Mechanochemical Degradation of an EPDM Polymer*

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Synopsis

A mill-mastication study of an EPDM polymer (DuPont, Nordel 1070) was conducted in the mill-roll temperature range of 68–480°F. The extent of degradation was determined by dilute-solution viscosity measurements. The role of oxygen in the polymer mastication was followed by infrared spectroscopy. The breakdown of the EPDM polymer on the mill is minimum in the temperature range of 185–315°F. Up to 315°F. the increase in temperature leads to a decreased amount of degradation. During cold mastication mechanical breakdown occurs. The use of a free-radical acceptor shows that this type of breakdown is caused by the mechanical rupture of C—C bonds in the polymer chain. At and above 350°F. thermooxidative degradation becomes dominant, the polymer degrading drastically, and the higher the temperature, the greater the extent of degradation for the same period of mastication. Infrared spectroscopy shows that hot mastication results in decreased double-bond concentration and increased amounts of carbonyl and, possibly, anhydride and lactone groups. Of the carbonyl groups formed 30% are due to the oxidation of double bonds in terpolymer and 70% to the oxidation of the main chain. A mechanism is proposed to account for these observations.

INTRODUCTION

The mastication of elastomers involves a number of mechanochemical processes. It has been demonstrated[1,2] that the structural and physical changes in the macromolecules during mastication are due to mechanical and oxidative degradation. These processes are frequently referred to as cold and hot mastication.

In two papers Mullins and Watson[1] and Bristow[2] have shown evidence that the mechanical breakdown of the polymer molecule is caused by mechanical rupture of primary carbon–carbon bonds in the polymer chain, giving polymer radicals. These radicals are due to the scission of only those polymer chains that are of a length in excess of a critical value.[3,4] Harmon and Jacobs[5] have provided some experimental evidence of the existence of a critical macromolecular chain length after a long period of mastication. These radicals are stabilized by a free-radical acceptor such as O_2, when mastication is carried out either in air or in an oxygen atmosphere.

Bueche's theory[4] predicts the effect of the original molecular weight of the polymer, shear rate, melt viscosity, temperature, and presence of a stabilizer on the mechanical degradation of a polymer. There exists a qualitative agreement between the theory[4] and the experimental data.[1,2,5] However, the theory needs quantitative verification.

Indirect evidence[1,2] is also present in the literature concerning the significant role of oxygen in hot mastication. Oxidative degradation has been found to be a nonrandom process[1] at moderately high temperatures but is expected to be a random process at very high temperatures.

The mastication work reported in the literature is on high diene polymers. The present investigation is concerned with cold and hot mastication of ethylene–propylene terpolymer, a polymer with saturated backbone. Direct evidence of the role of oxygen in high-temperature mastication of EPDM polymer is furnished by infrared analysis. A mechanism of polymer degradation is proposed.

EXPERIMENTAL METHODS AND MATERIAL

EPDM polymer (DuPont's Nordel 1070, containing 62 mole-% ethylene and $[\eta] = 3.55$) and EPM (ethylene–propylene copolymer, containing 63 mole-% ethylene and $[\eta] = 3.48$) polymers were hot-acetone-extracted for 32 hr. and dried under vacuum at 50°C. The dried polymers were stored in the dark in a nitrogen atmosphere until ready for mastication. The starting polymers were gel-free.

The mastication was done on a 4-in. open mill. The front roll had an rpm of 21; the rear roll, of 32. The nip distance was 0.030 in. A batch weighed 100 g. of polymer. For room-temperature mastication cold water was circulated through the rolls; for high-temperature mastication hot oil was circulated through the rolls. The roll-surface temperature was taken as the mastication temperature.

For sol–gel measurements 0.5 g. of polymer was dissolved in 100 ml. of cyclohexane.[6] After 2 days the solution was centrifuged for 75 min. at 2500 rpm.

If W_i is the initial weight of the polymer in 100 ml. of cyclohexane solution, and W_p is the weight of the polymer in 10 ml. of solution after centrifugation, then the gel content W_g (weight fraction) in the sample may be expressed as

$$W_g = (W_i - 10W_p)/W_i \tag{1}$$

The intrinsic viscosities in cyclohexane were measured[6] at 30 ± 0.01°C. The measurements were made in a Ubbelohde dilution viscometer.

For preparing a polymer and 1,1'-diphenyl-2-picryl hydrazine (DPPH) mixture a 5% polymer solution was prepared in cyclohexane. DPPH was dissolved in cyclohexane separately. The DPPH solution was then mixed with the polymer solution. The concentration of DPPH in this solution was 1 part per 100 parts of polymer. The mixture was freeze-dried.

The polymer–DPPH mixtures, with varying amounts of DPPH, were prepared similarly for calibration purposes.

The polymer–DPPH mixture was masticated in a Uni-Rotor[7] in a nitrogen atmosphere for different intervals of time at $75 \pm 2.5°F$. The samples were then cold-acetone-extracted for removal of DPPH. The extraction was carried out in a nitrogen atmosphere as long as it gave no colored acetone. The amount of combined DPPH was determined by infrared spectroscopy with the use of the calibration curves. Infrared studies of polymer films were made.

For determination of the minimum amount of carbonyl groups detectable by the spectrophotometer stearic acid in appropriate proportions was incorporated into EPDM polymer by mill-mixing at room temperature. The resulting samples were then studied by infrared spectroscopy.

RESULTS AND DISCUSSION

The extent of mechanical and chemical degradation was followed by intrinsic-viscosity and infrared spectroscopic changes.

Mastication for Different Intervals of Time

Figure 1 represents the intrinsic viscosities of polymers masticated at 68 and 150°F. It is obvious that degradation is much more severe at 68 than at 150°F. After 60 min. of mastication at 68°F. there is no appreci-
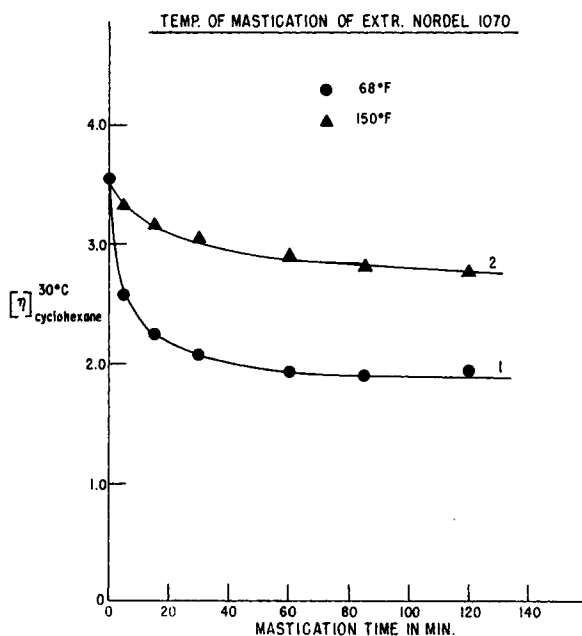

Fig. 1. Changes in intrinsic viscosity of EPDM with mastication time at (●) 68°F. and (▲) 150°F.
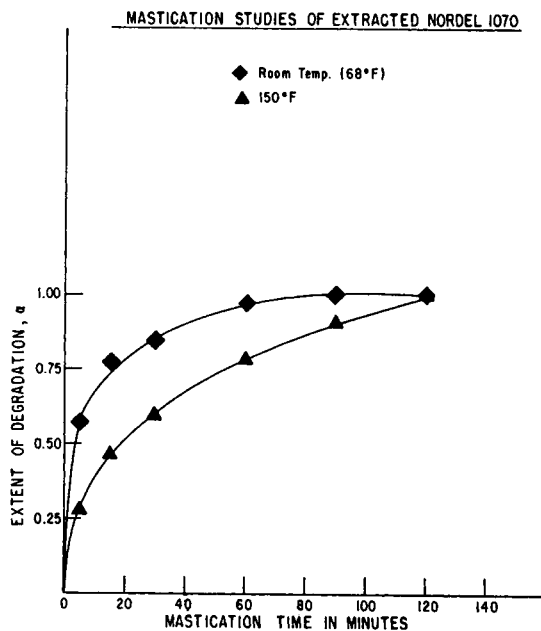
Fig. 2. Extent of degradation of extracted EPDM at (♦) 68°F. and (▲) 150°F.

able further degradation. However, at 150°F. the extent of degradation has not equilibrated in 120 min. The extent of degradation of both systems may be represented in a simple way, as follows. If $[\eta]_0$ is the intrinsic viscosity of unmasticated polymer, $[\eta]_t$ is that of polymer after time t of mastication, and $[\eta]_c$ is the critical intrinsic viscosity (no further degradation beyond this value), then the extent α_t of degradation at any time t may be written

$$\alpha_t = ([\eta]_0 - [\eta]_t)/([\eta]_0 - [\eta]_c) \qquad (2)$$

Figure 2 shows the plots of α_t versus t. At 68°F. about 57% of degradation occurs at 5 min. of mastication, whereas it takes 30 min. to obtain about the same amount of degradation at 150°F.

Curve 1 in Figure 1 may be represented by

$$[\eta]_t = [\eta]_c + \mu e^{-\beta t} \qquad (3)$$

where $\mu = [\eta]_0 - [\eta]_c$, and μ and β both are constant and depend on the polymer characteristics and temperature of mastication.

Mastication at Different Temperatures

For a study of the effect of heat and oxygen on the mastication of EPDM polymer the extracted polymer was masticated for 30 min. in the temperature range of 68–480°F. The intrinsic viscosities of the masticated samples are shown in Figure 3. The curve seems to have three very dis-
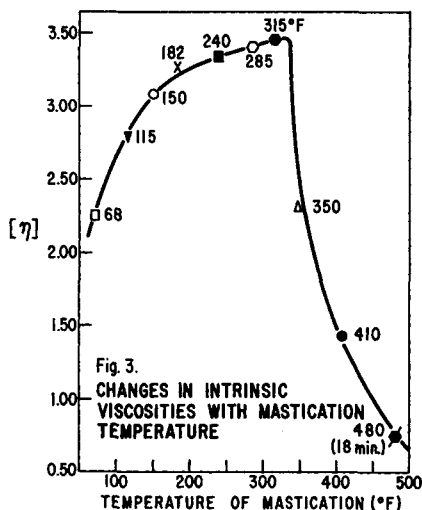
Fig. 3. Changes in intrinsic viscosity with mastication temperature.

tinct regions, one in the temperature range between 68 to 150°F., another between 150 and 315°F., another above 315°F.

Bueche's theory predicts that $F_0 \propto \eta\dot{\gamma}M_e^{1/2}/\rho$, where F_0 is the breaking tension at the center of the polymer chain, η and ρ are the melt viscosity and density of polymer, respectively, $\dot{\gamma}$ is the shear rate, and M_e is the molecular weight between entanglements. In the first region, where the temperature is low enough, η is high and, hence, the shearing force exerted on the polymer chains is greatest; this leads to a greater extent of degradation or lower intrinsic viscosity. As the temperature increases, η decreases with relatively small changes in ρ and M_e; hence, owing to a lower shearing force, the polymer shows a higher intrinsic viscosity after a given milling period.

In the second region, where the polymer becomes soft, there is a considerable decrease in η and a small decrease in ρ. Therefore, owing to a smaller shearing force, the extent of degradation is also smaller. If one desires to obtain a greater extent of degradation within this temperature change, the shear rate $\dot{\gamma}$ should be increased so as to compensate for the decrease in $\eta M_e/\rho$.

By the same argument, the shearing force is very small in the third region, but in this case an additional process, thermooxidation, comes into play. The intrinsic viscosities of masticated polymers decrease drastically with an increase in mastication temperature.

Mechanism of Cold Mastication

For determination of whether the cold mastication of EPDM polymer proceeds via the radical mechanism a mixture of polymer and DPPH was masticated at 75 ± 2.5°F. under a nitrogen atmosphere in a Uni-Rotor.[7]

The percentage of combined DPPH was obtained from the infrared calibration curve. The actual amount of combined DPPH with mastication time is shown in Figure 4. It is obvious from this figure that in the cold mastication of EPDM some polymer radicals are produced. The number of polymer radicals increases with mastication time at least up to 60 min. of mastication.

Another suggestion of radical mechanism is provided by more gel formation when the polymer is milled in an inert atmosphere. Table I gives the
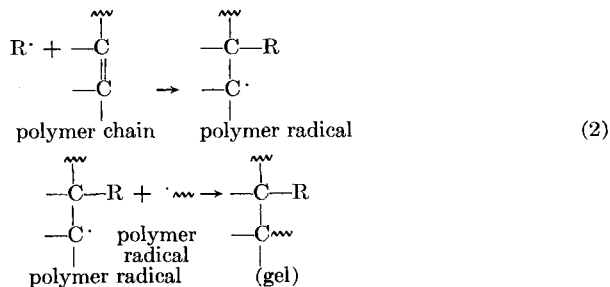
TABLE I
Gel Content in Masticated Polymer

Temp. of mastic., °F.	Time of mastic., min.	Gel, %	$[\eta]$
Mill mastication, in air:			
68	5	4.1	2.60
"	15	4.2	2.27
"	30	3.8	2.17
"	60	3.5	1.95
"	90	3.6	1.93
"	120	3.3	1.95
150	15	2.1	3.17
"	30	1.7	3.07
410	30	0.4	1.50
Unirotor mastication, air and N_2:			
75	10 (in Air)	1.6	3.05
"	10 (in N_2)	3.4	3.30

necessary data. The higher the mastication temperature, the less the gel content for the same duration of mastication in air. This is expected. At low temperature, owing to high viscosity, the shearing action is more severe than at higher temperature and produces more free radicals. Besides, at a high temperature these radicals are terminated by O_2 much faster than at a low temperature, producing less gel. The entire process may be represented schematically as
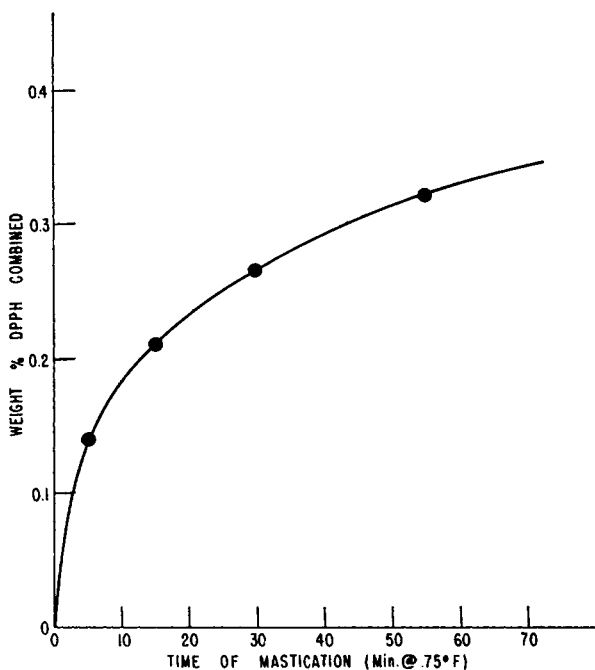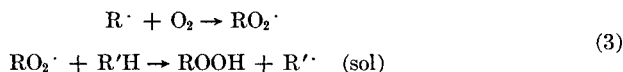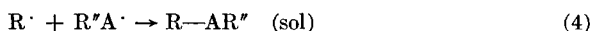
$$R\text{---}R \rightarrow 2R\cdot \tag{1}$$

In the presence of nitrogen:

(2)

Fig. 4. Weight per cent DPPH combined versus time of mastication.

In the presence of O_2:

$$R\cdot + O_2 \rightarrow RO_2\cdot$$

$$RO_2\cdot + R'H \rightarrow ROOH + R'\cdot \quad \text{(sol)} \tag{3}$$

In the presence of a radical acceptor $R''A\cdot$:

$$R\cdot + R''A\cdot \rightarrow R\text{---}AR'' \quad \text{(sol)} \tag{4}$$

As shown in Table I, the sample masticated in nitrogen has greater gel content than the one masticated in air for a 10 min. period. Therefore, the mechanical breakdown of EPDM polymer is due to the primary C—C bond rupture, caused by shearing action, which gives polymer radicals.

Mechanism of Degradation during Hot Mastication

Hot mastication will be referred to as the mastication done at temperatures above 315°F. It is evident in Figure 3 that the intrinsic viscosities of samples masticated at temperatures above 315°F. drop drastically. It was felt that at these temperatures the thermooxidative process becomes predominant. To verify this, infrared spectra of masticated samples were obtained.

Figure 5 shows the infrared spectra of unmasticated EPDM polymer and those of a sample mill-masticated at 315°F. for 30 min. Similar spectra were obtained for samples masticated at 68, 115, 150, 182, and 240°F. Cold mastication did not show the presence of any oxygen-containing groups

in the polymer.   Hot mastication showed the presence of ketonic groups at 1720 cm.$^{-1}$, anhydride and lactones at 1790–1720 cm.$^{-1}$, and hydroxyl groups at 3450 cm.$^{-1}$.   This is shown in Figure 6.

It is imperative to emphasize that, even though the spectra for 315°F. and below do not show the presence of any oxygen-containing groups, oxygen is not necessarily excluded from the polymer at these temperatures. The infrared spectrophotometer could detect a minimum of 0.05% carbonyl concentration on the polymer.   Field et al.[8] have shown that the
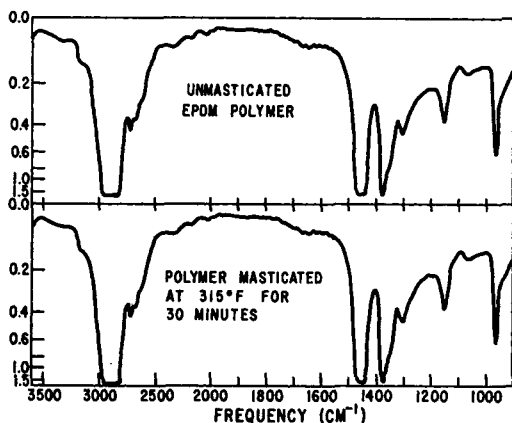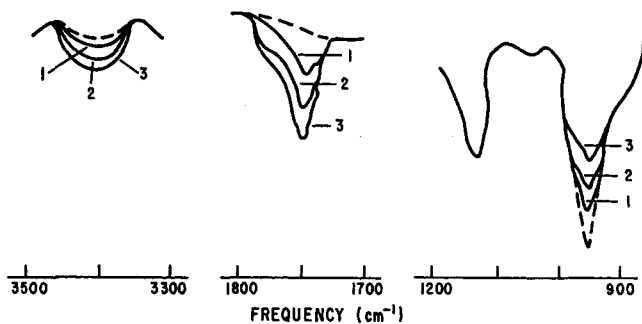

Fig. 5. Infrared spectra of EPDM polymers.

Fig. 6. Infrared spectra of EPDM samples masticated at (1) 350°F. for 30 min., (2) 410°F. for 30 min., and (3) 480°F. for 18 min.   Dashed lines represent spectra of unmasticated EPDM.

polymer that had absorbed 5% oxygen did not exhibit the presence of any oxygen-containing groups in its spectra.   Therefore, one is tempted to infer that at 315°F. and below the oxygen content of the polymer is beyond the detection limit of the spectrophotometer.   Qualitatively, one would expect an inevitable presence of oxygen even at these temperatures, because some oxygen is always used[1] for stabilizing the free radicals generated during mastication in air.

TABLE II
Infrared Spectra Peak Ratios for Masticated EPDM Polymer Samples

Temp. of mastic., °F.	Time of mastic., min.	$A_{965}{}^a/A_{1156}{}^b$	$A_{1720}{}^c/A_{1156}{}^b$	$A_{1780}{}^d/A_{1720}{}^c$
Unmast.	—	1.76	0	—
68	30	1.74	0	—
115	30	1.75	0	—
150	30	1.75	0	—
182	30	1.76	0	—
240	30	1.74	0	—
315	30	1.74	0	—
350	30	1.54	0.194	0.116
410	5	1.62	0.092	0
410	15	1.56	0.219	0.117
410	30	1.40	0.537	0.149
480	6	1.41	0.810	0.128
480	12	0.99	1.50	0.151
480	18	0.90	1.59	0.174

[a] Peak is due to propylene and double bond from third monomer.
[b] Peak is due to propylene and is a CH_3 rocking bond.
[c] Peak due to carbonyl groups.
[d] Peaks are generally due to anhydride and lactone groups.

A qualitative analysis of the spectra in Figures 5 and 6 are provided in Table II. The ratios A_{965}/A_{1156} and A_{1720}/A_{1156} are the relative measures of the concentrations of $>C{=}C<$ and $>C{=}O$, respectively. It is observed in the table that in hot mastication, with increasing milling temperature for constant milling time and also with increasing milling time at a given temperature, the number of double bonds decreases, and the carbonyl group concentration increases. However, this does not necessarily mean that all the carbonyl groups are formed because of double bonds only. Main-chain scission under hot-mastication conditions might lead to $>C{=}O$ formation.

It becomes necessary at this point to determine the relative contribution of double bonds to the carbonyl groups formed. For this purpose EPM
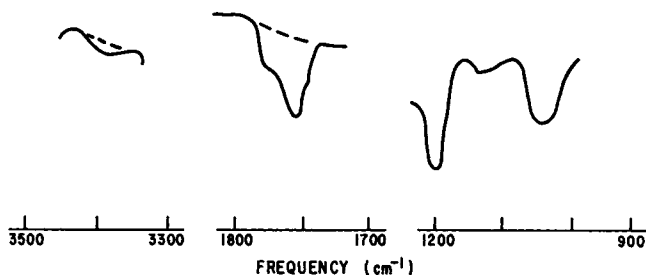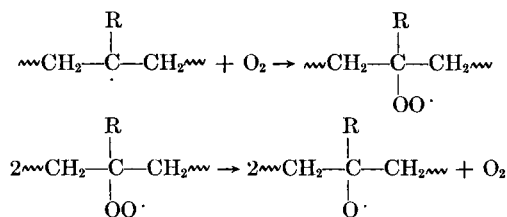

Fig. 7. Infrared spectra of EPM (63 mole-% ethylene) masticated at 410°F. for 30 min.; dashed lines represent spectra of unmasticated EPDM.

polymer, containing 63 mole-% ethylene, was masticated at 410°F. for 30 min. Figure 7 shows infrared spectra of this masticated sample. The spectra of unmasticated EPM polymer did not show the presence of any oxygen-containing groups. However, in the spectra of hot-masticated EPM polymer, Figure 7, peaks due to carbonyl, anhydride, and lactone appear in the 1790–1720 cm.$^{-1}$ region. Peak ratios of EPDM and EPM polymers are compared in Table III.
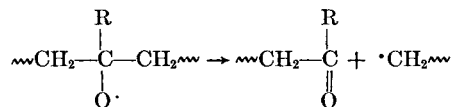
TABLE III
Thermooxidation of EPM and EPDM

Sample	Ethylene, mole-%	Temp. of mastic., °F.	Time of mastic., min.	A_{965}/A_{1156}	A_{1720}/A_{1156}	A_{1780}/A_{1720}
EPDM	62	unmasticated		1.76	0	0
"	62	410	30	1.40	0.537	0.149
EPM	63	unmasticated		0.493	0	0
"	63	410	30	0.490	0.376	0.117

The amount of carbonyl group formed in hot mastication of EPM is 70% of that of EPDM. This means that 30% of the total carbonyl group formed is due to the oxidation of the double bond in EPDM and 70% is due to the oxidation of the ruptured main chain. The main-chain oxidation can take place in two ways: the polymer chains are broken down, owing to shear, and so give polymer radicals, which are in turn terminated by oxygen a process that would give rise to oxygen-containing groups, and the weakest spot in EPDM and EPM is the tertiary hydrogen in the propylene unit, and it is therefore the most susceptible to abstraction that gives a radical. Bartlett and Traylor's result[9] on the interaction of cumylperoxy radicals may be applied to these elastomers to give
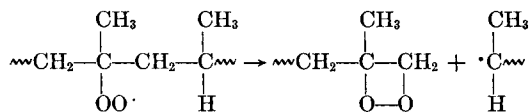
$$\sim CH_2-\overset{\overset{\textstyle R}{|}}{\underset{\cdot}{C}}-CH_2\sim \; + \; O_2 \rightarrow \sim CH_2-\overset{\overset{\textstyle R}{|}}{\underset{\underset{\textstyle OO\cdot}{|}}{C}}-CH_2\sim$$

$$2\sim CH_2-\overset{\overset{\textstyle R}{|}}{\underset{\underset{\textstyle OO\cdot}{|}}{C}}-CH_2\sim \rightarrow 2\sim CH_2-\overset{\overset{\textstyle R}{|}}{\underset{\underset{\textstyle O\cdot}{|}}{C}}-CH_2\sim \; + \; O_2$$

According to Kochi,[10] the alkoxy radical on cleavage gives

$$\sim CH_2-\overset{\overset{\textstyle R}{|}}{\underset{\underset{\textstyle O\cdot}{|}}{C}}-CH_2\sim \rightarrow \sim CH_2-\overset{\overset{\textstyle R}{|}}{\underset{\underset{\textstyle O}{\|}}{C}} \; + \; \cdot CH_2\sim$$

The alkyl radical thus produced rapidly adds oxygen, giving a primary peroxy radical, which terminates before abstracting hydrogen from RH. The termination may take place as[11]

$$2\sim CH_2OO\cdot \rightarrow \sim CH_2OH + \sim CHO + O_2$$

Others[12] have suggested that scission in polypropylene arises by isomerization:

$$\text{wCH}_2\text{—}\underset{\underset{OO\cdot}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{—CH}_2\text{—}\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{w} \rightarrow \text{wCH}_2\text{—}\underset{\underset{O—O}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{—CH}_2 + \cdot\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{w}$$

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