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STUDY OF THE THERMAL OXIDATION OF POLYOLEFINES—IX.

SOME DIFFERENCES IN THE OXIDATION OF POLYETHYLENE AND POLYPROPYLENE

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Abstract—In the thermal oxidations of polyethylene (PE) and polypropylene (PP), both similarities and differences are found. In the initial stage, the ratio of the hydroperoxide formed and the amount of oxygen absorbed is independent of both the nature of the polymer and the actual reaction conditions. With increased conversion, however, this ratio decreases to a greater extent in the case of PE than for PP. Most of the carbonyl groups formed in the PE chain during oxidation are ketones and carboxyls, but in PP there are also carbonyls with different structure. The amount of carbonyl groups in PE is approximately 1.5 times that observed for PP. The number of scissions involving considerable molecular weight decrease is higher for PE than for PP: for identical conversions, the ratio of scissions is $s_{PE}/s_{PP} \sim 6$.

INTRODUCTION

A number of similar features can be observed in the thermal oxidation of different polyolefines. The process is a degenerate branched radical chain reaction; overall oxygen absorption and the formation of end-products are autocatalytic; the concentration of polymer hydroperoxide (the intermediate product of oxidation) passes through a maximum. The curve indicating weight change shows a similar trend. These similarities are well illustrated by some kinetic curves for polyethylene (PE) and polypropylene (PP) in Fig. 1.

Owing to the analogies, kinetic analysis of the overall process is generally performed according to a mechanism independent of monomer structure and essentially identical for all polyolefines [1]. The oxidations of polyolefines, however, show some marked qualitative and quantitative differences, depending on the monomer structure. We point out some differences between the thermal oxidations of PE and PP.

EXPERIMENTAL

We used high pressure PE and isotactic PP films, using samples described in detail previously [2–3]. We studied overall oxygen absorption, the formation of hydroperoxide and carbonyl groups as well as organic volatile products, and also examined the time dependence of changes in the number average molecular weight under 20–760 Torr oxygen pressure in the temperature range 130–160°C. Detailed descriptions of the degradation and methods of measurement were given previously [2–5]. The notations are summarized in Table 1.

EXPERIMENTAL RESULTS

Comparison of the i.r. spectra of oxidized PE and PP shows characteristic differences. Figure 2 displays

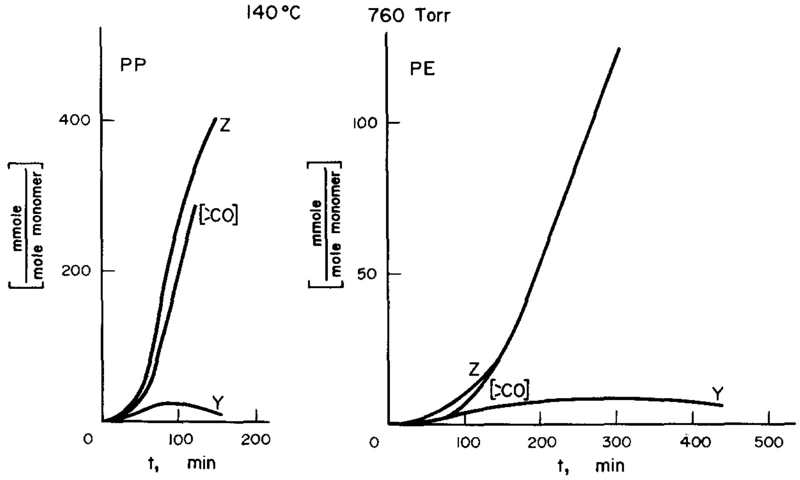

Fig. 1. Oxygen absorption, carbonyl formation and hydroperoxide content of PE and PP, plotted as a function of time.

Table 1. Notations of parameters studied

Parameters	Notation	Dimension
Oxygen absorption	Z	mmole/m.u.
Hydroperoxide concentration	Y	mmole/m.u.
Carbonyl concentration	[>CO]	mmole/m.u.
Average number of chain scissions per macromolecule	s	—
Amount of organic volatile products	chemical terms	mmole/m.u.
Oxygen content of volatile products	O_i	meq. O/m.u.

m.u. = monomeric unit.

spectra of PE and PP films with approximately corresponding oxygen content in the ranges of 2900–3700 and 1600–1800 cm^{-1} respectively.

In the range 2900–3700 cm^{-1} where hydroxyl groups with different chemical structures absorb, PP shows a significant band with 3380 maximum while the absorption of PE in this range is much lower without any sharp peak. This difference, as will be seen, can be attributed partly to quantitative difference and partly to the formation of hydroperoxide sequences in the PP sample, for which the absorption coefficient is much higher than that of isolated hydroperoxide groups formed in PE.

Figure 3 shows the change in hydroperoxide concentration as a function of oxygen absorbed by PE at 160°C under 20 and 760 Torr pressure and at 140°C under 760 Torr, and by PP at 130°C (80 and 760 Torr) and at 140°C (760 Torr).

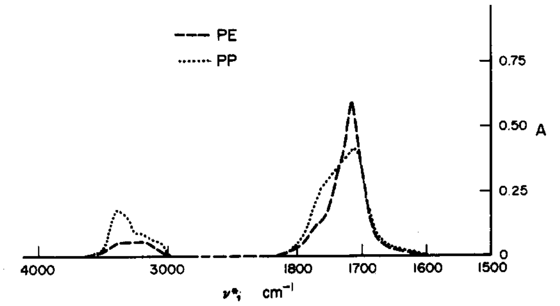

Fig. 2. i.r. Spectra of oxidized PE and PP samples.

It is apparent that, in the initial stage of the reaction, the number of hydroperoxide groups per molecule of absorbed oxygen is independent of both the type of the polymer and the reaction conditions and is close to unity. This points to almost quantitative formation of hydroperoxides from the oxygen absorbed.

At higher conversion, hydroperoxide content depends on the reaction conditions and the nature of the polymer. With both polymers, over the range of temperature and pressure studied, hydroperoxide concentration was strongly dependent on the pressure but scarcely, or not at all, on the temperature. Under comparable conditions (i.e. at nearly identical overall rates of oxidation, under 760 Torr oxygen pressure, e.g., at 160°C for PE and 130°C for PP), the amount of hydroperoxide assigned to an identical amount of total oxygen absorption is always higher in PP.

Extinction curves are quite different (see Fig. 2) also in the range of 1600–1800 cm^{-1}. In PE mainly keto- and carboxyl groups can be found (1700–1740 cm^{-1}) while in PP the formation of considerable amount of other carbonyl compounds is observed. The total amount of carbonyl formed from 1 mole of absorbed oxygen is also different in the two polymers (see Fig. 4).

In the case of PE, a larger fraction of the absorbed oxygen (approx. 1.5 times as much as in PP) is incorporated as carbonyl. The ratio of incorporation appeared to be independent of the reaction conditions. As stated earlier [2], in the thermal oxidation of PE, the oxygen absorbed is approx. half in the solid and half in the volatile phase. According to our new results, a smaller proportion of the absorbed oxygen is incorporated in PP in the form of carbonyl while most is built in partly in the form of higher hydroperoxide content and partly in the considerable amount of organic volatile products.

Figure 5 shows the amount of oxygen in the volatile product (O_i) plotted against the total amount of oxygen absorbed for both polymers under identical experimental conditions. (The oxygen content of the volatile product expressed in terms of oxygen-atom

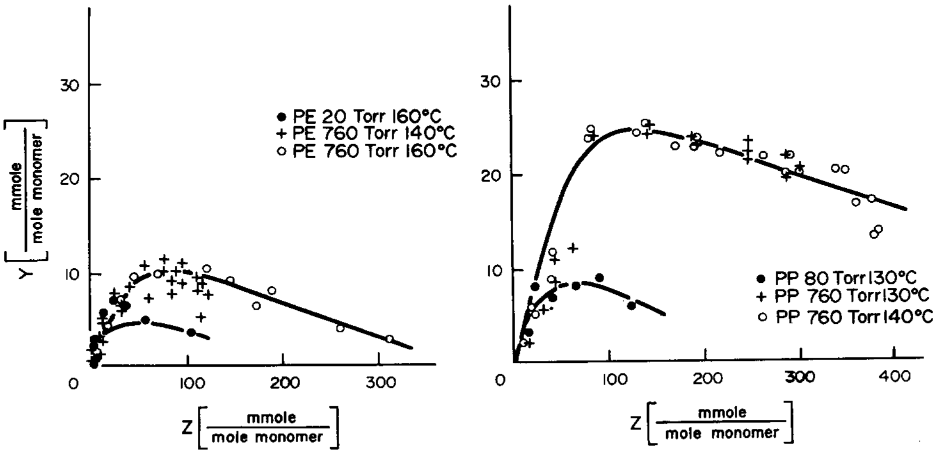

Fig. 3. Hydroperoxide concentration plotted as a function of oxygen absorbed.

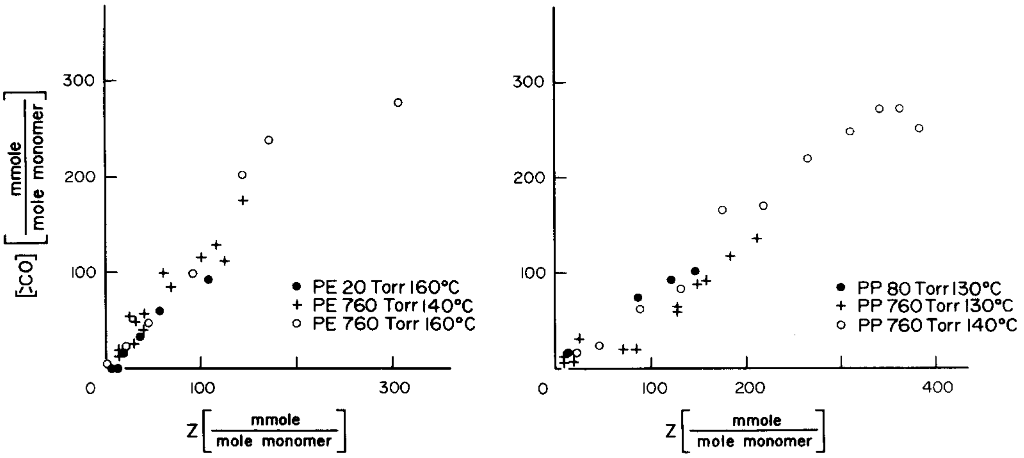

Fig. 4. Carbonyl concentration plotted as a function of oxygen absorbed.

equivalents was calculated with the use of $O_i = 2Z - ([>CO] + 2Y)$.)

Figure 6 gives the amount of the volatile C_2–C_4 organic oxo-compounds evolved during degradation plotted as a function of conversion. It can be seen that the formation of volatile products from identical amounts of absorbed oxygen is lower for PE than PP, over the whole range of conversion examined, due to the fact that the formation of volatile products is initially somewhat retarded compared to the oxygen absorption process.

Thus, except in the initial stages the amounts of volatiles produced from one mole oxygen absorbed by PE and PP are nearly equal, the total amount of the volatile products formed from PP is, however, higher than that of PE over the whole process (Figs 5 and 6).

The phenomenon may perhaps be explained by the different structures of polymeric hydroperoxides [6–7] formed as intermediate products from PP and PE during oxidation. As also pointed out in our description of the i.r. spectra, the hydroperoxide groups formed from PE during the oxidation are located along the polymer chain as isolated groups. Their thermal decomposition leads to the formation of isolated alkoxy radicals. On splitting of the C—C bond near the alkoxy radical, considerable decrease in the molecular weight can be observed, with the formation of hydrocarbon macroradicals and macromolecules with oxo end groups. Volatile oxo-compounds can be formed only after the accumulation of such macromolecules so that this process is delayed compared to oxygen uptake.

During PP oxidation, the formation of hydroperoxide sequences, mainly of dihydroperoxides, can be observed. During bifunctional decomposition of these groups, there may be a more complex transition state with several active centres containing possibly also small molecule organic oxo-compounds among the end-products. As in the case of PP, hydroperoxide sequences are formed even in the initial stage of the process; no delay can be observed even at the very beginning of the process in plotting organic volatile products as a function of absorbed oxygen.

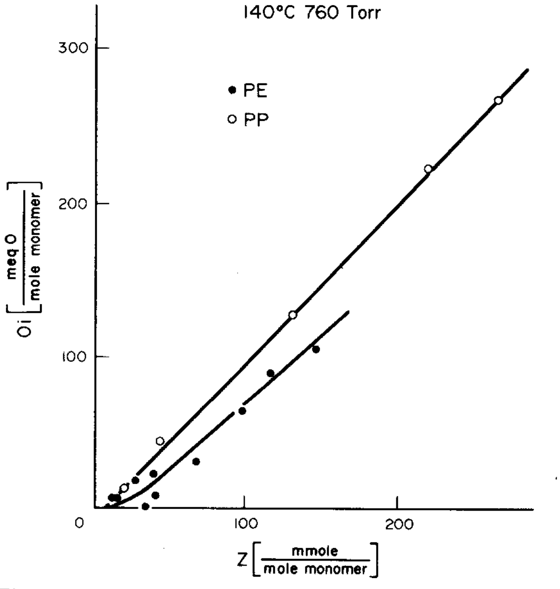

Fig. 5. Oxygen content of volatile products plotted as a function of total oxygen absorbed.

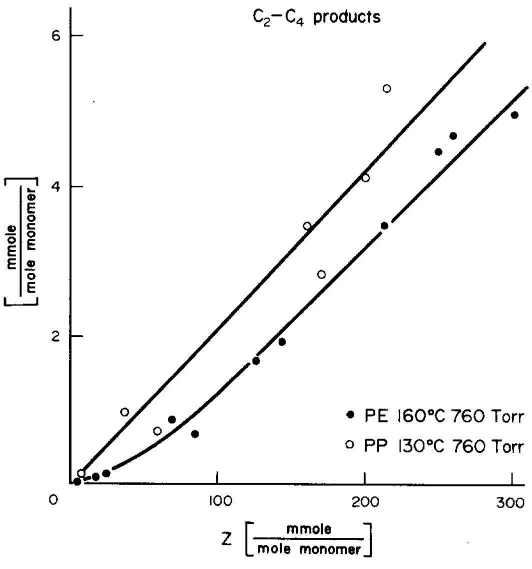

Fig. 6. Amount of low molecular weight organic oxo-compounds plotted as a function of oxygen absorbed.

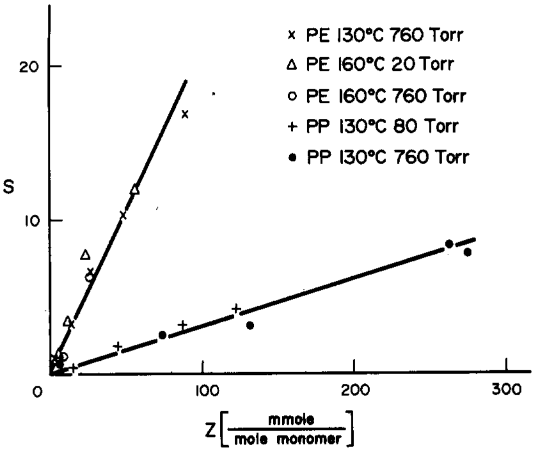

Fig. 7. Average number of scissions plotted as a function of oxygen absorbed.

In the thermal oxidations of PE and PP, the most remarkable difference can be observed in the changes of molecular weights of the two polymers. Figure 7 shows the average number of scissions within one polymer molecule as a function of conversion.

The *s* value determined from molecular weight measurements is characteristic of scissions involving considerable molecular weight decrease.

The number of scissions is much higher (six-fold) for identical degrees of oxidation in PE than in PP. The number of scissions in both polymers depends only on the amount of oxygen absorbed and is independent of the temperature and oxygen pressure.

This marked difference in the average number of scissions of identically oxidized PE and PP may be due to various reasons: different physical and hydroperoxide structures of the two polymers, various possibilities of the bimolecular recombination of macroradicals etc. Solution of these problems would be very useful for elucidation of the oxidation mechanism of PE and PP, and the problem will be approached by further experimental methods.

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