

Thermal Oxidation of Fractionated Polypropylene in Solution

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Synopsis

Thermal oxidation of fractionated polypropylene was carried out in trichlorobenzene under atmospheric oxygen at 125°C with conventional oxygen uptake. The oxidizability of the polymers is discussed on the basis of the oxygen uptake curves and the properties of the polymers. Fractions of atactic polypropylene oxidized easily at the initial stage of the oxidation and showed neither autoxidation phenomena nor the induction period observed in the isotactic polymer. Hydrogenation of the ether-soluble fraction by a Wilkinson catalyst gave a polymer which was, according to infrared spectrometry, free from impurity groups such as hydroperoxide, carbonyl, and unsaturation groups. The hydrogenated fraction was more stable to thermal oxidation than the unhydrogenated fraction and showed an induction period. The results indicate that the initiation process of the oxidation of polypropylene is apparently dependent on the impurities such as hydroperoxide, carbonyl, and unsaturation and that stereoregularity of the polymer affects the kinetic dependence of the oxidation.

INTRODUCTION

The initiation process either in thermal degradation or photodegradation of polymers is substantially affected by the presence of trace amounts of impurities such as hydroperoxide, carbonyl, and unsaturation, and contaminants such as catalyst residues and metallic compounds which are believed to originate in the production machine, in particular the pelletizer.¹⁻⁵ In addition, differences in stereoregularity of the polymers affect the kinetic dependence of the degradation of the polymers. Dulog et al.^{6,7} reported that autoxidation of isotactic polypropylene and poly(butene-1) in trichlorobenzene solution showed a kinetic behavior different from that of the atactic fractions of these polymers. Kamiya also observed similar results in the catalyzed oxidation of polypropylene⁸ and polystyrene.⁹ Dulog et al.^{6,7} attributed the difference to the favorable spatial configuration of the isotactic structure. They concluded that a bimolecular initiation step to the oxidation of the isotactic polymers involved attack by oxygen on the hydrogen on the tertiary carbon of the isotactic polymers, a further attack on the hydrogen of the adjacent tertiary carbon then being preferred. Van Sickle¹⁰ stated that the kinetic behavior of the amorphous and crystalline forms differs slightly and that the oxidation rate of the amorphous type is slower for a given polypropylene and initiator concentration. In a recent publication, Chien and Wang¹¹ carried out the thermal oxidation of polyolefin films for an initiated system, and the measurements were made for low conversion, from 0.6% to 2%. They observed that results are in contradiction with others obtained previously in solution oxidations.⁶⁻⁹

It is therefore preferable to discuss the oxidizability of the polymer in con-

nection with both stereoregularity of the polymer and impurities in the polymer independently. As an experimental approach to this problem, several fractions of polypropylene with different stereoregularity and a fraction reduced with a Wilkinson catalyst which was supposed to be free from impurity groups were prepared, and the thermal oxidation was carried out with a conventional oxygen uptake apparatus. The results obtained apparently demonstrate the important roles of both impurities and stereoregularity of the polypropylene in the thermal oxidation of the polymer.

EXPERIMENTAL

Samples

Neat powdery isotactic polypropylene (IPP) and atactic polypropylene (APP) were products of a manufacturing plant in Japan. APP (ca. 30 g; cut into ca. 1 mm³) packed into a filter paper thimble was placed in a Soxhlet extractor and was successively extracted with 700 ml ether, hexane, and heptane for 10 hr under a nitrogen atmosphere. The powdery IPP, finer than 100 mesh, was used without further extraction. After the extraction, ether was removed under reduced pressure, and the ether-soluble fraction was dried in vacuo at ambient temperature. In other fractions, large parts of solvents were removed under reduced pressure, and the polymers extracted were precipitated into a large amount of acetone. The precipitates were filtered through a sintered-glass disk and dried under reduced pressure at ambient temperature. The recoveries of each fraction and properties of the polymers are summarized in Table I.

Characterization of the Polymers

Molecular weight of the ether-soluble fraction and ether-insoluble-hexane-soluble fraction was measured in benzene at 30°C, and that of other polymers was measured in decalin containing a small amount of antioxidant (Topanol, product of I.C.I., Ltd.) at 135°C under nitrogen. The molecular weight of each polymer was determined with the aid of following equations¹²:

For ether-soluble and ether-insoluble-hexane-soluble fractions:

$$[\eta] = 33.8 \times 10^{-5} \bar{M}_w^{0.67}$$

For others:

$$[\eta] = 9.17 \times 10^{-5} \bar{M}_w^{0.8}$$

TABLE I
Properties of Samples

Sample	Fraction	Recovery, %	$\bar{M}_w \times 10^{-4}$	D.P.	Isotacticity, %
A	APP, original	—	2.60	618	31.9
B	APP, ether soluble	61.7	0.745	177	4.7
C	APP, ether insoluble, hexane soluble	12.8	2.858	679	48.4
D	APP, hexane insoluble, heptane soluble	22.3	2.894	688	70.6
E	IPP, original	—	14.54	3455	80.8
F	APP, ether soluble, hydrogenated	—	0.76	180	14.1

The infrared absorption spectrum of each sample was recorded on a double-beam grating spectrophotometer, Hitachi EpI-G3. Isotacticity of the polymers was calculated according to the following empirical equation,¹³ which was derived from the relationship between atactic percentage in the polypropylene and optical density ratio at 974 cm^{-1} and 995 cm^{-1} 14:

$$\text{Iso}(\%) = \left\{ 1 - \frac{k - 1}{0.853k - 0.113} \right\} \times 100$$

where k = optical density ratio ($D_{974\text{ cm}^{-1}}/D_{995\text{ cm}^{-1}}$).

Thermal Oxidation

In a ca. 20-ml flat-bottomed oxygen absorption cell containing 1 g (or 0.2 g) polymer, 10 ml (or 5 ml) 1,2,4-trichlorobenzene was added. The oxidation was carried out under atmospheric pressure at 125°C with a magnetic stirrer at a constant stirring rate of 700 rpm. The oxygen uptake measurements were made in the apparatus shown in Figure 1.

Hydrogenation of Ether-Soluble Fraction

Solution containing 3 g ether-soluble fraction in 50 ml benzene was degassed

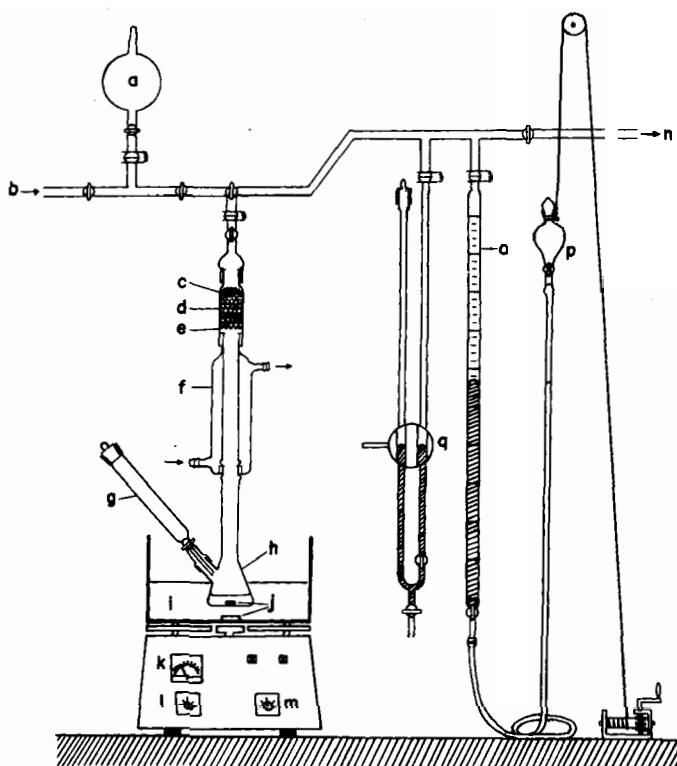


Fig. 1. Oxygen uptake apparatus: (a) oxygen reservoir; (b) oxygen; (c) glass wool; (d) silica gel (20–50 mesh); (e) glass filter; (f) cooler (water); (g) dropping funnel; (h) reaction cell; (i) oil bath; (j) magnetic stirrer; (k) tachometer (rpm); (l) stirrer control; (m) thermostat; (n) vacuum pump; (o) gasometer (40 ml); (p) leveling bulb; (q) magnifying glass.

by a freeze-melt method. Tris(triphenylphosphine chlororhodium) $[\text{RhCl}(\text{PPh}_3)_3]$, 150 mg], which had been prepared according to the procedures of Wilkinson et al.,^{15,16} was added to the solution under a nitrogen atmosphere, and hydrogen gas was bubbled into the solution at ambient temperature for 3 hr. After the reaction, benzene was removed under reduced pressure, and the residue was dissolved with heptane (light yellow solution). The solution was passed through a column containing activated alumina and active charcoal. Heptane was removed from the eluate, and the residue was poured into a large amount of methanol. The precipitate was filtered and dried in vacuo at ambient temperature.

RESULTS AND DISCUSSION

Oxygen uptake curves of each sample are shown in Figure 2. The figure shows differences in the thermal oxidation behavior of the fractionated samples. In the case of IPP (sample E), the rate of oxygen uptake is slow at the initial stage of the thermal oxidation, and an autoxidation phenomenon is observed after a certain period. On the other hand, the oxygen uptake curves of APP (samples A, B, and C) are different from that of the isotactic polymer. The shape of the curve is almost linear through the oxidation, and neither induction period nor autoxidation phenomena are observed.

The results apparently indicate that the maximum rate of the oxidation of IPP is faster than that of APP. When one discusses the oxidizability of the polypropylene on the basis of maximum rate of oxidation, the results are consistent with that of previous works.⁶⁻⁹ However, in this study, atactic fractions oxidize much faster than isotactic polymer at the initial stage of the oxidation. This implies the important role of the impurity groups in the polymer in the initiation process of the thermal oxidation of the polymer.

Significant differences in the characteristic infrared spectra of each sample were observed (Fig. 3). Infrared spectra of atactic fractions show the presence of a pendent-type unsaturation at 888 cm^{-1} .¹⁴ However, the unsaturated group was scarcely detected in isotactic polymer. The relative amount of the pen-

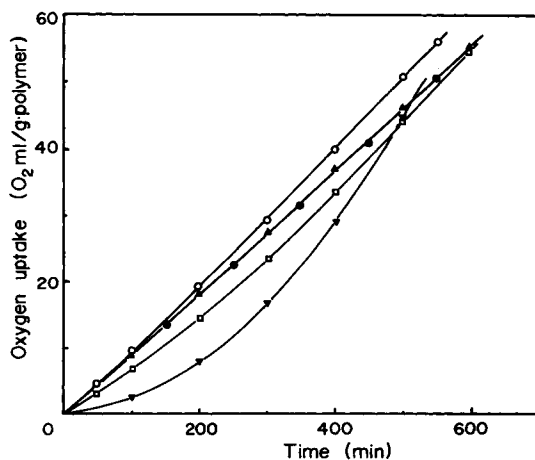


Fig. 2. Oxygen absorption curves of each sample at 125°C in TCB (PP 1 g/10 ml TCB): (O) B (APP ether); (●) A (APP original); (Δ) C (APP hexane); (\square) D (APP heptane); (\blacktriangledown) E (IPP original) (see Table I).

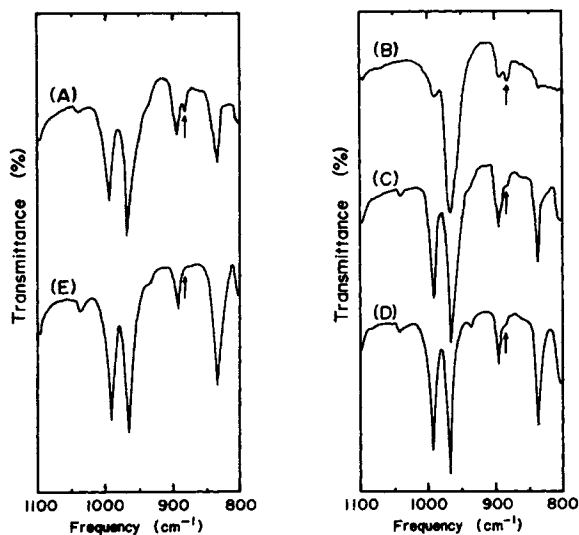


Fig. 3. Infrared spectra of samples A (APP original), B (APP ether), C (APP hexane), D (APP heptane), and E (IPP original). Relative absorbance ($A_{888 \text{ cm}^{-1}}/A_{2720 \text{ cm}^{-1}}$): A, 0.326; B, 0.472; C, 0.226; D, 0.136; E, 0.054. A, C, and D films were prepared by a vacuum press; B, sample was mounted on a NaCl plate; E, KBr pellet.

dent-type unsaturation was calculated using the absorption peak at 2720 cm^{-1} as an internal standard. The results noted in Figure 3 and data in Table I apparently show a correlation between the tacticity of the polymer and the relative amount of unsaturated groups, and the content of the unsaturation is highest in the ether-soluble fraction. For the initiation process in the oxidation of the polymer, it has been considered that hydroperoxide and carbonyl groups, as well as unsaturated groups, play very important roles.¹⁻⁵

It is desirable to use a polypropylene which is completely free of impurity groups such as hydroperoxide, carbonyl, and unsaturated groups in order to ascertain the role of these groups in the oxidation of the polymer. However, the ideal polymer is not available at present, and saturated hydrocarbons have been used as model compounds. It is assumed that reduction of atactic fraction may give a polymer which is free from impurity groups.

Thus, the ether-soluble fraction of APP was reduced by a Wilkinson catalyst in benzene solution. Infrared spectra of the ether-soluble fraction of APP before and after reduction were measured by mounting samples on a sodium chloride plate. The infrared spectra of the impurity group regions in both samples are shown in Figure 4. Before the hydrogenation, the ether-soluble fraction clearly shows the presence of associated hydroperoxide (at ca. 3350 cm^{-1}),¹⁷ carbonyl groups (at ca. 1720 cm^{-1}), and unsaturated groups (at 1645 and 888 cm^{-1}), while the reduced fraction shows none of these groups (Fig. 4). Therefore, one may say that the reduction of the ether-soluble fraction by a Wilkinson catalyst gave a polymer which is, according to infrared spectrophotometry, free from impurity groups such as hydroperoxide, carbonyl, and unsaturated groups.

The thermal oxidation of the reduced fraction was carried out and compared with that of the unreduced fraction. The oxygen uptake curves of both samples

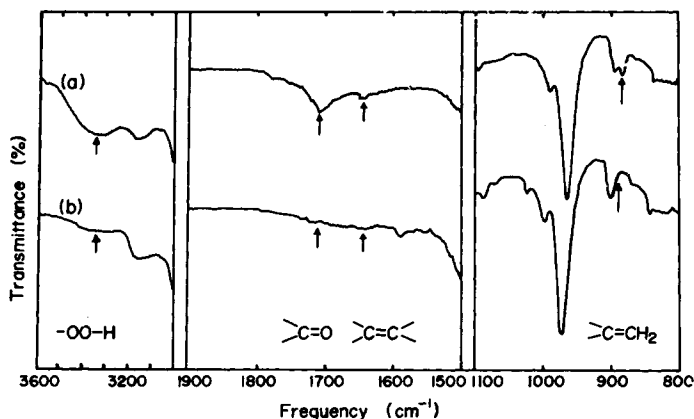


Fig. 4. Infrared spectra of sample B (APP ether) before (a) and after (b) reduction. Absorbance at 2720 cm^{-1} (internal standard): (a) 0.159; (b) 0.176.

are shown in Figure 5. As is apparent, the oxidizability of the ether-soluble fraction of APP is remarkably reduced by the hydrogenation of the polymer, and an induction period is observed. As mentioned above, at the initial stage of the thermal oxidation, the atactic fractions oxidize faster than the isotactic polymer and show no autoxidation phenomena. The results, therefore, apparently indicate the important role of the impurity groups such as hydroperoxide, carbonyl, and unsaturation in the initiation process of the thermal oxidation of the polymer. The Wilkinson catalyst is an effective one, and discriminative reduction of the impurity groups in the polymer is impossible as can be seen in the infrared spectra of Figure 5. Therefore, the relative importance of these groups for the oxidation of the polymer cannot be determined by the results obtained in this work. However, the hydroperoxide group may play the most important role in the thermal oxidation among these impurity groups.

The results indicate that the initiation process of the oxidation of polypropylene is apparently dependent on impurity groups such as hydroperoxide, carbonyl, and unsaturation groups, and stereoregularity of the polymer affects the kinetic dependence of the oxidation.

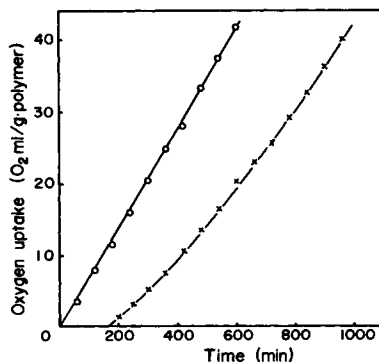


Fig. 5. Oxygen absorption curves of sample B (APP ether) at 125°C in TCB (PP $0.2\text{ g}/5\text{ ml TCB}$): (O) before reduction; (X) after reduction.

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