

Ozone Treatment of Water-Soluble Polymers. IV.

Ozone Degradability of Water-Soluble Polymers

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Synopsis

The ozone degradability of water-soluble polymers, i.e., polyethylene glycol, poly(vinyl alcohol), poly(vinyl pyrrolidone), polyacrylamide, and sodium polyacrylate, was studied in the aspects of ozonization rate and degradation efficiency. The reactions of ozone with polymers were first order, respectively, with respect to ozone and polymer, except poly(vinyl alcohol) under basic condition ($1/2$ order with respect to ozone). The reaction rate of poly(vinyl pyrrolidone) was the largest, while those of polyacrylamide and sodium polyacrylate were almost zero. The absorption rate of ozone into the polymer solution was affected by the reaction rate, the foaming property of solution, and the self-decomposition of ozone. In terms of chain breakage and complete oxidation to CO_2 , the degradation efficiency of polyethylene glycol was the best, and that of poly(vinyl pyrrolidone) was poor in spite of the high reaction rate. A little degradation was observed also in the case of polyacrylamide and sodium polyacrylate.

INTRODUCTION

Reactions of ozone with unsaturated hydrocarbons have been investigated very extensively. Much less work has been done on the corresponding reactions with saturated hydrocarbons.¹⁻³ In particular, the reaction in aqueous solution has been scarcely investigated.^{4,5} Ozonization in water is very complicated because the self-decomposition of ozone is catalyzed by hydroxyl ion,^{6,7} and is not always the same as that in organic solvents.

The preceding papers in this series have covered the ozonization of polyethylene glycol (PEG) and polyacrylamide (PAA) in water.^{8,9} The ozonizations of these water-soluble polymers have been found to be effective for lowering molecular weight, and consequently also effective for improving their biodegradability.¹⁰ However, the ozone degradabilities of the other water-soluble polymers are entirely obscure because of the reason mentioned above. Finding the oxidation efficiency in ozonization and the reaction rates of ozone with water-soluble polymers, as well as finding the mechanism of the reaction, is significant and indispensable for judging if an ozonization be suitable for treatment of each water-soluble polymer.

In this paper, therefore, the ozone degradabilities of five kinds of water-soluble polymers, i.e., PEG, PAA, poly(vinyl alcohol) (PVA), poly(vinyl pyrrolidone) (PVP), and sodium polyacrylate (PANa) were studied in the aspects of ozonization rate and degradation efficiency.

EXPERIMENTAL

Materials

PAA was prepared by radical polymerization in water at 80°C using potassium persulfate as initiator, and the polymerized product was then purified twice by precipitating with acetone. The other polymers were obtained from Wako Pure Chemical Industries Ltd. The approximate average molecular weights of these polymers were estimated by viscosity measurement as follows: PEG, 10,000; PVP, 27,000; PVA, 28,000; PANa, 410,000; and PAA, 280,000. All other chemicals used in this work were of special grade.

Methods

Ozonization Techniques. The ozonization apparatus and the techniques used in this work, except the case of measuring the rate constant of ozone-polymer reaction, were the same as those described in the previous paper.⁸ The ozonization of polymers was carried out at a concentration of 0.025% for TOC measurement, 0.1% for the measurement of ozone absorption rate and COD, and 1% for the measurement of solution viscosity. The solvents used were KCl-HCl buffer (pH 2), NaH₂PO₄-Na₂HPO₄ buffer (pH 7), and NaHCO₃-Na₂CO₃ buffer (pH 11).

Rate Constant of Ozonization. The rate constants of the reaction of ozone with polymers in water were determined at 3°C by the use of the apparatus illustrated in Figure 1. Solvent (the buffer solution of prescribed pH) was placed in a four-neck flask and in one syringe, and the polymer solution of prescribed concentration (100 ml) was placed in the other syringe which was separated from the solvent by a stopper. At first, the solvent was saturated with ozone and then the bubbles formed by blowing ozone were removed completely by pushing out all of the solvent into the flask from the syringe. At that time, the solvent saturated with ozone was circulated through a flow cell. Then, the polymer solution was injected into the flask from the syringe and stirred by operating the two syringes (initiation of reaction). The decay of ozone in the solution was determined on the basis of absorbance at 260 nm with an UV spectrophotometer. All of the solvents and the polymer solutions were filtered with a membrane filter

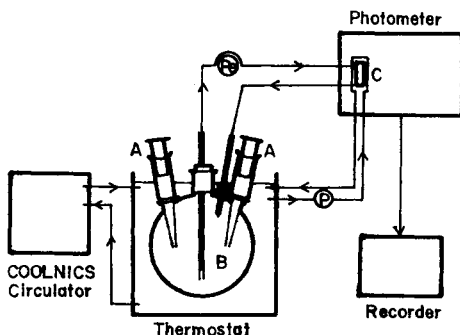


Fig. 1. Apparatus used for the kinetic study of the reaction of ozone with water-soluble polymers in water: (A) 100 ml syringe; (B) 300-ml four-neck flask; (C) thermostated flow cell; (P) pump; (Pe) perista pump for circulation of the solution (silicone tube was used).

with a pore size of 0.1 μm in order to remove contaminants which affect the decay rate of ozone. In this manner rate constants of reaction of ozone with polymers in water were determined by the isolation method.

Absorption Rate of Ozone. The amount of ozone consumed in the reactor, in which 100 ml of sample solution was placed, was calculated from the difference between the amount of residual ozone in the reactor and that of the ozone evolved. A plot of the ozone consumed against reaction time was linear in the initial period of reaction, and the slope of the straight line gave the absorption rate of ozone.

COD and TOC of Solution. The COD of solution was measured by the oxidation method with potassium dichromate, and the results were expressed in term of molar ratio of oxygen uptake/ozone consumed—the oxygen atom (mole) used for oxidation of polymer in 1 mole of ozone consumed. This value indicates an oxidation efficiency in the ozonization.

The TOC of solution was measured with a Shimazu TOC analyzer to determine the effect of ozonization on complete oxidation to CO_2 . The result was expressed in terms of oxidized carbon (mole) per mole of ozone consumed.

Estimation of Molecular Weight. The lowering of molecular weight was observed by means of viscosity measurement. The intrinsic viscosities of ozonized polymers were measured in following solvents at 30°C with an Ubbelohde viscometer, and the average molecular weights were estimated on the basis of the following equations for respective polymers:

$$\text{PEG; } [\eta] = 1.25 \times 10^{-4} M^{0.78}$$

in water,¹¹

$$\text{PVA; } [\eta] = 6.66 \times 10^{-4} M^{0.64}$$

in water,¹²

$$\text{PVP; } [\eta] = 1.40 \times 10^{-4} M^{0.70}$$

in water,¹³

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

in 1.0 M NaNO_3 aqueous solution,¹⁴ and

$$\text{PANa; } [\eta] = 12.1 \times 10^{-4} M^{0.5}$$

in 1.25 M NaSCN aqueous solution.¹⁵ The buffer solution used as a solvent in ozonization affected scarcely the estimation of molecular weight. The number of breaks in the polymer chain was estimated according to the method of Sakurada,¹⁶ and the amount of ozone consumed per one break of the polymer chain was further calculated on the basis of the number of breaks, the ozone consumed, and the molecular weight of the original polymer.

RESULTS AND DISCUSSION

Ozonization Rate

Figure 2 shows the pseudo-first-order plots of the ozone decay in various polymer solutions. These plots gave straight lines with most of the water-soluble polymers used, and indicated that the reactions of ozone with polymers in water

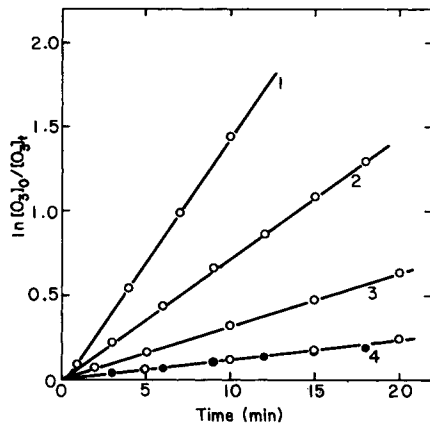


Fig. 2. Pseudo-first-order plots of ozone decay in various polymer solutions (pH 2, 3°C): (1) PVA; $13.1 \times 10^{-3}M$, (2) PVP; $8.69 \times 10^{-3}M$, (3) PEG; $21.9 \times 10^{-3}M$, (4) PAA; $27.1 \times 10^{-3}M$, PANa; $20.5 \times 10^{-3}M$, and buffer solution of pH 2.

were first-order with respect to ozone. Furthermore, these pseudo first-order rate constants (k') increased linearly with increasing polymer concentration (one monomer unit was taken as one mole) as shown in Figure 3. Consequently, the second-order rate constants concerning the ozone-polymer reaction were obtained from the slope of k' -polymer concentration plots. The results are shown in Table I. The most rapid reaction rate was observed in the case of PVP at pH 10. The rate constants, zero, in PAA and PANa mean that the decay rate of ozone in those polymer solutions is the same as the self-decomposition rate of ozone in the solvent (the rate constants at pH 2, 7, and 10 were 1.22×10^{-2} , 2.52×10^{-2} , and $12.92 \times 10^{-2} \text{ min}^{-1}$, respectively). That is to say, ozone does not react directly with PAA or PANa, except the slow reaction with PAA at pH 10. These results suggest that carboxyl group and amide group are resistant to ozone. Such resistance of amide group has been reported also in the previous paper.⁹ The reaction of ozone with PVA was $3/2$ -order reaction ($1/2$ -order with respect to ozone) only at pH 10. The pseudo-first-order rate constants of PEG at pH 7 and 10 were independent of the polymer concentration, and the reproducibility of

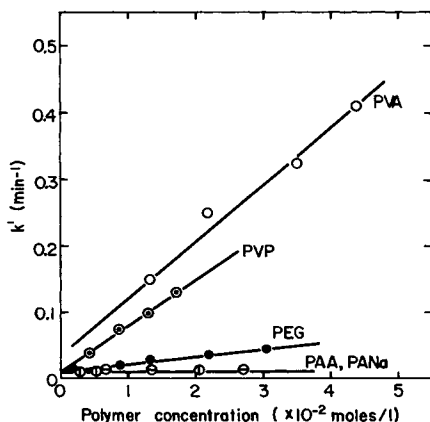


Fig. 3. Plots of pseudo-first-order rate constant (k') against polymer concentration in the ozonization at pH 2 and 3°C.

TABLE I
Rate Constants of the Reaction of Ozone with Water-Soluble Polymers in Water at 3°C
(l/mol-min)

Polymers	pH 2	pH 7	pH 10
EG	2.23	151.10	459.6
DEG	2.44	5.58	314.7
PEG	0.99	—	—
PVA	8.16	7.38	(3.72) ^a
PVP	7.02	24.56	3757
PAA	0	0	10.9
PANa	0	0	0

^a The $\frac{3}{2}$ -order reaction ($\frac{1}{2}$ -order with respect to ozone); dimension, l^{1/2}/mol^{1/2}·min.

the data was invariably poor. This abnormal phenomenon was not observed in ethylene glycol (EG) or diethylene glycol (DEG), which were measured for comparison. The cause of this phenomenon is obscure, but it is presumed to be due to the secondary reaction of ozone with a primary ozonization product. The rate constants concerning EG and DEG suggest that the ether bond is slow to react with ozone compared to a primary alcohol.

On the other hand, the rate of ozone treatment is governed essentially by the absorption rate of ozone into solution, and the absorption rate is an important factor in ozone treatment. However, the absorption rate of ozone is affected by many factors, e.g., contact time of gas-liquid, foaming property, solute concentration, reaction rate of ozone with solute, etc. The data of the absorption rate shown in Table II are relative values which were obtained under the same experimental condition with respect to solution volume (100 ml), polymer concentration (0.1%), temperature (room), and bubbling rate of ozone (10 mg/min). These values are not always compatible with the rate constants in Table I. The difference of the foaming property in each polymer solution is probably responsible for the disagreement. The large values in PEG and PVP at pH 11 are due to the high foaming properties and/or high reaction rate of ozone with the polymer. PVA foamed so vigorously that the absorption rate was not observed. The absorption rates in PAA and PANa solutions are about the same as those in buffer solutions. This is explicable by the rate constants in Table I. Such absorption of ozone in PAA, PANa, and the buffer solution is due to the self-decomposition of ozone in the solution. Accordingly, the absorption rate of ozone is not necessarily proportional to the degradation of polymer (which is manifested as the drop of TOC, COD, and solution viscosity).

TABLE II
Absorption Rate of Ozone into the Aqueous Solution (0.1%) of Water-Soluble Polymers

Polymers	Absorption rate (O ₃ mol/min) × 10 ⁵		
	pH 2	pH 7	pH 11
PEG	0.4	2.2	13.1
PVP	0.5	3.8	10.8
PAA	0.4	0.6	5.4
PANa	0.4	1.4	5.2
Solvent ^a	0.0	0.2	4.7

^a Buffer solution of respective pH.

Degradation Efficiency

One of the most important subjects in the ozone treatment of polymers is the lowering of molecular weight. The ozone absorbed into the polymer solution is not always consumed only so as to lower the molecular weight as mentioned above. Then, the amount of ozone consumed per one break of polymer chain was estimated from the measurement of solution viscosity and ozone consumed, and the values were shown in Table III. The values of ozone consumed include the ozone used in self-decomposition and to partial oxidations other than chain breakage. Accordingly, the values in Table III indicate the application efficiency of ozone for the breakage of polymer chains. That is to say, the larger the value is, the larger the amount of ozone used in reactions other than chain breakage.

As can be seen from Table III, the polymer chain of PEG was the most effectively broken by ozone. On the other hand, the large value concerning PVP, whose rate constant of ozonization was the largest, as mentioned previously, suggests that reactions other than chain breakage occurred appreciably in the ozonization. The large values in PAA and PANa, which do not react directly with ozone, may be due to the consumption of ozone by self-decomposition. These values, however, indicate simultaneously that polymer chain breakage results also from the self-composition of ozone without the direct attack of ozone on the polymer. This chain breakage seems to be due to the attack of the nascent oxygen produced in the self-decomposition process of ozone.

All of the chemical changes that result from ozonization are oxidative reactions, including the breaking of the polymer chain. The progress of degradation by ozone treatment, accordingly, can be appreciated by determining the degree of oxidation in solution, that is, COD of solution. The CODs of the polymers used in this work were approximately equal to the amount of oxygen required to completely oxidize the polymer to CO_2 and H_2O . Consequently, the utilization efficiency of ozone for oxidation could be calculated from the decrease in the COD of the solution.

Table IV shows the results in term of oxygen uptake (moles of oxygen atom) per ozone consumed (1-mole ozone). These values of oxidation efficiency were 2 to 3 in most of the polymers. This result means that two or all oxygen atoms of the ozone molecule consumed are used in the oxidation of polymer. The small values in PAA and PANa at pH 11 seem to be due to the contribution of the self-decomposition of ozone. However, even if a part of the ozone absorbed into the solution should be consumed by the self-decomposition, it is undoubtedly true that all of the polymers were oxidized and degraded effectively in proportion to the amount of ozone consumed. No such result in acidic solution was shown

TABLE III
Lowering in Molecular Weight of Water-Soluble Polymers by Ozonization—the Amount of Ozone Consumed per One Break of Polymer Chain

Polymers	pH 2	pH 7	pH 11
PEG	3.8	3.5	3.9
PVA	—	—	4.9
PVP	8.5	24.1	76.6
PAA	70.7	19.3	15.2
PANa	5.4	12.6	28.1

TABLE IV
Oxidation Efficiency of Water-Soluble Polymers in Ozonization

Polymers	Oxidation efficiency (O/O ₃) ^a	
	pH 7	pH 11
PEG	1.7	1.8
PVA	—	1.9
PVP	2.9	1.9
PAA	2.8	0.7
PANa	3.0	0.7

^a The amount of oxygen uptake per mole of ozone consumed: oxygen uptake was calculated from the drop in COD of the solution.

TABLE V
The Amount of Carbon Oxidized to CO₂ in Ozonization

Polymers	Oxidized C (mole)/O ₃ (mole) consumed	
	pH 7	pH 11
PEG	0.31	0.32
PVP	—	0.00
PVA	0.13	0.06
PAA	0.00	0.03
PANa	0.71	0.16

because the ozone consumed and COD drop was too low to be determined without large errors.

On the other hand, the drop of TOC results only in the case where the organic carbon of polymer leads to CO₂ by ozonization. The values in Table V show the amount of carbon (mole) oxidized to CO₂ by one mole of ozone consumed, which were calculated from the TOC drop in polymer solution. These values are very small compared with that of the oxygen uptake. This result indicates that the complete degradation of the polymers to CO₂ proceeded scarcely during the ozonization, except for PEG and PANa.

Above described results lead us to the conclusion that the ozone treatment of the water-soluble polymers in water is the most suitable for lowering of molecular weight, but unsuitable for the complete degradation to carbon dioxide.

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