Features of the silver nanoparticles formation in a photopolymer under uniform lighting

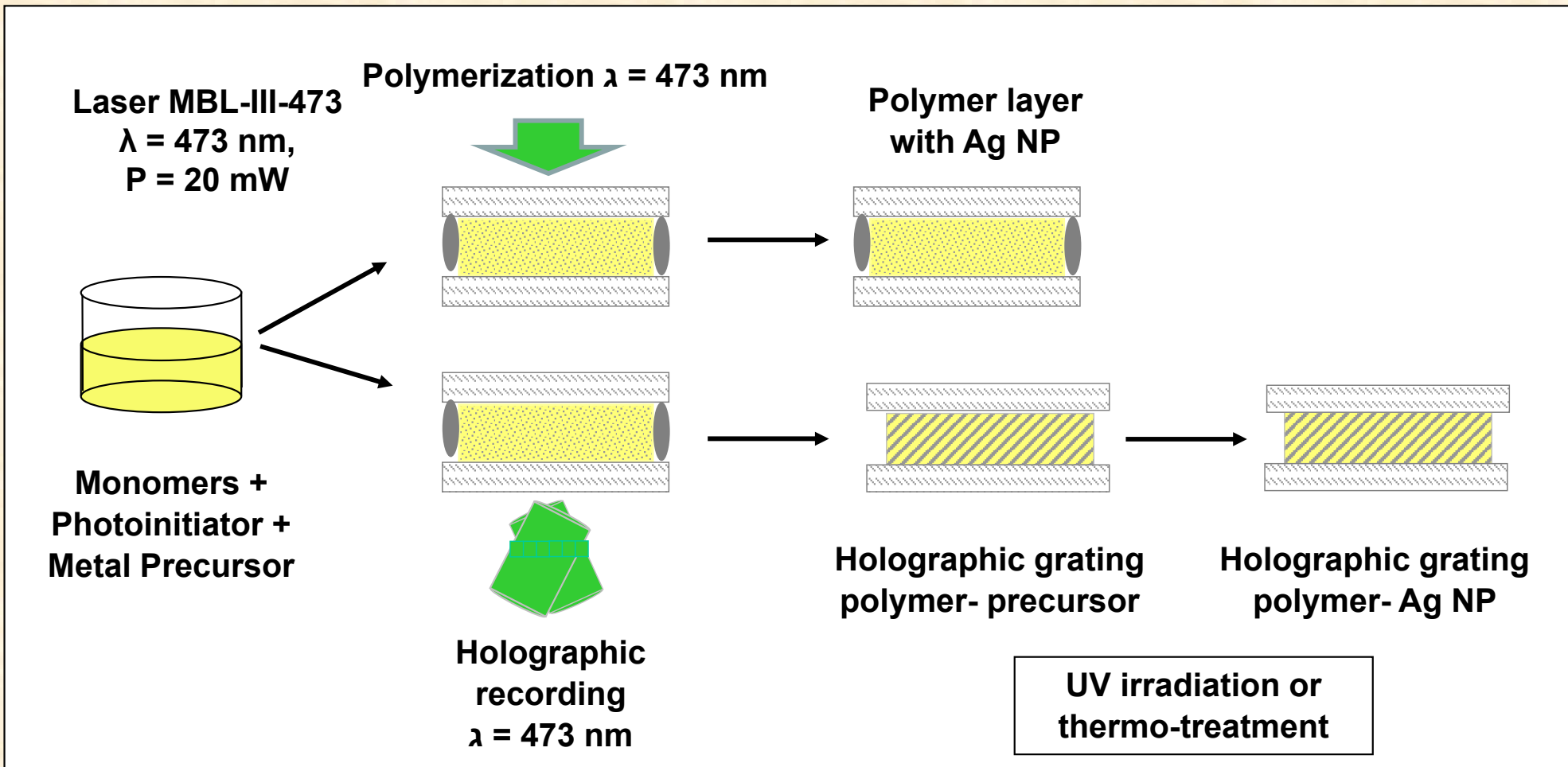*T.M. Smirnova[1], V.O. Hryn[1], D.O. Klymchuk[2], Y.M. Akimov[2]*

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The structure of the polymer layer was studied using a transmission electron microscope JEOL JEM-1230(Japan). Accelerating voltage was 80 kV, resolving power 0.2 nm.

A thickness of the layer was of 40-50 nm. The dimension of the sample was approximately (0.2-0.3) mm^2. The layers were placed on the microscope stage and scanned with an electron beam from the glass/polymer interface facing the radiation to the back polymer/glass interface.

In our studies, we used the method of simultaneous polymerization and in situ formation of silver NPs. The original composition was developed for the manufacture of diffraction gratings by the method of holographic lithography.

Laser MBL-III-473
λ = 473 nm,
P = 20 mW

Polymerization λ = 473 nm

Polymer layer with Ag NP

Monomers + Photoinitiator + Metal Precursor

Holographic recording λ = 473 nm

Holographic grating polymer- precursor

Holographic grating polymer- Ag NP

UV irradiation or thermo-treatment

Photosensitive layers for polymerization were fabricated by sandwiching a drop of initial liquid composition between two glass substrates, which were separated by calibrated Teflon spacers with a thickness of 20 μm.

The photosensitive layer was irradiated with a homogeneous beam of DPSS laser MBL-III-473 (λ = 473 nm, P = 20 mW).
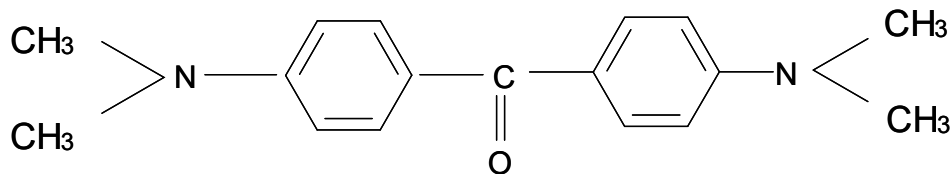
Photopolymer composite

The optimal composition includes two copolymerized monomers, that form a cross-linked polymer network and a solution of $AgNO_3$ in acetonitrile as a metal precursor – 30 vol.% relative to the mixture of monomers
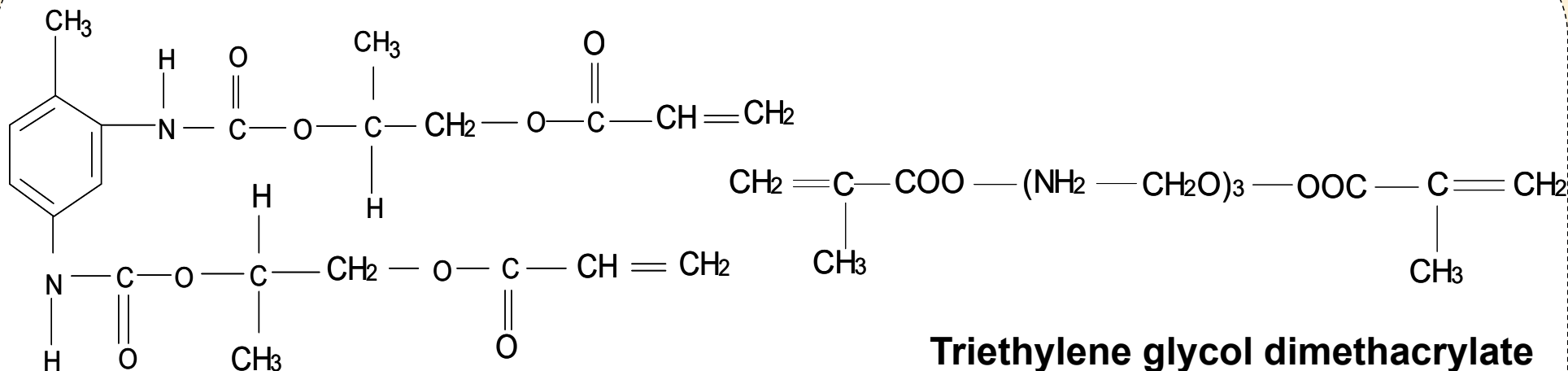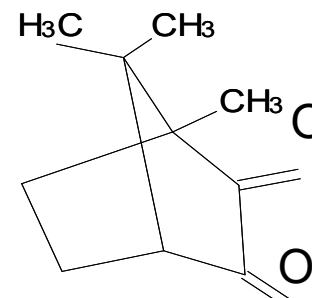
α,ω-Akryl-bis(propylene glycol)2,4- toluene diurethane - 30 w.%
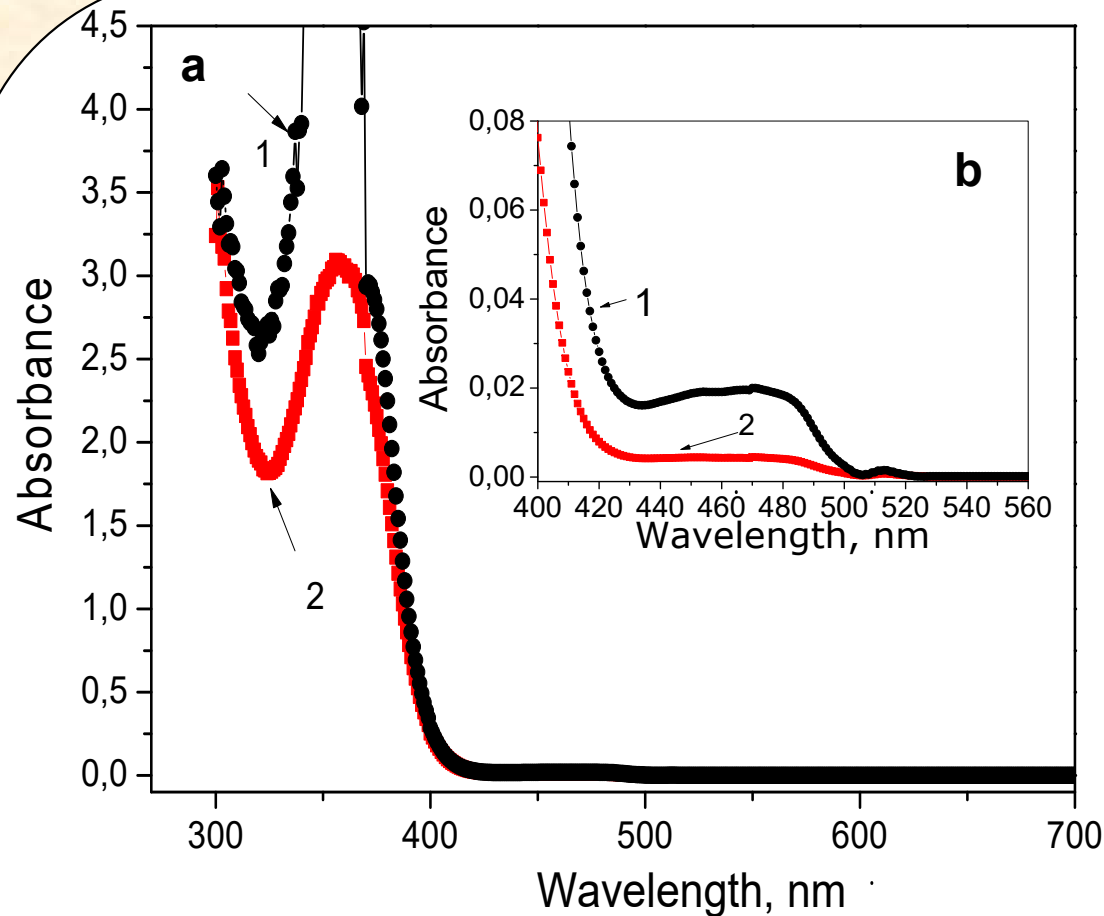
Triethylene glycol dimethacrylate
64 w.%

Michler's ketone (MK) – 1 w.%

Camphorquinone (CQ) – 5 w.%

Absorption of the photopolymerizable composite

Absorption spectra of the photopolymerizable composite, containing:
a) the Michler's ketone (MK) and camphorquinone as the initiator system;
b) the camphorquinone before (1) and after (2) polymerization.
Film thickness is 20 μm.

The short-wave absorption band with a maximum at $\lambda \approx 358$ nm belongs to MK. The weak long-wave absorption band at $\lambda_{max} \approx 450$ nm corresponds to the $n \rightarrow \pi$ transition in a CQ molecule. At the optimal CQ concentration, the absorption coefficient k ≤ 5 cm^{-1} at the wavelength of polymerizing radiation.

Therefore, if the thickness of a recording layer $d \leq 100$ μm, the polymerization and holographic recording practically take place in the given field, that provides the uniformity over the layer thickness.

Structure of the polymer Ag NP layer:
a) near the front substrate facing the radiation source;
b) in the middle of the polymer layer;
c) and near the back substrate.

The average radius of NPs in the polymer volume is 3.1±1.6 nm.

At the polymer/glass boundary, NPs of two types are observed: a layer of NPs with a radius of (4.07±1.91) nm and individual large NPs, the radius of which varies from 9.4 nm to 15 nm.
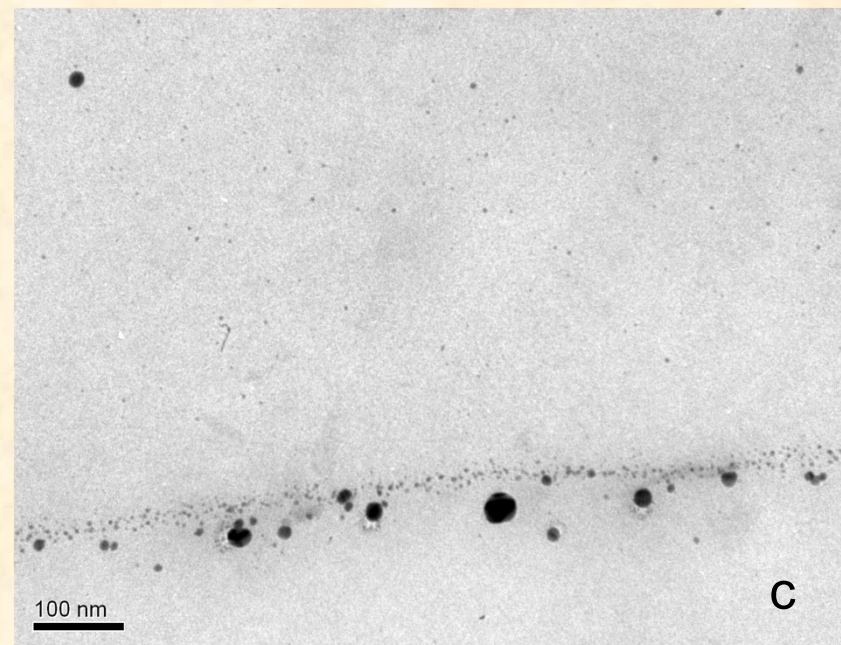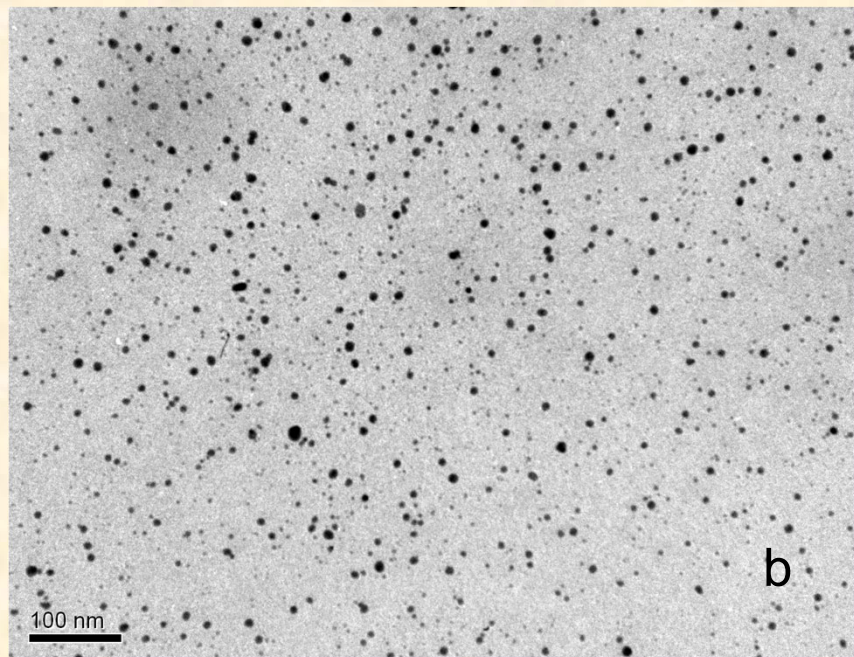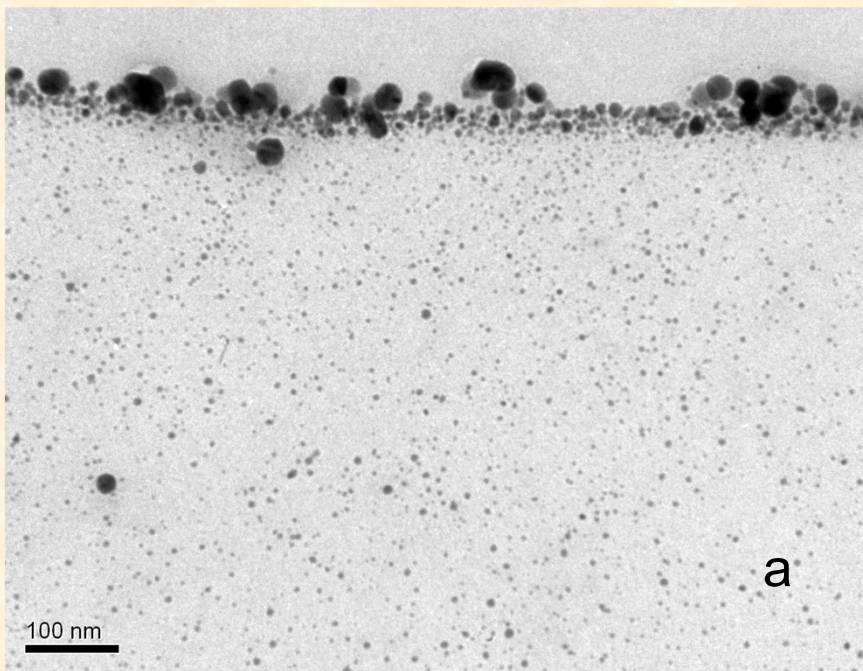
Absorption spectra of the polymer – Ag NPs layer
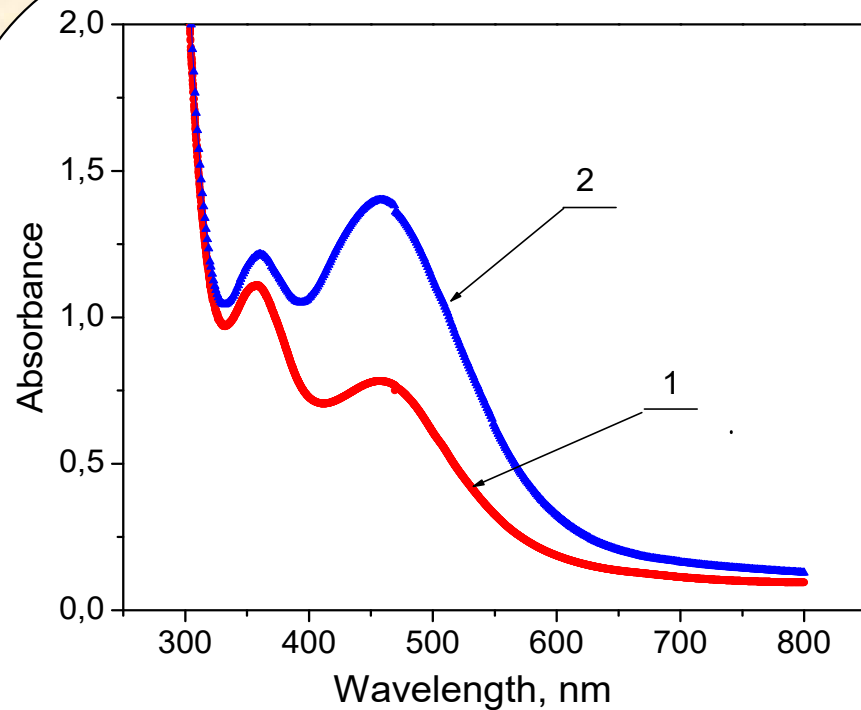
**Absorption spectra of the grating
after exposure (1)
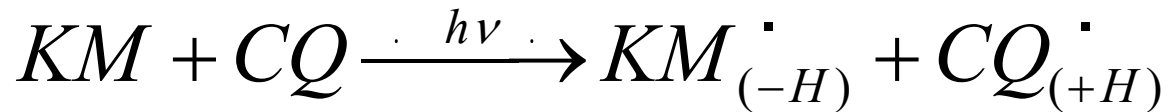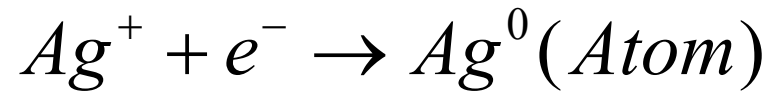and after thermo- processing for 60 min. (2).**

It was found that Ag NPs are formed in the polymer layer during polymerization. This is confirmed by the appearance of local surface plasmon bands of silver in the absorption spectrum in the range of 400–500 nm.

It was also shown that the intensity of the bands increases with post-processing of the layer by heating or UV radiation.

A distinctive feature of the formation of NPs in the polymer layer is the formation of a group of NPs of a larger size near the substrates.

In the initial state, the composition is an equilibrium mixture of liquid components. During the polymerization process, the thermodynamic equilibrium is disturbed and the precursor is displaced from the polymer body to the substrates, near which, under the influence of light, an accumulation of Ag NPs is formed.
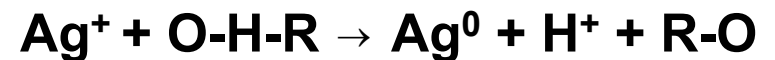
Possible mechanism of the formation of silver nanoparticles caused by free radicals as a reducing agent

$$Ag^+ + e^- \rightarrow Ag^0 (Atom)$$

$$xAg^0 \rightarrow Ag_X (Nanoparticle)$$

$$KM + CQ \xrightarrow{\quad h\nu \quad} KM^{\cdot}_{(-H)} + CQ^{\cdot}_{(+H)}$$

Monomer

Ag^+

Polymer network

$Ag^+ + O\text{-}H\text{-}R \rightarrow Ag^0 + H^+ + R\text{-}O$

The aminoalkyl radicals $KM^{\cdot}_{(-H)}$ initiate the reaction of photopolymerization of the monomers.

The ketyl radicals $CQ^{\cdot}_{(+H)}$ containing OH-groups can reduce Ag^+ to Ag^0 according to the mentioned scheme

Since the reduction of Ag NP occurs simultaneously with the formation of the polymer matrix and no additional reducing agents were introduced, the radicals that initiate the radical polymerization will reduce the Ag nanoparticles.

Conclusions

➢ We have observed for the first time the accumulation of Ag NPs near the substrates limiting the polymer layer with the simultaneous formation of a polymer network and Ag NPs under the action of uniform laser radiation. The NPs form a layer both near the front substrate facing the light source and near the back surface. The sizes of NPs in the polymer matrix and at the boundaries with substrates differ significantly.

➢ It was found that the reason for the formation of Ag NP near the substrates is the diffusion transfer of the metal precursor (AgNO3 solution in acetonitrile) to the substrates. As a result of the formation of the polymer network, the thermodynamic equilibrium of the monomers - precursor system is disrupted, which leads to the displacement of excess precursor solution from the polymer matrix and its accumulation near the substrates, where Ag NP are formed under the action of light.

➢ The most probable mechanism of photoreduction of Ag NP is the interaction of silver ions with ketyl radicals CQ· (+H), which are formed during the absorption of polymerizing radiation by the system, initiating a chain reaction of the composition polymerization.

➢ Since the nucleation and the growth of Ag clusters are controlled by the diffusion processes, the increase in the viscosity of the polymer matrix prevents the photo-induced generation of Ag NPs. Further photo- or thermo-processing can increase the diffusion and promote the reduction reaction.