

UV-Irradiated Ozonation of Water-Soluble Polymers

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Synopsis

The effect of ultraviolet light on the ozonation of some water-soluble polymers such as polyethylene glycol, polyacrylamide, carboxymethyl cellulose, and poly(vinyl alcohol) was investigated. Ultraviolet light irradiation accelerated the ozonation. Acceleration was caused by the decomposition of ozone by ultraviolet light, which produced active species.

INTRODUCTION

Water-soluble polymers are widely used as water-treatment agents, food additives, antifreeze, and in cosmetics. Their discharge into the environment may cause serious water pollution because some of them are inert to biological degradation and may accumulate in nature; although polyethylene glycol can be degraded by *Acinetobacter* SC 25, *Pseudomonas* KW 8, or *Flavobacterium* BT, the rate of degradation is slow.¹ Moreover, they are hard to remove completely and economically by ordinary physicochemical treatments such as adsorption or reverse osmosis.

Ozonation of waste water has been investigated extensively²⁻⁶; however, there has been little work on the ozonation of water-soluble polymers in the aqueous phase.^{7,8} Despite the powerful oxidizing ability of ozone, the efficiency of ozonation is low, owing to the gas-liquid heterogeneous nature of the reaction. Moreover, complete removal of organic compounds cannot be attained because refractory compounds are formed during ozonation. However, the use of ultraviolet light accelerated the ozonation of relatively low molecular weight organic compounds.⁹

In this work, ozonation of some water-soluble polymers was carried out under ultraviolet light irradiation in an attempt to degrade these polymers completely.

EXPERIMENTAL

The reaction apparatus is shown in Figure 1. Reactions were carried out usually at 30°C by use of a reaction vessel (liquid volume 180 ml) equipped with a 100-W high-pressure mercury lamp and a vessel (liquid volume 110 ml) equipped with a 15-W low-pressure mercury lamp. Unless otherwise stated, the 100-W high-pressure mercury lamp was used. Ozone was produced from oxygen by a Nippon Ozone 0-3-2 ozonizer. The flow rate of ozonized oxygen was 500 ml/min, and the ozone feed rate was 29 mg/min. The ozone concentrations at the inlet and outlet of the reaction vessel were measured using a Shimadzu UV-200S spectrophotometer.

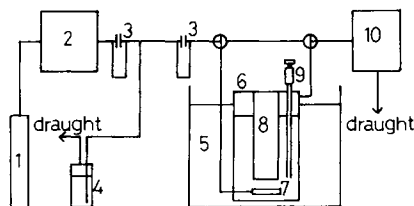


Fig. 1. Apparatus: (1) oxygen cylinder; (2) ozone generator; (3) flowmeter; (4) KI solution; (5) thermostat; (6) reactor; (7) gas distributor; (8) mercury lamp; (9) syringe; (10) UV spectrometer.

G.R.-grade polymers, buffers, or other reagents were used without further purification.

Total organic carbon (TOC) was analyzed using a Shimadzu TOC-10A TOC analyzer, and chemical oxygen demand (COD) was measured by oxidation with potassium permanganate (COD_{Mn}) and with potassium dichromate (COD_{Cr}). Molecular weight of polyethylene glycol (PEG) was estimated using the viscosity-molecular weight relationship derived by Bailey et al.,¹⁰ and the number of chain scissions of PEG was calculated according to the method of Sakurada et al.¹¹

RESULTS AND DISCUSSION

Effect of Ultraviolet Light Irradiation on Ozonation of PEG

PEG with a molecular weight of 2000 (PEG-20000), 20000 ppm of an aqueous solution, was ozonized and the effect of ultraviolet light (UV) was investigated. The result is shown in Figure 2. Although the molecular weight decreases considerably by ozonation alone, the rate of the decrease is much higher under UV irradiation; ozonation alone requires more than 100 min to decrease molecular weight to 2000, while with UV irradiation only 40 min is required.

The rate of ozonation is accelerated markedly in alkaline media, which suggests that active species are produced in the decomposition of ozone catalyzed by hydroxide ion.^{12,13} Therefore, the effect of pH was investigated in the UV-irradiated ozonation.

Figure 3 shows the effect of pH on the time course of the change of intrinsic viscosity $[\eta]$ and of ozone consumption. The rate of the decrease of $[\eta]$ is much higher and the quantity of ozone consumed is much larger at pH 12 than at pH

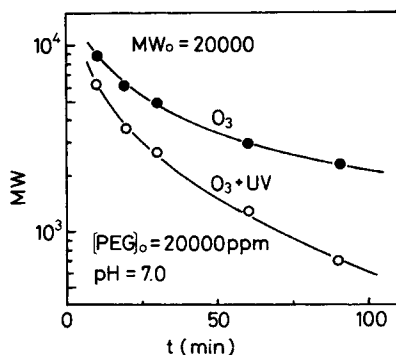


Fig. 2. Effect of UV on the ozonation of 20000 ppm PEG-20000.

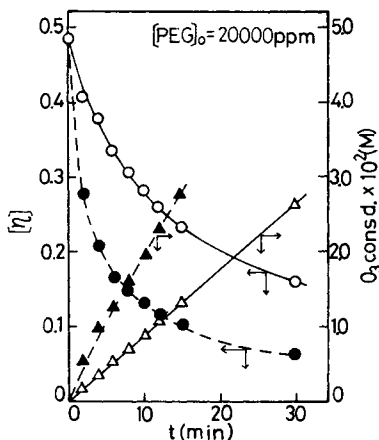


Fig. 3. Plot of t vs. $[\eta]$ and ozone consumed. (—), pH = 4; (---), pH = 12.

4. The number of chain scissions per one molecule PEG, n , and $[\eta]$ were plotted against the quantity of ozone consumed in Figure 4. More chains are broken at pH 12 than at pH 4 and the number of chain scissions ranged from 0.13 to 0.23 at the pH 2–12. Hydroxide ion accelerates the UV-irradiated ozonation.

Figure 5 shows the effect of pH on the degree of ozone absorption, ξ , in pure water. Ozone absorption is remarkably increased by UV irradiation in the acidic and neutral regions, which is in accord with the strong oxidizing ability of the

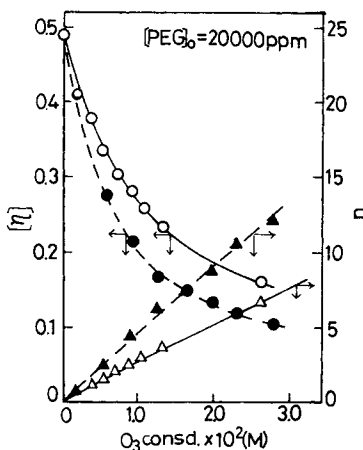


Fig. 4. Ozone consumed vs. $[\eta]$ and n . For legend, see caption on Fig. 3.

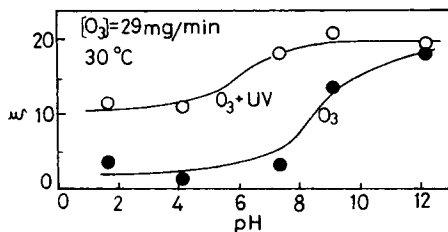


Fig. 5. Effect of pH on ozone absorption in water.

ozone-UV system discussed above. As pH increases, both ξ 's with and without UV irradiation increase and reach about the same value at pH 12. Raising the pH of the solution has an accelerating effect on ozonation by the same degree as UV irradiation, and UV has no effect at pH above 12. In order to examine this, ozonation was carried out at pH 7 and 13 and the effect of UV was investigated. The effect of UV irradiation is remarkable both at pH 7 and 13; the rate of the decrease of TOC is higher under UV irradiation (Fig. 6). At pH 7 the amount of acid (assumed to be monobasic acid) accumulated after 3 hr was 0.013M in the UV-irradiated ozonation, while only 0.006M acid was detected in the ozonation without UV. Thus, the reaction proceeds more extensively under UV irradiation in the whole pH range. Reactions were carried out in the neutral region without pH adjustment.

In the ozonation of 20,000 ppm PEG-20000, ozone is mainly consumed in the degradation of the polymer chain and TOC is scarcely removed. Therefore, PEG-20000 in low concentration (200 ppm) was ozonized and the effect of UV on the decrease in TOC or COD was investigated.

The initial value of COD_{Mn} (68 ppm) is considerably lower than theoretical (360 ppm) (Fig. 7). As the reaction proceeds, it increases to a maximum in both ozone alone and ozone-UV cases, which suggests that the polymer is decomposed to lower molecular weight compounds which are sensitive to COD_{Mn} analysis. However, the maximum of COD_{Mn} under UV is much higher than that in ozonation alone, and it decreases to zero as the reaction proceeds. Ozonation alone cannot remove it completely. Although TOC scarcely decreases with ozonation, its complete removal is achieved by the combined use of UV after some induction period. As COD_{Mn} increases during the induction period of TOC decrease, the degradation to lower molecular weight compounds precedes TOC decrease. Complete removal of COD_{Cr} is also observed under UV irradiation.

Figure 8 shows the effect of molecular weight of PEG on the rate of the decrease of TOC in the UV-irradiated ozonation. Although TOC decrease in the ozonation of PEG-20000 has some induction period, TOC of other relatively low molecular weight PEGs easily decreases. Decrease in the molecular weight occurs during the induction period of TOC decrease.

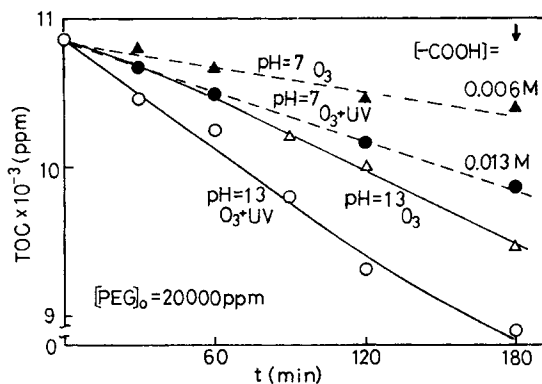


Fig. 6. Effect of UV on TOC decrease.

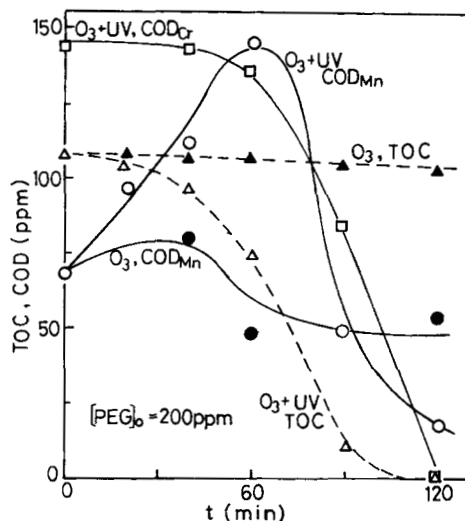


Fig. 7. Effect of UV on the ozonation of 200 ppm PEG-20000.

UV-Irradiated Ozonation of Other Polymers

The effect of UV on the ozonation of carboxymethyl cellulose (CMC), poly(vinyl alcohol) (PVA), and polyacrylamide (PAA) is presented. Time course of the change in relative viscosity, η_{rel} , is shown in Figure 9. The decrease in η_{rel} of CMC is very rapid, and no difference in the rate can be seen between the UV-irradiated ozonation and the ozonation alone. UV irradiation accelerates the decrease of η_{rel} of PVA and PAA; however, the effect is small. Judging from the decrease in η_{rel} , UV has little effect on the ozonation of these polymers. Therefore, we observed a change in TOC and COD in the ozonation of low concentration (200–300 ppm) of these polymers. The results are shown in Figures 10–12. The effect of UV is also noteworthy as in the case of the ozonation of PEG. UV-irradiated ozonation of PVA results in a decrease in TOC to zero after 120 min (Fig. 10), while ozonation alone scarcely removes it. COD_{Mn} is at

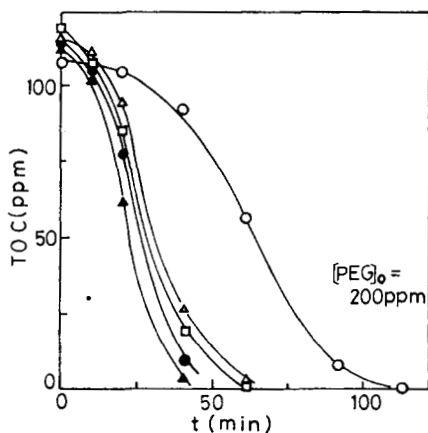


Fig. 8. UV-Irradiated ozonation of 200 ppm PEG. Effect of molecular weight. MW: (○), 20,000; (Δ), 7500; (□), 3000; (●), 1000; (▲), 400.

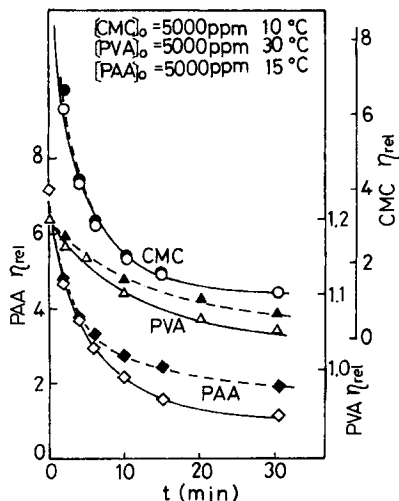


Fig. 9. Effect of UV on the ozonation of some polymers. t vs. η_{rel} \circ (---), O_3 ; (—), $O_3 + UV$.

maximum after 20 min in both UV–ozone and ozone cases. However, it decreases rapidly to zero in the former case while ozone cannot remove it completely. Almost the same phenomena are seen in the ozonation of CMC and PAA. From the results obtained thus far, it is clear that UV has a remarkable effect on the ozonation of the polymers and that their complete degradation is possible.

Consideration on the Effect of UV

Plengle et al.⁹ states that UV activates the ozonation of organic compounds and produces radical species. In order to examine their deduction, we conducted the ozonation of acetic acid (a model compound as a degradation product of the

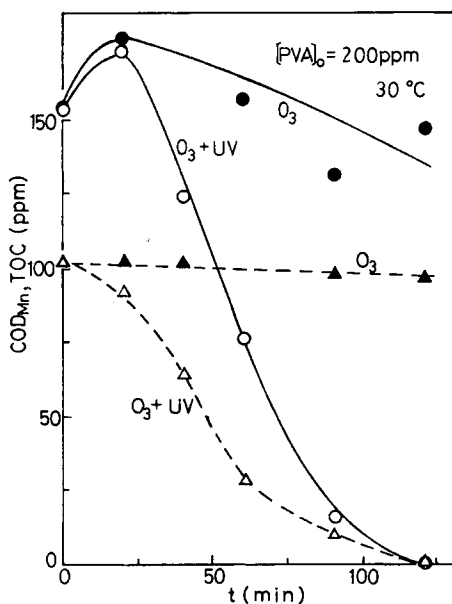


Fig. 10. Effect of UV on the ozonation of 200 ppm PVA. (—), COD_{Mn} ; (---), TOC.

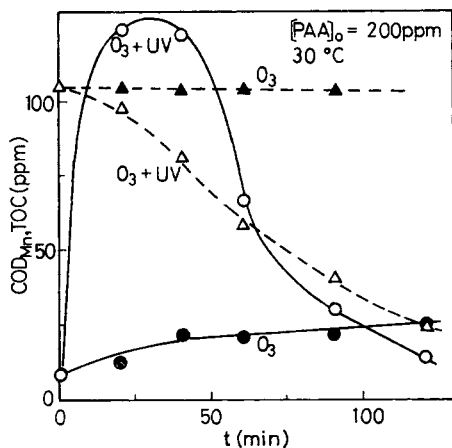


Fig. 11. Effect of UV on the ozonation of 200 ppm PAA. For legend, see caption in Fig. 10.

TABLE I
Effect of UV on Ozone Absorption in Water^a

	Degree of ozone absorption, (%)	
	UV	Without UV
15-W low-pressure lamp	18.0	3.0
100-W high-pressure lamp	10.1	3.0

^a 30°C, ozone feed rate = 29 mg/min.

polymers) using a 15-W low-pressure mercury lamp as a radiation source. It has a main radiation of 2537 Å and acetic acid has little absorption in this wavelength region. Although activation of acetic acid does not occur, UV-irradiated ozonation rapidly reduces TOC to zero while ozonation alone has no effect (Fig. 13). Therefore, the effect of UV is not an activation of reactants.

Figure 14 illustrates a comparison between the effect of the 100-W high-pressure mercury lamp and that of 15-W low-pressure mercury lamp in the ozonation of acetic acid and PEG-20000. The effect of the 15-W low-pressure lamp is greater than that of the 100-W high-pressure lamp, although the total radiation energy of the latter is much higher. When PEG-20000 was ozonized

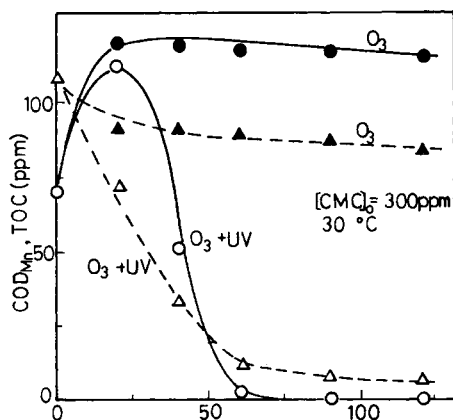


Fig. 12. Effect of UV on the ozonation of 300 ppm CMC. For legend, see caption in Fig. 10.

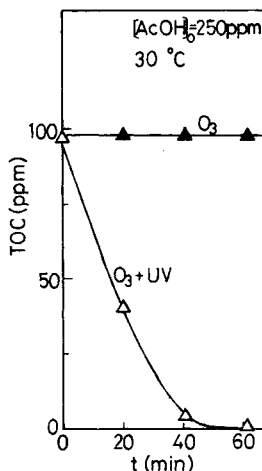


Fig. 13. Effect of 15-W low-pressure mercury lamp on the ozonation of acetic acid.

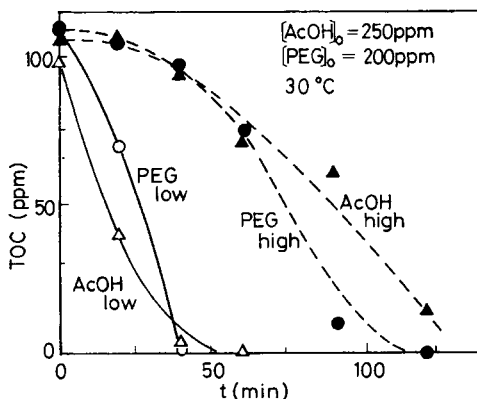


Fig. 14. Comparison between the effect of 15-W low-pressure lamp and that of 100-W high-pressure lamp.

under radiation with $\lambda > 3100 \text{ \AA}$ using aqueous sodium biphthalate as a filter solution, a decrease in TOC was not observed. The 2537 \AA resonance line, which corresponds to the maximum absorption of ozone, is effective. Ozone is decomposed by the radiation of this resonance line to produce active species. This is also supported by the fact that the radiation by the 15-W low-pressure lamp resulted in a higher degree of ozone absorption in water than that by the 100-W high-pressure lamp (Table I).

Ozone is decomposed by radiation with $\lambda < 3100 \text{ \AA}$ to produce $O(^1D)$ and $O_2(^1\Delta)$.¹⁴ The singlet oxygen atom has a strong oxidizing ability, and this may be the active species in the UV-irradiated ozonation. However, details are not known and are currently under investigation.

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