

# Characterization of Copolymeric Poly(2-vinylimidazoline)

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## SYNOPSIS

Copolymeric poly(2-vinylimidazoline), comprising the ring-closed 2-imidazoline and ring-opened linear amide repeat units, was characterized by <sup>13</sup>C-NMR spectroscopy. This was facilitated by the <sup>13</sup>C-NMR analyses of the model compound forms of the copolymer's repeat units, 2-ethylimidazoline and *N*-propionylethylenediamine. Quantitative determinations were made for the percentages of ring-opened, linear amide, repeat units and residual ethylenediamine present in different batches of the poly(2-vinylimidazoline) copolymer. © 1995 John Wiley & Sons, Inc.

## BACKGROUND

Thin-film composite polyamide membranes have been developed for desalination by the pressure-driven membrane process of reverse osmosis (RO).<sup>1</sup> Such membranes can be prepared, *in situ*, by an interfacial polycondensation reaction between an aqueous precursor solution of a multifunctional amine and an organic-soluble aromatic acid chloride cross-linking agent, upon a porous support, at the interface of the two immiscible solvents.<sup>2</sup> The search for water-soluble amine-containing polymeric precursors from which novel polyamide RO membranes could be created led to the study of poly(2-vinylimidazoline).<sup>3</sup>

The synthesis of poly(2-vinylimidazoline) during an amine-condensation reaction between polyacrylonitrile (PAN) and ethylenediamine (EDA), and isolation of the crude product, is described in the literature.<sup>4</sup> The product PVI I was a copolymer of ring-closed poly(2-vinylimidazoline) (PVI) and its hydrolyzed form of ring-opened, poly(*N*-aminoethylacrylamide) (PVAM-Hy). The model compounds of the copolymer's repeat units, 2-ethylimidazoline (MC) and *N*-propionylethylenediamine (HMC), were synthesized and then characterized by NMR spectroscopy. Based on the <sup>13</sup>C-NMR data of these monomers, the PVI I copolymer was char-

acterized by <sup>13</sup>C-NMR spectroscopy, as will be discussed in this article. Quantitative determinations were made for the amounts of hydrolyzed repeat units of PVAM-Hy and residual EDA monomer present in successive batches of the PVI I copolymer. These quantitative analyses were important in assessing whether each newly synthesized batch of PVI I was suitable for use in making membranes that would exhibit adequate RO performances (salt-retention and permeate flux). PVI I, which contained too much EDA and too high a ratio of hydrolyzed groups, appeared to be unsuitable; membranes of below-standard performance were made from such a precursor. 3-Chlorosulfonylbenzoyl chloride (X) was used throughout as the cross-linking reagent for the PVI I precursor in the making of PVI I/X membranes.

The following aspects of these membranes have been discussed in previous articles: the method of membrane fabrication, including the use of various cross-linking agents, and some early test results<sup>5</sup>; and the RO performances of the membranes, tested under various stringent test conditions<sup>6</sup> and the chemical composition of the membrane, based on model compound studies.<sup>7</sup>

## EXPERIMENTAL

### Preparation of PVI I

The preparation of PVI I by the amine condensation reaction between PAN and excess EDA, and isola-

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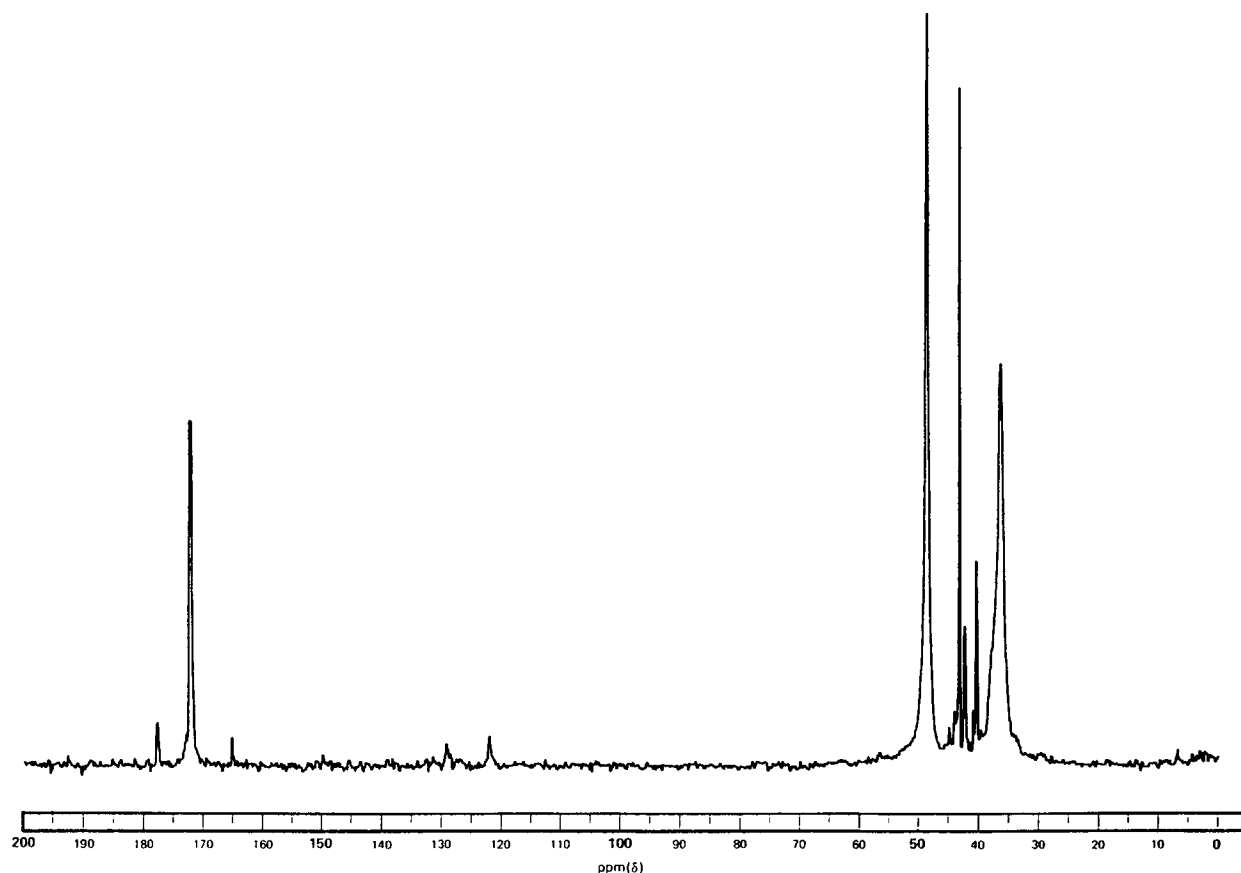
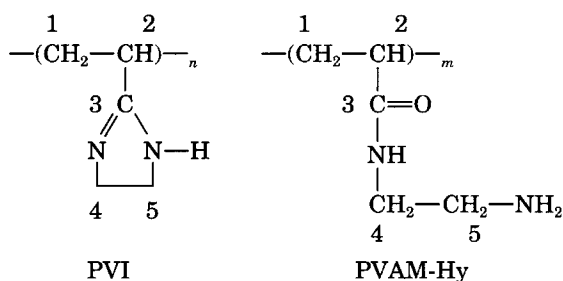


Figure 1  $^{13}\text{C}$ -NMR spectrum of PVI I (batch 8). Assignment of data is given in Table I.

Table I  $^{13}\text{C}$ -NMR Data of PVI I (8)



$\delta$ ( $\text{D}_2\text{O}$ ) PVI	Carbon Atom	$\delta$ ( $\text{D}_2\text{O}$ ) PVAM-Hy
36.48–38.56	1	36.48–38.56
36.48–38.56	2	36.48–38.56
172.1; 172.3	3	177.60
48.82	4	42.59
48.82	5	40.58

25% w/v in  $\text{D}_2\text{O}$  at  $34^\circ\text{C}$ ; dioxane at  $\delta$  67.3 was used as external standard.

tion by freeze-drying, has been described in an earlier paper.<sup>5</sup> A typical  $^{13}\text{C}$ -NMR spectrum of PVI I is shown in Figure 1 and the data are given in Table I.

#### Preparation of Poly(*N*-aminoethylacrylamide) (PVAM-Hy)

An aqueous 10% solution of PVI I (pH 10.9) was boiled gently overnight under reflux cooling. The hydrolysis product was isolated by removing most of the water by evaporation on a rotary evaporator at  $50^\circ\text{C}$  and then allowing it to dry completely on a freeze-dryer. This entailed drying of several small quantities (about  $40 \text{ cm}^3$ ) of the viscous, concentrated polymer solution over periods of a few days. The product was isolated in a quantitative yield as a coarse brown powder and was characterized by  $^{13}\text{C}$ -NMR spectroscopy. The  $^{13}\text{C}$ -NMR spectrum of homopolymeric PVAM-Hy is given in Figure 2 and the following data were obtained:  $^{13}\text{C}$ -NMR (20

MHz, D<sub>2</sub>O, 34°C)  $\delta$  178.17–177.48; 44.05–42.88; 41.67; 40.39; and 37.21–35.21 ( $\delta$  values measured relative to external dioxane at  $\delta$  67.3).

### Preparation of Model Compound Materials

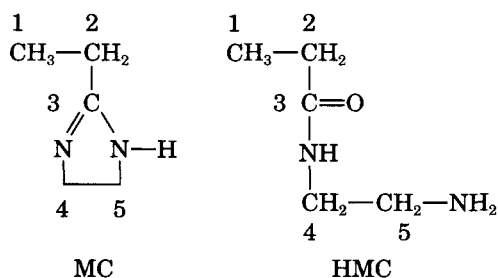
#### 2-Ethylimidazoline (MC)<sup>8</sup>

Ethylenediamine (EDA) (60 g; 1 mol) and propionitrile (55 g; 1 mol) were heated together with sulfur powder (1.5 g) for 4 h at 100°C under reflux conditions. After the reaction mixture had cooled, zinc powder (15 g) was added and the reaction allowed to run for a further 2 h. The crude reaction mix was then sublimed under vacuum at 75°C/2 mmHg to yield the very hygroscopic product of MC (72 g; 73.5% yield). This product was characterized by mass spectrometry and <sup>13</sup>C- and <sup>1</sup>H-NMR spectroscopy: <sup>13</sup>C-NMR (20 MHz, DMSO-*d*<sub>6</sub>, 34°C) assignments are given in Table II and <sup>1</sup>H-NMR (80 MHz, DMSO-*d*<sub>6</sub>, 30°C) assignments are  $\delta$  3.41 (s, 2 × 2H);  $\delta$  2.09 (q, *J* = 7.6 Hz, 2H); and  $\delta$  1.06 (t, *J* = 7.5 Hz, 3H). MS (*m/z*, relative intensity) was 98 (M<sup>+</sup>, 47), 97(56), 69(100), 68(28), 54(47), 42(28), and 41(29). MC required storage, under vacuum, in a dessicator.

#### N-Propionylethylenediamine (HMC)<sup>9</sup>

Ethylpropionate (51 g; 0.5 mol) and EDA (90 g; 1.5 mol) were heated together to 100°C for 42 h under

**Table II** <sup>13</sup>C-NMR Data of the Model Compounds of PVI I: 2-Ethylimidazoline (MC) and N-propionylethylenediamine (HMC)



$\delta$ (DMSO- <i>d</i> <sub>6</sub> )	Carbon Atom	$\delta$ (DMSO- <i>d</i> <sub>6</sub> )
10.98	1	9.95
22.10	2	28.58
168.56	3	173.08
49.33	4	42.31
49.33	5	41.44

TMS at  $\delta$  0.0 was used as the internal standard.

a nitrogen atmosphere. The low-boiling excess of EDA and the byproduct of ethanol were removed under reduced pressure. HMC was then distilled at 130°C/3 mmHg to yield a yellow liquid. The yield was 42 g (72%). Structure was confirmed by <sup>13</sup>C- and <sup>1</sup>H-NMR spectroscopy. <sup>13</sup>C-NMR (20 MHz, DMSO-*d*<sub>6</sub>, 34°C) assignments are given in Table II and <sup>1</sup>H-NMR (80 MHz, DMSO-*d*<sub>6</sub>, 30°C) assignments are  $\delta$  8.0–7.42 (s broad, 1H amide);  $\delta$  2.7–2.34 (m, 2 × 2H);  $\delta$  2.12 (s, 2H amine);  $\delta$  2.07 (q, *J* = 7.5 Hz, 2H); and  $\delta$  0.98 (t, *J* = 7.5 Hz, 3H).

### Determination of the Rate of Hydrolysis of PVI I

The course of the conversion of PVI to PVAM-Hy, in aqueous medium, was followed by <sup>13</sup>C-NMR spectroscopy. A solution (28%) of PVI I (16) (120 mg) was made up in deuterated water (0.430 cm<sup>3</sup>) in a 5 mm NMR tube. This was allowed to hydrolyze at 22°C. At frequent intervals of days, a <sup>13</sup>C-NMR spectrum of the reaction product was recorded. As the hydrolysis reaction proceeded, the peak height of the C=N carbon belonging to the 2-imidazoline group decreased, with a corresponding increase in the peak height of the carbonyl carbon in the ring-opened, linear amide group of the newly formed hydrolysis product. Upon <sup>13</sup>C-NMR analysis of the initial sample, at *t* = 0, the signal of the C=N carbon was recorded at  $\delta$  172.18 and that of the carbonyl carbon was recorded at  $\delta$  177.58. The changes in intensities of peaks were measured, and from these, the relative percentages of the two different groups present in the reaction product could be calculated. The rate constant was then calculated to be  $k = 1.87 \times 10^{-7} \text{ s}^{-1}$ ,  $t_{1/2} = 42.8$  days.

### Analytical

High-resolution <sup>13</sup>C-NMR spectra were recorded at 34°C using a Varian FT 80 spectrometer operating at 20 MHz. <sup>1</sup>H-NMR spectra were recorded at 30°C using a Varian FT 80 spectrometer operating at 80 MHz.

<sup>13</sup>C-NMR spectra of PVI I samples were obtained using solutions of about 25% concentration in deuterium oxide (D<sub>2</sub>O) as solvent, which was added just prior to recording to minimize interaction with PVI I. <sup>13</sup>C- $\delta$  values in D<sub>2</sub>O were determined relative to dioxane at  $\delta$  67.3 as the external standard. All spectra obtained in DMSO-*d*<sub>6</sub> were calibrated using TMS as the internal standard. <sup>13</sup>C spin-lattice relaxation times (*T*<sub>1</sub>) were determined by means of the spin-inversion-recovery technique, using a Varian VXR-300 NMR spectrometer.

## DISCUSSION

Copolymeric PVI I has two model compounds: ring-closed, unhydrolyzed, 2-ethylimidazoline (MC) and ring-opened or hydrolyzed linear, N-propionylethylenediamine (HMC). Their chemical structures and  $^{13}\text{C}$ -NMR data are presented in Table II and will often be referred to in the discussion of the elucidation of the  $^{13}\text{C}$ -NMR spectra of PVI I.

Due to the hydrolytic instability of MC, it was not possible to obtain spectra for the model compounds using the solvent  $\text{D}_2\text{O}$  that had been used to obtain the spectra of PVI I. The  $^{13}\text{C}$ -NMR spectrum of a sample of PVI I (batch 8) is shown in Figure 1. (The assignments subsequently made are given in Table I.) The expected chemical shifts for the carbon atoms in the PVI I structure could be calculated with the aid of empirical parameters<sup>10</sup> from the data of the model compounds given in Table II. Consideration was given first to elucidating the structure of PVI I in the ring-closed form (PVI) whose model compound equivalent is MC.

The methyl carbon ( $\text{C}_1$ ) of MC resonates at  $\delta$  10.98. Calculation of the  $\alpha$ ,  $\beta$ , and  $\gamma$  shift effects showed that the corresponding methylene carbon ( $\text{C}_1$ ) in the polymeric form should resonate at  $\delta$  35.98. The methylene carbon ( $\text{C}_2$ ) in MC resonates at  $\delta$  22.10 and calculation of the  $\alpha$ ,  $\beta$ , and  $\gamma$  shift effects indicated that the corresponding methine carbon ( $\text{C}_2$ ) of the polymer should resonate at  $\delta$  38.10. Both carbon atoms of the PVI backbone structure could therefore be expected to be found in the region of  $\delta$  35–39. The broad signal at  $\delta$  36.48–38.56 in the  $^{13}\text{C}$ -NMR spectrum of PVI I (8) (Fig. 1) was therefore assigned to these two carbon atoms.

The two equivalent methylene carbon atoms ( $\text{C}_4$  and  $\text{C}_5$ ) of MC resonate at  $\delta$  49.33. These carbons are equivalent since MC is able to assume a tautomeric form. The signal at  $\delta$  48.82 in the  $^{13}\text{C}$ -NMR spectrum of PVI I (8) was therefore assigned to the equivalent methylene carbons of the 2-imidazoline ring.

The  $\text{C}=\text{N}$  carbon of the model compound (MC) resonates at  $\delta$  168.56 ( $\text{DMSO}-d_6$ ). The signal at  $\delta$  172 ( $\text{D}_2\text{O}$ ) in the spectrum of the polymer was subsequently assigned to the  $\text{C}=\text{N}$  carbon. The slight shift in value could have been due to a solvent effect.

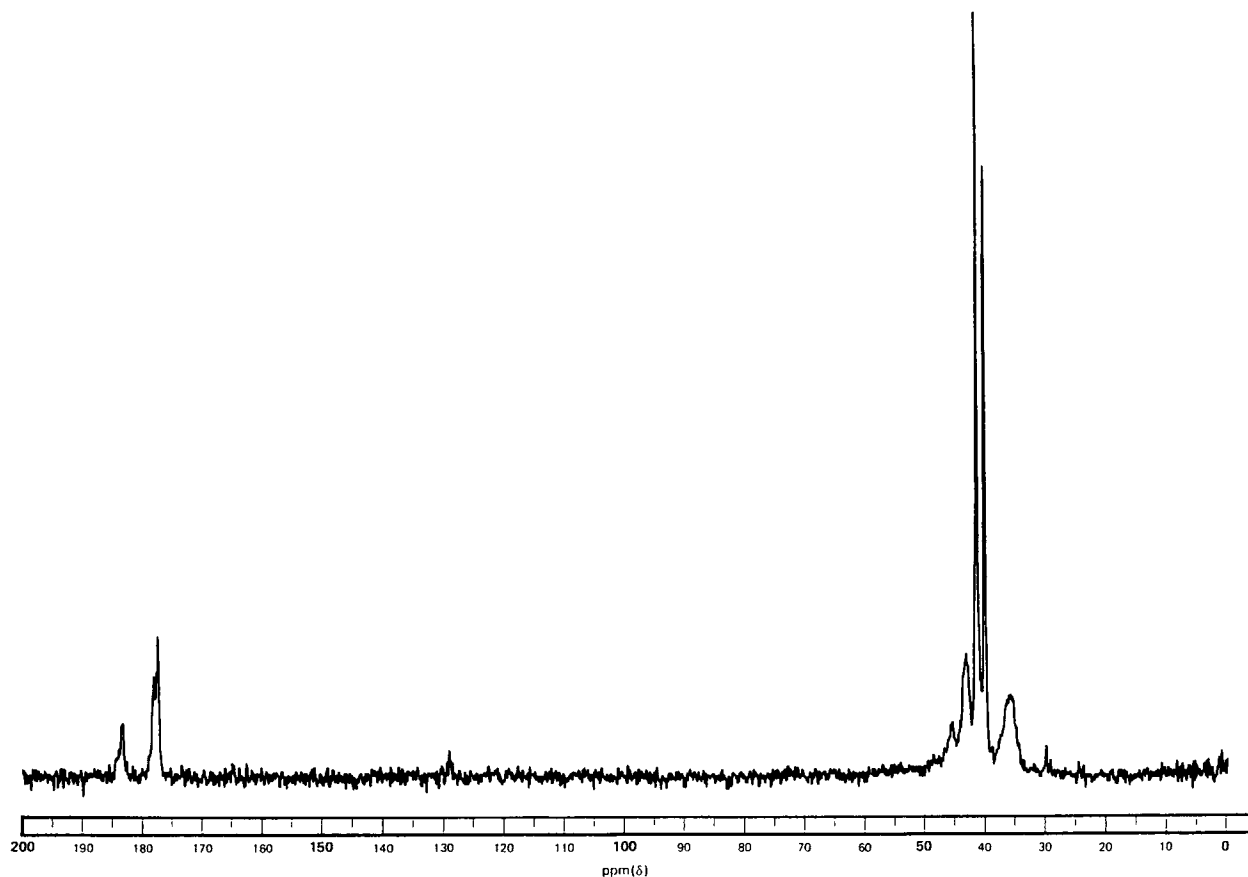
The signal of the  $\text{C}=\text{N}$  group ( $\text{C}_3$ ) of the polymer was observed to be split into two bands (in other PVI I samples, this signal was split into as many as seven bands). This phenomenon could be explained by the presence of the different configurations that could be formed at this site. In the spectrum of the PAN reagent, the nitrile group was also split into

seven bands. The appearance of three bands for the proton broadband noise-decoupled nitrile and methine carbon absorptions for 20% (w/v) solutions of PAN in  $\text{DMSO}-d_6$  has been reported. These were assigned to hetero-, iso-, and syndiotactic triads. Upon further dilution of the sample (to 5% w/v), resolution was improved and up to six pentad lines were observed.<sup>11</sup> As PVI I is prepared from PAN with the reaction taking place at the nitrile carbon site, configurations similar to those described for PAN<sup>12</sup> can be expected to be found in PVI I.

Assignment of the remaining signals (as yet unidentified) in the spectrum under discussion was possible only after consideration was given to the presence of the ring-opened, hydrolyzed repeat unit of PVAM-Hy in PVI I. The model compound of the PVAM-Hy repeat unit is HMC. The amide carbon of HMC ( $\text{C}_3$ ) resonates at  $\delta$  ( $\text{DMSO}-d_6$ ) 173.08 ( $\text{DMSO}-d_6$ ). The position of the signal at  $\delta$  177.60 ( $\text{D}_2\text{O}$ ) in PVI I (8) is characteristic of an amide carbon. Ring-opening of the 2-imidazoline-type structure would render the two methylene carbons ( $\text{C}_4$  and  $\text{C}_5$ ) no longer equivalent, resulting in their having different shift values. This is clear in the  $^{13}\text{C}$ -NMR spectrum of HMC in which shift values  $\delta$  ( $\text{DMSO}-d_6$ ) 42.31 and 41.44 were obtained. Hence, the small signals at  $\delta$  ( $\text{D}_2\text{O}$ ) 42.59 and 40.58 in the PVI I (8)  $^{13}\text{C}$ -NMR spectrum were assigned to the two now nonequivalent methylene carbons of PVAM-Hy. The assignments made for PVAM-Hy here were later verified after the  $^{13}\text{C}$ -NMR spectrum of the fully hydrolyzed PVI I material had been recorded (see Fig. 2).

A very strong sharp signal at  $\delta$  43.41 in the  $^{13}\text{C}$ -NMR spectrum of PVI I (8) remained unaccounted for. From the appearance of the signal, it was suspected to be due to the presence of a monomeric species. EDA was added to a sample solution of PVI I in deuterium oxide, of which a  $^{13}\text{C}$ -NMR spectrum had been recorded, and the  $^{13}\text{C}$ -NMR spectrum of this admixture was recorded.

Addition of the excess of EDA gave a  $^{13}\text{C}$ -NMR spectrum with a very intense signal at  $\delta$  43.84. The  $^{13}\text{C}$  chemical shift for EDA is  $\delta$  44.06 ( $\text{D}_2\text{O}$ ). In the light of the closeness of these shifts to the  $\delta$  43.41 in PVI I (8), it was concluded that EDA was present as a monomeric impurity (freeze-drying was not absolutely effective in removing the solvent from the polymer).  $^{13}\text{C}$ -NMR spectra of all PVI I samples showed a sharp signal at about  $\delta$  44, indicating the presence of EDA. EDA could be partly washed out of PVI I samples, by an acetone extraction, to yield PVI II, which had about half the content of the monomer.<sup>3,5</sup>



**Figure 2**  $^{13}\text{C}$ -NMR spectrum of poly(*N*-aminoethylacrylamide) (PVAM-Hy) (25% w/v in  $\text{D}_2\text{O}$ ,  $34^\circ\text{C}$ ).

The NMR data finally assigned to the PVI I copolymer are presented in Table I.

#### Quantitative Determination of PVAM-Hy in PVI I

Calculations of the percentages of hydrolyzed repeat units (PVAM-Hy) present in successive batches of PVI I were initially based on the technique of comparing the peak heights (height of resonance signal) of the carbons belonging to the respective functional groups of the two different repeat units in the  $^{13}\text{C}$ -NMR spectra. The  $\text{C}=\text{N}$  carbon of ring-closed PVI, resonating at  $\delta$  ( $\text{D}_2\text{O}$ ) 172, was compared with the  $\text{CONH}_2$  (amide) carbon of the ring-opened PVAM-Hy product, resonating  $\delta$  ( $\text{D}_2\text{O}$ ) 177. This approach is acceptable and may be used on condition that the relaxation times, and, thus, the line widths at half-height of the carbons being compared, are similar. This technique had the advantage that the spectrum did not need to be integrated before calculations could be made. It has further been assumed that the nuclear Overhauser effects (NOE)<sup>13</sup> for these two

nonprotonated carbon were similar and relatively small in comparison to the NOEs experienced by the protonated carbons under conditions of broadband proton decoupling.

The spin-inversion-recovery technique<sup>14a</sup> was used to determine the spin-lattice relaxation times. The amide carbon of the PVAM-Hy repeat unit was found to have a relaxation time ( $T_1$ ) of 1.73 ( $1.73 \pm 0.1$ ) s and the  $\text{C}=\text{N}$  group of the PVI I repeat unit had a relaxation time ( $T_1$ ) of 1.63 ( $1.63 \pm 0.39$ ) s. These are relatively long relaxation times for polymers but they are considered similar enough to justify the use of the method of quantitation under discussion, for which it was assumed that relaxation times of the  $\text{CONH}_2$  and  $\text{C}=\text{N}$  carbons were similar.

Peak heights were substituted in eq. (1) to calculate the approximate percentage of hydrolyzed product (% PVAM-Hy) present in batches of PVI I. An alternative approach for calculating the approximate percentages of PVAM-Hy present in PVI I samples was based on integration. The lower region

**Table III Percentages of PVAM-Hy Present in Batches of PVI I (Calculations Based on <sup>13</sup>C-NMR Data of "Non-Fully Relaxed" Spectra)**

PVI I Batch No.	M1	M2
E4	11.0	12.0
E6	9.7	9.2
8	11.4	—
13	11.5	—
15	14.4	—
16	14.6	—
19	11.4	—
24	19.5	—

M1, Method 1: using peak heights of C=N (of PVI) and amide (of PVAM-Hy) signals, measured in millimetres, using the largest intensity for each of the peaks. M2, Method 2: using integration of the C=N signal (of PVI) and amide signal (of PVAM-Hy).

of the spectrum could be integrated to include the —C=N and amide carbons at  $\delta$  172 and 177, respectively. Calculations for only two batches of PVI I (E4 and E6) were done using this method:

% PVAM-Hy

$$= \frac{\text{peak height (or integral) amide signal}}{\text{peak height (or integral) (amide + C=N) signals}} \times 100 \quad (1)$$

The calculated percentages of PVAM-Hy present in batches of PVI I, as determined by the two methods, are given in Table III.

### Hydrolysis of PVI I

PVI I readily hydrolyzes in the presence of moisture. RO performance results of PVI I/X membranes pointed to the fact that an effective PVI I aqueous

**Table V Hydrolysis of a PVI I Solution as a Function of Time**

Age of PVI I Solution (Days)	PVAM-Hy in PVI I (%)
0	14.6
10	43.2
25	52.2
60	71.0
390	100.0

solution did not have a very long shelf life.<sup>15</sup> Table IV contains data that illustrate this. There was a marked deterioration in performance of membranes fabricated from aged aqueous solutions of PVI I.

A controlled <sup>13</sup>C-NMR experiment was then carried out to determine how readily this hydrolysis reaction takes place in aqueous medium. Results, presented in Table V, indicated that there was an initial fast hydrolysis reaction, which later slowed down considerably.

### Quantitative Determination of Residual Ethylenediamine (EDA)

Once all the signals in the <sup>13</sup>C-NMR spectrum of a sample of PVI I had been identified, the results obtained from integration of the spectrum were used to determine the percentage of EDA present in the sample. The integrated spectrum of PVI I (8) ( $\delta$  20–70) is shown in Figure 3, with identification of the various signals.

Considering the number of carbon atoms in PVI I (8) and with reference to the information contained in the integrated spectrum shown in Figure 3, the following was proposed:

$$\text{Areas under the signals: } A + B + A_1 + B_1 = C + C_1 + C_2.$$

Then (after measuring the integrals): 50  $\approx$  55 mm.

**Table IV Effect of Age of Aqueous Solutions of PVI I on RO Performances of PVI I/X Membranes<sup>15</sup>**

PVI I Solution Age (Days)	PVI I Solution pH	Membrane Performance		
		Salt Retention (%)	Permeate Flux (Lmd)	A <sup>2</sup> /B <sup>a</sup> ( $\times 10^{-5}$ )
0	12.0	98.4 $\pm$ 0.2	370 $\pm$ 52	8.9
1	11.8	98.4 $\pm$ 0.3	270 $\pm$ 51	8.0
12	11.3	98.5 $\pm$ 0.1	230 $\pm$ 5	5.4
26	11.2	90.2 $\pm$ 1.0	1540 $\pm$ 114	7.3

<sup>a</sup> This is a figure of merit, introduced by Lonsdale,<sup>16</sup> to compare performances of different membranes.

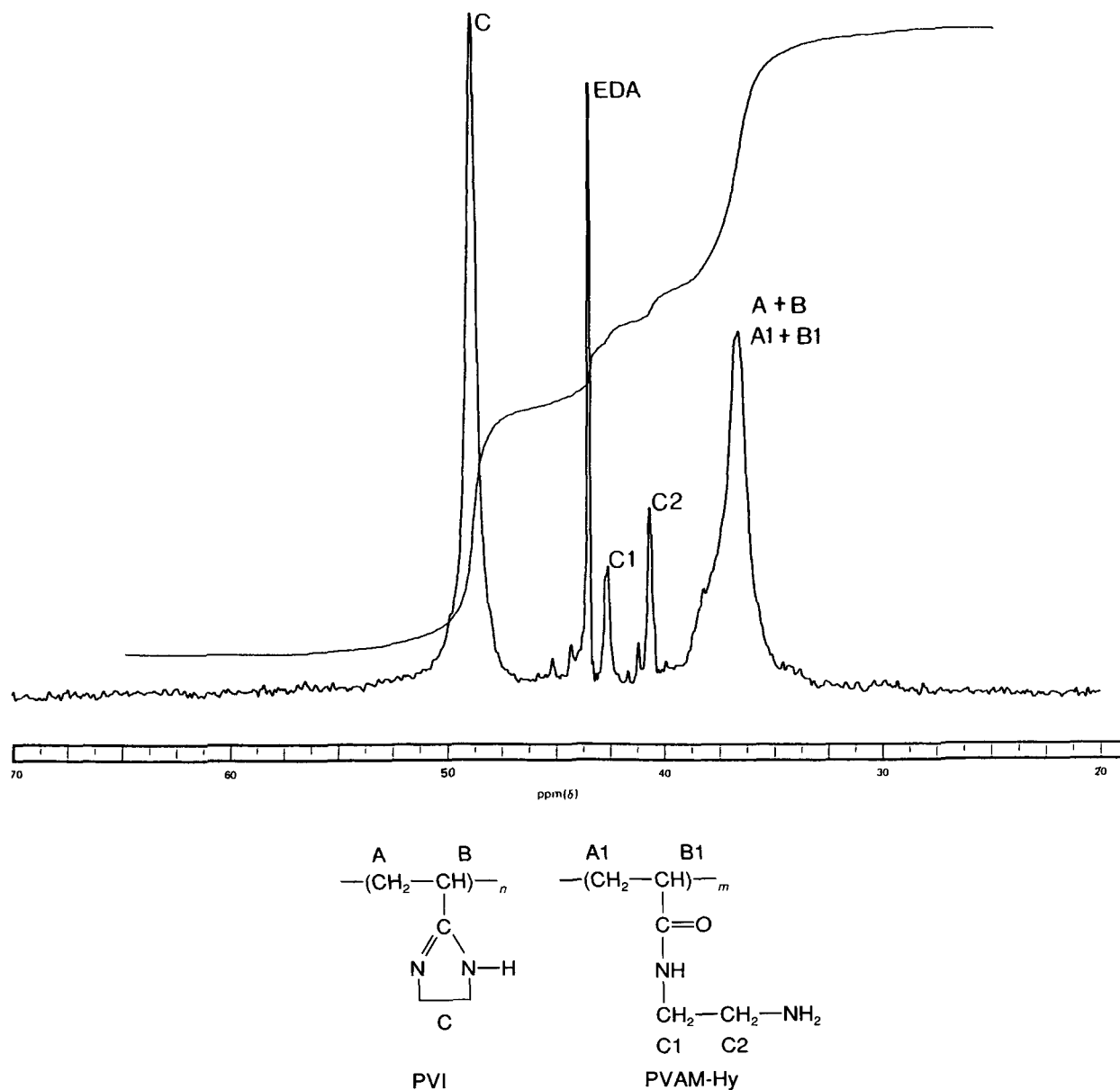


Figure 3 Integrated  $^{13}\text{C}$ -NMR spectrum of PVI I (8) ( $\delta$  20–70 ppm).

Hence, an integral of 105 mm represents  $4 \times \text{C}$  atoms: ( $\text{A} + \text{B} + \text{C}$  or  $\text{A}_1 + \text{B}_1 + \text{C}_1 + \text{C}_2$ ).

Hence, an integral of 26.25 mm represents  $1 \times \text{C}$  atom in the integrated PVI I (8) spectrum.

In the same spectrum, the integral of the signal assigned to the two equivalent carbon atoms of EDA ( $\delta$  44) was 8.5 mm. The integral for one carbon atom of EDA was therefore 4.25 mm.

Hence, the percentage of EDA (% EDA) present in PVI I (8) was calculated as follows:

$$\begin{aligned} \% \text{ EDA} &= \frac{\text{EDA}_i}{\text{EDA}_i + \text{PVI I}_i} \times 100 \\ &= \frac{4.25}{4.25 + 26.25} \times 100 \\ &= 13.9 \end{aligned}$$

where  $\text{EDA}_i$  is the integration count for one carbon atom of ethylenediamine in the PVI I sample, and  $\text{PVI I}_i$ , the integration count for one carbon atom of PVI I in the sample.

Quantitative measurements from  $^{13}\text{C}$ -NMR spectra depend on the range of relaxation times<sup>14b</sup> and the range of NOEs experienced by the different carbons. For the quantitative determination of EDA by the method described above, the assumption was made that the relaxation time of the  $\text{CH}_2$  carbons of EDA was similar to the relaxation times of the protonated carbons of the polymer. To verify this assumption, a separate NMR experiment was run, using PVI I (16), during which all the carbon atoms were allowed to relax completely between pulses.

A relaxation time ( $T_1$ ) of  $2.7 \pm 0.12$  s, which had been determined for the carbon atoms of EDA in PVI I (16), was used to set up the experiment for obtaining the fully relaxed spectrum of PVI I (16). A waiting period of  $5 \times T_1$  between pulses was selected. After integration of the fully relaxed spectrum, the new intensities were used to calculate the percentage of EDA present. This was found to be 17.2% EDA. From the integrated spectrum of a sample of PVI I (16) recorded under normal experimental conditions ( $26^\circ$  pulses, 0.41 s pulse repetition time, i.e., non-fully relaxed spectrum), 11.4% EDA had been calculated to be present. These results indicated that the calculated percentage of EDA from the integrated non-fully relaxed spectra was about 34% too low.

The only assumption then made that was not verified was that the NOE for the protonated carbons was the same for all the protonated carbons. A relaxation agent could have been used to make the relaxation times of all the carbons equal and short in order to quench any possible differences in the NOE. In practice, this was not advisable due to such reagents causing substantial line broadening that would confuse the integration.

**Table VI Percentages of Ethylenediamine (EDA) Present in Batches of PVI I (Calculations Based on  $^{13}\text{C}$ -NMR Data of Non-Fully Relaxed Spectra)**

PVI I Batch No.	EDA (%) <sup>a</sup>
8	13.9
16	11.4
18	21.1
19	22.2
24	9.8
25	14.5
E4	14.0
E6	15.5

<sup>a</sup> These values are estimated to be too low by about 34%. This is evident from values calculated from fully relaxed spectra.

When integrated,  $^{13}\text{C}$ -NMR spectra (non-fully relaxed spectra) of further PVI I samples had been obtained, the percentages of EDA present in these samples were also calculated. These results are shown in Table VI.

Determination of the percentages of EDA present in PVI I batches 18 and 19, from which membranes of below expected standard had been made, showed that both batches contained more than 20% of the monomer. Membranes of satisfactory performance had been made from PVI I batches 8 and 25, containing 13.9 and 14.5% EDA, respectively.<sup>15</sup> On the basis of the data gathered and observations made to date, it is suggested that the concentration of EDA in PVI I to be used as precursor in adequate membrane fabrication should preferably not exceed 15% (percentage EDA determined from integration of non-fully relaxed spectra).

PVI I (24), containing approximately 9.8% EDA, was washed with acetone to remove excess EDA present. Calculations based on the  $^{13}\text{C}$ -NMR analysis of the washed product, PVI II, indicated that approximately 4.8% EDA remained. The RO performances of PVI II tubular membranes were very good, having higher fluxes than those made from PVI I, and have been described in an earlier article.<sup>17</sup>

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## REFERENCES

1. J. E. Cadotte and R. J. Petersen, *Thin-film Composite Reverse Osmosis Membranes: Origin, Development and Recent Advances*, ACS Symposium Series, American Chemical Society, Washington, DC, 1981, Vol. 153, pp. 305-326.
2. J. E. Cadotte, R. S. King, R. S. Majerle, and R. J. Petersen, in E. E. Carraher, Jr. and J. Preston, Eds., *Interfacial Synthesis: Recent Advances*, Marcel Dekker, New York, 1982, Vol. 3.
3. M. J. Hurndall, PhD Thesis, University of Stellenbosch, Stellenbosch, South Africa, 1991.
4. M. J. Hurwitz and H. Aschkenasy, Belg. Pat. 637,380 (March 1964); *Chem. Abstr.*, **62**, 7892b (1965).
5. M. J. Hurndall, E. P. Jacobs, and R. D. Sanderson, *J. Appl. Polym. Sci.*, **46**, 523-529 (1992).
6. M. J. Hurndall, E. P. Jacobs, and R. D. Sanderson, *Desalination*, **86**, 135-154 (1992).
7. M. J. Hurndall, E. P. Jacobs, and R. D. Sanderson, *J. Membr. Sci.*, **78**, 283-298 (1993).
8. N. Sawa, Jpn. Pat. 39-24965 (1964); *Chem. Abstr.*, **62**, 118020d (1965).



9. A. J. Hill and S. R. Aspinall, *J. Am. Chem. Soc.*, **61**, 822–825 (1939).
10. F. W. Wehrli and T. Wirthlin, in *Interpretation of Carbon-13 NMR Spectra*, Heyden, London, 1976, p. 37.
11. J. B. Stothers, *Organic Chemistry—A Series of Monographs*, Academic Press, New York, London, 1972, Vol. 24, p. 457.
12. J. Schaefer, *Macromolecules*, **4**(1), 105–107 (1971).
13. D. Neuhaus and M. P. Williamson, in *The Nuclear Overhauser Effect in Structural and Conformational Analysis*, VCH, New York, 1989.
14. J. K. M. Sanders and B. K. Hunter, *Modern NMR Spectroscopy, A Guide for Chemists*, Oxford University Press, Oxford, 1989, (a) p. 182; (b) p. 180.
15. E. P. Jacobs, PhD Thesis, University of Stellenbosch, South Africa, March 1988.
16. H. K. Lonsdale, Recent advances in reverse osmosis membranes. *Desalination*, **13**, 317–332 (1973).
17. M. J. Hurndall, E. P. Jacobs, A. J. Van Reenen, and R. D. Sanderson, *Desalination*, **89**, 203–222 (1992).

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