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# Spatial transfer of matter as a method of holographic recording in photoformers

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## Abstract

A theoretical model is proposed for hologram recording in photoformers (polymer aggregates with polymerization-diffusion mechanism of refractive index modulation and/or absorption coefficient modulation). The main attention is concentrated on binary (bi-component) photoformers. The latter are a mixture of monomers (or monomer and neutral component) with different refractive indexes  $n_1 \neq n_2$  or absorption coefficients  $\alpha_1 \neq \alpha_2$ . The importance of nonlinear diffusion under inhomogeneous photopolymerization is underlined. The generalization of the Fick's law for diffusion in the systems with the phase transformations of the mixture components is discussed. The holographic technique is successfully used for experimental evaluation of some photopolymer parameters: polymer chain termination order, diffusivity, etc. © 2000 Published by Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Recently, polymer materials have been investigated as the media for volume phase hologram recording [1–6]. The interest in photopolymer media is due to their practical advantages, such as relative cheapness, high diffraction efficiency of the recorded gratings and absence of the ‘wet’ development process.

Among the variety of photopolymers there exist materials, where the hologram recording involves a spatial transfer of several molecular components [3–5]. We call these materials, in what follows, photo-

formers (PF). The distinguishing features of photoformers are:

1. the mixture consists of at least two components (monomers) that photopolymerize independently, with substantially different rates;
2. the refractive indices (or absorption coefficients) for the components are different; and
3. spatial mass transfer takes place during the spatially inhomogeneous polymerization process when the mixture is exposed to light fringes.

Mutual diffusion of the components or local shrinkage of the materials during polymerization could cause mass transfer. Both the refractive index  $n(\mathbf{r}, t)$  and absorption coefficient  $\alpha(\mathbf{r}, t)$  can be modulated in this way. This means that the light fringes

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can produce phase and amplitude holograms in photoformers.

The spatial transfer of components was suggested as a mechanism of hologram recording in Ref. [5]. A number of papers devoted to the theoretical description of hologram recording in photopolymers has been published during the last decade [7–10]. The variety and complexity of photochemical processes, however, makes any attempt to create a general theory very difficult. Different classes of polymers need different approaches and different descriptions.

The present work is devoted to the development of a theoretical model of hologram formation in photoformers with the polymerization-diffusion mechanism of spatial separation of components (the composition PPC-488 [4] is considered as an example).

The structure of the article is as follows: First we formulate the set of rate equations describing the sequence of chemical transformations in the considered mixture under the influence of light, discussed in Section 2. Then we underline the nonlinear nature of the diffusion for the considered chemical reactions and develop the relevant description in Section 3. A complete set of equations is derived in Section 4 for the description of photoformer photopolymerization. Next, Section 5 is devoted to the description of light-induced changes of optical parameters and interrelate the refractive index with the densities of certain chemical substances. Finally, in Sections 6 and 7 the results of computer simulation are displayed and compared with the experimental data.

## 2. Theoretical description of photopolymerization process

In its initial state, a photoformer consists of a liquid mixture of two monomers (oligomers)  $M_1$ ,  $M_2$ . To specify monomer properties we suppose monomer  $M_1$  is characterized by a high polymerization rate and  $M_2$  by a low rate. Under illumination of an active layer, monomer  $M_1$  polymerizes first in the fringe maxima. The polymer  $P_1$  being formed from  $M_1$  is thermodynamically incompatible with monomer  $M_2$ . For this reason, monomer  $M_2$  is forced out of high intensity regions. As a result, the

relative concentration of  $M_2$  decreases in the interference fringe maxima. In a final stage (after long-term illumination), the photoformer turns to a solid phase totally.

As a special case of the binary system we examine a photoformer consisting of a mixture of monomer  $M$  and liquid neutral component  $N$ . The molecules of the neutral component do not form chemical bonds under the influence of light, but can move in space at a macroscopic distance that is comparable with the light wave length. Note that the neutral component of the photoformer can be considered as a photopolymer component with a zero polymerization rate.

If the optical parameters of the mixture components are different, the modulation of refractive index  $n(\mathbf{r}, t)$  or absorption coefficient  $\alpha(\mathbf{r}, t)$  appears as a result of the spatial redistribution of the initial components. Such a photoformer layer can be used as a medium for holographic recording. It should be noted that if the polymerization process is finished, the further transport of the mixture components is impossible. Thus, the stability of the recorded hologram can be ensured.

In view of the complexity of the system, the theoretical description of the dynamics of hologram recording inevitably requires certain approximations. Even in the simplest cases, the real photopolymerization processes are multistage. We believe the following stages should be taken into consideration [11,12]:

1. photo (thermo-) excitation of the initiator:  $C + h\nu \rightarrow k_i(k_i)C^*$ . The molecules  $C$  are transformed into the intermediate (unstable) state  $C^*$  known as ‘radicals in cage’ [13];
2. dissociation of the intermediate state  $C^*$  (so-called ‘going radicals out of cage’) is completed by forming either a free initial radical couple  $C^* \rightarrow k_d 2R_1$  or both the initial radical and macroradical:  $C^* + M \rightarrow k_m R_1 + R_a$  (note that radicals ‘in cage’ can also recombine; the result is the formation of either initiator molecule  $C$  or inactive products  $Q$ :  $C^* \rightarrow k_b C$ ,  $C^* \rightarrow k_q Q$ );
3. formation of the active macroradical  $R_a$  as the result of the reaction between the initial radical  $R_1$  and monomer molecule  $M$ :  $R_1 + M \rightarrow k_a R_{a(1)}$ ;
4. polymer chain growth (consecutive addition of monomer molecules to the macroradical  $R_a$ ):  $R_{a(m)} + M \rightarrow k_p R_{a(m+1)}$ ; and

5. termination of reactionary chain (transformation of macroradicals to the inactive-phase polymer  $P$ ).

The letters above the arrows designate the constants of appropriate reactions.

Therefore, we have to consider more than ten constants of the elementary reactions. However, the following conditions are usually realized which allow simplifying the description of photopolymerization kinetics:

1. reactionary ability of the active macroradical  $R_{a(m)}$  does not depend on the amount of monomer links 'm';
2. the build-up time of (quasi)stationary concentration of both  $R_1$  and  $C^*$  is small compared with the characteristic time of polymerization  $\tau_p$ ; and
3. the expenditure of monomer is negligible in the initiation reactions.

In accordance with the stages mentioned above, the following equations for local kinetics of photopolymerization can be derived [12,14]:

$$\frac{dC}{dt} = -(k_t + k_1 I)C + k_b C^*, \quad (1a)$$

$$\frac{dC^*}{dt} = (k_t + k_1 I)C - (k_d - k_m M - k_b - k_q)C^*, \quad (1b)$$

$$\frac{dR_1}{dt} = (2k_d + k_m M)C^* - k_a R_1 M, \quad (1c)$$

$$\frac{dR_a}{dt} = k_a R_1 M + k_m C^* M - [b_1 R_a + b_2 R_a^2], \quad (1d)$$

$$\frac{dM}{dt} = -[k_p R_a + k_a R_1 + k_m C^*]M, \quad (1e)$$

$$\frac{dP}{dt} = b_1 R_a + b_2 R_a^2. \quad (1f)$$

Here  $k_i$  are the constants of the reactions mentioned above (which are related to the probabilities of relevant transformations).  $P$ ,  $M$ ,  $R_a$ ,  $R_1$ ,  $C^*$  stand for the volumetric parts (normalized concentrations) of polymer, monomer, active macroradicals, initial radicals and molecules of the initiator in an intermediate state ('radicals in cage'), respectively. It should be mentioned that all the stages of the transformations, except the initiator dissociation, occur without the assistance of light quanta. It was taken into consider-

ation in Eqs. (1d) and (1f) that the chain termination reaction can take place within both the monomolecular mechanism (with coefficient  $b_1$ ) and the bimolecular one (with coefficient  $b_2$ ). Note also, that under typical conditions, the following inequality holds:

$$C + C^* + R_1 \ll M + P + R_a. \quad (2)$$

In agreement with the experimental data [11–14], both the build-up time of the steady-state concentration of initial radicals  $R_1$  and the lifetime of initiator molecules in the intermediate state are typically much smaller than the characteristic time of a polymerization process. Therefore the states of  $R_1$  and  $C^*$  can be considered below as (quasi) stationary ones:

$$\frac{dR_1}{dt} \approx \frac{dC^*}{dt} \approx 0. \quad (3)$$

The parameters  $b_{1,2}$  are in fact not constant, but depend on the stage of the reaction [15,16]. Therefore, a more convenient term 'function of chain termination' will be used hereinafter.

The evaluation of reaction constants and the functions of chain termination are the special problems usually solved by traditional methods (viscosity dynamics analysis, dilatometric measurement analysis, etc. [14,16]). To simplify the processing of the experimental data the model approximations for chain termination functions can be introduced. Coefficient  $b_2$  is the rate of bimolecular recombination process (when polymer molecule formation is the result of the coupling of two macroradicals). Using the chain model for a long polymeric molecule, it is reasonable to assume that the mobility of the active tips has an activation nature. The presence of inactive components near the macroradical active tip hinders the movement of the latter, creating additional potential barriers. These conditions can be described as the increase of activation energy  $E_a$  if the volumetric part of the high-molecular components grows.

As polymer macroradicals differ from polymer molecules only in terms of the properties of a terminal tip (i.e., the presence or absence of an active radical group), function  $b_2$  has to depend on the sum  $P_\Sigma = P + R_a$ . Supposing for the sake of simplicity that  $E_a(P_\Sigma) = E_a^0 + a_1 P_\Sigma$ , we can obtain the approximation for the bimolecular recombination function:

$$\begin{aligned} b_2(P_\Sigma) &= c_2^0 \exp(-E_a(P_\Sigma)/k_0 T) \\ &= b_2^0 \exp(-\gamma P_\Sigma), \end{aligned} \quad (4)$$

where  $T$  is the temperature of the system and  $\gamma = a_1/k_0T$ .

Admixtures and/or ‘capture’ of active macroradicals by surrounding inactive molecules can cause the monomolecular recombination.

The single-monomer media (without shrinkage) can be used for hologram recording only in dynamic regime. This peculiarity can be explained in the following way. In photopolymers, the optical characteristics  $n_m$ ,  $\alpha_m$  of the liquid phase (monomer, oligomer) usually differ from those of the solid (polymer) phase  $n_p$ ,  $\alpha_p$  ( $n_i$ ,  $\alpha_i$  are refractive and absorption indexes of the  $i$  phase). When recording a hologram, the light intensity distribution consists of alternating maxima and minima. The polymer concentration  $P$  becomes higher in bright regions of fringes and therefore the refraction index becomes spatially modulated. However, this index modulation disappears in the steady state (large exposure time) since sooner or later all the matter is transformed into a homogeneous (polymer) phase.

### 3. Mutual diffusion as matter transfer mechanism

A mixture of a few non-copolymerizing monomers can be used to record the holograms which are stable in the stationary state. For that the monomers should have substantial difference in polymerization rates and small chemical affinity.

Further, we consider the mixture to be consisting of two monomers only. One of them (with volume fraction  $M_1$ ) polymerizes quickly (the characterized time is  $\tau_{p1}$ ), and the other (with volume fraction  $M_2$ ) polymerizes slowly (the characterized time is  $\tau_{p2} \gg \tau_{p1}$ ). In the case of hologram recording, component  $M_1$  polymerizes and at initial recording stage ( $t \leq \tau_{p1}$ ) turns into polymer  $P_1$  in the regions of maximum illumination. Then, component  $M_2$  is forced into the minimum illumination regions, where it will be transformed into the solid (polymer) phase  $P_2$  some later (when  $t > \tau_{p2} \gg \tau_{p1}$ ). If the optical characteristics of mixture components are not the same, the obtained inhomogeneous polymer material is a holographic grating that is stable at  $t \rightarrow \infty$ . As the copolymerization effect decreases the modulation depth of the optical constants, monomers  $M_{1,2}$  have

to be chosen from the set of materials being polymerized independently.

The physical reason for spatial transfer of the mixture components under inhomogeneous polymerization can be explained in the following way. The equilibrium condition of two liquid components with volume fraction  $M_1$  and  $M_2$  is:

$$\begin{aligned} M_1(\mathbf{r}_a, t)/M_2(\mathbf{r}_a, t) &= M_1(\mathbf{r}_b, t)/M_2(\mathbf{r}_b, t) \\ &= \text{const}, \end{aligned} \quad (5)$$

where  $\mathbf{r}_a$  and  $\mathbf{r}_b$  are coordinates of physically infinitesimal elements of the volume that accept mutual flow of components. Note that diffusion is the only physical reason of intermixing if convection is absent. It is possible to use the term ‘interdiffusion’ when the considerable amount of both components is interchanged.

The condition of volume conservation requires that the total matter flow is absent, i.e.,  $\mathbf{j}^{M1} + \mathbf{j}^{M2} = 0$ , where  $\mathbf{j}^{M1}$ ,  $\mathbf{j}^{M2}$  are the flow densities of  $M_1$  and  $M_2$ , respectively. When writing this condition we suppose that solidified polymer fractions  $P_1$  and  $P_2$  are motionless. The long molecules of macroradicals  $R_{a1}$ ,  $R_{a2}$  are also supposed to be motionless, therefore we can consider one of two flows only, for instance  $\mathbf{j}^{M1}$ . Within the diffusion mechanism of matter transfer,  $\mathbf{j}^{M1}$  depends on both the volume fractions  $M_{1,2}$  and their gradients  $\nabla M_{1,2}$ . Taking into account the first derivatives only, it is possible to obtain:

$$\mathbf{j}^{M1} = D_1^f(M_1, M_2) \nabla M_1 + D_2^f(M_1, M_2) \nabla M_2. \quad (6)$$

Of course, in the steady state,  $\mathbf{j}^{M1,2} = 0$ , but it does not mean that in this case  $\nabla M_{1,2} = 0$ . This feature can be explained in a following way. For inhomogeneous polymerization the volume fractions of solidified components becomes spatially dependent  $P_{1,2} = P_{1,2}(\mathbf{r})$  and therefore the total concentrations of movable components also become spatially dependent. As we neglect possible shrinkage of the material, the volume conservation law leads to the normalization condition:

$$M_1(\mathbf{r}, t) + M_2(\mathbf{r}, t) + P_{\Sigma 1}(\mathbf{r}, t) + P_{\Sigma 2}(\mathbf{r}, t) = 1, \quad (7)$$

where  $P_{\Sigma 1,2}(\mathbf{r}, t) = P_{1,2}(\mathbf{r}, t) + R_{a1,2}(\mathbf{r}, t)$  are the volume fractions of the immobile components. Taking into consideration Eq. (2), the contributions of both

the initiator  $C$  and initial radicals  $R_1$  are to be neglected in the equations of conservation of volume.

Coefficients  $D_1^f$  and  $D_2^f$  are not independent. To show this we consider the equilibrium (steady) state  $\mathbf{j}_e^{M_1} = D_1^f(M_{1,2}^e)\nabla M_1^e + D_2^f(M_{1,2}^e)\nabla M_2^e = 0$ . For this case, it follows from Eq. (5) that  $\nabla[M_1^e/M_2^e] = 0$  or  $-M_2^e\nabla M_1^e + M_1^e\nabla M_2^e = 0$ . (8)

Comparing Eqs. (6) and (8) one can conclude that  $D_1^f = -D_0M_2$ ,  $D_2^f = D_0M_1$ , where  $D_0$  is the diffusion constant of the system. The signs of both terms in Eq. (6) were determined by comparison with the Fick's law for special cases. The result can be generalized for the case of nonequilibrium states. Finally, the total flow of component  $M_1$  can be written in the following form taking into consideration the interdiffusion effect:

$$\mathbf{j}^{M_1}(\mathbf{r}, t) = D_0 [M_1(\mathbf{r}, t)\nabla M_2(\mathbf{r}, t) - M_2(\mathbf{r}, t)\nabla M_1(\mathbf{r}, t)]. \quad (9)$$

We emphasize that the new diffusion law (9) is essentially nonlinear (second order nonlinearity). Under certain conditions, however, this nonlinearity may be only apparent. Consider, for example, a special case of chemically inactive materials (i.e., if components  $M_{1,2}$  do not undergo photochemical transformations and can only diffuse). Then, the conservation condition  $M_1 + M_2 = 1$  holds, reducing Eq. (9) to the usual Fick's law [17]:

$$\mathbf{j}^{M_1}(\mathbf{r}, t) = -D_F\nabla M_1(\mathbf{r}, t). \quad (10)$$

It is obvious that the diffusivity in this case coincides with that in Fick's law. It follows from the example that the diffusion law tends to become nontrivial (nonlinear) only if the third substance is present.

Of course, Eq. (9) can be formally given in a form similar to Fick's law:

$$\mathbf{j}^{M_1}(x, t) = -D_{ef}(M_1, M_2)\partial M_1(x, t)/\partial x, \quad (11)$$

although an effective diffusivity appears instead of  $D_F$

$$D_{ef}(M_1, M_2) = D_0 \left[ M_2 - M_1 \frac{\partial M_2 / \partial x}{\partial M_1 / \partial x} \right], \quad (12)$$

which depends on the degree of polymerization. We restricted ourselves above, for the sake of simplicity,

to consideration of the one-dimensional case and have taken into account the conservation law (7). As follows from Eq. (12), the value of  $D_{ef}(M_1, M_2)$  depends on the concentrations even if  $D_0 = \text{const}$ . It is also clear that the dependence of  $D_0$  on component concentration is equivalent to a higher order nonlinearity of the diffusion. Therefore, our restriction  $D_0 = \text{const}$  in Eq. (9) is not equivalent to  $D_F = \text{const}$  in Fick's law (10). It should be mentioned, that the diffusivity  $D_{ef}$  [12,14,16] can change their values tens and hundreds of times when measured in the course of the polymerization.

Let us remind that according to their definitions the values  $M_{1,2}$  can vary only within the range  $0 \leq M_{1,2} \leq 1$ .

#### 4. Photoformer polymerization equations

In this section the photopolymerization Eqs. (1) are generalized for the case of diffusion in multicomponent system.

The transfer kinetics of any component are defined by the usual continuity equation:

$$\frac{\partial M_{1,2}(\mathbf{r}, t)}{\partial t} + \text{div } \mathbf{j}^{M_{1,2}}(\mathbf{r}, t) = S_{1,2}(\mathbf{r}, t), \quad (13)$$

where  $S_{1,2}$  are source functions.

The volume fraction of initiator  $C$  is considered to be small:  $C \ll 1$ , so that it has been neglected in the conservation law (7). Only one initiator  $C$  is considered to be interacting with different monomers. It can form different active radicals labeled  $R_{a1}$ ,  $R_{a2}$ . In what follows, we will consider  $R_{a1,2}$  radicals that interact only strictly selectively with their 'own' monomers (i.e., no copolymerization occurs). Then, for the case of two-component mixture Eqs. (1) can be generalized as follows (see Appendix A):

$$\frac{\partial P_{\Sigma 1,2}}{\partial t} = k_{p1,2} R_{a1,2} M_{1,2}, \quad (14a)$$

$$\frac{\partial M_{1,2}}{\partial t} = -k_{p1,2} R_{a1,2} M_{1,2} + D_0 [M_{2,1} \Delta M_{1,2} - M_{1,2} \Delta M_{2,1}], \quad (14b)$$

$$M_1 + P_{\Sigma 1} + M_2 + P_{\Sigma 2} = 1, \quad P_{\Sigma 1,2} = P_{1,2} + R_{a1,2}. \quad (14c)$$

If the initiator volume fraction does not depend on the intermixing of monomer components, a spatially local equation such as Eq. (A.1b) can be written for each of radicals  $R_{a1}$  and  $R_{a2}$ , but with the different material constants. Both the polymer molecules and active radicals being large, their diffusion can be neglected. Diffusion of both  $C^*$  and  $R_1$  is also not important, because of the small lifetime of those states.

The initiator  $C$  is considered to be common for both of the monomers, and its dissolubility is supposed to be the same for both of the monomers. Thus, we can write the initiator balance equation in the following form:

$$\frac{\partial C}{\partial t} = -k_c CG(M_1, M_2)[I + I_t] + D_c \Delta C. \quad (15)$$

The function  $G(M_1, M_2)$  is defined in Appendix A.

Next, the photoformers with a neutral component (being one particular case of a binary system) are to be considered. The neutral component is a liquid which is not dissolved by polymers, but it can diffuse in accordance with the results of Section 3. Then under the approximation (2), the equations for photoformers with a neutral component take the following form:

$$\begin{aligned} \frac{\partial N(\mathbf{r}, t)}{\partial t} &= D_0 [M(\mathbf{r}, t) \Delta N(\mathbf{r}, t) - N(\mathbf{r}, t) \Delta M(\mathbf{r}, t)], \\ & \quad (16a) \end{aligned}$$

$$\tau_p^0 \frac{\partial P_\Sigma(\mathbf{r}, t)}{\partial t} = R'_a(\mathbf{r}, t) M(\mathbf{r}, t), \quad (16b)$$

$$\begin{aligned} \tau_r^0 \frac{\partial R'_a(\mathbf{r}, t)}{\partial t} &= C'(\mathbf{r}, t) F(M) [1 + I(\mathbf{r}, t)/I_t] \\ &\quad - L_1(P_\Sigma) R'_a(\mathbf{r}, t) - L_2(P_\Sigma) R_a^2(\mathbf{r}, t), \\ & \quad (16c) \end{aligned}$$

$$\begin{aligned} \tau_c^0 \frac{\partial C'(\mathbf{r}, t)}{\partial t} &= -C'(\mathbf{r}, t) G(M) [1 + I(\mathbf{r}, t)/I_t] \\ &\quad + D_c \tau_c^0 \Delta C'(\mathbf{r}, t), \\ & \quad (16d) \end{aligned}$$

$$P_\Sigma(\mathbf{r}, t) + M(\mathbf{r}, t) + N(\mathbf{r}, t) = 1, \quad (16e)$$

where  $L_1(P_\Sigma) = b_1(P_\Sigma)/[I_t k_r b_2^0 C_0]^{1/2}$ ,  $L_2(P_\Sigma) = b_2(P_\Sigma)/b_2^0$ , and  $N$  is the volume fraction of the

neutral component. The motionless components (polymer  $P$  and macroradicals  $R_a$ ) enter equations only as the sum  $P_\Sigma = P + R_a$ . The concentrations of both the initiator and radicals are normalized as follows:  $C' = C(\mathbf{r}, t)/C_0$ ,  $R'_a = R_a(\mathbf{r}, t)/R_{a0}$ ,  $R_{a0} = [k_r I_t C_0/b_2^0]^{1/2}$  ( $C_0$  is the initial concentration of the initiator and  $R_{a0}$  is the stationary concentration of active radicals in the dark at  $M=1$ ). The other functions  $F(M)$ ,  $G(M)$  in Eqs. (16) are defined in Appendix A.

The dynamics of the polymerization processes in photoformers is characterized by three parameters: the polymerization constant with the dimension of time  $\tau_p^0 = [I_t k_r k_p^2 C_0/b_2^0]^{-1/2}$ ; the dark lifetime of the active radicals  $\tau_r^0 = [I_t k_r b_2^0 C_0]^{-1/2}$ ; the constant of the initiator dissociation in the dark  $\tau_c^0 = 1/k_c I_t$ .

In general case, the set of Eqs. (16) has to be complemented by the initial conditions:

$$\begin{aligned} M(\mathbf{r}, 0) &= 1 - N_0, \quad N(\mathbf{r}, 0) = N_0 \leq 1, \\ P(\mathbf{r}, 0) &= 0, \quad R'_a(\mathbf{r}, 0) = 1, \quad C'(\mathbf{r}, 0) = 1. \end{aligned} \quad (17)$$

As the molecules of both the monomer and initiator are of comparable size, the diffusivities are suggested to be the same  $D_c \approx D_0$ .

The general set of Eqs. (16) describes the kinetics of polymerization of binary photoformer (with a neutral component) for the systems with the polymerization-diffusion mechanism of mass transfer.

## 5. Kinetics of holographic grating record

Two types of photopolymer materials were used in our experiments for holographic recording. First, mixtures of type PP-A (see Table 1) were used, which consist of materials of the dimethacrylate/ethylene glycol group [4,18,19] with the addition of a small amount of photopolymerization initiator. As all the monomers (oligomers) of the mixture copolymerize, this medium is considered to be an ordinary photopolymer.

Second, modified PPC-488 compositions (see Table 2) were investigated, which were obtained by admixing an unpolymerizable material (bromonaphthalene) [4,19] and PP-A. This medium belongs to binary photoformers with a neutral component. The optimum volume fraction  $N$  of the neutral com-

Table 1  
Ordinary photopolymer PP-A

Component	Composition	Weight share (%)	Refractive index
Monomer ( <i>M</i> )	Mixture of acrylic oligomers	98.0–99.9	1.478 (liquid), 1.516 (polymer)
Initiator ( <i>C</i> )	System based on $\alpha$ -diketone	0.1–2.0	–

ponent was 43%, but it was varied over the range from 10% up to 60% if necessary. Recording layers with a thickness of  $h_0 = 10\text{--}100\ \mu\text{m}$  were formed between two glass plates by means of calibrated spacers.

In the experiments, only fresh mixtures were used, pre-illuminated by the spatially homogeneous light from a mercury lamp (prepolymerization) to deactivate the inhibitors (among them, dissolved oxygen [18,19]).

To record a transmission hologram, the photopolymer layer was illuminated by two coherent beams of an argon laser (wavelength  $\lambda = 488\ \text{nm}$ ) with intensities  $I_1$  and  $I_2$ . Both beams impinged upon the layer symmetrically at an angle  $\theta_0$  to normal ( $z$ -axis). The diffraction efficiency of the grating was monitored with a He–Ne laser beam ( $\lambda = 632.8\ \text{nm}$ ) passing through the photopolymer layer at the Bragg angle  $\theta_B$ . We neglect possible self-diffraction effects leading to the dependence of light fringes on the propagation coordinate because two beams with identical intensities are used with the bisectrix parallel to the layer normal. In this case, the distribution of light intensity inside the active layer substantially depends on only one spatial variable  $x$

$$I(\mathbf{r}, t) = I_0 f(x), \quad f(x) = 1 + m \cos(2\pi x/\Lambda). \quad (18)$$

Here  $\Lambda$  is a grating spacing,  $I_0 = I_1 + I_2$  is the total intensity of the beams and  $m = 2\sqrt{I_1 I_2}/I_0$  is the

fringe visibility. The axis  $x$  is chosen at the plane of the beams crossing.

The hologram recording in the photopolymer is a nonlinear process, i.e., the refractive index is generally a nonlinear function of the light intensity  $I(\mathbf{r}, t)$ . The profile of the refractive index  $n(\mathbf{r}, t)$  therefore contains several Fourier harmonics:

$$n(\mathbf{r}, t) = \sum_l n_l^f(t) \exp(i2\pi l x/\Lambda), \quad (19)$$

$$l = 0, \pm 1, \pm 2, \dots$$

If the thickness of a photosensitive layer  $h_0$  meets the requirement  $h_0 \lambda \geq \Lambda^2$  [20], the reconstructed image depends only on the first harmonic of refractive index distribution  $n_1(t) = 2|n_1^f(t)|$ .

The kinetics of temporal variation of the refractive index contains information on photochemical processes and on interdiffusion in photoformers that can be obtained from the diffraction efficiency  $DE(t)$  of a holographic grating (see Fig. 1). In particular, for the case of transmission phase holograms (realized in our experiments), the first harmonic  $n_1$  can be found using the Kogelnik formula [20,21].

In the materials under investigation two processes can contribute to hologram formation in the steady state ( $t \rightarrow \infty$ ):

- spatial redistribution of mixture components;
- inhomogeneous shrinkage leading to surface relief formation or to appearance of microcavities in the bulk of the material.

Table 2  
Binary photopolymer PPC-488

Component	Composition	Weight share (%)	Refractive index
Monomer ( <i>M</i> )	Mixture of acrylic oligomers	55	1.478 (liquid), 1.516 (polymer)
Neutral component ( <i>N</i> )	Bromonaphthalene	43	1.660
Initiator ( <i>C</i> )	System based on $\alpha$ -diketone	2.0	–

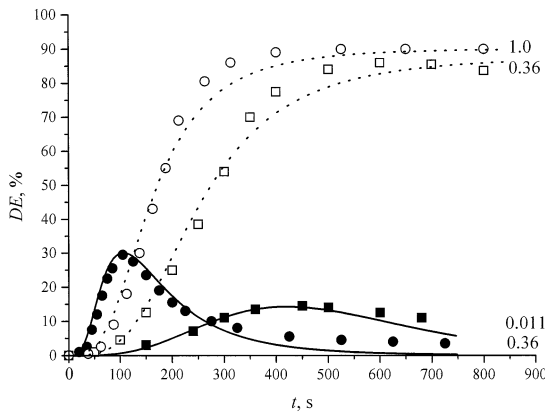


Fig. 1. Kinetics of hologram diffraction efficiency for the photoformer PPC-488 (open dots and open squares) and ordinary photopolymer PP-A (filled dots and filled squares). Numbers at the curves are the light intensity  $I_0$  (mW/cm<sup>2</sup>). The layer thickness is  $h_0 = 20 \mu\text{m}$  and the fringe spacing is  $\Lambda = 1 \mu\text{m}$ . Lines represent the best fit to the theory for the set of parameters given in Table 3.

It should be noted that in the mixture with no neutral component (PP-A) the first of two processes mentioned above does not occur at all. Nevertheless, the experimentally measured steady state diffraction efficiency is in this case 10–20 times smaller compared to binary photoformer PPC-488 (i.e., a mixture of PP-A with the neutral component). In our opinion, this proves that the main process of grating formation in PPC-488 is related to the spatial redistribution of the mixture components. This justifies our further calculations where the shrinkage is neglected.

It should be emphasized that the relative smallness of the shrinkage is related to the special features of the materials used. In particular, the difference of the refractive indexes of a neutral medium ( $n_n^0$ ) and polymer ( $n_p^0$ ) for PPC-488 is extremely large and reaches the value  $\Delta n_{\text{max}} = n_n^0 - n_p^0 \approx 0.14$  (see Tables 1 and 2).

**6. Main features of holographic recording in photoformers: Comparison with the experimental data**

For photoformers used in our experiments, the absorption coefficient is small enough that we can consider the phase holograms only. Certainly, the

refractive index of PF is determined by the parameters of mixture components. Using the Lorentz–Lorenz equation, it is possible to obtain the linear approximation:

$$n(\mathbf{r}, t) = n_p^0 P_\Sigma(\mathbf{r}, t) + n_m^0 M(\mathbf{r}, t) + n_n^0 N(\mathbf{r}, t) = n_p^0 + M(\mathbf{r}, t) [n_m^0 - n_p^0] + N(\mathbf{r}, t) [n_n^0 - n_p^0], \tag{20a}$$

and the analogous relations for the Fourier-components

$$n_l^f(t) = M_l^f(t) [n_m^0 - n_p^0] + N_l^f(t) [n_n^0 - n_p^0], \quad l \geq 1, \tag{21b}$$

where

$$X_l^f(t) = \frac{1}{\Lambda} \int_{-\Lambda/2}^{+\Lambda/2} X(x, t) \exp(i2\pi lx/\Lambda) dx, \tag{21c}$$

Here,  $X(x, t)$  is the volume fraction of an appropriate substance ( $P_\Sigma, M, N$ ) and  $X_l^f$  are the Fourier harmonics of the  $l$ th order. Both the polymer and active macroradicals are considered to be motionless components with identical optical properties. From this point of view, they should be characterized by the combined volume fraction  $P_\Sigma = P + R_a$ .

The typical kinetic curves for the amplitude of the first harmonic of the volume fraction of the motionless component  $P_{\Sigma 1}$  and neutral media  $N_1$  are shown in Fig. 2. They have been calculated from Eqs. (16) for  $F(M) = 1, G(M) = 1$  and parameters  $L_1(P_\Sigma) =$

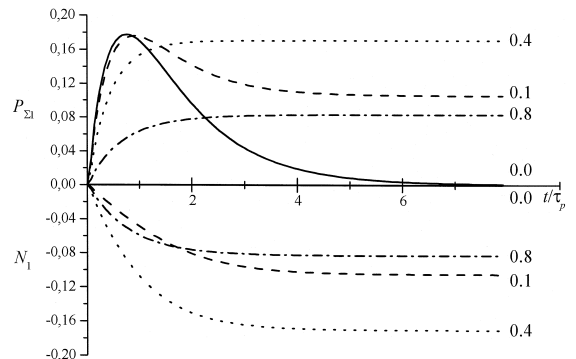


Fig. 2. Temporal variation of first spatial harmonics for the polymer  $P_{\Sigma 1}$  and neutral component  $N_1$ . Numbers at the curves are the initial concentration of the neutral component  $N_0$ .



0,  $L_2(P_{\Sigma}) = 1$ ,  $C'(t) = 1$ ,  $\tau_p^0/\tau_r^0 = 10$ ,  $m = 0.9$ ,  $\tau_p D_0/\Lambda^2 = 10$ . For a small amount of the neutral component, the function  $P_{\Sigma_1}$  (parameter of modulation of the motionless component) demonstrates typically transient behavior with the maximum at  $t \approx \tau_p$  and decrease at  $t \rightarrow \infty$  (it is clear that if  $N_0 = 0$ , then  $P_{\Sigma_1}(t \rightarrow \infty) = 0$ ). Here,  $\tau_p$  is a parameter that characterizes the time scale of polymerization process (see Appendix B).

The (inter)diffusion coefficient  $D_0$  essentially affects the dynamics of  $P_{\Sigma_1}(t)$ ,  $N_1(t)$ . For any nonzero  $D_0$  we get steady state grating ( $P_{\Sigma_1}(t \rightarrow \infty) \neq 0$ ). Of course, its influence on holographic grating recording depends on the scale  $\Lambda$  of the transversal inhomogeneity of the light field. In our experiments, the dependence of  $n_1^{st} = n_1(t \rightarrow \infty)$  on the fringe spacing  $\Lambda$  was investigated in a steady state. As follows from the results shown in Fig. 3, the characteristic diffusion length  $L_D$  is about 5–7  $\mu\text{m}$  (at  $I_0 = 14 \text{ mW/cm}^2$ ). When polymer becomes solid, diffusion is able to transfer a neutral component practically completely from the regions of maximum illumination to the regions of minimum illumination if  $\Lambda \leq L_D$ .

On the contrary, when the fringe spacing is large ( $\Lambda \gg L_D$ ), the diffusion process has not enough time to redistribute the material between maxima and minima of the light pattern during the solidification time. When  $D_0 = 0$ , the case of an ordinary composition is realized, for which  $n_1^{st} = 0$ .

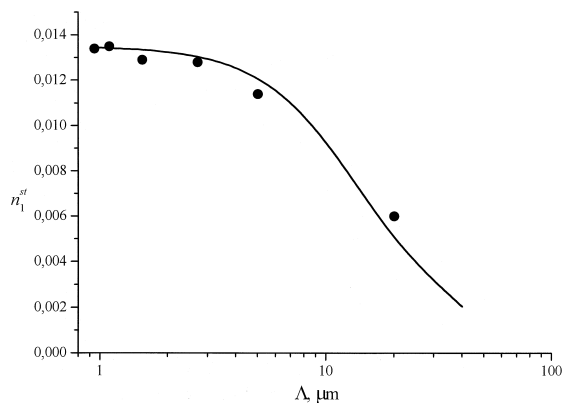


Fig. 3. Amplitude of the refractive index modulation  $n_1^{st}$  versus fringe spacing  $\Lambda$  at  $I_0 = 14 \text{ mW/cm}^2$  for PPC-488. The calculation parameters are given in Table 2 and Table 3. The solid line shows the best fit to the theoretical calculations.

Thus, in the general case, the behavior of the function  $n_1^{st}(\Lambda)$  essentially depends on the value of  $D_0$ . Comparing the refractive index kinetics for different  $\Lambda$ , we found for our case  $D_0 \approx 1.5 \times 10^{-9} \text{ cm}^2/\text{s}$ . On the order of value,  $D_0$  correlates with the usual Fick's coefficient  $D_F$  for diffusion of small molecules in concentrated gels [22].

It should be noted that the predicted decreasing of the recording efficiency with the increase of  $\Lambda$  is confirmed by experimentally observed dependence  $n_1(\lambda)$  for different media with diffusion separation of the components [5].

## 7. Kinetics of holographic grating recording as a method of determination of polymerization process parameters

Determination of the predominant mechanism of the polymer radical recombination in a specific photopolymer is an independent problem. It can be shown that the investigation of the recording kinetics of the holographic gratings in photopolymers can be used as the basis of the method for the determination of the recombination process order.

Suppose, for instance, that the binary recombination prevails (it leads to  $L_1 = 0$ ,  $L_2 \neq 0$  in Eqs. (16)). The polymerization kinetics dependence on the total light intensity  $I_0$  can thus be found. Let us consider the phase (stage) of the polymerization process corresponding, for example, to 90% polymerization. In accordance with Appendix C, the normalized (dimensionless) time of reaching this phase  $t'_{0,9} = \text{const}$  is constant and does not depend on  $I_0$ . This means that the real time of reaching the 90%-polymerization stage depends on  $I_0$  according to the rule:

$$t_{0,9} = \tau_p^0 t'_{0,9} / I_0^{1/2}, \quad (22)$$

(it has been taken into account that  $I_0 \gg I_1$ ). In the case of linear recombination ( $L_1 \neq 0$ ,  $L_2 = 0$ ) it could be similarly found that  $t_{0,9} \sim 1/I_0$ . Thus, it can be determined whether the recombination is linear or quadratic by studying the dependence of  $t_{0,9}$  on  $I_0$ .

The function  $t_{0,9}(I_0)$  was experimentally found for both ordinary photopolymer PP-A and photopolymer PPC-488. The results are shown in Fig. 4 (in double logarithmic scale). As is obvious, a linear approximation can be applied over the medium in-

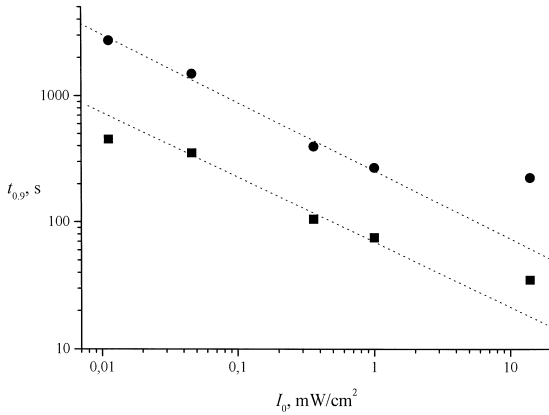


Fig. 4. Pump intensity dependence of characteristic polymerization time  $t_{0.9}$  (time of reaching of 90% level of  $n_1^{\text{st}}$  modulation). Dots are the experimental data for the binary photoformer PPC-488, squares are that for the photopolymer PP-A, the lines are the best fit to linear approximation.

tensity range (over the large intensity range, the assumption of the Appendix C are no more valid). The experimentally determined average tangent of the inclination of  $\ln t_{0.9}$  relative to  $\ln I_0$  is  $\tan \alpha = -0.52 \pm 0.02$ . On the other hand, it follows from Eq. (22) that in the case of binary recombination:

$$\tan \alpha = \frac{\partial(\ln t_{0.9})}{\partial(\ln I_0)} = -0.50. \quad (23)$$

Therefore, we can arrive at the conclusion that bimolecular recombination prevails in the investigated materials PP-A and PPC-488. Thus, linear recombination may be neglected in our calculations, i.e., it can be supposed that  $L_1 = 0$ .

To check the validity of the approximation for the parameter of bimolecular chain termination suggested above (see Eq. (4)), the experiments on the photopolymerization of the PP-A by homogeneous laser radiation beam ( $\lambda = 488$  nm) have been performed. The degree of polymerization of the photopolymer composition was determined by measurement of the refractive index  $\tilde{n}(t)$  (using the interferometric method) for the plane samples investigated.

Let us suppose that the initial refractive index is  $\tilde{n}_1$  and the final one is  $\tilde{n}_2$ . Then, within a linear approximation, the degree of polymerization  $P_\Sigma$  (the volume fraction of all the high-molecular compo-

nents) at the moment of time  $t$  can be found to be  $P(t) = [\tilde{n}(t) - \tilde{n}_1]/[\tilde{n}_2 - \tilde{n}_1]$ . The data obtained allow plotting of the graph of the auxiliary function  $d\eta/dt'$ , where  $\eta(P_\Sigma) = 2(1-P_\Sigma)^{-1/2}$  (see Fig. 5). In the experiment, the light intensity  $I_0$  was chosen in such a way so that the inequalities  $\tau_r \ll \tau_p \ll \tau_c$  hold (this is not complicated if the initiator dissociates slowly, but the polymer radicals decay quickly). In this case, as follows from Eq. (C.1) (see Appendix C):

$$\frac{d\eta(P_\Sigma)}{dt'} = \exp(\gamma P_\Sigma/2). \quad (24)$$

It has been taken into account that  $F(M) = M$ ,  $C = C_0$  and, in absence of a neutral component,  $M = 1 - P_\Sigma$ . One can see from the results shown in Fig. 5 that the theoretical dependence (24) is confirmed well by the experimental data. The slope of the function  $d\eta/dt'$  (taken on the logarithmic scale) allowed us to determine parameter  $\gamma$  in Eq. (4) directly. We found  $\gamma \approx 6.0$  for photoformer PPC-488.

The modulation depth of the refractive index  $n_1^{\text{st}}$ , in a steady state, certainly depends on the presence of a neutral component. The theoretical dependence  $n_1^{\text{st}}(N_0)$  is shown in Fig. 6. In the same figure, the experimental data for the steady state modulation depth of the refractive index  $n_1^{\text{st}}$  are shown. It is clear that, in the absence of a neutral component ( $N_0 = 0$ ), there is no stationary modulation of the refractive index  $n_1^{\text{st}}(N_0 = 0) = 0$ . The same results

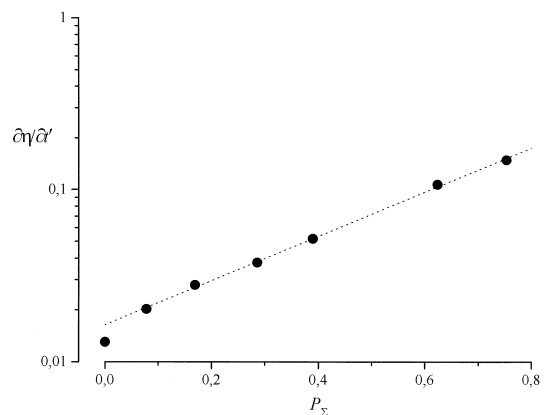


Fig. 5. Dependence of  $\partial\eta/\partial t'$  on the polymer fraction under homogeneous illumination. Dots are the experimental results, the line is the best fit to linear dependence.

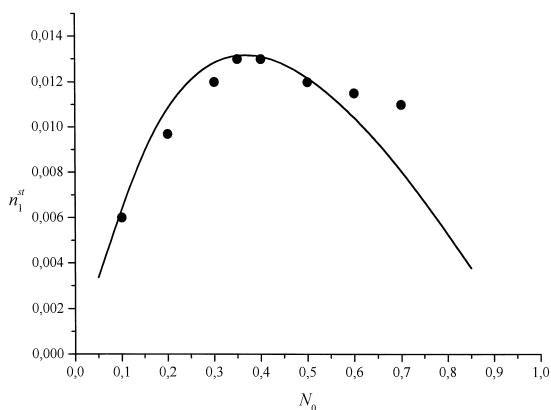


Fig. 6. Neutral component influence on refractive index modulation in PPC-488 (under steady-state conditions). The calculation parameters are given in Table 3. The solid line represents the theoretical results, the dots represent the experimental data.

would also be obtained in the case of  $N_0 = 1$  (i.e., the monomer is completely absent). Thus, we conclude that the optimum composition of mixtures should be about equal concentration  $N_0 \approx M_0 \approx 0.5$ . However the large concentration  $N$  decreases the average rate of polymerization and makes the condition of the spatial modulation  $P_{\Sigma}(r, t)$  worse. Therefore, the optimum value  $N_0^{\text{opt}}$  (that ensures the maximum modulation depth) is less than 0.5. The calculations gave the optimum concentration of a neutral component as being in the range of  $N_0^{\text{opt}} = 0.35$ – $0.45$ , depending on both the recording condition and mixture parameters. This corresponds fairly well to the results of our measurements.

## 8. Conclusion

Photoformers are a special kind of photopolymerizing compositions with essential differences when compared with other photopolymers. The following features should be taken into account for their description:

1. the spatial inhomogeneity of photopolymerization; and
2. the regular (macroscopic) spatial transfer of the mixture components.

For substantial phase transition due to photostimulated polymerization, mass diffusion becomes highly nonlinear. In this case the mutual diffusion of both

components of the mixture takes place and the usual Fick's law has to be changed by the law of nonlinear diffusion.

As a consequence of the large difference of the refractive indexes of movable components ( $n_n^0 - n_p^0 \approx 0.14$ ) the holograms recorded in PPC-488 are characterized by the large diffraction efficiency (up to 90%, see Fig. 1). It is clear that the diffusion processes restrict the minimum values of the spatial frequencies  $\Omega$  of holographic gratings. For example, at  $I_0 = 14 \text{ mW/cm}^2$ , the diffraction efficiency of recorded holograms begins to decrease for  $\Omega < 300 \text{ mm}^{-1}$ . However, the maximum line resolution of PPC-488 is large enough and allows for the recording of information with density up to  $5000 \text{ mm}^{-1}$ .

To study both the polymerization kinetics and spatial transfer of substances in the photoformers, optical (holographic) methods can be used. Based on these methods, it has been shown that the biradical mechanism of reactionary chain termination takes place in PPC-488. The dependence of the chain termination function on polymer concentration is well approximated by the exponential dependence (4) under  $\gamma \approx 6.0$ .

The developed theory describes the main features of holographic grating recording in photoformers and is in good agreement with the experimental data. It allows for the evaluation of such photoformer parameters as dark photopolymerization constant  $I_t$ , diffusivity  $D_0$ , and relaxation times for different processes. The results obtained for both ordinary photopolymer PP-A and binary photoformer PPC-488 are presented in Table 3.

It should be mentioned that our theory describes binary photoformers with the main contribution to holographic recording caused by the polymeriza-

Table 3  
Parameters of photopolymers

Parameter of system	Ordinary photopolymer PP-A	Binary photoformer PPC-488
$D_0$	–	$1.5 \times 10^{-9} \text{ cm}^2/\text{s}$
$I_t$	$6 \text{ }\mu\text{W/cm}^2$	$10 \text{ }\mu\text{W/cm}^2$
$\gamma$	6.0	6.0
$\tau_p^0$	9.3 min.	9.2 min.
$\tau_r^0$	4.3 min.	5.8 min.
$\tau_c^0$	166.7 min.	300.0 min.

tion-diffusion mechanism of mass transfer. Generalization of the present theory by taking into account shrinkage in hologram formation is a subject for further investigations.

### Acknowledgements

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### Appendix A

The simplified system of photopolymerization equations follows from Eq. (1a)–Eqs. (1f), (2) and (3):

$$\frac{dP_{\Sigma}}{dt} = -\frac{dM}{dt}, \quad \frac{dM}{dt} = -k_p R_a M, \quad (\text{A.1a})$$

$$\frac{dR_a}{dt} = k_r CF(M)(I + I_t) - (b_1 R_a + b_2 R_a^2), \quad (\text{A.1b})$$

$$\frac{dC}{dt} = -k_c CG(M)(I + I_t), \quad (\text{A.1c})$$

where

$$I_t = k_t/k_1, \quad k_r = 2k_1 \frac{k_d + k_m}{k_b + k_q + k_d + k_m},$$

$$k_c = k_1 \frac{k_q + k_d + k_m}{k_b + k_q + k_d + k_m},$$

$$F(M) = \frac{k_d + k_m M}{k_b + k_q + k_d + k_m M} \bigg/ \frac{k_d + k_m}{k_b + k_q + k_d + k_m},$$

$$G(M) = \frac{k_q + k_d + k_m M}{k_b + k_q + k_d + k_m M} \bigg/ \frac{k_q + k_d + k_m}{k_b + k_q + k_d + k_m}. \quad (\text{A.2})$$

The system (A.1) describes the polymerization process of the ordinary photopolymer.

The functions  $F(M)$  and  $G(M)$  describe the influence of the monomer on the kinetics of initiator dissociation. They are determined to be monotonous, non-decreasing and satisfying the following relations:  $F(1) = 1$ ,  $G(1) = 1$  and  $F(0) \geq 0$ ,  $G(0) \geq 0$ .

If monomers of a few types are present, the function  $G$  gets the following form

$$G(M_1, M_2, \dots, M_i) = \frac{k_q + k_d + \sum_i k_m^{(i)} M_i}{k_b + k_q + k_d + \sum_i k_m^{(i)} M_i} \bigg/ \frac{k_q + k_d + \sum_i k_m^{(i)}}{k_b + k_q + k_d + \sum_i k_m^{(i)}}. \quad (\text{A.3})$$

We checked from the analysis of photopolymerization dynamics that the following conditions hold for PPC-488

$$k_b + k_q \gg k_m \gg k_d. \quad (\text{A.4})$$

Therefore the approximation following from Eqs. (A.2) and (A.3) is used in the theory:

$$F(M) \approx M, \quad G(M) \approx 1. \quad (\text{A.5})$$

### Appendix B

The set of Eqs. (16) can be solved analytically in the particular case of homogeneous illumination  $I = I_0 = \text{const}$  under the following assumptions: (a) the initiator dissociates slowly, so that  $C \approx C_0$  during the polymerization process; and (b)  $F(M) = 1$ ,  $L_1(P_{\Sigma}) = 0$ ,  $L_2(P_{\Sigma}) = 1$ . Then the solution can be written in the following form:

$$P_{\Sigma}(t) = (1 - N_0) \times \left\{ 1 - \left[ \text{ch}\left((1 + I_0/I_t)^{1/2} t/\tau_r^0\right) \right]^{-\tau_r^0/\tau_p^0} \right\} \quad (\text{B.1a})$$

$$R'_a(t) = (1 + I_0/I_t)^{1/2} \text{th}\left[(1 + I_0/I_t)^{1/2} t/\tau_r^0\right]. \quad (\text{B.1b})$$

As it follows from Eq. (B.1b), the characteristic relaxation time of polymer radical concentration is  $\tau_r(I_0) = \tau_r^0/(1 + I_0/I_t)^{1/2}$ . Note also that for  $t \gg \tau_r$ , the expression (B.1a) can be rewritten in the following form

$$P_\Sigma(t) = (1 - N_0) \times \left\{ 1 - 2^{\tau_r^0/\tau_p^0} \exp\left(- (1 + I_0/I_t)^{1/2} t/\tau_p^0\right) \right\} \quad (\text{B.2})$$

It is evident from Eq. (B.2), the value  $\tau_p(I_0) = \tau_p^0/(1 + I_0/I_t)^{1/2}$  is the characteristic time of the polymerization process (i.e., the process of the accumulation of high-molecular components). This is valid for  $\tau_p > \tau_r$ , what, as a rule, takes place in practice [12,14,23].

As it follows from Eq. (16d), in the case of homogeneous illumination, the characteristic time of initiator dissociation is  $\tau_c(I_0) = \tau_c^0/(1 + I_0/I_t)$ .

## Appendix C

Note first of all, that in a particular case of bimolecular recombination, the system (16) can be written in the form that (formally) does not depend on the writing beam intensities:

$$\frac{\partial N}{\partial t'} = \frac{D_0 \tau_p}{\Lambda^2} \left[ M \frac{\partial^2 N}{\partial x'^2} - N \frac{\partial^2 M}{\partial x'^2} \right] \quad (\text{C.1a})$$

$$\frac{\partial P_\Sigma}{\partial t'} = R_a'' M \quad (\text{C.1b})$$

$$\frac{\partial R_a''}{\partial t'} = \frac{\tau_p}{\tau_r} \left[ F(M) f'(x') - L_2(P_\Sigma) R_a''^2 \right] \quad (\text{C.1c})$$

$$P_\Sigma + M + N = 1 \quad (\text{C.1d})$$

where  $R_a'' = R_a' \sqrt{1 + I_0/I_t}$ ,  $\tau_r = \tau_r^0/(1 + I_0/I_t)^{1/2}$ ,  $\tau_p = \tau_p^0/(1 + I_0/I_t)^{1/2}$ , and the new arguments  $t' = t/\tau_p$ ,  $x' = x/\Lambda$  are introduced.

It was taken into account that, according to the experimental data, the characteristic time of initiator dissociation satisfies inequality  $\tau_c \gg \tau_p$ . It means, we can assume  $C \approx C_0 = \text{const}$  ( $C_0$  is the initial concentration of the initiator) over the range of  $0 < t \leq \tau_p$ .

Let us consider the case of small grating spacing. For  $\Lambda \ll L_D$  the neutral component follows the inhomogeneities of the polymerization process practically without inertia according to the equation

$$M \frac{\partial^2 N}{\partial x^2} = N \frac{\partial^2 M}{\partial x^2}, \quad M = 1 - P - N. \quad (\text{C.2})$$

The solution of Eq. (C.2) can be represented in the following form

$$N(r, t) = N_0 \frac{1 - P_\Sigma(r, t)}{1 - P_{\Sigma 0}(t)} \quad (\text{C.3})$$

where  $P_{\Sigma 0}(t)$  is the amplitude of the zero harmonic of a polymer distribution (that coincides with the volume fraction of a polymer averaged over the grating spacing). The spatial distribution of a function  $f'(x') = 1 + m' \cos(2\pi x')$  (see Eq. (C.1c)) is determined by the effective modulation index  $m' = m/(1 + I_0/I_t)$ . Over the range  $I_0 \gg I_t$ , that we are restricted to  $m' = m$ , and does not depend on  $I_0$ . In this case, the functions  $P_\Sigma(x, t)$ , calculated at different intensities, are similar and differ from each other only by temporal scale, as follows from Eqs. (C.1a), (C.1b), (C.1c), (C.1d) and (C.3).

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