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Abstract

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ON THE THERMAL DESTRUCTION OF POLYFORMALDEHYDE

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The thermal decomposition of polyformaldehyde proceeds from the ends of the molecule (1); moreover, practically the only product of destruction is formaldehyde (2). Kern and Cherdron (3,4) have argued in favor of an ionic mechanism for the destruction processes of polyoxymethylenes. By analogy with other polymers (5–6) (polypropylene, epoxy resins, etc.), whose thermal decomposition is a radical reaction, we assumed that the thermal decomposition of polyformaldehyde may also proceed by a radical mechanism. In the initial stage of the process, as a result of the initiation reaction, two types of free radicals may be formed:

$$\sim C - CH_2 - O - CH_2 - O\cdot, \tag{1}$$

$$\sim C - CH_2 - O - \dot{C}H_2. \tag{2}$$

From the energetic point of view, the most favorable is the rupture of such a bond as is accompanied by the formation of a double bond. Isomerization of the radicals formed is also possible. Thus, during the thermal destruction of polypropylene and of some vinyl polymers, isomerization of the polymer radicals formed takes place (6,7).

Isomerization of radicals (1) and (2) may proceed according to the following scheme, with formation of formic acid and methyl formate:

$$(1') \quad \sim O{-}CH_2{-}O{-}CH_2{-}O\cdot \longrightarrow \sim O{-}CH_2{-}O{-}\dot{C}H{-}OH \longrightarrow R_1\cdot{+}HCOOH$$

(formic acid)

$$(2) \quad \sim O - CH_2 - O - \dot{C}H_2 \longrightarrow \sim O - \dot{C}H - O - CH_3 \longrightarrow R_2\cdot{+}HCOOCH_3$$

Fig. 1. Chromatogram of the decomposition products of polyformaldehyde: 0 —gas peak, 1 —methyl formate, 2 —methyl alcohol, 4 —water, 3 and 5 —not identified

Figure 1: Fig. 1. Chromatogram of the decomposition products of polyformaldehyde: 0 —gas peak, 1 —methyl formate, 2 —methyl alcohol, 4 —water, 3 and 5 —not identified

(methyl formate)

If isomerization occurs by the transfer of hydrogen from more distant carbon atoms, methyl alcohol may be formed:

$$(1) \quad \sim \mathrm{O{-}CH_2{-}O{-}CH_2{-}O{-}CH_2{-}O}\cdot \longrightarrow \sim \mathrm{O{-}CH_2} \overset{a}{-} \mathrm{O{-}\dot{C}H{-}O} \overset{b}{-} \mathrm{CH_2{-}OH}$$

This radical may decompose by two pathways:

$$\text{a)} \quad \sim \mathrm{O - CH_2 - O - \dot{C}H + O = CH - O - CH_2 - OH};$$

$$\text{b)} \quad \sim \mathrm{O{-}CH_2{-}O{-}C(=O)H{+}\dot{C}H_2OH}; \qquad \mathrm{\dot{C}H_2OH \rightarrow CH_3OH} \quad \text{(methyl alcohol)}.$$

In addition, more complex molecules of the type –C–O–C–O–C–, with various functional groups at the ends of the molecule, may also be formed.

Thus, it could be assumed that if methyl formate, formic acid, methanol, and certain other substances of more complex structure were found among the products of the thermal decomposition of polyformaldehyde, this would be important evidence in favor of a radical mechanism of the decomposition reaction.

Fig. 1. Chromatogram of the decomposition products of polyformaldehyde: 0 —gas peak, 1 —methyl formate, 2 —methyl alcohol, 4 —water, 3 and 5 —not identified.

The thermal destruction of polyformaldehyde (with protected ends) was carried out by us in a special circulation apparatus at a temperature of 300°. Since the main product of thermal destruction is formaldehyde, for successful analysis it was necessary to separate it from the other decomposition products, the amount of which is 2-3 orders of magnitude smaller than the amount of formaldehyde formed. We separated formaldehyde by using its property of spontaneous polymerization into Eu-polyoxymethylene at the temperature of dry ice. The yield of formaldehyde was about 98% of the weight of the destructed polymer. After its separation, the decomposition products were subjected to chromatographic

Fig. 2. IR spectrum of the decomposition products of polyformaldehyde

Figure 2: Fig. 2. IR spectrum of the decomposition products of polyformaldehyde

separation (by retention time); the following were identified: methyl alcohol, methyl formate, water, hydrogen, and methane (Fig. 1).

Fig. 2. IR spectrum of the decomposition products of polyformaldehyde.

In the IR spectrum of the decomposition products, shown in Fig. 2, the dotted line indicates absorption bands corresponding to pure methyl formate. The resulting agreement of the frequencies and the ratio of the band intensities confirms the presence of methyl formate in the destruction products. Intense absorption bands corresponding to 1100 and 1030 cm^{-1}, in the spectrum of the destruction products of polyformaldehyde, are also observed for simple ethers and correspond to stretching vibrations of ether bonds in compounds of the type: $-C-O-C-O-C-$.

The indicated products of the thermal destruction of polyformaldehyde were also detected by mass-spectrometric analysis.

In chromatographic, mass-spectrometric, and polarographic analyses, formic acid could not be detected in the decomposition products of polyformaldehyde. The absence of formic acid argues in favor of the predominant formation of radical (2), $\sim C-CH_2-O-\dot{C}H_2$.

Thus, the results obtained by us indicate that the thermal decomposition of polyformaldehyde is a complex process that also includes a radical mechanism.

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Note: Figure translations are in progress. See original paper for figures.