REASON FOR THE LUMINESCENCE OF POLYCAPROAMIDE AND CAPROLACTAM

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The monomer ε-caprolactam (CL) is always present in polycaproamide (PCA). During the polyamidation process and in later processing stages, thermal oxidation of the CL may take place. Therefore oxidation products of the CL are contained in the PCA; these may react with the polymer macromolecules. We have previously [1] shown the possibility of using a luminescence method of analysis to evaluate the quality of PCA at various stages of manufacture. Using this method, we have established the dependence of the quality indices of the PCA on the properties of the CL [2]. In the present article we show a very probable route for the formation of luminescent impurities in PCA due to thermal oxidation products of CL which, on being incorporated into the macromolecular chain, form a luminescing copolymer.

Literature data relative to the luminescent properties of CL are scarce [3, 4]. Since pure CL does not absorb radiation in the UV region above \( \lambda = 210 \) nm, it does not luminesce in the visible region of the spectrum. However, on thermal oxidation of crystalline CL (All-Union State Standard 7850-74) in air, the intensity of luminescence rises rapidly (Fig. 1).

Conditions for the measurement of the intensity of luminescence, \( I_7 \), and also the spectra for PCA specimens have been given previously [1]. In relative units, \( I_7 \) for 50% solutions of CL and solutions of the oxidation product, CL ε-hydroperoxide (CLHP) having a concentration of \( 2.5 \times 10^{-4} \) g/ml in twice-distilled water was determined similarly to [1] on a KFL-2-1 fluorimeter (glass-standard ZhS 10, glass-equivalent ZhS-18). For the CL specimens, the coefficient of variation in 10 measurements was not over 3%, and the relative error in measurement was not over 4%.

*Instead of the term "fluorescence," we use the broader term "luminescence," since neither quantum-yield nor lifetime is known or has been determined in the case of thermally oxidized CL.

Fig. 1. Luminescence spectra of CLHP (1), CL (2), and PCA (3), oxidized in air at 130° C for 2 h.

As a result of analysis of a large number of specimens, it was found that the \( I_Z \) figure for CL from various manufacturing plants and various methods of manufacture differs only slightly and is rather small \([2]\). However, thermal oxidation of the CL causes a tenfold increase in \( I_Z \), which indicates a peculiar sensitivity of this method to CL oxidation products.

In conformity with the data of \([5]\), thermal oxidation of CL in air leads to the formation of CLHP, which, later on, gives such oxidation products as adipimide, adipic acid monoamide, adipamide, adipic acid, and the like. We have found that, of the compounds listed, products or one of the products from the decomposition of CLHP have a definite ability to luminesce. To ascertain the conditions for its formation, we have investigated the process of thermal oxidation of CLHP in air. A temperature of 130°C is optimum for the formation of the luminescing product (Fig. 2). At 131°C, more than 97% by wt. of the CLHP is decomposed to form adipimide \([6]\). In \([4]\) an analogous mechanism of the thermo-oxidative reactions of CL is examined, which lead to the formation of CLHP (2), adipimide (3), and later to the formation of the \( \alpha \)-ketoimide (4), copolymerization of which with CL or with PCA macromolecules gives a luminescing copolymer:

\[
\begin{align*}
&\text{Copolymerization of the adipimide with CL is also possible. Further oxidation of this inside structure at the carbon atom neighboring the carbonyl group then leads to the luminescing } \alpha\text{-ketoimide structure.}
\end{align*}
\]

The position of the maximum, the form of the luminescence spectra of thermally oxidized CLHP, PCA, and CL (Fig. 1), and also the feature of luminescence analysis that complication in the structure of molecules, for example an increase in molecular weight, does not lead to complication in the spectra, permit one to speak of an identical nature of the luminescence of these compounds. This conclusion agrees with those of \([4]\), where the authors observed similar pictures for the luminescence of substances isolated from thermally oxidized PCA and CL, and on the basis of the studies performed explained the reasons for luminescence both in CL and also in PCA by a content of identical groups, which had the \( \alpha \)-ketoimide structure. There are also the reports by \([7]\) about the possibility of forming imide structures in PCA as a result of thermal oxidation:

\[
\begin{align*}
\text{RCONHCHR'} & \xrightarrow{70-130^\circ C} R'\text{OH} \\
\text{OOH} & \xrightarrow{+\text{H}_2\text{O}} \text{RCONHCHR'} \\
\end{align*}
\]

where R and R' are terminal alkyl macroradicals.