U.V. MAHILNY[1]
D.N. MARMYSH[1]
A.I. STANKEVICH[1]
A.L. TOLSTIK[1]
V. MATUSEVICH[2,✉]
R. KOWARSCHIK[2]

Holographic volume gratings in a glass-like polymer material

[1] Physical Department of Belarussian State University, 4 F. Scorina Ave., 220050 Minsk, Belarus
[2] Friedrich-Schiller-University Jena, Institute of Applied Optics, Max-Wien-Platz 1, 07743 Jena, Germany

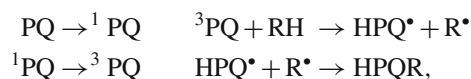**ABSTRACT** We demonstrate a possibility to write efficient and thermally stable volume holographic gratings in a glassy polymer material based on PMMA and phenanthrenequinone with layers prepared, by casting the liquid solution of ingredients on a substrate and drying to a solid state. A high concentration of phenanthrenequinone (up to 4 mol. %) makes it possible to use photosensitive layers of lower thicknesses (50–180 μm) for the recording of efficient holographic gratings. The exposing is followed by a thermal amplification of the grating due to diffusion of residual phenanthrenequinone molecules and fixation by an incoherent optical illumination. We present experimental temporal curves of the refractive index modulation and diffraction efficiency both under the exposure and the heating process. The behavior of the gratings under temperatures up to 140 °C has been studied.

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1   Introduction

Polymeric recording media containing phenanthrenequinone (PQ) as a photosensitive additive belong to the category of phase holographic media with diffusion amplification. Investigations of the recording and transformation processes of holographic diffraction gratings in such media have been performed mainly for layers with low contents of the additive (~ 0.5 mol.%) [1–4]. Samples with a thickness up to 1 mm for hologram recording were produced by block polymerization of the PQ solution in a monomer. The principal photoreaction in this medium is photoreduction with subsequent photoaddition of the product to macromolecules and may be given in the following general form [5]:

$$PQ \rightarrow {}^1PQ \qquad {}^3PQ + RH \rightarrow HPQ^\bullet + R^\bullet$$
$$^1PQ \rightarrow {}^3PQ \qquad HPQ^\bullet + R^\bullet \rightarrow HPQR,$$

where ^1PQ and ^3PQ characterize the phenanthrenequinone in the singlet and triplet excited states, respectively; $HPQ^\bullet$ is the semiquinone radical; RH is the hydrogen donor represented by the macromolecules. Under the influence of a sinusoidally modulated field of interfering light beams, the recording medium reveals the opposite phase distributions of

✉ Fax: 03641-947659, E-mail: Vladislav.Matusevich@uni-jena.de

the unreacted PQ and photoproduct associated with antiphase contributions into the refractive index distribution. Owing to their superposition, the general distribution of the refractive index within the layer is formed. Being added to the polymeric matrix, the photoproduct is not mobile as the unreacted PQ, and the diffusion degradation of the concentration distribution of the latter proceeds according to the diffusion equation with the initial sinusoidal distribution:

$$\Delta c = \Delta c_0 \exp(-\gamma t), \tag{1}$$

where Δc_0 is the initial concentration modulation amplitude, t – time, $\gamma = D(2\pi/d)^2$ – rate constant of the process, D – diffusion coefficient, d – light-induced grating period. The change of the modulation amplitude of the refractive index Δn is described by:

$$\Delta n = \Delta n_{FP} - \Delta n_{PQ} \exp(-\gamma t), \tag{2}$$

where Δn_{FP} is the photoproduct contribution to the refractive-index modulation amplitude, Δn_{PQ} – contribution of the unreacted PQ to the refractive-index modulation amplitude at the instant the exposure is terminated. The degradation of the PQ distribution results in a homogeneous concentration within the grating structure and its amplification. The homogeneity of the final distribution of PQ enables the fixation of the amplified grating by exposure with uniform incoherent radiation. Thus, the amplified phase hologram is formed by the photoproducts bound to the macromolecules. The thermodegradation of the holograms occurs due to the diffusion of the polymer [2].

Based on polymeric PQ-containing recording media, transmission and reflection volume holograms may be produced with high diffraction efficiency and as a rule with high angular and spectral selectivity. Volume holograms with high diffraction efficiency and lower selectivity would be useful as coupling elements between light beams with considerable divergence and planar lightguides, for instance. In this case the diffraction efficiency may be retained by increasing the attainable modulation amplitude of the refractive index. One of the most obvious ways is to increase the concentration of PQ within the PQ-containing polymeric media. But this is relatively complex with regard to the block polymerization method due to the inadequate solubility of PQ in the monomer. Small thicknesses of the recording layers make it possible to generate the layers by a technologically

more straight-forward method: pouring of the dissolved polymer and PQ onto the substrate. Changes in the production technique of recording layers as well as the increasing concentration of PQ may affect the recording process, amplification and degradation of phase structures.

This paper describes the recording and transformation of phase holographic gratings within polymeric layers with high content of PQ produced by pouring of dissolved ingredients.

2   Experiment

For recording of volume phase holograms, the used polymeric material was a solid solution of PQ in polymethyl methacrylate. The recording layers with a thickness of 60–180 µm and with a concentration of PQ amounting to 0.5–4 mol.% were formed by pouring a liquid solution of PQ and polymethyl methacrylate in organic solvent onto the glass substrate and subsequent drying.

Using these samples, we recorded symmetric volume holographic gratings with periods $d = 0.9$–3.5 µm with Ar-laser beams ($\lambda = 514.5$ nm). During the recording process and in the post-exposure period the diffraction efficiency of the grating was controlled at the 633-nm wavelength of a He-Ne laser. The diffraction efficiency is the ratio of the signal beam intensity to the total intensity of the beams:

$$\eta = \frac{I_s}{I_s + I_0}, \tag{3}$$

with I_s – intensity of the diffracted beam, I_0 – intensity of the beam transmitted without diffraction.

Based on the measured values of the diffraction efficiency the modulation amplitude of the refractive index Δn can be calculated using the formula:

$$\Delta n = \frac{\lambda \cos\theta \arcsin(\sqrt{\eta})}{\pi h}, \tag{4}$$

with λ – probe wavelength, θ – incidence angle of the probe beam, h – recording layer thickness.

Figure 1 shows the diffraction efficiency as a function of the recording time t_e for gratings written in samples with different concentrations of PQ. The diffraction efficiency follows a monotonic increase to a maximum value that is higher for stronger PQ concentrations. E.g., the diffraction efficiency was 20% for the sample with a thickness of 180 µm thick and a PQ concentration of 4 mol.%. For longer recording times, the diffraction efficiency again decreased.

During the recording process not only the first-order diffraction but also higher order diffraction appears. This is associated with gratings having spatial frequencies which are multiples of the recorded grating frequency with regard to the period of the interference structure. Figure 2 demonstrates the typical relationship between the first- and second-order diffraction and the exposure time. The second-order diffraction increases with stronger first-order diffraction. Measurements of the samples under test show that a change of the optical density in the PQ absorption region, on exposure associated with the initial moment of recording the second-order diffraction, was below 5%.

After recording the holographic gratings were thermally treated. Figure 3 shows the typical relationship between the
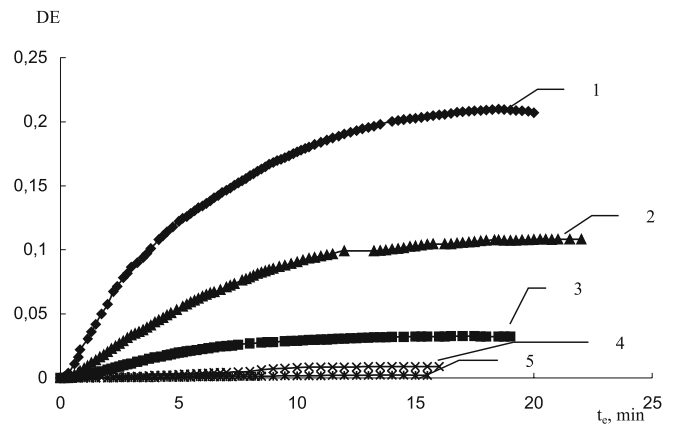

FIGURE 1   The diffraction efficiency kinetics during exposure. PQ concentrations: 4 (1), 3 (2), 2 (3), 1.2 (4) and 0.55 (5) mol.%. Layer thickness: 180 (1), 170 (2), 155 (3), 125 (4), 135 (5) µm. Grating periods: 1.65 (1, 2, 3) and 2.66 (4, 5)
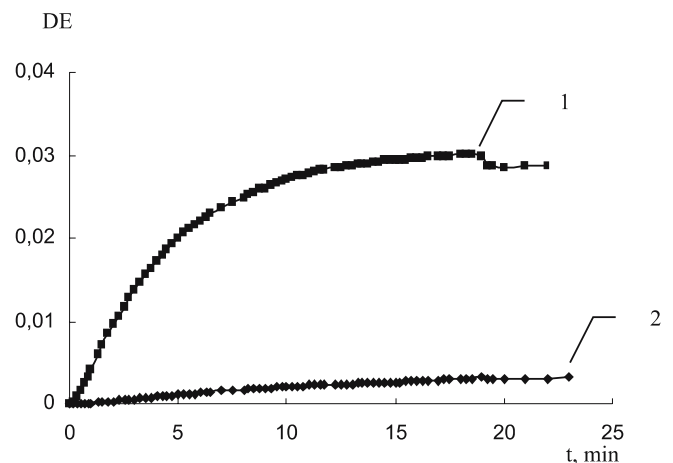

FIGURE 2   The diffraction efficiency kinetics of the first (1) and the second (2) orders during exposure (4 mol.% PQ, $h = 85$ µm, $d = 1.65$ µm)

relative modulation amplitude of the refractive index and the time of the post-exposure annealing at different temperatures. Curve 1 represents the first-order diffraction and curve 2 the second-order diffraction, respectively.

The modulation amplitude was increasing for longer periods of thermal treatment both for the first- and second-order diffraction; the temperature growth was contributing to the rate of their increase. In the case of the second-order this increase was much more rapid. At a temperature of 63 °C the amplitude of the refractive index modulation of the second-order diffraction reached a maximum value, remaining stable up to a temperature of 85 °C. A further increase of temperature up to 100 °C caused a decrease in Δn. After a maximum value of the refractive index modulation amplitude of the first-order was reached, the layer with a grating was exposed to uniform irradiation of the Xe lamp leading to a 85%-decrease of the optical density at a wavelength of PQ absorption. During this process the refractive index modulation amplitude of the grating was not lowering.

Figure 4a shows the relative modulation amplitude of the refractive index as a function of the annealing time for gratings with different exposure. Post-exposure annealing was performed at 80 °C. In the process of annealing the refractive
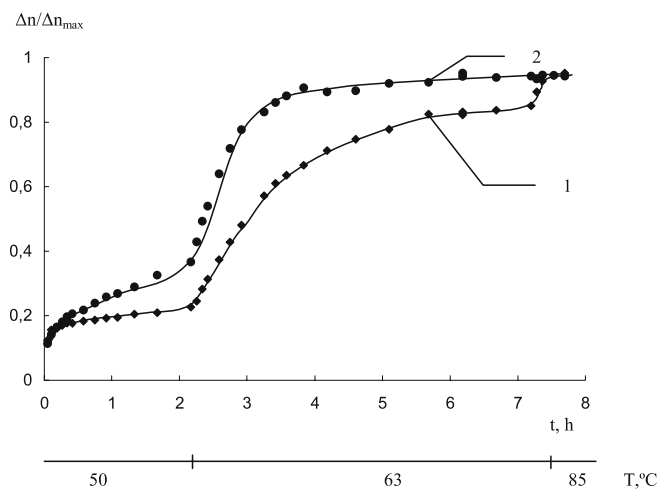
FIGURE 3   The relative modulation amplitude of the refractive index for the first (1) and the second (2) diffraction orders during postexposure annealing (4 mol.% PQ, $h = 85\,\mu\mathrm{m}$, $d = 1.65\,\mu\mathrm{m}$)
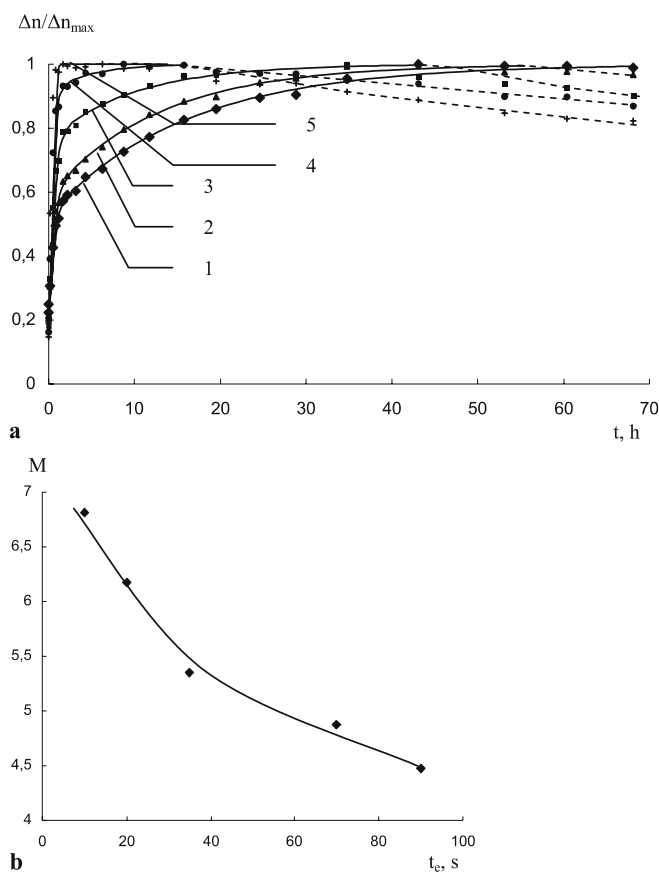

FIGURE 4   **(a)** The refractive index modulation dependence on the annealing time ($T = 80\,^\circ\mathrm{C}$, exposure time 90 (1), 70 (2), 35 (3), 20 (4), 10 (5) s). *Solid line* is the result of approximation accordingly to the expression (2). **(b)** The amplification coefficient dependence of the modulation amplitude on exposure time (3 mol.% PQ, $d = 2\,\mu\mathrm{m}$)

index modulation amplitude was increasing to a maximum value, the time of this increase was longer for gratings with longer exposure. Two different sections may be distinguished for the rising parts of the corresponding curves: rapid rising and slow rising. The contribution to the rapidly-rising component is growing with a decrease in exposure time, and for

gratings with a minimal exposure this rising is associated with the rapid component only. After reaching its maximum value, the refractive index modulation amplitude was stable for some time; and then dropped down with a rate well below the rising one. The decrease of the modulation amplitude was higher for shorter exposure times of the grating. The amplification factor M was calculated as the ratio of the maximum modulation amplitude of the refractive index during annealing to that obtained at the instance the recording is terminated, decreasing with exposure time (Fig. 4b).

Figure 5 demonstrates the typical dependence between the relative modulation amplitude of the refractive index and the annealing time at temperatures varying from 100 to 140 °C for the first- and second-order diffraction of the gratings, previously subjected to enhancement and fixation at lower temperatures by a uniform light field. High-temperature annealing results in lowering of the refractive-index modulation amplitude both for the first- and second-order diffraction, whereas the process rates are practically identical.

As seen in Fig. 1, a growing concentration of PQ within the layer causes higher maximum values of the diffraction efficiency. Figure 6 presents a relative value of Δn for the first-order diffraction as a function of PQ concentration in a layer with gratings recorded before a maximum value of the diffraction efficiency was reached. The maximum value of Δn increases essentially in a linear manner with growing concentration of PQ. Changing the concentration of PQ from 0.5 to 4 mol.% increases the value of Δn nearly by a factor of 6.

The appearance of the second-order diffraction during the recording process indicates that the refractive index profile deviates from the sinusoidal one determined by the interference pattern. Such an effect is described in [6]. To realize the second-order diffraction, an in-depth recording was performed, with the second-order diffraction emerging when the first-order diffraction was decreasing in the process. Distortions of the grating profile were attributed to the depletion of the photosensitive species at the maxima of the interference pattern. In our case the onset of the second-order diffraction was registered at the initial portion of the kinetic curve for
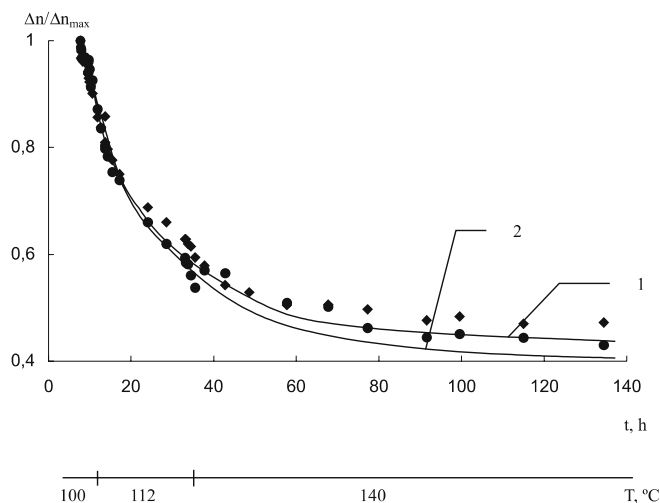

FIGURE 5   The first (1) and the second (2) order grating degradation in the temperature range of 100–140 °C (3 mol.% PQ, $h = 75\,\mu\mathrm{m}$, $d = 2.66\,\mu\mathrm{m}$). After amplification the grating was fixed with uniform irradiation
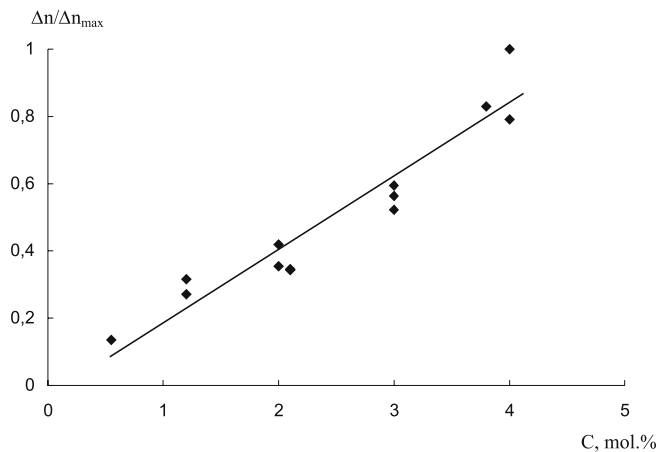
FIGURE 6 The concentration dependence of refractive index modulation for the first order gratings under recording to the maximum value of the diffraction efficiency

the first-order diffraction (Fig. 2). At that point the values of Δn for the first order were lying above the interval $(1–5) \times 10^{-5}$ for the gratings with various periods recorded in the samples, characterized by different concentrations of PQ, and their maxima being at least ten times higher. Considering minor changes in the optical density at the appearance of the second-order diffraction, it can be inferred that distortions of the refractive index profile in case under test could not be attributed to the exhausting of PQ. This distortion may be due to a specific character of the photochemical reaction (radicals formation and their diffusion until the moment of addition to the macromolecules) as well as to deformations of the material as a result of the photochemical reaction.

The amplification process of the recorded gratings (Figs. 3a, 4) is non-exponential in nature because the increasing kinetics of Δn could not be described by the diffusion of only one component with a constant diffusion coefficient. The growing of Δn can be adequately approximated by the following expression:

$$y = y_0 - a_1 \exp(-\gamma_1 t) - a_2 \exp(-\gamma_2 t), \tag{5}$$

taking rates into consideration the contributions of at least two processes with different rates. Table 1 summarizes the results obtained for the rising parts of the refractive-index kinetics with the use of expression (5). The factor γ_1 determines the rate of increase of Δn due to the rapid component, whereas factor γ_2 – characterizes the slow one. Note that they reveal more than a 10-fold difference practically for all gratings. The increase rate was lowering with growing exposure time both for rapid and slow components. The value a_2/a_1 deter-

mines the relative contribution into the increase of each of the components, growing with exposure time. This indicates a stronger contribution of the rapid component compared to the slow one if the exposure time is decreasing.

The contribution made by the diffusion of PQ to the process of grating amplification is obvious. This is supported by the homogeneous distribution of PQ within the layer after the amplification process and ensures the stability of the gratings when exposed to a uniform light field. There are at least two processes capable of proceeding simultaneously with PQ diffusion and result in the non-exponential nature of the amplification. The first process is the addition of a semiquinone radical to the macromolecules and the associated increase of the refractive index of the layer [7]. In this case any kinetics of the increase of Δn should have two components. However, in the case under test for the grating with minimum exposure (Fig. 4, curve 5), the increase is described by a rapid component only. Taking this into consideration, one can find that the addition of a semiquinone radical has a minor effect on the process of Δn-increasing with post exposure annealing. The second process is connected with the redistribution of the local density [8, 9] within the material due to deformations resulting from the photoreaction. This effect should be stronger for higher concentrations of the photoproduct as seen by the lower amplification factor for longer exposure times (Fig. 4b). This process may be responsible for the grating degradation at high-temperature annealing too, indicating no signs of diffusion.

3   Conclusion

This paper presents the recording and transformation processes of phase holographic gratings in polymeric layers containing phenanthrenequinone and produced by the pouring method. It is demonstrated that a growing concentration of PQ from 0.5 to 4 mol.% leads to an increase of amplitude of the refractive index modulation by six times. The amplification process shows no mono-exponential behavior, but has to be described by two exponential functions with characteristic constants differing by a factor of ten in practically all experimental cases. It has been found that for longer exposure times the amplification factor of the refractive index modulation amplitude falls down. The degradation rate of holographic gratings during the process of thermal annealing does not follow the typical diffusion behavior.

Grating	t_e, s	T, °C	a_2/a_1	γ_1	γ_2
1	90	80	1.6	4.97×10^{-4}	1.71×10^{-5}
2	70	80	1.1	4.88×10^{-4}	2.15×10^{-5}
3	35	80	0.45	5.55×10^{-4}	5.28×10^{-5}
4	20	80	0.13	6.94×10^{-4}	9.51×10^{-5}
5	10	80	–	1.08×10^{-3}	–

TABLE 1 Recording and transformation characteristics of phase holographic gratings ($d = 2\,\mu$m) in a sample with 3 mol.% of PQ

REFERENCES

1 O. Andreeva, O. Banduk, A. Paramonov, A. Cherkasov, E. Gavrilyuk, P. Andreev, Opticheski Zh. (rus) **67**, 12 (2000)
2 A. Veniaminov, Y. Sedunov, A. Popov, O. Banduk, Opt. Spectrosk. (rus) **81**, 676 (1996)
3 J. Mumbru, J. Solomatine, D. Psaltis, Sh.H. Lin, K.Y. Hsu, W.-Zh. Chen, W.T. Whang, Opt. Comm. **194**, 103 (2001)
4 A. Popov, I. Novikov, K. Lapushka, I. Zyuzin, Yu. Ponosov, Yu. Ashcheulov, A. Veniaminov, J. Opt. A: Pure Appl. Opt. **2**, 494 (2000)
5 O. Banduk, N. Shelehov, A. Popov, M. Danilova, Zh. Prikl. Khimii (sov) **61**, 4 (1988)
6 A. Veniaminov, H. Sillescu, Chem. Phys. Lett. **303**, 499 (1999)
7 A. Veniaminov, V. Goncharov, A. Popov, Opt. Spectrosk. (rus) **70**, 864 (1991)
8 U.V. Mahilny, Y. Gritsai, A. Stankevich, A. Tolstik, L. Wenke, Proc. SPIE **5135**, 111 (2003)
9 U.V. Mahilny, Y. Gritsai, S. Kovalev, Zh. Tech. Fiz. (rus) **69**, 8 (1999)