Polymer Holography – New Theory of Image Growth

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Summary: The image forming process in photopolymer holographic film has been studied thoroughly. Many grow-curves, i.e. the curves describing the time dependence of the image grow, have been obtained by the special equipment (described in[1]) under varying conditions. The varying concerns both the changes in film composition and exposition. The S-type form of the measured grow curves bring out some problem in interpreting them in the framework of the usual diffusion theories of photopolymer image growth. To overcome the problem we add the idea that polymer loses its mobility as it grows to the usual only diffusion theories and put down the more general immobilization-diffusion theory.[2]

Keywords: diffusion; hologram; holography; photopolymer; polymer kinetics

Introduction

The hologram is formed by photo-polymerization. During this process, monomer units the refractive index of which is different from that of the matrix (difference Δn_e) are absorbed by the growing polymers and so the number of free monomers, and also its concentration, is reduced. The mobility of a polymer is much lower than that of a monomer and so the diffusion of monomers towards polymers is much larger than the diffusion in the opposite direction. Usually the opposite diffusion is neglected. It is not correct for the early stages of the polymer growth. Therefore we have put down a theory which does not neglect the opposite diffusion. We call this theory immobilization–diffusion theory (ID-theory) to emphasize the fact that we take into account the decreasing mobility of a polymer instead of supposing its fixed position from the very beginning of its growth as is done in the usual theories which take into account only diffusion (e.g. [3,4]).

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Immobilization – Diffusion Theory

Single Polymer Case

The ideas of the theory will be at first described on the case of one polymer which starts to grow at the plane $x = 0$. The schematic view of holographic film with the coordinate system used in the further calculations is given in Figure 1. The number of monomers in a unit volume of the holographic film is denoted as density $\rho = \rho(x, y, z)$.

The forthcoming calculations will be limited to the case when only the x-direction dependence is supposed; $\rho = \rho(x, y, z) = \rho(x)$. The polymer grows as the monomer units transporting the elementary refractive index Δn_e join it. In the intervals Δt_k monomers are added to the growing polymer chain, and so after k intervals the refractive index of the polymer is $\Delta n_k = k\Delta n_e$; k is the polymerization degree. The polymer loses its mobility with increasing k; its probable deviation $\Delta x_k = |x - x_0|$ (actual value of the deviation for quadrimer – $k = 4$ –is denoted d in Figure 1) from the initial position ($x_0 = 0$) decreases. We assume that

$$\Delta x_k = \frac{\Delta x_1}{k^m}, \quad k = 1, 2, 3 \ldots \tag{1}$$

The exponent m describes the rate of the decrease and so the rate of the polymer

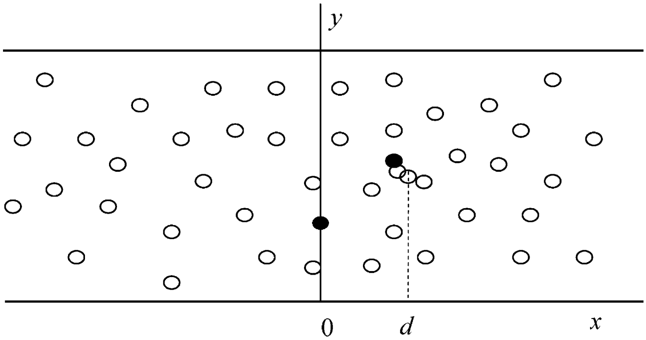

Figure 1.
Schematic view of the holographic film with one quadrimer which actual distance *d* from the plane $x = 0$, where the polymer have started to grow, is *d*.

immobilization. The exponent m has values between 1/2 and 1 if viscous random motion of linear polymer is supposed. Higher values of m are obtained if some branching or cross–linking occurs. The exponent m is zero if no immobilization is supposed and the position of a polymer is thought to be fixed from the very beginning of the polymerization process. It is the case which is assumed in the only diffusion theories.

The next important point of our theory is that we identify the deviation Δx_k with the probable deviation δ_k of the Gaussian distribution function [5];

$$2\sigma_k/3 = \delta_k = \Delta x_k = \Delta l_k/3. \tag{2}$$

Thus we obtain for the probability $p_k(x)$ to meet the polymer of polymerization degree k at the distance $|x|$ from the plane $x = 0$ the expression

$$\begin{aligned} p_k &= \frac{1}{\sigma_k\sqrt{2\pi}}\exp\left(-\frac{x^2}{2\sigma_k^2}\right) \\ &= \frac{2}{\Delta l_k\sqrt{2\pi}}\exp\left(\frac{-2x^2}{\Delta l_k^2}\right). \end{aligned} \tag{3}$$

The mean free path of a monomer molecule $\Delta l_k = \Delta x_k/3$ at polymerization degree k is introduced in the second equation. Each monomer transports the elementary refractive index Δn_{e} and so the whole refractive index modulation due to the polymer growth may be expressed as

$$\begin{aligned} \Delta n_k(x) &= k\Delta n_e p_k(x) \\ &= \frac{k^{m+1}\Delta n_{\mathrm{e}}\sqrt{2}}{\Delta l_1\sqrt{\pi}}\exp\left(\frac{-2k^{2m}x^2}{\Delta l_1^2}\right), \end{aligned} \tag{4}$$

if we put $\Delta l_1/k^m$ instead of Δl_k according to (1) and (2). The drift of the refractive index modulation towards the plane $x = 0$ with the increasing polymerization degree is demonstrated in Figure 2 for two values of the exponent m. The stabilization of polymers in the vicinity of $x = 0$, where they have started to grow, is evident. The rate of stabilization is much larger for $m = 1$ than for $m = 0.5$.

Continuous Spatial and Time Distribution of the Growing Polymers

We shall introduce the density of polymers $c(u, T)$ which start to grow in the place of the coordinate $x = u$ at time $t = T$. We assume that c may be expressed as

$$c = AI(u, T)\rho(T). \tag{5}$$

The constant A is the efficiency of initiation and I the intensity of illumination (intensity of the applied laser light), $\rho(T)$ is the actual density of free monomers at time T. With the density $c = c(u,T)$ we may express the refractive index modulation density $\Delta n(x,t)$ distribution in space (along coordinate x) at time t by integrating the modulation process via coordinate u and

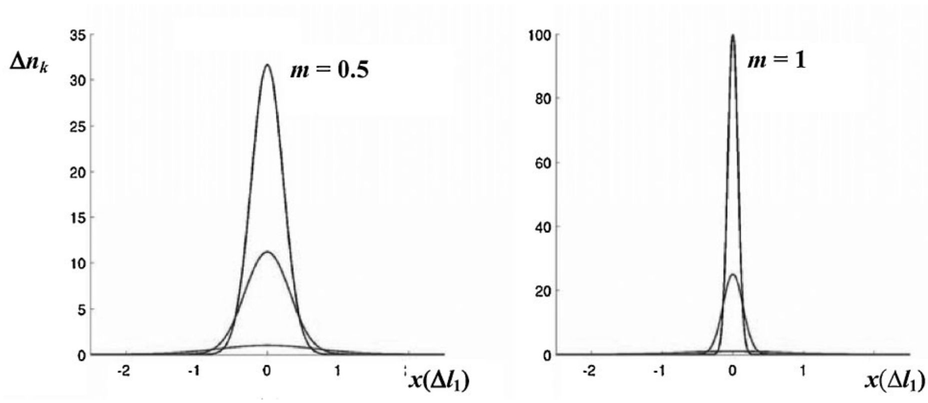

Figure 2.
The Δn_k against x dependence for $m = 0.5$ and 1. Coordinate x is expressed in Δl_1 units, refractive index modulation Δn_k is expressed in the same arbitrary units in both the figures. The lowest curves belong to polymerization degree $k = 1$, the middle curves to $k = 5$ and the upper ones to $k = 10$.

process time T;

$$\Delta n(x,t) = \int_0^t \int_{-\infty}^{+\infty} \Delta n_e c(u,T) p(x-u)\, \mathrm{d}u \mathrm{d}T. \tag{6}$$

If we introduce c from Eq. (5), p from Eq. (3) modified for the continuous case and the relation between conversion degree s and time T,

$$s = \left[1 - \exp\left(-\frac{cT}{\rho}\right)\right] = \left[1 - \exp\left(-\frac{T}{\tau}\right)\right], \tag{7}$$

we obtain the final result

$$\Delta n(x,t) = \frac{2A\Delta n_e \rho_0}{\Delta l_1 \sqrt{2\pi}} \int_0^t \int_{-\infty}^{+\infty} I(u,T)\left[1 - \exp\left(-\frac{T}{\tau}\right)\right]^{m+1} \exp\left[\frac{2(x-u)^2}{\Delta l_1^2}\left[1 - \exp\left(-\frac{T}{\tau}\right)\right]^{2m}\right] \mathrm{d}T \mathrm{d}u \tag{8}$$

The relaxation time

$$\tau = \rho/c = \rho_0/c_0 \tag{9}$$

of the whole image forming process has been introduced in eq. (7). Typical solutions of eq. (8) will be given in the next chapter.

Results of Model Calculations

Fidelity of Reproduction

To test how the eq. (8) describes the image forming process, the reproduction of an illuminated box-type profile has been used (see Figure 3). The exponent $m = 2$ has been put down in eq. (8). We see that with increasing conversion degree s the image of the box type illumination changes from the wide Gaussian-like curve at $s = 0.2$ to the nearly true reproduction of the box-type illumination at $s = 1$. The sine-like illumination profile which we use in experiments reproduces even more quickly.

Refractive Index Modulation Grow-Curves, Dependence on Exponent m

The depence of the modulation of refractive index n on time t (the grow-curve) at the coordinate $x = 0$ for the sine-like illumination profile are given for three different values of m in Figure 4. The refractive index first rises with increasing grow-rate, goes through an inflexion point and with decreasing grow-rate it achieves

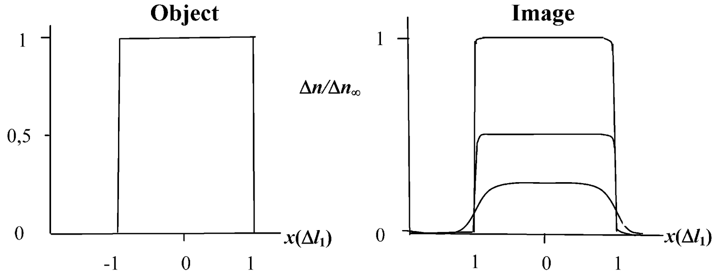

Figure 3.
The reproduction of the box-type object. The fidelity of reproduction grows with increasing conversion s. The lowest curve of the image corresponds to $s = 0.2$, the middle curve to $s = 0.5$, the upper one to $s = 1$.

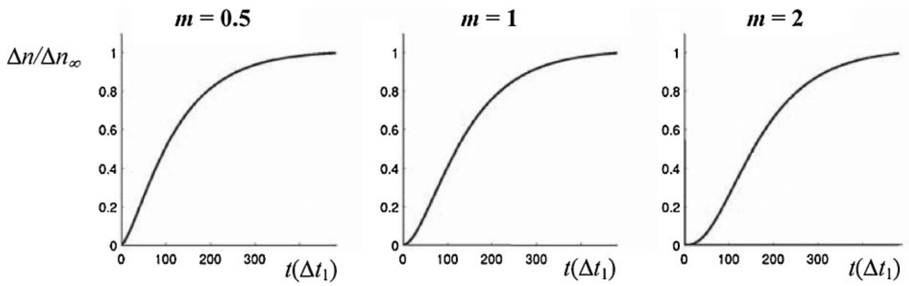

Figure 4.
The grow curves for three different values of exponent m. The same conditions for the three curves were chosen. Time is measured in Δt_1 units, Δt_1 is the mean time which a monomer needs to overcome the distance Δl_1.

its maximum value. With increasing exponent m the inflection point reaches higher values and the grow curve changes its form appropriately.

Dependence of the Grow-Curves on the Intensity of Illumination I

The form of the grow-curve depends substantially on the relaxation time τ and if we compare equations (5) and (9) we see that it means dependence on the intensity of illumination I. The dependence is seen in Figure 5 where the intensities are changed in large scales. Other parameters than the intensity are the same in all the three cases. Refractive index modulation Δn is expressed relatively to its terminal value Δn_∞ ($\Delta n_r = \Delta n/\Delta n_\infty$), time relatively to Δt_1 value ($t_r = t/\Delta t_1$). The intensity dependence of grow-curves predicted by the ID-theory which is seen in Figure 5 is in good agreement with our experimental

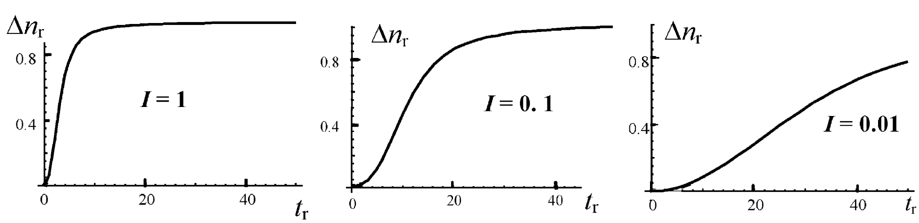

Figure 5.
Intensity dependence of the grow-curves. Time and refractive index modulation are given in relative units.

results. Some of the typical results supporting our theory are reproduced in references [1] and [2] and will be published also in our second contribution[6] to these proceedings.

Conclusion

The ID-theory coming out from very natural assumptions has been put down. It is able to describe the experimentally observed *S*-type form of the grow-curves and their dependence on the intensity of illumination. Branching or cross-linking during the polymerization process may be detected through specifying the exponent m from the measured grow-curves. The presented form of the theory is elementary with many approximations and simplifications. Further refinements of it will lead to other forecasting possibilities. We hope that the ID-theory will be a good tool for optimizing the exposition parameters of existing polymer holographic materials and can also help in preparation of new types of them.

Acknowledgements: The research was supported by the Ministry of Education Research Plan (projects No.60840770022, 0021620835) and Grant Agency of the Czech Republic (projects No. 102/05/H039, 203/03/0262).

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