DEMONSTRATION OF THE RADICAL CHARACTER OF THE MECHANISM OF THE THERMAL DECOMPOSITION OF POLYACRYLATES


The accepted free-radical chain mechanism of the thermal decomposition of polyacrylates consists of a cleavage of the chain, followed by transfer of an \( \alpha \)-hydrogen atom and the formation of the radical \( \cdot\text{CH}_2\cdot\text{C} \sim (I) \), which is the source of the basic readily volatile products, \( \text{CO}_2 \) and alcohol \([1, 2]\). The kinetic data of the thermal decomposition of polyacrylates in the presence of an inhibitor of free-radical reactions served as evidence of such a mechanism. The introduction of negligible amounts of 1,4-dianthraquinone substantially lowers the rate of decomposition of the polymer on account of chain termination on inhibitor molecules. However, the reaction of stripping of a \( \text{H} \) atom with the formation of a radical (I), which is the source of all the decomposition products, was not established \([1-5]\).

For an independent demonstration of the radical nature of the mechanism of the thermal decomposition of polyacrylates, proceeding with the participation of the indicated radicals, we investigated the thermal decomposition of polybutyl acrylate (PBA) and polymethyl acrylate (PMA) in the presence of dicumyl peroxide (CP) and the tert-butyl ester of \( \beta \)-(triethylsilyl)perpropionic acid \((\text{C}_2\text{H}_5)_3\text{Si(CH}_2\text{)C(O)OOC(CH}_3)\) (TBE).

Figures 1 and 2 present the curves of the weight loss under vacuum for PBA and PMA at various temperatures. As can be seen, additions of CP and TBE substantially accelerate the rate of thermal decomposition of polyacrylates; additions of peroxides cause a decomposition of the polymers under conditions \((220^\circ)\) in which the polyacrylates are stable in the absence of peroxides.

Chromatographic analysis of readily volatile products of the thermal decomposition of polyacrylates in the presence of each of the indicated peroxides and without them has shown that in both cases qualitatively identical decomposition products of the polymer units are contained: \( \text{CO}_2 \), alcohol, monomers, and butylene (in the decomposition of PBA). Moreover, in the decomposition of the polymers in the presence of CP,

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Conditions of thermal decomposition</th>
<th>Total weight loss</th>
<th>Readily volatile fraction</th>
<th>Fragments of chain</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBA*</td>
<td>220(^{\circ}), 2,5 h</td>
<td>11.2</td>
<td>6.5</td>
<td>4.7</td>
</tr>
<tr>
<td>PBA + 3% CP</td>
<td>220(^{\circ}), 2,5 h</td>
<td>29.4</td>
<td>9.8</td>
<td>19.4</td>
</tr>
<tr>
<td></td>
<td>250(^{\circ}), 3 h</td>
<td>13.9</td>
<td>4.7</td>
<td>9.2</td>
</tr>
<tr>
<td>PBA + 3% CP</td>
<td>220(^{\circ}), 2 h</td>
<td>20.9</td>
<td>7.2</td>
<td>13.7</td>
</tr>
<tr>
<td>PMA</td>
<td>300(^{\circ}), 2,5 h</td>
<td>15.7</td>
<td>3.4</td>
<td>12.3</td>
</tr>
<tr>
<td>PMA + 3% CP</td>
<td>220(^{\circ}), 3 h</td>
<td>10.3</td>
<td>2.2</td>
<td>8.1</td>
</tr>
</tbody>
</table>

*Data of [1, 3, 5].

methane, acetophenone, and dimethylphenylcarbinol (DMPC), which are the products of radical decomposition of the peroxide, were detected. In an investigation of the products of thermal decomposition (250°) of PBA in the presence of 3% TBE, (C2H5)4Si, methane, and acetone were detected. The identified decomposition products of peroxides are characteristic of the decomposition of peroxides in the presence of compounds that are hydrogen donors [6, 7]. The thermal decomposition of PBA in the presence of 3% PC was studied in more detail. Tables 1 and 2 present the data on the thermal decomposition of PBA and PMA in the presence of dicumyl peroxide and an analysis of readily volatile products. As can be seen from Table 2, the yield of methane and DMPC is negligible, while the amount of the latter increases with decreasing temperature of decomposition.

The possibility remains that the stripping of hydrogen by peroxide radicals occurs not only from the tertiary carbon atom, but also from the methylene group. To demonstrate the preferential stripping of an α-H atom we analyzed readily volatile products of the thermal decomposition of polymethyl methacrylate (PMMA), which does not have a labile hydrogen atom at the tertiary carbon atom, with an addition of 3% CP, conducted under conditions analogous to the thermal decomposition of PMA. It was found that the ratio of the amount of DMPC to the amount of acetophenone is 0.35 for PMA, 0.14 for PMMA. The substantial increase in the yield of DMPC in the case of decomposition of the peroxide in polyacrylate is evidence of a predominant stripping of the α-H atom.

The data obtained permit us to represent the following scheme of the interaction of peroxide with polyacrylate in thermal decomposition:

\[
\text{C}_6\text{H}_5\text{C} = \text{O} + \frac{1}{2}\text{C}_6\text{H}_5\text{C} = \text{O} \rightarrow \text{C}_6\text{H}_5\text{C} = \text{O} + \text{C}_6\text{H}_5\text{C} = \text{O}
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