08

Experimental study of the mechanism of relief formation in liquid photopolymerizing compositions

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A theoretical and experimental study of the mechanism of microrelief formation on layers of liquid photopolymerizing compositions was carried out. A direct experiment was carried out to prevent diffusion mass transfer during the post-exposure period. From the experiment it became clear that there is no diffusion of the liquid oligomer from dark to light zones during the post-exposure period. It is concluded that, due to the microheterogeneous mechanism of polymerization, the increase in relief during the post-exposure period is due to the swelling of polymer globules in their own remaining oligomer..

Keywords: liquid photopolymerizing compositions, microrelief, degree of conversion, microheterogeneous mechanism, radical polymerization.

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Introduction

Techniques for fabrication of optical elements have always been relevant and retain their relevance today. One of the authors of the present study has discovered the effect of mass transfer in liquid photopolymerizing compositions (LPPCs) in 1987 [1]. Both IR focusators and visible-range diffraction optical elements have been constructed based on this effect [2–21]. Continuous relief ranging from fractions of a micrometer to hundreds of micrometers was obtained by exposing LPPC layers held between glasses to a projection of a half-tone image of an optical element. After exposure, when a liquid layer of the oligomer composition turned into a rubber-like layer and the glasses forming this layer were separated, a subtle relief image of the optical element remained on the surface of this layer. The relief then grew tens of times over the course of several hours. It was monitored in a non-contact manner with an interference microscope. This growth could be stopped at any moment to obtain the required relief height. It was believed that the relief growth is sustained by the transfer of unpolymerized oligomer in the LPPC layer from dark zones of the half-tone image to light zones. The hypothesis regarding relief formation in the dark (post-exposure) period was proposed in [4–6,21]. The present study is focused on theoretical and experimental verification of this hypothesis.

1. Theoretical analysis of the mechanisms of LPPC polymerization

The concept of associative structure of liquid reactive oligomers (LROs) [22–25], which is based on hypotheses regarding the structure of low-molecular liquids [26–29], is the dominant one at present.

Having discovered a strict orientation of molecules in alcohols, Stewart [30] has introduced the concept of cybotactic microregions in isotropic liquids. In contrast to microcrystals, these ordered areas do not have clear outlines: these are groups of molecules with above-average ordering that emerge and disappear through fluctuations.

In their study of oligoester acrylates A.A. Berlin and G.V. Korolev [31] have suggested that the formation of associates with an oriented anisotropic order, which were called „cybotaxises“ in [23], leads to an increase in the rate of their polymerization. This effect is observed due to a „kinetically favorable order“ with terminal unsaturated bonds located on the periphery of these aggregates, which facilitates polymerization. Notably, this implies a hereditary transition of the oligomer morphology to the morphology of a network polymer. The probability of formation of ordered associates in oligomers, where strong intermolecular interaction centers (IICs) are present, is high. They differ from chaotic density fluctuations in their high stability (due to cooperative bonding) and discrete nature (the sizes are limited by the possibilities of energy compensation for the „chaos-order" entropy loss) [25].

A.A. Berlin devoted many years of work to the study of LROs and has substantiated and proven experimentally the existence of kinetically favorable and unfavorable arrangements of molecules in „labile blanks" [31,32]. Labile blanks function most efficiently in oligoester acrylates [33] when they transform into network polymers during polymerization. The authors consider two cases. In the first case, the arrangement of functional groups in a „blank" is close to the one realized during the reaction. In other words, oligomer molecules are arranged in a kinetically favorable order, and the lifetime of associates (τ_s) is longer than the lifetime of an active center or a transition state (τ^*). In this case ($\tau_s \geq \tau^*$), the reaction rate in ordered regions is many ($5-10$) times higher than in disordered (inter-associate) ones. If this order is disturbed by, e.g., vibration, the polymerization rate decreases [23]. The second case is the one of a kinetically unfavorable order, where, although $\tau_s \geq \tau^*$, no favorable packing is found in the associates. The reaction in the associates then proceeds slowly, but is accelerated in inter-associate regions. The introduction of solvents into such a system weakens the intermolecular interaction, facilitates the destruction of kinetically unfavorable associative blanks, and increases the mobility of functional groups, thus contributing to the acceleration of oligomer polymerization [34–36].

A significant role in orientational acceleration of the reaction of oligomer molecules is played not only by the arrangement of reactive groups (which is the main factor in polymerization via double bonds of, e.g., oligoester acrylates), but also by the activation of these groups due to the formation of hydrogen bonds with other types of functional groups belonging to neighboring molecules in the associate. The initiating role of H-bonds has been demonstrated convincingly by T.E. Lipatova [37] in the context of formation of polyurethanes.

Of particular interest is the transfer of structural order in oligoester acrylate oligomers to network polymers formed from them [36]. It was found [34,38,39] that vitrified oligomeric liquids with $M \leq 1200$, where M is the molecular weight, are characterized by the presence of globular formations $200-500$ Åin size. Tetwork polymers obtained from these oligomers also feature a well-defined globular structure or variously shaped formations of fused globules. A layered structure with lamella thicknesses of $100-130$ and $150-180$ Å was observed in vitrified melts of oligomers [40] with $M = 1000$ and 2500, respectively. The morphological pattern of network polymers based on them is no different from the supramolecular structure of the original oligomers.

Thus, the associative structure of reactive oligomers affects the kinetics of reactions of their transformation into polymers and has a direct influence on the structure. This opens up the possibility of altering the structure of network polymers by subjecting the initial oligomers to a certain targeted influence that changes the rigidity of their molecules or (and) the intermolecular interaction. This should result in a change in the associative structure (arrangement, hierarchy, weight fraction). A modification of this kind may be induced by introducing solvents with different solvating abilities or via exposure to force fields: magnetic, electrical, or mechanical.

2. Experimental procedure

It was assumed earlier [2–21] that the growth of relief after UV exposure of the LPPC through a photomask with a periodic structure of a black-and-white image is due to the diffusion of the remaining unpolymerized oligomer from dark to light zones. In the present study, we prove experimentally that the relief formation mechanism is not rooted in diffusion. To do this, we exclude physically the oligomer transfer in the direction of illumination variation gradient in the course of exposure of the sample to UV light. The idea is that the motion of matter in a sufficiently wide and long elliptical zone, which has a minimum of illumination on one side and a maximum on the other side, should proceed along the width of the zone from its dark region to the light one. If a part of the sample is cut out (removed) within the elliptical zone, the mass transfer of the oligomer will be disrupted at this point (the cut). In other words, the oligomer substance will not be able to move from the dark part to the light part. If the diffusion theory is correct, the relief height in the light part of the zone bordering on the removed section of the sample should be lower than the relief height in the light part that transitions continuously into the dark part of the zone in the remaining intact section of the sample. The cut was made with a thin scalpel after exposure.

The sample was prepared with the use of a glass photographic plate with a black-and-white half-tone image of a Fresnel lens. The elliptical structure of a focusator of the Fresnel lens type is seen in Fig. 1, *b*. The central ellipse is assumed to be the zero zone, the next ellipse-shaped zone is considered the first, the next ellipse-shaped zone is considered the second, etc. A thin polymer layer with a thickness of $10\,\mu$m was formed in advance on the surface of the photographic plate emulsion to create a uniform flat surface and isolate the photoemulsion from the subsequent photopolymerization reaction. Spacers with a thickness of $100\,\mu$m were placed along the edges of the plate. The LPPC was then poured onto the prepared photographic plate surface and covered carefully with clean glass treated for good adhesion to the LPPC layer. At the next stage, this structure was subjected to UV irradiation. The LPFC layer was exposed through a photomask with a half-tone image (Fig. 1, *b*), which altered smoothly the optical density across the Fresnel lens zone. The attenuation of intensity of transmitted light in the dark part of the zone was three times stronger than in the light part.

After approximately $10-15$ min of exposure, the glasses were separated, and a soft rubber-like layer of a relief copy

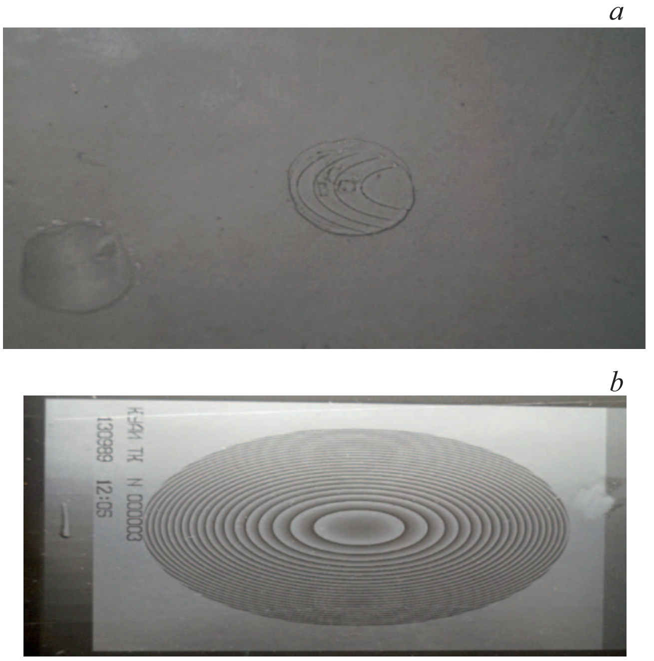

Figure 1. Preparation of the sample for study. To study the process, the optical element was filled with the MDF-2 LPPC only partially. *a* — MDF-2 prepolymer circle with a thickness of 100 μm in the center of the figure is the exposed sample of a fragment of the focusator image with the first and second zones of the Fresnel lens cut out in the central part; a fragment of the prepolymer layer with a relief diffraction grating, which was used to monitor the polymerization process, is seen at the bottom left; *b* — photomask of the Fresnel lens on a glass photographic plate; a photometric wedge is seen on the left, and a diffraction grating with a frequency of 10 lines/mm is on the right at the edge of the field.

of the black-and-white image of the Fresnel lens formed from the initially liquid LPPC layer (Fig. 1, *a*) on the surface of the glass that covered the photographic plate with the Fresnel lens image.

3. Experimental results

The LPPC, which contained 98% of MDF-2 oligomer and 2% of i-BEB (isobutyl ether of benzoin) photoinitiator, was irradiated using an EM-5006 industrial lithography unit with a DRSh 500 lamp. The illumination power was set to 70 W. The thickness of the LPPC layer was set to 100 μm by the spacers used.

The degree of conversion was monitored by non-actinic (non-polymerizing) red light from a red laser pointer with a wavelength of 530 nm.

Irradiation was interrupted at the maximum difference in polymerization depth between the light and dark zones, which was identified as the moment when the number of orders of diffraction of the laser beam off the diffraction grating reached its maximum (Fig. 2).

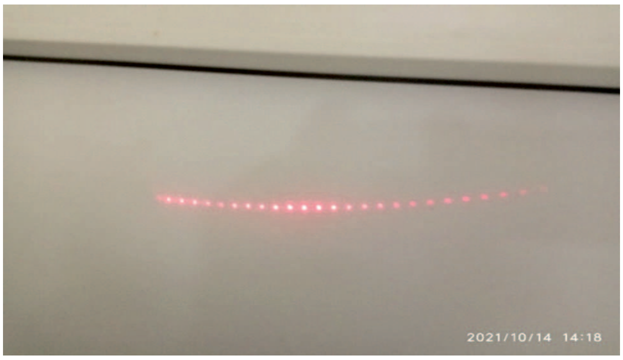

Figure 2. Maximum number of diffraction orders (26) in monitoring of the degree of conversion. Prior to polymerization, three orders were visible. The irradiation procedure was stopped at the moment when the number of diffraction orders began decreasing.

Within 10 min after exposure and separation of the glasses (one of which retained the LPPC layer with the formed relief), cuts were made in the central regions of the first and second zones of the optical element sample. Within 5 min after cutting, the relief height was measured with an MII-4 interferometric microscope. Measurements were performed along the normals to the tangents of zones of the Fresnel lens (i.e., in the directions of light intensity gradient during exposure). One normal went through the center of the cut section, while the other passed at a distance on the order of the zone width (3 mm) from the edge of the cut, where the zone was continuous. The maximum relief height at the ridge (i.e., at the sites of transition from the light part of zone 1 to the dark part of zone 2 and from the light part of zone 2 to the dark part of zone 3) was measured.

The results of measurements along the normal in the center of the cut section and along the normal away from it in the continuous zone were the same. Immediately after measurements, the relief height was 8.8 μm both near the cut and away from it. A day later, 95 interference periods, which correspond to 26.125 μm, were found in the cut section, and 90 periods (24.75 μm) were observed at a distance from the cut. (1 period = 0.275 μm). Measurements were carried out for five samples with an accuracy within the margin of error; the results were the same for all samples. This suggests that no mass transfer occurs in the direction of illumination gradient during exposure, since the same increase in relief height is observed in regions where the expected flow of the oligomer substance is interrupted. Therefore, it is fair to assume that swelling occurs due to internal effects in the local region of the observed zone.

Spectrometric studies of the main LPPC component (MDF-2 oligomer) were carried out (Fig. 3). The double bonds of this oligomer, which is shown in Fig. 4, have a maximum at a frequency of 1637 cm^{-1}. The other maxima are irrelevant to the process in question. The double bonds are opened during polymerization, and gelation occurs at a

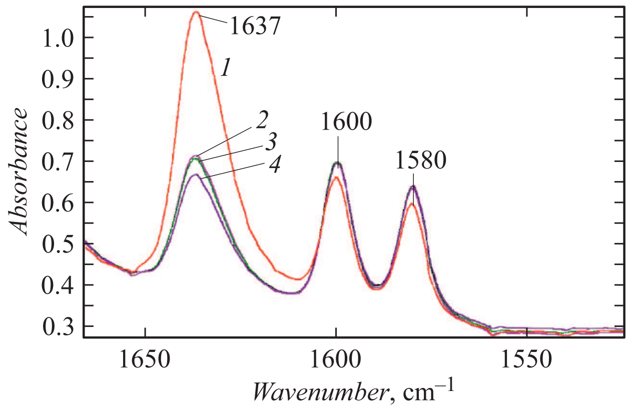

Figure 3. Spectrum of the MDF-2 oligomer. Curve *1* — spectrum before UV exposure; *2* — spectrum immediately after UV exposure; *3* — spectrum 1 h after UV exposure; *4* — spectrum 24 h after UV exposure.

conversion degree of 2–3%. The degree of conversion of the prepolymer after exposure was measured by examining double bonds with an IR spectrometer. The spectra of the MDF-2 oligomer are shown in Fig. 3. The thickness of layers measured with the spectrometer was $30\,\mu$m.

The spectra were recorded in absorbance coordinates. The absorbance is a logarithmic characteristic of concentration. Therefore, according to the Bouguer–Lambert–Beer absorption law, the number of consumed double bonds is $\Gamma = (D_0 - D_1)/D_0$, where D_0 is the absorption of the MDF-2 liquid oligomer prior to polymerization and D_1 is the absorption of the prepolymer after polymerization.

The degree of conversion was 39.4% and 30.4% in light and dark areas, respectively; i.e., 60–70% of the oligomer are left after exposure.

The obtained results suggest that there is no post-exposure diffusion of the oligomer from dark zones to light zones. If, as was previously assumed, it did occur, there would be a significant (several-fold) difference in relief height between the intact (without cuts) zones and the zones where the central parts were removed in the experiment. The observed difference was just several percent with fluctuations in both directions.

Thus, the mechanism of relief growth in the post-exposure period differs in nature from the previously assumed diffusion after UV illumination.

4. Discussion

Let us apply the above theoretical reasoning to the examined MDF-2 oligomer. Its chemical formula is shown in Fig. 4.

The polymer chain contains a benzene ring grafted to acrylate chains. In the present case, this group will be a strong IIC during the formation of a prepolymer from the oligomer in radical polymerization. It was demonstrated in [24] that attraction constant F of the phenyl group is 741.5, while the attraction constants of the other groups present in the chain are 2–3 times smaller. Attraction constant F is a complex energy characteristic of the physical network: $F = (E_{cohesion} V_{298\,\mathrm{K}})^{0.5}$, where $V_{298\,\mathrm{K}}$ is the molar volume at a temperature of 298 K and $E_{cohesion}$ is the cohesive energy. By definition, cohesive energy is the energy needed to break all intermolecular contacts per mole of contacting atomic groups. According to Stewart [33], associates of the first type—density fluctuations and anisotropic fluctuations: formations with close order—are formed. These associates are seen clearly under a microscope at high magnification both during and after polymerization. They are commonly called microhetero-

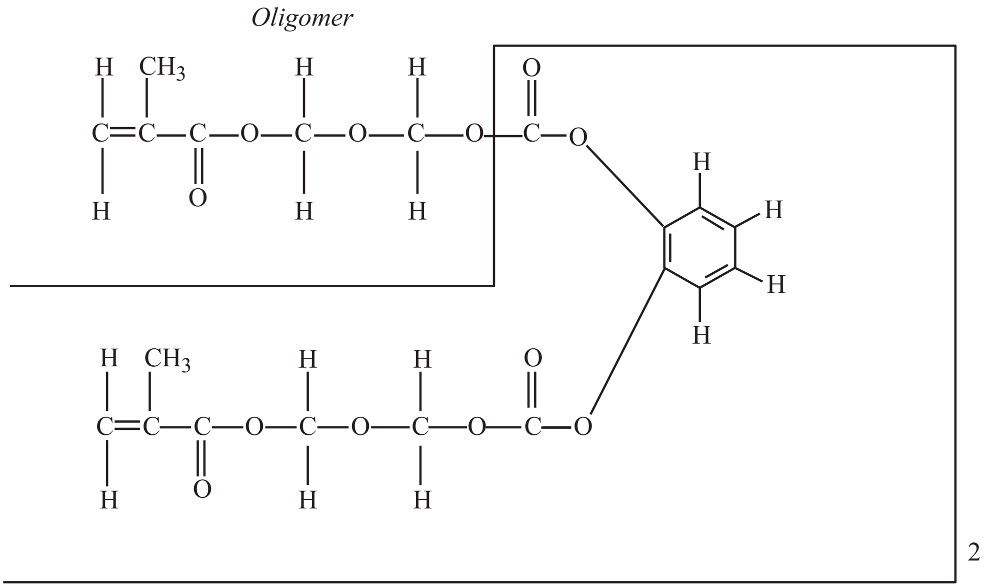

Figure 4. Chemical formula of the MDF-2 oligomer (number „2“ denotes the structure repeating two times).

geneous formations in literature and shaped like tangles of highly twisted long polymer molecules.

In the present case, mechanical stress, which arises during polymerization of the initial liquid oligomer, builds up in the course of polymerization. Glass surfaces, which limit the change in volume, force the resulting polymer to pack tightly under exposure to UV light. According to the experimental data, the difference in degrees of conversion in light and dark zones varies from 30 to 40%. This is already a fairly dense prepolymer. The maximum conversion of MDF-2 in the center during UV polymerization is as high as 90%. A further increase in conversion is achieved by additional measures, such as raising the temperature or introducing thermal initiators. Therefore, fairly strong compaction of the associative-globular structure of the polymer, which still remains immersed in its own unpolymerized liquid oligomer, occurs in the process of oligomer transfer in diffusion under UV illumination. When the glasses are separated after polymerization, the associates (globules) formed as a result of heterogeneous polymerization begin to relax and grow in volume, swelling in their own remaining oligomer. Thus, the relief grows in the dark not due to mass transfer from the dark zone to the light one, but due to IIC-initiated processes.

If the middle part of the polymer composition zone is cut out after exposure, the oligomer mass transfer may be prevented. A comparison of the formed relief a day after the experiment revealed that the relief at the edges of the zone (at the ridge, where a fragment was cut out, and in the adjacent intact region) was of the same height. This suggests that there is no post-exposure diffusion of the oligomer from dark zones to light ones. If, as was previously assumed, it did occur, there would be a significant (several-fold) difference in relief height in the experiment. The observed difference was just several percent with fluctuations in both directions. In other words, it was demonstrated experimentally that the mechanism of relief growth in the post-exposure period differs in nature from the previously assumed diffusion.

A new concept of mass transfer in the period after exposure of the sample to UV light was formulated based on the obtained results.

Mass transfer proceeds under illumination only. At this time, a concentration gradient of free radicals arises under the influence of actinic UV radiation within one zone of the optical element (which is a strip of a certain width) and at the boundaries of zones with a sharp dark–light transition. The produced free radicals cleave the double bonds of the oligomer and initiate polymerization, which proceeds in such a way that the oligomer is drawn from dark zones into light ones. Therefore, the process leads to an increase in density (mass) of the prepolymer in light areas. Under the specified conditions of polymerization within the gap between two solid glasses, the prepolymer accumulates in light zones due to an increase in its density and compression. Since the concentration of globules during exposure is proportional to the received UV dose, swelling and, consequently, volume expansion will be more profound at the sites where more globules are present (i.e., in better illuminated areas). The result is a linear relief growth as a function of intensity. The mechanism of polymer shrinkage is virtually irrelevant to mass transfer, since the relief in experiments may grow by up to 50% of the initial layer thickness, reaching greater height levels in light areas. The concept of polymer shrinkage is applicable when an oligomer is polymerized in samples without modulation of the light intensity throughout them to almost the highest degrees in a given technological process (on the order of 90% and higher). In the present case, the light intensity is modulated along the sample layer, and light zones border on dark ones and draw the liquid oligomer from them during exposure, while the prepolymer becomes denser. Since the degree of conversion does not exceed 40%, the concept of shrinkage is not applicable here. When one compares individual samples in a conventional experiment without spatial amplitude modulation of UV light, shrinkage is observed in samples with a high degree of conversion. The relief height increases in the dark mode due to the fact that areas with different degrees of conversion form within each zone of the optical element. In the experiment, rigid glass surfaces prevented the variation of local polymer volume inside the zone in the process of irradiation. In other words, the glasses prevented the oligomer from moving from the dark zone to the light one, which is why the polymer was compacted in light zones. This was observed when the optical element was exposed on a test diffraction grating illuminated with laser light. After a certain exposure time, the number of diffraction orders increased from the initial three to 20–30. When the maximum difference in polymer density between the light and dark zones was reached, the number of diffraction orders started decreasing, eventually dropping to the initial level of three orders. Virtually no relief was observed after disassembly of the system in this state; only its traces a fraction of a micrometer in height were visible. Therefore, the irradiation process was interrupted when the number of diffraction orders reached its maximum.

Conclusion

1. When LPPC layers are exposed to a periodic UV light field, relief forms due to mass transfer, which proceeds during exposure only.

2. In the post-exposure period, diffusion is either nonexistent or plays an insignificant role in the relief formation mechanism. The relief formation is driven by strong IICs arising from the chemical structure of the MDF-2 oligomer.

3. The depth of polymerization was determined by IR spectroscopy as the ratio of consumed double bonds to the initial number of double bonds in the MDF-2 oligomer. The degree of polymerization averaged over the sample aperture and determined immediately after exposure and separation of the glasses was 30–40%. This depth of polymerization

allows one to produce high-quality diffractive optical elements.

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Conflict of interest

The authors declare that they have no conflict of interest.

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