Oxidative Degradation of Polyolefins. I. Thermal Oxidative Degradation of Atactic Polypropylene in Solution

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Synopsis

Atactic polypropylene was oxidized in solution with radical initiator in the absence and presence of metal catalyst to considerably high conversion over the temperature range of 70° to 125°C, and oxidation products and the change in molecular weight distribution were measured. The unoxidized polypropylene had no ultraviolet absorption at 253.7 nm, whereas the oxidized polypropylene showed distinct absorption over a wide range of molecular weights. It was found that oxygen was incorporated into the polymer chain as hydroperoxide, acid, carbonyl, and hydroxy groups. Much of the absorbed oxygen was found to be involved in smaller fraction of low molecular weight products. Although the average molecular weight of the oxidized polypropylene decreased significantly, the formation of low-boiling products was quite small.

INTRODUCTION

The production of polyolefins is enormous in these days, and much polymer waste are formed in the industries and in urban life. Extensive efforts have been devoted recently to solve this waste problem, and much of the work has been aimed at the recovery of fuel by thermal cracking at high temperature. However, it may be preferable to recover useful organic chemicals from polymer waste. Thus, we have started our study on the accelerated oxidative degradation of polymers in an attempt to recover oxygenated products useful in the petrochemical industries. The behavior of polymers under air is important from the viewpoint of environmental science as well. The present paper deals with the thermal oxidative degradation of atactic polypropylene in solution, the primary objective being to measure the oxidation products and change in the molecular weight distribution during oxidation at relatively high conversion.

Polypropylene is one of the four major polymers used commercially and is quite susceptible to oxidation by molecular oxygen since it has alternate tertiary hydrogens in the main chain. Therefore, much work has been performed to understand the mechanism and kinetics of the oxidation and also to inhibit the oxidative ageing of polypropylene.[1] Accordingly, much of the work so far reported has been carried out at low conversion of the initial stage, and the

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oxidation products at high conversions have not received much attention. Although the formation of low-boiling products such as acetone, acetaldehyde, and acetic acid has been reported in the oxidation of polypropylene,[2,3,4] the yields of these products are usually not known or quite small.

EXPERIMENTAL

Materials

Commercial polypropylene was purified by the conventional procedure using benzene and methanol as solvent and precipitant, respectively. An example of the purification procedure is as follows. About 107 g polypropylene was first soaked in 500 ml benzene at room temperature for several days. The insoluble fraction was separated by filtration and the filtrate was slowly added into 1 liter distilled methanol to obtain polypropylene precipitate. This precipitate was dissolved into 300 ml benzene and introduced into 600 ml methanol. This procedure was repeated three times. Finally, the precipitate was dried to constant weight at room temperature under vacuum in about 40 hr. Thus, 60 g purified polypropylene was obtained. The infrared spectrum of the purified polypropylene in carbon tetrachloride showed strong absorption at 975 cm^{-1} and little absorption at 995 cm^{-1}, indicating that this polypropylene is mostly atactic and little isotactic polypropylene was present.[5] The intrinsic viscosity of the purified polypropylene measured at 45°C in benzene was obtained as 0.164 dl/g, and the viscosity-average molecular weight calculated from this intrinsic viscosity by the relation of Kinsinger and Hughes[6] was 8420.

Chlorobenzene and o-dichlorobenzene were distilled prior to use. Commercial azobisisobutyronitrile (AIBN) and azobiscyclohexanecarbonitrile (ACN) were recrystallized from methanol. Di-tert-butyl peroxide (DBP) supplied by Nippon Oils and Fats Co. was used without further purification.

In some oxidations, commercial metal salts such as cobalt, manganese, copper, and iron were used as catalyst. These metals were used as either naphthenate, decanoate, or acetate as indicated in the text.

Oxidation Procedure

Purified polypropylene, radical initiator, and metal catalyst when required were dissolved in a solvent to obtain an appropriate solution. The mixture was transferred to an about 50-ml round-bottom reaction vessel, which was then connected to a vacuum line equipped with a manometer for measuring the oxygen uptake at constant pressure. The oxidation was carried out under atmospheric pressure of pure oxygen in an oil bath maintained at constant temperature. After the oxidation, the reaction mixture was analyzed as described in a following section.

Analyses

Peroxides. Peroxide formation was determined by iodometric titration. Two types of procedures were employed: one was to determine only hydroperoxide, and the other was to determine both hydroperoxide and dialkyl

peroxide. In the first procedure, 1 ml product solution was added to a solution of 40 ml isopropyl alcohol and 5 ml glacial acetic acid containing 2 ml NaI-saturated isopropyl alcohol solution. After 10 min of refluxing, 10 ml water was added from the top of the condenser, and the liberated iodine was titrated with an aqueous solution of $0.01N$ $Na_2S_2O_3$. In the second procedure, hydrochloric acid was used instead of acetic acid as described in the literature.[1]

Carbonyl and Hydroxy Compounds. These groups were determined by infrared spectroscopy using bands at 1710 and 3350 cm^{-1}, respectively. The extinction coefficients were measured by using model compounds such as 2-octanone, propionaldehyde, acetic acid, n-capric acid, azeraic acid, *tert*-amyl alcohol, and *tert*-butyl hydroperoxide. Spectra were recorded on a Jasco spectrometer Model IR-G. Liquid samples were analyzed in a 0.1-mm potassium bromide or calcium fluoride cell. An unoxidized polypropylene solution was placed in the reference beam.

Acid. Acid was determined by titration with $0.1N$ alcoholic sodium hydroxide. It was assured that the hydroperoxide present did not interfere this acid titration.

Low-Boiling Products. Gas–liquid chromatographic analyses were employed to measure the low-boiling products. Chromatograms were recorded on Shimadzu 4APTF and 4BPT gas chromatographs equipped with digital integrator. Three kinds of columns were employed: 3 mm × 7 m column packed with 10 wt-%, 80–100 mesh polyethylene glycol $20M$ on Uniport B (70° and 110°C), 3 mm × 3 m column packed with 15 wt-%, 80–100 mesh Apiezon grease L on Uniport B (150°C), and 3 mm × 2 m column packed with 50–80 mesh Porapak-Q (110°C). Volatile gasses were analyzed by molecular sieve 13X and activated charcoal columns. Helium was used as a carrier gas for all columns.

Molecular Weight Distribution. The change in the molecular weight distribution was followed by gel permeation chromatography (GPC) using du Pont Liquid Chromatograph Model 830. Two crosslinked polystyrene gel column combinations (0.5 m each of HSG-10 and HSG-15 supplied by Shimadzu) were employed 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.

Viscosity. Viscosities of initial and oxidized polypropylene were measured at 45°C in benzene using a calibrated modified Ostwald viscosimeter. Viscosity-average molecular weight was calculated from intrinsic viscosity by the relation of Kinsinger and Hughes.[6]

Elemental Analysis. Elemental analyses were performed for initial and oxidized polypropylene at Mitsui Toatsu Chemical Co.

RESULTS AND DISCUSSION

AIBN-Initiated Oxidation of Polypropylene at 70°C in Chlorobenzene

The results of oxidations of polypropylene in chlorobenzene at 70°C in the presence of AIBN as radical initiator are summarized in Table I. The conversion, amount of oxygen absorbed per monomer unit, reached to about 8%

TABLE I
Oxidation of Polypropylene in Chlorobenzene at 70°C Under 1 atm Oxygen for 5 Hours

Expt.	1	2	3	4	5	6	7
[PP],[a] M	2.40	2.34	2.47	2.41	2.38	2.34	2.38
[AIBN] × 10^2, M	1.02	4.10	8.13	3.90	4.16	4.15	4.01
Metal[b]				Co	Fe	Mn	Cu
[Metal] × 10^2, M				0.99	1.06	1.02	1.05
ΔO_2 × 10^2,[c] M	3.08	9.25	17.97	11.99	16.60	16.41	19.96
$(\Delta O_2/[PP])$ × 10^2, %	1.3	3.6	7.3	5.0	7.0	7.0	8.4
hpo × 10^2,[d] M	1.99	5.43	9.37	2.13	3.85	2.27	3.16
$(hpo/\Delta O_2)$ × 10^2, %	64.6	58.7	52.1	17.8	23.2	13.8	15.8
$[\eta]$[e]		0.150		0.119		0.125	

[a] Polypropylene concentration in monomer unit.

[b] As metal naphthenate.

[c] Total oxygen consumed, corrected for nitrogen evolution from AIBN.

[d] Total hydroperoxide formed.

[e] Intrinsic viscosity of oxidized polypropylene at 45°C in benzene, $[\eta]$ for initial polypropylene was 0.168.

in 5 hr. The rate of oxidation increased with increasing initiator concentration. The addition of metal catalyst increased the rate of oxidation, though not so significantly, and the metals were effective in the order of Cu > Mn ≈ Fe > Co. The primary major product was hydroperoxide as observed in the oxidation of simple hydrocarbons. The yield of hydroperoxide was as high as 65%, but it decreased with increasing initiator concentration. This may be partly because the kinetic chain length decreased with increasing initiator
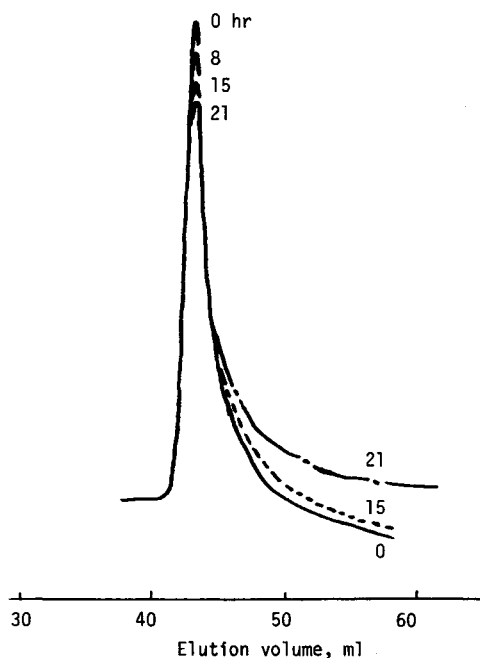

Fig. 1. Gel permeation chromatograms of polypropylene oxidized at 90°C in chlorobenzene with 1.98 × $10^{-2}M$ ACN.
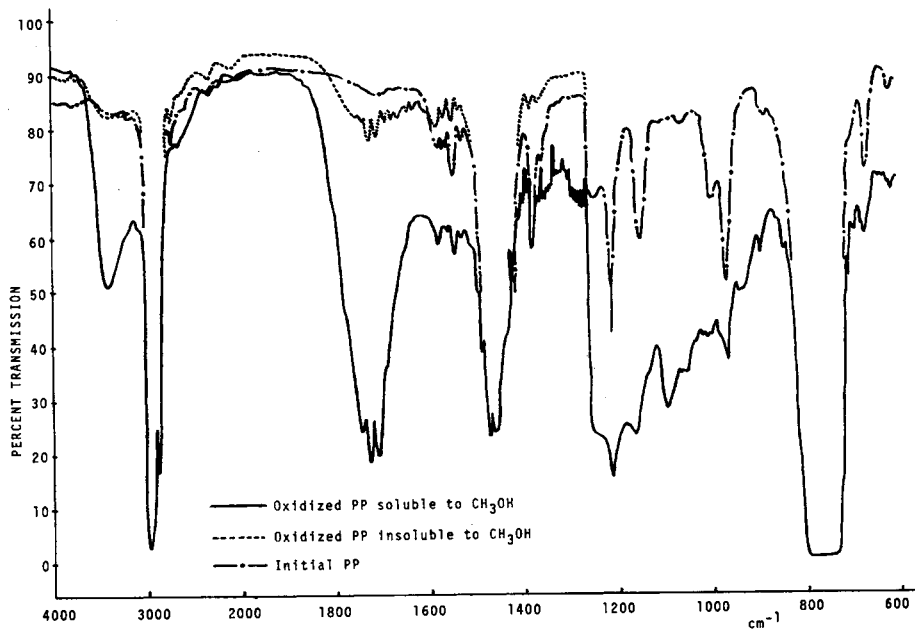
Fig. 2. Infrared spectra of polypropylene solutions in carbon tetrachloride.

concentration and partly because hydroperoxide was subjected to secondary reactions at higher conversion. Bawn[7] and Van Sickle[8] also found that the yield of polypropylene hydroperoxide decreased with increasing conversion. A much lower yield of hydroperoxide in the presence of metal catalyst should be apparently due to the redox decomposition of hydroperoxide by the metal catalyst.[9] Other major products were carbonyl compounds and alcohol, as determined by infrared spectra. The formation of these products was larger as predicted in the presence of metal catalyst.

The intrinsic viscosity of the oxidized polypropylene was measured and compared with the initial polypropylene. As shown in Table I, the oxidized polypropylene had considerably lower intrinsic viscosity than the unoxidized polypropylene. However, little low-boiling products could be observed by GLC.

ACN-Initiated Oxidation of Polypropylene at 90°C in Chlorobenzene

When 2.39M polypropylene was oxidized in chlorobenzene at 90°C with 1.98 × 10^{-2}M ACN under atmospheric pressure of oxygen, 0.152M oxygen uptake was observed in 21 hr, corresponding to a conversion of 6.4%. The total hydroperoxide formed was found to be 0.043M, which was 28% of oxygen absorbed. Little low-boiling products were found by GLC. The change in molecular weight distribution with time measured by gel permeation chromatography is shown in Figure 1, which indicates that the molecular weight of polypropylene decreased with time.

In order to obtain a higher conversion, 2.0M polypropylene was oxidized in chlorobenzene at 90°C in the presence of 2.0 × 10^{-2}M ACN and 1.05 ×
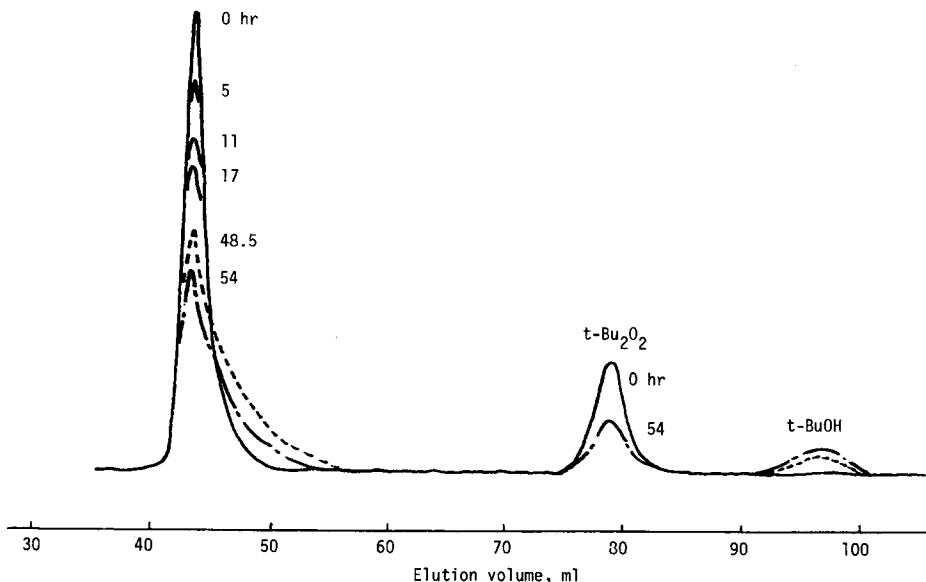
Fig. 3. Gel permeation chromatograms of polypropylene oxidized at 110°C in chlorobenzene with DBP.

$10^{-2}M$ copper naphthenate for 50 hr. The half-life of ACN at 90°C is approximately 5 hr, and $1.0 \times 10^{-2}M$ ACN was added to the reaction mixture in every 5 hr. The observed oxygen uptake was $0.74M$, and the conversion reached 37%. However, little low-boiling products could be found by GLC except acetone, which increased with conversion. The total acid formation was found as high as 29% of oxygen absorbed. The product solution was colored brown, and the hydroperoxide could not be determined accurately by iodometric titration.

The oxidation product solution was introduced slowly into ten times as much by volume of methanol. About two thirds of polypropylene was found to be soluble, and only one third was recovered as precipitate. Figure 2 shows the infrared absorption spectra of the initial and oxidized polypropylenes. It can be seen that the oxidized polypropylene soluble in methanol has strong absorption of hydroxy and carbonyl groups, whereas oxidized polypropylene insoluble in methanol has only small absorption by these groups.

DBP-Initiated Oxidation of Polypropylene at 110° and 125°C

Polypropylene was first oxidized at 110°C in chlorobenzene using DBP as an initiator. The change in molecular weight distribution of polypropylene with time is shown in Figure 3, which shows the monotonous decrease in the molecular weight of polypropylene with conversion. However, the decrease in molecular weight was not so significant.

Table II summarizes the results of DBP-initiated oxidation of polypropylene in o-dichlorobenzene at 125°C. The maximum conversion was as high as 26%. In contrast to the results in Table I at 70°C, manganese decanoate accelerated the oxidation of polypropylene but cobalt and copper showed nega-

TABLE II
Oxidation of Polypropylene at 125°C
in o-Dichlorobenzene Initiated with $3.0 \times 10^{-2}M$ DBP

Expt.	8	9	10	11	12	13	14
PP, g	1.003	1.042	1.020	1.019	1.003	0.706	0.709
[PP], M	2.38	2.48	2.42	2.42	2.38	1.68	1.68
Solution, ml	10	10	10	10	10	10[a]	10[a]
Catalyst			Cu[b]	Co[b]	Mn[b]	Cu[b]	Co[c]
[Cat] $\times 10^2$, M			2.0	2.0	2.0	2.0	2.0
Time, hr	8	16	8	8	8	8	8
ΔO_2, M	0.447	0.664	0.379	0.246	0.613	0.180	0.257
Conversion, %	18.8	26.0	15.6	10.2	25.7	10.7	15.3
Products, % oxygen absorbed							
hpo	8.8	7.3	3.9	2.3	1.8	4.3	1.1
acid	19.4	19.4	22.8	28.2	24.9		
alcohol[d]	72.0	36.7	62.8				
$>C{=}O$[d]	5.6	10.9	7.9	12.4	3.3		

[a] With 3 ml acetic acid.
[b] As decanoate.
[c] As cobaltous acetate with $1.1 \times 10^{-2}M$ NaBr.
[d] Alcohol and ketone (and aldehyde) determined by IR after correction for hydroperoxide and acid, respectively.

tive effect on the rate of oxidation. The addition of acetic acid or sodium bromide was not so effective (expts. 13 and 14), although they were found previously[10] to be quite effective at lower temperature. The yield of hydro-

TABLE III
Elemental Analyses of Initial and Oxidized Polypropylene

Compound	C, %	H, %	O, %
Initial polypropylene			
obsd.	85.77	14.25	
calcd.	85.71	14.29	0.00
Oxidized polypropylene,[a] obsd.	73.43	11.38	15.19
Precipitated polypropylene,[b] obsd.	78.88	12.70	8.42
$[{-}(CH_2{-}\overset{CH_3}{\underset{}{CH}}{)_3}CH_2{-}\overset{CH_3}{\underset{OOH}{C}}{-}]$, calcd.	72.0	12.0	16.0
$[{-}(CH_2{-}\overset{CH_3}{\underset{}{CH}}{)_3}CH_2{-}\overset{}{\underset{O}{\overset{\|}{C}}}{-}]$, calcd.	78.6	11.9	9.5
$[{-}(CH_2{-}\overset{CH_3}{\underset{}{CH}}{)_3}CH_2{-}\overset{CH_3}{\underset{OH}{C}}{-}]$, calcd.	78.3	13.0	8.7
$[{-}(CH_2{-}\overset{CH_3}{\underset{}{CH}}{)_3}CH_2{-}\overset{CH_3}{\underset{O{-}}{C}}{-}]$, calcd.	78.7	12.6	8.7

[a] Oxidized polypropylene, dried by removal of solvent and volatile materials from the reaction mixture under vacuum.
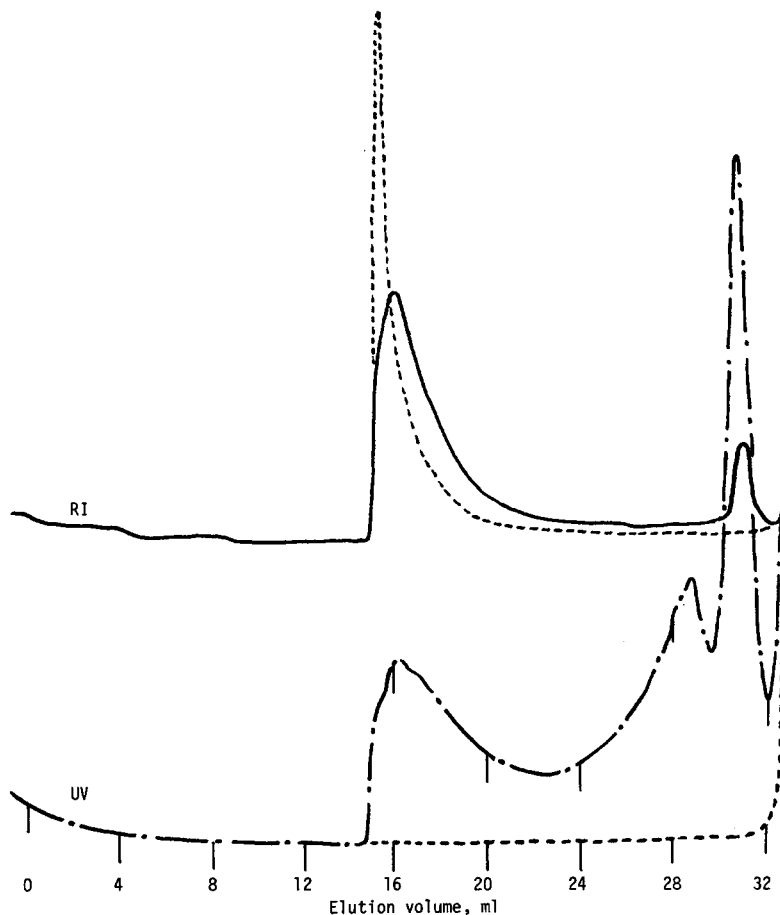[b] Oxidized polypropylene precipitated from methanol and dried.

Fig. 4. Gel permeation chromatograms of polypropylene oxidized at 125°C in o-dichloroben-zene, conversion = 18.8% (expt. 8): (- - - - -) initial PP; (———) oxidized PP by RI; (— - —) oxidized PP by UV.

peroxide was less than 10%, and more acid, alcohol, and carbonyl compounds were produced at 125°C.

Gel permeation chromatograms obtained in experiments 8, 9, 11, and 12 are shown in Figures 4, 5, 6, and 7, respectively. These figures show that the molecular weight of oxidized polypropylene drifted to lower fractions. It is interesting that the initial polypropylene had no absorption at 253.7 nm, whereas the oxidized polypropylene had strong absorption, indicating the introduction of oxygen into the main chain. Although the chromatograms measured by refractive index do not clearly show the formation of low molecular weight products, the ultraviolet analyses show the formation of low molecular weight fractions which contained relatively more carbonyl or hydroxy group than that of high molecular weight fraction. Figures 4 and 5 show the effect of conversion: more decrease in the molecular weight and more ultraviolet absorption at lower molecular weight fraction are observed as the conversion increased.

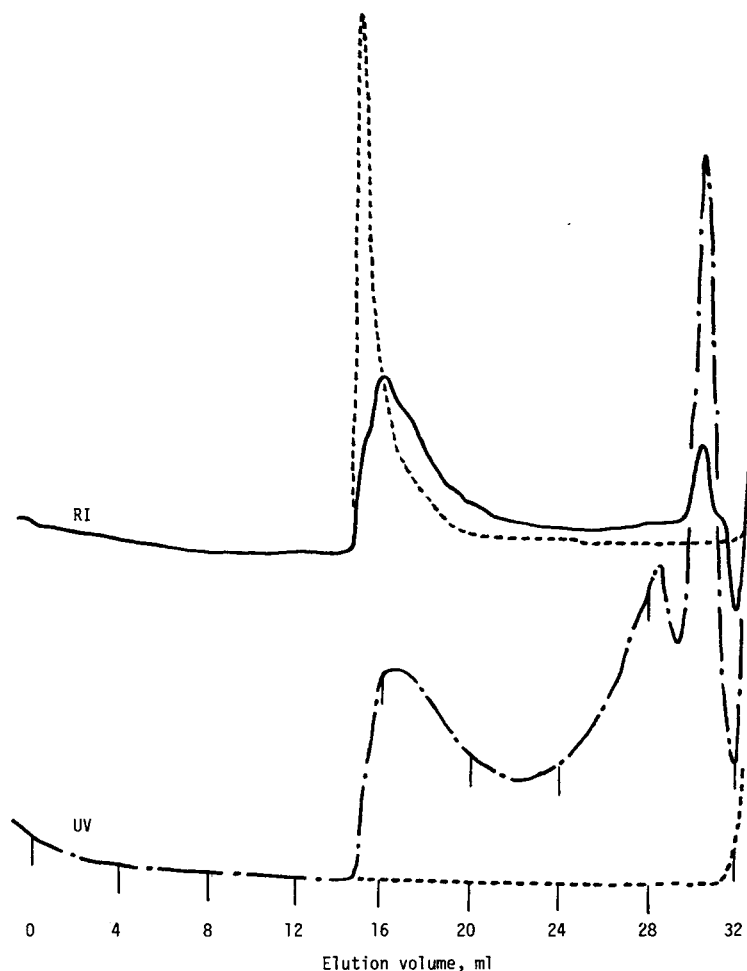In order to obtain more information on the oxidation products of polypro-

Fig. 5. Gel permeation chromatograms of polypropylene oxidized at 125°C in o-dichloroben-zene, conversion = 26.0% (expt. 9): (- - - - -) initial PP; (———) oxidized PP by RI; (— - —) oxidized PP by UV.

pylene, 3.17 g polypropylene was oxidized at 125°C in 20 ml o-dichloroben-zene with three portions of 0.12M DBP, added three times at an appropriate time intervals. In 20 hr, 418 ml oxygen uptake was observed, corresponding to 24.7% conversion. The amounts of hydroperoxide and acid formed were found by titration as 3.3% and 19% of oxygen absorbed, respectively. An aliquot of the reaction mixture was taken out, and solvent and volatile materials were removed under vacuum to obtain dried, oxidized polypropylene. The molecular weight of this polypropylene was about 1800, much smaller than the initial 11300.

When 5 ml product solution was introduced into 30 ml cold methanol, about 90% polypropylene was insoluble and precipitated. The precipitate was washed with methanol several times and dried at room temperature under vacuum. It was found that this precipitated polypropylene contained approximately 2%, and 10% oxygen absorbed as hydroperoxide and acid, respectively. The infrared absorption spectra showed that about 5% absorbed
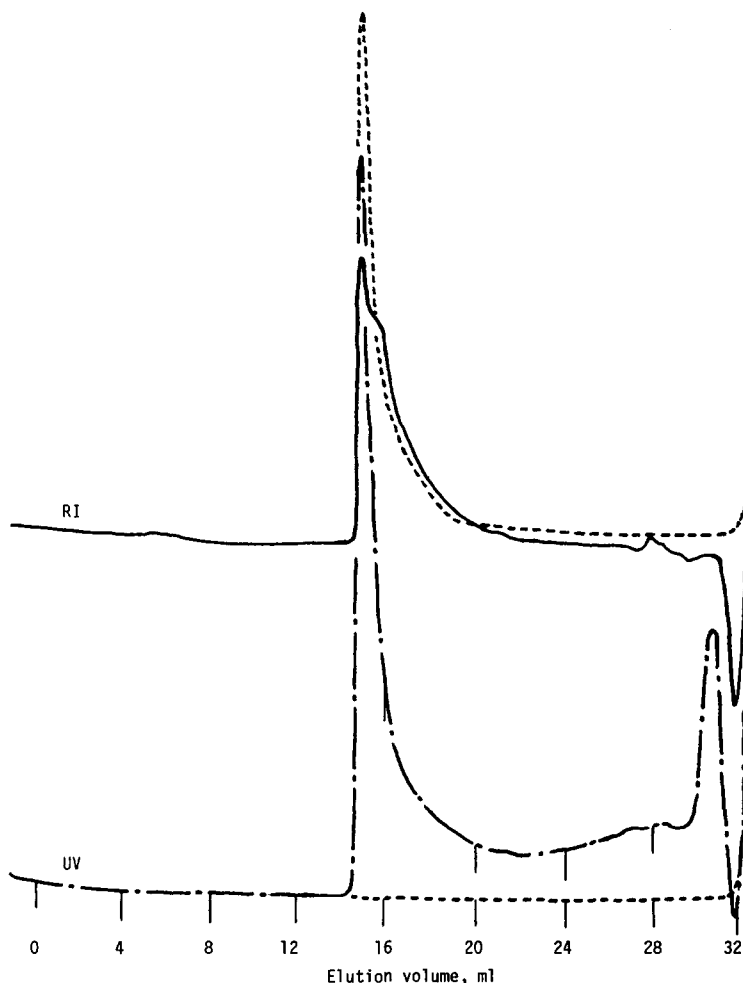
Fig. 6. Gel permeation chromatograms of polypropylene oxidized at 125°C in o-dichloroben-
zene with cobalt decanoate (expt. 11): (- - - - -) initial PP; (———) oxidized PP by RI; (— · —) oxi-
dized PP by UV.

oxygen was present as carbonyl group in this precipitate. The hydroxy group
content was small. The molecular weight of this precipitated polypropylene
was obtained as 2480.

The results of elemental analyses of the initial and oxidized polypropylene
are given in Table III. The results of initial polypropylene agreed satisfacto-
rily with the calculated numbers. The oxygen content in the precipitated
polypropylene was significantly lower than that of total oxidized polypropyl-
ene. This may be because the precipitated polypropylene contained less hy-
droperoxide and acid. Table III implies that much of the oxygen absorbed is
taken into polymer chain as either acid, ketone, alcohol, or dialkyl peroxide,
which is a peroxide crosslinking. This crosslinking may be the reason why as
high as 90% of the oxidized polypropylene did not dissolve into methanol but
precipitated in spite of relatively high conversion when the product mixture
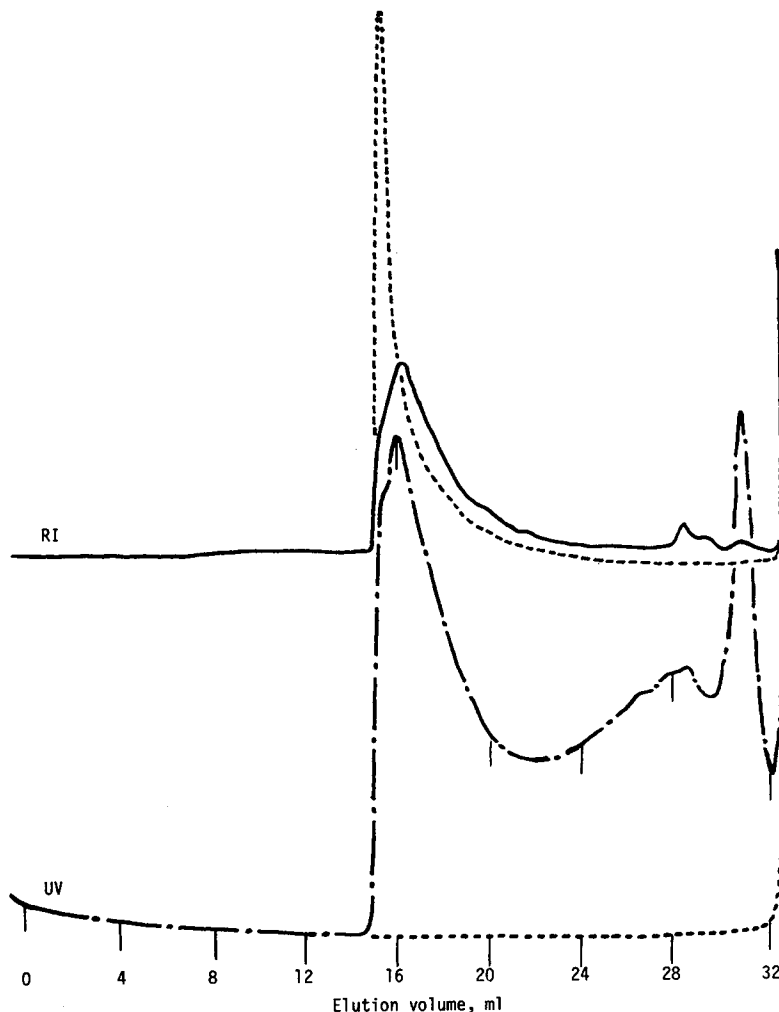was added to cold methanol. Abu-Isa[11] found in the thermal oxidation of

Fig. 7. Gel permeation chromatograms of polypropylene oxidized at 125°C in o-dichloroben-zene with managanese decanoate (expt. 12): (- - - - -) initial PP; (———) oxidized PP by RI; (— · —) oxidized PP by UV.

polypropylene film that the degree of crystallinity increased with the degree of oxidation.

Figures 8 and 9 show, respectively, the gel permeation chromatograms of the oxidized polypropylene obtained by removal of solvent and volatile materials from whole reaction mixture and polypropylene precipitated from cold methanol. It is clear that oxygen was incorporated into the polymer chain over a wide range of molecular weight and polypropylene precipitated had little low molecular weight fraction. The results mentioned above suggest that much of the absorbed oxygen is involved in smaller fraction of soluble, low molecular weight products. However, the GLC analyses showed that the formation of low-boiling products was quite small.

Most of the cleavage of the backbone of polypropylene under the reaction conditions employed in this study must arise from the β-scission of the terti-
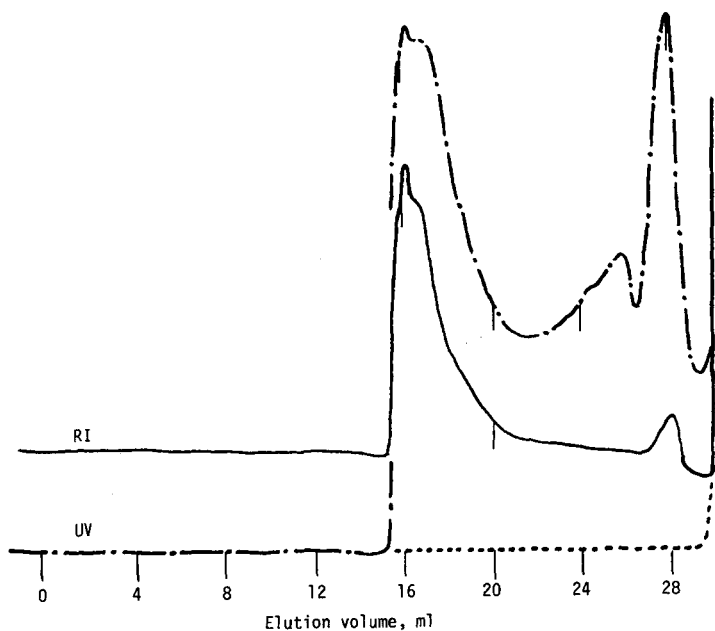
Fig. 8. Gel permeation chromatograms of oxidized polypropylene obtained by removal of solvent from whole reaction mixture: (- - - - -) initial PP; (———) oxidized PP by RI; (— · —) oxidized PP by UV.

ary alkoxy radical formed by the nonterminating interactions of polypropylene peroxy radicals and by the decomposition of polypropylene hydroperoxide.[1,12]   From this viewpoint, aromatic or polar solvent may be preferable since β-scission of alkoxy radical is favored over hydrogen atom abstraction in these solvents.[13]   However, the results shown above suggest that this type of cleavage alone is not sufficient to give much low-boiling products even in the
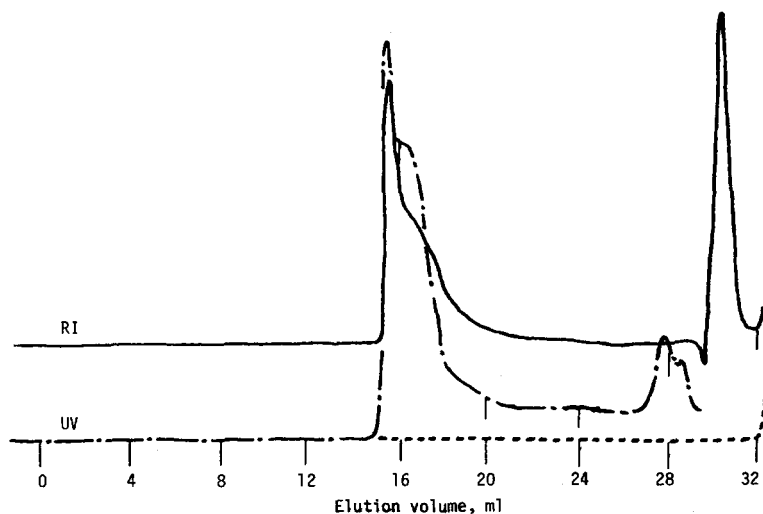
Fig. 9. Gel permeation chromatograms of oxidized polypropylene precipitated from methanol: (- - - - -) initial PP; (———) oxidized PP by RI; (— - —) oxidized PP by UV.

presence of metal catalyst. The oxidation at higher temperature may be required for this purpose. Considering that major primary oxidation products are hydroperoxide and carbonyl compounds, another possible approach may be the photochemical oxidative degradation[3,14] since ultraviolet light is known to be effective in the cleavage of these compounds by either radical or nonradical process. The catalytic cleavage of oxidized polypropylene by, for example, acid[15] or base may also be promising. These studies are now in progress in our laboratory.

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