1548 © 1981 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 54, 1548—1553 (1981) [Vol. 54, No. 5

Wet Oxidation of Water-soluble Polymers

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(Received September 19, 1980)

Wet oxidation of various water-soluble polymers was carried out with particular attention given to the reactivity of polyethylene glycol. Polymers with high molecular weight were more reactive than their low molecular weight analogues or monomer models. It is suggested that the high reactivity of the polymers can be attributed to the ease of an intramolecular hydrogen abstraction in the propagation step of oxidation. Bio-degradability of the polymers was highly improved by wet oxidation. Wet oxidation is especially effective for the treatment of waste water containing water-soluble polymers.

Wet oxidation of organic compounds is carried out under a high pressure of air and at an elevated temperature between 100 °C and a critical temperature of water, 372 °C. This method has been successfully applied to the treatment of various sludges,[1,2)] waste water from organic chemicals manufacturing process,[3)] and pulp and paper mill waste matters.[4)] Under appropriate conditions, organic pollutants can be completely removed. However, the severe reaction conditions require higher running and installation costs than other processes, and practical application of this method is limited.

The reaction mechanism of the process has not been clarified as yet. Mitigation of the conditions is desirable by the development of effective catalysts or improvement of the process of the operation.[5)] Previously investigation was carried out on the wet oxidation of various low molecular weight organic compounds including dyes and amides.[6—8)] The reactivity of these compounds is correlated with the carbon content in a molecule. Compounds with higher carbon content seem to lose carbon monoxide or carbon dioxide more easily in the course of their degradation to refractory lower carboxylic acids, giving rise to faster decrease in total organic carbon. If this reactivity-carbon content relationship can be applied to the wet oxidation of polymers, the reactivity of homologous polymers would be independent of their molecular weight.

We have investigated the wet oxidation of water-soluble polymers with an emphasis on polyethylene glycol. Water-soluble polymers are widely used as water treatment agents, food additives, antifreeze, and in cosmetics. Their discharge into environment might cause serious water pollution because some of them are inert to biological degradation and accumulate in the environment.[9)] Their complete removal is difficult when ordinary physicochemical treatment such as adsorption or reverse osmosis is carried out. Improvement of the bio-degradability of the polymers by the treatment has also been examined.

Experimental

Material. Commercial reagents were used without further purification. Polyethylene glycol (PEG), polypropylene glycol (PPG), poly(vinyl alcohol) (PVA), polyacrylamide (PAM), pol(acrylic acid) (PAA), carboxymethylcellulose (CMC), 2-hydroxyethylcellulose (HEC), and methylcellulose (MC) were used as the water-soluble polymers. Their molecular weights, except for PEG and PPG, were determined from the corresponding molecular weight-viscosity relationship.[10)] The results are given in Table 1.

TABLE 1. MOLECULAR WEIGHT OF POLYMERS

Polymer	Molecular weight
PEG-200	190—210
PEG-400	380—420
PEG-1000	950—1050
PEG-2000	1800—2200
PEG-4000	3000—3700
PEG-6000	7800—9000
PEG-20000	24900
PPG	1000
PVA	21500
PAM	485000
PAA	38000
CMC	17500
HEC	82600
MC	58200

Apparatus and Procedure. Deionized water, nitrogen (0.98 MPa), and Oxygen (1.96 MPa) were placed in the reaction vessel, a 1—1 autoclave equipped with a sample injector and a valve for sampling. The vessel was heated with an electric furnace. A polymer solution was injected through the injector under pressure, the solution being stirred magnetically. It was confirmed that the reactions were not controlled by the diffusion of oxygen into the liquid phase. At appropriate time intervals, an aliquot of the solution was withdrawn through a cooling jacket and subjected to analysis.

The reactivity of polymers was determined on the basis of the decrease in total organic carbon during the course of reaction.

Analysis. Total organic carbon (TOC) analysis was carried out with a Sumitomo Model GCT-12N TOC analyzer and gas chromatographic (GPC) analysis with a Shimadzu GC-6A gas chromatograph equipped with a flame ionization detector using nitrogen as the carrier gas. Polyester FF 10% on Neosorb NFH, 3 mm × 2 m, was used for the GPC analysis of ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG) and formaldehyde, and chromosorb 101, 3 mm × 2 m, for ethanol and propionamide. Ion chromatographic analysis was performed on a Dionex Model 10 ion chromatograph using an anion separating column and 2.5×10^{-3} mol dm^{-3} Na_2CO_3 plus 3.0×10^{-3}

mol dm^{-3} $NaHCO_3$ as an eluent. Proton NMR spectra were taken on a Varian Model T-60A spectrometer using tetramethylsilane as a standard and deuteriochloroform as solvent, and infrared spectra on a Hitachi Model 215 grating spectrophotometer. Molecular weight of PEG was determined on a Toyo Soda Model HLC-802 UR gel permiation chromatograph using commercial PEG samples as standard.

Results and Discussion

Effect of Molecular Weight on the Wet Oxidation of PEG. Figure 1 shows the time courses of the TOC decrease in the wet oxidation of PEG-20000 at various temperature. The temperature dependency is remarkable as in the oxidation of benzyl alcohol reported previously.[6] The rate of the reaction was found to be independent of the oxygen pressure above 0.98 MPa.

The reactivity of PEG depends upon the molecular weight (Fig. 2). Ethylene glycol does not react under the conditions, but the reactivity of PEG increases with an increase in molecular weight. Although there is a maximum in the rate of TOC decrease at a molecular weight around 2000, PEG with higher molecular weight is more reactive as compared with its low molecular weight analogues. Thus, successive reaction was carried out with PEG-200 and PEG-20000.

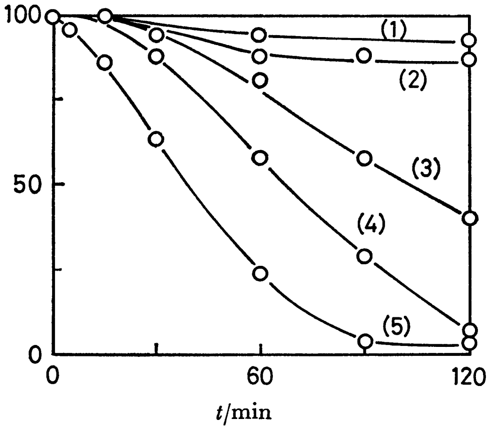


Fig. 1. Wet oxidation of PEG-20000. Effect of temperature.
[PEG]$_0$=5000 ppm, $P(O_2)$=1.96 PMa. (1): 160 °C, (2): 180 °C, (3): 200 °C, (4): 210 °C, (5) 220 °C.

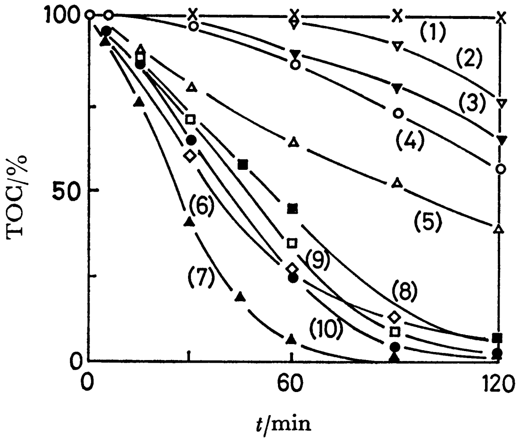


Fig. 2. Wet oxidation of PEG. Effect of molecular weight.
[TOC]$_0$=2500 ppm, $P(O_2)$=1.96 MPa, 220 °C.
(1): EG, (2): DEG, (3): TEG, (4): PEG-200, (5): PEG-400, (6): PEG-1000, (7): PEG-2000, (8): PEG-4000 (9): PEG-6000, (10): PEG-20000.

Accumulation of Acids during the Course of Reaction. Figure 3 shows the changes in pH and acid accumulation during the course of wet oxidation of PEG-200 and PEG-20000. The pH decreases at the initial stage of the reaction, recovering gradually. In the case of PEG-20000, the change in pH is more rapid as compared with PEG-200. The amount of acid increases at an early stage of the reaction, then decreasing. Both accumulation and decrease of acids were faster with PEG-20000 than with PEG-200, which can be explained in terms of the difference in molecular weight. Acids formed from PEG-20000 should have higher molecular weight than those from PEG-200, and should be more reactive. The molecular weight determined in the course of oxidation of PEG-20000 was *ca.* 600 after 5 min, and *ca.* 300 even after 30 min.

Product Analysis. Gas chromatographic analysis of the reaction mixture of the wet oxidation of PEG-200 and PEG-20000 showed formation of formaldehyde, EG, DEG, and TEG during the course of oxidation. The amount of these products, shown as functions of the reaction time in Figs. 4 and 5, increased with the progress of reaction in the case of PEG-200. Oxidation of PEG-20000 gave a large

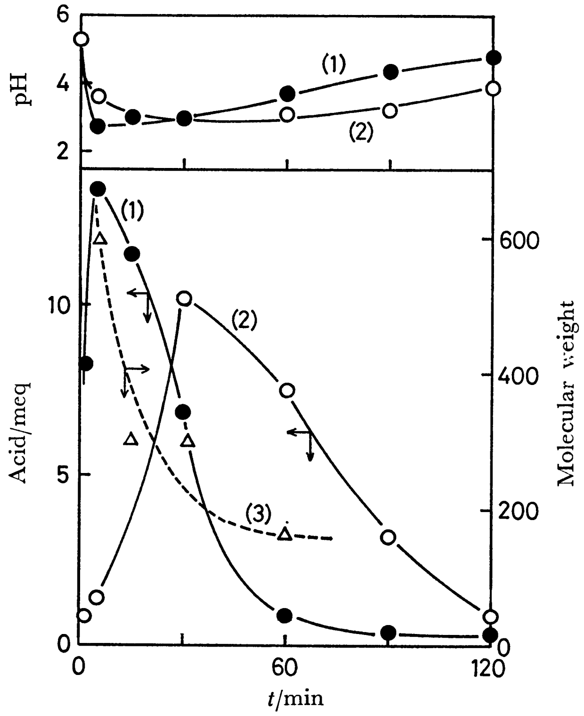


Fig. 3. pH change and acid accumulation during the wet oxidation of PEG-200 and PEG-20000.
[TOC]$_0$=500 ppm, $P(O_2)$=0.98 MPa, 220 °C. (1): PEG-20000, (2): PEG-200, (3): Molecular weight of oxidized PEG-20000.

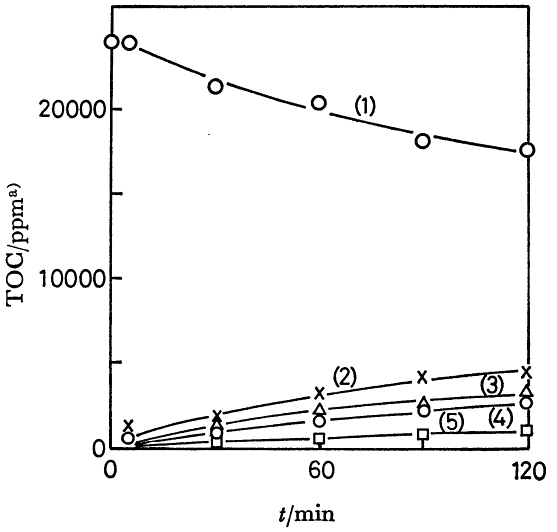


Fig. 4. Accumulation of EG, DEG, TEG, and formaldehyde during the wet oxidation of PEG-200. $P(O_2)=1.96$ MPa, 220 °C. (1): Decrease of TOC, (2): TEG, (3): EG, (4): DEG, (5): Formaldehyde. a) Accumulation of EG, DEG, TEG, and formaldehyde is expressed by TOC contained in these compounds.

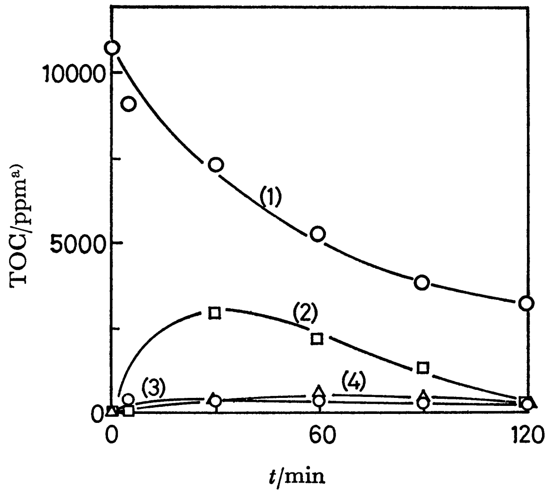


Fig. 5. Accumulation of EG, DEG, and formaldehyde during the wet oxidation of PEG-20000. $P(O_2)=1.96$ MPa, 220 °C. (1): Decrease of TOC, (2): Formaldehyde, (3): EG, (4): DEG. a) Accumulation of EG, DEG, and formaldehyde is expressed by TOC contained in these compounds.

amount of formaldehyde at an early stage of the reaction, decreasing with the progress of reaction. Only trace amount of EG and DEG were detected in this case.

Ion chromatographic analysis of the reaction mixture in the oxidation of PEG-20000 showed the formation of formic acid and acetic acid. Proton NMR spectra of the oxidation products of PEG-20000 showed unresolved signals at δ 4.4—4.7 and 3.6. A signal observed at δ 8.1 was assigned to formyl protons. The results indicate the formation of formic acid and/or formic esters. Infrared spectra of these products indicate the presence of carboxylic acids.

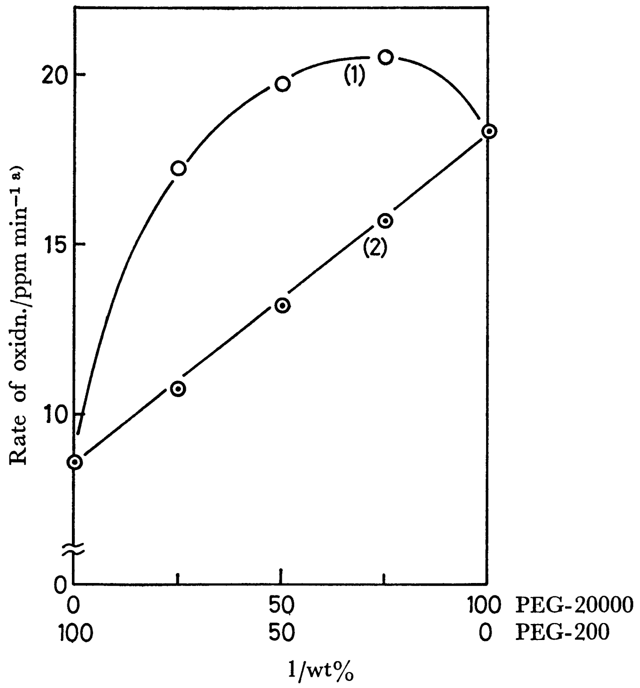
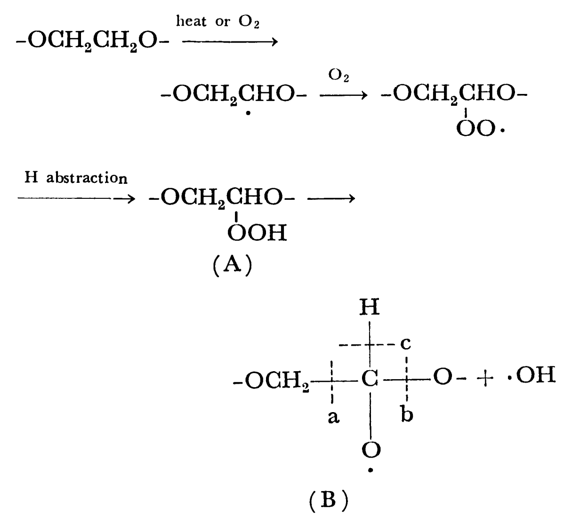


Fig. 6. Co-oxidation of PEG-200 and PEG-20000. $P(O_2)=1.96$ MPa, Total $[TOC]_0=2500$ ppm, 220 °C. (1): obsd, (2): calcd. a) The rate was calculated from TOC decrease.

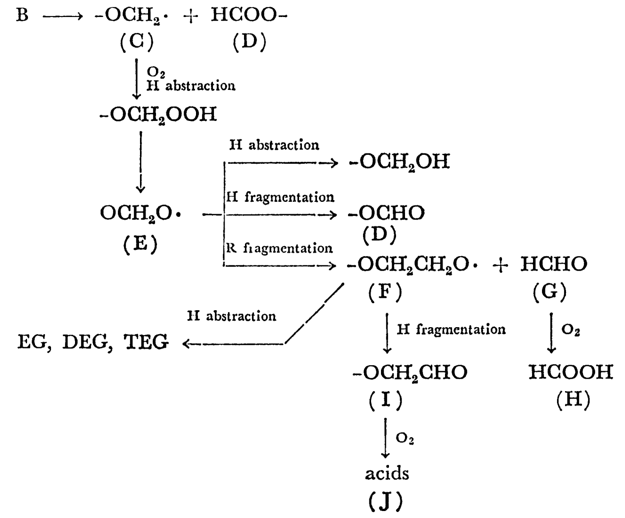
Co-oxidation of PEG-200 with PEG-20000. First, the effect of the concentration of the polymers on the rate of oxidation was examined. The curves of TOC decrease show an induction period (Fig. 2), the rate of oxidation being expressed by the mean velocity of TOC decrease at the reaction time of 60 min. The apparent reaction orders with respect to TOC were found to be 1.0 and 0.75 for PEG-20000 and PEG-200 respectively.

Figure 6 shows the dependence of the rate of oxidation on the ratio of the concentrations of PEG-200 and PEG-20000. The calculated line was obtained by taking the reaction order into consideration. The experimental data lie far above this line, suggesting that the reaction proceeds in a radical mechanism, where active species produced from PEG-20000 attack PEG-200. Co-oxidation of reactive compounds with less reactive reactants would thus be useful in practical waste water treatment. The apparent activation energy for the oxidation of PEG-20000 was 97.9 kJ/mol in the temperature range 180—220 °C.

Mechanism of Product Formation in Wet Oxidation of PEG. The following scheme is proposed for an explanation of the formation of the identified products. A radical mechanism seems to support the result. Goglev and Neiman reported that the thermal oxidation of PEG proceeds in a radical mechanism in which the first step is the formation of hydroperoxide of PEG.[11] The first step would be the formation of a hydroperoxide A, which undergoes thermal decomposition to produce an alkoxyl radical B and a hydroxyl radical. The hydroxyl radical is highly reactive and would give rise to further degradation of PEG.



Hydrogen atom fragmentation at bond c or hydrogen abstraction of the intermediate B might lead to the formation of an alcohol or an ester, although they were not characterized.



Fragementation at bond a of the radical B might produce formic ester D. The radical C is converted into an alkoxyl radical E, which undergoes an alkoxyl radical fragmentation (R fragmentation) to give another alkoxyl radical F and formaldehyde G. The latter might undergo further oxidation to produce formic acid H. Alkoxyl radical F would give EG, DEG, or TEG by hydrogen abstraction. Radical F might also produce aldehyde I, from which carboxylic acid J would be formed.

Fragmentation at bond b of the radical B can explain the formation of aldehyde and alkoxyl radical; their behaviour would be the same as discussed above.

$$\mathrm{B} \longrightarrow \text{-}\mathrm{OCH_2CHO} + \cdot\mathrm{OCH_2CH_2O}\text{-}$$

Consideration on the Effect of Molecular Weight on the Reactivity of PEG. The reactivity of a hydrocarbon in the autoxidation depends upon the rate of the propagation step.

$$\mathrm{ROO}\cdot + \mathrm{RH} \longrightarrow \mathrm{ROOH} + \mathrm{R}\cdot$$

This step generally occurs intermolecularly, although intramolecular reaction is also possible. Intramolecular hydrogen abstraction *via* cyclic intermediate occurs easily in the oxidation of acyclic ethers.[11,12] It is assumed that intramolecular process plays an important role when the concentration of PEG is low. Ease of cyclization depends upon the stability of the ring formed and on the activation entropy of cyclization. In the lactone formation from hydroxy acid, five to seven membered rings are easily produced, rings with more than fourteen atoms being also possible.[13] In the oxidation of PEG, cyclic transition state with five, six, and more than fourteen membered rings including peroxy oxygen atoms seems favorable. However, in the oxidation of PEG with a low molecular weight, *e.g.* PEG-200, intramolecular hydrogen abstraction would be difficult after several chain scissions. On the other hand, PEG with a high molecular weight holds a long chain during the course of oxidation (Fig. 3) and would undergo further intramolecular reaction.

Although the above explanation is possible for the effect of molecular weight on the wet oxidation of PEG, it does not necessarily follow that the higher the molecular weight, the higher the reactivity. A maximum in the reactivity was observed for PEG with a molecular weight *ca.* 2000, further increase in molecular weight showing little effect (Fig. 2). This suggests that the propagation step is a competition between intra- and intermolecular hydrogen abstraction as Goglev and Neiman indicated.[11] Intermolecular reaction should decrease with the increase in the molecular weight of PEG as a result of the reduced rate in the diffusion of the molecule.

Wet Oxidation of Other Polymers. Reactivity of other polymers in the wet oxidation was also investigated. In the case of CMC, HEC, and MC, viscosity of the aqueous solution of these polymers was very high, making the use of the sample injector impossible. Thus, reactions were carried out by heating a sample solution under a nitrogen atmosphere followed by injecting oxygen into the vessel. Viscosity and pH of the solution decreased during the course of pre-heating, indicating that thermal degradation occurred during this period. As shown in Fig. 7, all polymers were equally or even more reactive than PEG-20000. The reactivities of PVA, PPG, PAM, and PAA and their respective monomer models, ethanol, 1,2-propanediol, propionamide, and propionic acid were compared (Figs. 8 and 9), the sample injector being used. The reactivity of PVA was high, but TOC decrease in the oxidation of ethanol was slow, the amount of residual TOC being in line with the residual amount of ethanol determined by gas chromatography. Propionamide gradually decomposed, but TOC remained unchanged. On the other hand, PAM oxidized rapidly. Similar results were observed for PPG and PAA.

The results indicate that the polymers are reactive to a greater extent than the corresponding low molecular weight analogues due to a significant polymer effect, and that wet oxidation is particularly effective for the treatment of these water-soluble polymers. The reactivity-carbon content relationship, observed in the oxidation of low molecular weight compounds, is not applicable to the wet oxidation of polymers.

Improvement of Bio-degradability of Polymers. Synthetic polymers are generally inert to biological treatment. Although PEG can be degraded by some microorganism, the rate of degradation is low.[9)]

We have examined the improvement of bio-degradability of the polymers by wet oxidation. The results are given in Table 2. The bio-degradability is expressed by $(BOD_5/COD_{Cr})\times 100$ of the sample solution. Although all the polymers examined were inert to biological degradation, their bio-degradability was remarkably improved by wet oxidation. Treatment for only 5 min considerably improved the reactivity. After 2 h of oxidation, complete reactivity in the biological treatment was attained with PEG-1000 and PEG-2000. The effects of atmosphere and temperature of wet oxidation on the improvement of the bio-degradability of PEG-20000 are given in Table 3. Although degradation of the polymer chain occurs under a nitrogen atmosphere, scarcely any improvement in bio-degradability was observed. Incorporation of oxygen atoms into the reactant is inevitable. The bio-degradability was considerably improved by the wet oxidation at 160 °C, although there

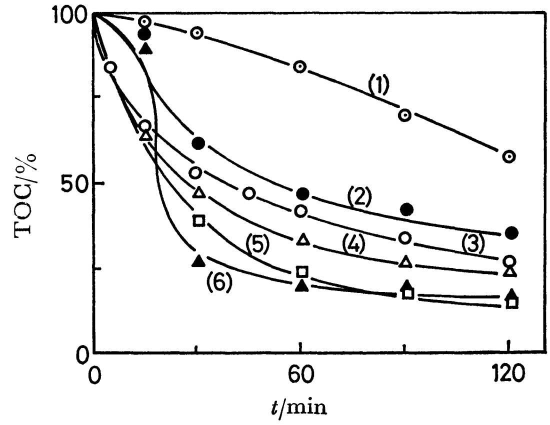


Fig. 7. Wet oxidation of water-soluble polymers. $P(O_2)=2.94$ MPa, $[\text{Polymer}]_0=5000$ ppm, 220 °C. (1): PEG-200, (2): PEG-20000, (3): PVA, (4): MC, (5): PAA, (6): PAM.

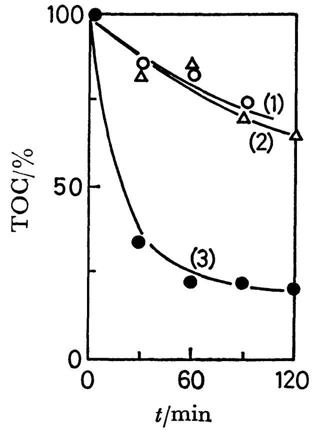


Fig. 8. Wet oxidation of PVA and ethanol. $P(O_2)=1.96$ MPa, $[TOC]_0=2500$ ppm, 220 °C. (1) Ethanol, (2) Ethanol determined by gas chromatograph and expressed by the TOC content, (3) PVA.

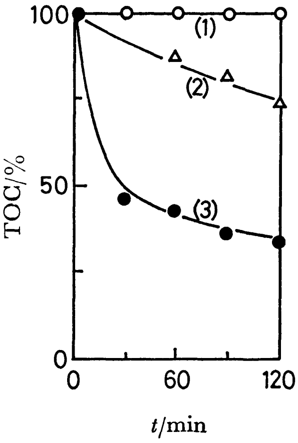


Fig. 9. Wet oxidation of PAM and propionamide. $P(O_2)=0.98$ MPa, $[TOC]_0=500$ ppm, 220 °C. (1): Propionamide, (2): Propionamide determined by gas chromatograph and expressed by the TOC content, (3): PAM.

TABLE 2. BIODEGRABILITY OF POLYMERS[a)]

Polymer	Reaction time/min		
	0	5	120
EG [b)]	76.0	—	—
PEG-200	4.0	23.0	49.0
PEG-400	0.2	36.0	65.0
PEG-1000	0	51.0	100
PEG-2000	2.0	50.0	100
PEG-4000	2.0	73.0	80.0
PEG-6000	6.0	57.0	91.0
PEG-20000	0.4	61.0	64.0
PVA	1.0	17.0	86.0
PPG [c)]	1.3	33.0	58.0
Ethanol	63.0	—	—
PAM	1.0	15.0	53.0
PAA	1.5	47.0	46.0

a) Expressed by $(BOD_5/COD_{Cr})\times 100$. b) Reaction conditions shown in Fig. 3. c) Reaction conditions: $[\text{Reactant}]=1000$ ppm, $P(O_2)=0.98$ MPa, 220 °C.

TABLE 3. BIO-DEGRADABILITY OF PEG-20000.[a)] EFFECTS OF TEMPERATURE AND ATMOSPHERE IN THE TREATMENT OF PEG-20000

Reaction time / min	220 °C N_2[b)]	220 °C N_2-O_2[c)]	200 °C N_2-O_2[c)]	180 °C N_2-O_2[c)]	160 °C N_2-O_2[c)]	100 °C N_2-O_2[c)]
5	6.0	61.0	23.0	43.0	41.0	1.7
120	8.0	64.0	38.0	62.0	61.0	30.0

a) Expressed by $(BOD_5/COD_{Cr})\times 100$. b) $P(N_2)=1.96$ MPa. c) $P(O_2)=1.96$ MPa.

was scarcely any decrease in TOC. Moreover, the oxidation at as low as 100 °C was still effective when sufficient reaction time as 2 h was employed. This shows that wet oxidation under mild conditions is sufficient for the improvement of bio-degradability. Thus wet oxidation is an effective pre-treatment for the biological purification of waste water containing those water-soluble polymers.

We thank Dr. J. Yoshida and Dr. S. Kojiya, Kyoto Institute of Technology, for their helpful advice and discussions.

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