

## **Study of the inhibition period prior to the holographic grating formation in liquid crystal photopolymerizable materials**

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### ***ABSTRACT***

*We theoretically describe the experimentally observed inhibition period prior to the holographic grating formation in liquid crystal photopolymerizable materials. The proposed model explains the inhibition period of grating formation by the presence of oxygen, or other inhibitor molecules, which initially suppress the creation of free radicals. The theoretical dependence of inhibition period on the recording intensity is in good accordance with experimental results.*

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## INTRODUCTION

Photopolymerizable materials that are sensitive in the infrared spectra increasingly attracted the attention of researchers as convenient media for optical storage applications [1-7]. One of the most useful properties of photopolymeric materials is the real time recording of holographic gratings. A particular interest represent the so called polymer dispersed liquid crystals (PDLC) [7-9]. Such composite materials are interesting since they possess the well known advantages of polymers and the electrically controllable anisotropy of liquid crystals. The anisotropic properties of liquid crystal droplets, dispersed into polymers, allow the control of the recorded diffraction gratings by an electrical field through reorientation of liquid crystal molecules [10]. The diffraction properties of PDLC gratings can also be controlled by temperature thanks to the strong temperature dependence of liquid crystal refractive indexes [7]. However, there are still a number of key phenomena taking place during the recording of those holograms that require further exploration. Among them we can note the inhibition period of polymerization, dependence of diffraction efficiency of the hologram on pre-polymerization intensity and so on [2, 6, 11].

The aim of the present work is to explore the complete kinetics of holographic recording by considering a four components system: polymer + monomer + liquid crystal + oxygen. To record the hologram, the cell is exposed to the interference pattern of light (see details in section IV). The non-uniform exposition and polymerization create concentration gradients in these materials. Typically, a diffusion of monomers is initiated from dark zones to the more illuminated zones. Thus, a spatial modulation of the density of the final polymer and of its refractive index are formed. The solution of the diffusion equation of polymerization with two components "polymer + monomer" was considered earlier [12, 13]. However, experiments show that the spatial modulation of the polymer density, as well as the corresponding diffraction efficiency, begin to increase only after some preliminary illumination of the monomer solution. This period of time during which the polymerization and diffraction are not yet detected, while the solution is illuminated by the periodic interference pattern, is known as the inhibition period. We present in this work a model which corresponds well to the experimentally observed of inhibition period. The essence of this effect is that, at the initial stage, doped inhibitor molecules (such as oxygen) suppress the polymerization process[14]. When the concentration of such molecules becomes less than some critical value, the chain reaction of polymerization begins.

## DIFFUSION MODEL

As for usual H-PDLCs, the initial monomer is chosen in such a way that the liquid crystal can be well dissolved in it. However, the liquid crystal is pushed out from the area where the polymer is formed as a result of polymerization. Since the liquid crystal does not participate in the process of polymerization and, in rather good approximation, does not influence the spatial distribution pattern of the polymer, its concentration is not included in the diffusion equation<sup>1</sup>. At relatively small concentration of liquid crystal, the monomer and liquid crystal can be considered as occupying the same volume since they are well mixed. The situation is different in the case of the polymer. Phase separation takes place between polymer and liquid crystal since they cannot

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<sup>1</sup> In a better approximation we could take into account the fact that the opposed diffusion of the LC would easily slow down the monomer diffusion.

occupy the same volume. Since the diffusion mobility of the liquid crystal is much higher than the mobility of the polymer, it is pushed out of the volume where the polymer was formed and the pattern of spatial distribution of polymer does not significantly change.

Let's consider the equation of polymerization under the influence of light with periodically modulated intensity, taking into account the molecular diffusion. Let's denote the concentration of monomer as  $U(\vec{r}, t)$ , and  $N(\vec{r}, t)$  as the concentration of polymer. We assume that the growth rate of the concentration of polymer  $N(\vec{r}, t)$  is proportional to the concentration of the remaining monomer:

$$\frac{\partial N(\vec{r}, t)}{\partial t} = F(\vec{r}, t)U(\vec{r}, t), \quad (1)$$

where  $F(\vec{r}, t)$  is the coefficient of proportionality named as "local polymerization rate". The spatio-temporal variation of the concentration of monomer is given by the standard equation of diffusion along with an additional term in its right side representing the decline of the monomer concentration due to polymerization.

$$\frac{\partial U(\vec{r}, t)}{\partial t} + \vec{\nabla} \vec{j}(\vec{r}, t) = -\frac{\partial N(\vec{r}, t)}{\partial t} \quad (2)$$

where  $\vec{j}(\vec{r}, t)$  denotes a flow density due to monomer diffusion,

$$\vec{j}(\vec{r}, t) = -D(\vec{r}, t)\vec{\nabla}U(\vec{r}, t) \quad (3)$$

where  $D(\vec{r}, t)$  stands for a local value of the diffusion coefficient.

In the case of standard holographic exposure the polymer sample is illuminated by a pair of symmetrically incident mutually coherent laser beams. Thus the distribution of light is periodic and may be described by the expression  $I(x) = I_0(1 + V \cos(Kx))$ , where  $I_0$  is the average intensity of light,  $V$  - the interference contrast and  $K = 2\pi/\Lambda$ , where  $\Lambda$  - is the period of modulation that is defined by the angle  $\alpha$  between the recording beams:  $\Lambda = (\lambda/2)\sin(\alpha/2)$ .

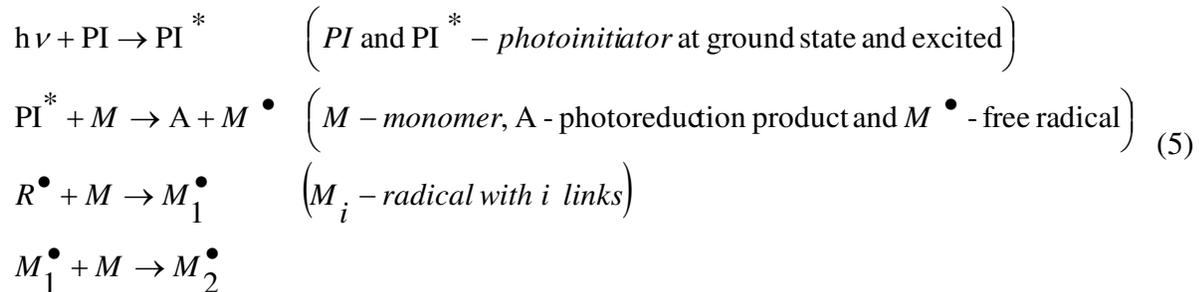
Thus, in the approximation of local spatial response<sup>2</sup> the spatial dependence of  $F$  can be written as follows

$$F(x, t) = F_0(t)(1 + V \cos(Kx)) \quad (4)$$

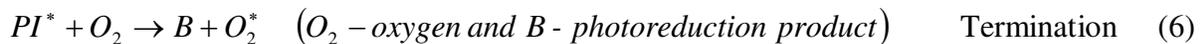
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<sup>2</sup> The non-local model of photopolymerization was explored by Sheridan et al. in Ref.[15].

We can notice that the presence of oxygen (or other molecular species) may act as an inhibitor for the polymerization process. The photoactivated molecules of dye will thus react with the oxygen and the reaction of polymerization cannot take place if the concentration of oxygen is too high [14,16,17].



It is important to note that the photoinitiator (PI) participates in the chemical reaction only once. It then turns into the passive product A. If there is oxygen in the solution at the initial stage, it can deactivate the photoinitiator from its excited triplet state. Then, the radical formation, and thus the chain reaction, does not occur [11].



However, if the concentration of photoinitiator is high enough, a certain amount of radicals will be formed. Nevertheless, these radicals may also react with oxygen, resulting in a reaction of peroxidation:



Each of these mechanisms of polymerization and its impact on the photopolymerization has its own probability. If the sum probability of the interruption of polymerization is more than the probability of polymerization, it means that the total coefficient of polymerization is less than 1, i.e. the polymerization dies away. When the probability of polymerization is more than the probability of interruption, then the total coefficient of polymerization is more than 1. It means that due to light illumination, more radicals are formed than consumed due to oxygen (or other inhibitors) and thus a chain reaction may start. [18]

Thus, the question of whether there will be a reaction of photopolymerization or not depends on the concentration of monomer, photoinitiator (dye - complex) and oxygen. From aforementioned it is clear that the concentration of the photoinitiator should be above some critical value. If it is the case, then the rate of polymerization does not depend upon the concentration of dye. We shall therefore assume that the concentration of dye is big enough. The outcome of polymerization then depends on the ratio between the concentration of monomer and oxygen. Similarly if the concentration of oxygen in the solution exceeds a certain limit, polymerization does not start at all, i.e. the polymerization rate  $F_0(t) = 0$ . As soon as the concentration of oxygen becomes less than this limit, the normal process of polymerization can start. Let's find the corre-

sponding function  $F_0(t)$  in its explicit form. As the oxygen consumes a part of the dye, the critical value of oxygen concentration, at which the reaction is inhibited, will be expressed as a certain percentage ( $\chi$ ) of the monomer concentration. Taking this into account, it is possible to write  $F_0(t)$  as an explicit function of the concentration of oxygen (inhibitor) and initial concentration of monomer as follows :

$$F_0(t) = f_0 \theta \left( \frac{U^0}{i_d} - \rho(t) \right), \quad (8)$$

where  $\rho(t)$  is the concentration of oxygen ,  $\theta$  is a step function,  $f_0 = kI_0$ ,  $k$  is a proportionality constant,  $U^0$  is the initial concentration of monomer and  $i_d$  specifies how many times the concentration of oxygen should be less than the monomer concentration.  $U^0/i_d$  then shows the threshold concentration of oxygen below which polymerization can occur. Let us call this concentration value as the “inhibition threshold”. To describe the oxygen concentration dynamics , we shall make the following assumptions. Since oxygen is a gas and its diffusion constant is great enough, then, during illumination, its distribution inside the sample remains uniform. The rate of change of the concentration of oxygen during the process of illumination of the solution is directly proportional to the concentration of oxygen. Reacting with the dye, the oxygen turns into an inert component which cannot further influence the process of polymerization. The differential equation for the concentration of oxygen  $\rho$  has the following form,

$$\frac{d\rho(t)}{dt} = -\beta\rho(t) \quad (9)$$

where  $\beta$  is a constant that is proportional to the average light intensity  $\beta = k'I_0$  (at low intensities), where  $k'$  is a constant for a given solution at a fixed temperature. The solution of this equation will be  $\rho(t) = \rho_0 \exp(-\beta t)$  , where  $\rho_0$  is the initial concentration of oxygen.

As a result, the local polymerization rate  $F_0(t)$  takes the following form:

$$F_0(t) = f_0 \theta \left( \frac{U^0}{i_d} - \rho_0 \exp(-\beta t) \right) \quad (10)$$

Since the intensity of light varies only along the  $x$  axis, the spatial dependence of  $U(\vec{r},t)$  and  $N(\vec{r},t)$  has a one-dimensional dependence along the  $x$ -coordinate. Substituting the equations (1), (3) and (10) in (2), we shall obtain the following system of equations:

$$\frac{\partial U(x,t)}{\partial t} = \frac{\partial}{\partial x} \left[ D(x,t) \frac{\partial U(x,t)}{\partial x} \right] - f_0 \theta \left( \frac{U^0}{i_d} - \rho_0 \exp(-\beta t) \right) (1 + V \cos(Kx)) U(x,t) \quad (11)$$

$$\frac{\partial N(x,t)}{\partial t} = f_0 \theta \left( \frac{U^0}{i_d} - \rho_0 \exp(-\beta t) \right) (1 + V \cos(Kx)) U(x,t) \quad (12)$$

The initial condition for equation (11) will be written as  $U(x,0) = U^0$ . We can represent the solution of equation (11) as Fourier series. Knowing that the polymerization is initiated by periodically modulated light,  $U(x,t)$  and  $N(x,t)$  are also expressed as periodic and even functions of  $x$ , neglecting diffusion nonlinearities. Hence, the Fourier series of these functions contain only terms with cosines:

$$U(x,t) = \sum_{i=0}^{\infty} U_i(t) \cos(iKx) \quad (13)$$

Similarly we shall expand the coefficient of diffusion  $D(x,t)$  in Fourier series:

$$D(x,t) = \sum_{i=0}^{\infty} D_i(t) \cos(iKx) \quad (14)$$

The Fourier coefficients  $D_i(t)$  hereinafter will be called diffusion coefficient of order  $i$ . Substituting (6), (11), (14) and (15) in equation (12), we get

$$\begin{aligned} \sum_{i=0}^{\infty} \frac{dU_i(t)}{dt} \cos(ikx) = & \left[ \sum_{i,j=0}^{\infty} ijK^2 D_i(t) U_j(t) \sin(iKx) \sin(jKx) \right] + \\ & + \sum_{i,j=0}^{\infty} (iK)^2 D_j(t) \cos(jKx) U_i(t) \cos(iKx) - \\ & - f_0 \left( \frac{U^0}{i_d} - \rho_0 \text{Exp}(-\beta t) \right) (1 + V \cos(Kx)) \sum_{i=0}^{\infty} U_i(t) \cos(iKx) \end{aligned} \quad (15)$$

Expanding equation (15) on components and making transformations similarly as in [12], we obtain a system of differential equations for Fourier component of monomer's concentration. We assume that the harmonics above the third order can be neglected since their contribution is  $\sim 10^6$  times less than contributions of the first terms. If we neglect diffusion nonlinearities, it will be justified to retain only the first two terms in (15).

$$D(x,t) = D_0(t) + D_1(t) \cos(Kx) \quad (16)$$

Since it is known that mobility is reduced during polymerization, the coefficient of diffusion is decreasing and in accordance with [12] for Fourier-component we obtain

$$D_0(t) = \frac{1}{2} [D_{\max}(t) + D_{\min}(t)] = D_a \exp(-\mu F_0 t) \text{ch}(\alpha F_0 V t) \quad (17)$$

$$D_1(t) = \frac{1}{2} [D_{\min}(t) - D_{\max}(t)] = -D_a \exp(-\mu F_0 t) \text{sh}(\alpha F_0 V t) \quad (18)$$

where  $D_a$  represents the initial coefficient of diffusion and  $\mu$  is a constant. Having substituted (17) and (18) in the equation for Fourier-components of monomer concentration and replacing  $\xi = f_0 t$  as in [12], we obtain

$$\frac{dU_0(\xi)}{d\xi} = -H(\xi)U_0(\xi) - \frac{1}{2}H(\xi)VU_1(\xi) \quad (19)$$

$$\begin{aligned} \frac{dU_1(\xi)}{d\xi} = & -H(\xi)VU_0(\xi) - [H(\xi) + R \exp(-\mu\xi)ch(\mu V\xi)]U_1(\xi) - \\ & - \left[ \frac{1}{2}H(\xi)V - R \exp(-\mu\xi)sh(\mu V\xi) \right]U_2(\xi) \end{aligned} \quad (20)$$

$$\begin{aligned} \frac{dU_2(\xi)}{d\xi} = & - \left[ \frac{1}{2}H(\xi)V - R \exp(-\mu\xi)sh(\mu V\xi) \right]U_1(\xi) - \\ & - [H(\xi) + 4R \exp(-\mu\xi)ch(\mu V\xi)]U_2(\xi) - \\ & - \left[ \frac{1}{2}H(\xi)V - 3R \exp(-\mu\xi)sh(\mu V\xi) \right]U_3(\xi) \end{aligned} \quad (21)$$

where  $R = \frac{D_a K^2}{f_0}$ ,  $H(\xi) = \theta\left(\frac{U^0}{i_d} - \rho_0 \exp\left(-\frac{\beta}{f_0}\xi\right)\right)$

The concentration of polymer at the moment  $\xi$  is described by the expression

$$N(x, \xi) = \int_0^\xi F(x, \xi')U(x, \xi')d\xi' \quad (22)$$

Let's substitute (4) (8) and (13) in equation (22) and present  $N(x, \xi)$  as the sum of its harmonics. With regard to diffraction we are interested only in the first two terms of the Fourier series. The first high harmonics in Fourier series of  $N(x, t)$  are small since Bragg angles for gratings with periods  $2K$ ,  $3K$  etc differ from Bragg angles for period  $K$  [19]. Moreover, during monitoring, the presence of gratings of higher order is not detected.

$$N(x, t) = N_0(t) + N_1(t) \cos(kx) \quad (23)$$

For Fourier components we obtain

$$N_0(\xi) = \int_0^\xi \theta\left(\frac{U^0}{i_d} - \rho_0 \exp\left(-\frac{\beta}{f_0}\xi'\right)\right) \left[ U_0(\xi') + \frac{1}{2}VU_1(\xi') \right] d\xi' \quad (24)$$

$$N_1(\xi) = \int_0^\xi \theta\left(\frac{U^0}{i_d} - \rho_0 \exp\left(-\frac{\beta}{f_0}\xi'\right)\right) \left[ VU_0(\xi') + U_1(\xi') + \frac{1}{2}VU_2(\xi') \right] d\xi' \quad (25)$$

Now we can analyze the distribution of liquid crystals. We have already mentioned that there is phase separation between polymer and liquid crystal. Let  $L(x, t)$  be the concentration of liquid crystal and  $c$  the ratio between average concentration of liquid crystal and polymer

( $c = L_0/N_0$ ). In a first approximation we can assume that the modulation of concentration of liquid crystal, similarly to its average value, is  $c$  times less than the modulation of concentration of polymer ( $c = L_1/N_1$ ). Hence, the concentration of liquid crystal at the moment  $\xi$  and in a point  $x$  can be expressed as:

$$L(x, \xi) = L_0(\xi) + L_1(\xi)\cos(Kx) = cN_0(\xi) - cN_1(\xi)\cos(Kx) \quad (26)$$

Having the expressions for the concentration of polymer, monomer and liquid crystals, it would now be possible to find the distribution of the composite material refractive index. According to the Lorenz-Lorenz formula [20], the material density  $\varphi$ , molar weight  $M$  and molar refractivity  $n_{mol}$  determine the refractive index  $n$  in the following way.

$$\frac{n^2 - 1}{n^2 + 2} = \frac{\varphi}{M} n_{mol} \quad (27)$$

According to [13], it follows from (27)

$$n_1 \sim U_1 \frac{n_m^2 - 1}{n_m^2 + 2} + N_1 \frac{n_p^2 - 1}{n_p^2 + 2} - L_1 \frac{n_{LC}^2 - 1}{n_{LC}^2 + 2} = U_1 \frac{n_m^2 - 1}{n_m^2 + 2} + N_1 \left( \frac{n_p^2 - 1}{n_p^2 + 2} - c \frac{n_{LC}^2 - 1}{n_{LC}^2 + 2} \right) \quad (28)$$

where  $n_1$  is the modulation of refractive index,  $n_m$  the refractive index of monomer,  $n_p$  the refractive index of polymer and  $n_{LC}$  the refractive index of liquid crystals<sup>3</sup>. The last, obviously, has an anisotropic value and depends on the polarization of incident light.

## II. NUMERICAL RESULTS

Solving (19) - (21) and (24) - (25) by numerical methods using “Mathematica 4.0” and returning variable  $\xi$  to  $t$ , we obtain Fourier-components of monomer and polymer concentrations. Figure 1 plots the curves of Fourier components of the monomer  $U_0(t)$ ,  $U_1(t)$ ,  $U_2(t)$  with the following parameters :  $U_0 = 1, V = 1, k' = 0.01, k = 0.01, \mu = 0.5, R = 0.1, \rho_0 = 0.5, I_0 = 15mW/cm^{-2}, i_d = 100$  (i.e. for the reaction to start, the concentration of oxygen or other inhibitors must be by two orders of magnitude smaller than monomer concentration). The components for polymer concentration are presented in figure 2 . Note that the inhibition period is present in both graphs. According to formula (26) we find the distribution of liquid crystal concentration, i.e. its Fourier-components  $L_1$ . From formula (28) we find the modulation of refractive index for the whole composition. According to the coupled waves theory of Kogelnik [19], the diffraction efficiency of a thick holographic grating can be calculated with the following formula.

<sup>3</sup> We use  $n_{LC} = n_o$  for a s-polarized probe beam since the the optical axis direction that is defined by the average molecular orientation of LC is along the grating vector [21]

$$\eta = \sin^2\left(\frac{\pi\Delta n d}{\lambda \cos\theta}\right) \quad (29)$$

where  $d$  is the thickness of the grating,  $\lambda$  the probe wavelength,  $\Delta n$  the modulation of refractive index, and  $\theta$  the Bragg angle. The theory of coupled waves for the case of anisotropic gratings was generalized by Montemezani and Zgonic [22]. Nevertheless, the diffraction efficiency can be calculated by (29) in the case of incidence at Bragg angle using the refractive index modulation at a given (S or P) readout (probe) polarization. The temporal dependence of diffraction efficiency (solid line) during polymerization is presented in figure 3. It can be noticed that the diffraction efficiency begins to grow after some preliminary illumination of the monomer solution as in the case of real experiment.

Let's now consider the dependence of this inhibition period  $t_i$  on the intensity of illumination. It can be determined by the condition

$$\frac{U^0}{i_d} - \rho_0 \exp(-\beta t_i) = 0 \quad (30)$$

Since we assume a large concentration of dye, we can roughly suggest that every photon getting in the environment activates one molecule of photoinitiator which results in the deactivation of one molecule of oxygen. As already mentioned, since the diffusion coefficient of oxygen is high it will rather have a uniform spatial distribution. Solving equation (30) for  $t_i$  we obtain

$$t_i = -\frac{\ln(U^0/(i_d \rho_0))}{k'I_0} \quad (31)$$

Figure 4 plots the dependence of the inhibition period on the average intensity of polymerizing light. Polymerization obviously won't start at all at zero intensity, and the inhibition period tends to zero at very high intensities.

## EXPERIMENTAL RESULTS

Transmission holograms were recorded in a near infrared photopolymerizable solution using two collimated laser beams (from a cw Ti-Sa operating at 823 nm) symmetrically incident on the film. The photopolymerizable solution consisted (see details in Ref.[5]) of monomer DPEPA (Di-Penta-Erithriol-Penta-Acrylate), electron donor, initiator EDMAB<sub>z</sub> (Ethyl-di Methyl-Amino-Benzoate), nematic liquid crystal E7 (with refractive indexes for ordinary and extraordinary waves, respectively  $n_o=1.5211$ ,  $n_e=1.7464$ ) and a second monomer 2EEEA (2-Ethoxy-Ethoxy-Ethyl Acrylate Ester). The diffraction efficiency was monitored during recording using a He-Ne laser (operating at  $\lambda=543\text{nm}$ ) at the corresponding Bragg angle ( $16.8^\circ$ ). A set of transmission holograms was recorded at a fixed cross angle of  $50.18^\circ$  between the two beams, which results in

a pattern with a spacing of  $\Lambda = 0.94 \mu\text{m}$ . The experimental diffraction efficiency as a function of recording time is plotted in figure 3 (square dots). Let us note that the bleaching of the dye takes place without any threshold or inhibition period [23]. It continues up to saturation when the majority of the dye is already degraded and the polymerization is over. The experimental dependence of the inhibition period on the total recording intensity is presented on Fig. 4.

## CONCLUSIONS AND DISCUSSIONS

We have experimentally observed and theoretically described the inhibition period in the recording of holographic gratings in liquid crystal photopolymerizable materials. Within the framework of our approximation it is supposed that diffusion nonlinearities are absent in the solution and the polymerization rate is directly proportional to the intensity of light. The occurrence of the inhibition period is explained by the presence of oxygen in our monomer solution, which damp the excited molecules of dye and prevent the monomers from being activated. Our experiment and theoretical analysis are in good agreement.

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## Figure Caption

**Fig.1. Dependence of monomer concentration Fourier components  $U_0(t)$ ,  $U_1(t)$ ,  $U_2(t)$  on exposition time.**

**Fig.2. Dependence of polymer concentration Fourier components  $N_0(t)$ ,  $N_1(t)$  on exposition time.**

**Fig.3. Experimental (solid line) and theoretical (boxes) dependence of diffraction efficiency during polymerization.**

**Fig.4. Experimental (solid line) and theoretical (boxes) dependence of duration of a dead zone on average intensity of polymerizing light**

Fig.1.

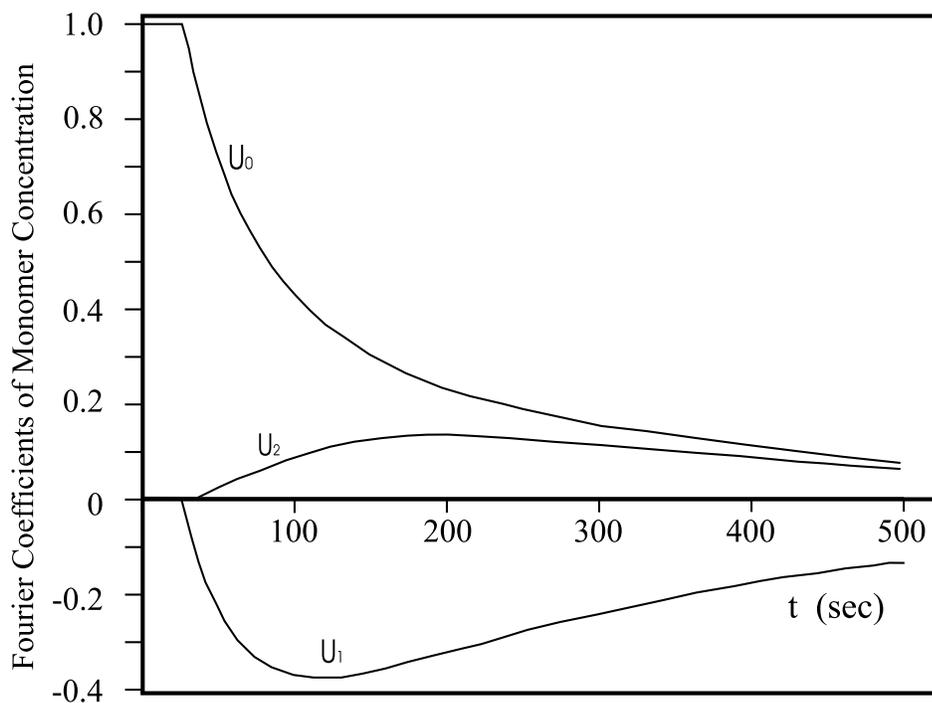


Fig.2.

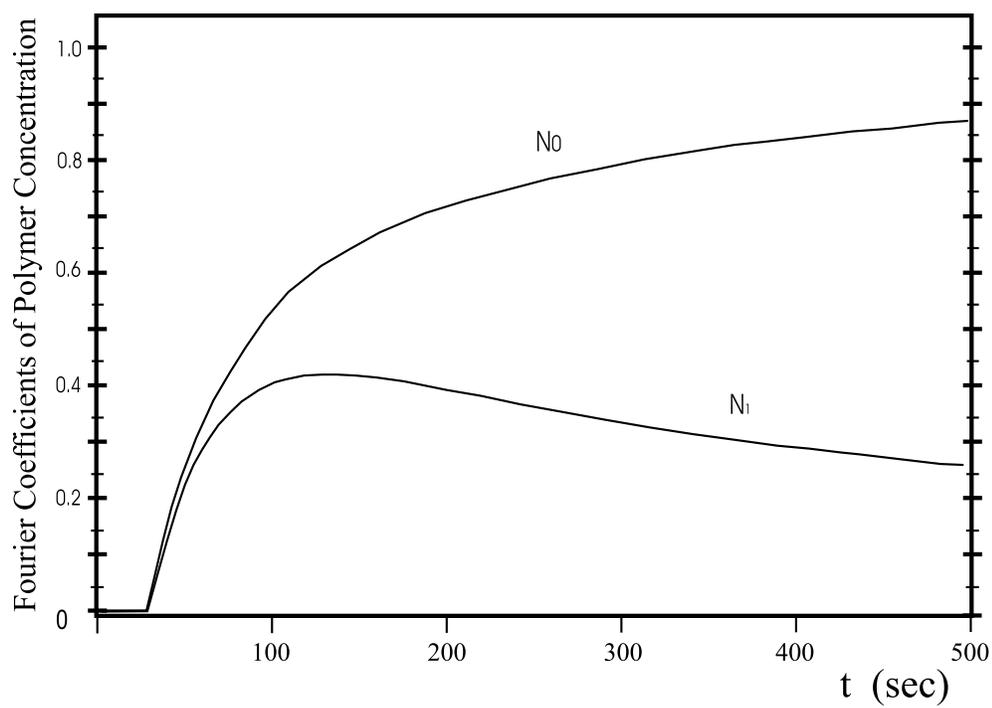


Fig.3.

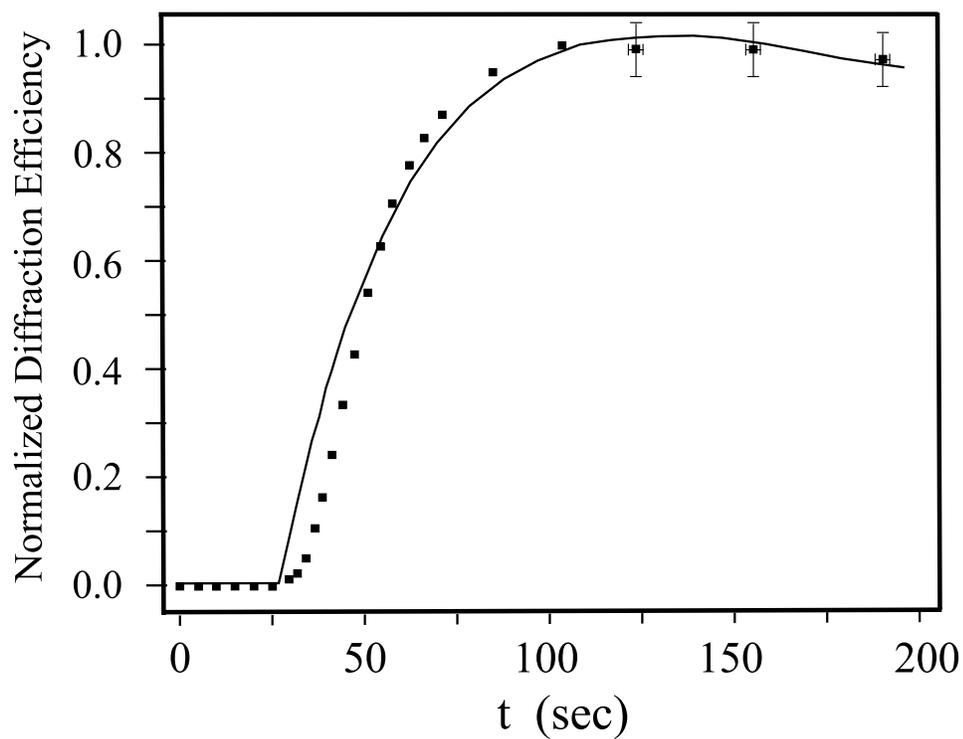


Fig.4.

