The thermal degradation of poly(\textit{iso}-butyl methacrylate) and poly(\textit{sec}-butyl methacrylate)

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The non-oxidative thermal degradation of poly(\textit{iso}-butyl methacrylate) and poly(\textit{sec}-butyl methacrylate) was investigated by studying changes in the polymer residue. Due to the different number of $\beta$-hydrogens in their ester substituents, these two polymeric isomers behave differently when subjected to elevated temperatures. Poly(\textit{iso}-butyl methacrylate) degrades quantitatively by depolymerisation with zip lengths of the same order of magnitude as those of poly(methyl methacrylate). Poly(\textit{sec}-butyl methacrylate) degrades by a combined degradation mechanism of depolymerisation and de-esterification. De-esterification becomes a significant thermolysis route at temperatures higher than 240 °C.

Keywords: poly(butyl methacrylate), isomers, thermal degradation, mechanism, depolymerisation, de-esterification.

INTRODUCTION

It is generally considered that most polymethacrylates thermally degrade by depolymerisation. Grassie and his co-workers initiated and carried out investigations of thermal degradation of numerous polymethacrylates, placing most emphasis on the major represen-

\begin{align*}
\text{CH}_2 & \text{C} \quad + \quad \text{CH}_2 & \text{C} \\
& \text{O} \quad \text{H} & \text{C} \quad \text{H} \\
& \text{R} & \text{H} & \text{H}
\end{align*}

Scheme 1. The de-esterification of a polymethacrylate with 2$\beta$-hydrogens

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tative of this class of compounds, poly(methyl methacrylate) (PMMA). Although PMMA degrades practically quantitatively to its monomer, the thermolysis mechanism of other polymethacrylates is not that simple and is determined predominantly by the structure of the ester substituent. If there are β-hydrogen atoms present in the substituent, de-esterification may and does occur (Scheme 1).

The influence of β-hydrogens on the thermolysis mechanism of polymethacrylates is shown in Table I. De-esterification competes with depolymerisation as a relevant degradation path when the monomer unit has five or more β-hydrogens. Consequently, isomeric structures such as poly(iso-, n-, sec- and tert-butyl methacrylate) (PiBMA, PnBMA, PsBMA and PtBMA) have different thermolysis mechanisms. Grassie studied the thermal degradation of PnBMA nad PtBMA and found that the former predominantly degraded by depolymerisation and the latter by de-esterification.

<table>
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<th>Substituent</th>
<th>No. of β-Hs</th>
<th>Substituent</th>
<th>No. of β-Hs</th>
<th>Substituent</th>
<th>No. of β-Hs</th>
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<td>sec-Butyl</td>
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</tr>
<tr>
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<td>n-Butyl</td>
<td>2</td>
<td>tert-Butyl</td>
<td>9</td>
</tr>
<tr>
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<td>n-Hexyl</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>n-Heptyl</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>n-Octyl</td>
<td>2</td>
<td></td>
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</table>

The goal of this study was to investigate the thermal degradation of PiBMA (Structure I) and PsBMA (Structure II) and determine their basic thermolysis mechanisms by studying changes in the polymer residue.

EXPERIMENTAL

The monomers, iso-butyl methacrylate and sec-butyl methacrylate, were synthesised by the standard acid catalysed esterification of methacrylic acid (Aldrich, p.a.) with iso-butanol (Kemika, p.a.) and sec-butanol (Kemika, p.a.), respectively. After the normal work-up procedure, the monomers were vacuum distilled immediately prior to polymerisation. The polymerisations were performed in bulk at 50 °C in glass ampoules sealed under high vacuum using 0.5 mol % α,α'-azo-
bisisobutyronitrile (AIBN) as the initiator. The polymers were isolated by precipitation with metha-
ol (Zorka Pharma, p.a.) containing about 5% water and freed of residual monomer by repeated pre-
cipitation from acetone (Zorka Pharma, p.a.) solutions using methanol containing 5% water. The
polymers were dried to constant mass at room temperature.

The values of the limiting viscosity numbers (LVN) of the samples were determined in ace-
tone at 25 °C using an Ubbelohde viscometer; LVN\textsubscript{PiBMA} = 0.123 m\textsuperscript{3}/kg and LVN\textsubscript{PsBMA} = 0.0686 m\textsuperscript{3}/kg. The mean number-average molar mass, $\overline{M}_n$ of PiBMA was calculated from the obtained LVN value using the Kuhn-Mark-Houwink-Sakurada equation and literature values for the coefficients $K$ and $a$:

$$\overline{M}_n = 4.33 \times 10^5 \text{ g/mol}.$$ 

Thermal degradation experiments were performed using a small furnace, the temperature of
which was controlled by a rheostat. The temperature of the furnace, measured by a Ni-NiCd thermo-
couple, was kept constant to ±1°C. Experiments were performed in the range 180 – 200 °C for PiBMA
and 200 – 260 °C for PsBMA under a nitrogen flow of 50 cm\textsuperscript{3}/min for 5 to 30 min. The sample masses
were about 120 mg.

After determining the mass loss, the PiBMA residues were analysed by measuring the LVN.
The content of free acid groups in degraded PsBMA samples was determined by dissolving or swell-
ing the residue in methanol, adding a known amount of methanolic 0.1 mol/dm\textsuperscript{3} NaOH solution and
back titrating the excess alkali with 0.1 mol/dm\textsuperscript{3} aqueous HCl using phenolphthalein as indicator.

RESULTS AND DISCUSSION

Thermal degradation of PiBMA

The isothermal mass loss of PiBMA as a function of degradation time at various ther-
molysis temperatures is shown in Fig. 1. Significant mass loss can be noticed at longer
degradation times and at 200 °C. Based on the fact that PiBMA has one β-hydrogen in its
ester substituent, it may be assumed that depolymerisation is the main thermal degrada-
tion mechanism. This assumption was confirmed by thermal volatilisation analysis
(TVA), which indicated almost quantitative degradation to monomer. Therefore, it is in-
teresting to follow changes in the molar mass of the residue during thermal degradation,
Fig. 2. The molar mass of PiBMA decreases considerably during degradation.

![Fig. 1. The dependence of PiBMA mass loss on time at various degradation temperatures.](image-url)
The number of main chain scissions per monomer unit can be determined on the basis of changes in the mass and molar mass of the degraded sample.\textsuperscript{8} The number of bond scissions per monomer unit, \( \frac{s}{P_0} \), may be calculated from the equation:

\[
\frac{s}{P_0} = \frac{1 - x}{P_t} - \frac{1}{P_0}
\]

where \( s \) is the number of scissions, \( x \) the fraction of evaporated thermal degradation volatiles, and \( P_0 \) and \( P_t \) the degrees of polymerisation of the initial and degraded polymer, respectively. The results of this calculation are shown in Fig. 3 where \( s/P_0 \) is plotted against time at various temperatures. It may be noticed that the values of

Fig. 2. The change in \( \overline{M_w} \) of PiBMA degraded at various temperatures.

Fig. 3. Dependence of the number of bonds broken per monomer unit of PiBMA, \( s/P_0 \), on time at various degradation temperatures.
s/P₀ tend toward constant values at longer degradation times. As expected, higher values of s/P₀ are observed at higher degradation temperatures.

The relative change in the molar mass of the polymer residues, Mₙ/Mₙ₀, as a function of mass loss is shown in Fig. 4. The shape of the Mₙ/Mₙ₀ vs. conversion curve indicates the occurrence of random main chain scission, which initiates depolymerisation, and/or that the zip length of depropagation, Z, is smaller than the degree of polymerisation of the polymer.⁸

An attempt was made to determine the zip length of depropagation by the equation proposed by Kashiwagi et al.:⁹

\[
\frac{W}{W_0} = \frac{P_t^2}{P_0^2} \left( \frac{Z + P_0}{Z + P_t} \right)^2
\]  

(2)

where W/W₀ is the ratio of the mass of the residue and the mass of the initial polymer. The results of the calculation are shown in Fig. 5. The value of Z increases with degradation temperature. Also, as expected from the shape of the dependence Mₙ/Mₙ₀ vs. mass loss, the values of Z are lower than the initial degree of polymerisation of PiBMA, P₀ = 3050. Similar calculations for PMMA degraded in the temperature range 260–300 °C yielded Z values between 1000 and 2000.⁹ The values for PiBMA are lower most probably because they were derived from data obtained at lower thermolysis temperatures. If one extrapolates the obtained dependence of Z vs. degradation temperature to the temperatures 260 and 300 °C, one obtains Z values of 1455 and 2080, respectively, which compare very well with the values determined for PMMA and indicate the similar depropagation behaviour of PMMA and PiBMA.

However, detailed results obtained for the thermolysis of the structurally similar isomeric butyl diesters of poly(itaconic acid) showed that although depolymerisation
was the main degradation mechanism of poly(di-isobutyl itaconate) (PDiBI) more alkene was evolved than was the case of poly(di-n-butyl itaconate) (PDnBI). This is contrary to the assumption that the amount of ester decomposition is dependent on the number of β-hydrogen atoms. This fact was explained by the special lability of the lone tertiary hydrogen atom present in the ester substituents of PDiBI. This mechanism is also likely to occur in the thermal degradation of PiBMA. Further results would be necessary to confirm this assumption.

Thermal degradation of PsBMA

The isothermal mass loss of PsBMA as a function of degradation time at various thermolysis temperatures is shown in Fig. 6. Significant mass loss can be noticed at 220 °C.
Compared to PiBMA, PsBMA seems to be more thermally stable (the mass loss of PiBMA after 30 min at 200 °C is 55.2 % and for PsBMA 7.4 %). As PsBMA has five β-hydrogens in the ester substituent, it may be assumed that de-esterification significantly competes with depolymerisation as the main thermal degradation mechanism.

Attempts to determine the LVN of degraded PsBMA were not successful as $\eta_{sp}$/c increased with decreasing polymer concentration. Such behaviour indicates that the structure of the polymer residue changes during thermal degradation implying that depolymerisation is not the only degradation mechanism and that the residue has ionic properties in dilute solution. The ionic properties can only result from the existence of free acid or anhydride groups in the polymer residue.

\[ \text{Fig. 7. The dependence of the number of COOH groups evolved per monomer unit of PsBMA as a function of time at various thermolysis temperatures.} \]

\[ \text{Fig. 8. The dependence of the number of COOH groups evolved per monomer unit of PsBMA as a function of temperature, degradation time 30 min.} \]
The acid groups formed in the PsBMA residue were determined quantitatively by acid-base titrations of the residues. The determined amounts of acid groups, expressed as mol COOH per mol monomer unit, are shown as a function of time and temperature of degradation in Figs. 7 and 8, respectively. The number of evolved COOH groups increases exponentially with degradation temperature indicating that de-esterification is a relevant degradation route at temperatures higher than 240 °C. These data agree well with the TVA data of McNeill on the evolution of 1- and 2-butene during thermolysis.7 Similar behaviour was found for the thermal degradation of the structurally similar poly(di-sec-butyl itaconate).10

CONCLUSIONS

On the basis of our own findings and the TVA work of McNeill,7 it may be concluded that the assumptions made by Grassie and coworkers1–4 concerning the mechanism of thermal degradation of polymethacrylates were generally correct, although the importance of the lone tertiary hydrogen atom in the ester substituent structures still needs to be established. Poly(iso-butyl methacrylate) degrades quantitatively by depolymerisation with zip lengths of the same order of magnitude as those of PMMA. Poly(sec-butyl methacrylate) degrades by a combined degradation mechanism of depolymerisation and de-esterification. De-esterification becomes a significant thermolysis route at temperatures higher than 240 °C.

ИЗВОД

ТЕРМИЧКА ДЕГРАДАЦИЈА ПОЛИ(iso-БУТИЛ МЕТАКРИЛАТА) И ПОЛИ(sec-БУТИЛ МЕТАКРИЛАТА)

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Нексицидативна термичка деградација поли(iso-бутил метакрилата) и поли(sec-бутил метакрилата) испитана је праћењем промена у полимерном остатку. Због различитог броја β-вodonика у естарском супституту, ова два полимера изомера се различито понашају приликом излагања повишеним температурама. Поли(iso-бутил метакрилат) деградира квантитативно деполимеризацијом док мономер са кинетичким дужинама депропагације истог реда величине као код деградације поли(метил метакрилата). Поли(sec-бутил метакрилат) деградира комбинованим механизмом деградације: деполимеризацијом и дестерификацијом. Дестерификација постаје значајна реакција термолизе на температурама вишим од 240 °C.

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