

Acidic and Basic Hydrolysis of Poly(*N*-vinylformamide)

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ABSTRACT: Poly(*N*-vinylformamide) (PNVF) was synthesized and hydrolyzed to poly(vinylamine) (PVAm) in both HCl and NaOH solutions. The hydrolysis kinetics and the equilibrium hydrolysis were examined experimentally at different temperatures, polymer concentrations, and acid- or base-to-amide molar ratios. The hydrolysis kinetics strongly depended on temperature, polymer, and HCl or NaOH concentrations, but showed little dependence on PNVF molecular weight. The acid hydrolysis of PNVF exhibited limited conversions because of the electrostatic repulsion among the cationic amine groups generated during hydrolysis and proton hydrates. In the basic hydrolysis, complete amide conversions were observed when the NaOH/amide molar ratios were greater than unity. The effects of temperature and

PNVF concentration on the equilibrium amide conversion appeared to be negligible in both acidic and basic hydrolysis. The equilibrium conversions of base hydrolysis were higher than those of acidic hydrolysis under the same reaction conditions. At NaOH/amide ratios of less than unity, the equilibrium hydrolysis experiments revealed that one base molecule could induce the hydrolysis of more than one amide group. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3412–3419, 2002

Key words: poly(*N*-vinylformamide); poly(vinylamine); acidic hydrolysis; basic hydrolysis; hydrolysis kinetics; equilibrium hydrolysis; polyelectrolytes; water-soluble polymers

INTRODUCTION

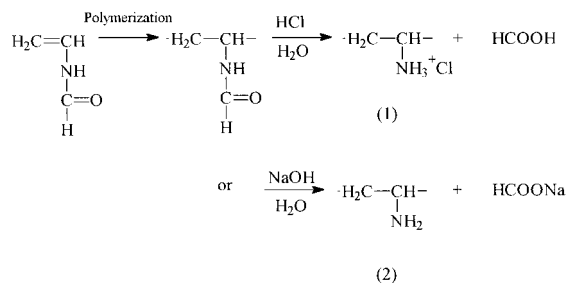
Poly(vinylamine) (PVAm) is a water-soluble polymer with a high density of reactive amino groups in its chain. PVAm and partially hydrolyzed poly(*N*-vinylformamide) (PNVF) have various applications in such industries as water treatment, papermaking, textile finishes, personal care products, adhesives, coatings, and oil field chemicals.^{1–5} However, PVAm cannot be synthesized directly from a vinylamine monomer. The common synthesis routes of PVAm involve modifications of other polymers that are readily available, such as polyacrylamide (PAM),⁶ polyacrylic acid (PAA),⁷ polyacrylonitrile (PAN),⁸ and poly(*N*-vinyl *tert*-butylcarbamate).^{9,10} These modifications, always complicated and costly, usually consist of a series of reactions followed by a final hydrolysis step to PVAm.

N-Vinylformamide (NVF) was developed as a precursor for simple and economical production of PVAm. PNVF can be easily converted into PVAm by hydrolysis in either acidic or basic aqueous solution. Acid hydrolysis produces cationic polymers, whereas base hydrolysis yields polymers with free amine functional groups. Base hydrolysis is usually a more effective approach, with almost 100% completion.¹¹ However, the electrostatic repulsion between cationic

amine groups and proton hydrates prevents acid hydrolysis from a complete conversion. On the other side, the byproduct from NaOH hydrolysis, sodium formate salt, needs to be removed by dialysis or precipitation at a great expense. In contrast, acid hydrolysis conducted in the mixture of methanol and aqueous solvent produces methylformate, which can be easily stripped as a light component. An alternative approach recently developed was a catalyzed thermal hydrolysis.¹² The synthesis routes of PVAm via base or acid hydrolysis of PNVF are shown in Scheme 1.

Industrial interests in PNVF and its hydrolysis products are growing constantly because of its potential applications in various fields. This synthesis route will probably become the most effective approach to prepare high-molecular-weight polyelectrolytes and/or amine functional polymers. However, there is a clear lack of fundamental understanding in the mechanistic and kinetic aspects of the free-radical polymerization of vinylformamide as well as the hydrolysis process of PNVF to PVAm. Recently, we reported a systematic experimental investigation of the polymerization kinetics in bulk and in aqueous solution and presented a mathematical model to correlate the monomer conversion and polymer molecular weight data.¹³ We also observed the formation of PNVF gels at high conversions under certain reaction conditions and elucidated that the gelation was caused by chain transfer to the amide group.¹⁴ In this paper, we report the results of an experimental investigation on the hydrolysis of PNVF in acidic and basic aqueous solutions. The effects of

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Scheme 1 Synthesis route of polyvinylamine (PVAm) via (1) acidic and (2) basic hydrolysis of poly(*N*-vinylformamide) (PNVF).

temperature, polymer concentration, and acid or base concentrations on the hydrolysis kinetics and hydrolysis equilibrium were systematically examined.

NVF, as a precursor to high molecular weight amide and amine functional polymers, has shown attractive high reactivities in polymerization, copolymerization, and hydrolysis. It was first synthesized more than three decades ago.¹⁵ Different synthetic routes to NVF have since been reported.¹⁶ A recently developed production technology used two simple chemicals, acetaldehyde and formamide, to synthesize the precursor of NVF, ethylideneformamide. The latter was then heated to produce NVF via cracking with the help of a catalyst.¹ This synthetic route has become commercially attractive and renewed industrial and academic research interest in NVF and its polymers. PNVF has good potential to replace polyacrylamide (PAM) in many applications because of its low toxicity, ease for high molecular weight, and functional polyelectrolyte. This experimental investigation contributes to the understanding of the PNVF hydrolysis kinetics and equilibrium under various conditions. This type of data is also desirable for designing and optimizing industrial processes.

EXPERIMENTAL

NVF monomer (Aldrich) was used to synthesize PNVF for the hydrolysis study. NVF was distilled under vacuum at <70°C and stored at -15°C before polymerization.

Two batches of PNVF with different molecular weights were prepared. The low molecular weight PNVF was produced by a precipitation polymerization in toluene medium. The weight-average molecular weight, \bar{M}_w is 579,000, with a polydispersity index of 5.84. The high molecular weight PNVF was synthesized by an inverse emulsion polymerization. The molecular weight was determined by a viscosity measurement and was found to be ~2 million.¹⁷ Both samples were dried under a vacuum for 48 h and recovered as fine powder. Sodium hydroxide, (NaOH;

ACP Chemicals Inc.) and hydrochloric acid (HCl; Fisher Scientific) were used as received. Millipore water was used for the experiments.

The hydrolysis kinetic experiments were conducted in nitrogen-sealed glass vials. All the samples were immersed in a circulating water bath set at a desired temperature. One vial was taken out at each preset time and cooled down immediately. The hydrolyzed polymer samples from basic hydrolysis were acidified with a concentrated HCl solution for ~5 min prior to precipitation by methanol. Acid-hydrolyzed polymer samples were precipitated directly from water with a mixture of methanol and concentrated HCl solution. All samples were dried in a vacuum oven at room temperature for 48 h.

For the equilibrium hydrolysis, three polymer concentrations were tested: 2, 5, and 10 wt %. The acid or base/amide group molar ratios investigated were 0.1, 0.3, 0.5, 0.8, 1.0, 1.2, 1.5, and 2.0. The equilibrium hydrolysis was carried out for 48 h at preset reaction temperatures with an exception that the time for acidic equilibrium hydrolysis at 60°C and 2 wt % polymer concentration was 7 days. The polymer samples were recovered by precipitation and dried.

The amide molar conversion of hydrolyzed sample was determined by proton nuclear magnetic resonance spectroscopy (¹H NMR). Spectrum of pure PNVF and acidified, partially hydrolyzed PNVF in D₂O are shown in Figure 1. The chemical shift of the amide groups is at 7.4–8.2 ppm. The chemical shift of the backbone —CH₂— groups is at 1.2–2.4 ppm. The area of the amide group peak diminishes with increasing degree of hydrolysis. The molar conversion of hydrolysis can be calculated by monitoring the change in the amide group peak area. Equation 1 gives the calculation of hydrolysis conversion:

Amide conversion

$$= 1 - \frac{2 \times \text{amide group peak area}}{\text{CH}_2 - \text{peak area}} \quad (1)$$

RESULTS AND DISCUSSION

Hydrolysis kinetics

Acidic hydrolysis kinetics

The effect of temperature on the acidic hydrolysis kinetics is shown in Figure 2. The amide group concentration was 0.704 mol/L, with a 1 : 1 acid/amide group molar ratio. An increase in temperature yielded a higher initial hydrolysis rate.

Acidic hydrolysis was also conducted at 70°C, with three different acid/amide molar ratios (0.5, 1.0, and 2.0). The amide group concentration was 0.704 mol/L (5 wt % PNVF in water). The initial hydrolysis rate

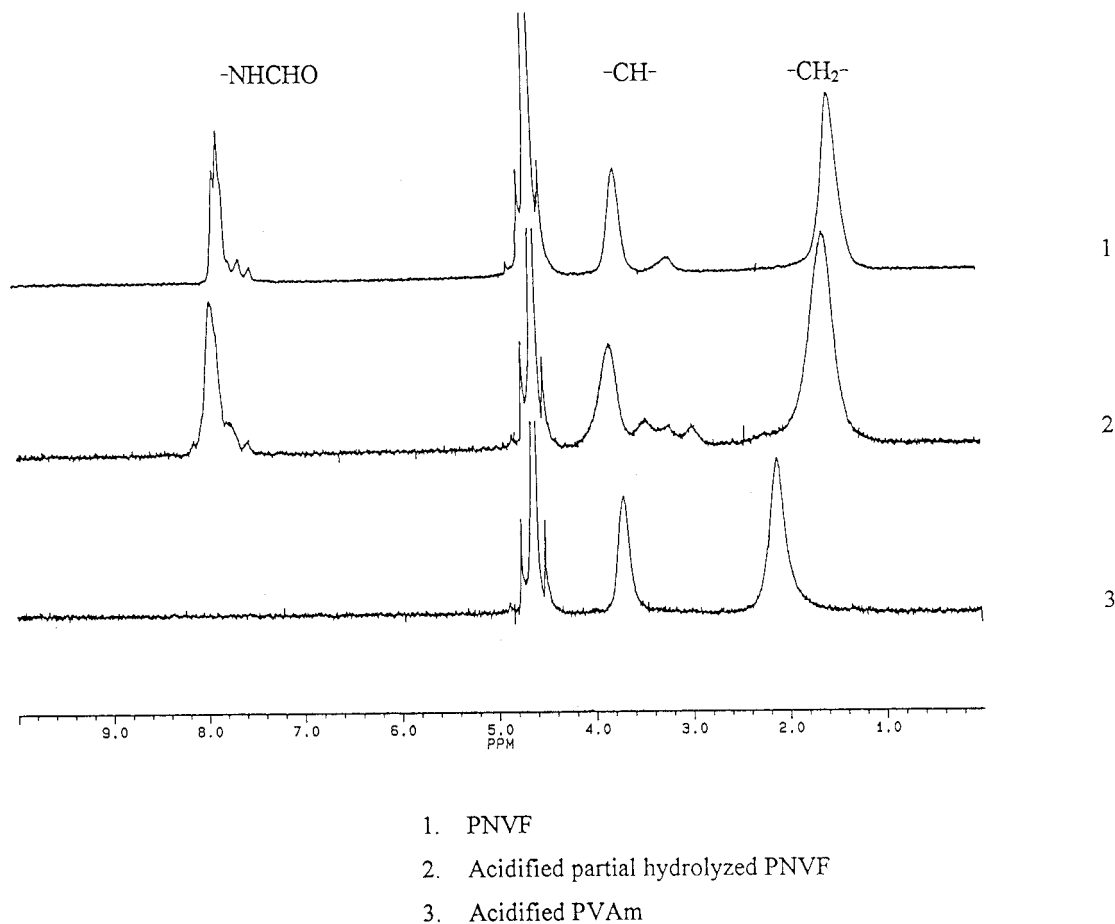


Figure 1 ^1H NMR spectra of PNVF and hydrolyzed PNVF in D_2O : (1) pure PNVF, (2) acidified partially hydrolyzed PNVF; and (3) acidified PVAm.

increased with increasing the acid concentration, as shown in Figure 3.

The effect of the polymer concentration on the acidic hydrolysis kinetics is shown in Figure 4. The amide group concentration was set at 0.282, 0.704, and 1.408 mol/L. When the molar ratio of acid/amide group was 1 : 1, the initial rate increased with increasing the amide concentration.

The acidic hydrolysis reactions did not reach an equilibrium conversion in the 10-h period for the kinetic experiments. The hydrolysis reaction slowed down dramatically after 8 h because of the electronic repulsion among cationic groups generated during hydrolysis and the depletion of the reactants.¹⁸

Basic hydrolysis kinetics

The basic hydrolysis kinetics at 60, 70, and 80°C are shown in Figure 5. The polymer concentration was 0.704 mol/L, with a 1 : 1 base/amide molar ratio. A higher temperature gave a higher initial conversion rate. However, the final hydrolysis reached the same level at different temperatures. At the same polymer

concentration, the degree of hydrolysis was determined only by the base/amide ratio.

The effect of the base concentration on the hydrolysis kinetics is shown in Figure 6. The base/amide ratios were 0.5, 1.0, and 2.0, with an amide concentration of 0.704 mol/L. A higher base concentration not only yielded a higher initial rate, but also gave a higher degree of hydrolysis. At the highest base concentration, the hydrolysis reaction was completed within 5 h.

The effect of the polymer concentration on the hydrolysis kinetics is shown in Figure 7. The polymer concentrations were 0.282, 0.704, and 1.408 mol/L. The base concentrations were set at two different levels of 0.282 and 1.408 mol/L. The initial hydrolysis rates at the high base concentration were higher than those at the low base concentration. However, changing the polymer concentration made almost no difference in the initial rate when the base concentration was 1.408 mol/L. At a base concentration of 0.282 mol/L, the initial rate decreased with increasing the polymer concentration from 0.282 to 1.408 mol/L.

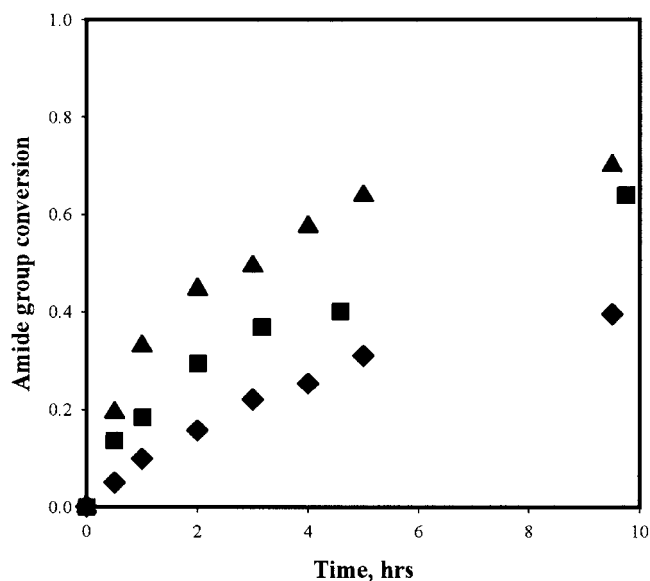


Figure 2 Acidic hydrolysis kinetics at different temperatures with 0.704 mol/L (5 wt %) amide group and 1:1 HCl/amide molar ratio. Key: (◆) 60°C; (■) 70°C; (▲) 80°C.

Compared with the acidic hydrolysis, the basic hydrolysis kinetics displayed higher initial hydrolysis rate and higher equilibrium amide conversion at the same reactant concentrations, temperature, and time span.

The data presented in Figures 2–7 were obtained from the low molecular weight ($M_w = 579,000$) PNVF sample. The basic hydrolysis kinetics at 70°C of the low molecular weight PNVF are compared with those of the high molecular weight PNVF sample in Figure

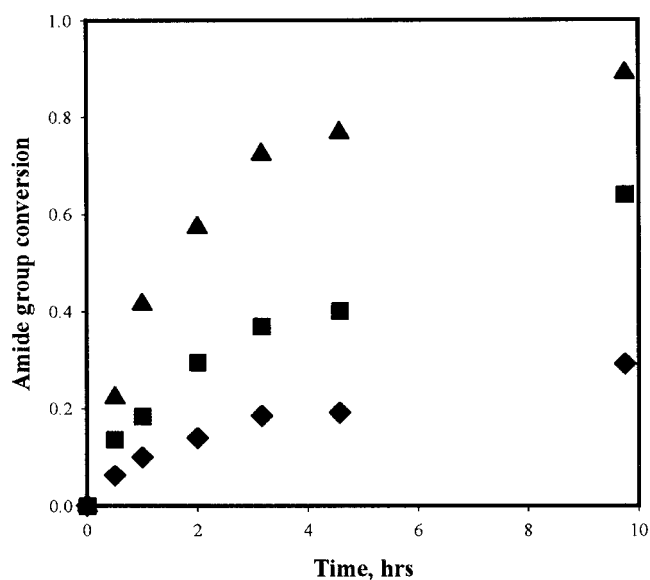


Figure 3 Effect of HCl/amide molar ratio on hydrolysis kinetics at 70°C and 0.704 mol/L amide group. Key: (◆) 0.353 mol/L HCl; (■) 0.704 mol/L HCl; (▲) 1.408 mol/L.

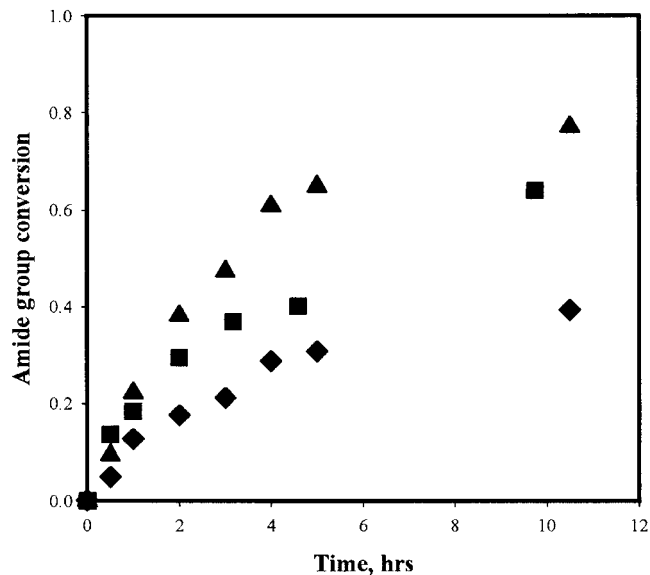


Figure 4 Effect of PNVF concentration on acidic hydrolysis at 70°C. Key: (▲) 1.408 mol/L PNVF; (■) 0.704 mol/L PNVF; (◆) 0.282 mol/L PNVF.

8. The amide and base concentrations were the same (0.704 mol/L). The lower molecular weight sample gave a slightly higher initial rate up to ~70% conversion. However, the discrepancy was not significant and disappeared at the final stage of the reaction. A possible explanation for this result is that the high molecular weight sample has a higher viscosity. The result may suggest a weak viscosity effect on the hydrolysis kinetics at the early stage.

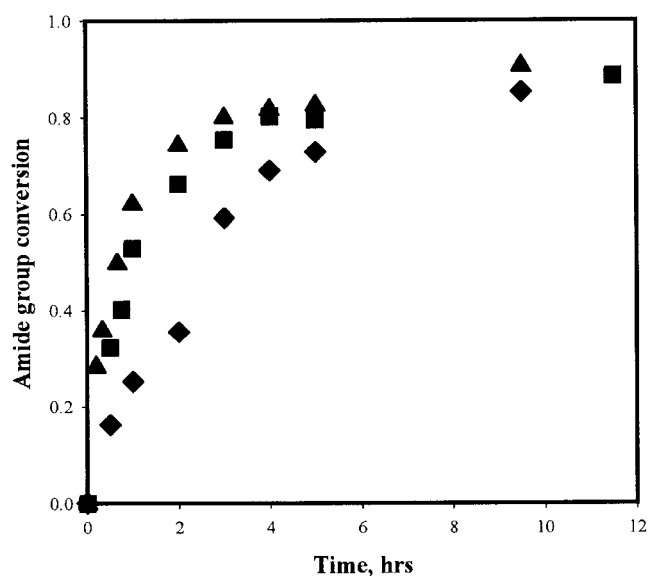


Figure 5 Basic hydrolysis kinetics at different temperatures with 0.704 mol/L (5 wt %) amide group and 1:1 NaOH/amide molar ratio. Key: (◆) 60°C; (■) 70°C; (▲) 80°C.

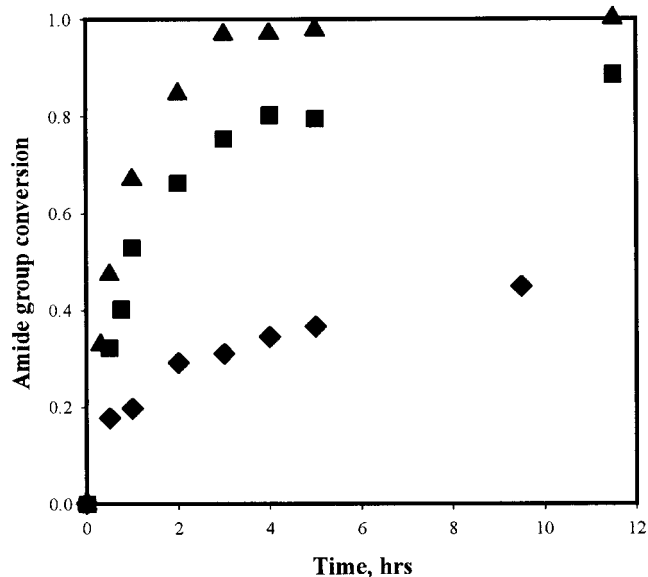


Figure 6 Effect of NaOH/amide molar ratio on hydrolysis kinetics at 70°C and 0.704 mol/L amide group. Key: (◆) 0.353 mol/L NaOH; (■) 0.704 mol/L NaOH; (▲) 1.408 mol/L NaOH.

Equilibrium hydrolysis

The equilibrium conversions of the PNVF hydrolysis at different temperatures, polymer concentrations, and acid or base/amide molar ratios are shown in Figures 9–14. The data can be divided into two groups: the results of the acidic equilibrium hydrolysis

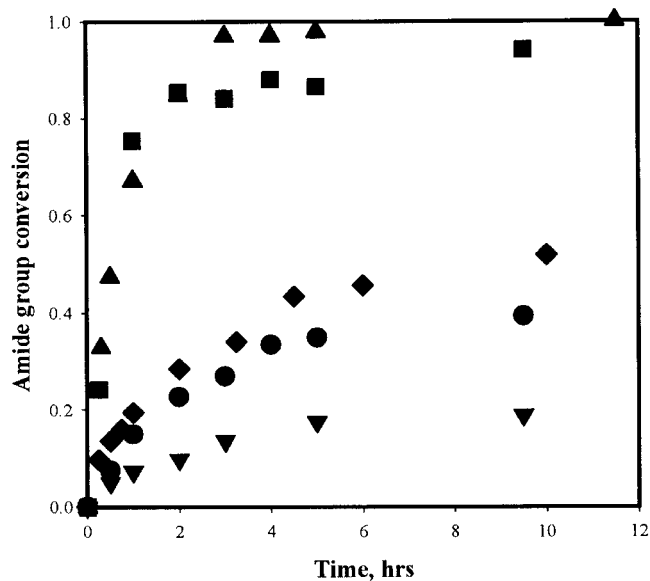


Figure 7 Effect of PNVF concentration on basic hydrolysis kinetics at 70°C. Key: (▲) 0.704 mol/L PNVF and 1.408 mol/L NaOH; (■) 1.408 mol/L PNVF and 1.408 mol/L NaOH; (◆) 0.282 mol/L PNVF and 0.282 mol/L NaOH; (●) 0.704 mol/L PNVF and 0.282 mol/L NaOH; (▼) 1.408 mol/L PNVF and 0.282 mol/L NaOH.

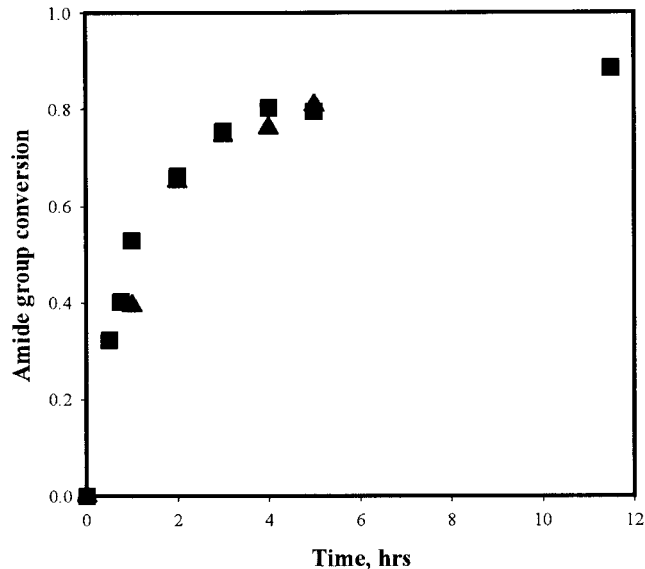


Figure 8 Effect of PNVF molecular weight on basic hydrolysis kinetics at 70°C and 0.704 mol/L amide group. Key: (■) $M_w = 0.58 \times 10^6$; (▲) $M_w = 2 \times 10^6$.

at 60, 70, and 80°C are shown in Figures 9, 10, and 11, respectively; and the results of basic equilibrium hydrolysis at the same three temperatures are shown in Figures 12, 13, and 14, respectively. The equilibrium hydrolysis conversion is plotted against the initial acid or base/amide molar ratio. In each figure, an equal molar line is also plotted.

In general, the data show that the equilibrium conversion increased with increasing acid or base/amide molar ratio. There was no sign of hydrolysis in parallel

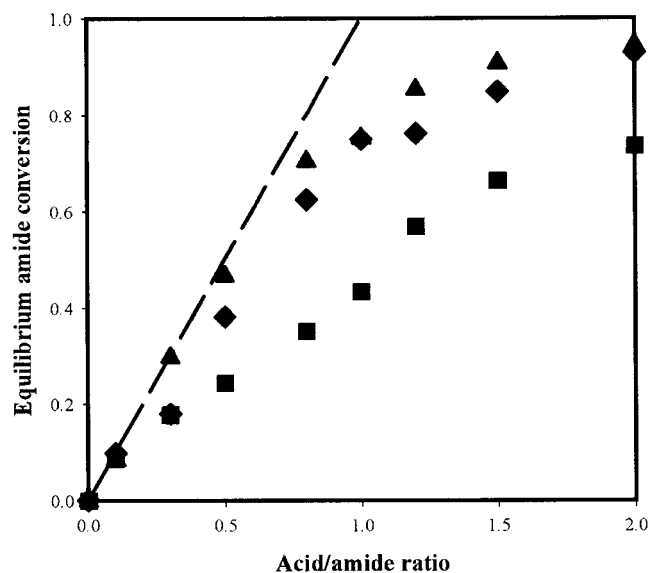


Figure 9 Equilibrium amide conversion versus HCl/amide ratio at 60°C. Key: (---) the equal molar line; (■) 0.282 mol/L amide group; (◆) 0.704 mol/L amide group; (▲) 1.408 mol/L amide group.

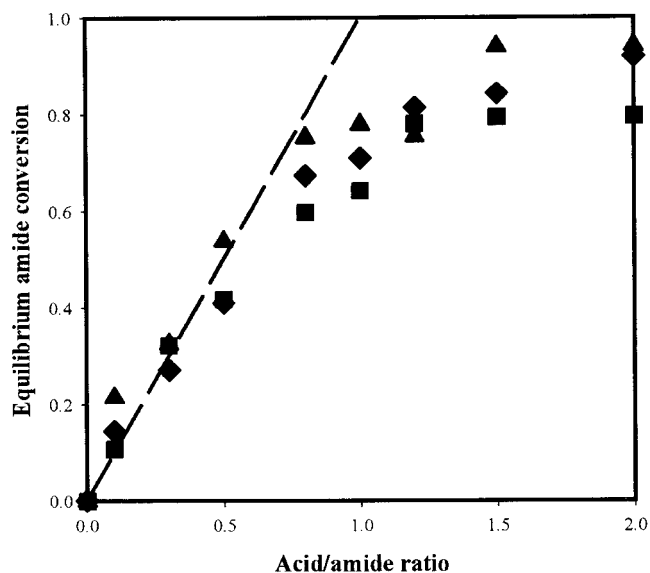


Figure 10 Equilibrium amide conversion versus HCl/amide ratio at 70°C. Key: (— — —) the equal molar line; (■) 0.282 mol/L amide group; (◆) 0.704 mol/L amide group; (▲) 1.408 mol/L amide group.

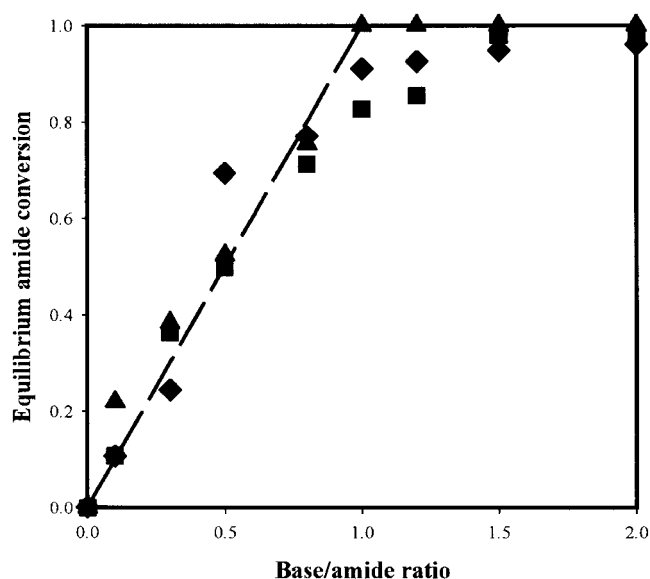


Figure 12 Equilibrium amide conversion versus NaOH/amide ratio at 60°C. Key: (— — —) the equal molar line; (■) 0.282 mol/L amide group; (◆) 0.704 mol/L amide group; (▲) 1.408 mol/L amide group.

blank samples after being heated to the same temperature and held for the same period of time. This result excludes the possibility of thermal hydrolysis. The experimental results suggest that the equilibrium conversion of hydrolysis was determined only by the acid or base/amide molar ratio.

The equilibrium conversions of acidic hydrolysis were generally lower than those of basic hydrolysis at

the same temperature, polymer concentration, and acid or base/amide molar ratio.

The acidic hydrolysis did not proceed to 100% conversion under current experimental conditions, as shown in Figures 9–11. This result can be explained by the fact that the acidic hydrolysis introduced cationic charges onto the polymer chains (Figure 15). When the neighboring amide groups were hydrolyzed and be-

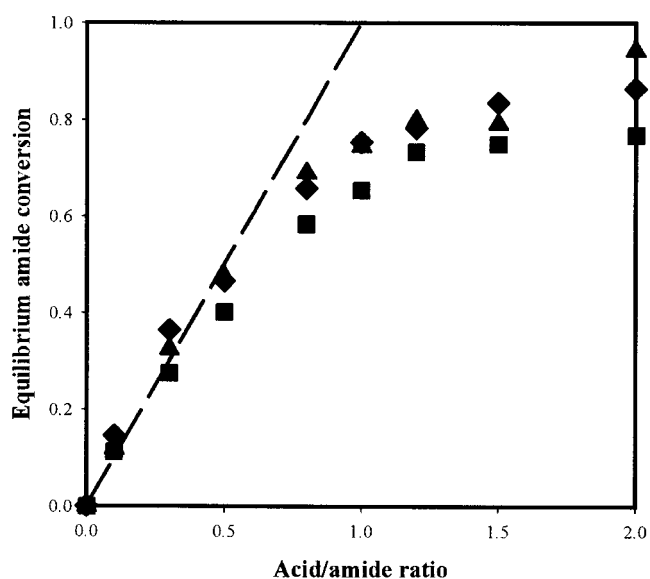


Figure 11 Equilibrium amide conversion versus HCl/amide ratio at 80°C. Key: (— — —) the equal molar line; (■) 0.282 mol/L amide group; (◆) 0.704 mol/L amide group; (▲) 1.408 mol/L amide group.

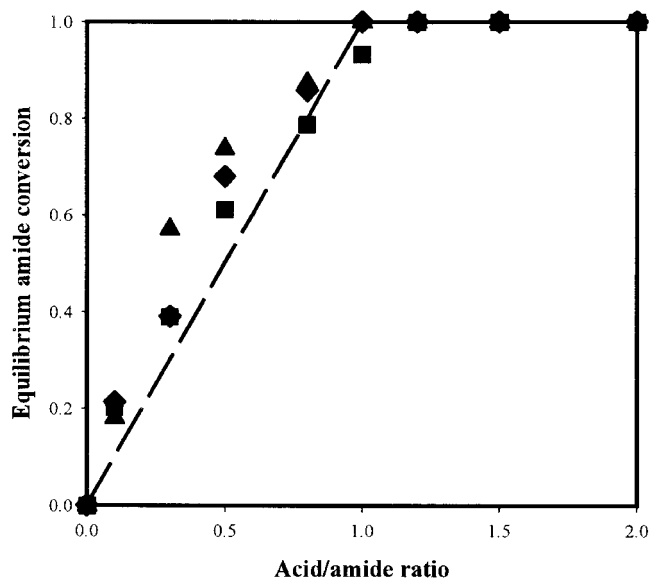


Figure 13 Equilibrium amide conversion versus NaOH/amide ratio at 70°C. Key: (— — —) the equal molar line; (■) 0.282 mol/L amide group; (◆) 0.704 mol/L amide group; (▲) 1.408 mol/L amide group.

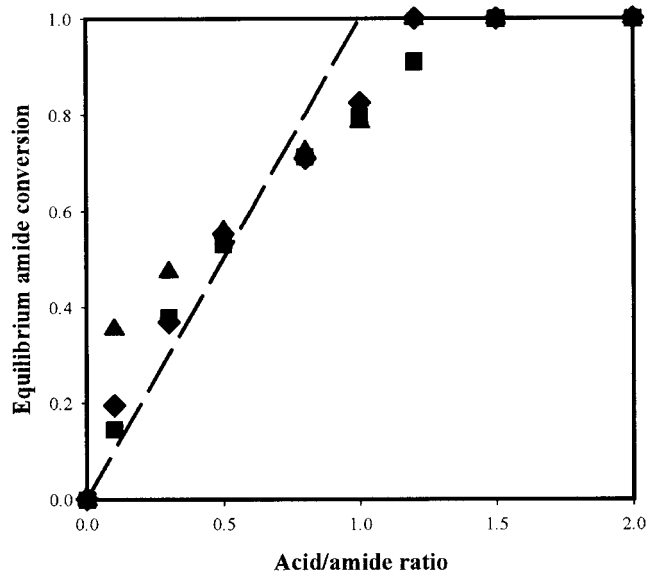


Figure 14 Equilibrium amide conversion versus NaOH/amide ratio at 80°C. Key: (— — —) the equal molar line; (■) 0.282 mol/L amide group; (◆) 0.704 mol/L amide group; (◆) 1.408 mol/L amide group.

came cationic amino groups, the remaining amide groups were shielded by these cationic charged amino groups. The electrostatic repulsion between these cationic amino groups and the attacking H_3O^+ species prevented a complete amide conversion in the hydrolysis. It was also observed that under most experimental conditions, the equilibrium conversions of acid hydrolysis did not exceed the equal molar line in the figures; that is, the experimental points were always on or below the line.

An interesting observation with the basic hydrolysis was that at the base/amide ratios below 1.0, the base hydrolysis often gave an equilibrium conversion higher than the theoretical value based on the stoichiometry of the hydrolysis route shown in Scheme 1. These experimental points were above the equal molar

lines in the figures (Figures 12–14). The data revealed that 1 mol of base (OH^-) induced the hydrolysis of >1 mol of amide group. When the base/amide molar ratio was <1, the initial NaOH should be completely consumed before all the amide groups are hydrolyzed. However, the basic hydrolysis of an amide group produces an amine group, which is also a weak base. The hydrolysis of amine groups provides additional OH^- anions (eq. 2).



These additional OH^- anions can continue the hydrolysis of amide groups, which can explain why the basic hydrolysis had a higher amide conversion than the equal molar line in the figures. This “overshoot” phenomenon was more pronounced at the lower base/amide molar ratios (<0.5).

The experimental data also show that the basic hydrolysis usually proceeded to a complete amide conversion when the base/amide ratio was >1.0.

CONCLUSIONS

The basic hydrolysis gave higher reaction rates and higher equilibrium conversions than its acidic counterpart at the same reactant concentrations, temperature, and time span. The equilibrium hydrolysis data reveal that 1 mol of base induced the hydrolysis for >1 mol of amide groups, particularly at the NaOH/amide group ratios <1.0. The basic hydrolysis of PNVF proceeded to a complete conversion when the NaOH/amide ratio was >1.0. The acidic equilibrium hydrolysis did not reach 100% completion within the scope of this experimental investigation. The acidic hydrolysis also gave lower equilibrium amide conversion than the basic hydrolysis at the same reaction conditions. This result was explained by the cationic repul-

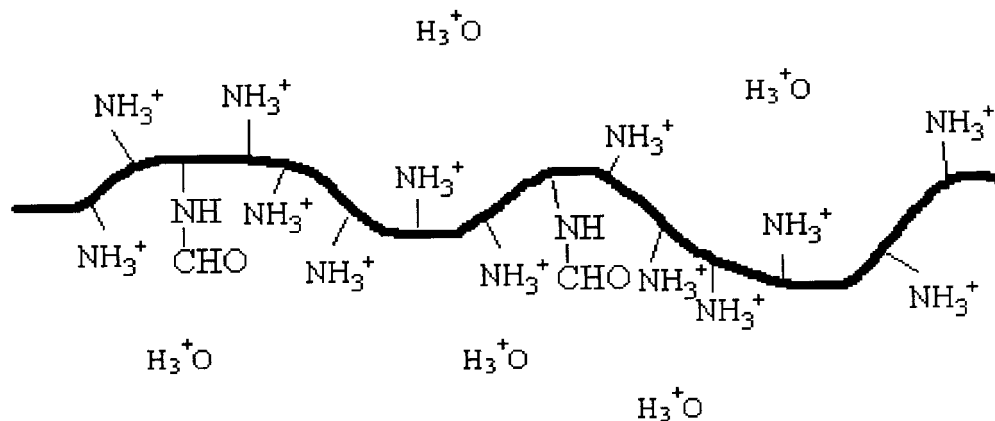


Figure 15 Electrostatic repulsion prevented a complete conversion in PNVF acidic hydrolysis.

sion established between charged polymer chains and the approaching acid (H^+).

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