefore the conformational restrictions, which are imposed on the unplasticized PVC-NH<sub>2</sub> powders based on the present TSC measurements, are markedly diminished in those materials that can be readily poled. In other words, PVC-NH<sub>2</sub> batches that can be screened in the powdered state not only are in a more convenient form but also are evaluated under more discriminating conditions.

<sup>1</sup>A referee has pointed out that  $T_g$  values determined by DSC and dynamic mechanical measurements do not exactly correlate under all conditions. Mixing methods to characterize a reduction in the  $T_g$  by nearly 140°C from plasticization is legitimate, however, because the difference between the methods of measurement is likely to be only a few degrees.

## 5. Conclusions

From DSC and TGA measurements some general characteristics of PVC-NH<sub>2</sub> powders can be obtained. However, it is by TSC measurements that the depolarization currents show that the number of dipoles and their molecular mobilities do differ in otherwise comparable batches, and that the best products are those that display pH Nernstian behavior. These outcomes suggest that the PVC-NH<sub>2</sub> powders can be screened in the solid state, before the plasticizer and other ingredients are added and without preparing membrane electrodes for subsequent electrochemical measurements. When combined with the more conventional nitrogen analyses and EMF measurements, the PVC-NH<sub>2</sub> powders are best discriminated with respect to their potential as membrane electrodes by such thermoelectric methodologies as TSC.

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