Polymeric materials containing phenanthrenequinone (PQ) have been used in phase holography for a rather long time and now belong to the list of classical holographic media [1]. The photoinduced attachment (photoaddition) of PQ derivatives to macromolecules of a polymer matrix is accompanied by the diffusion of unreacted PQ molecules, which leads to a significant postexposure enhancement of the phase holograms recorded in such media. This mechanism accounts for large values of the enhancement coefficient, the final refractive index modulation amplitude \( \Delta n \), and, hence, the diffraction efficiency of diffusion-enhanced phase gratings. The range of spectral sensitivity of the PQ-containing polymeric media covers the wavelength interval from 350 to 600 nm (for layers with thicknesses of about one hundred microns, the effective spectral sensitivity range reduces to 450–550 nm). Therefore, an important practical task is the search for new related materials for holographic recording with postexposure enhancement, ensuring an increased coefficient of enhancement and possessing sensitivity in different spectral intervals.

This Letter reports on a new photorecording material for phase-modulated optical recording, which provides for a postexposure diffusion-induced enhancement of holograms and is sensitive to radiation in the near-UV spectral range.

The postexposure diffusion-induced enhancement of holograms stimulated by a pseudomonomolecular photoaddition reaction in a polymeric recording medium can be schematically described as follows. The optical recording process creates a sinusoidal distribution (in phase with the recording light field) of the photoaddition reaction product (photoproduct) attached to the polymer matrix in a layer of the medium, with a concentration modulation amplitude of \( \Delta c_p \). Simultaneously, there arises a counterphase distribution of the unreacted photosensitive component. Assuming that all photoproduct is attached to macromolecules of the matrix, the subsequent diffusion of the photosensitive component will restore its homogeneous distribution in the layer, while retaining the \( \Delta c_p \) modulation [1].

The resulting refractive index modulation amplitude \( \Delta n \) can be evaluated (to within terms on the order of \( \Delta n/n \), where \( n \) is the average refractive index of the layer) using the Lorenz–Lorentz formula as

\[
\Delta n = \frac{(n^2 + 2)^2}{6n} \sum \Delta c_i R_i,
\]

where \( \Delta c_i \) and \( R_i \) are the concentration modulation amplitude and the molar refraction of the \( i \)th component. In the case under consideration, the \( \Delta n \) value immediately upon termination of the recording exposure is

\[
\Delta n_0 = \frac{(n^2 + 2)^2 \Delta c_p (R_p - R_s)}{6n},
\]

where \( R_p \) and \( R_s \) are the molar refractions of the photoproduct and the initial sensitive component. Upon termination of the postexposure diffusion process, the enhanced refractive index modulation amplitude is

\[
\Delta n_e = \frac{(n^2 + 2)^2 \Delta c_p R_p}{6n}.
\]

Therefore, the corresponding enhancement coefficient \( M \) (with respect to the refractive index modulation
amplitude) can be determined as

$$M \equiv \frac{\Delta n_e}{\Delta n_{02}} = \frac{R_p}{|R_p - R_i|}. \quad (4)$$

For holographic recording applications, the $\Delta n_e$ value determines the achievable diffraction efficiency $\eta$ and, hence, must be rendered as large as possible. At the same time, small $\Delta n_{02}$ values (at a sufficiently high gain $M$) are favorable for eliminating distortions caused by diffraction on the recorded structures and by their mismatch with the interference pattern related to a change in the average refractive index of the working layer. As can be seen from expressions (3) and (4), the $\Delta n_e$ value is limited by the molar refraction of the photoproduct and by the achievable modulation amplitude of the photoproduct concentration. The smaller the difference between molar refractions of the initial material and the photoproduct, the greater the enhancement coefficient. For a PQ-containing photoproduct, the $R_p$ value estimated from data on the atomic refraction for the sodium $D$ lines [2] is 64.6 cm$^3$/mol and the molar refraction increment is $R_p - R_i = 4.3$ cm$^3$/mol. This implies that the enhancement coefficient in this system cannot exceed the level of about 15 (the maximum gain achieved in practice, $M = 8$, corresponds to the photoaddition of approximately half of the PQ molecules [3]).

The achievable modulation amplitude $\Delta c_p$ of the photoproduct concentration is limited by the initial concentration $c_s$ of the photosensitive component and, as a rule, $\Delta c_p$ must be much smaller than $c_s$ in order to avoid distortions (related to the lack of the photosensitive component) at the maxima of the interference pattern. For PQ in polymer matrices, $c_s$ is limited by the crystallization and does not exceed $5 \times 10^{-4}$ cm$^{-3}$.

We have used PMMA matrices doped with xanthon (Xn) as a photosensitive component. The choice of Xn is determined primarily by the possibility of photoaddition of this ketone molecule to a polymer matrix via a photoreduction reaction according to the following scheme [4]:

$$\begin{align*}
\text{O} & \quad \text{C}=\text{O} + \text{RH} \xrightarrow{\text{hv}} \quad \text{O} \quad \text{C}^-\text{O} \quad \text{H}.
\end{align*}$$

Estimates of the molar refraction of the photoproduct ($R_p = 54.65$ cm$^3$/mol) and the resulting change upon photoaddition ($R_p - R_i = 0.5$ cm$^3$/mol) suggested that the achievable enhancement coefficient is much greater than that for PQ at a comparable final diffraction efficiency. Another important factor is that Xn molecules can be introduced into a poly(methyl methacrylate) (PMMA) matrix at a concentration up to $10^{-3}$ cm$^{-3}$, which is much greater than the possible content of PQ under otherwise equal conditions. The spectral sensitivity range of the Xn-containing material falls within the near-UV region (with a maximum optical absorption at 330 nm). For a layer thickness of about 100 µm (most convenient in holography), the appropriate optical density of 0.1–0.2 is achieved in the wavelength range of widely used radiation sources operating at $\lambda = 355$ and 365 nm. It should be noted that polymer layers containing a converted Xn photoproduct exhibit shrinkage on heating [4], which is probably related to a decrease in the molar volume upon photoconversion. This shrinkage must not produce obstacles to the diffusion of relatively large Xn molecules.

We have studied PMMA layers with a thickness of 20–50 µm and an Xn content of 5–6%. The samples were prepared by casting a PMMA:Xn solution onto a substrate, followed by drying to constant weight. In some cases, we also used cover glass plates pressed to the samples in order to eliminate surface relief formation in the course of drying. The phase gratings were recorded by exposure of the samples to UV light $\lambda = 365$ nm (for which the indicated layers are optically thin) through a mask that provided a periodic intensity distribution with a period of 20–80 µm. Then, the gratings were probed with He–Ne laser radiation (633 nm) and the diffraction efficiency $\eta$ was determined in the first and higher orders of diffraction. When necessary, the influence of the surface relief component (in the samples prepared without cover glasses) was eliminated by filling the relief with immersion fluid having an average refractive index close to that of the polymer layer.

![Fig. 1. Plots of the relative modulation of the refractive index $\Delta n_r$ versus time for the phase gratings of periods $d = 80$ (1, 3) and 30 µm (2) in the course of a three-stage heat treatment at $T = 80^\circ$C (0–32 h), 100°C (32–100 h), and 110°C (100–200 h) for the PMMA:Xn layers (1, 2) without and (3) with cover glass plates. The final treatment (110°C) was performed upon homogeneous irradiation of the samples. Points indicate the experimental data; solid curves show approximation of the initial buildup regions.](image-url)