# Cleavage of Polypropylene Chains during Autoxidation

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ABSTRACT: Polypropylene has been autoxidized in benzene solution with initiation by di-*tert*-butyl peroxide, and the change in molecular weight has been determined by ebulliometry. Experiments were performed with both fractionated amorphous polypropylene and unfractionated crystalline polymer. The amount of carbon–carbon bond cleavage effected by the oxidation reaction averages one bond broken per 20 to 30 molecules of oxygen consumed. The cited number is nearly insensitive to the usual experimental variables of conversion, temperature, rate of initiation, and substrate concentration. The current evidence supports the conclusion that the cleavage reaction accompanies the oxidation propagation reaction and not the termination reaction.

The fundamental basis for the degradation of physical properties of polymers on aging (or oxidation) is the cleavage of polymer chains by the chemical reactions taking place. However, little information is available on the quantitative aspects of this problem; that is, how many chain cleavages are effected per oxygen molecule consumed or per initiating radical introduced. Some previous data are available from the work of Bawn and Chaudhri[1] which was subsequently analyzed by Reich and Stivala.[2] More recently, Mayo and Decker[3] reported the cleavage rate of polypropylene during $\gamma$ radiation initiated oxidation. A possible shortcoming of all of these investigations is that they rely on viscosity measurements and approximate relationships between the intrinsic viscosity $[\eta]$ and the number average molecular weight ($\overline{M}_n$). The relationship of $[\eta]$ and $\overline{M}_n$ may be changed by the autoxidative functionalization of the polymer. The availability of relatively low molecular weight crystalline polypropylene coupled with the capability of determination of number average molecular weight of these materials by ebulliometry[4] allows a direct approach to the problem. The benzene solution oxidation technique previously developed[5,6] seemed like an attractive procedure for effecting the oxidation, in as much as the parameters of the reaction can be closely controlled. In the course of other work it has been observed that substantial reductions in molecular weight were effected during the solution oxidation of crystalline polypropylene even though no effort had been made to obtain a narrow molecular weight range starting material.

The objective of this work was to measure the number of polymer chain cleavages effected by autoxidation as a function of conversion, temperature, and polymer and initiator concentrations. Some experiments were performed with fractionated amorphous polypropylene, but, because of difficulties during the isolation of the oxidation product, most of the effort was concentrated on the crystalline material.

## Experimental Section

**Materials.** Amorphous polypropylene was obtained by extraction of production line samples of (mostly) crystalline material as previously described.[6] The material was fractionated by preparative gel permeation chromatography as a benzene solution. The benzene solutions of the fractions were evaporated to near dryness, the product taken up in *n*-hexane, and the hexane solutions poured down a column (1 in. × 4 in.) of activated, neutral alumina. Final isolation of the polypropylene was by precipitation from the hexane solution by the dropwise addition of acetone. The polymer was dried by heating in vacuo (0.1 Torr) at 100–120 °C. For the highest molecular weight fraction $\overline{M}_n = 11\,200$ by ebulliometry; $\overline{M}_w/\overline{M}_n = 1.7$ by gel permeation chromatography.

Crystalline polypropylene was obtained from commercial material by the extraction and precipitation techniques previously described.[6] It was used without fractionation. By an average of five (23 300; 19 400; 22 000; 22 500; and 24 800) determinations the $\overline{M}_n$ of this material was taken as 22 400; $\overline{M}_w/\overline{M}_n = 5.5$ by gel permeation chromatography.

**Oxidation Procedure.** Techniques for the oxidation of polymers as benzene solutions have been previously described.[6] Crystalline polypropylenes of the molecular weight used here form homogeneous, nonopalescent solutions in benzene at the temperatures used in these experiments.

Several variations of work-up procedure were tried for the isolation of samples of oxidized amorphous polypropylene, but the apparently most successful involved reduction by lithium aluminum hydride (LAH) in the following manner. One gram of LAH was dissolved in 50 ml of absolute ether and a 10-ml aliquot of the benzene solution of oxidized polymer was introduced with a syringe. After 1 h of reflux, a wet slush of sodium sulfate was added to destroy the excess LAH. The clear supernatant liquid of the mixture was decanted and saved. The residue of sodium sulfate and lithium and aluminum hydroxides was extracted overnight in a Soxhlet extractor. The extract was combined with the supernatant liquid before evaporation of the solvents to recover the polymer. Drying was accomplished by taking up the polymer in benzene (10 ml) and distilling away the solvent, then finally pumping at 0.1 Torr at 100 °C overnight. Recovery of polymer by this procedure was about 95% theoretical.

Isolation of crystalline polypropylenes was much simpler than isolation of the amorphous form. Three variations of a precipitation technique were used to obtain samples for analysis. First, the polymer that precipitated from the benzene solvent on cooling was isolated by direct filtration and further washings with cold benzene. The other samples for analysis were obtained by pouring the benzene suspension of polymer into cold 2-propanol or methanol (10/1 volume ratio of alcohol to suspension volume) and then filtering. Evaporation of the washings from several of the precipitation experiments indicated negligible nonvolatile material was present in the filtrates of the isolation procedure. It has been recently reported that, even with high conversions, the solution oxidation of amorphous polypropylene gives very low yields of volatile products.[7]

**Molecular Weight Determination.** All number average molecular weights ($\overline{M}_n$) were measured by ebulliometry.[4] Experiments from another investigation showed that triphenyl phosphine reduction of the hydroperoxide groups on the oxidized polymer only slightly affects the molecular weight determination. Some measurements of $\overline{M}_n$ were attempted by membrane osmometry on the amorphous polypropylene samples. This technique gave erratic results which failed to show the regular diminution of molecular weight with increasing oxidation of the polymer.

## Results and Discussion

The experiments with amorphous polypropylene were not considered as satisfactory as those with crystalline material because of the uncertainties in the work-up procedure, i.e., some material may have been lost and a further fractionation of the polymer effected. This was shown most dramatically in experiments (not shown in Table I) where a direct precipitation for polymer recovery was attempted. The recovered material had a higher $\overline{M}_n$ than the starting polymer. Slight cross-linking coupled with loss of low molecular weight fragments may explain this result. Nevertheless, the experiments with amorphous polypropylene reported in Table I do show that under most conditions of oxidation and work-up, about 20 molecules of oxygen are absorbed to cleave one bond of the polymer. The numbers of the last column were calculated with

Table I
Oxidation of Polypropylene in Benzene Solution[a]

| | | | | | Final $\overline{M}_n$ on polymer isolated by | | | |
|---|---|---|---|---|---|---|---|---|
| Expt No. | $[\text{Polyprop}]_0$,[b] M | $[t\text{-Bu}_2\text{O}_2]_0$, $\times 10^2$, M | Time, min | $[\text{O}_2]$, $\times 10^2$, M | Direct filtration | $i$-PrOH pptn | MeOH pptn | $\text{O}_2$ molecules[c] consd/bond broken |
| 1[d] | 1.54 | 2.40 | 320 | 4.5 | 7 800[e] | | | 17 |
| [f] | | | 765 | 8.2 | 5 700[e] | | | 14 |
| 2[g] | 1.46 | 1.53 | 270 | 4.1 | 8 000[e] | | | 20 |
| [f] | | | 695 | 8.6 | 5 700[e] | | | 17 |
| 3 | 2.50 | 2.27 | 75 | 2.7 | 14 100 | 18 400 | | 27 |
| 4 | 2.51 | 2.56 | 140 | 5.5 | 15 700 | 15 200 | 14 000 | 24 |
| 5 | 2.52 | 2.52 | 300 | 10.8 | 12 200 | 12 700 | | 30 |
| 6 | 2.53 | 2.45 | 535 | 18.2 | 9 500 | 10 500 | 9 500 | 34 |
| 7 | 2.49 | 1.02 | 465 | 11.4 | 11 300 | 12 100 | 12 100 | 29 |
| 8 | 2.52 | 9.70 | 130 | 10.3 | 11 600 | 13 100 | 11 200 | 31 |
| 9 | 5.23 | 2.48 | 295 | 19.8 | | 11 000 | | 19 |
| 10 | 1.08 | 2.51 | 220 | 5.1 | | 12 500 | 14 500 | 32 |
| 11[h] | 2.48 | 2.48 | 120 | 10.6 | | 12 900 | 12 100 | 31 |
| 12[i] | 5.00 | 2.60 | 185 | 19.5 | | 10 500 | | 18 |
| 13[j] | 4.99 | 2.44 | 130 | 21.3 | | 10 100 | | 19 |

[a] Experiments with crystalline polypropylene of $\overline{M}_n = 22\,400$ at 120 °C unless otherwise noted; solution volumes were ca. 57 ml. [b] In monomer units, mol wt = 42.1 g/mol. [c] Computed from the $\overline{M}_n$ of polymer isolated by $i$-PrOH precipitation where more than one determination was available. [d] Amorphous polypropylene, $\overline{M}_n = 11\,400$. [e] Work-up by reductive technique as described in the text. [f] Continued oxidation of the preceding experiment. [g] Amorphous polypropylene, $\overline{M}_n = 10\,000$. [h] 130 °C. [i] Starting solution was 0.76 M in *tert*-butyl hydroperoxide. [j] Starting solution was 1.53 M in *tert*-butyl hydroperoxide.

the aid of the relationship:

$$\frac{\text{No. of bonds cleaved}}{\text{mol of starting polymer}} = \frac{\overline{M}_n(\text{initial})}{\overline{M}_n(\text{final})} - 1$$

The remaining discussion centers on the results obtained with crystalline polypropylene. Experiments 3, 4, 5, and 6 were identical except that the extent of oxidation was increased from 1.1 to 7.2%. There appears to be a discernable but not monotonic, trend downward in the efficiency of the oxidation for cleavage of the polymer chain, with the highest efficiencies for cleavage occurring at lowest conversions. Secondary oxidation processes on small product molecules, which produce no new polymeric particles, could account for this observation; or, conversely, new chains are being produced through cross-linking.

The remaining variables investigated include temperature, polymer, and initiator concentration. Within the narrow range investigated (10 °C), temperature has no effect on the efficiency of chain cleavage. This also applies to the rate of initiation as indicated by experiments 7 and 8 where the concentration of *tert*-butyl peroxide was varied by a factor of 9.

The negligible effect of initiator concentration as mentioned above along with the experiments in which *tert*-butyl hydroperoxide were added compel one to conclude that chain cleavage accompanies the propagation reaction and is not dependent on the termination reaction. From the expression

$$\text{total radicals} = 2[t\text{-Bu}_2\text{O}_2]_0[1 - \exp(-k_d t)]$$

it is calculated that, at 120 °C, the number of bonds broken per radical introduced into the oxidizing system varies from 1 to ⅓ for the various conversions and initiator concentrations used. While the amount of *tert*-butyl hydroperoxide added in experiments 12 and 13 is probably not sufficient to totally convert all polymer peroxy radicals present to *tert*-butylperoxy radicals,[8] the termination reaction should have at least been altered to that of one polymer peroxy radical interacting with one *tert*-butylperoxy radical. Comparison of experiments 12 and 13 with experiment 9, where no hydroperoxide has been added, indicates little alteration of the cleavage efficiency of the oxidation.

The assertion that chain cleavage accompanies the radical chain propagation reaction and is not readily related to the termination reaction is contrary to the traditional view of the source of polymer chain cleavage and requires some amplification. Tobolsky, Norling, Frick, and Yu[9] concluded that, for lightly cross-linked samples of atactic polypropylene, one initiating radical produces one chain scission during oxidation at 110 °C. In light of careful and more recent work of Mayo and colleagues[10] on oxidations of neat polypropylene with incorporated initiator, Tobolsky's results probably need to be reevaluated. The radical yield from benzoyl peroxide decomposition in the very viscous polymer matrix was probably very much less than the anticipated 0.6 of theoretical. The apparently linear dependence of chain scission rate on initiator concentration should, according to Mayo's work, be reanalyzed in terms of geminate (first order in initiator) and statistical (half-order) interactions of radical pairs. In our work at relatively low viscosities, we expect that there is very little, if any, geminate radical reaction and that we observe only the results of random or statistical interaction of radicals. According to Decker and Mayo's[3] analysis of the $\gamma$ radiation initiated oxidation of polypropylene at 22 °C, where $G_{\text{scission}}$ was independent of dose rate, about half of the observed cleavage can be ascribed to geminate radical pair reactions and the rest to radiolysis and product decomposition reactions.

Since polypropylene hydroperoxides obtained in these liquid-phase oxidations have modest thermal decomposition rates,[6] it is tempting to ascribe our results to decomposition of these product molecules. But we would expect the relationship of cleavage to conversion to be more complex than the nearly one-to-one relationship found. That is, cleavage efficiency would be higher in higher conversion oxidations. Since this is not the observed result, we can only speculate at this time about the nature of a cleavage reaction which would accompany or compete with the radical chain propagation reaction. Cleavage reactions of the type which compete with propagation have been identified as part of the mechanism for the oxidation of unsaturated hydrocarbons.[12] Trace amounts of some transition metal ions, which strongly catalyze hydroperoxide decompositions,[11] might also produce the observed result.

There appears to be an unexpected, and possibly spurious, effect of polymer concentration on the efficiency of chain cleavage. Oxidations at 1.08 and 2.5 M in polymer gave nearly identical chain cleavage efficiencies while doubling the polymer concentration again to 5.0 M (experiment 9) reduced the cleavage efficiency by one-third.

It should be kept in mind that the amount of cleavage reported in Table I is actually net cleavage; that is, the figure is total cleavage minus the amount of cross-linking effected by the oxidation. The lower scission efficiency at 5.0 M polymer concentration would be consistent with the proposal of enhanced cross-linking. However, there is no reason to suspect that a cross-linking reaction plays a major role under the reaction conditions used here. In oxidations of neat amorphous polypropylene at 22 °C, Decker and Mayo[3] assigned all of the cross-linking reaction to the geminate radical pairs reactions. In our relatively low viscosity system, we anticipate little cage reaction of this type. Also, the recent investigation by Niki, Shiono, Ido, and Kamiya[7] of amorphous polypropylene oxidation in solution under a variety of conditions indicates little likelihood of major cross-linking. They published the gel permeation chromatograms for the reactant polypropylene superimposed on the chromatograms of the oxidation products. In all cases there was no indication that any materials were being formed which had a higher molecular weight than the starting polymer.

Finally, the results here can be compared with those reported by Decker and Mayo.[3] In their analysis of the oxidation of neat, amorphous polypropylene at 22 °C, chain cleavage was equated to a linear dependence on total initiation while oxygen absorption was analyzed as a composite of first and half-order initiation processes. For their experiments where initiation was by Co-60 irradiation, the values of $G_{O_2}/G_{\text{scissions}}$, which are to be compared with the values in the last column of Table I, range from 29 to 16. The agreement between the two sets of data is remarkably good when the number of variables that have been changed is considered.

In conclusion, the reaction which leads to cleavage of polypropylene chains during oxidation is a relatively minor one and appears to accompany the propagation reaction. In the oxidation of a model compound, 2,4,6-trimethylheptane,[13] yields of hydroperoxides were lower than those in the oxidation of 2,4-dimethylpentane and substantial amounts of products corresponding to carbon–carbon chain cleavage were found. In so far as carbon–carbon bond breaking is concerned, the trend seems to have actually been reversed somewhat in the polymer case.

## References and Notes

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# Comments on the Theory of Steric Stabilization

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ABSTRACT: Steric stabilization of colloidal particles in theta and good solvents is examined theoretically. For near-theta solvents an analytic solution to the equations solved numerically by Dolan and Edwards is presented and the domain of validity of their approach delineated. In good solvents a scaling analysis is employed which makes use of the analogies between magnetic systems and polymers to give asymptotic expressions for the interaction potential between the colloidal particles. In both types of solvent it is found that metastable stabilization by a potential barrier can be produced for polymer coverages of the particles insufficient to cause stability right at the theta point.

## I. Introduction

A dispersion of colloidal particles may be stabilized against flocculation by the adsorption or attachment of flexible polymer molecules onto the particles of the suspension. In the absence of a macromolecular covering of the particles, flocculation will rapidly take place because of the attractive van der Waals forces between the particles which causes them to stick together. The presence of polymers between the surfaces of the particles gives rise to a repulsive force between the particles; when two such particles approach, the reduction in the number of configurations available to the flexible polymer chains gives rise to an "entropic" repulsive force between the particles. This may keep two colliding particles so far apart that the van der Waals interaction energy is insufficient for coherence. For a recent reappraisal of current theory and references to other relevant work, the reader is referred to the article by Osmond et al.[2a]

We shall distinguish between (i) theta solvents, (ii) worse than theta solvents, and (iii) better than theta solvents (good solvents). Most theoretical work to date has concentrated on theta solvents since, for such solvents, the statistics of the polymer chains will be of the simple random-flight type.[2b,3] The essential features are summarized in section II. For