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Polymer holography II - The theory of hologram growth

Polymer growth detected by holographic method

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Summary

The theory describing in molecular terms radical photopolymerization due to which the refractive index modulation distribution producing a hologram is formed. The theory extends the usual only-diffusion concept to early stages of polymerization, where the opposite diffusion of short polymers (oligomers) is possible which is reduced with increasing polymerization degree. The results of the theory are compared with our experimental results. The idea that, inversely, the experimentally detected curves describing the hologram growth may be used for the study of polymerization kinetics is put forward.

Introduction

The hologram is formed by photopolymerization. Light (in our case in the form of a grid) activates an initiator and so the radical polymerization process starts. 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 monomer molecules, 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 to polymers is much larger than the diffusion of polymers to monomers. To neglect this opposite diffusion is the usual assumption used in the theories describing hologram growth [1-3] (see also our introductory article [4]). As this assumption is not adequate for the early stages of polymer growth, and therefore also of the image growth, we have outlined a theory which does not neglect the opposite diffusion. We call this theory immobilization-diffusion theory to emphasize the fact that we take into account the decreasing mobility of a polymer instead of assuming its fixed position from the very beginning of its growth, as is done in common only-diffusion theories.

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Immobilization-diffusion theory of hologram growth

Single polymer case

The process of polymer stabilization will at first be modeled on one polymer which starts to grow in the illuminated part of a holographic polymer film. In Figure 1 a schematic view of holographic film with the coordinate system used in further calculations is given. Monomers are represented by open circles, the growing polymer is pictured as a tetramer, its actual deviation at time *t* from the plane x=0 is *d*; the radical at the tetramer end is drawn as a full circle.

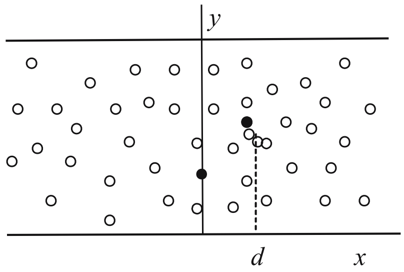

Figure 1. Scheme of the photopolymer film.

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 where only the dependence of ρ on the x-coordinate will be assumed; $\rho(x,y,z)=\rho(x)$. Neglecting the finite dimensions of the exposed film in y direction leading to ignoring the y-dependence of ρ is not a crude approximation. But the dependence of ρ on the z-coordinate may be important as the thickness of the film (~10μm) is substantially larger than monomer dimensions and the illumination profile may be changed substantially along the z-coordinate. In more refined calculations, the dependence of ρ on z will be taken into account but here it is neglected.

Now, we will study how the polymer that starts to grow at the plane $x = 0$ moves. (The radical which starts the polymerization at $t = 0$ is depicted by a full circle at $x = 0$ in Figure 1). As was declared, we will study only the movement in the x-direction. The probabilities to move in $+x$ and $-x$ directions are the same and so, as the mobility of a polymer decreases with increasing polymerization degree *k*, the polymer moves closer and closer to the plain $x = 0$ at which it starts to grow. The polymer carries elementary refractive index differences Δn_e and therefore also these differences concentrate near the plain $x = 0$. So the homogeneity of the refraction index of the film is disrupted and its modulation occurs. The modulation of refractive index is the value which creates the hologram. The described process of polymer growth and accompanying refractive index modulation is a main motive of our theory. We will now outline its mathematical description.

The polymer grows as the monomer units transporting the elementary refractive index modulation 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 modulation 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 $\left|\Delta x_k\right|$ (actual value of this deviation for tetramer – (k=4) is denoted *d* in Figure 1) from the initial position ($x = 0$) decreases. We assume that

$$|\Delta x_k| = \frac{|\Delta x_1|}{k^m},\ k = 1,2,3,... \qquad (\mathbf{1})$$

The exponent m describes the rate of the decrease and so the rate of the polymer immobilization. The exponent m has values between 1/2 and 1 if viscous random motion of linear polymer is assumed. Higher values of m are obtained if some branching or crosslinking occurs. The exponent $m = 0$ if no immobilization is assumed as is the case in the only-diffusion theories where the polymer has the fixed position from the very beginning.

The probable deviation $|\Delta x_1|$ is set to one third (the factor 1/3 reflects the fact that deviations only in the x-direction are concerned) of the value Δl_0; $|\Delta x_1| = \Delta l_0/3$. The value Δl_0 is the mean distance which a monomer molecule must undergo to reach another monomer molecule at the beginning of the polymerization process. For evaluation of these distances at polymerization degree k we have used the expression

$$\Delta l_k = \frac{1}{\sqrt{2}S\rho_k(x)} \qquad (\mathbf{2})$$

in analogy to the method how the mean free path of molecules is evaluated in the kinetic theory of gases (e.g. [5]). In our analogy $\rho_k(x)$ is the density of free monomers when the growing polymer reaches the polymerization degree k and S is the effective cross-section of the radical through which the polymerization proceeds. The complicated trajectory that a monomer must undergo through the gel to reach another monomer or growing polymer is replaced by a uniform straight movement through distance Δl_k with velocity v, inversely proportional to the viscosity η of the gel in our model.

The Δl_k increases as the monomers are consumed by polymers (ρ_k from Eq. 2 decreases) and so the average time necessary for the monomer to reach the polymer also increases. Together with the rapid growth of the refraction index modulation in the early stages of a polymer growth this retardation of its growth caused by the decrease in free monomer molecules gives the typical S-shape of the grow-curves obtained by experiment and discussed later in the article.

The next important point of our theory is that we identify the deviation $|\Delta x_k|$ with the probable deviation of the Gaussian distribution function [5];

$$|\Delta x_k| = \delta_k \doteq 2/3\sigma_k \qquad (\mathbf{3})$$

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

$$p_k(x) = \frac{1}{\sigma_k\sqrt{2\pi}}\mathrm{e}^{-\frac{x^2}{2\sigma_k^2}} = \frac{\sqrt{2}k^m}{\Delta l_0\sqrt{\pi}}\mathrm{e}^{-\frac{2k^{2m}x^2}{\Delta l_0^2}} \qquad (\mathbf{4})$$

Each monomer transports the elementary refractive index modulation Δn_e and so the whole refractive index modulation due to polymer growth may be expressed as

$$\Delta n_k(x) = k\Delta n_e p_k(x) = \frac{k^{m+1}\Delta n_e\sqrt{2}}{\Delta l_0\sqrt{\pi}}\mathrm{e}^{-\frac{2k^{2m}x^2}{\Delta l_0^2}} \qquad (\mathbf{5})$$

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 increasing rate of the drift with increasing exponent m is seen.

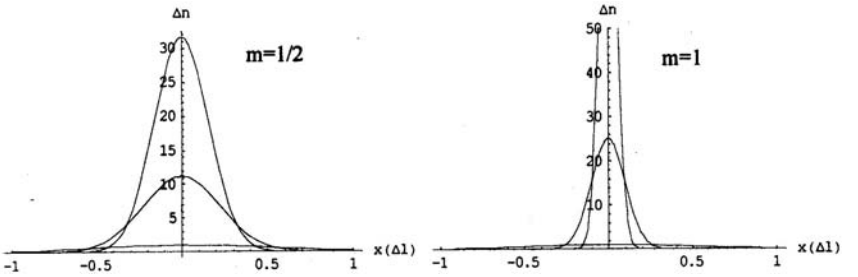

Figure 2. The stabilization of the polymer near its initial position for two values of the exponent m. For each of the two drawings the lowest curve belongs to k=1, the middle curve to k=5 and the upper one to k=10.

The stabilization of polymers in the vicinity of the lighted places where they have started to grow is the main idea also in our further treatment of the problem. We replace a polymer that starts to grow at $x = 0$ in time $t = 0$ by a group of polymers which start to grow in the illuminated places of the film during the whole exposition interval. Instead of measuring the progress of the refractive index modulation by polymerization degree k we express it in the exposition time t_s.

Continuous spatial and time distribution of the growing polymers

We introduce the density $c(x,t)$ of polymers which starts growing in the place of coordinate x at time t. The meaning of $c(x,t)$ comes out from the following expressions

$$C = \int_{t_1}^{t_2}\int_{x_1}^{x_2} c\left(x,t\right)\mathrm{d}x\mathrm{d}t; \quad \mathrm{d}C = c\left(x,t\right)\mathrm{d}x\mathrm{d}t \tag{6}$$

C is the total number of polymer molecules the growth of which is initiated in a stripe of width $\langle x_1, x_2\rangle$ and unit lengths in the y and z directions during the time interval $\langle t_1, t_2\rangle$. We assume that c may be expressed as

$$c = AI\left(x,t\right) \tag{7}$$

The constant A is the efficiency of initiation and I the intensity of illumination (intensity of the applied laser light). We introduce the actual degree of conversion

$$d = \frac{\rho_0 - \rho\left(t\right)}{\rho_0} \tag{8}$$

where $\rho(t)$ is the actual and ρ_0 the initial density of the free monomers. The degree of conversion d is the ratio of the monomers remaining free at time t to the initial number of monomers.

If we now introduce in our calculations the two times, the time t_i when the initiated monomers started to polymerize and time t_s when we observe the actual state of the refractive index modulation $\Delta n(x,t_S)$, we obtain the expression:

$$\Delta n(x,t_\mathrm{s}) = \int_0^{t_\mathrm{s}} \int_{-\infty}^{+\infty} \frac{dn_e}{dt}(t_\mathrm{i},x_\mathrm{i})\, c(t_\mathrm{i},x_\mathrm{i})\, \rho(t_\mathrm{i})\, \mathrm{d}x_\mathrm{i}\mathrm{d}t_\mathrm{i} \qquad \mathbf{(9)}$$

If we introduce modified expression (5) and *c* given by (7) into (9), we obtain

$$\Delta n(x,t_\mathrm{s}) = B\Delta n_\mathrm{e} \frac{\sqrt{2}}{\sqrt{\pi}}(m+1) \int_0^{t_s} \int_{-\infty}^{\infty} \frac{t_i^{\mathrm{m}}}{\Delta t_0^{\,m} \Delta l_0} A\, I(x_\mathrm{i},t)\, \rho(t_\mathrm{i})\, \mathrm{e}^{\frac{-t_\mathrm{i}^{2\mathrm{m}}(x-x_\mathrm{i})^2}{\Delta t_0^{2\mathrm{n}} \Delta l_0^2}}\, \mathrm{d}x_\mathrm{i}\mathrm{d}t_\mathrm{i} \qquad \mathbf{(10)}$$

The modification of Eq. (5) means that the starting polymerization point x=0 is replaced by x_i and the polymerization degree is replaced by time t_i. The constant *B* is the unifying factor. The initial mean free path of a monomer Δl_0 and time $\Delta t_0 = \Delta l_0 / v$, which is necessary for a monomer to travel through this path by constant velocity *v,* are introduced in the expression (10). The mean free path $\Delta l(\rho)$ and therefore also the time necessary to travel through it $\Delta t(\rho)$ are growing as monomers are consumed by polymers, i.e. with decreasing density ρ and increasing conversion *d*. The dependence of conversion *d* on time t_i is given by a simple function

$$d = 1 - \mathrm{e}^{-\frac{t_i}{\tau}} = 1 - \mathrm{e}^{\frac{-t_i c t_s}{\Delta t_0}} = 1 - \mathrm{e}^{\frac{-t_i A I \rho_0 t_s}{\Delta t_0}} \qquad \mathbf{(11)}$$

in which the value of the relaxation time τ is expressed in more detail in the second and third equation.

We will treat the general expression (10) in more detail for two profiles of the initiating light intensity. The first of these is that we really use in the experiments:

$$I = I_0 (\cos \pi b x)^2 = \frac{I_0}{2}(1 + \cos 2\pi b x) \qquad \mathbf{(12)}$$

We obtain

$$\Delta n(x,t_\mathrm{s}) = B\Delta n_\mathrm{e}(m+1) \frac{\rho_0}{\sqrt{2\pi}} \int_0^{t_s} \int_{-\infty}^{\infty} t_\mathrm{i}^{\mathrm{m}} (1 + \cos 2\pi b x_\mathrm{i}) A I_0 \left(\mathrm{e}^{-A I_0 t_\mathrm{i}}\right) \mathrm{e}^{-t_\mathrm{i}^{2\mathrm{m}}(x-x_\mathrm{i})^2} \mathrm{d}x_\mathrm{i}\mathrm{d}t_\mathrm{i} \qquad \mathbf{(13)}$$

In Eq. (13) the coordinate *x* is measured in Δl_0 units and times t_i and t_s in Δt_0 units. So we obtain reduced curves more convenient for further studies.

The second initiating light intensity profile studied in more detail is the box-type one:

$$\begin{aligned} &I = 0 \text{ for } x \in (-\infty, -a),\ I = I_0 \text{ for } x \in \langle -a, +a \rangle \\ &\text{and } I = 0 \text{ for } x \in (+a, \infty) \end{aligned} \qquad \mathbf{(14)}$$

We have obtained the following refractive index modulation after time $t_\mathrm{S} = s\Delta\, t_0$

$$\Delta n(x,t_\mathrm{s}) = B\Delta n_\mathrm{e}(m+1) \frac{\sqrt{2}\rho_0}{\sqrt{\pi}} \int_{-a}^{+a} \int_0^{t_\mathrm{s}} t_i^{\mathrm{m}} A I_0 \mathrm{e}^{-A I_0 t} \mathrm{e}^{-t_i^{2\mathrm{m}}(x-x_i)^2} \mathrm{d}x_i \mathrm{d}t_i \qquad \mathbf{(15)}$$

Results of model calculations

Accuracy of reproduction

To test the fidelity of image forming we have used Eq. (15) to evaluate $\Delta n(x, s\Delta t_0)$ for several values of time $t_\mathrm{S} = s\Delta\, t_0$. The box type illumination profile (14) with a = 1 and the factor m = 2 has been assumed. The results are given in Figure 3.

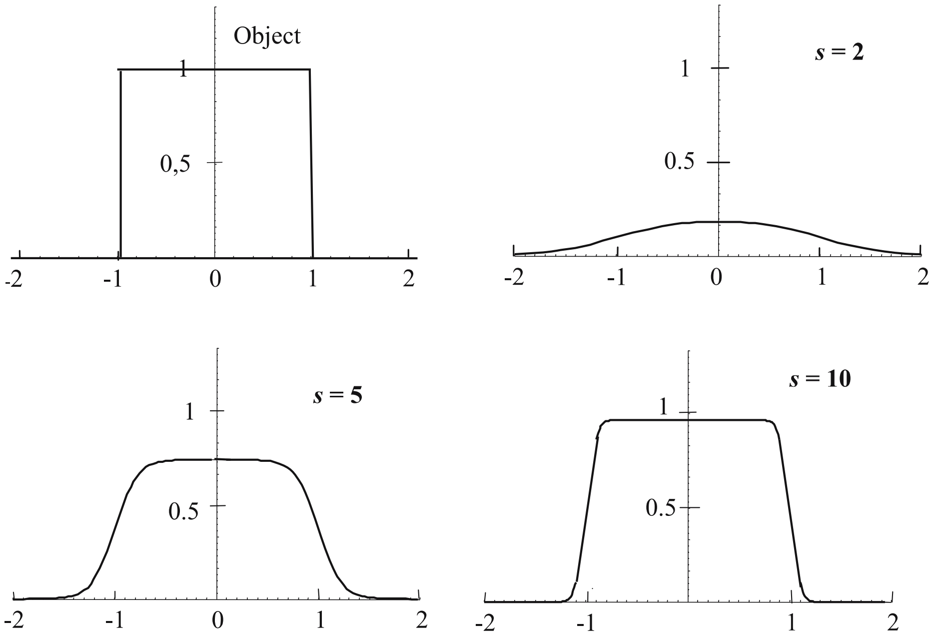

Figure 3. The reproduction of the object with increasing exposition time $\Delta t_s = s\Delta t_0$. On x-axes distances in Δl_0 units are given, on y-axes of the s-labeled curves refractive index modulation is plotted. Intensity I of the "object" is arbitrary.

We see that with increasing s the image of the box type illumination develops from the wide Gaussian-like curve at $s = 2$ to the nearly true reproduction of the box-type illumination profile at $s = 10$. The accuracy of reproduction grows more quickly for the illumination profile given by Eq. 12 as in this case the monomer transport distances necessary for obtaining good image are shorter.

Refractive index modulation grow curves

The predicted reduced refractive index modulation Δn versus exposition time $t_S = s\Delta t_0$ curves (grow-curves) are given in Fig. 4. The curves were calculated as Δn values for x=0 from Eq. (12) and divided by the final value $\Delta n_{\max}$. The refractive index modulation at first rises with increasing grow-rate, goes through an inflexion point and with decreasing grow rate it achieves its maximum value $\Delta n_{\max}$ at which all the monomers are consumed by polymers. The rate of this process rises with increasing concentration c, i.e. with increasing intensity of illumination I (see Eq. (7)).

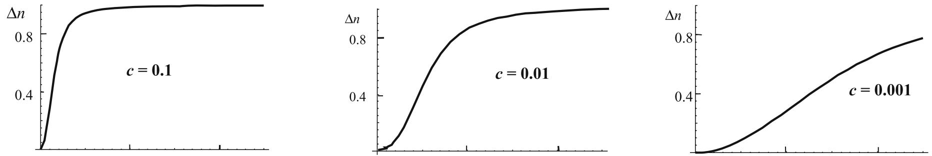

Figure 4. The normalized grow-curves for three concentrations c.

The grow-curves have an S-type shape. The rise rate increases when the polymers (oligomers) start to grow and it decreases when the depletion of free monomers becomes substantial. The grow-curves are measured in our experiments [4]. The S-type shape of them inspired us to design the immobilization - diffusion theory. The diffusion theory only cannot simply explain the increasing growing rate in the early stages of the exposition as it assumes fixed position of polymers in the lighted parts of holographic films from the very beginning of the polymer growth. In the initial part of their growth the polymers are only very short oligomers the mobility of which is not negligible.

Dependence of grow-curves on exponent m

The dependence of grow-curves on exponent m is illustrated by Figure 5 where the calculated reduced curves for three different m-values are given.

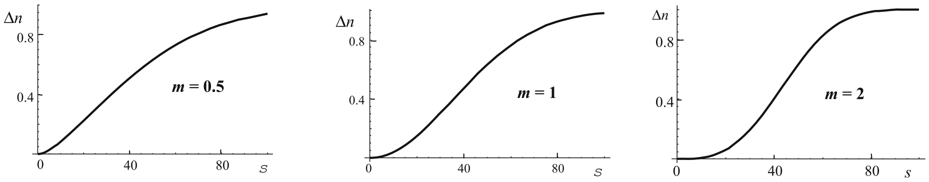

Figure 5. Reduced grow-curves for the exponents $m = 0.5$, 1 and 2.

It is seen that with increasing m the curves become more abrupt and their points of inflexion occur at higher reduced time values. The grow-curves corresponding in form to higher values of m are often observed in experiments. This indicates that some faster mechanisms of polymer growth, such as branching or network formation, are to be assumed in hologram growth.

Experimentally obtained grow-curves; comparison with theoretical predictions

Measured grow-curves

In Figure 6 three grow-curves obtained by our measurements [4] are presented. All curves in their rising parts have the predicted S-type form. The upper curve was illuminated with intensity $I = 7$ mWcm^{-2}, the lower two curves were illuminated with intensity $I = 3$ mWcm^{-2}. The higher rate of growth of the upper curve than that of the lower two curves is though in agreement with the prediction visualized in Figure 4. The higher c value means also higher intensity I. The exposition time of the upper curve was $t_e = 3$ s, one of the lower curves was exposed for $t_e = 15$ s, the exposition was not switch off for the second one.

The different maximum values of the two curves are not predicted by the theory, neither the decrease in the refractive index modulation after the maximum of the curves is reached. A small decrease in the maximum values of the curves exposition of which was stopped when maximum modulation was reached can be explained by the inverse diffusion which occurs for the short polymers (oligomers) that had started to grow at times very close to the moment when the exposition was stopped. To avoid this process the exposition is usually stopped before the maximum of Δn is reached [4]. After switching off the exposition, no new polymers start to grow and the monomers are bonded to the already existing ones. The process is then the normal diffusion to the well fixed polymers as is the case described by the classical theories of hologram growth.

Degradation under influence of the initiating light evidently occurs if the exposition is not stopped (the lowest curve) and the modulation nearly completely disappears. It may be caused by chemical reasons, by physical processes in the exposed layer or by long-term instabilities of the exposition equipment.

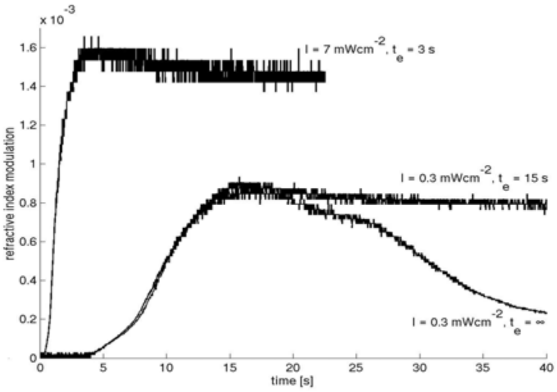

Figure 6. Examples of the experimentally obtained grow-curves.

Inverse problem - how the polymer growth kinetics can be derived from the measured grow-curve

The subtitle of this article is “Polymer growth detected by holographic method”. So far it has only been the idea supported by some preliminary results. The main point of the idea is: If we are able to detect in situ how the hologram grows and the theory describing in molecular terms this process is available, we can in principle say from the form of the detected grow-curve, how the polymeric system forming the hologram grows. In other words, we presume that polymer holography may be a useful tool for study of polymerization kinetics [6, 7] or possibly the network-forming process [8].

One hint supporting the idea is that if we find the grow curve of the form corresponding to $m>1/2$ (Figure 5), we can assume that polymerization is more effective than linear growth. The detected curves have often values of m much higher than 1/2, especially in samples where bis-acrylamide (crosslinking agent) is present. Such samples (films) are insoluble after exposition and so the assumption that the exposed hologram in this case is formed by micronetworks seems to be very probable.

A second hint comes out from the measurement of molecular weight distribution of the exposed sample. We obtained a very preliminary result by dynamic light scattering which shows that at high exposition intensity I the molecular weight distribution is narrow and at lower intensity the distribution broadens on the high-molecular-weight tail. This result may be predicted by the presented theory. The sample used in this experiment was without bis-acrylamide as the sample must be soluble.

Conclusions

1) A method of model computing of the holographic image growth has been developed.
2) The model gives a framework for the systematic experimental study of the processes by which holograms are created on photopolymeric films.
3) The model used in the theory is based on the linear polymer growth. Our experiments have shown that network formation seems to be important for obtaining a good hologram. In the present form of the theory this fact may be taken into account only by taking a higher value of the exponent m. We will try to incorporate branching and crosslinking to the roots of the theory.
4) We believe that the grow-curve study may be conversely used for studying the polymerization, branching and network formation processes. We are studying this problem now but only preliminary results are available.

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