Optical control of microphase separation of the photopolymerized composition based on oligo(ester acrylates) for the preparation of polymer materials with the nonuniform nanopore distribution

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The possibility of control of microphase separation in the photocured composition bulk with the non-polymerizable component (NC) soluble in the monomer and restrictedly compatible with the polymer was studied for manufacturing polymer materials with the spatially non-uniform nanopore distribution. It is shown by numerical simulation that NC redistribution occurs under the action of radiation with the nonuniform over the surface area intensity distribution in the initial step of photopolymerization when the composition is single-phase. Microphase separation of the composition occurs during polymerization in the regions with an enhanced content of an additive, whereas the composition remains single-phase in the regions with a decreased concentration of NC. After NC removal from the final polymer, a material is obtained in which regions with nanopores and regions of the uniform polymer would coexist. The dependences of the size of these regions on the initial concentration of the neutral component in the composition, diffusion parameters of the polymerized medium, and parameters of actinic radiation were studied. The conclusions of numerical simulation were checked experimentally.

Key words: photopolymerization, multicomponent photopolymerized composition, oligo-(ester acrylates), nanoporous polymer, diffusion redistribution.

Interest in nanoporous polymer materials with specified structure increases at the present time.[1–3] These materials can be used, for example, in the preparation of separation membranes[3–6] and microreactors for the formation of nanoparticles of inorganic compounds,[7] in liquid or gas chromatography,[8] as well as in microelectronics as layers with ultimately low dielectric permeability.[9] In addition, the pore surface can be modified by functional groups or active sites to impart specified properties to a porous material.[2,4–6] This approach makes it possible to solve a series of problems of controlling heterogeneous catalysts,[10] development of new supports for chromatography,[2,4] and manufacturing nanofilters having the effect of selective separation of complicated water—organic mixtures.[5,6]

Porous polymer materials can be formed during curing of compositions based on oligo(ester acrylates) due to the phase separation of components of a polymerized composition.[2,3] We discovered and studied the effect of pore formation during curing of a photopolymerized composition (PPC) based on oligo(ester acrylate) OCM-2 in the presence of a non-polymerizable component (NC).[11] In these systems, the polymerization of oligo(ester acrylate) (OEA) results in the formation of a three-dimensional cross-linked polymer, which is restrictedly compatible with NC. At a small content of an additive to PPC, the system remains single-phase during the whole polymerization process to form a uniform polymer monolith. Microphase separation occurs at a higher content of NC. After NC removal, a monolithic sample with open bound nanopores is formed. However, it should be mentioned that thus synthesized nanoporous materials are rather friable. To prepare efficient filtering membranes from them, it is necessary to improve their strength properties by the introduction of reinforcing elements. This problem can also be solved if one sample simultaneously contains regions with nanopores and without nanopores.

The possibility of optical control of the microphase separation process in PPC based on oligo(ester acrylates) containing NC for the preparation of polymer materials in which regions of uniform polymer alternate with regions containing nanopores is considered in this work.

Results and Discussion

Mechanism of redistribution of PPC components under the action of nonuniform radiation. A wide series of NC forming a true solution with the monomer and restrictedly compatible with the polymer obtained during curing is known for polyfunctional monomers.[12] At a certain content of NC, this can result in the microphase separation of the polymerized medium and, as a consequence, in the formation of a dispersion of NC droplets in the solid polymer.[2,3,11] For example, microphase separation occurs during the curing of PPC based on oligo(ester acrylate) OCM-2 in the presence of methanol at its content in PPC higher than 25 wt.% to form a two-phase system solid polymer—solvent.[11] If a nonuniform distribution of the neutral component concentration is created at the initial stage of polymerization in such a way that regions with enhanced and lowered NC contents would coexist, then a nonuniform polymer monolith can be prepared with the simultaneous coexistence of two regions: in one of them microphase separation occurs, and in the second region the system remains single-phase. The redistribution of components of photosensitive media can be obtained due to diffusion processes that occur in these systems under the action of nonuniform radiation.[13—16] The necessary distribution of the neutral component can be formed, for example, by the photoinitiation with the space-nonuniform periodical distribution of the intensity in the following form:

$$I(x´,y´) = I_0 \cdot I´(x´,y´) =$$
$$= I_0 \cdot (1 + \Delta I \cdot \cos(2\pi \cdot u \cdot x´ \cdot L)), \qquad (1)$$

where $x´ = x/L$ and $y´ = y/L$ are dimensionless coordinates, I_0 is the average intensity, ΔI is the depth of light field modulation, $u = 1/d$ is the spatial frequency of intensity distribution, d is the period of intensity distribution, and L is the length of analyzed realization. This intensity distribution can easily be obtained due to the interference of two planar waves.

In the course of photopolymerization NC is redistributed over the composition volume and is not involved in the chemical reaction and, therefore, its total amount in the PPC composition remains unchanged. At the same time, the monomer participates not only in mutual diffusion processes but, unlike the neutral component, is also consumed to the formation of polymer molecules. If neglecting the change in the PPC volume (in shrinkage processes and dissolution) and a difference in the densities of the composition components, at the initial stage of polymerization, when the monomer conversion is low and PPC is single-phase at any content of the neutral component, processes of component redistribution of this composition during its curing can be studied using the multicomponent diffusion model.[16] In terms of this model, the system of equations describing changes in the concentrations of the PPC components (monomer, polymer, and NC) is the following:

$$\partial N/\partial t´ = \beta_{NM}(M\Delta N - N\Delta M) + \beta_{PN}(P\Delta N - N\Delta P) +$$
$$+ (\beta_{PN}/P^*)(N(\nabla P)^2 - P(\nabla N \nabla P),$$

$$\partial M/\partial t´ = \beta_{NM}(N\Delta M - M\Delta N) + \beta_{MP}(P\Delta M - M\Delta P) +$$
$$+ (\beta_{MP}/P^*)(M(\nabla P)^2 - P(\nabla M \nabla P) -$$
$$- \gamma \cdot I´(x´,y´) \cdot M(-\ln(M/(1 - N)^{(\gamma - 1)/\gamma})), \qquad (2)$$

$$P(M, N) = 1 - N - M,$$
$$\beta_{PN}(P) = \beta_{NM}\exp\{-P/P^*\},$$
$$\beta_{MP}(P) = \beta_M\exp\{-P/P^*\},$$

where M, P, and N are the mass fractions of the monomer, polymer, and neutral component, respectively; $t´$ is dimensionless time; and P^* is the fraction of the polymer at which the characteristic increase in viscosity is observed. The main dimensionless parameters of the model are determined by the following equations:

$$\beta_M = t_P/t_D = H_0 \cdot D_M/(I_0 \cdot L^2),$$
$$\beta_{NM} = H_0 \cdot \alpha_{NM}/(I_0 \cdot L^2), \qquad (3)$$

where $t_P = H_0/I_0$ is the characteristic polymerization time, $t_D = L_2/D_M$ is the characteristic diffusion time, D_M is the diffusion coefficient of the monomer, α_{NM} is the coefficient characterizing mutual diffusion of the NC and monomer, and H_0 and γ are the parameters determining the contrast of the polymerized medium.

This model makes it possible to calculate numerically the instant spatial distribution of components in a thin layer of the PPC during initiation with photoirradiation having a specified intensity distribution. The system of Eqs (1) and (2) with free boundary conditions was solved using the "explicit scheme" for the case of periodical intensity distribution $I(x´,y´)$.[17] Since the intensity distribution $I(x´,y´)$ is periodical only by the coordinate $x´$ and is constant by another coordinate ($y´$), then in this case one can be restricted by the solution of a one-dimensional problem by the coordinate $x´$. It should be mentioned that the dimensionless parameters β_M and β_{NM} (see Eq. (3)) combine both diffusional properties of the polymerized system (D_M and α_{NM}, respectively) and the value of average intensity I_0 of the initiating radiation $I(x´,y´)$.

The results of computer simulation at the parameters $\gamma = 4$, $P^* = 0.1$, $\beta_M = 4 \cdot 10^{-7}$, $\beta_{NM} = 4 \cdot 10^{-6}$, $L = 500$ µm, $\Delta I = 0.99$, and $u = 0.256$ µm^{-1} ($d = 3.9$ µm) are presented in Fig. 1. The initial distributions $P(x´)$ and $N(x´)$ were specified constant: $P_0 = 10^{-6}$, $N_0 = 0.2$. It is seen that polymerization occurs with a higher rate in the regions
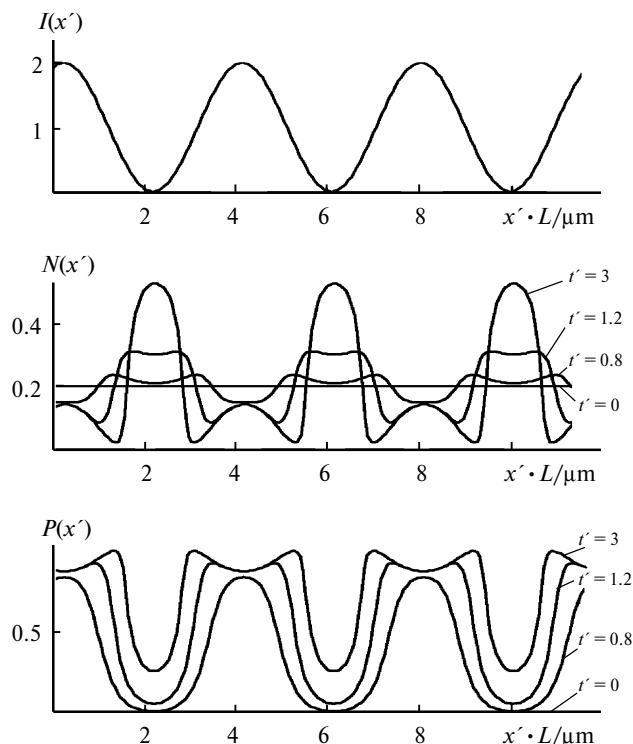
Fig. 1. Distribution of the initiating radiation intensity $I(x')$ and characteristic distributions $N(x')$ and $P(x')$ in different steps of PPC polymerization.

where the actinic radiation intensity is higher. Polymerization results in the redistribution of the PPC components: a neutral additive is displaced from the regions with high conversion to the regions with a lower content of the polymer. The most efficient redistribution of the PPC components is observed in the regions, where the intensity distribution gradient $I(x',y')$ of the incident light is maximum. As a result, in these regions of the content of NC decreases substantially compared to the initial value N_0 and the conversion $P(x')/(1 - N(x'))$ approaches a limit-

ing value. At the same time, the fraction of NC increases by several times in the regions where the initiating radiation intensity is low and, correspondingly, the conversion is lower.

The concentration redistribution of the PPC components occurs in the direction perpendicular to the gradient of the actinic radiation intensity. Correspondingly, if the system is yet single-phase due to the irradiation with light with the periodical intensity distribution (Eq. (1)), alternating regions with the elevated or lowered content of the neutral component are formed in the PPC layer. The monomer conversion is insignificant in the regions with a high NC concentration (see Fig. 1). At the initial stage of polymerization, this nonuniform distribution of concentrations of the components of the PPC based on oligo(ester acrylates) can substantially affect the structure of the final sample. Microphase separation should take place at an elevated content of NC because of its restricted compatibility with the polymer[18] and, correspondingly, a two-phase system solid polymer—liquid should be formed.[11] In the regions with a lowered content of NC, the latter will remain in the polymer network, and the system will be single-phase. this can qualitatively be explained using the phase diagrams of a monomer—polymer—NC mixture[11,18] (Fig. 2). Two areas can be isolated in these diagrams: *1*, single-phase and *2*, two-phase in which the NC is incompatible with the polymer and microphase separation occurs. The NZN_1* curve is a boundary of these areas, where N_1* is the limiting concentration of the NC at which the NC is compatible with the polymer network. For the uniform initiation of the PPC with a small content of the neutral polymer ($N_0 < N_1*$), the system remains single-phase during the whole polymerization process and, as a result, a uniform polymer is formed (see Fig. 2, *a*, movement of the figurative point along the *ab* line). At $N_0 > N_1*$, the system transits to the two-phase region during polymerization (see Fig. 2, *a*, movement of the figurative point along the *cd* line), where two phases are formed during the subsequent polymerization due to
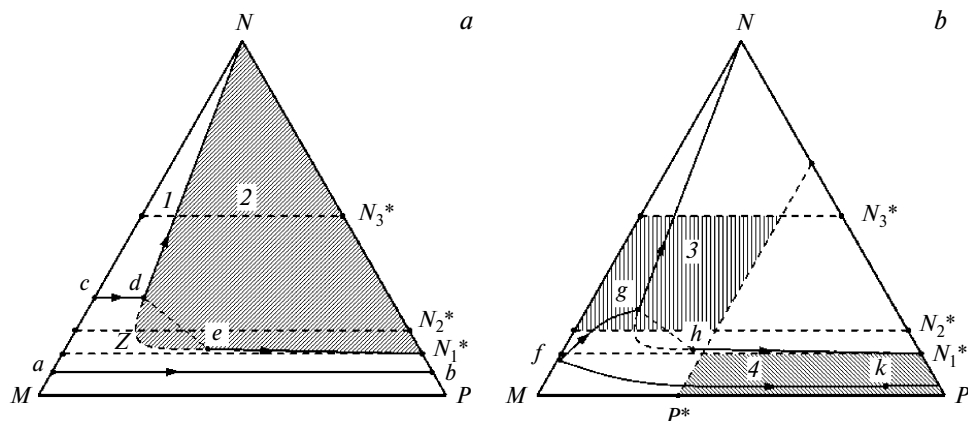

Fig. 2. Phase diagrams of the three-component medium (monomer—polymer—NC (M—P—N)). Possible movements of the figurative point are presented for uniform (*a*) and nonuniform (*b*) photoinitiation of polymerization.

microphase separation: the phase enriched in NC (see Fig. 2, *a*, line *dN*) and the phase enriched in polymer (see Fig. 2, *a*, line *eN*$_1$*). The PPC based on oligo(ester acrylates) are characterized by short curing times and, therefore, separation occurs in the microscale.[11] However, the fulfillment of the conditions $N_0 > N_1$* is insufficient for the formation of nanosized regions of the liquid phase from which pores are formed later. As shown by the experimental studies,[11] the final polymer material with open bound pores is formed at a higher content of the NC. For example, for the PPC based on OCM-2 in the presence of methanol, N_1* = 0.1 and N_2* = 0.25. There is another restraint: a friable, decomposing to individual parts polymer material is formed at the content $N_0 = N_3$* > 0.5.

The figurative points moves in the phase diagram in another way for the curing of the multicomponent PPC by nonuniform radiation with the periodical intensity distribution for different regions of the polymerized layer (see Fig. 2, *b*). In the regions with a high luminosity, the NC content will decrease (see Fig. 1) and the movement of the figurative point can be presented by the line *fk* (see Fig. 2, *b*). At this point even under the condition $N_0 > N_1$*, the system can remain single-phase during the whole polymerization process. Simultaneously, in the adjacent regions with lowered luminosity the content of the neutral component, on the contrary, will increase (see Fig. 1) and can exceed the critical concentration of phase separation (N_2*) even at $N_0 < N_1$* (see Fig. 2, *b*, movement of the figurative point along the *fg* line). Two phases will be formed in these regions during the next polymerization: the phase enriched in NC (see Fig. 2, *a*, line *gN*) and the phase enriched in polymer (see Fig. 2, *a*, line *hN*$_1$*). This results in the formation of a dispersion of droplets of the liquid phase in the solid polymer. Therefore, initiation with nonuniform radiation makes it possible to localize regions in which microphase separation of the PPC should occur. However, the necessary concentration redistribution of the PPC components in the homophase state is possible only until the viscosity of the composition would not be too high ($P < P$*).

Thus, the condition of formation of the two-phase morphology solid polymer—solvent during the curing of the PPC based on OCM-2 with methanol, for which P* = 0.1, is as follows:

$$0.25 < N(x´) < 0.5,$$

$$P(x´) < 0.1, \tag{4}$$

which corresponds to region *3* (see Fig. 2, *b*). Therefore, in the regions where the system remains single-phase during the whole polymerization process (Fig. 2, *b*, region *4*), the combined fulfillment of the conditions is necessary

$$N(x´) < 0.1,$$

$$P(x´) < 0.1. \tag{5}$$

After the subsequent removal of the NC from the final polymer sample, open bound pores are formed in the regions with two-phase morphology for which the condition (4) is fulfilled, and a uniform polymer is formed in the regions satisfying the conditions (5). The ratio of sizes of the regions with nanopores and uniform polymer can quantitatively be estimated from the fraction of surface areas (Q_{pore} and $Q_{no-pore}$) of the corresponding regions (Fig. 3). The value of Q_{pore} is determined as the sum of all regions satisfying the condition (4) normalized by *d* on the period (*d*) of the formed periodical distribution of the PPC components. The value of $Q_{no-pore}$ will be determined by the condition (5) on the period (see Fig. 3).

Dependence of the size of the regions with nanopores and uniform polymer on the parameters of the PPC and radiation. The efficiency of diffusion processes in multicomponent PPC at the initial stage of polymerization depends on both parameters of the composition and the polymerization rate.[16] Therefore, we studied the influence of the parameters of the polymerized medium (N_0, β_M, and β_{NM}) and actinic radiation (ΔI, *u*) on the structure of the final polymer material, namely, on the size of the regions in which nanopores or a uniform material are formed. For this purpose, computer simulation was performed in two stages. First, on the basis of the diffusion model (Eq. (2)) we performed the numerical analysis of the redistribution of components in the thin layer of the PPC when the latter is initiated by radiation with the periodical intensity distribution (Eq. (1)). Then, the values of Q_{pore} and $Q_{no-pore}$ satisfying the conditions (4) and (5) were determined from the obtained distributions of the concentrations of the polymer and NC, respectively. For numerical simulation, the initial distributions $P(x´)$ and $N(x´)$ were specified constant: P_0 and N_0. The value of N_0 was varied from 0 to 0.4, and $P_0 = 10^{-6}$. The values of other parameters of the model were the following: $\gamma = 4$, P* = 0.1, and $L = 500 \, \mu m$. The β_M and β_{NM} parameters were varied from $4 \cdot 10^{-9}$ to $4 \cdot 10^{-3}$, ΔI changed from 0.3 to 0.99, and the spatial frequency *u* ranged from 0.016 to 1 μm^{-1}.

The influence of the initial content of the neutral component (N_0) and the modulation depth of the initiating
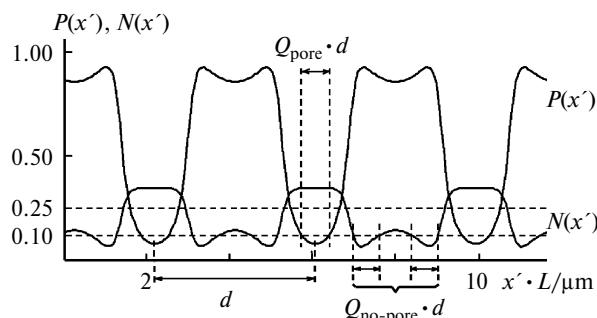

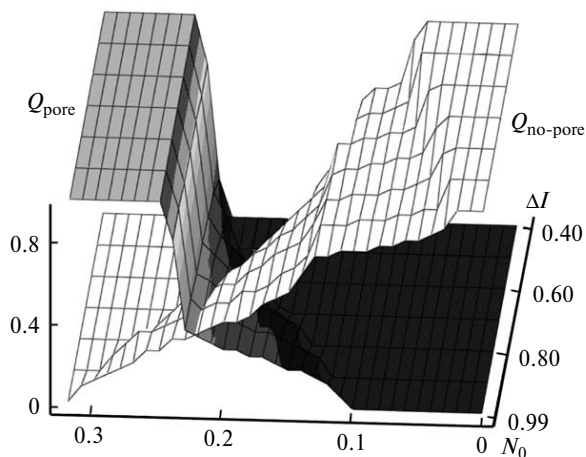**Fig. 3.** Determination of the size of nanopore formation regions (after NC removal) and uniform polymer.

Fig. 4. Fractions of the surface areas Q_{pore} and $Q_{no-pore}$ *vs* N_0 and ΔI ($\beta_M = 4 \cdot 10^{-7}$, $\beta_{NM} = 4 \cdot 10^{-6}$, $u = 0.256\ \mu m^{-1}$).

radiation (ΔI) on Q_{pore} and $Q_{no-pore}$ was studied at $\beta_M = 4 \cdot 10^{-7}$, $\beta_{NM} = 4 \cdot 10^{-6}$, and $u = 0.256\ \mu m^{-1}$. The numerical simulation results showed that the fraction of regions with nanopores (Q_{pore}) increased with an increase in N_0 (Fig. 4). On the contrary, the fraction of regions ($Q_{no-pore}$) in which a uniform monolithic polymer is formed decreases with an increase in N_0 (see Fig. 4). In this case, Q_{pore} and $Q_{no-pore}$ depend not only on the initial content of the neutral component but also on the modulation depth ΔI of the intensity distribution of the initiating radiation. For example, for $\Delta I = 0.8$ even at $N_0 = 0.15$ (at which the system is single-phase during the whole polymerization process and a uniform polymer is formed during initiation with the radiation with $I(x´,y´) = const$), the nonuniform initiation results in the appearance of regions in the polymer bulk, where the microphase separation of the polymerized medium occurs and nanopores are formed after the removal of the NC. The value of Q_{pore} increases with an increase in the modulation depth of the initiating radiation intensity (see Fig. 4). Similar differences in polymer structure formation under the action of uniform and nonuniform radiation are also observed for elevated N_0. At $N_0 = 0.25$, when nanopores are formed over the whole surface area of the sample during uniform polymerization, the initiation with light with the periodical intensity distribution with $\Delta I = 0.7$ results in the regions with the uniform polymer (see Fig. 4).

This behavior of the polymerized medium during polymerization with nonuniform radiation leads to the range of N_0 values for which both regions with an elevated NC content (in which microphase separation will occur and, correspondingly, nanopores will be formed after NC removal) and regions with a lowered NC content (in which the system is single-phase during the whole polymerization process) can be formed. Therefore, a uniform polymer is formed (see Fig. 4). Changing the values of N_0 in

this range, one can control the ratio of Q_{pore} and $Q_{no-pore}$, thus specifying permeability and strength of the formed nanoporous polymer material. There is the initial NC content (for our simulation parameters, $N_0 = 0.23$) at which Q_{pore} and $Q_{no-pore}$ are comparable. The range of N_0 in which non-zero values of Q_{pore} and $Q_{no-pore}$ simultaneously exist also depends on the contrast ΔI of the actinic radiation. For the parameter $\beta_M = 4 \cdot 10^{-7}$, $\beta_{NM} = 4 \cdot 10^{-6}$, and $u = 0.256\ \mu m^{-1}$, the combined formation of regions with nanopores and regions of uniform polymer is possible at the modulation depth ΔI of the intensity distribution $I(x´,y´)$ is not lower than 0.5 (see Fig. 4). The range of N_0 at which the polymer with the nonuniform distribution of nanopores extends with an increase in ΔI. At the maximum value of contrast of the polymerized light ($\Delta I = 0.99$), the nonuniform nanoporous structure in the polymer is formed at the NC content in the composition from 10 to 30 wt.% (see Fig. 4).

Nanoporous polymers can be synthesized from the PPC containing different oligomers and solvents.[2,3,11] The viscosity of these compositions can vary in a wide range. Therefore, we studied the influence of the β_M and β_{NM} parameters and the scale of the detected periodical distribution of the intensity (spatial frequency u) on the efficiency of the NC distribution in the PPC layer in the course of its curing. It was found that the dependences of Q_{pore} and $Q_{no-pore}$ on the β_M parameter and spatial frequency (u) of the photoirradiation intensity distribution $I(x´,y´)$ are nonmonotonic (Fig. 5). There is an optimum spatial period d_{opt} of the $I(x´,y´)$ distribution for which the sizes of the regions, where nanopores or uniform polymer are formed after NC removal, are maximum. The maximum values of Q_{pore} and $Q_{no-pore}$ shift to lower spatial frequencies with an increase in β_M. Correspondingly, an optimum spatial period at which the fractions Q_{pore} and $Q_{no-pore}$ maximum exists for each composition. It should be mentioned that the β_M parameter (Eq. (3)) is determined by both the viscosity of oligomer and the average intensity I_0 of the initiating radiation, which, in turn, provides an additional possibility for optical control of the formation of a nonuniform nanoporous structure: d_{opt} can be varied due to a change in I_0.

Similar dependences of Q_{pore} and $Q_{no-pore}$ on the ratio of parameters β_{NM}/β_M (at the fixed parameter $\beta_M = 4 \cdot 10^{-7}$) and spatial frequency (u) can also be observed (Fig. 6). The maximum values of Q_{pore} and $Q_{no-pore}$ also shift to the region of lower spatial frequencies u with an increase in the β_{NM} parameter. That is, if more viscous neutral components are added to the PPC to form a nonuniform polymer structure with the maximum values of Q_{pore} and $Q_{no-pore}$, polymerization should be initiated by the nonuniform radiation with a shorter spatial period.

Thus, there is an optimum spatial frequency of the intensity distribution of polymerizing light at which the fractions of regions with nanopores and regions of uni-
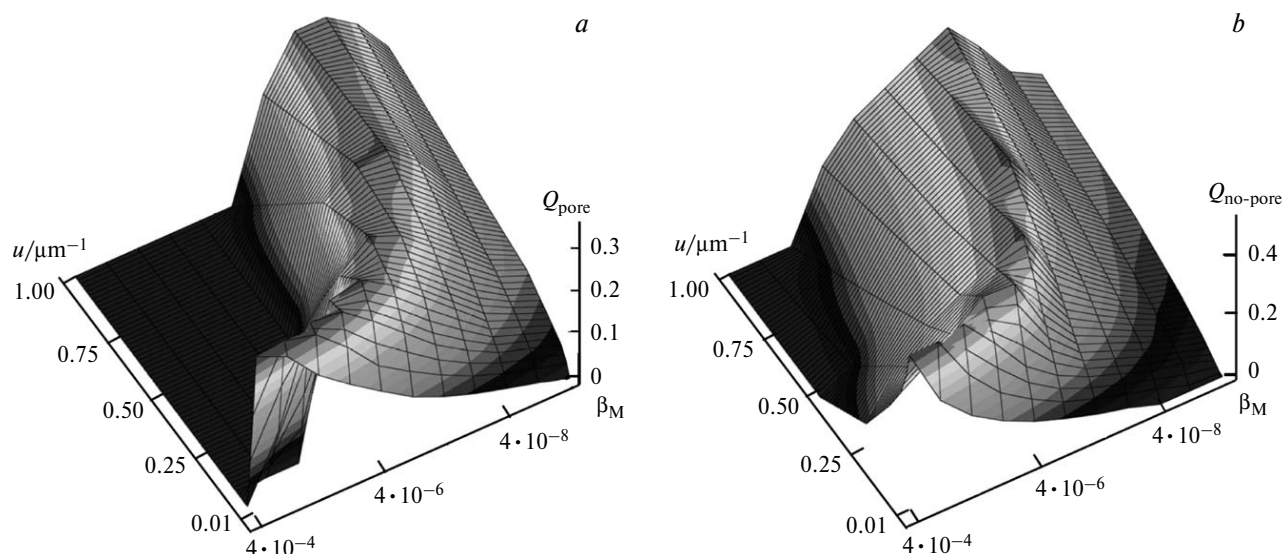
Fig. 5. Ratios of the surface areas Q_{pore} (*a*) and $Q_{no-pore}$ (*b*) *vs* β_M and *u* ($N_0 = 0.23$, $\beta_{NM}/\beta_M = 10$, $\Delta I = 0.99$).

form polymer are maximum. For example, for the manufacturing of the polymer material with the periodical distribution of the nanopore concentration with the spatial frequency $u \approx 0.5$ μm^{-1}, it is necessary that the dimensionless parameters would take the following values: $\beta_M \approx 10^{-7}$ and $\beta_{NM} \approx 10^{-6}$. This means that for the PPC based on oligo(ester acrylate) OCM-2 in the presence of butanol characterized by the diffusion coefficients $D_M \approx 0.01$ μm^2 s^{-1} and $\alpha_{NM} \approx 0.1$ μm^2 s^{-1} the polymerization time at which a nonuniform structure begins to form in the polymer bulk is several minutes.

Experimental checking of the numerical simulation results. To check the obtained computer simulation results, we experimentally studied the possibility of development of the polymer material with the nonuniform nanopore

distribution with the light with the periodical intensity distribution during the curing of the PPC based on polyfunctional monomer α,ω-bis(methacryloyloxyethylenoxycarbonyloxy)ethylenoxyethylene oligo(carbonate methacrylate) (OCM-2).

The influence of the NC content N_0 in the PPC on the polymer structure was studied at the modulation depth of the initiating radiation intensity $\Delta I \approx 0.97$. It was found (Fig. 7) that a periodical relief structure with the uniform surface is formed at a low content of the neutral component (10 wt.% and lower). A structure with the periodical nanopore distribution is formed at the NC fraction in the PPC higher than 10 wt.%: pores with a size of several hundreds of nanometers are formed in the sites of holes of the polymer lattice, whereas pores are not formed in the
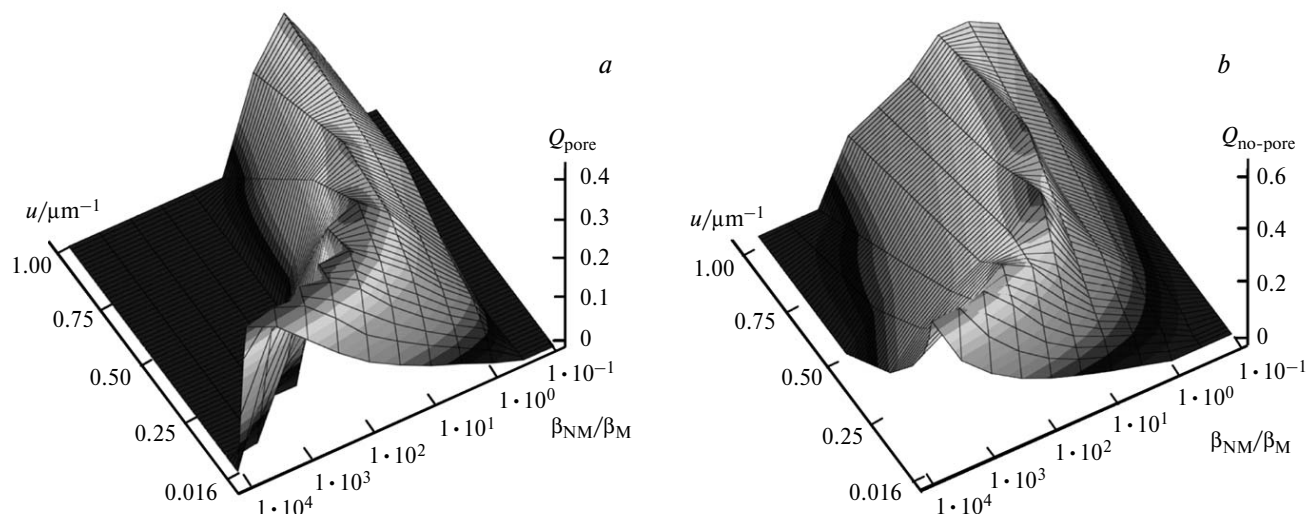

Fig. 6. Fractions of the surface areas Q_{pore} (*a*) and $Q_{no-pore}$ (*b*) *vs* β_M/β_{NM} and *u* ($N_0 = 0.23$, $\beta_M = 4 \cdot 10^{-7}$, $\Delta I = 0.99$).
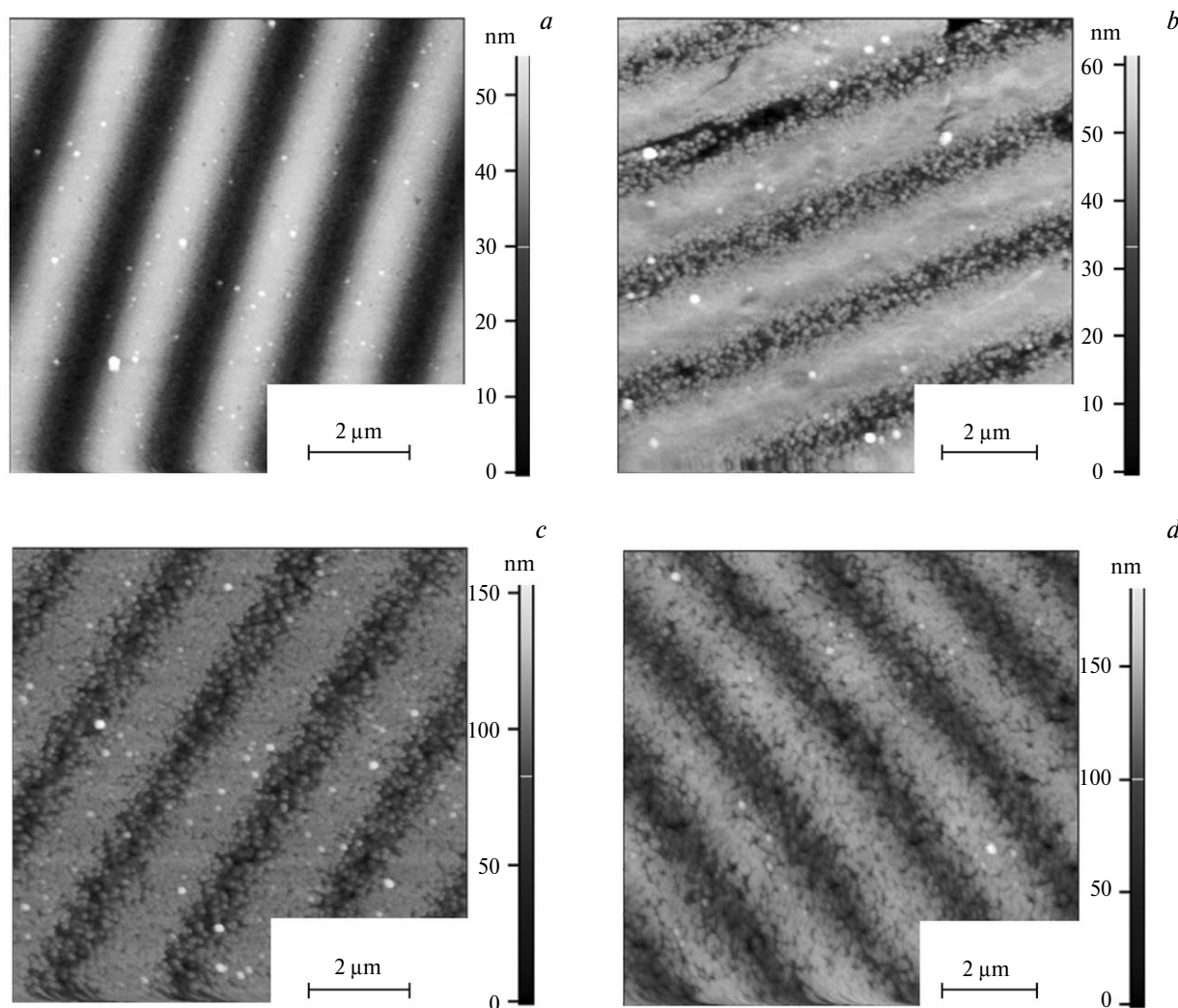
Fig. 7. AFM images of the surface of the polymer synthesized from PPC with different contents of butanol: 10 (*a*), 15 (*b*), 20 (*c*), and 25 wt.% (*d*) ($\Delta I \approx 0.97$).

regions of heights. Nanopores are formed on the whole surface of the polymer sample with the further increase in the butanol content.

The influence of the modulation depth of the actinic radiation intensity (ΔI) was studied at a neutral additive content of 15 wt.% (Fig. 8). The region of pore formation narrowed with a decrease in ΔI, which is consistent with the computer simulation results.

To conclude, polymer materials with the nonuniform concentration of nanopores can be formed during the curing of the PPC containing the neutral component under the action of light with the periodical spatial intensity distribution. In the regions with a low intensity of the initiating radiation, the NC concentration increases, resulting in the microphase separation of the polymerized medium, whereas in the regions with a high luminosity the NC content decreases and the system remains sing-phase during the whole polymerization process. As a result, after the removal of the non-polarizable component, a polymer material is formed with a nonuniform nanoporous structure. In this case, the efficiency of formation of such a material is determined by both the actinic radiation intensity and depends substantially on the spatial period of the nonuniform intensity distribution of the initiating light. These materials contain regions with nanopores along with regions of uniform polymer, which makes it possible to improve their physicomechanical properties. This also provides a possibility to perform one-stage processes of optical design of nanoporous materials: formation of monolithic cowlings and other nanoporous filters. The nanoporous structure will be formed in the regions initiated with light with the periodical intensity distribution, whereas a uniform polymer will simultaneously be formed in the regions initiated by uniform radiation.
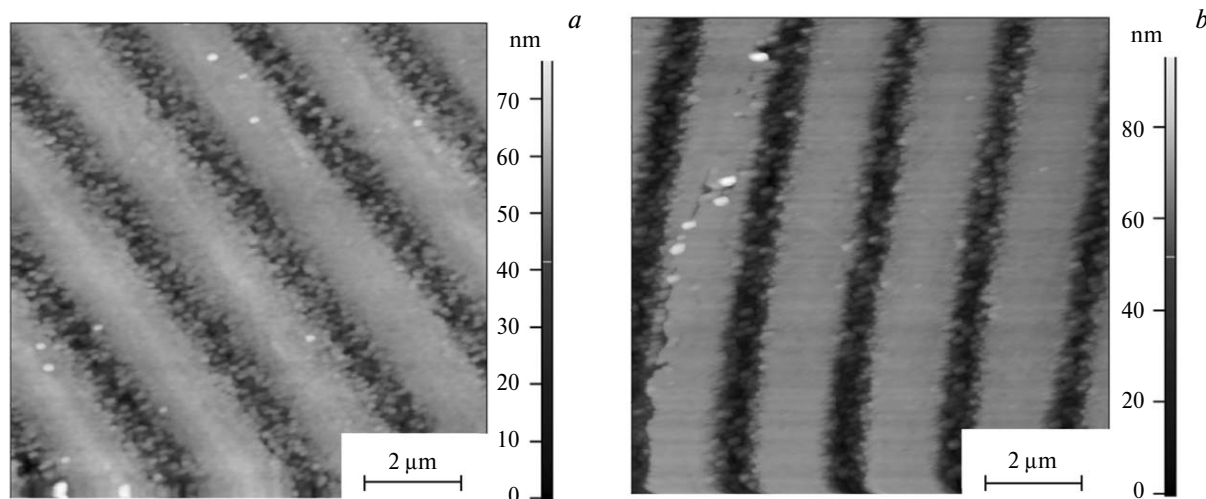
Fig. 8. AFM images of the surface of the polymer synthesized from PPC with 15 wt.% of butanol at different modulations of the incident light intensity (ΔI): (*a*) 0.74 and (*b*) 0.49.

Experimental

Monomer oligo(carbonate dimethacrylate α,ω-bis(methacryloyloxycarbonyloxy)ethylenoxyethylene) oligo(carbonate dimethacrylate) (OCM-2) was used without additional purification, and the content of impurities (toluene) in the initial OCM-2 was 0.4% according to high-performance liquid chromatography (HPLC) (Knauer gel permeation chromatograph). The PPC was prepared by the dissolution of the initiator in a mixture of OCM-2 and neutral component. The following photoinitiating system was used: substituted *ortho*-benzoquinone (0.05 wt.%) and *N,N*-dimethylethanolamine (1 wt.%). This system makes it possible to perform polymerization by the optical radiation of the visible range.[19] Butanol preliminarily purified using a known procedure[20] was used as NC.

Periodical distribution of the light intensity (Eq. (1)) was obtained due to the interference of two planar waves. The scheme of the experimental setup is presented in Fig. 9. The spatial frequency *u* was specified by changing the angle α between interfering beams. The depth of light field modulation (ΔI) was varied using a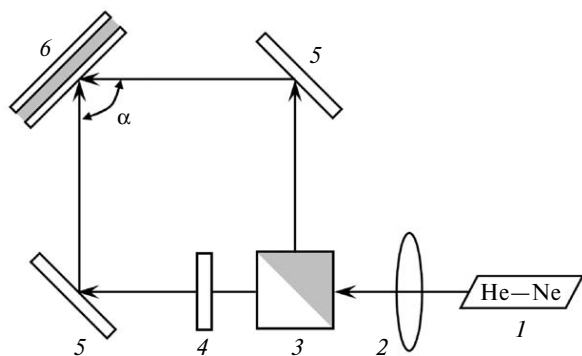 light filter. The PPC was polymerized inside the cavity of the mold formed by two silicate glasses with a damping interlayer between them (50 μm). According to the parameters presented above for the PPC based on the polyfunctional monomer OCM-2 with butanol, the parameters of the initiating radiation for recording the periodical structure with the spatial frequency $u \approx 0.5\,\mu m^{-1}$ were determined. A He—Ne laser ($\lambda = 0.63\,\mu m$) was used as a radiation source. The average intensity of interfering beams was ~4 mW cm^{-2}. The exposure time was selected in such a way that the maximum possible conversion would be achieved on all regions of the polymer sample in both areas with high intensity, where the system is single phase during the whole polymerization process and a uniform polymer should be obtained, and areas with low intensity in which microphase separation occurs and nanopores should be formed. The polymerization of the PPC with light with a nonuniform spatial intensity distribution was carried out for 40 min. Then the samples were additionally polymerized by scattered polychromatic light with an intensity of ~14 mW cm^{-2} for 20 min.

The obtained polymer samples were taken out of the glass mold and analyzed (after butanol was removed from pore cavities) and analyzed by atomic force microscopy (AFM) on a Solver P47 microscope (NT-MDT). Scanning was carried out in the tapping mode. The size of the analyzed regions was varied from tens of nanometers to tens of microns. The AFM images were formed using the Nova software (NT-MDT).

Fig. 9. Scheme of the experimental setup: *1*, helium—neon laser; *2*, collimator; *3*, light dividing cube; *4*, light filter; *5*, mirrors; and *6*, reactor with PPC.

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