In recent years numerous research papers have been published on the changes in chemical structure and in physical properties of polymers when they are exposed to heat over a range of temperatures. For example, these changes can occur at any time during the injection moulding of the plastic, in the subsequent processing and in its end-use application when exposed to elevated temperatures.

Thermal stability is a very important parameter which must be taken into account when selecting polymers whether for their use as constructional or engineering applications or in the packaging of food at high temperatures.

The mechanisms by which such changes occur are many and it is important to know what these are and to be able to measure the rate of change of polymer structure and its dependence on temperature and time. Development of an understanding of the mechanisms of thermal degradation will help the chemist to develop materials with better thermal stability. This is particularly important in newer developments in engineering and aerospace.

This book reviews in nine chapters the measurement of these properties in the main types of polymers in use today. Numerous techniques are discussed ranging from thermogravimetric analysis, differential scanning calorimetry, infrared and nuclear magnetic resonance based methods to pyrolytic techniques such as those based on pyrolysis, gas chromatography and mass spectrometry.

The book is aimed at those engaged in the manufacture of polymers and the development of end-use applications. It is essential that students of polymer science should have a thorough understanding of polymer stability and an additional aim of the book is to help in the development of such an interest.
Thermal Stability of Polymers

T.R. Crompton
In recent years a considerable amount of work has been done on the elucidation of the changes in chemical structure and in physical properties of polymers when they are exposed to heat over a range of temperatures.

These changes can occur at any time between the injection moulding of the plastic, in subsequent processing and in its end-use application when exposed to elevated temperatures.

Thermal stability is a very important parameter, which must be taken into account when selecting polymers for a wide range of applications whether in their use as constructional or engineering applications or in the packaging of food at elevated temperatures.

The mechanisms by which such changes occur are many and it is important to be able to elucidate these and to be able to measure the rate of change of polymer structure and its dependence on temperature and time.

This book reviews in nine chapters the measurement of these properties in the main types of polymers in use today.

Numerous techniques have been applied to such measurements ranging from thermogravimetric analysis, differential scanning calorimetry, infrared and nuclear magnetic resonance spectroscopy based methods and pyrolytic techniques such as those based on pyrolysis, gas chromatography and mass spectrometry.

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1 Carbon Hydrogen Polymers

1.1 Polyethylene

Thermal degradation of polymers usually proceeds via a number of possible mechanisms, which can generally be grouped into three classes: (a) random scission, (b) depolymerisation, and (c) side group elimination.

1.1.1 Random Scission

Random scission results from the production of free radicals along the backbone of the polymer, which causes the macromolecule to be fragmented into smaller molecules of varying chain lengths. On chromatographic analysis these fragments reveal a repeating series of oligomers frequently differing in chain length by the number of carbons in the original monomer:

```
\text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{CH}_3
```

Producing

```
\text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{CH}_3
```

(1.1)
Polyolefins generally degrade through a random scission mechanism, and polyethylene (PE) is a good example of this behaviour. When a free radical is formed along the chain of PE, chain scission occurs, producing a molecule with an unsaturated end and another with a terminal free radical. This free radical may abstract a hydrogen from a neighbouring carbon, producing a saturated end and a new radical, or it may combine with another free radical to form an alkane. Multiple cleavages produce molecules small enough to be volatile, with double bonds at both ends, one end, or neither end. Since the scission is random, molecules are made with a wide variety of chain lengths. These appear in the pyrogram as a series of triplet peaks. Each triplet consists of an alkane, an alkene, and a diene of a specific chain length. The hydrocarbons in each triplet have one more carbon than the molecules in the triplet that eluted just prior to it.

The chromatogram resulting from the pyrolysis of PE at 750 °C shows oligomers containing up to 30 carbons.

It is interesting to compare results obtainable by gel permeation chromatography (GPC) of PE, polypropylene (PP), and an ethylene–propylene copolymer. The pyrolysis products were hydrogenated at 200 °C by passing through a small hydrogenation section containing 0.75% platinum on 30/50 mesh aluminium oxide. The hydrogenated pyrolysis products were then separated on squalane on a fireback column, and the separated compounds detected by a katharometer. Under these experimental conditions only alkanes up to C₉ could be detected.

It can be seen that major differences occur in the products of thermal degradation that are obtained for these three similar polymers. PE produces major amounts of normal C₂ to C₈ alkanes and minor amounts of 2-methyl and 3-methyl compounds such as isopentane and 3-methylpentane, indicative of short-chain branching on the polymer backbone. For PP, branched alkanes predominate, these peaks occurring in regular patterns, e.g., 2-methyl, 3-ethyl, and 2,4-dimethylpentane and 2,4-dimethylheptane, which are almost absent in the PE pyrolysate. Minor components obtained from PP are normal paraffins present in decreasing amounts up to n-hexane. This is to be contrasted with the pyrogram of PE, where n-alkanes predominate. The ethylene–propylene copolymer, as might be expected, produces both normal and branched alkanes. The concentrations of 2,4-dimethylpentane and 2,4-dimethylheptane are lower than those that occur in PP.

A mechanism [1] involving two equilibrium stages, i.e., the formation of free radicals and abstraction of hydrogen atoms by these radicals, has been suggested for the thermal degradation of polyalkenes. The initiation of polyalkene degradation consists of the cleavage of the carbon–carbon bond and the macromolecules to form free radicals:
Such cleavage occurs at the weakest bonds (the tertiary carbon atom in groups containing other atoms, and so on).

The scission of the chain, with the elimination of small amounts (1%) of monomer, occurs at its free-radical ends, a process which has been termed ‘unzipping’:

$$\sim\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2~\longrightarrow~\sim\text{CH}_2-\text{CH}_2+\text{CH}_2=\text{CH}_2$$  \hspace{1cm} (1.2)

Chain scission occurs because of the recombination of two free radicals with the formation of one linear or branched chain and, in some cases, of a crosslinked polymer. As is seen from the reaction schemes given, free radicals formed during polyalkene degradation are involved in two competing reactions: free radical transfer of an hydrogen atom and chain scission to form monomer. The number of hydrogen atoms in the chain determines which reaction will predominate. Since PE is the polyalkene most saturated with hydrogen atoms, the chain transfer reaction predominates. The low yield of monomer during the thermal degradation of PE may thus be associated with this mechanism.

If a fraction of the hydrogen atoms in the polyalkene chain are replaced by methyl or other small groups, then the hydrogen atom transfer process becomes difficult; this leads to the formation of free radicals which continue polymer degradation to produce monomer. For example, during the thermal degradation of polyisobutylene, the cleavage of a fraction of the carbon–carbon bonds causes the formation of free radicals which promote chain scission to produce monomer (in up to 18% yield):

$$\sim\text{CH}_2-\text{C(CH}_3)_2-\text{CH}_2~\longrightarrow~\sim\text{CH}_2+\text{C(CH}_3)_2=\text{CH}_2$$  \hspace{1cm} (1.5)
Thermal Stability of Polymers

The thermal decomposition of polyalkenes may be presented as described next. In contrast to low molecular mass substances, for example alkanes, macromolecules do not behave as a single kinetic unit: some of their elements may acquire greater amounts of energy, while the others may acquire less. At the same time all three types of motion of these elements of the macromolecule are limited by their being chemically bound to the remainder of the macromolecule with its large dimensions. The resultant fluctuation in tensions leads to the cleavage of chemical bonds occurring in different parts of the macromolecule. If, as in PE, there are sufficient quantities of mobile hydrogen atoms in the chain, then such a macromolecular scission is accompanied by the abstraction of a hydrogen atom from the carbon atom nearest to the site of scission. However, when the hydrogen atom content is low, as in polyisobutylene and propylene, the occurrence of chain scission is not accompanied by the transfer of hydrogen atoms. Instead, the free radicals formed continue the process of chain cleavage to form monomer.

1.1.2 Depolymerisation

Depolymerisation is a free radical mechanism in which the polymer essentially reverts to a monomer or monomers. Unlike random scission, which produces fragments of a variety of chain lengths, depolymerisation generates a simple chromatogram consisting of large peaks for the monomers from which the polymer or copolymer was produced:

\[ (~\text{CH}_2\text{Ph} - \text{CH}_2\text{Ph}~)_n \rightarrow n\text{PhCH} = \text{CH}_2 \]

1.1.3 Side Group Elimination

This is usually a two-stage process in which the polymer chain is first stripped of atoms or molecules attached to the backbone of the polymers, leaving an unsaturated chain. This polyene then undergoes further reactions, including scission, aromatisation, and char formation.

It is known that, in the absence of oxygen, PE is thermally stable. The thermogravimetric analysis (TGA) of this polymer shows that decomposition of this polymer begins at about 280 °C, and when the temperature is near to 350 °C, its thermal degradation proceeds rapidly with the elimination of considerable quantities of volatile materials. The half-life temperature (i.e., that leading to 50% weight loss on heating for 40–45
minutes) of PE is 406 °C. Only 1% of monomer is formed during the thermal degradation of PE, which indicates the absence of the chain depolymerisation reaction of this polymer. Since all carbon–carbon bonds in PE (except for those sited at the chain ends, at branching sites and at other side-groups) possess the same strength, then the probability of their degradation on heating is the same. Thus, the pattern of thermal degradation of PE macromolecules is random.

It has been found that, on the thermal degradation of comparatively low molecular mass PE under vacuum or in a nitrogen atmosphere under normal pressure, the volatile products of degradation consist of molecular fragments of PE macromolecules. The viscosity-average molecular mass of the residue falls sharply on a 10 hours exposure above 315 °C (Figure 1.1). Subsequent heating leads to a smoother decrease in the molecular mass of the polymer. The degradation of PE in a nitrogen atmosphere results in growth of its unsaturation with the extent of its decomposition; this may be associated with the disproportionation of more low molecular mass macroradicals at their end-groups or with the transfer of hydrogen atoms from two neighbouring carbon atoms of the main chain.

![Figure 1.1](image)

**Figure 1.1** Variation in relative intrinsic viscosity of the residue from polymethylene decomposition ([W] is the degree of conversion: △ at 375 °C; □ at 480 °C; X at 390 °C; ○ at 400 °C; the solid curve is that calculated.
Source: Author’s own files

Analysis of the degradation products of PE produced under vacuum and under atmospheres of nitrogen and helium at different temperatures made it possible to establish that the higher the decomposition temperature, the lower the molecular mass
Thermal Stability of Polymers

of the decomposition products, and the larger the fraction of gaseous compounds. Thus, the fraction of ethylene is 0% at 500 °C, 5.5% at 800 °C and 26.4% at 1,200 °C. This may be explained by the fact that, at temperatures above 800 °C, both competing reactions proceed, i.e., the cleavage of chains into comparatively high molecular mass fragments with the transfer of hydrogen atoms, and the cleavage of free macroradicals via the chain mechanism to form monomer. The rate and significance of the latter process increase at higher temperatures.

Studies on the thermal degradation of PE samples with different molecular masses in the isothermal regime at different temperatures have shown that the kinetic curves have linear plots up to 70% weight loss (Figure 1.2), which point to a zero-order reaction. The activation energy of thermal degradation increases with the molecular mass of the polymer from 192.3 kJ/mol (molecular mass 11,000) up to 276.3 kJ/mol (molecular mass 23,000) [2].

Figure 1.2 Kinetic curves of the thermal degradation of polyethylene with molecular mass (a) 23,000, (b) 16,000 and (c) 11,000 at different temperatures: (a) 1 – 405 °C, 2 – 393 °C, 3 – 412 °C, 4 – 436 °C; (b) 1 – 317 °C, 2 – 376 °C, 3 – 388 °C, 4 – 403 °C, 5 – 402 °C; (c) 1 – 374 °C, 2 – 393 °C, 3 – 410 °C, 4 – 420 °C, 5 – 396 °C. Source: Author’s own files
A comparison of the decomposition processes of three PE samples (commercial PE having a molecular mass of 20,000, unbranched high molecular mass polymethylene and strongly branched PE) differing in structure and molecular mass has enabled the characterisation of substantial differences in their thermal degradation.

The dependence of the degradation rate upon the extent of degradation was calculated from weight loss curves of commercial PE (Figure 1.3). It was found that in its initial stage (up to 10–40%) the rate of the process is very high, but then it is sharply reduced and transforms into a virtually linear dependence, which is extrapolated to zero at 100% decomposition. Such a kinetic pattern derives from two main factors: (i) the polydisperse nature of the polymer, whose low molecular mass fractions are easily removed in the initial degradation stages, and (ii) the presence of weak bonds in the main polymer chain caused by the presence of hydroperoxide and other groups. The weak links lead to the splitting of carbon–carbon bonds and other reactions in the initial stages of the process. These particular factors diminish in significance over the course of degradation, and the rate of the process decreases sharply.

![Figure 1.3](image-url)  

**Figure 1.3** Dependence of the rate of thermal degradation ($v$) of commercial PE with molecular mass 20,000 on the degree of decomposition at temperatures: 1 - 392 °C, 2 – 387 °C, 3 – 382 °C, 4 – 377 °C, 5 – 372 °C. Source: Author’s own files

Studies on the rate of thermal degradation of unbranched high molecular mass PE (polymethylene) have shown that the process follows almost ideal first-order kinetics. The rate of thermal degradation is directly proportional to the temperature of the process. The dependence of the rate of elimination of volatiles on their quantity
Thermal Stability of Polymers

shows complex behaviour. The rate curves pass through a maximum of degrees of decomposition from 2% to 10%, and then become gradually straight, finally falling to zero at 100% decomposition of the polymer.

For the thermal degradation of branched PE, as in the case of low molecular mass commercial PE, high rates of decomposition are observed in the initial stages of the process. After 15–30% decomposition of the polymer, the rate falls sharply.

Anderson and Freeman [2] found that in the thermal decomposition of high-pressure PE (low-density polyethylene; LDPE) under vacuum there were three stages of decomposition. In the first stage, up to 3% conversion, zero-order kinetics was followed and the value of the energy of activation (E) was about 48 kcal/mole; in the second stage, 3–15% conversion, the order was still zero and the value of E was found to be about 6 kcal/mole (Figure 1.4). From 15–35% conversion, the reaction appeared to involve the transition from zero-order to first-order kinetics, and above 35% conversion, the kinetics were first-order and the value of E was found to be about 67 kcal/mole (Figure 1.5). The initial stage was attributed to the degradation of branched chains of short length since these should require less energy for bond rupture. The second stage was attributed to end chain cleavage, and the final stage, to the random rupture of carbon–carbon bonds, which requires an energy similar to that found for this stage.

![Figure 1.4](image)

**Figure 1.4** Temperature dependency plot of the low temperature thermal degradation of polyethylene in vacuum: (1) up to 3% degradation, (2) from 3 to 15% degradation. Reproduced with permission from D.A. Anderson and E.S. Freeman, *Journal of Polymer Science*, 1961, 54, 253, ©1961, Wiley [2]
1.1.3.1 Differential Thermal Analysis

Irgashi and Kambe [3] also studied the thermal degradation of polyethylene and used dynamic thermal analysis (DTA) as well as TGA techniques. The experiments were carried out in both air and nitrogen. The PE studied were, two low-density samples. By means of DTA, the crystallinities of the high-pressure samples were found to be 33% and 36% while those for the low-pressure samples were 64% and 77%, and the melting points of the latter samples were higher than those of the former.

Figure 1.6 shows DTA curves for a high-density PE (HDPE) in air and in nitrogen. The initial large peaks represent the melting of the sample while the two final peaks denote thermal decomposition. The upper curve also shows two small exothermic peaks, which presumably are due to oxidation. From such curves it would appear that thermal decomposition for high and low-pressure PE occurs in one stage. The weight losses of the two low-density samples began at about 360 °C, which is about 20 °C higher than for the high-pressure samples. These results were attributed to the branching present in the high-pressure samples. A branched PE is presumably more thermally unstable than a linear one since thermal decomposition may be initiated at a branched point with a tertiary hydrogen atom. Isothermal experiments [4] support these findings.
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Figure 1.6 Differential thermal analysis curves for high-density Hisex 5000. Upper curve, in air; lower curve, in a nitrogen atmosphere. Reproduced with permission from S. Irgashi and H. Kambe, Polymer Preprints, 1964, 5, 333. © 1964, American Chemical Society [3]

In Figure 1.7 are shown weight losses for a paraffin in comparison with an HDPE. The weight loss of the paraffin began at 180 °C and that of the polymer at 380 °C. The degradation products were trapped and gave melting points, for paraffin and the polymer of 55.0–55.5 °C and 51.0–67.0 °C, respectively. The melting point of the trapped products for paraffin corresponds well with the original one, indicating vaporisation of the paraffin, while the wide melting point range of the polymer degradation products indicates the presence of a large number of hydrocarbons. On the basis of isothermal methods, Madorsky [5] has found that in the degradation of PE, a whole spectrum of chain fragments was obtained, each containing from one to fifty or more carbons, depending upon the pyrolysis temperature. These results would appear to support the view that random chain scission is involved in the degradation of PE. However, it may be interesting to note that on the basis of isothermal methods, others [6] have reported that in the degradation of PE, a large amount of ethylene is formed at higher temperatures than they used (about 600 °C). The apparent activation energy for the degradation in nitrogen was 14 kcal/mol for both LDPE and HDPE. However, some workers obtained reaction orders of zero and some of one (compare the results reported by Madorsky [5] with those obtained by Jellinek [7]). This seems to be dependent on details in the method of measurement and clearly needs to be resolved.
1.1.3.2 Differential Scanning Calorimetry

Camacho and Karlsson [8] have examined the thermal stability of recycled HDPE, PP and their blends in their discussion of environmental concerns and producers’ liability concerning the dispersal, collection and recycling of these polymers.

These studies included a comparison of results obtained by differential scanning calorimetry (DSC), TGA and chemiluminescence.

All these techniques demonstrate that the blend and its components alone undergo substantial degradation after the first or second extrusion. Accordingly, upgrade of the resin through the addition of a re-stabilising system becomes necessary to avoid their premature failure.

The thermogravimetric (TG) measurements on the reprocessed blend were shifted towards higher temperatures than the simulated curve indicating that the blends,
despite the multiple extrusions are more stable than expected in nitrogen. The HDPE has a stabilising effect on the PP.

DSC and TG can be used to determine the thermal/oxidative stability of PP, PE and their blends. The oxidation induction time (OIT) and the oxidation temperature (T_{ox}) provide relatively, rapid information about the total amount of effective antioxidants in the reprocessed resin, which is important to establish the need for re-stabilisation or upgrade of the resins.

Figure 1.8 shows the DSC thermograms of the multi-extruded resins. According to Figure 1.8a and Figure 1.8b the DSC traces of PP and HDPE remained practically unaltered after the first and second extrusion, whereas further reprocessing induced changes in the peaks’ shape probably due to chain scission in PE and PP. For example, the thermogram of HDPE after the second extrusion pass exhibits a bimodal melting peak that might be attributed to the presence of species with a lower molecular weight (M_w) than the original material formed as a result of severe chain scission and not able to co-crystallise. Even though bimodality was not observed in the re-processed PP an increase in the low molar mass tail after each extrusion was noticed.
Figure 1.8 DSC thermograms of multi-extruded: (a) polypropylene, (b) polyethylene and (c) PP/HDPE (20/80 blend). Reproduced with permission from W. Camacho and S. Karlsson, Polymer Degradation and Stability, 2002, 78, 385. © 2002, Elsevier [8]
**Thermal Stability of Polymers**

**Figure 1.9a** and **Figure 1.9b** display the TG curves of PP after the corresponding extrusion pass in nitrogen and oxygen, respectively. The differences are clearer in the experiments under nitrogen, where a systematic drop in the degradation temperature is observed after every extrusion pass. This is due to the chain scission of PP during processing. Under oxygen, $T_{ox}$ drops sharply for samples extruded up to four times and remains almost constant for the samples processed further. These results are in good agreement with the measurements obtained with OIT.

**Figure 1.9** Thermogravimetric traces of multi-extruded polyolefins under different atmospheres: (a) nitrogen and (b) oxygen, I – PP, II – PE. Reproduced with permission from W. Camacho and S. Karlsson, *Polymer Degradation and Stability*, 2002, 78, 385. © 2002, Elsevier [8]

Hussain and co-workers [9] also investigated the thermomechanical degradation of LDPE during the conditioning of samples in a batch blender using a variety of techniques including DSC, high-performance chromatography, GPC, nuclear magnetic resonance and dynamic viscosity measurements.
DSC was discussed as it was not expected to show any significant shifts in glass transition temperature or melting temperature, which are relatively insensitive to moderate changes in $M_w$, resulting from polymer degradation. However, melt viscosity measurements are highly sensitive to $M_w$ changes and these workers used them as a tool for monitoring polymer degradation.

The objective of this study was to make sure that degradation of PE was prevented during the conditioning process. Different techniques were used to examine the stability of PE in the melt blender. Small-strain dynamic oscillatory measurements of viscoelastic properties ($\eta'$) in a mechanical spectrometer as well as $M_w$ and molecular weight distribution from GPC analysis were used to assess the stability of samples of linear low-density polyethylene (LLDPE) and LDPE in the melt blender.

The study included samples with and without additional antioxidants - results were compared to the properties of the ‘as-received’ samples. The results of using the different techniques can be integrated to explain: (a) the modifications that can occur due to the melt blending of PE, (b) their relation to the polymer chemistry, and (c) the possible means for detection and prevention of degradation.

If degradation is to take place, then $M_w$ will either increase (chain build-up) or decrease (chain breakdown) and the polydispersity will be broadened. Four measurements were carried out for each of the six samples. Results are shown in Table 1.1 and indicate that there is a decrease in $M_w$ accompanying the higher polymer conditioning temperatures. The $M_w$ and polydispersity of the four different measurements were averaged and the standard deviation, given in parentheses, was calculated for each case.

<table>
<thead>
<tr>
<th>Blender conditions</th>
<th>$M_w$ (SD)</th>
<th>$t_o$</th>
<th>PD (SD)</th>
<th>$t_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S229: none</td>
<td>105,313 (1285)</td>
<td>-</td>
<td>3.57 (0.07)</td>
<td>-</td>
</tr>
<tr>
<td>S229: $T_{\text{conditioning}}$ = 190 °C</td>
<td>95,794 (1750)</td>
<td>8.770</td>
<td>3.32 (0.10)</td>
<td>4.096</td>
</tr>
<tr>
<td>S229: $T_{\text{conditioning}}$ = 220 °C</td>
<td>93,530 (2163)</td>
<td>9.367</td>
<td>3.39 (0.22)</td>
<td>4.097</td>
</tr>
<tr>
<td>S216: none</td>
<td>99,464 (902)</td>
<td>-</td>
<td>6.45 (0.36)</td>
<td>-</td>
</tr>
<tr>
<td>S216: $T_{\text{conditioning}}$ = 190 °C</td>
<td>100,255 (1818)</td>
<td>0.78</td>
<td>5.98 (0.14)</td>
<td>2.434</td>
</tr>
<tr>
<td>S216: $T_{\text{conditioning}}$ = 220 °C</td>
<td>108,934 (1696)</td>
<td>9.86</td>
<td>6.48 (0.56)</td>
<td>0.090</td>
</tr>
</tbody>
</table>

SD = Standard deviation
1.1.3.3 Other Techniques

Wang and co-workers [10] used Fourier-transform infrared spectroscopy, pyrolysis gas chromatography–mass spectrometry (Py-GC-MS) and TGA in their studies of thermal degradation of magnesium hydroxide (MH) and red phosphorus flame retarded LDPE composites. They calculated the apparent activation energy ($E_a$) of the degradation of LLDPE, and LLDPE/magnesium hydroxide and LLDPE/magnesium – red phosphorus composites in nitrogen atmosphere using the Kissinger and Flynn–Wall methods based on TG data. The $E_a$ values obtained from both methods agree well. The peak temperature ($T_k$) obtained from the derivative TG curves and $E_a$ values of the degradation of the PE and its composites are listed in Table 1.2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heating rate (°C/min)</th>
<th>$T_k$ (°C)</th>
<th>Degradation state</th>
<th>$E_a$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLDPE</td>
<td>10</td>
<td>492</td>
<td>Whole process</td>
<td>247</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>500</td>
<td></td>
<td></td>
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<td></td>
<td>20</td>
<td>509</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>40</td>
<td>517</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LLDPE/50% magnesium hydroxide</td>
<td>10</td>
<td>496</td>
<td>2nd</td>
<td>245</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>503</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>LLDPE/40% MH/10% red phosphorus</td>
<td>10</td>
<td>507</td>
<td>2nd</td>
<td>234</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>514</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>523</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>536</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The Py-GC-MS results show that the addition of magnesium hydroxide and phosphorus to LLDPE resin leads to great changes of the ratio of heavy compounds and light compounds. The LLDPE/40% magnesium hydroxide/10% red phosphorus composite produces heavier compounds than the LLDPE/50% magnesium hydroxide composite.

El-Goudy and El Shansbury [11] used a combination of x-ray fluorescence spectroscopy, TGA and DSC in their studies of the effects of radiation on PE.

### 1.2 Polypropylene and Polyisobutylene

Since on the PP macrochain every second carbon atom is tertiary and in polyisobutylene (PIB) it is quaternary, then the strength of the carbon–carbon bonds falls going from PE, through PP to PIB.

This is clearly confirmed by the data on the thermal degradation of propylene and PIB under vacuum (Table 1.3). Comparison of the number of volatile products released at corresponding temperatures has shown that PIB is less thermally stable than PP; thus the PP half-life temperature is 387 °C, while that of PIB is 344 °C.

<table>
<thead>
<tr>
<th>Table 1.3 Thermal degradation of PP and PIB (0.5 h under vacuum)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PP</strong></td>
</tr>
<tr>
<td>Decomposition temperature (°C)</td>
</tr>
<tr>
<td>328</td>
</tr>
<tr>
<td>374</td>
</tr>
<tr>
<td>380</td>
</tr>
<tr>
<td>384</td>
</tr>
<tr>
<td>393</td>
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<td>395</td>
</tr>
<tr>
<td>400</td>
</tr>
<tr>
<td>410</td>
</tr>
<tr>
<td>800</td>
</tr>
</tbody>
</table>

Source: Author’s own files
Mass spectroscopic analysis of the volatile fractions released by PP during its half-life at 380–410 °C has shown that butane, butane, hexane, hexene, pentane, pentene and propylene are the main products of decomposition.

In PP, the tertiary hydrogen atom is more reactive, undergoing scission more readily than the secondary hydrogen atom. Accordingly, bond cleavage in the polymer chain occurs mainly with the transfer of an hydrogen atom:

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_2–\text{CH}–\text{CH}_2–\text{CH}–\text{CH}_2 & \quad \rightarrow \text{CH}_2–\text{C(CH}_3\text{)=CH}_2 + \text{CH}_2–\text{CH}_2
\end{align*}
\]

With PP, the cleavage of carbon–carbon bonds with the formation of free radicals and the subsequent elimination of monomer molecules is more frequent than for PE.

The presence of two methyl groups at every second carbon atom in the PIB chain causes steric difficulties for cleavage followed by the transfer of an hydrogen atom. This results in a considerable increase in the number of chain breaks with the formation of free radicals, which, on decomposition by a chain mechanism, produce monomer:

\[
\begin{align*}
\sim\text{C(CH}_3\text{)2–CH}_2–\text{C(CH}_3\text{)2–CH}_2–\text{C(CH}_3\text{)2–CH}_2 & \quad \rightarrow \text{C(CH}_3\text{)2} \\
\sim\text{CH}_2–\text{C(CH}_3\text{)2 + CH}_2–\text{C(CH}_3\text{)2–CH}_2 & \quad \sim\text{C(CH}_3\text{)2–CH}_2–\text{C(CH}_3\text{)2} – \rightarrow \sim\text{C(CH}_3\text{)2 + CH}_2=\text{C(CH}_3\text{)2}
\end{align*}
\]

Simultaneously a significant number of C–C scissions occur with the transfer of hydrogen atoms, leading to the formation of compounds with saturated and unsaturated groups at the chain ends.

Studies on the rate of thermal degradation of PP and PIB have shown that the reaction order determined over the linear sections of the kinetic curves is 1, and the activation energies for the degradation of PP and PIB are 242.4 and 204.8 kJ/mol, respectively.
The results of studies on the influence of molecular mass and molecular mass distribution of PIB on the kinetics of its thermal degradation are of interest because of the effect of chemical structure on the thermal stability of the polymer. Several high and low molecular mass fractions and non-fractionated samples of PIB with high and low molecular masses have been used in these studies. It has been found that the molecular mass of PIB sharply decreases from about two million to about 25,000 in the initial period (10% of weight loss) of polymer degradation under vacuum at 300 °C. Thereafter the decrease in molecular mass of the polymer decelerates.

In their initial stages of decomposition, the pattern of the dependence of the rate on the degree of decomposition differs for low molecular and high molecular mass samples of PIB (Figure 1.10). While a drastic decrease in the degradation rate is typical of low molecular mass fractions (Figure 1.10, curves 1–3), the occurrence of maxima in the rate curves within the same range of polymer degradation (10–20%) is typical of high molecular mass samples of PIB.

![Graph](image.png)

**Figure 1.10** Dependence of the rate of thermal degradation on the degree of decomposition of polyisobutylene with different molecular masses: 1 – 23,400, 2 – 40,000, 3 – 440,000, 4 – 100,000, 5 – 198,000 and 6 – 700,000.

Source: Author’s own files

The high values of the initial rate of degradation of low molecular mass PIB are probably associated with the presence of very short chains, leading to the formation of monomer which volatilises.

At later stages of the process, the decomposition curves (Figure 1.10) reveal that the initial values of the molecular mass of the polymer and its distribution have no critical
influence on the rate of thermal degradation. This is explained by the fact that even in
the initial stages of decomposition, the molecular mass of even high molecular mass
PIB is sharply reduced through cleavages of the carbon–carbon bonds of the main
chain to form low molecular mass (about 25,000) polymer and monomer.

Gomez-Elvira and co-workers [12] studied thermal stability at 90 °C to 140 °C of
predominantly isotactic metallocene catalysed PP samples ranging from 3,000 to
41,000 molecular weight by chemiluminescent analysis and compared results with
those obtained for predominantly isotactic Ziegler-Natta PP (ZNiPP) of increasing
molecular weight. The structural differences of these two types of polymer is
sufficiently different to expect very different thermal stability behaviour between them.

Gomez-Elvira and co-workers [12] presented oxidation kinetics at 90 °C, 100 °C,
120 °C and 140 °C for metallocene polymerised PP. The oxidation was carried out
on powder. The chemiluminescence curves were recorded all along the induction
period and the auto acceleration stage, and stopped well after auto acceleration had
finished. An example of the kinetic curves obtained is shown in Figure 1.11, together
with the way in which the induction period has been estimated. For these samples a
bimodal distribution was always found, no matter what the molecular weight and
the isotacticy were (Figure 1.12). As in the case of ZNiPP, the low temperature
component appears about 15 °C before the main melting peak, the only difference
being its lower relative intensity in the higher number average molecular polymer
weight ($M_n = 41,000$).

This work revealed that the microstructural control of tactic errors, provided by
metallocene catalysis, ensured that the configurational microstructure is a parameter
which can lead to improve the iPP thermal stability over 100 °C.

Brambilla and co-workers [13] studied the outdoor degradation of iPP plates by
means of positron annihilation lifetime spectroscopy (PALS), absorption infrared
spectroscopy, DSC and density measurements. Infrared spectra reveal the presence of
oxygenated species in the exposed polymer induced by external agents. Results from
thermal and density analysis suggest an increase of crystallinity of the sample with
exposure time. Positron data strengthened such a conclusion, showing a reduction
of the amorphous zones as monitored by the corresponding decrease of positronium
(Ps) formation. Furthermore, an estimation of the average sizes of the free volume
holes and of the defects in the crystalline regions was obtained. PALS is a relatively
simple technique which can probe the properties of the free volume holes in a non-
destructive way. It is based on the fact that some of the positrons injected into the
material under investigation are trapped in regions with reduced electron density
where they may form a bound positron–electron positronium system.
Figure 1.11 An example of the chemiluminescence experiment showing the determination of the induction time. The curve corresponds to a sample of metallocene catalysed PP $M_n = 19,000$, oxidised in $O_2$ at 140 °C. Reproduced with permission from J.M. Gomez-Elvira, P. Tiemblo, M. Elvira, L. Matisova-Rychla and J. Rychly, *Polymer Degradation and Stability*, 2004, 85, 873. © 2004, Elsevier [12]

Figure 1.12 Normalised first DSC scans of M-iPP samples: 5 (---), 4 (- - -), 3 (-----) and 2 (-- --). Reproduced with permission from J.M. Gomez-Elvira, P. Tiemblo, M. Elvira, L. Matisova-Rychla and J. Rychly, *Polymer Degradation and Stability*, 2004, 85, 873. © 2004, Elsevier [12]