

Study on Alkaline Hydrolysis of Polyacrylamide by ^{13}C NMR

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ABSTRACT: Alkaline hydrolysis of a polyacrylamide sample was performed in aqueous sodium hydroxide (NaOH) solutions at various NaOH concentrations to investigate the effects of hydrolysis conditions on the sequence distribution of the hydrolyzed products. For this purpose, ^{13}C NMR spectra for the aqueous solutions of the products were measured, in order to determine the sequence distribution based on carboxyl (on acrylic acid residue) and carbamoyl (on acrylamide residue) carbon peak assignments. It was first found that the specific concentration of aqueous sodium hydroxide solution gives a product with a sequence distribution greatly differing from the conventional product whose sequence distribution is almost completely alternative of acrylic acid and acrylamide residues. Under the other hydrolysis conditions employed here, the products with almost alternative sequence distribution were found to be commonly produced. Possible hydrolysis mechanisms are discussed based on the structures of aq NaOH solutions.

KEY WORDS ^{13}C NMR / Polyacrylamide / Alkaline Hydrolysis / Sequence Distribution /

Many studies have been carried out on the alkaline hydrolysis of the carbamoyl group in polyacrylamide (PAA) to carboxyl group. Moens *et al.*¹ investigated the process of alkaline hydrolysis as change in electric conductivity of the system by measuring the increase of negative charge due to conversion of the carbamoyl group to the ionic carboxyl group. Gunari *et al.*² analyzed its kinetics by measuring the viscosity of the aqueous (aq) solution of hydrolyzed PAA, because the viscosity varied in proportion to the degree of hydrolysis of PAA. Moens *et al.*¹ and Gunari *et al.*² speculated that the carbamoyl group was not randomly hydrolyzed and the carbamoyl group in the acrylamide (A) monomer unit adjacent to the acrylic acid (B) monomer unit produced by alkaline hydrolysis of PAA was strongly resistant to further alkaline hydrolysis, finally leading to the formation of

ABABAB type polymer. This kind of autoretarded reaction has already been proposed by Fuoss *et al.*³ in the case of quaternization of poly(4-vinylpyridine) by alkyl halide. Higuchi *et al.*⁴ supported the above speculation on the hydrolysis model of PAA using experimentally determined rate constants of hydrolysis of A unit in AAA, ABA, and BAB sequences. Halverson *et al.*⁵ directly measured the ^{13}C NMR spectra of the alkaline solution of PAA, in which PAA was hydrolyzed to the desired degree. Here, note that they used a hydrolysis media consisting of water and sodium chloride (0.75 mol l^{-1}) or isopropanol (2 wt%) and stoichiometrical amount of sodium hydroxide (NaOH) (0.23—0.7 mol) for the desired hydrolysis degree of PAA using the polymer solution with its concentration of 5 and 9 wt%. They analyzed carbonyl carbon peaks for A and B monomer units and suggested that

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carboxyl groups have a well-spaced distribution along the polymer chain, supporting the previous speculation proposed by Moens *et al.*¹ and Gunari *et al.*² Very recently, Truong *et al.*⁶ analyzed the rate constant of hydrolysis of PAA (0.1 mol l^{-1}) in 0.25 mol l^{-1} (1%) of aq NaOH from the stand point of the rate equilibria concept proposed by Fuoss *et al.*³ and Higuchi *et al.*⁴ They also gave ^{13}C NMR peak assignments on carbonyl, carbamoyl and methine carbons. They clearly showed that BBB type moiety was hard to produce even at a hydrolysis degree more than 0.5.

All these literature data seem to point out that the hydrolyzed product of PAA in aq NaOH has mainly the ABAB type moiety although the reaction was not carried out in very high concentrations of NaOH. However, our very recent study⁷ on the structure of aq NaOH solution by adiabatic compressibility, electroconductivity, ^1H - and ^{23}Na NMR and Raman spectroscopic measurements as a function of NaOH concentration has revealed that a 9–10 wt% aq NaOH solution has a specific structure in which Na^+ and OH^- ions are surrounded with three water molecule layers. The 1st layer consists of 4 mol of steadily solvated water, the 2nd layer is the weakly bonded water (average 0.2 mol) and the 3rd layer consists of free water. The 2nd layer serves as energy transfer media. In fact, we found that a 9.1 wt% aq NaOH solution has the most powerful dissolving ability for cellulose.⁸ In this connection, it is interesting to study whether the aq NaOH having a specific structure influences the product in alkaline hydrolysis of PAA.

In this study, we attempt to elucidate in more detail the sequence distribution of A and B units in the hydrolyzed PAA obtained at an equilibrium state in aq sodium hydroxide (NaOH) solution at high NaOH concentration. For this purpose, the carbonyl carbon peak region of ^{13}C NMR spectra of the aq solution of the hydrolyzed PAA samples obtained was analyzed.

EXPERIMENTAL

Preparation of the Hydrolyzed PAA Samples

A PAA sample (the viscosity average-molecular weight $\bar{M}_v = 9.0 \times 10^6$) was supplied by Kishida chemicals (Japan) and used as received. The hydrolysis of PAA was carried out under the two different conditions:

1) At the different NaOH concentrations and the same polymer concentration (2 wt%): Two grams (g) of PAA were mixed with 98 g of 5, 9.1, and 20 wt% of aq NaOH solution and dissolved completely at 4°C . Then, the temperature of the system was elevated to 50°C followed by standing for 60 min with intermittently shaking for complete hydrolysis. When 20 wt% aq NaOH was used for dissolution and hydrolysis of PAA, PAA was not so readily dissolved at 4°C that the mixture of PAA and 20 wt% aq NaOH solution was to stand overnight at 4°C and then heated to 50°C for hydrolysis. The hydrolysis was stopped by adding 20 wt% aq acetic acid into the system and the reaction product was precipitated by the addition of a large amount of methanol. The precipitates were washed several times by a mixture of water–methanol (1:4, v/v) and by acetone and finally dried *in vacuo* at 60°C for 8 h.

2) At the same NaOH concentration (9.1 wt%) and different polymer concentrations: In a 9.1 wt% aq NaOH solution PAA was dissolved at polymer concentrations of 2, 4, and 6 wt% at room temperature and the resultant solutions were subjected to hydrolysis and recovery process as described in the above section.

NMR Measurement

Each 0.2 g of the hydrolyzed product was put into NMR sample tube (10 mm ϕ) together with 3.8 g of deuterium oxide (D_2O) (Merck & Co., Inc., Ralway, U.S.A.) to give a clear solution. The ^{13}C NMR spectra of the sample solutions were recorded on a FT-NMR spectrometer (JNM FX-200, JEOL, Japan) under

the following operating conditions: 45° pulse, acquisition time, 0.68 s; pulse delay time, 2.5 s; accumulation, more than 7,000 times; complete proton decoupled mode, temperature, 50–60°C; internal reference, DSS (sodium 2,2-dimethyl-2-silapentane 5-sulfonate) as 0 ppm.

RESULTS AND DISCUSSION

Figures 1 and 2 show the ^{13}C NMR spectra of the hydrolyzed products obtained under the same polymer concentration (2 wt%) in 5 and 20 wt% aq NaOH solutions and the products obtained in 9.1 wt% aq NaOH with different polymer concentrations (2, 4, and 6 wt%), respectively. Five envelopes around 185, 182, 47, 45, and 38 ppm are assigned to carboxyl, carbamoyl, methine bonded to carboxyl, methine bonded to carbamoyl, and methylene carbons, respectively.^{4,5} These envelopes had fine structures. The carboxyl carbon peaks of the products in Figure 1 appeared as one strong broad signal having very weak shoulder peaks and the methine carbons attached to carboxyl group consisted of 3 broad peaks. A close inspection revealed that the carbamoyl carbon peak for the hydrolyzed PAA in Figure 1 consisted of at least two peaks, irrespective of the concentrations of alkali used for the hydrolysis. In this case, higher is the alkali concentration and lower is the intensity of the peak at higher magnetic field side. The spectra for all the products hydrolyzed in 9.1 wt% of aq NaOH (Figure 2) were found to be similar and peak separation relatively good, irrespective of polymer concentrations in the hydrolysis reactions. These spectra are distinctively different from those in Figure 1: First, both the carboxyl and the carbamoyl carbon peaks clearly consist of 2 and 3 peaks, respectively. Secondly, the peaks for the methine carbon attached to carboxyl group is finely separated into 4 peaks. Halverson *et al.*⁵ and Truong *et al.*⁶ reported three separate peaks both for carboxyl and carbamoyl carbon en-

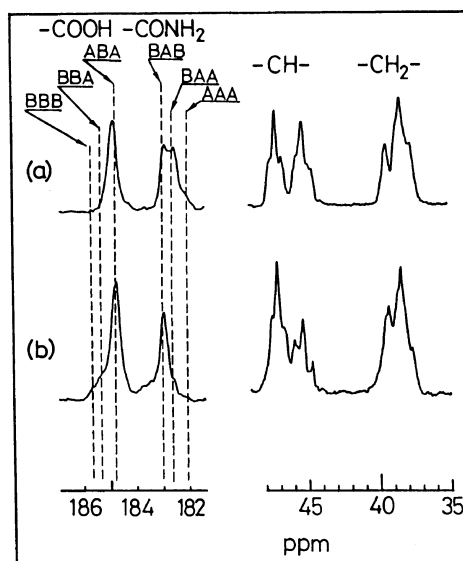


Figure 1. ^{13}C NMR spectra of hydrolyzed products obtained in 5(a) and 20(b) wt% aq NaOH.

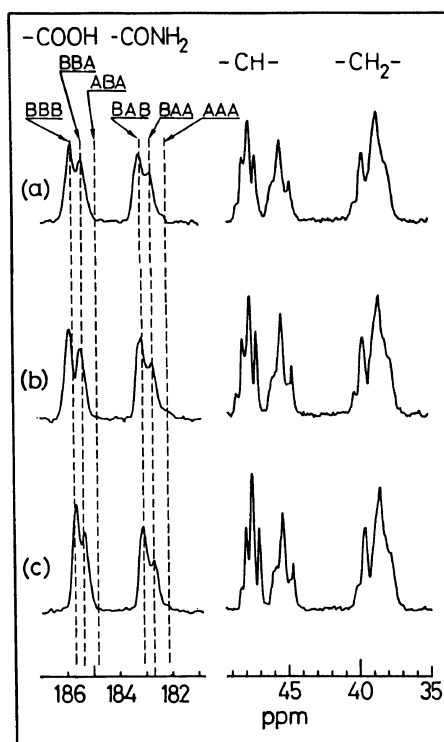


Figure 2. ^{13}C NMR spectra of hydrolyzed products obtained in 9.1 wt% aq NaOH: a, polymer concentration 2 wt%; b, 4 wt%; c, 6 wt%.

Table I. ^{13}C NMR chemical shifts and their assignments of hydrolyzed polyacrylamide (PAA)^a

| Sample | Chemical shifts (in ppm) | | | | | | | |
|------------------------------------|--------------------------|------------------|------------------|------------------|------------------|------------------|------------------|-------|
| | Carboxyl carbon | | | | Carbamoyl carbon | | | |
| | (BBB) | BBB | BBA | ABA | BAB | BAA | AAA | (AAA) |
| PAA/5 wt% NaOH (=2/98, w/w) | | | 185.35 (0.03) | 184.85 (0.44) | 182.87 (0.30) | 182.55 (0.21) | 182.05 (0.02) | |
| PAA/20 wt% NaOH (=2/98, w/w) | | 185.75 (0.02) | 185.38 (0.07) | 184.74 (0.50) | 182.96 (0.37) | 182.57 (0.03) | 182.10 (0.01) | |
| PAA/9.1 wt% NaOH (=2/98, w/w) | | 185.66 (0.30) | 185.31 (0.23) | | 183.10 (0.30) | 182.69 (0.16) | 182.10 (0.01) | |
| PAA/9.1 wt% NaOH (=4/96, w/w) | | 185.84 (0.30) | 185.47 (0.22) | | 183.10 (0.30) | 182.70 (0.16) | 182.08 (0.02) | |
| PAA/9.1 wt% NaOH (=6/94, w/w) | | 185.62 (0.32) | 185.32 (0.21) | | 183.07 (0.32) | 182.69 (0.13) | 182.11 (0.02) | |
| Original PAA Poly(acrylic acid) | | 186.99 | | | | | | 182.0 |

^a A, acrylamide monomer unit; B, acrylic acid monomer unit. Values in parenthesis denote relative peak intensities.

velopes, assigned from lower magnetic field as those of centered monomer units for BBB, BBA, and ABA, and BAB, BAA, AAA, respectively. Chemical shifts and peak intensities of all carbonyl and carbamoyl peaks detected are collected in Table I. Table I also shows assignments for the carboxyl and carbamoyl carbon peak groups according to Halverson *et al.*⁵ and Truong *et al.*⁶ Their assignments were made on the basis of the experimental fact that an addition of B monomer unit to the centered monomer unit (A or B) in question tends to shift the original peak position of the carbonyl carbon in the centered monomer towards lower magnetic field. Since both the carboxyl and carbamoyl carbon peaks in poly(acrylic acid) and PAA do not separate by differences in their stereoregularity, their assignments are acceptable. The validity of the assignments can also be supported by more detailed sequence distribution and the corresponding methine and methylene peak shape analysis, although detailed discussion is not described here. The experimental fact that a carboxyl or carbamoyl carbon peak responsible for the centered A or B unit in a given triad sequence has some

chemical shift range suggests that chemical shifts might be influenced by pentad or higher sequence distribution. Since we applied a complete proton decoupling mode in NMR measurements, as described in the experimental section, each carbon peak may be susceptible to different Overhauser effects. However Table I indicates that in this case the above suspection is not true because the peak intensity ratio of the total carbonyl to total methine carbon peaks was found to be exactly 1:1. Thus, more quantitative analysis on sequence distribution is possible and from Table I we can conclude that 1) the hydrolyzed product prepared in 5 wt% aq NaOH mainly has triad sequences of ABA, BAB and BAA, 2) the hydrolyzed product prepared in 20 wt% aq NaOH mainly has triad sequences of ABA and BAB, 3) the hydrolyzed product prepared in 9.1 wt% aq NaOH has triad sequences of BBB, ABB, BAB, and BAA. Therefore, the main sequence of the hydrolyzed products obtained in 5 and 20 wt% aq NaOH is the alternative of A and B, confirming the previous conclusion. But, this is the first demonstration indicating the hydrolyzed product

Table II. Extent of sample hydrolysis E_h

| Sample | $E_h/\%$ | | Average |
|----------------------------------|----------------------|---------------------|---------|
| | from carbonyl carbon | from methine carbon | |
| PAA/5 wt% NaOH (=2/98, w/w) | 47.0 | 47.9 | 47.5 |
| PAA/20 wt% NaOH (=2/98, w/w) | 58.8 | 64.5 | 61.7 |
| PAA/9.1 wt% NaOH (=2/98, w/w) | 52.5 | 53.9 | 53.2 |
| PAA/9.1 wt% NaOH (=4/96, w/w) | 51.6 | 53.9 | 52.8 |
| PAA/9.1 wt% NaOH (=6/94, w/w) | 53.0 | 54.0 | 53.5 |

to have BBB, ABB, BAB, and BAA as main sequences. The extent of hydrolysis E_h was calculated by the relation,

| | | | | | | | |
|------------------------|-------------------------------------|---|---|----------------------------------|---|-------------------------|-----|
| AAA | $\rightarrow P_0, P_0' \rightarrow$ | BAA | + | ABA | + | AAA | (1) |
| | | $2P_0'$ | | P_0 | | $(1 - P_0 - 2P_0')$ | |
| BAA | $\rightarrow P_1, P_0' \rightarrow$ | BAB | + | BBA | + | BAA | (2) |
| $2P_0'$ | | $2P_0'^2$ | | $2P_0'P_1$ | | $2P_0'(1 - P_1 - P_0')$ | |
| ABA | $\rightarrow P_1' \rightarrow$ | BBA | + | ABA | | | (3) |
| P_0 | | $2P_0P_1'$ | | $P_0(1 - 2P_1')$ | | | |
| BAB | $\rightarrow P_2 \rightarrow$ | BBB | + | BAB | | | (4) |
| $2P_0'^2$ | | $2P_0'^2P_2$ | | $2P_0'^2(1 - P_2)$ | | | |
| BBA | $\rightarrow P_1' \rightarrow$ | BBB | | | + | BBA | (5) |
| $2(P_0P_1' + P_0'P_1)$ | | $2P_1'(P_0P_1' + P_0'P_1) + 2P_0'^2P_2$ | | $2(1 - P_1')(P_0P_1' + P_0'P_1)$ | | | |

Here, P_n ($n=0, 1, 2$) denotes the reaction probability of A unit in the center of AAA, BAA, and BAB, respectively. P_n' ($n=0, 1$) denotes those of A unit in the center of AAX and BAX, and X means A or B connected to the triads given above. Thus, P_0' is the average of P_0 and P_1 and P_1' , the average of P_1 and P_2 . The quantities shown under the hydrolyzed products means the relative molar concentrations of the products in the system. We can roughly estimate parameters such as $P_0, P_0', P_1, P_1',$ and P_2 at a reaction time of 60 min (or at half hydrolysis point) by putting experimen-

$$E_h (\%) = 100 \times \text{FB}/(\text{FA} + \text{FB})$$

Here, FA and FB denote carboxyl and carbamoyl carbon peak intensities, respectively. The E_h obtained from carbonyl and methine carbon peak intensities are collected in columns 1 and 2 of the Table II and they are in excellent agreement with each other. From Table II, it is obvious that the E_h remains almost constant for all hydrolyzed PAA samples being 50% on the average (maximum; 62%, minimum; 47%).

If the hydrolysis route of PAA by alkali is assumed to be a step-wise reaction on a given triad sequence and the reaction probabilities of A units in the center of the arbitrary triads considering the monomer units existed in both sides of the given triads are assumed different, then the route may be illustrated as follows:

tally determined fractions of the triads shown in Table I into the corresponding relative molar concentrations shown in the above scheme. For deriving these parameters for the hydrolysis of PAA in 5 wt% aq NaOH, fractions of BBB, BBA, and AAA were regarded as zero and for the hydrolysis of PAA (2 wt%) in 20 wt% aq NaOH, fractions of ABA and AAA were regarded to be zero. Several combinations of P_n and P_n' values were obtained as solutions. By considering $0 \leq P_n \leq 1.0$ and $0 \leq P_n' \leq 1.0$, we obtained $P_0=0.22, P_0'=0.39, P_1=0.34, P_1'=-0.5 (=0),$ and $P_2=0$ for the

former hydrolysis. This means that the BBA triad is hard to be produced from ABA, and BBB is not obtained from BAB and BBA. Thus, auto-retarded hydrolysis is proved here.

Contrary to this, for hydrolysis of PAA (2 wt%) in 9.1 wt% aq NaOH, $P_0=0.12$, $P_0'=0.44$, $P_1'=0.50$, $P_1=0.38$, $P_2=0.23$ were estimated as the suitable combinations of P_n and P_n' . This means an A unit next to B tends to be hydrolyzed faster than A unit adjacent to A unit but interestingly the A unit surrounded with B is relatively resistant to hydrolysis as is the case observed for the hydrolysis in 5 and 20 wt% aq NaOH. The reason why 9.1 wt% aq NaOH gives a specific hydrolyzed products of PAA is not clear at present. But, the following mechanism might be considered: In 5 wt% and 20 wt% aq NaOH solutions, 1 mol of Na^+ and OH^- ions in a system is strongly solvated to the same extent by about 5 or 3 mol of water at 4°C, although temperature rise lowers these numbers slightly.⁷ These masses, surrounded by only free water react as cationic and anionic masses.

On the other hand, in a 9.1 wt% aq NaOH, both Na^+ and OH^- ions are strongly solvated by 4 mol of water and on this layer there is a weakly bonded water layer, which is surrounded by free water.⁷ The weakly bonded layer was proved to act as energy transfer media.⁷ When a carboxyl group is introduced in the AAA sequence, a cationic mass will approach the carboxyl group for ion exchange, taking along an anionic mass. Provided that carboxylation of amide group starts with a nucleophilic addition reaction, the anionic mass react with an amide adjacent to the carboxyl group. However, if the anionic mass has no weakly bonded water, the anionic mass mainly plays the role as a neutralizing agent for protons departing from the carboxyl group as a result of ion exchange, losing the power as a nucleophilic reagent. Thus, in this case it is difficult to produce a BBA type triad (see Figure 3a). On the other hand, an anionic mass having weakly bonded layer approaches a B unit, and this

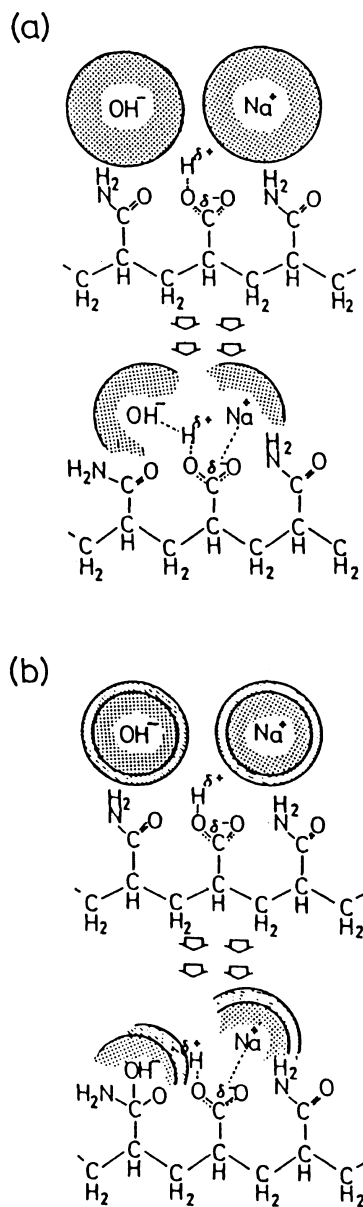


Figure 3. Schematic representation of the mechanism for alkaline hydrolysis of PAA in a, 5 and 20 wt%; b, 9.1 wt% aq NaOH.

weakly bonded water, which is more reactive than free water can initiate a nucleophilic reaction on the adjacent amide group besides function as a neutralizing agent, leading to the production of a BBA triad (see Figure 3b).

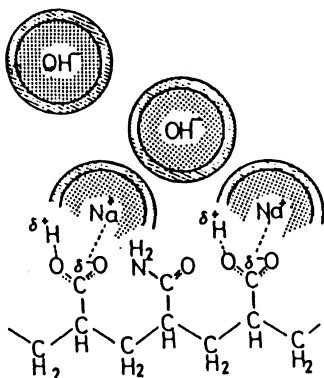


Figure 4. Schematic representation of a hindrance mechanism for A unit in BAB type triad of PAA in 9.1 wt% aq NaOH to be hydrolyzed.

Even in the latter case, if there is a BAB type triad, the anionic mass, whose ionic radius is more than 1 Angström, tends not to approach the A unit or the initiating power of nucleophilic reaction of the anionic mass might be hindered by the stiff affiliation of cationic mass with the adjacent two B units as illustrated in Figure 4.

This paper is the first to demonstrate that

the hydrolysis of PAA in a specific concentration (9.1 wt%) of aq NaOH medium gives a specific product having a sequence distribution of BBB, BBA, and BAB, ABB. Under other hydrolysis conditions, conventional products having alternative sequence distributions of acrylic acid and acrylamide residues were confirmed to be produced. A tentative hydrolysis mechanism is presented.

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