

Oxidative Degradation of Polymers. II. Thermal Oxidative Degradation of Atactic Polypropylene in Solution Under Pressure

TAKEO SHIONO, ETSUO NIKI, and YOSHIO KAMIYA, *Department of Reaction Chemistry, Faculty of Engineering, University of Tokyo, Hongo, Tokyo 113, Japan*

Synopsis

Atactic polypropylene was oxidized in solution in the presence and absence of radical initiator over the temperature range of 140° to 200°C under oxygen pressure of 3.3 to 12.4 kg/cm², and the effects of metal catalyst and additives on the rate, products, and change in molecular weight distribution were measured. The synergistic effect was observed with cobalt and manganese salts. The deactivation of the metal catalysts was suppressed by the addition of acetic acid and acetic anhydride as solvent. The rate of oxidation increased with increasing temperature, but the decrease in molecular weight was nevertheless not so significant as to give many low-boiling products. However, the production of mixtures of acid, ketone, alcohol, and ester with molecular weights of several hundreds was promising. The refractive index of polypropylene decreased markedly as the oxidation proceeded, and the complications involved in the determination of the change in molecular weight distribution measured by gel permeation chromatography are discussed.

INTRODUCTION

The interactions of polymers and molecular oxygen are the fundamental processes in aging and degradation of plastics and rubber and also in the deterioration of lipids and foods.¹⁻³ In the course of our study on the oxidation of polymers by molecular oxygen, we have been working on the accelerated degradation of polymers in order to elucidate the course of oxidation and the possibility of recovering useful chemicals from the polymers.

In the previous paper,⁴ the oxidative degradation of atactic polypropylene was carried out in solution over the temperature range of 70° to 125°C under atmospheric pressure of oxygen. Although considerable amounts of oxygen were introduced into the polymer chain or at its ends, the decrease in molecular weight and the formation of low-boiling products were relatively small. In this paper the results of the oxidations of atactic polypropylene at higher temperatures and under pressure of oxygen are given. The effects of metal catalysts, solvents, and additives were also studied. Furthermore, the oxidation products were fractionated using gel permeation chromatography, and each fraction was dried, weighed, and analyzed by infrared spectroscopy, refractive index, and ultraviolet absorption.

TABLE I
Oxidation of Polypropylene in Benzene at 140°C With and Without Metal Decanoate,
[DBP] = $3.1 \times 10^{-2}M$, P_{O_2} = 6.3 kg/cm²

	Expt. 1	2	3	4	5	6
Catalyst	none	Mn	Mn ^a	Mn ^a	Co ^a	Co + Mn ^a
Catalyst $\times 10^2$, <i>M</i>		2.01	2.00	2.01	2.00	2.0, 0.20
NaBr $\times 10^2$, <i>M</i>	none	none	none	1.96	2.05	2.06
Time, hr	9	32	16	16	16	16
Recovery, % ^b	100	97	77	70	24	0
Products, ^c mole/100 mole monomer unit						
Acid	0.33	0.61	1.55	1.89	2.21	6.21 ^e
Ketone	0.49	0.74	1.51	1.72	4.20	9.79 ^e
Ester	0.22	0.34	1.07	1.04	3.00	5.41 ^e
Alcohol	trace	trace	trace	trace	2.97	4.07 ^e
MW ^d	5500	4000	4000	3500	1300	1000 ^e

^a With 10 volume per cent each of acetic acid and acetic anhydride.

^b Per cent of oxidized polypropylene precipitated from methanol.

^c Analyzed for recovered polypropylene.

^d Molecular weight of oxidized polypropylene measured by viscosity. The molecular weight of initial polypropylene was 11300.

^e Analyzed for polymers which was obtained by removal of solvent from reaction mixture.

EXPERIMENTAL

Materials

The purification of commercial atactic polypropylene has been described previously.⁴ Benzene was distilled prior to use. Di-*t*-butyl peroxide (DBP) purchased from Nippon Oils and Fats Co. was used without further purification. Commercial cumyl hydroperoxide (CHP) was purified from its sodium salt and distilled under reduced pressure. Cobaltous and manganous decanoates used as catalyst in some oxidations were prepared from corresponding chlorides.

TABLE II
Low-Boiling Products in the Oxidation of Polypropylene at 140°C^a

	Expt. 1 ^b	2	3	4	5
H ₂ O	4.19	6.05	10.9	20.9	26.1
CH ₃ OH	0.34	0.19	0.02	t	0.02
HCHO	t	t	t	t	t
HCOOH		t	1.67	2.45	0.38
HCOOCH ₃	0.07	0.21	0.16	0.05	0.02
CH ₃ CHO	0.15	0.35	0.35	0.09	0.33
C ₂ H ₅ OH		t	t	t	t
CH ₃ COOH	0.55	5.17	s	s	s
CH ₃ COOCH ₃		t	3.25	2.69	1.16
CH ₃ COCH ₃	1.29	1.19	1.29	0.23	1.03

^a Concentrations in 10²*M*; t, trace; s, solvent. Carbon dioxide was always observed, but its quantitative amount is not available.

^b Experiment number in Table II correspond to experiment number in Table I.

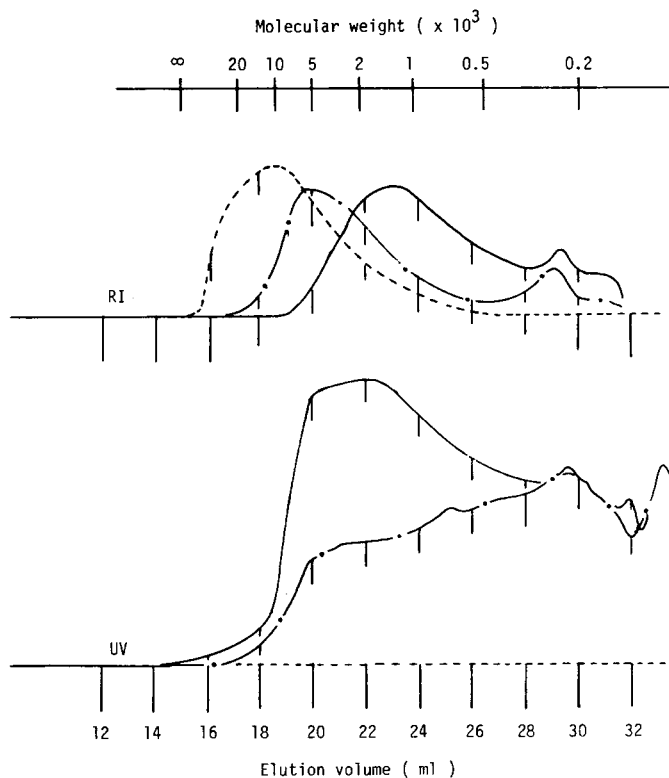


Fig. 1. Gel permeation chromatograms of polypropylene oxidized at 140°C in benzene, acetic acid, and acetic anhydride (8:1:1 by volume) under 6.3 kg/cm² oxygen; reaction time = 16 hr: (-----) initial PP; (—) oxidized with MnDe₂ and DBP; (—) oxidized with CoDe₂, NaBr, and DBP.

Oxidation Procedure

Atactic polypropylene, radical initiator, metal catalyst, and sodium bromide, when required, were dissolved in benzene to obtain an appropriate solution. In several experiments, acetic acid and acetic anhydride were also added to the solution. The concentration of polypropylene was kept constant at 2.4M by monomer unit. The mixture was transferred to a 100-ml glass or stainless steel autoclave, then oxygen was introduced to the reactor, and the oxidation was carried out either at 140°, 170°, or 200°C. After the oxidation, the reaction mixture was analyzed as described in the following section.

Analyses

The analyses of *peroxides, carbonyl and hydroxy compounds, acid, and low-boiling products* have been described previously.⁴

The change in *molecular weight distribution* was followed by gel permeation chromatography (GPC) using du Pont-Shimadzu Liquid Chromatography Model 830. Two types of column combinations were employed: one 0.5 m each of HSG-15 and HSG-30, and the other 0.5 m each of HSG-10 and HSG-15. These are crosslinked polystyrene gel columns supplied by Shimadzu. The column oven

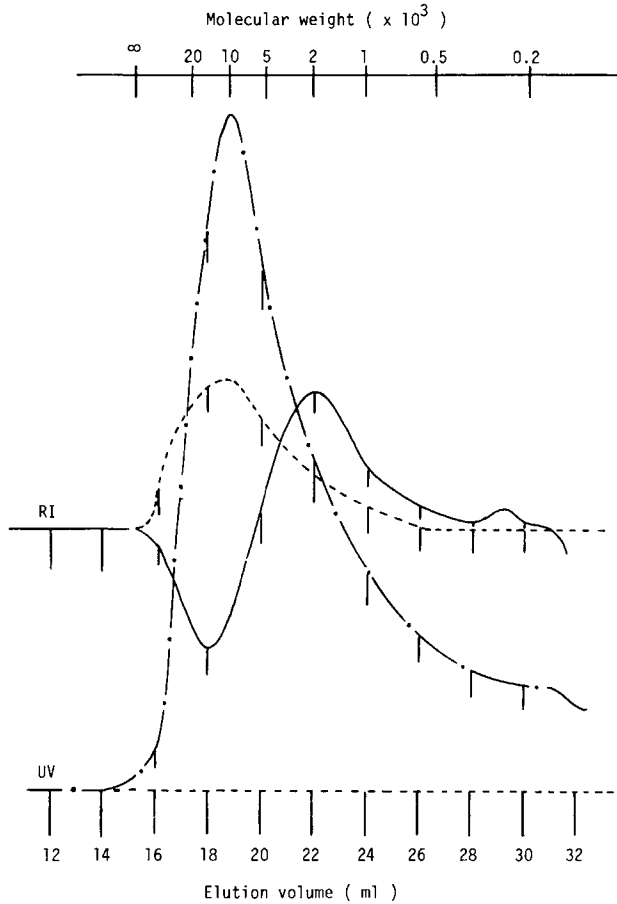


Fig. 2. Gel permeation chromatograms of polypropylene oxidized at 170°C in benzene, acetic acid, and acetic anhydride (8:1:1 by volume) with CoDe_2 , NaBr and DBP; $P_{\text{O}_2} = 3.6 \text{ kg/cm}^2$, reaction time = 16 hr: (-----) initial PP; (—) oxidized PP by refractive index; (— · —) oxidized PP by UV.

was maintained at 40°C. Tetrahydrofuran was used as a carrier liquid at a speed of 1 ml/min. Both refractive index (at 30°C) and ultraviolet absorption at 253.7 nm were used for analyses.

The polypropylene recovered and dried after oxidation was dissolved into carbon tetrachloride and analyzed by *ultraviolet absorption spectroscopy* at room temperature using a Hitachi spectrophotometer Model 124. Carbon tetrachloride was placed in the reference beam.

RESULTS AND DISCUSSION

Oxidation at 140°C

The results of oxidation of atactic polypropylene under pressure of oxygen at 140°C are summarized in Table I. The oxidized solution was added slowly into 30 times as much cold methanol to precipitate polypropylene, which was

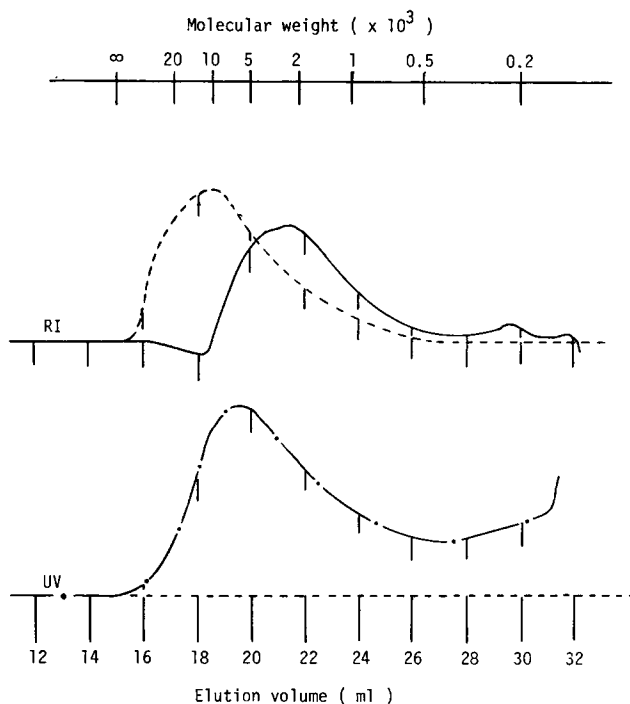


Fig. 3. Gel permeation chromatograms of polypropylene oxidized at 200°C in benzene, acetic acid, and acetic anhydride (8:1:1 by volume) with CoDe_2 and NaBr ; $P_{\text{O}_2} = 9.0 \text{ kg/cm}^2$, reaction time = 8 hr: (-----) initial PP; (—) oxidized PP by refractive index; (-·-) oxidized PP by UV.

then washed with methanol several times and dissolved into pentane. The precipitated metal complexes were removed by filtration, and the filtrate was evacuated and dried under vacuum at room temperature. The recovery of polypropylene thus obtained is shown in Table I. The table indicates that the molecular weight and recovery of the oxidized polypropylene decrease as the formations of acid, ketone, ester, and alcohol increase. The results of gas-liquid chromatography analyses for low-boiling products are summarized in Table II.

The oxidation in the presence of radical initiator but absence of metal catalyst was slow, and the polypropylene could be recovered quantitatively after oxidation. Since the remaining hydroperoxide was considerably high and the decrease in molecular weight measured by gel permeation chromatography was not significant, the oxidation was carried out under similar conditions but in the presence of manganous decanoate. The oxidation was carried out for 32 hr, but after 8 hr, manganese salt precipitated and the rate of decrease in molecular weight diminished markedly. It was found that the addition of 10 volume per cent each of acetic acid and acetic anhydride was effective in suppressing the deactivation of metal catalyst and increased the rate of oxidation.⁵ Sodium bromide was also effective in the presence of both manganous and cobaltous decanoates.⁵

Figure 1 shows the gel permeation chromatograms of initial and oxidized polypropylene measured by both refractive index and ultraviolet absorption at 253.7 nm. As observed previously,⁴ the initial polypropylene had no ultraviolet absorption, whereas the oxidized polypropylene showed a marked absorption

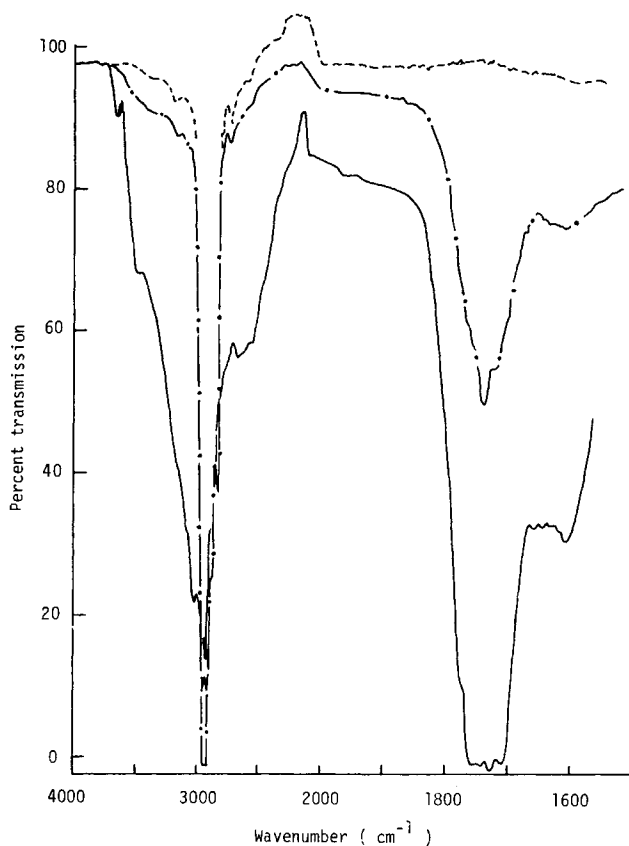


Fig. 4. Infrared absorption spectra of polypropylene: (- - - -) unoxidized PP; (— · —) PP oxidized at 170°C for 16 hr with DBP, CoDe_2 , and NaBr; (—) PP oxidized further for another 8 hr at 140°C with DBP, MnDe_2 , and NaBr.

over a wide range of molecular weight. It is noteworthy that much of the polypropylene oxidized in the presence of cobaltous decanoate and sodium bromide was soluble in methanol, indicating that many functional groups were introduced into the polymer chain and at its ends. The last column of Table I shows the synergistic effect of manganese and cobalt salts; that is, the combination of cobalt and manganese salts was most effective in reducing molecular weight and introducing functional groups. It is quite remarkable that no polypropylene precipitated from methanol.

Oxidations at 170° and 200°C

Oxidations of atactic polypropylene were performed at 170°C for 16 hr with added di-*t*-butyl peroxide or cumyl hydroperoxide as a radical initiator. The gel permeation chromatograms of the oxidized polypropylene are shown in Figure 2, which indicates the formation of products that have lower refractive index than tetrahydrofuran.

Oxidation of polypropylene proceeded smoothly at 200°C in the presence of cobaltous decanoate and sodium bromide but without added radical initiator.

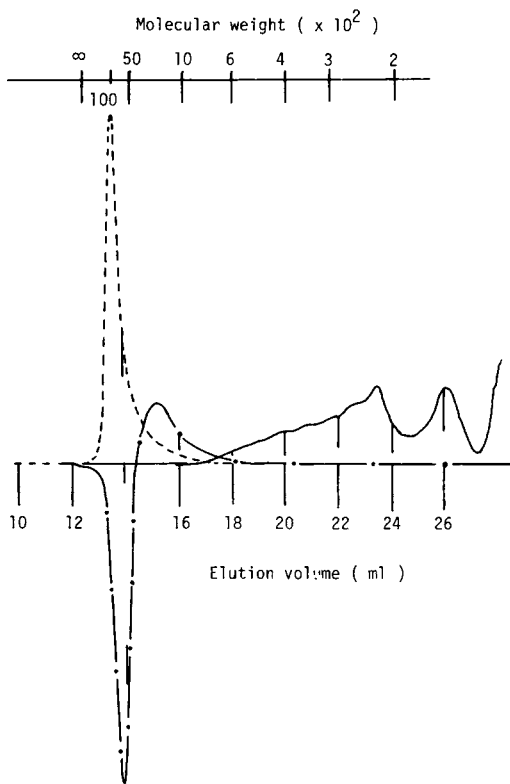


Fig. 5. Change in gel permeation chromatograms of polypropylene by oxidation measured by refractive index (see text): (-----) unoxidized PP; (----) PP oxidized at 170°C for 16 hr with DBP, CoDe_2 , and NaBr; (—) PP oxidized further for another 8 hr at 140°C with DBP, MnDe_2 , and NaBr.

Figure 3 shows the change in gel permeation chromatograms of initial and final polypropylene. The formation of products that have lower refractive index than tetrahydrofuran is again observed. At 200°C, more carbon dioxide and water were formed than at lower temperatures.

Figures 1, 2, and 3 show that the oxidations at 170° and 200°C are not efficient as compared with those at 140°C from the viewpoint of cleaving the polymer chain. However, it was found that polypropylene preoxidized at 170°C by cobalt decanoate and sodium bromide could be degraded quite efficiently by the subsequent oxidation at 140°C in the presence of manganese decanoate. Polypropylene was first oxidized at 170°C for 16 hr in benzene, acetic acid, and acetic anhydride (8:1:1 by volume) in the presence of cobalt decanoate, sodium bromide, and DBP, and the reaction mixture was introduced into cold methanol to obtain precipitated oxidized polypropylene. The preoxidized polypropylene thus obtained was then oxidized at 140°C for 8 hr in benzene, acetic acid, and acetic anhydride (5:1:1 by volume) in the presence of manganous decanoate, sodium bromide, and DBP. The color of the solution changed from dark brown to light yellow.

The change in the infrared absorption spectra and gel permeation chromatograms are shown in Figures 4 and 5, respectively. Figure 4 shows that much

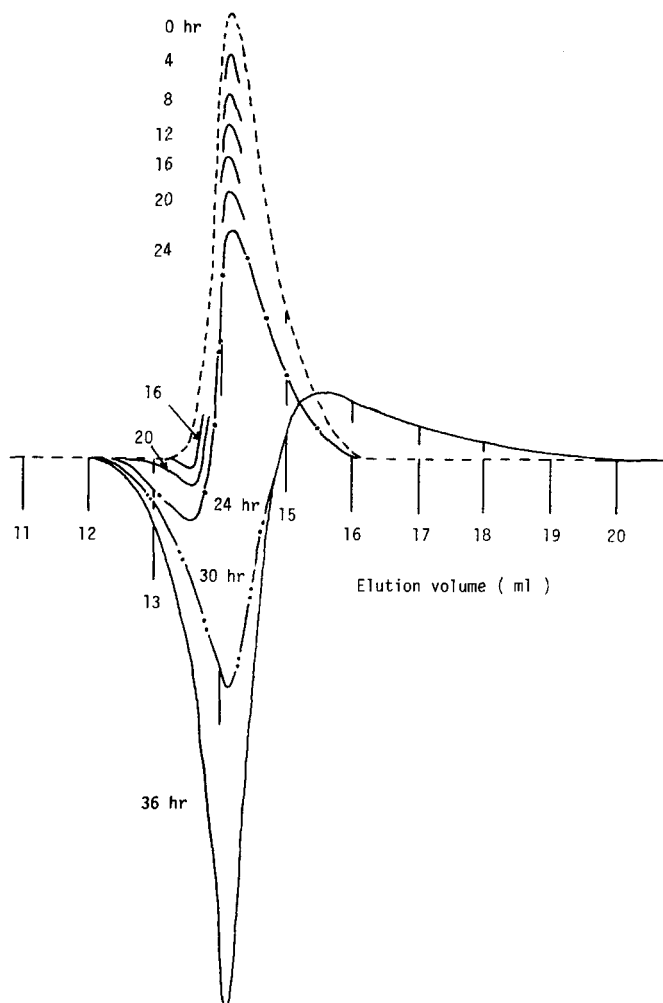


Fig. 6. Gel permeation chromatograms by refractive index of polypropylene oxidized at 170°C in benzene, acetic acid, and acetic anhydride (8:1:1 by volume) with DBP, CoDe_2 , and NaBr.

carbonyl and hydroxy groups were introduced into polymer by the second oxidation. The change in the gel permeation chromatograms is more drastic. Although the extent of decrease in molecular weight is not significant in the oxidation at 170°C, the second oxidation was quite effective in reducing the molecular weight of polypropylene, and Figure 5 implies that much of the oxidized polypropylene had a molecular weight of lower than 1000. It may be noteworthy that the final polypropylene was soluble in methanol, partly soluble in benzene and chloroform, but insoluble in carbon tetrachloride.

Fractionation of Oxidized Polypropylene

More detailed study was carried out to elucidate the formation and nature of products that have a lower refractive index than tetrahydrofuran. This is im-

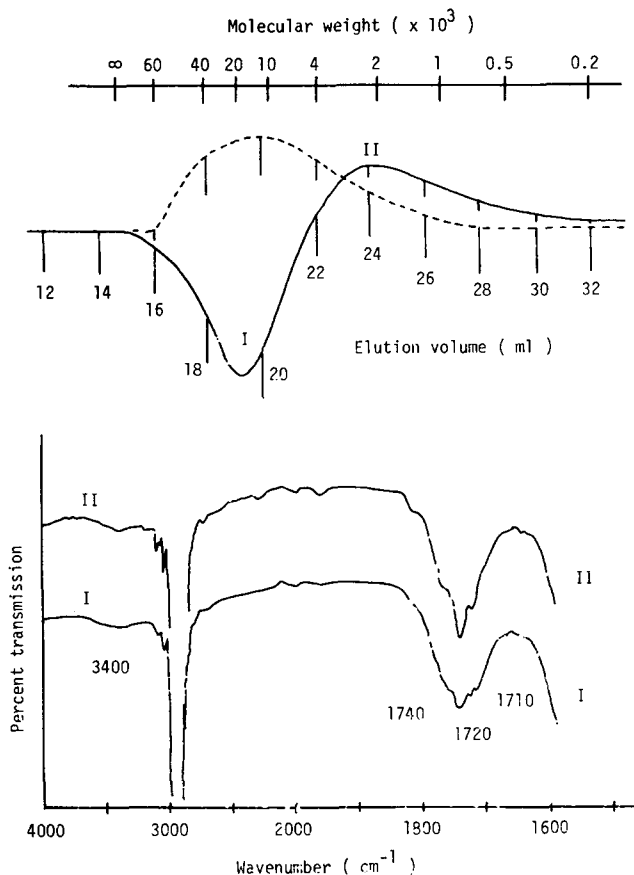


Fig. 7. Gel permeation chromatograms and infrared absorption spectra of oxidized polypropylene.

portant since under these circumstances the change in molecular weight distribution cannot be deduced directly from the gel permeation chromatograms obtained by refractive index.

Figure 6 shows the change in gel permeation chromatograms with time measured by refractive index in the oxidation of polypropylene at 170°C. It can be seen clearly that the refractive index as well as the molecular weight decrease markedly as the oxidation proceeds.

In order to examine the effect of peroxide crosslinking products, the oxidized polypropylene which had a lower refractive index than tetrahydrofuran was heated in benzene at 170°C for 4 hr under nitrogen atmosphere on the premise that the peroxide, if any, would be thermally decomposed under these conditions and reduce the molecular weight of oxidized polypropylene. However, the gel permeation chromatograms before and after thermal treatment showed no substantial change, and no products could be found at all by gas-liquid chromatography. These results imply that the peroxide content is small and contributes little to the lowering of the refractive index.

Figure 7 shows the infrared absorption spectra of two fractions of oxidized polypropylene, one with a lower and the other with a higher refractive index than

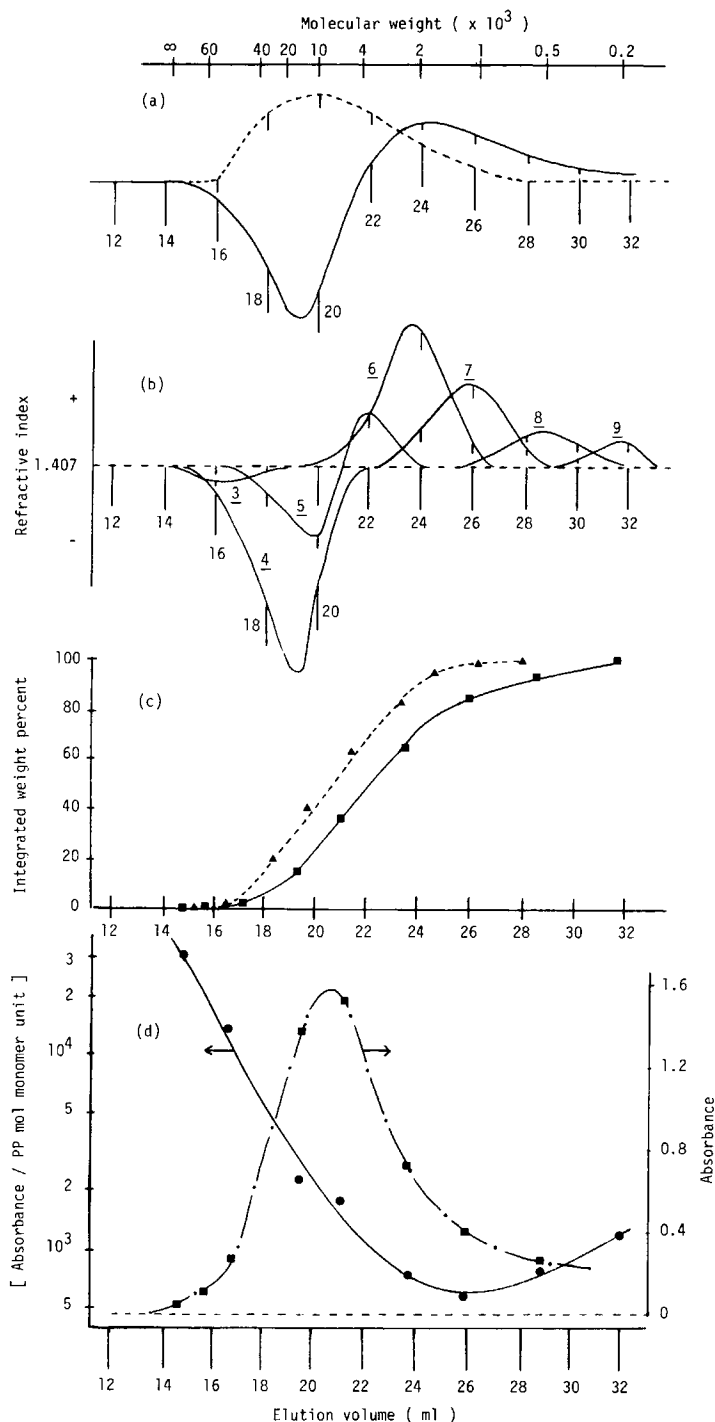


Fig. 8. (a) Gel permeation chromatograms of oxidized polypropylene before fractionation: (-----) Initial PP; (—) oxidized PP. (b) Gel permeation chromatograms of oxidized polypropylene of each fraction by refractive index. Numbers underlined correspond to the fraction number. The refractive index of tetrahydrofuran is 1.407. (c) Integrated weight per cent of initial (-----) and oxidized (—) polypropylene. (d) Ultraviolet absorptions at 260 nm of oxidized polypropylene and per monomer unit. The unoxidized polypropylene had no adsorption at 260 nm.

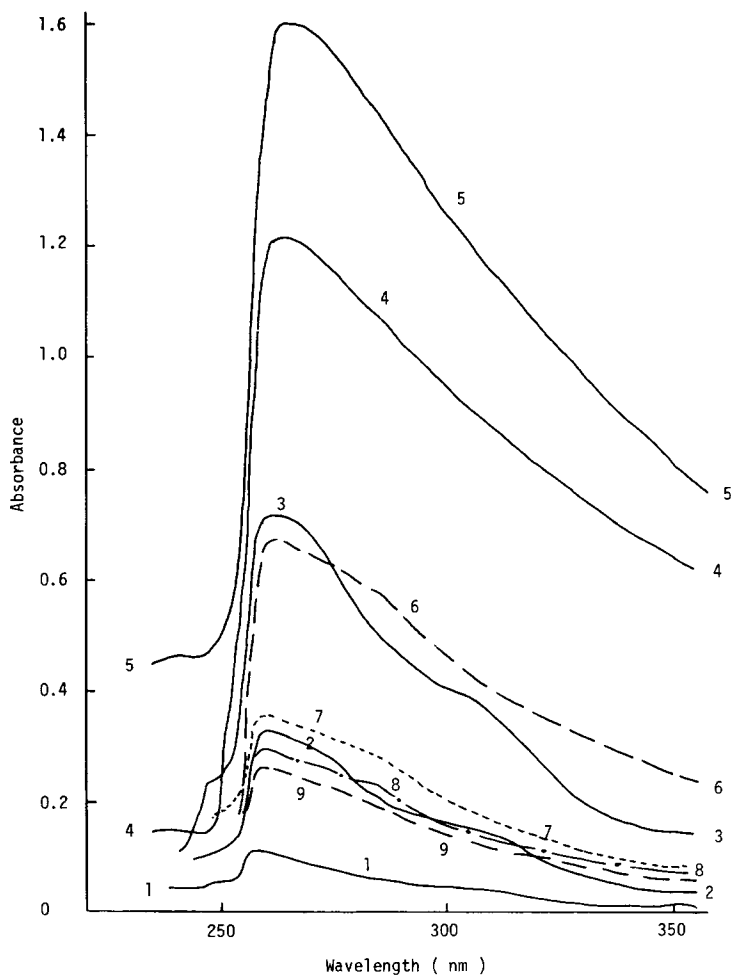


Fig. 9. Ultraviolet absorption spectra of each fraction of oxidized polypropylene. Numbers correspond to the fraction number.

tetrahydrofuran. Formations of hydroxy group (3400 cm^{-1}), ester, acid, and ketone ($1710\text{--}1740\text{ cm}^{-1}$)⁶ are observed for both fractions, and the two spectra resemble each other closely.

The oxidized polypropylene was then fractionated into nine fractions by using gel permeation chromatography. Each fraction was dried under vacuum at room temperature and weighed. Figure 8a shows the gel permeation chromatograms of oxidized polypropylene before fractionation, and Figure 8b illustrate the gel permeation chromatograms of each fraction measured by refractive index. Fractions 1 and 2 contained little products (see Fig. 9). The refractive indices of fractions 3 and 4 were lower than that of tetrahydrofuran, while those of fractions 6, 7, 8, and 9 were higher. The integrated weights per cent of initial and oxidized polypropylene are shown in Figure 8c, which clearly indicates the decrease in molecular weight of the oxidized polypropylene. As shown in Figure 9, similar ultraviolet absorption spectra were obtained for each fraction with λ_{max} at about 260 nm. Figure 8d shows the absorption at 260 nm of fractions of oxi-

dized polypropylene and also the absorbance per polypropylene monomer unit. These figures clearly indicate the change in molecular weight distribution which cannot be deduced by gel permeation chromatograms measured by refractive index alone. It may also be concluded that the decrease in refractive index is ascribed to the high concentrations of functional groups introduced into the polymer chain.

The results shown above indicate that the rate of oxidation of atactic polypropylene in solution under pressure of oxygen increases with temperature, but the decrease in molecular weight is nevertheless not as significant as expected. Although the production of low-boiling oxygenated chemicals seems to be not very promising, production of mixtures of acid, ketone, alcohol, and ester with molecular weights of several hundreds may be possible, especially with cobalt and manganese salts and sodium bromide as catalyst in the presence of acid.

References

1. C. H. Bamford and C. F. H. Tipper, Ed., *Comprehensive Chemical Kinetics*, Vol. 14, *Degradation of Polymers*, Elsevier, Amsterdam, 1975.
2. J. Guillet, Ed., *Polymers and Ecological Problems*, Plenum Press, New York, 1973.
3. L. Lundberg, *Autoxidation and Antioxidants*, Interscience, New York, 1962.
4. E. Niki, T. Shiono, T. Ido, and Y. Kamiya, *J. Appl. Polym. Sci.*, **19**, 3341 (1975).
5. Le. K. Bi and Y. Kamiya, *J. Polym. Sci. A-1*, **7**, 1131 (1969).
6. J. N. Lomonte, *Anal. Chem.*, **36**, 192 (1964).

Received April 5, 1976

Revised May 17, 1976