Oxidative Degradation of Polymers. V. Ozonization of Polypropylene and Polystyrene in Carbon Tetrachloride

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The rates and products of ozonization of atactic polypropylene and polystyrene were studied in carbon tetrachloride at 30 and 70 °C. Atactic polypropylene underwent cleavage statistically by ozone to give oxygenated products. The molecular weight of polypropylene decreased with the progress of ozonization. Most chain ends of ozonized polypropylene were suggested to be carboxylic acids. Ozonization of polystyrene brought about crosslinking as well as chain scission, giving rise to broadening of molecular weight distribution. The major product from polystyrene was carboxylic acid.

Plastics and rubber deteriorate in the presence of ozone because of its powerful oxidizing action.[1] Ozonization of organic compounds, especially olefins, has been studied extensively.[2,3] The ozonization of polyethylene is reported to give peroxide, carbonyl and carboxylic compounds,[4-8] while polystyrene becomes brittle and discolored.[6,9] Razumovskii *et al.* found peroxide, carbonyl and carboxylic groups on the surface of ozonized polystyrene.[9] Both atactic and isotactic polypropylene films are also ozonized at ambient temperatures without induction period.[10] The attack of ozone on polymers was observed to result in chain scission.[11-13] However, the results so far obtained are qualitative and the arguments are speculative. More information is needed in order to clarify the nature of ozonization of polymers. In the course of our study on the oxidative degradation of polymers, we have studied the ozonization of atactic polypropylene and polystyrene in carbon tetrachloride.

Experimental

Materials. Polypropylene, kindly supplied by Mr. Fujita, Mitsui Petrochemical Ind. Co. was purified as follows. 92 g of chopped polypropylene was first soaked in 500 ml benzene at room temperature for about a week. The insoluble fraction was separated by filtration and the soluble fraction was repeatedly precipitated from the benzene solution by addition to excess methanol. It was finally dried in a vacuum at room temperature. The infrared spectrum of the purified polypropylene showed little absorption at 997 cm^{-1} but strong absorption at 975 cm^{-1}, indicating that little isotactic polypropylene was present. The intrinsic viscosity at 45 °C in carbon tetrachloride and the number average molecular weight of the purified atactic polypropylene were found to be 0.213 dl/g and 1.2×10^4, respectively.

Commercial polystyrene was purified by the conventional method using benzene and methanol as solvent and precipitant, respectively. The polystyrene solution was then washed successively with acid, water, alkali and water. Finally its 2% solution in chloroform was introduced slowly into excess methanol under vigorous stirring to give white powder polystyrene, which was dried in a vacuume at room temperature. The purified polystyrene dissolved completely into methyl ethyl ketone, indicating that it is atactic. The intrinsic viscosity at 45 °C in carbon tetrachloride was found to be 0.770 dl/g. The number average molecular weight was calculated as 2.1×10^5 by means of following equation obtained from the standard mono-dispersed polystyrenes.

$$[\eta] = 1.34 \times 10^{-4} \bar{M}_n^{0.706} \quad (1)$$

Carbon tetrachloride was treated with ozone prior to the oxidation reaction. Ozone was produced in a standard ozone generator, Nippon Ozone Co., Ltd. Model O-3-2, by charging pure oxygen dried with silica gel. The concentration of ozone in the feed gas determined by iodometric titration was 2—4%.

Procedures. Oxidation was carried out in a *ca.* 100 ml vessel equipped with a condenser. The oxidation was started by bubbling O_3–O_2 gas through the reaction mixture which was stirred vigorously with a magnetic stirrer. The amount of ozone consumed was calculated from the difference of the ozone concentration in the exhaust gases in the absence and the presence of substrate.

The reaction mixture was analyzed as follows. Viscosity was measured at 45 °C in carbon tetrachloride using a modified Ostwald viscosimeter. The molecular weight distribution was measured at 40 °C by gel permeation chromatography (DuPont-Shimadzu Model 830). Various types of crosslinked polystyrene gel columns (Shimadzu) were employed according to the molecular weight measured. Tetrahydrofuran (THF) was used as a carrier liquid at a speed of 1 ml/min. Both refractive index and ultraviolet absorption were used as a detector device. The calibration curve for the molecular weight of polystyrene was prepared by using standard, monodispersed polystyrenes; it was corrected for polypropylene with the *Q*-values given by Ouano and Mercier.[14]

Low-boiling products were determined by gas liquid chromatography. The conditions are given in Table 1.

Total amount of peroxides and acids formed was determined by iodometric and neutralization titrations, respectively. The

TABLE 1. GAS LIQUID CHROMATOGRAPHIC ANALYSIS

Column	Temp, °C	Carrier gas	Detector
Porapak-Q, 2 m, 50/80 mesh	100, 140, 170	N_2	FID
15 wt % Apiezon-L, 5m, on 80/100 mesh Uniport B	80, 140, 160	He	TCD
20 wt % PEG 20M, 7m, on 80/100 mesh Uniport B	75, 84	He	TCD
Chromosorb 101, 3m, 60/80 mesh	80	He	TCD

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oxidized polymers were analyzed by IR, UV, and ^1H NMR spectra and also by elemental analysis. Low molecular weight acids were determined by isotachophoretic analysis. An aqueous solution of 0.01 M gultamic acid was used as the terminal solution, and an aqueous solution containing 0.01 M L-histidine and 0.01 M L-histidine hydrochloride as the leading solution.

Results and Discussion

Ozonization of Polypropylene. The results of ozonization of polypropylene are summarized in Table 2. Although the initial solution of polypropylene in carbon tetrachloride was colorless, it became pale yellow after about 30 min. Discoloration increased with increase in reaction time. The change in molecular weight can best be visualized by the analysis of gel permeation chromatography. Figure 1 shows an example of the gel permeation chromatogram of the ozonized polypropylene. The molecular weight of polypropylene decreases markedly with the progress of ozonization (Fig. 1 and Table 2). The molecular weight decreased from 12000 to 500 in 10 h. The absorption at 260 nm also increased with increase in reaction time, stronger absorption being observed for lower molecular weight fractions (Fig. 1). The infrared spectrum of the product solution showed the formation of hydroxyl (3400 cm^{-1}) and carbonyl (1710 cm^{-1}) groups. Formation of methanol, acetone, acetaldehyde and acetic acid, observed by gas liquid chromatographic analysis, was very slight except for acetic acid at high conversion: acetic acid accounts for not more than 20% of total acid observed. Acetic acid was also observed by isotachophoretic analysis.

The total number of chain ends calculated from the initial weight of polypropylene and its final average molecular weight are given in Table 2. The results would underestimate the total number of chain ends as expected from the molecular weight distribution shown in Fig. 1. However, they correspond remarkably well with those of observed acid, indicating that much of the chain ends of the ozonized polypropylene is carboxylic acid.

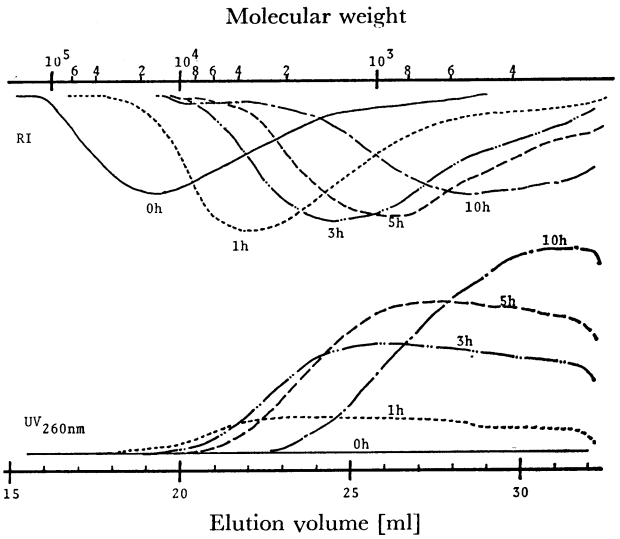

Fig. 1. Gel permeation chromatograms of polypropylene ozonized at 30 °C in carbon tetrachloride (Run No.5).

The results of elemental analysis for initial and ozonized polypropylenes are summarized in Table 3. It was confirmed that ozonized polypropylene contains no chlorine. This suggests that polymer carbon radical reacts with oxygen immediately before it attacks carbon tetrachloride and abstracts chlorine atom. Tables 2 and

TABLE 2. OZONIZATION OF ATACTIC POLYPROPYLENE AT 30 °C IN 50 ml CARBON TETRACHLORIDE

Run No.	1	2	3	4	5
APP,[a] mmol	47.5	47.8	12.0	12.5	11.9
Time, h	1	4	2	9	10
O_3 supplied/APP, mol/mol	0.16	0.62	1.23	5.31	6.25
Molecular weight by GPC at time t (h)					
$t=0$	12000	12000	12000	12000	12000
0.5		9000	6200		
1	7000	6800	3400	4400	3400
2		5400	1900	2000	
3		3000		1700	1300
4		2400		1400	
5				1100	900
7				800	
9				700	
10					500
Total number of chain ends, mmol	0.57	1.68	0.53	1.50	2.01
Total acid, mmol	0.70	1.9		1.9	2.1
Peroxide, mmol	0.68	2.6		0.42	0.49
Low boiling products, mmol					
Methanol		trace		trace	trace
Acetaldehyde		trace		trace	trace
Acetone	trace	small		small	small
Acetic acid	trace	trace		0.09	0.37

a) By monomer unit.

Table 3. Elemental analysis of initial and ozonized polypropylene

Run No.	Initial		1	2	3
	Calcd	Found			
Molecular weight		12000	7000	2400	1900
C, %	85.63	85.53	81.29	78.08	75.74
H, %	14.37	14.95	14.02	13.52	12.15
O,[a] %	0		4.69	8.40	12.11
H/C	2.00	2.08	2.05	2.06	1.99
$\Delta O/C_3H_6$	0		0.13	0.24	0.36
Peroxidic oxygen,[b] %	0		1.6		
Carboxylic oxygen,[c] %	0		0.4		

a) By difference. b) Determined by iodometric titration. c) Determined by neutralization titration.

3 show that the lower the molecular weight, the higher the content of oxygen and that the ratio of carbon to hydrogen atoms remains constant. Oxygen is incorporated not only as carboxylic acid but also as other functional groups such as hydroperoxide, alcohol and ketone.

The ^1H NMR analysis showed new peaks at 6.2 ppm and 5.0 ppm for ozonized polypropylene. However, they were not identified. The formation of carbon dioxide was confirmed by the formation of white precipitate when the exhaust gas was passed through the aqueous barium hydroxide solution.

Ozonization of Polystyrene. The ozonization of polystyrene was performed in a similar way to that for polypropylene. Distinct results were obtained. Discoloration of the reaction mixture to pale yellow was also observed for polystyrene. A white gummy substance was precipitated with the progress of ozonization. The substance was insoluble in carbon tetrachloride but partly soluble in acetone and tetrahydrofuran.

The pertinent results of the ozonization of polystyrene are summarized in Table 4. The effect of temperature was found to be small. Figure 2 shows an example of the gel permeation chromatograms of ozonized polystyrene. Broadening of molecular weight distribution was observed in each reaction, both lower and higher molecular weight fractions being formed. Since the column we used can not separate polymers with molecular weight higher than 10^6, the formation of crosslinked polymers, is indicated in Fig. 2.

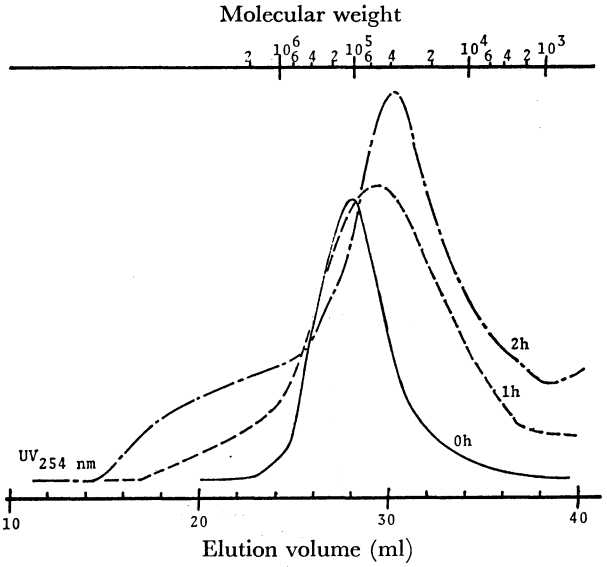

Fig. 2. Gel permeation chromatograms of polystyrene ozonized at 70 °C in carbon tetrachloride (Run No. 7).

Figure 3 shows the infrared spectra of the reaction mixture and the production of hydroxyl (3400 cm^{-1})

Table 4. Ozonization of polystyrene in 50 ml carbon tetrachloride

Run No.	Initial	6	7	8	9	10
PS,[a] mmol		9.62	9.62	9.61	9.60	4.82
Temperature, °C		70	70	70	30	30
Time, h		1	2	4	1.5	2
O_3 supplied/PS, mol/mol		0.63	1.54	2.87	1.08	3.07
Peroxide,mmol					0.83	
Acid, mmol					3.22	
Elemental analysis of ozonized polystyrene						
C, %	92.26		74.44	68.40	84.66	72.94
H, %	7.74		6.18	5.69	7.29	6.31
O,[b] %	0		(19.38)[c]	(25.91)[c]	8.05	20.75
H/C	1.00		0.99	0.99	1.02	1.03
$\Delta O/C_8H_8$					0.57	1.71
Peroxidic oxygen, %			1.1	0.9	0.3	
Carboxylic oxygen, %			4.9	3.9	3.6	

a) Polystyrene by monomer unit. b) By difference. c) Containing some chlorine due to incomplete removal of carbon tetrachloride.

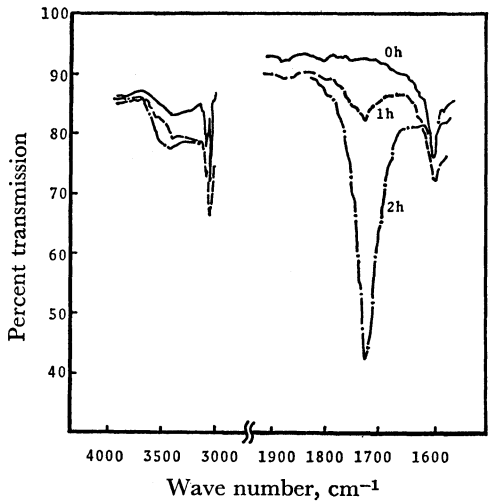

Fig. 3. Infrared spectra of ozonized polystyrene (Run Nos. 6 and 7).

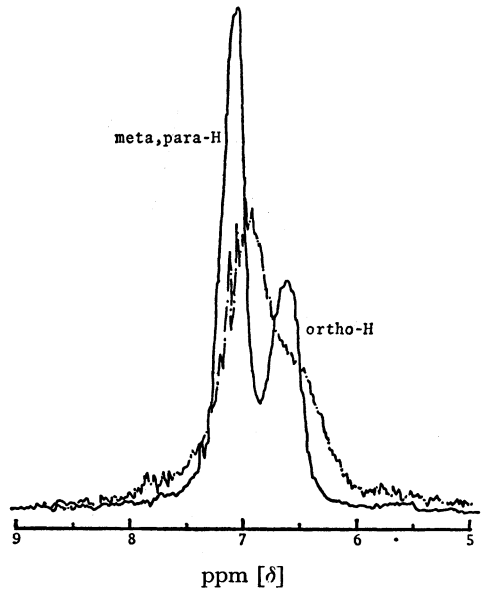

Fig. 4. NMR spectra of initial and ozonized polystyrene (Run No. 8).
——: Initial,
-·-·-: ozonized, 70 °C, 4 h.

and carbonyl (1730 cm^{-1}) groups. The UV spectrum showed the formation of a new band at 283 nm.

The results of elemental analyses, summarized in Table 4, show that much oxygen is incorporated into the polymer chain. Major products are carboxylic acid. Much of the chain ends should be acid.

Figure 4 shows the ^1H NMR spectra of initial and ozonized polystyrenes. The spectra of 6.63 and 7.10 ppm correspond respectively to *ortho* hydrogen and *meta*- and *para*-hydrogens of aromatic ring. The ratio is 2 to 3. The spectrum of ozonized polystyrene indicates the cleavage of aromatic ring. It was found by isotachophoretic analysis that formic acid was formed from polystyrene.

The results show that polypropylene is cleaved by ozone at ambient temperature to give dibasic acids as major products, polystyrene being both crosslinked and cleaved.

It has not yet been established how the initiation reactions proceed in the ozonization of saturated hydrocarbons.[15] It appears that the ozonization of carbon-hydrogen bond involves a hydrotrioxide, but the exact mode of formation of this intermediate and how it is converted into products has not been clarified. Hellman and Hamilton[16] postulated a scheme in which the ozonization of carbon-hydrogen bond proceeds through carbon radical and/or carbonium ion. The formation of 1-chloro- and 1-bromoadamantane in the ozonization of adamantane in the presence of bromotrichloromethane[17] suggests the presence of carbon radical. However, high ratio of retention of stereoregularity in the ozonization of saturated hydrocarbons[17,18] implies that this radical is not entirely free. The important role of ozone in the ozonization of polypropylene should be in the initial production of free radicals, which is supported experimentally by ESR analyses.[19,20] The adventitious impurities involved in polypropylene such as hydroperoxide, alcohol and carbonyl compounds might also contribute in the initiation reactions. Since polypropylene is relatively reactive toward oxygen, these impurities might be formed inevitably during the course of processing and storing.

After the initial production of radicals, the ozonization should resemble oxidation by molecular oxygen, where peroxyl and alkoxyl radicals are important chain carrying species.[21] The reported kinetic isotope effect and relative reactivities observed in the ozonization of aliphatic hydrocarbons[16,22] suggest the preferential attack of ozone on tertiary carbon-hydrogen bond of polypropylene to yield tertiary polypropylene radical. The characteristic feature of ozonization, when compared with autoxidation by molecular oxygen, is the rapid cleavage of polymer chain and high yield of carboxylic acid. It is not clear whether ozone is effective in direct scission of the carbon-carbon sigma bond. Carbon-carbon double bond is cleaved quite rapidly by ozone. Since the molecular weight of polypropylene decreases monotonously as the ozonization proceeds, the contribution of residual double bond involved in the initial polypropylene, if any, should be small. Since not much double bond should be formed in the autoxidation of polypropylene under sufficient oxygen, we assume that chain scission arises mostly from the β-scission of polypropylene alkoxyl radical. Primary alcohol is easily oxidized to aldehyde, which is then oxidized to carboxylic acid by ozone.

It is not clear why polystyrene behaves quite differently from polypropylene toward ozone. Ozone may attack either tertiary benzylic hydrogen or aromatic ring of polystyrene. The reactivity of the tertiary hydrogen of polystyrene is much lower than that of corresponding model compounds and polypropylene.[23] The crosslinking is not so important in the oxidation of polystyrene in solution by molecular oxygen as in the ozonization. Therefore, the cleavage of the aromatic ring should play a key role in the formation of crosslinked polystyrene. The ozonization of aromatic

compounds has been examined by many investigators, most extensively by Wibaut and his colleagues.[24] Ozone is able to function as a 1,3-dipole, an electrophile, or as a nucleophile, but it behaves primarily as an electrophilic reagent in its reactions with aromatic compounds.[24] In fact, the relative ozonization rates correlate well with the electron donating properties of alkyl substituted benzenes.[25] Thus the zwitter ion may play an important role and might be responsible for the crosslinking. The detailed mechanism of the crosslinking is now being studied with model compounds. It may be worth noting that the ozonization of simple aromatic compounds such as benzene, toluene and phenol gives insoluble polymeric materials.

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