Ozone Treatment of Water-Soluble Polymers. III. Ozone Degradation of Polyacrylamide in Water

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Synopsis

Polyacrylamide (MW 350,000) was ozonized at pH 2 and pH 10 buffer solution. There was little ozonization at pH 2, but at pH 10 the COD and the viscosity of the solution decreased upon ozonization, and a linear relationship existed between the ozone consumed and the number of breaks calculated from the viscosity. This relationship apparently indicated that 45 molecules ozone were consumed for one cleavage of the polymer chain. Such random cleavage was confirmed also by the observation of molecular weight distribution by means of gel filtration chromatography. The amide group decreased scarcely by the ozonization, while a small amount of aldehyde was observed in the ozonized solution. No remarkable change was observed in the IR spectra of the ozonized sample, except for a weak absorption band at 1725 cm^{-1} which arose from the carbonyl of aldehyde or ketone. Although no variation was observed in the ^{13}C NMR spectra either, a strong absorption peak at 266 nm appeared in the UV spectra of the ozonized solution and increased with the ozonization time. This phenomenon was presumed to be due to the formation of a certain ring structure between the amide group and the small amount of ketone produced in the main chain. However, the details of the ozonization mechanism could not be ascertained.

INTRODUCTION

Polyacrylamide (PAA) is widely used as a flocculation water-treatment agent. Although there is no report on PAA residues in secondary effluents, a significant amount of PAA seems to be emptied into river water. Furthermore, no bacteria capable for utilizing PAA have yet been found. Consequently, if the polymer is abundant, it has to be removed or treated so that it can be degraded in nature.

We have been studying ozone degradation as a means for solving this problem and in previous papers reported the ozone degradation of polyethylene glycol[1] and bacterial utilization of ozonized polyethylene glycol.[2]

There is no report on the ozonization of PAA or any other amide compounds. Therefore, the aim of this report is to investigate the characteristics of ozone degradation of PAA in water.

EXPERIMENTAL

Polyacrylamide was prepared by radical polymerization in water at 80°C using potassium persulfate as initiator. The polymerized products were purified two times by precipitating with acetone. The molecular weight was measured by a viscometer and was found to be 350,000. The other chemicals used were commercial products.

The ozonization of PAA was carried out in 0.1% and 1% aqueous solutions

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prepared to pH 2 with hydrochloric acid–potassium chloride buffer (0.2*M*) or to pH 10 with carbonate–bicarbonate buffer (0.2*M*). The other ozonization techniques were the same as those described previously.[1] The chemical oxygen demand (COD) of the ozonized solution was measured by the oxidation method with potassium dichromate.

The intrinsic viscosity of the ozonized PAA, after $NaNO_3$ was added to the ozonized solution and the concentration was made 1.0*M*, was measured in 1.0*M* $NaNO_3$ aqueous solution at 30°C with an Ubbelohde viscometer. Under these conditions the effect of the base which constituted the original buffer solution on the solution viscosity was controlled within the experimental error. Consequently, the following equation concerning PAA was used to estimate molecular weight of the ozonized PAA[3]:

$$[\eta] = 3.73 \times 10^{-4} M^{0.66}$$

at 30°C in 1.0*M* $NaNO_3$ aq. solution. The number of breaks of PAA polymer chain was calculated previously described.[1]

The molecular weight distributions of the ozonized samples were measured by gel filtration chromatography with Sephadex G-100 gel (column size 2.6 cm $\phi \times 100$ cm). Sodium chloride solution, 1*M*, was used as solvent in order to prevent the adsorption of solute on the swollen gel. The sample volume was 5 ml, and the effluent was fractionated into 5-ml portions. The concentration of the solute in each fraction was measured with a Toshiba Beckman TOC analyzer. The relationship between elution volume and molecular weight was calibrated by using the following proteins as standards: γ-globulin (MW 160,000), albumin (MW 67,000), ovalbumin (MW 45,000), chymotrypsinogen-A (MW 25,000), myoglobin (MW 17,800), cytochrome C (MW 12,400), and bacitracin (MW 1450).

The aldehyde group in the ozonized solution was determined colorimetrically by the 2-hydrazinobenzothiazol method[4] using formaldehyde as standard. The UV spectra of the ozonized solutions were obtained with a Hitachi 323 recording spectrophotometer.

In order to avoid interference of the buffer solution and the salts with the analysis, a 1% PAA solution that was prepared to pH 12 with 1*M* NaOH at the beginning of the experiment was ozonized, and the amide group of the ozonized PAA was determined by Conway's diffusion method.[5] The ozonized solution was then lyophilized, and the IR spectra of the dried samples were observed by the KBr disk method with a Hatachi 225 infrared spectrophotometer.

The ^{13}C NMR spectra of the samples were measured with a JEOL PFT-100 NMR spectroscope under the following conditions: in about 20% aqueous solution, at room temperature, at a frequency of 25.03 MHz, and under proton noise decoupling. Chemical shifts were given in δ values using tetramethylsilane as external standard.

RESULTS AND DISCUSSION

Effect of pH on the Ozonization of PAA

PAA aqueous solutions of 0.1% were ozonized at pH 2 and 10. Figure 1 shows the plots of ozone consumed and COD of the solution versus ozonization time.

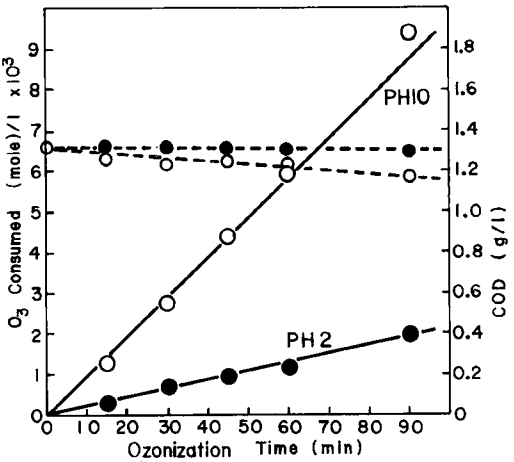

Fig. 1. Effect of pH on ozonization of PAA: full line, amount of ozone consumed; dashed line, COD of solution (0.1%); (○) pH 10; (●) pH 2.

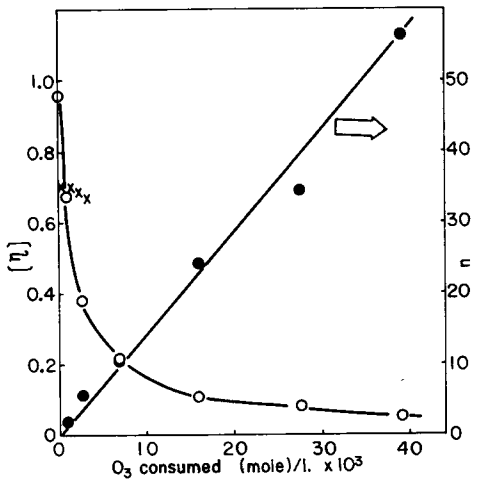

Fig. 2. Relationship between ozone consumed and intrinsic viscosity or number of breaks: (○) intrinsic viscosity at pH 10; (×) intrinsic viscosity at pH 2; (●) number of breaks at pH 10.

The ozone consumed at pH 10 was much larger than that at pH 2, but the decrease in COD was small even at pH 10 and was about 10% of the COD of the untreatment solution. The molar ratio of oxygen uptake to ozone consumed, as mentioned in the previous paper, was about 1 in the basic solution. This value indicates that one oxygen atom of one ozone molecule was used for the oxidation of PAA in basic solution. On the other hand, the decrease in COD of the acidic solution was slight and was within the range of experimental error. Consequently, the ozonization of PAA, as well as that of polyethylene glycol mentioned in the previous paper, was found to progress scarcely under acidic conditions.

Variation of Molecular Weight

The intrinsic viscosities of the 1% PAA solutions ozonized at pH 2 and 10 were measured in order to evaluate the lowering of molecular weight caused by the ozonization. Also the number of breaks of the polymer chain was calculated from

the viscosity data. The results were plotted against the ozone consumed per liter of PAA solution, as shown in Figure 2. In the basic solution, the intrinsic viscosity was lowered exponentially with increase in ozone consumed, while it was barely lowered in the acidic solution in spite of the ozone consumed, which was slight. A linear relationship was observed under basic condition between the number of breaks and the ozone consumed. This result shows that the main chain of the PAA was cleaved in proportion to the amount of ozone consumed. The straight line gave the value of the ozone consumed per one cleavage, which was 1.3×10^{-3} mole/l. Based on the molecular weight (350,000) of the original PAA and the concentration (1%) of the ozonization solution, this value signifies that 45 molecules ozone were consumed per one cleavage of molecular chain. Even if the measurement error of molecular weight and of ozone consumed is taken into consideration, this value is too large. Accordingly, it must be considered that ozone is consumed not only for the cleavage of the main chain.

The variation in molecular weight caused by the ozonization was observed not only by the solution viscosity but also by gel filtration chromatography. Figure 3 shows elution patterns of the solution ozonized at pH 10. The gel used was Sephadex G-100 and had exclusion limits of 1,000–150,000 (by dextran). Since the molecular weight of the original PAA was 350,000, the elution pattern of original PAA in Figure 3 appears in the outer exclusion volume. Therefore, it should be noted that the sharp elution pattern of the original PAA does not indicate the narrowness of molecular weight distribution. The elution volume of glucose (MW 180) which exceeded the separation limits of the gel was 470 ml. Consequently, the elution patterns of the samples ozonized for 60 and 120 min reflect the molecular weight distribution. Also, the area of each pattern is made equal in order to easily observe the variation of the molecular weight distribution. That is to say, the value of the ordinate in each fraction of the elution pattern refers to the proportion of the TOC of the fraction over the total TOC of the elution pattern. From the change in these patterns it was found that the PAA main chain was cleaved randomly by ozone and that the molecular weight was lowered with broadening of distribution.

The molecular weight of the two elution patterns was estimated on the basis

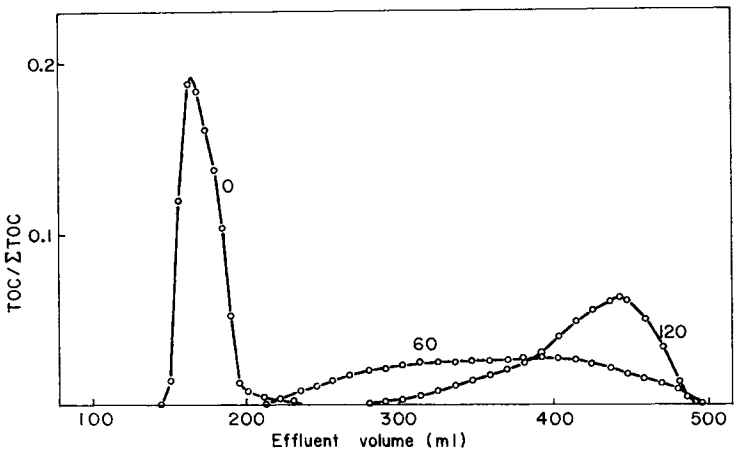

Fig. 3. Gel filtration chromatogram of original and ozonized PAA. Figures in each pattern show ozonization time. Column specifications: gel, Sephadex G-100; column size, 2.6 cm $\phi \times 10$ cm; solvent, 1.0 *M* NaCl aq. solution; detection, TOC.

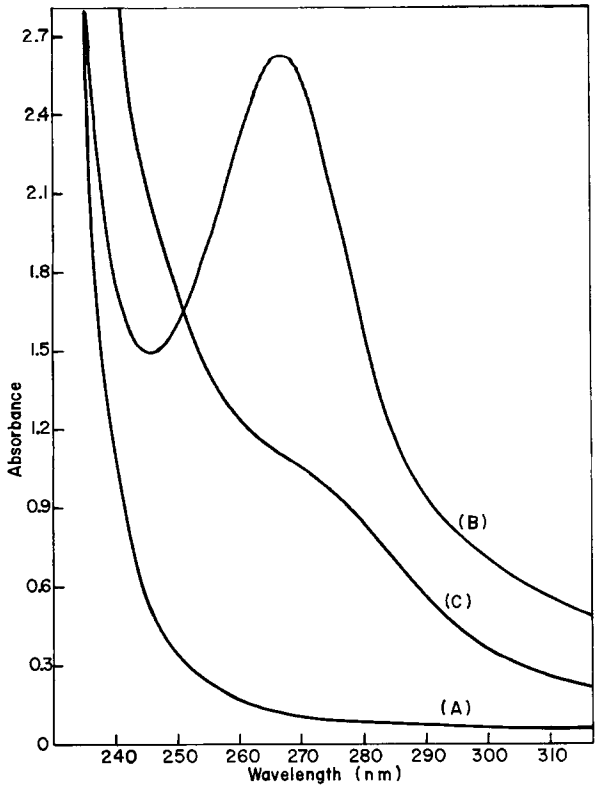

Fig. 4. UV spectra of ozonized PAA solution (1%): (a) original PAA solution; (b) PAA solution ozonized for 15 min at pH 10; (c) spectrum when concentrated HCl was added to the solution with spectrum B.

of the calibration curve, which was prepared using seven proteins of known molecular weights as standard. According to the method of Cazes, as well as a previous paper[1], the number-average and weight-average molecular weights of the sample ozonized for 60 min were 4500 and 20,000, respectively, and those of the sample ozonized for 120 min were 2800 and 5000, respectively. On the other hand, the viscosity-average molecular weight (data in Fig. 2) of the samples ozonized for 60 and 120 min were 15,000 and 4700, respectively. These values are consistent with the weight-average molecular weight obtained from the gel filtration chromatography.

Formation of New Functional Group

Ozonization is an oxygen oxidation, and it is expected that the carbonyl of aldehyde, carboxylic acid, or ketone is formed as a new functional group. Accordingly, the aldehyde in the ozonized solution was determined by the 2-hydrazinobenzothiazole method. The results are shown in Table I. Under basic conditions, the amount of aldehyde reached a maximum by 15 min of ozonization and then decreased on further ozonization. On the other hand, under acidic conditions, although the amount of aldehyde reached a maximum at the initial ozonization, the amount remained unchanged upon further ozonization. These results suggest that the aldehyde formed as a result of the polymer chain cleavage

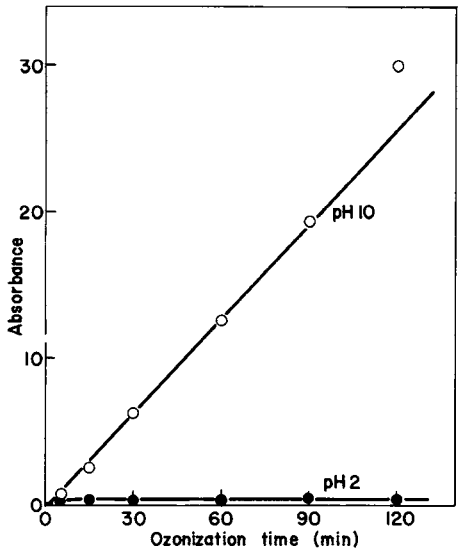

Fig. 5. Variation of absorbance in PAA solution at 266 nm by ozonization at pH 2 (●) and pH 10 (○).

TABLE I
Production of Aldehyde by Ozonization of PAA

Reaction time, min	pH 2		pH 10	
	Ozone consumed, (moles/l.) × 10^3	Aldehyde,[a] (moles/l.) × 10^3	Ozone consumed, (moles/l.) × 10^3	Aldehyde,[a] (moles/l.) × 10^3
15	0.4	10.58	2.8	5.66
30	0.7	10.76	7.0	4.52
60	1.6	10.53	15.9	1.28
90	2.7	9.60	27.6	0.21
120	3.5	9.56	39.0	0.06

[a] These values indicate the amount of aldehyde groups corresponding to that of formaldehyde.

was further oxidized to carboxylic acid by ozone under basic conditions but was stable under acidic conditions. The carboxylic acid formed by ozonization could not be determined, because the amide carbonyl interfered with the determination of carboxyl groups by the conventional methods.

Next, the amide group was determined to determine its stability against ozone attack. The results are shown in Table II. The analytical values are almost unchanged during the ozonization and indicate that the amide group hardly reacts with ozone. The same result was confirmed also by means of IR and ^{13}C NMR spectra as described below.

In UV spectra of the ozonized solutions, a strong absorption maximum appeared freshly at 266 nm. Figure 4 shows the absorption spectra of the solution ozonized for 15 min at pH 10 (spectrum B) and of original PAA (spectrum A) without the absorption maximum. Figure 5 shows the ozonization-caused variation in absorbance of the PAA solution at 266 nm. From these results, the absorption intensity at 266 nm at pH 10 was found to increase in proportion to

TABLE II
Amide Group of Ozonized PAA

Reaction time, min	Ozone consumed, (moles/l.) × 10^3	Amide group, (moles/l.) × 10^2
0	0	10.75
5	1.24	10.75
15	4.14	10.75
30	9.37	10.63
60	18.60	10.75
90	25.07	10.75

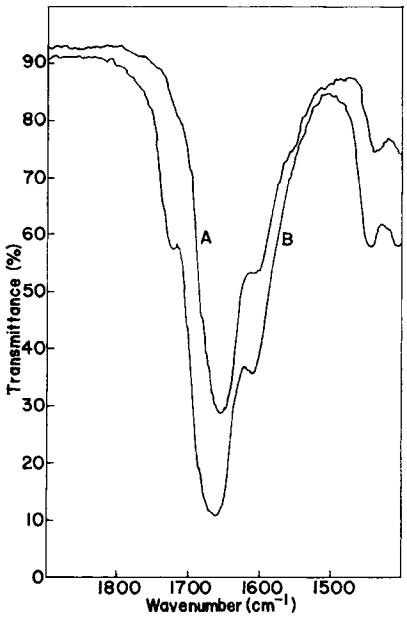

Fig. 6. IR spectra of ozonized PAA (KBr disk): (a) original; (b) PAA ozonized for 120 min.

the ozonization time. Although the absorption maximum appeared also in acidic ozonization, the intensity increased only at the initial ozonization and remained approximately constant afterward. Furthermore, the absorption maximum disappeared when concentrated HCl was added to the solution (at that time, the acidity of the solution was less than pH 1). The spectrum C in Figure 4 shows the alteration in spectrum B by the addition of HCl. The absorption maximum, however, appeared again with the same intensity upon addition of strong base. In the ozonized solution of pH 2, the absorbance did not change upon addition of strong base.

Now, it is known that primary amide adds to the carbonyl group of aldehyde and ketone and leads to the carbinolamine derivative and that such addition of amide is both reversible and catalyzed by acids and bases.[6] However, such carbinolamine derivatives as are produced from PAA and formaldehyde cannot have a UV absorption band at 266 nm, and in fact it was not observed. Therefore, the above phenomena suggest that a new functional group, perhaps aldehyde or ketone which was produced in the polymer chain by ozonization, combined with the amide group to form a certain ring structure.

On the other hand, the gel filtration pattern of the sample ozonized for 120 min was observed again by measuring the absorbance of each fraction at 266 nm. As a result, the pattern agreed completely with that of Figure 3 that was depicted on the basis of TOC. If the functional group that contributed to the UV spectra is a terminal group of the ozonized PAA, the two patterns ought not to agree with each other. And the intensity in the low molecular weight region of the pattern by the UV method ought to be stronger than that of the pattern by the TOC method, because the more the molecular weight decreases the more the number of terminal groups increases. Therefore, this result indicates that the new functional group responsible for the UV spectra is not the terminal group of the ozonized PAA but the group in the main PAA chain, probably ketone.

In order to determine the new functional group, IR and ^{13}C NMR spectra were observed with freeze-drying samples ozonized in 1% solution at pH 12; the solution naturally had the absorption maximum at 266 nm. Figure 6 shows the IR spectra in the wavelength region of 1400–1900 cm^{-1} of the original PAA and of the sample ozonized for 120 min. Both spectra have two absorption peaks, at 1660 cm^{-1} and 1610 cm^{-1}, which were assigned to the —C=O stretching and —N—H bending vibrations of the amide group, respectively. In the case of the ozonized sample a new absorption peak was observed at 1725 cm^{-1} in addition. This absorption band may be due to —C=O stretching of aldehyde or ketone. However, the absorption intensity was weak and approximately constant in the ozonization subsequent to the initial ozonization (30 min). Consequently, no correlation was observed between the absorption intensity of IR spectra and that of UV spectra at 266 nm already described.

Figure 7 shows the ^{13}C NMR spectrum of the sample ozonized for 90 min. Also the spectrum of original PAA was the same as that in Figure 7 and had only three signals, of 179.7 ppm, 42.2 ppm, and 35.1 ppm, which were all due to PAA and assigned to the carbon of —C(=O)—NH_2, —CH, and —CH_2, respectively. Consequently, none of new signals, not even the signal that arose from a new terminal

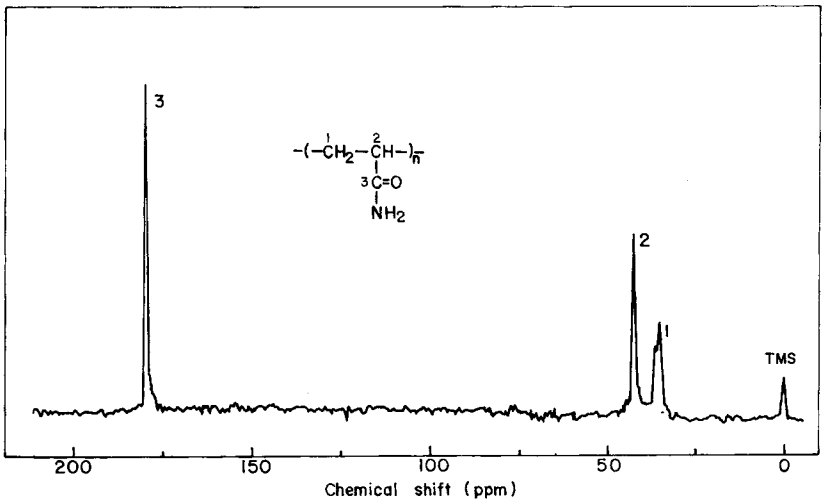

Fig. 7. ^{13}C NMR spectrum of ozonized PAA: instrument, JEOL PFT-100 NMR spectroscope; frequency, 25.03 MHz (complete proton decoupling); pulse width, 11 μsec (for ca. 45° pulse); pulse interval, 3.0 sec (2000 scans); chemical shift of each signal, (1) 35.11 ppm, (2) 42.19 ppm, (3) 179.72 ppm.

group and, needless to mention, the signal that arose from a new group in the main chain, was observed in the ozonized sample. These results appear to indicate that the new functional group responsible for the UV absorption band is too small to be detected by means of IR and NMR spectra.

Thus, it can be presumed that the new functional group responsible for the UV spectra is ketone produced in the main chain through attack of ozone on α-hydrogen and that the ketone also contributes to the cleavage of the polymer chain. However, the details of the ozonization mechanism were not ascertained from the experiment described above. An experiment concerning the model compound of PAA seems to be necessary to ascertain the mechanism.

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