THERMAL DESTRUCTION OF
POLY-[2, 5-(4', 4''-DIPHENYLENEPHTHALIDE)-1, 3, 4-OXADIAZOLE]

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As a result of an investigation of the thermal stability of poly-1,3,4-oxadiazoles [1], it was established
that decomposition of the polymers begins with the oxadiazole ring; moreover, the weakest carbon-oxygen
bonds break down first. It is also known that in polyesters based on phenolphthalein and various aromatic
dicarboxylic acids (polyarylates) [2], the ester bond and the lactone ring are responsible for the conver-
sions that occur during their aging. We were interested in evaluating the resistance to the action of high
temperatures of a polymer containing both a lactone and an oxadiazole ring and possessing the following
structure:

\[
\begin{array}{c}
\text{N} \\
\text{C} \\
\text{C} \\
\text{N} \\
\end{array}
\]

EXPERIMENTAL

Thermal destruction was studied at temperatures from 150 to 500° for 1 h on an apparatus permitting
the process to be conducted under vacuum with simultaneous collection of a sample of gas and its analysis
on a chromatograph, as well as on a Hungarian derivatograph, produced by MOM Company, in an inert
atmosphere. Changes in the structure of the polymer at low degrees of conversion were judged according
to the change in the intrinsic viscosity and the molecular weight, as well as the results of turbidimetric titra-
tion. The low-molecular products were investigated by thin-layer chromatography, while the residue after
destruction was evaluated according to the IR spectra and the data of elemental analysis.

Fig. 1. Measurement of the intrinsic viscosity (1) and molecular weight (2) during the heating of poly-
oxadiazole under vacuum for 1 h.

Fig. 2. Integral (a) and differential (b) curves of turbidimetric titration of polyoxadiazole: 1) initial;
2) 225°; 3) 275°; 4) 325°.

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR. Translated from Izvestiya
June 14, 1968.
At relatively low temperatures (150-325\(^\circ\)C), the macromolecule is not subject to destructive processes, which is evidenced by the absence of changes in the IR spectra and elemental analysis in comparison with the original sample. However, a measurement of the intrinsic viscosity revealed that its value begins to increase above 175\(^\circ\)C, reaching a maximum value of 200\(^\circ\)C, but then it decreases (Fig. 1). The molecular weight of the polymer increases continuously during heating above 175\(^\circ\)C. Up to 200\(^\circ\)C, the molecular weight and decrease in the intrinsic viscosity are evidence of the presence of branching in the polymer.

The nature of the processes that occur is distinctly evident on the curves of the molecular weight distribution, obtained by the method of turbidimetric titration (Fig. 2). The doubling of the maximum on the curves permits us to conclude that when the original polymer is heated, two processes occur simultaneously: structuration and destruction. Above 325\(^\circ\)C, the processes of branching turn into processes of cross-linking, which affects the solubility of the samples. Thus, at 350\(^\circ\)C a gel fraction is isolated, which swells greatly in solvents. With increasing temperature, the amount of the soluble fraction drops sharply; the ability of the gel to swell is also reduced. Up to 375\(^\circ\)C, inclusively, the polymer loses practically no weight. Only at 400\(^\circ\)C is a negligible evolution of gaseous and low-molecular products noted. At these temperatures a small fraction of the weight loss is comprised of water. As is shown in [1], water is liberated on account of further cyclization of the non-cyclized hydrazide fragments remaining in the polymer gel.

Destructive processes develop at 425\(^\circ\)C. At this temperature (Table 1) oxides of carbon and nitrogen are found; at higher temperatures (above 450\(^\circ\)C), small amounts of hydrogen, dicyanogen, and hydrocyanic acid are found. The low-molecular products consisted of benzonitrile, triphenylmethane, benzene, and the dinitrile of 4,4'-diphenyldicarboxylic acid (DN). Diphenyl and benzoic acid were detected in very small amounts. The change in the composition of the volatile products with increasing temperature is presented in Figs. 3 and 4. The residue represents an infusible dark mass, which shows limited swelling in organic solvents.

An analysis of the products of thermal destruction of the investigated polymer permits us to suggest that their formation occurs as a result of homolytic radical cleavage of the lactone and oxadiazole rings.

### Table 1. Composition of Products of Thermal Decomposition of Poly-[2,5-(4',4''-diphenylenephthalide)-1,3,4-oxadiazole] for 1 h

<table>
<thead>
<tr>
<th>T. °C</th>
<th>Total weight loss, %</th>
<th>Amount of water, %</th>
<th>(A \cdot 10^{-1})</th>
<th>(A \cdot 10^{-2})</th>
<th>(A \cdot 10^{-3})</th>
<th>(A \cdot 10^{-4})</th>
<th>Gaseous products</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>2,5</td>
<td>0,2</td>
<td>0,3</td>
<td>1,5</td>
<td>Traces</td>
<td>Traces</td>
<td>Traces</td>
</tr>
<tr>
<td>425</td>
<td>18,2</td>
<td>0,4</td>
<td>1,2</td>
<td>5,6</td>
<td>0,5</td>
<td>1,5</td>
<td>0,9</td>
</tr>
<tr>
<td>450</td>
<td>25,8</td>
<td>0,5</td>
<td>1,6</td>
<td>7,2</td>
<td>1,1</td>
<td>3,4</td>
<td>2,9</td>
</tr>
<tr>
<td>500</td>
<td>30,0</td>
<td>0,6</td>
<td>1,8</td>
<td>8,3</td>
<td>1,4</td>
<td>4,1</td>
<td>3,3</td>
</tr>
</tbody>
</table>

* In moles of the substance per mole of the structural unit.
† DN represents the dinitrile of 4,4'-diphenyldicarboxylic acid.