The action of ultraviolet radiation on a polymer in the presence of oxygen usually leads to the production of carbonyl and carboxyl groups [1, 2], with a corresponding marked increase in the absorbing power of the polymer in the ultraviolet range. This fact has provided a qualitative explanation for the so-called surface effect, namely that the change in the color of articles made of various polymers under the influence of ultraviolet radiation takes place chiefly on the surface as a result of the screening effect of the carbonyl and carboxyl groups produced [2]. No quantitative estimation of this effect has been made, however, and the influence of the groups produced on the rate of degradation of the polymer and its spectral characteristics has not been determined.

In the present work an attempt was made to examine analytically the role of carbonyl and carboxyl groups in the photodegradation of a polymer, the elementary unit of which did not contain unsaturated groups, and also the changes in the spectrum of the polymer in the range of the characteristic absorption of these groups.

Let us consider a polymer situated in a plane-parallel beam of ultraviolet radiation. The cross sectional area, for simplicity, can be taken as unity. The coordinate directed parallel to the beam will be denoted by the symbol \( x \). The equation for the transmission of radiant energy along the \( x \) axis through an element of volume \( dx \) can then be written

\[
\frac{\partial U}{\partial x} + \frac{1}{c} \frac{\partial U}{\partial t} = -kU, \tag{1}
\]

where \( U \) is the density of the radiation, \( k \) is the absorption coefficient, \( c \) is the velocity of light in the given substance, and \( t \) is the time.

Let us assume that the radiation is absorbed only by carbonyl groups, the quantity of which in unit volume is equal to \( n \). The action of the radiation brings about a photochemical reaction with the formation of a new carbonyl group, with quantum yield \( W \). We shall assume that the yield is constant. This is applicable so long as the damage to the original polymer and hence the concentrations of carbonyl groups are not too great. For long durations of irradiation, i.e., for high doses of absorbed energy, the changes in the polymer molecule are so great (a marked decrease in the degree of polymerization, the accumulation of decomposition products with low molecular weight) that they lead unavoidably to a change in the yield of the photochemical reaction. The quantity \( n \) will naturally be a function of time and the coordinate, since the rate of formation of the new groups is determined by the density of the radiation at the given point. Thus the absorption coefficient is

\[
k = \frac{nhv B}{c}, \tag{2}
\]

where \( B \) is the Einstein coefficient, and the density of radiation \( U \) will also be a function of time and the coordinate.

We can determine the rate of change in the absorption coefficient in the element of volume \( dx \). In accordance with Bouger's law, the number of quanta absorbed in unit volume in unit time will be \( kcU/\nu \). By multiplying this quantity by the yield \( W \), we obtain the number of carbonyl groups formed \( kcUW/\nu \). Using Eq. (2), we obtain


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Fig. 1. Distribution of the density of radiation in the specimen for different durations of irradiation: 1) $t = 0$; 2) 10; 3) 20; 4) 30; 5) 50 h. The density of radiation in relative units is plotted on the axis of ordinates, and the distance from the surface being irradiated, in $\mu$, is plotted on the axis of abscissae.

Fig. 2. Dependence of the intensity of the 1740 cm$^{-1}$ band (a) and the optical density of the specimen in the region of 220 nm (b) on the duration of irradiation $t$, h. The broken line was calculated from Eq. (12).

\[
\frac{\partial k(x, t)}{\partial t} = BWk(x, t)U(x, t).
\]

(3)

If we neglect the time of propagation of light in the volume being considered, Eq. (1) becomes

\[
\frac{\partial U(x, t)}{\partial x} = -k(x, t)U(x, t).
\]

(4)

Equations (3) and (4) form a system of differential equations of first order with respect to two unknown functions $k(x, t)$ and $U(x, t)$. The initial and boundary conditions for these will be $k(x, 0) = k_0$ and $U(0, t) = U_0$.

By solving this system of equations we find the explicit form of the functions $k(x, t)$ and $U(x, t)$, and this makes it possible to determine the changes in the absorption spectra of the polymer as a result of the irradiation, and also the distribution of the density of radiation on the polymer during irradiation at any moment of time, and hence to estimate the surface effect.

We formally integrate Eq. (3) with respect to time

\[
\int_{k_0}^{k} \frac{\partial k}{k} = \int_{0}^{t} BWU\,dt,
\]

(5)

Substituting Eq. (5) in Eq. (4), we obtain

\[
\frac{\partial U}{\partial x} = -k_0 \delta \frac{BW_0}{U}\delta U\delta t.
\]

(6)

and integrate Eq. (6) with respect to time

\[
\int_{0}^{t} \frac{\partial U}{\partial x} \,dt' = -k_0 \int_{0}^{t} BW_0 \delta U\delta t'.
\]

(63)