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# Mechanism of surface landscape formation in liquid photopolymerized compositions

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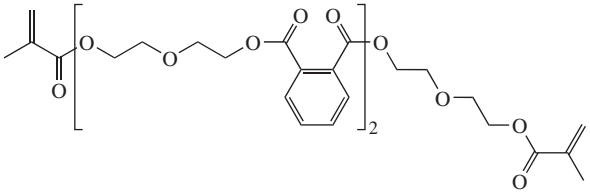
**The spatial modulations of the degree of polymerization of an oligomer in the layer of liquid photopolymerized compositions can initiate diffusion leading to the rise of surface landscape.**

The process of diffusion usually leads to the homogenization of a single-phase system, and it can generate spatial phase separation in two-phase and multiphase systems. Here we propose a new mechanism of diffusion in a single-phase system, when initial spatial modulation of conversion of the oligomer, initiated by photopolymerization, results in an essentially non-uniform spatial profile on the surface of the material.

It is important to emphasise significant difference of proposed mass-transfer mechanism from those leading to spatial phase separation in multiphase systems: there is no driving force for the directed motion of monomers (for example, chemical potential gradient). Instead, mass transfer is provided by diffusion (truly random motion) of the oligomer and its localization at lighten areas with formation of a chemical or physical network. The creation of such a network is the reason of observable rise of landscape on the surface of a thin film.

Along with its theoretical significance, the proposed mass-transfer mechanism is also of considerable practical interest. The effect of directed mass transfer in liquid photopolymerized compositions (PPCs) is widely used to synthesize diffraction optical elements (DOEs).[1–4] To obtain the well-shaped DOE landscape, a half-tone light-pattern with a band structure was prepared. The width of zones ranges from tens of microns to a few millimeters, depending on the aperture and the focal length. The optical density was modulated within each zone, so that a change in the light contrast between dark and light areas varies by a factor of 3–4. UV light projects DOE image on a thin layer (10–600 μm) of PPC. We used isobutyl ester of benzoin as light initiator, and the main component of PPC was the oligomer with the following structure:



During the exposure, the power of radiation was chosen to get an optimal exposure time within the range of 7–10 min. At short exposure time, that is, high power of light flux, a too dense network was formed both in dark and in light areas, hindering the diffusion of the oligomer through the network. At too long exposure times, there was a squashing of the landscape, formed during the transfer of the oligomer from dark zones to light ones. Optimal exposure time was determined to achieve a maximum difference of polymer conversion in light and dark areas.[1–4]

We think that the formation of a landscape by spatially modulated radiation in a thin layer of PPC happened because of the diffusion of oligomer from shaded to lighted areas. Since concentration of free radicals is maximal in lighted areas, these zones correspond to the outflow of the oligomer due to its polymerization with the formation of a polymeric network. Monomers diffuse toward the maxima of the landscape from adjoining areas, which were darker during the exposure. This diffusive process leads to an observable growth of the surface landscape.

We denote by $D_0$ the diffusion coefficient of oligomer in the absence of the network. In dense network, the diffusion of the oligomer is strongly slowed down $D << D_0$, due to the decrease in the size of a cell of polymeric network, and its commensurableness with the size of oligomer molecule. We will simulate the dependence of $D$ on conversion $p$ by the expression $D(p) = D_0\exp[-(p/p_c)^2]$, where $p$ is local conversion

$$p = n/(n + c) \quad (1)$$

and $p_c$ is about critical conversion of network formation. Here, $n(x,t)$ is the local concentration of the network, and $c(x,t)$ is the concentration of the oligomer. Explicit form of the dependence $D(p)$ is not essential for our consideration.

The equation of balance of oligomer concentration $c(x,t)$ has the form:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right) - \frac{\partial n}{\partial t}. \quad (2)$$

Here, the first term describes the effective diffusion of oligomer in the presence of the network, while the second term gives the rate of outflow of oligomer because of its localization in the polymeric network.

In our model, radicals are tightly bound to polymeric network, which is linked to the substrate. Thus, during the exposure time the image of the light-pattern is converted to the corresponding change in the concentration of polymer network. The concentration of free radicals $r(x,t)$, stucked in nodes of the network, is proportional to the concentration of the polymeric network. Therefore, after the exposure (in the shadow mode), the rate of polymerization is proportional to the concentration of polymeric network formed during the exposure.

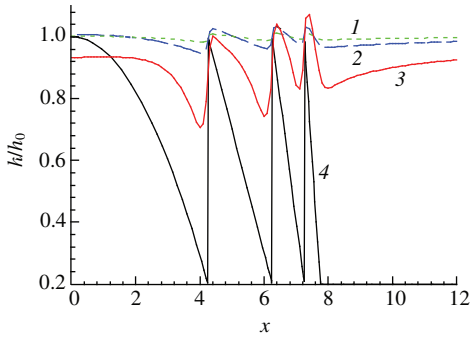



**Figure 1** Calculated profiles $h(x,t)/h_0$ of the thickness of the film as function of coordinate $x$ for three times $t$ (arbitrary units): (*1*) 0.3, (*2*) 1 and (*3*) 8 (we used Maple mathematical engine). The profile of dimensionless radical concentration $r(x)$ is shown by thin line (*4*). Parameters of this plot are: $D_0 = 50$, $k = 0.15$ and $\rho_n/\rho_c = 0.85$. The contrast of the profile $h(x,t)/h_0$ increases with time $t$, saturating at large times because of quick decrease of the diffusion coefficient $D(p)$ with the rise of conversion $p$.

Polymerization of the oligomer takes place only in the presence of free radicals, and the rate of this process is proportional to the product of concentrations of oligomer $c(x,t)$ and free radicals $r(x,t)$:

$$\partial n/\partial t = -knr, \quad (3)$$

where $k$ is the polymerization constant.

The above system of equations has to be solved with boundary conditions of absence of flows through outer surfaces. In the case of thin films, it is possible to ignore a change of the concentration in the direction perpendicular to the film surface. In this case, only coordinate $x$ along the surface comes into equations, and local thickness of the film is determined by the expression

$$h(x,t) = h_0[\rho_n n(x,t) + \rho_c c(x,t)], \quad (4)$$

where $h_0$ is the initial film thickness, $\rho_n$ and $\rho_c$ are surface densities of polymerized and free oligomers, respectively, and $\rho_n < \rho_c$ due to the reduction in the monomer volume as the result of polymerization.

In the case of one-dimensional profile of concentration of free radicals $r(x)$ the numerical solution of equations (2) and (3) for the relation $h(x,t)/h_0$ (4), with local diffusion coefficient $D(p)$, is shown in Figure 1. Thus, the oligomer will diffuse from regions, which were darker during exposure time, to lighter regions.

A similar set of experimental data was obtained.[1–3] The observed time $t = 5$–$10$ h of landscape formation is in good agreement with time estimation $t = L^2/D$ of diffusion to the characteristic scale $L \approx 1$ mm of the surface profile for typical oligomer diffusion coefficient $D \approx 10^{-10}$ m$^2$ s$^{-1}$.

In this work, we found that the diffusion of monomers in thin films can result in directed mass-transfer. This phenomenon is responsible for the formation of a spatially heterogeneous landscape on the surface of thin films, which was observed experimentally in preliminary lighted samples of PPCs. We propose and solve a new theoretical model, which allows optimizing the choice of materials and conditions of synthesis of diffractional optical elements.

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