Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Witek, Ewa , Pazdro, Marcin and Bortel, Edgar(2007) 'Mechanism for Base Hydrolysis of Poly(N-vinylformamide)', Journal of Macromolecular Science, Part A, 44: 5, 503 — 507

To link to this Article: DOI: 10.1080/10601320701235461

URL: http://dx.doi.org/10.1080/10601320701235461

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry (2007) **44**, 503–507

ISSN: 1060-1325 print/1520-5738 online
DOI: 10.1080/10601320701235461

Mechanism for Base Hydrolysis of Poly(N-vinylformamide)

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Received September, 2006, Accepted October, 2006

The industrial production of poly(N-vinylformamide), PNVF, was started a few years ago, making the desired polyvinylamine, PVAm, accessible on a large scale via hydrolysis of PNVF. According to the literature, the key to achieving a 100% conversion of PNVF into PVAm is to employ basic hydrolysis conditions. However, results disclosed in the present note contradict such statements.

A radically obtained PNVF polymer, assigned further on as PNVF-000 with $\bar{M}_w = 2.63 \times 10^5$ g/mol, was submitted to a stepwise hydrolysis in aq. NaOH solution with periods lasting 0, 5 20, 40, 90, 175, and 240 min. Aliquots ware taken, neutralized, precipitated and purified. For each polymer thus obtained the ^{13}C NMR spectra was recorded, providing evidence for transient formation of amidine rings. These rings while decomposing leave not only primary amine functions attached to the backbone, but also OH groups. Elementary analysis of PNVF-240, the polymer fully deprived of formaldehyde groups, confirm these findings. From the $C/N = 3.17$ ratio the share of vinyl-alcohol units present in the chains is estimated to be 42 mol%. Considering all the experimental results, the mechanism of basic hydrolysis was established.

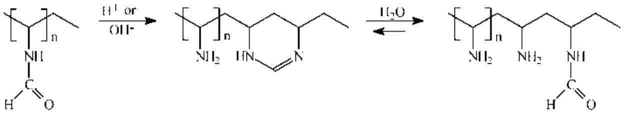
Keywords: poly(N-vinylformamide); hydrolysis; polyvinylamine; NMR spectroscopy

1 Introduction

Synthesis of polivinylamine, PVAm, has been a challenge for generations. The simplest monomer to provide this polyelectrolyte is not available because vinylamine, VAm, does not exist in a free state. Therefore, it was necessary to find a precursor. Among many proposals (1, 2) poly(N-vinylformamide), PNVF, proved to be by far the best for the purpose and was accepted for industrial production (3). Thus, at the beginning of the present century NVF, PNVF and PVAm have become commodity chemicals. The focus is now on exploring their potential uses in various fields. For example, PVAm has been utilized as a chelating agent for heavy metals (4, 5), as a support for enzymes (6), it found utility in water and waste-water treatment (7), and as an additive in petroleum production and papermaking (8).

In all these practical uses, the amount of primary amine groups attached to the backbone plays a significant role. Consequently, hydrolysis should be regarded as a key feature in the synthesis of polyvinylamine from PNVF. However, opinions presented in the literature on that issue are ambiguous. According to Yamamoto et al. (9) hydrolyses accomplished with base or acid experience, if proper conditions exist, there is a 100% transformation of PNVF into PVAm. This suggests that the PVAm backbones consist exclusively of -CH_2-$CH(NH_2)$- or -CH_2-$CH(NH_3^+)$- units, respectively.

In contrast, Pinschmidt *et al.* (10) maintained that such a complete transformation is only possible in the case of basic hydrolysis. If acid is employed, the conversion cannot surpass the 80% level due to mutual repelling of positive charges. It should be noticed, however, that the same authors detected in the ^{13}C-NMR spectrum obtained during hydrolysis, a signal around 150 ppm which they assigned to the carbon atom present in amidine rings formed transiently in accordance with the hydrolysis profile shown below (1, 10).



(1)

According to our experience, neither basic nor acid hydrolyses proceed with the exclusive formation of vinylamine or vinylammonia units. During the base hydrolysis of PNVF, for example, a distinct smell of ammonia is always perceptible. We first reported it, although earlier, Spange et al. (11), discovered the release of NH_3 due to acid hydrolysis of an oligo(N-vinylformamide). We also found the

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analytically determined nitrogen content in polyvinylamines to be lower than predicted by theory.

Therefore, the aim of the present work was to carry out ^{13}C-NMR and ^{1}H-NMR structure analyses on purified samples obtained stepwise from a basic hydrolysis of PNVF in order to establish a reliable mechanism for that process.

2 Experimental

2.1 *Materials*

NVF monomer from Aldrich was distilled in vacuum over a Vigreux column before use. Free radical initiator, 2,2′-azobis (2-methylpropionamidine)dihydrochloride (AIBA), also from Aldrich, was used as obtained. Analytical grade sodium hydroxide and hydrochloric acid, both from POCH Gliwice, Poland, were used as obtained. Acetone from POCh Gliwice, reagent grade, was distilled at 56°C, and water was twice redistilled. Solvents used for the spectroscopic measurements were of spectral grade (from ARMAR AG) and were used as received. Cellulose dialysis tubings for separating compounds with molecular weight <12,400; were supplied by Sigma-Aldrich.

2.2 *Polymerization of NVF*

A three-necked round bottom flask equipped with a reflux condenser, thermometer and an inlet capillary for argon was charged with 15 g (0.21 mole) NVF and 80 cm^3 of degassed water. The mixture was heated up to 60°C with constant argon flushing. The addition of 0.5695 g (0.0021 mole) AIBA, dissolved in 5 cm^3 water, followed. The polymerization lasted 3 h at 60°C under argon atmosphere. The resulting solution was dialyzed to water from a cellulose dialysis tubing over 3 days, exchanging the water every 24 h. The polymer was precipitated in acetone and dried in vacuum to constant weight. The poly(N-vinylformamide), PNVF, thus obtained, was designated as PNVF-000 and submitted to physicochemical characterization and to multi-stage base hydrolysis.

2.3 *Hydrolysis of PNVF*

A three-necked round bottom flask, equipped with a reflux condenser, thermometer and magnetic stirrer, was charged with 12 g PNVF-000 dissolved in 240,0 cm^3 2M$_{aq}$ NaOH (polymer concentration 5 wt%). During uninterrupted stirring, the solution was heated quickly to 50°C and at intervals of 5, 20, 40, 90, 175, and 240, an aliquot of 40 cm^3 was taken from the flask and neutralized with conc. HCl to pH 6 in order to stop further hydrolysis. Each of the six solutions was dialyzed over 3 days to water, exchanging the water every 24 h. The purified polymers were precipitated in acetone, vacuum dried to constant weight, and labeled with the following acronyms in which the numbers relate to the respective times of hydrolysis: PNVF-005, PNVF-040, PNVF-090, PNVF-135, and PNVF-240.

2.4 *Measurements*

The ^{13}C-NMR spectra were recorded on a Bruker 500 MHz Avance II spectrometer using the following conditions: pulse with 3,20 μs (30°), spectral with 3 437,5 Hz, acquisition time 1,4 s, transients 22000, solvent D$_2$O, internal reference TSP-d$_4$, maximal concentration ca. 20% estimated.

The ^{1}H NMR spectra were obtained with the same instrument by using the following conditions: pulse with 3,95 μs (30°), spectral with 4901,9 Hz, acquisition time 13,37 s, transients 256, solvent D$_2$O, internal reference TSP-d$_4$, maximal concentration ca. 20% estimated.

Fourier transformation, visualizations and the working up to the FID's obtained have been accomplished by use of the MestReC 4.8.6. program. Elemental analyses were performed on a EuroVector EURO EA 3000 C, H, N analyzer.

Molecular weight of PNVF was determined by static light scattering (SLS) experiment using a Brookhaven Instrument BIC-200 SM goniometer at 25 ± 0.02°C on five solutions of polymer in the range concentration from 0.200 to 0.600 mg/ml in 0.1 M NaCl. The wavelength was 632.8 nm. The Zimm plot was constructed with the standard BI-MwA/ZP software and the weight average molecular weight ($\bar{M}_w$) determined.

3 Results and Discussion

Figure 1 shows the ^{1}H-NMR spectrum of poly(N-vinylformamide), PNVF−000, with $\bar{M}_w = 2.63 \times 10^5$ g/mol, recorded at pH 6,5 in D$_2$O. Two multiplets at ^{1}H δ 7.92−8.07 ppm, labeled as a_1, and at ^{1}H δ 7.72−7.81 ppm, labeled as a_2, derived from formamide protons accommodated in chains with diversified tacticity. The signals a_1 appears to be much more intensive than signal a_2. A similar relationship concerns the b_1 and b_2 labeled methane-carbon protons signals at ^{1}H δ 3,92 ppm and ^{1}H δ 3,40 ppm.

Integration of the respective peak areas renders the following ratios:

$$\frac{a_1}{a_2} = \frac{0.42}{0.07} \quad \text{and} \quad \frac{b_1}{b_2} = \frac{0.43}{0.07}$$

Similarity of both the relationships confirms the assumption that a stereoregular structure prevails in the polymer. The shear of this structure amounts in PNVF to (0.42/0.49) × 100 = 84%. That statement appears to be important to explain the mechanism of hydrolysis.

Structures of PNVF−000 products, resulting from base hydrolyses, carried out at stepwise increasing reaction times, were first investigated with ^{13}C-NMR spectroscopy. Figure 2 shows seven patterns divided into 5 regions which cover the following shift intervals: region **1** (δ 169−173 ppm); region **2**

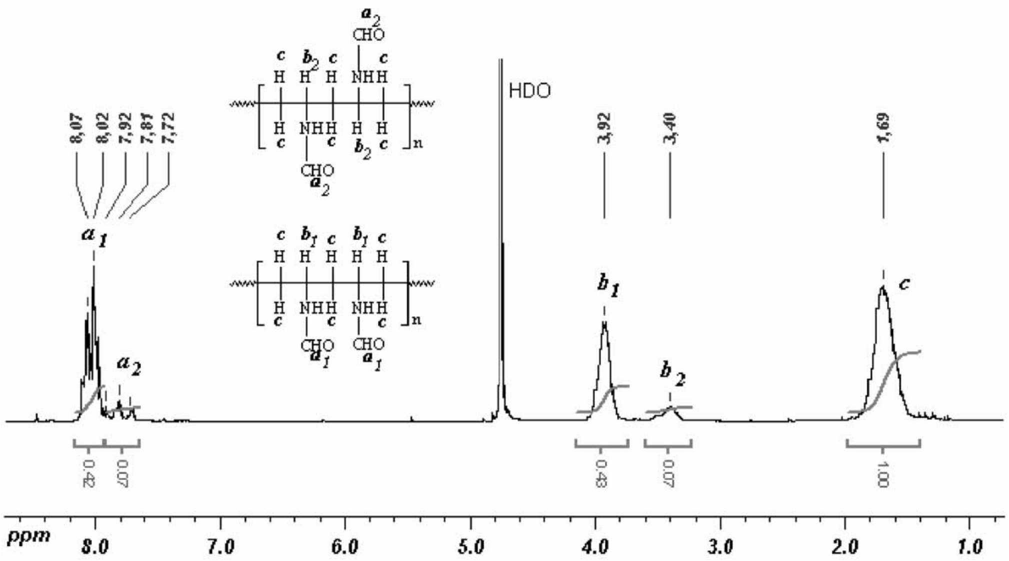


Fig. 1. ^{1}H-NMR spectrum (500 MHz, D_2O) of poly(N-vinylformamide), PNVF-000, and assignment of signals to the structure of polymer.

(δ 163–168 ppm); region **3** (δ 149–153 ppm); region **4** (δ 64–73 ppm), and region **5** (δ 20–48 ppm).

For a better illustration of structure changes occurring during the hydrolysis, chain units were incorporated in Figure 2. NMR signals, corresponding with particular C-atoms in the respective units, were designated with the same roman letter.

Aldehyde signals appearing in regions **1** and **2**, labeled as *a* and *a′*, were derived from the formaldehyde group. Before hydrolysis, however, in the case of PNVF–000, only the *a*

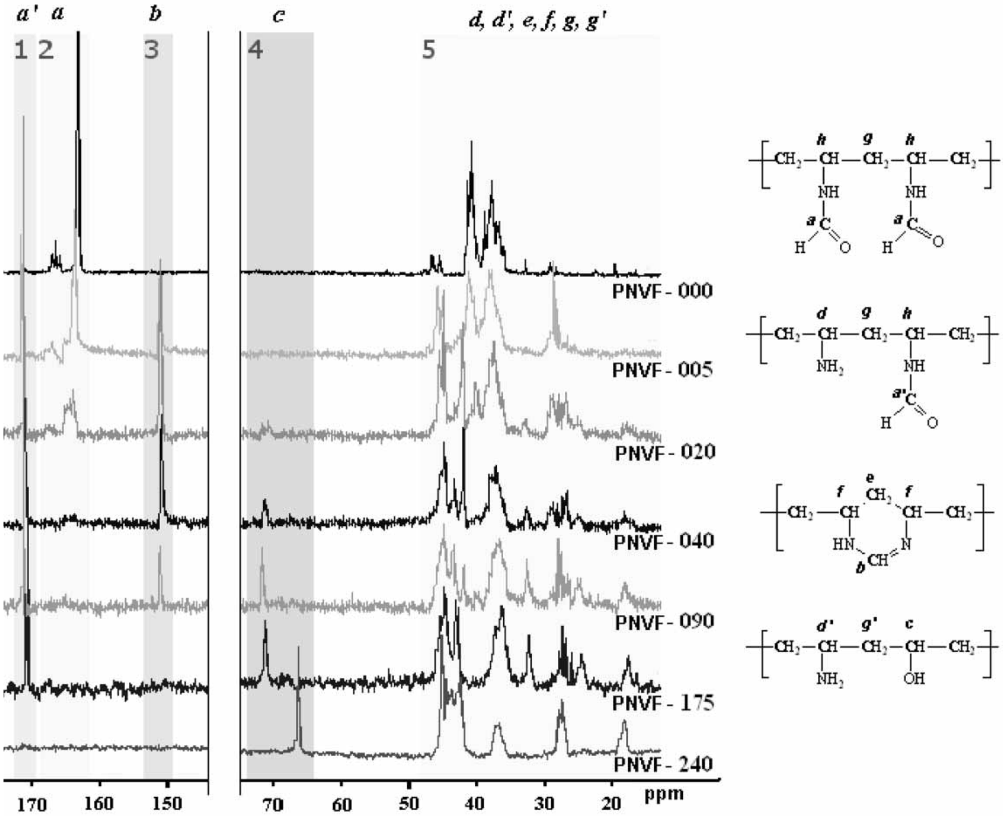


Fig. 2. ^{13}C-NMR spectra (500 MHz, D_2O) of polymers from base hydrolysis of PNVF, carried out stepwise at increasing reaction times, and assignment of signals to the structure changes occurred during the hydrolysis.

labeled signal appears in region **2**. But as early as after 5 min, the second *a′* labeled signal becomes visible in region **2**. Nevertheless, if hydrolysis is continued beyond 20 min, again only one, the *a′* labeled signal remains in region 1 of the proper pattern. The existence of two frequencies derived from formaldehyde can be explained on the grounds that in the course of hydrolysis part of the formaldehyde groups undergo transformatin into amine functions, which exert a lesser shielding effect on atoms in their neighborhood. After 240 min, both the aldehyde signals vanish. In region **3**, also after 5 min., the *b* labeled signal appears, which belongs to the transient amidine ring (cf. Pinschmidt (10)). These rings disappear after 90 min. Region **4** deserves special attention because the *c* labeled signal located there is derived from the OH substituted carbons. It should be recognized, that not all formaldehyde groups are transformed into a primary amine function. Part of them seems to be the source of ammonia, which gives the characteristic smell. The *c* labeled signal increases in intensity, while the time of hydrolysis lengthens. Signals in region **5** belong to methine - and metylene-carbons. Since the frequencies recorded there are tightened too much, the shifts range between δ 30–50 ppm was divided into five subregions designed as: 5.1; 5.2; 5.3 ^{13}C-NMR spectra of the subdivided region are shown separately in Figure 3.

It is easy to recognize that peaks appearing in the subregion **5.3** at δ 42–43 ppm derive from the *h* labeled, -NHCHO substituted methine-carbon. Intensity of this signal decreases to zero after 240 min. From polymers being hydrolyzed over 5, 20, 40, and 90 min. a peak appears at about δ 43 ppm in subregion **5.2**. Since its existence is connected with the signal of the *b*-labeled carbon atom located in the amidine ring, one can assume that the δ 43 ppm shift belongs to the *f*-labeled carbons of this transient ring. In subregion **5.1** at δ 43–48 ppm, visible peaks are derived from *d*-, *d′*-and *d″*-labeled NH_2, showing substituted carbons. Their intensities rise during the hydrolysis process. No signals derived from CH_3- head groups are visible in the ^{13}C-NMR patterns.

From all evidence provided by the NMR structure analyses of products, which were submitted to base hydrolysis over various time periods, the most relevant conclusion is that not all formaldehyde groups situated in PNVF are transformed into primary amine groups, since also partly OH functions are being formed. The amount of these OH groups attached to the backbone of PNVF-240 can be estimated from the C/N weight ratio resulting from the elementary

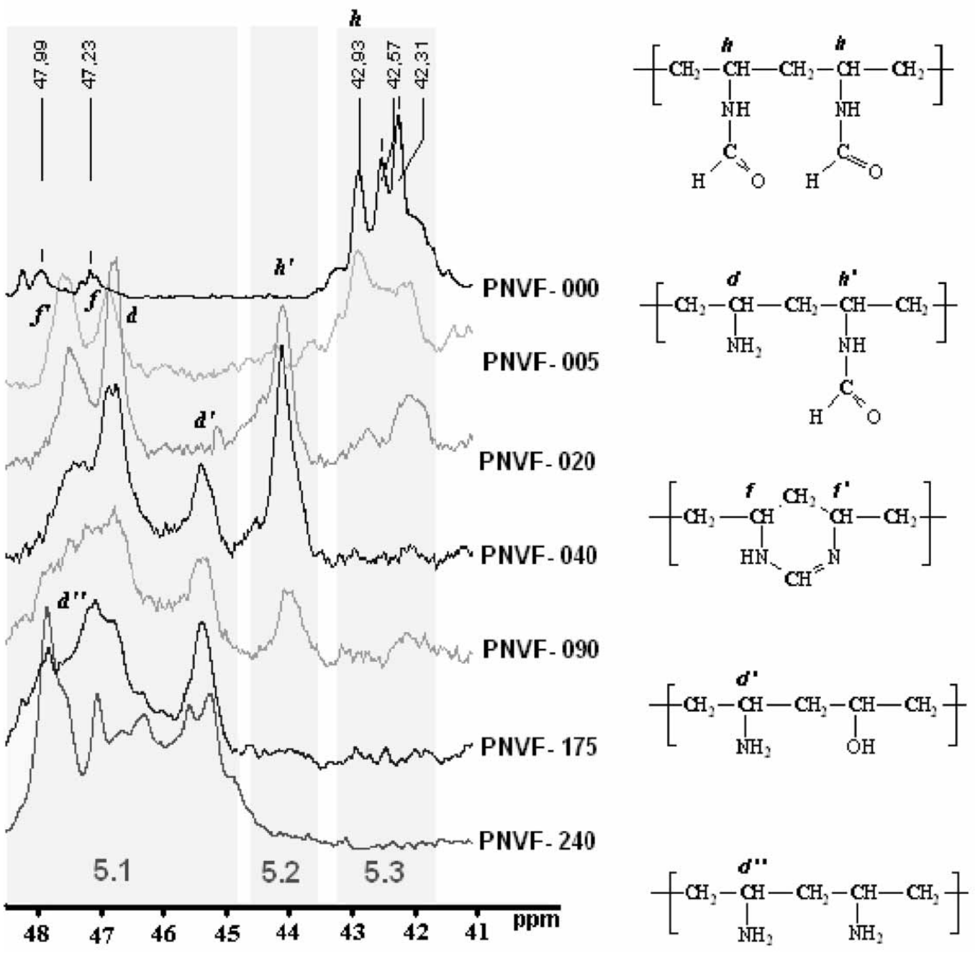
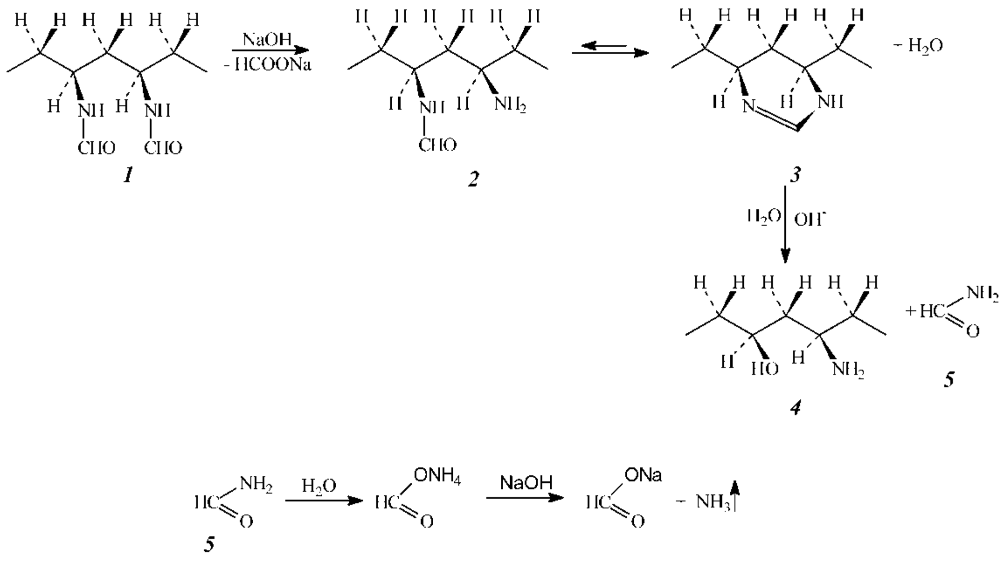


Fig. 3. Portions of the methine region of ^{13}C-NMR spectra shown at Figure 2 (500 MHz, D_2O).



Sch. 1. Mechanism of base hydrolysis of poly(N-vinylformamide).

analysis:

$$\text{PNVF} - 240\,\text{Found C}\,57.28,\,\text{H}\,10.00,\,\text{N}\,18.06,\,\frac{\text{C}}{\text{N}}3.17$$

$$\text{PVAm}\,(C_2H_5N)_n\,(43,027)_n:$$

$$\text{Calcd. C}\,55.73,\,\text{H}\,11.71,\,\text{N}\,32.55,\,\frac{\text{C}}{\text{N}}1.71$$

Taking the ratio $C/N = 3.17$ for granted, the formula for PNVF-240 should be:

$$-\!\!\left[CH_2{-}CH(NH_2){-}CH_2{-}CH(OH)\right]_{0.85n}\!\!-\!\!\left[CH_2{-}CH(NH_2)\right]_{0.15n}$$

Thus, the end-product of hydrolysis is a copolymer consisting of vinylamine and vinylalcohol units. The content of the latter reaches ca 42 mol%. This value is in agreement with the quantity of 84% regular chain structure found in PNVF-000, which structure, as suggested, consists of meso dyads enabling the formation of amidine rings.

Based on the experimental data, the mechanism of base hydrolysis of PNVF was established, which is shown in Scheme 1.

4 Conclusions

Contrary to opinions represented in literature no homopolymers of polyvinylamine, PVAm, can be obtained via basic hydrolysis of poli(N-vinylformamide), PNVF. This fact should be taken into account when chemical modifications are attempted involving NH_2 groups attached to the backbone. The degree of conversion may be below expectations.

NMR patterns indicate the PNVF chains to be highly stereoregular with likely a large amount of meso dyads. During hydrolysis these dyads enhance the formation of transient amidine rings, the decomposition of which renders beside a primary amine function always one hydroxyl group. As a consequence a copolymer results, namely poly (vinylamine-co-vinylalcohol), with a significant share of vinylalcohol units.

At present we continue the investigations focusing on the acid hydrolysis of poly(N-vinylformamide).

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