ISSN 0018-1439, High Energy Chemistry, 2006, Vol. 40, No. 3, pp. 131–141. © Pleiades Publishing, Inc., 2006.
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REVIEW

Photopolymerizable Recording Media for Three-Dimensional Holographic Optical Memory

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Received November 10, 2005

Abstract—The development of investigations in recent years on photopolymerizable recording holographic media for using as photosensitive layers of holographic optical disks, which satisfy the conditions for the application in archive optical memory is analyzed. It is shown that the main emphasis in the development of photopolymerizable holographic recording media is put on the improvement of their component composition. Formulations that permit joint radical and cationic photopolymerization were designed for thermally stable holographic recording. The holographic characteristics achieved for these media ensure the fabrication of single-layer optical disks 150 mm in diameter with the information capacity of 200 GB instead of 5 GB for modern optical disks. Ways of improving photopolymerizable holographic recording media for the manufacture of optical disks with an information capacity of more than 1 Tb cm^{-3} are considered.

DOI: 10.1134/S0018143906030015

The development of information technologies requires the creation of new information storage media, since the information capabilities of magnetic media appear to be reaching a limit now [1]. Note, however, that such information storage media are still used quite extensively.

Along with further improvement of magnetic media, optical disks (ODs), which substantially extend the capabilities of information technologies, find widespread application [2–4].

At present, three types of OD are used, which are designed for (1) only multiple reading of information recorded earlier (compact disks, or CD), (2) single information recording in a personal computer and multiple reading of information recorded (WORM OD), and (3) multiple processes of information recording, erasing, and reading in a personal computer (WERM OD).

The considered OD types find progressively increasing application. However, their limited information capacity becomes a retarding factor. This is due to the fact that only one or two surfaces of the information storage units are used for information recording. At present, ODs are actually two-dimensional (2D) storage systems.

Further progress in information technologies calls for development of three-dimensional (3D) OD. In this respect, investigations are performed aimed at designing multilayer OD structures (with more than 100 layers) with the use of a nonlinear two-photon process of bit-by-bit information recording and retrieval with an information capacity of more than 1 Tb cm^{-3} [5–7].

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An alternative way of realization of three-dimensional information carriers is the use of the holographic method of information recording in a thick photosensitive medium [8, 9]. This method permits recording and reading optical information with the use of a great number of holograms written on the same area of a photosensitive medium at different angles. All leading companies of the United States, Japan, and European Union working in the field of OD design and manufacture are trying to solve this problem.

Photosensitive media based on photopolymerization processes of organic compounds referred to as photopolymerizable or photopolymer materials (PPM) are the most suitable and promising for the fabrication of holographic CDs with an ultrahigh data storage capacity [10]. They belong to self-developed materials and ensure simultaneous real-time writing and reading of holograms, a property that determines their suitability for optical memory devices.

In spite of the theoretical possibility of using these materials to manufacture ODs of ultrahigh data storage capacity, which was shown by investigations, it is obvious now that they need improvement, especially in the line of elimination of recording-layer shrinkage during hologram writing [11].

To comprehend some specific requirements imposed on holographic recording media, we will briefly consider the holographic parameters that determine the possibility of their application.

Holograms are interference patterns that appear in a photosensitive layer as a result of interference of reference and object laser beams. The reference beam is used thereafter to retrieve information from the holo-

grams, and the object beam carries information about the object.

The main parameters of recording media determining the possibility of their use in holography are as follows:

(1) The efficiency of information reading determined by the brightness or the diffraction efficiency (DE) of holograms [12]

$$\mathrm{DE} = \eta = I_{\mathrm{dif}}/I_{\mathrm{inc}} = I_{+1}/I_0,$$

where $I_{\mathrm{dif}} = I_{+1}$ is the intensity of the light wave of the first diffraction order and $I_{\mathrm{inc}} = I_0$ is the incident light intensity.

Note that the highest value of DE is achievable only for phase holograms that do not absorb restoring light. This is possible only in the case of recording media that change their refractive index or thickness under the action of light.

(2) Photosensitivity of the medium

$$S = \sqrt{\eta/EV},$$

where V is the visibility of the information pattern recorded and E is the energy of recording light.

(3) Angular sensitivity

$$\theta = \Lambda/d,$$

where $\Lambda - 2\pi K$ is the period of the holographic diffraction grating and d is the thickness of the photosensitive medium. It follows from the above equation that the maximum angular sensitivity determining the capability of writing and reading holograms in the same area of the layer is achieved only for layers of large thickness.

The main requirements imposed on PPM for 3D holographic disks are a high diffraction efficiency of recorded holograms, which is achieved only by a photoinduced change in the refractive index of the medium without changing its absorbance; high photosensitivity of the medium necessary for achieving the maximum speed of writing holograms; a high angular sensitivity of the medium for writing holograms and restoring image, which is necessary for realization of 3D holographic optical memory; a large thickness of the photosensitive layer (0.5–2 mm), which provides writing holograms in the entire layer (deep holograms) and, as a consequence, a high angular sensitivity and writing a large number of holograms in the same area of the recording medium; and a low shrinkage of the photosensitive layer during hologram writing, which provides the distortion-free restoring of images from holograms.

Based on these requirements, we will consider the results that have been achieved to the present in the development of photopolymer materials for 2D holographic disks.

PHOTOPOLYMERIZABLE MATERIALS FOR THREE-DIMENSIONAL HOLOGRAPHIC OPTICAL DISKS

Photopolymerizable materials for three-dimensional holographic OD include, as a rule, the following components: a multifunctional monomer or oligomer, a photoinitiating system (photoinitiator or photosensitizer), a polymeric binder, and various additives that increase the photosensitivity of the recording medium (co-initiators).

The dry photopolymerizable systems are used for holographic ODs, in which the photosensitive composition is sandwiched between polymer or glass covers or is placed in microporous structured silicate glass.

PPMs are based on the reactions of radical, cationic, and mixed radical and cationic photopolymerization. To obtain holograms, two photoinduced processes are used:

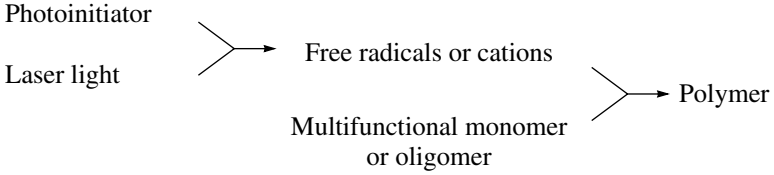
(1) a photoinduced change in the density of a photopolymerizable system [13]

$$\frac{n^2 - 1}{n^2 + 1} = \frac{4\pi\alpha N_L}{3},$$

where α is the molecular polarizability and $N_L = \rho N_A/M$ is the molecular density of the compound;

(2) photoinduced diffusion of the components during irradiation.

Polymer is formed in irradiated areas (Scheme 1).

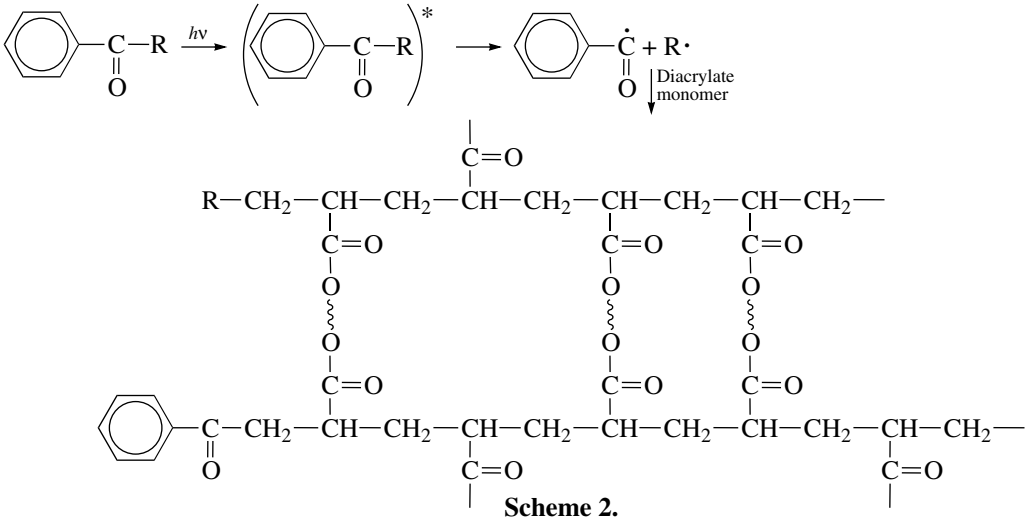


Scheme 1.

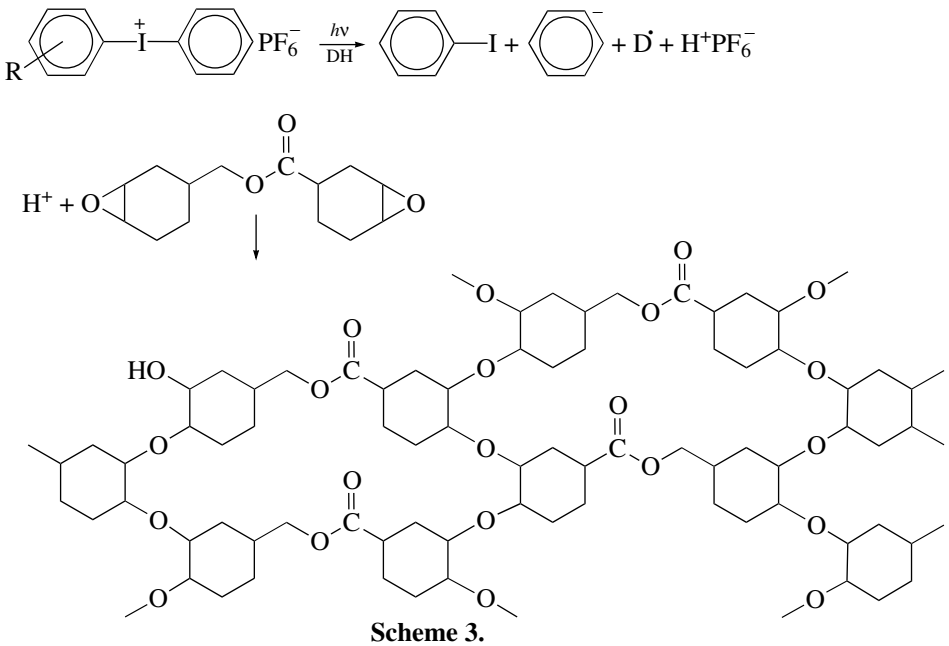
Owing to the spatial concentration gradient of the polymer created by the action of light, unreacted monomer and oligomer molecules diffuse to unilluminated areas of the layer. Note that the formation of holograms in such media is a nonlinear process depending on the ratio between the rates of diffusion of components and polymerization [14]. Further irradiation of the PPM layer with an incoherent or restor-

ing reference laser beam leads to photopolymerization of the whole layer. As a result, nonuniform concentration of the polymer is formed in the layer, which provides writing holograms of two types: relief and volume holograms. The value of the photoinduced change in the refractive index can be as high as $\Delta n = 10^{-2}$ [15].

Schemes 2 and 3 exemplify the radical polymerization of an acrylic monomer and the cationic polymerization of bisepoxide, respectively [16]:



Scheme 2.



Scheme 3.

Photoinitiating systems are one on the most important PPM components. They include only a photoinitiator if holograms are written with short-wavelength laser light, or a mixture of an initiator and a photosensitizer in the case of recording holograms with long-wavelength UV or visible light [16].

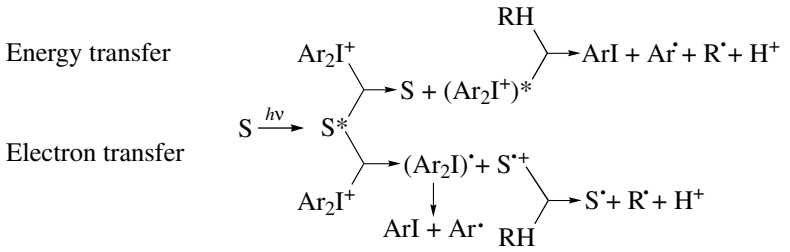
The spectral characteristics of photoinitiating systems are determined by the wavelength of laser light used for recording holograms.

The efficiency of photoinitiating systems is determined by the molecular absorption coefficient at the wavelength of writing light, the quantum yield of radicals or cations, the reactivity of the photoproducts, and the possibility of photobleaching in the course of photopolymerization for obtaining the maximum conversion of monomers or oligomers in the bulk of PPM.

A number of organic compounds are known as photoinitiators of radical and cationic photopolymerization [17].

The photopolymerization efficiency depends on the nature of photoinitiators (Fig. 1).

The use of photosensitizers is based on photoexcitation energy transfer or electron transfer (Scheme 4) [18]:



Scheme 4.

The structure (Fig. 2) and the spectral characteristics (Fig. 3) of the most popular photosensitizers provide their efficient application in PPM [19]. For photopolymerization with visible light, apart from the dyes shown above, dyes that, like camphorquinone, ensure photoinduced proton abstraction and the subsequent polymerization of maleimide vinyl and maleimide allyl ethers are suitable [20].

Dye mixtures, in particular, Rose Bengal and Methylene Blue, turned out to be efficient in holographic recording [21].

Recently, it has been found that the radical yield can be increased by introducing some additives into the photoinitiating system (carbon tetrabromide, diphenyliodonium salt, *N*-methyldiethanolamine, etc.) and, thus, the efficiency of the photoinitiation process can be enhanced [17]. The idea behind the use of these additives consists in the fact that radicals that are generated by photoexcitation and inhibit the polymerization process interact with introduced additives to form new radicals active in polymerization [18]. Figure 4 shows the dependences of conversion of an acrylate monomer into polymer, which illustrate the high efficiency of 2(4'-methoxyphenyl-4,6-bis(trichloromethyl)-1,3,5-triazine used as an additive of this kind [19]. An example of equally effective three-component systems is given by a PPM containing a dye (Methylene Blue), an electron donor (*N*-methylethanolamine), and the third component (diphenyliodonium chloride) [22], as well as by the systems photosensitizer (2-[*p*-(diethylamino)styryl]naphtho[1,2-*d*]thiazole)–initiator (2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetraphenyl-1,1'-bi-1*H*-imidazole)–co-initiator (2-mercaptobenzothiazole) [23].

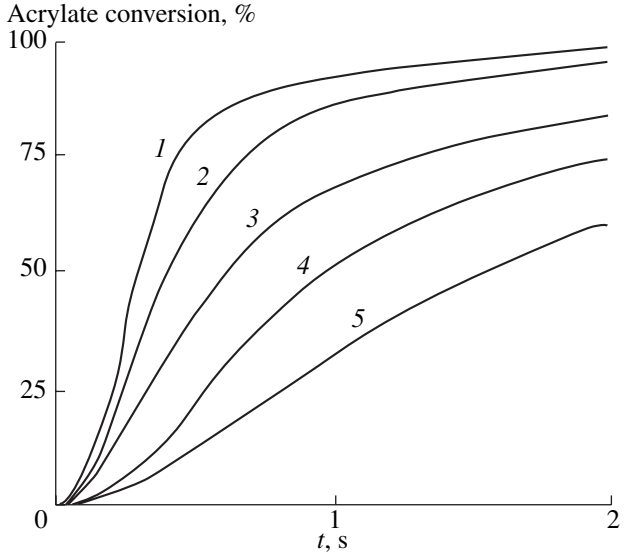


Fig. 1. Kinetic curves for the photopolymerization of the urethane acrylate system containing (*1*) bisacylphosphine oxide, (*2*) morpholinoketone, (*3*) dimetoxyacetophenone, (*4*) hydroxyphenylketone, and (*5*) benzophenone as photoinitiators by the action of UV light.

Efficient photobleaching of photoinitiating systems in the course of photopolymerization is of particular importance for 3D holographic recording media [24, 25]. It provides penetration of laser light into the bulk of the recording layer and writing "deep" holograms. This effect was studied using, as an example, the photoreduction of phenanthrenequinone in poly(methyl methacrylate) (PMMA) containing the residual monomer [26–29]. In this context, the use of photoinduced forms of photochromic compounds as photosensitizers seems to be attractive [30–33].

Two-quantum hologram recording processes were used for the same purpose [34].

To realize efficient two-photon writing of holograms [35, 36], benzyldimethylketal was suggested as a photoinitiator, which exhibits strong two-photon absorption ($\sigma > 1.250 \times 10^{-50}$ cm^4 s photon^{-1} [37, 38]), as well as amino- and carbazole-substituted diphenylpyridinevinylphenylvinylphenyls [39].

In relation to the growing application of cationic photopolymerization, photoinitiating systems for this type of PPM are of particular importance. In such systems, it is suggested to use onium compounds, which include iodonium and sulfonyl derivatives [40]. Under the action of light, these compounds generate both acids and radicals. A number of photosensitizers were

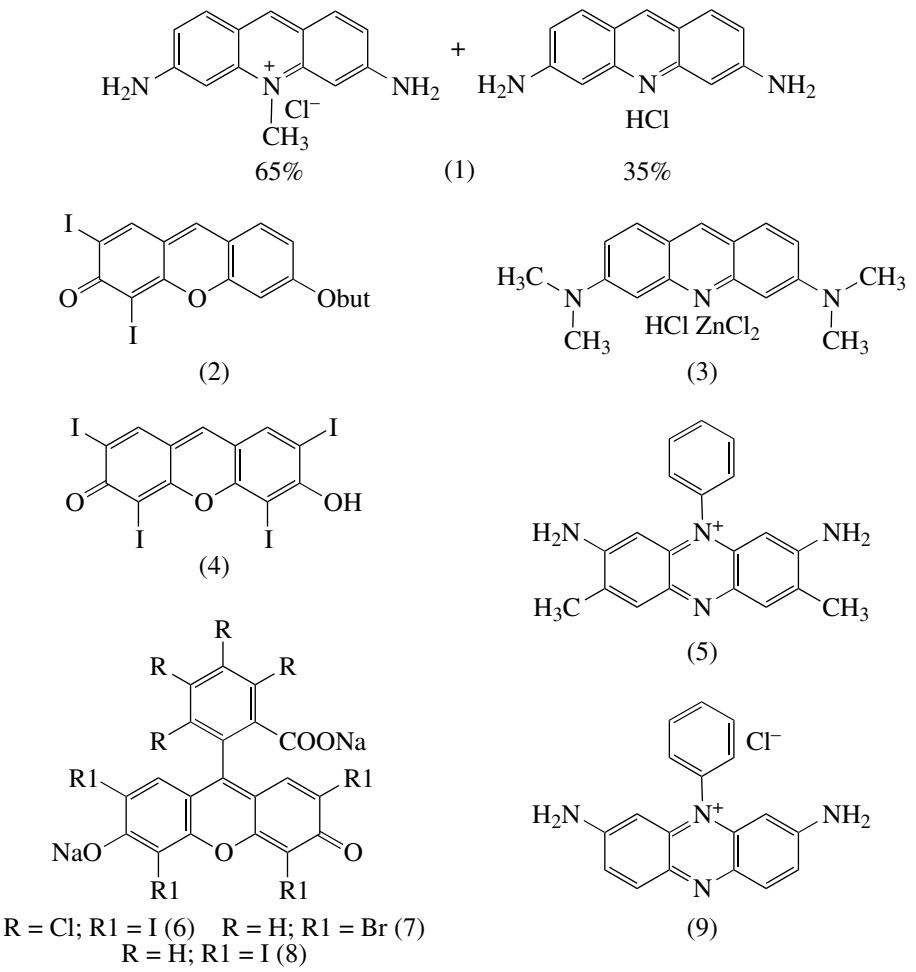


Fig. 2. Structures of dyes used as photosensitizers of radical photopolymerization: (*1*) acriflavine, (*2*) 3-butoxy-5,7-diiodo-6-fluorenone, (*3*) Acridine Orange, (*4*) 3-hydroxy-2,4,5,7-tetraiodo-6-fluorenone, (*5*) Safranine O, (*6*) Rose Bengal, (*7*) Eosin Y, (*8*) Erythrosine B, and (*9*) phenosafranine.

developed for onium photoinitiators [40–42], including merocyanine dyes [41] and titanocene [42].

Reactive PPM components that take part in radical photopolymerization are most often acrylate monomers in polymeric binders of various types. In the case of cationic photopolymerization, vinyl ethers and epoxides are generally used.

The selection of monomers is based on the requirement that photoinduced changes in the refractive index, which depend on the difference between the refractive indexes of the polymer matrix and the monomer, be maximum (table) [43].

An increase in the photoinduced change of the refractive index is facilitated by introducing aromatic monomers that contain heavy atoms, such as Zn-methacrylate or polycyclic aromatic substituents, in particular, 2,4,6-tribromomethane, *N*-vinylcarbazole, and other compounds [29, 44].

To increase the value of the photoinduced change in the refractive index, monomer mixtures are also used, thus allowing values of $\Delta n = 1.5 \times 10^{-2}$ to be attained [45, 46]. In such mixtures, monomers should differ in the reactivity and refractive index. During recording holograms, one of the monomers is readily photopolymerized and the other (less reactive) readily diffuses in the layer.

Photoinduced changes in the refractive index Δn_{phot} as a function of the constitution of photopolymerized compositions

Polymer	Monomer	Δn^{phot}
Cellulose acetate butyrate	2-Phenoxyethyl acrylate	1.05×10^{-5}
Poly(methyl methacrylate)	2-Phenoxyethyl acrylate	0.81×10^{-2}
Polystyrene	2-Phenoxyethyl acrylate	0.52×10^{-2}

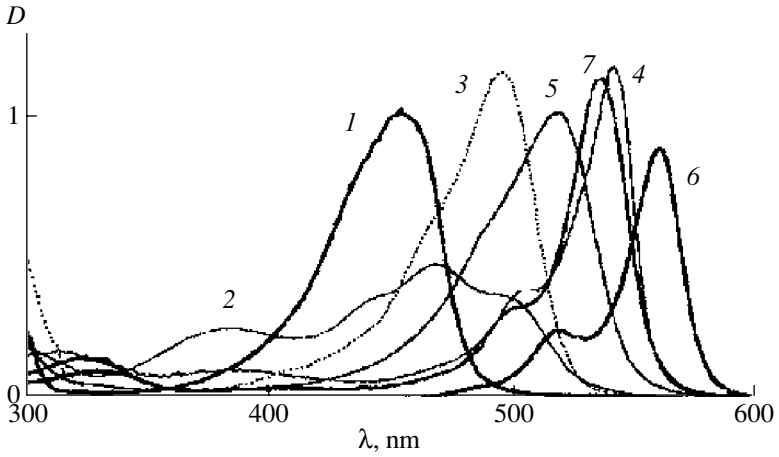


Fig. 3. Absorption spectra of the dyes in acetonitrile. The curve numbers corresponds to dye numbering in Fig. 2.

It was suggested to use, as an effective monomer, 2-hydroxyethyl methacrylate in PMMA containing the dye 1,3,5,7,8-pentamethyl-2,6-diethylpyrromethene difluoroborate as a photoinitiator [47]. Recording layers containing this PPM and having 500 μm thickness ensured obtaining holograms with DE = 60% at an exposure of $E = 1$ J cm^{-2}. Using modified PMMA, holograms with DE = 90% were recorded [48].

A photopolymerizable material based on cellulose acetate butyrate (50.4 wt %) was proposed, in which the cellulose ester was used as a polymeric binder containing 2-phenoxyethyl acrylate (29.2 wt %) and *N*-vinylcarbazole (17.2 wt %) as monomers, 1,1',2,2'-bis(*o*-chlorophenyl)-4,4',5,5'-tetraphenylbisimidazole (1.2 wt %) as a polymerization initiator, 4-methyl-4*H*-1,2,4-triazole-3-thiol (1.92 wt %) as a co-initiator, and 2,5-bis[(4-(phenylamino)phenyl)methylene]cyclopentanone (0.07 wt %) as a photosensitizer [49].

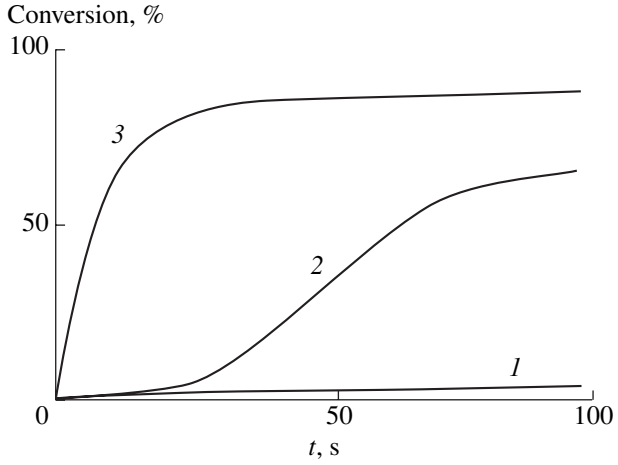


Fig. 4. Kinetics of photopolymerization of an acrylate PPM of 50 μm thickness in the presence of (*1*) Acridine Orange and 2-(4'-methoxyphenyl)-4,6-(trichloromethyl)-1,3,5-triazine; (*2*) Acridine Orange and Acridine Orange *N*-methyldiethanolamine; and (*3*) Acridine Orange, *N*-methyldiethanolamine, and 2-(4'-methoxyphenyl)-4,6-(trichloromethyl)-1,3,5-triazine.

Photopolymerizable materials with the polymeric binder poly(vinyl acetate-*co*-vinyl alcohol) containing acrylic mono-, bis-, and trifunctional monomers were also developed [50–52].

Attempts to increase the photoinduced change in the refractive index have led to realization of PPMs containing, in addition to a monomer and a photoinitiating system, neutral components (in particular, bromonaphthalene) that have a high refractive index and are not involved in the photopolymerization reaction [53, 54]. Such PPMs are referred to as photopolymer composites. Refractive index modulation in such composites is due not only to the photopolymerization process but also to the spatial change in the chemical composition of the medium as the result of mutual diffusion of the components between the illuminated and unilluminated areas. As neutral components, other unreactive compounds can be used, in particular, liquid crystals [55, 56], as well as photopolymerizable methacrylic, acrylic, styryloxy, and vinyl ester monomers containing liquid crystal moieties [57].

Holographic recording media on the basis of TiO_2 [58] and SiO_2 [59, 60] nanoparticles dispersed in PMMA layers were developed. The value of DE in such media can reach 95% at minimum layer shrinkage [61].

Sol–gel organic–inorganic composites with a thickness greater 200 μm on the basis of aromatic methacrylates were also proposed [62]. In such media, holograms with DE > 95% were recorded under the action of visible laser light (532 nm).

Acrylamides introduced into poly(vinyl alcohol) (PVA) at concentrations up to 6% found the most extensive application in holographic PPMs [63]. The highest photosensitivity was found for the bifunctional monomer *N*,*N*'-methylenebisacrylamide [64]. To decrease the noise parameters, *N*,*N*'-dihydrooxyethyleneacryla-

mide and dihydroxyethylenemethacrylate were introduced into these PPMs. The photopolymerization kinetics depended on the intensity of laser light [65].

By optimizing the writing light intensity, the layer thickness, and the concentration of each component, PPM samples containing Methylene Blue, acrylamide, and PVA were prepared, which provided recording holograms with DE = 80% at an exposure of E = 35 mJ cm^{-2} and a resolution of R = 1000 mm^{-1} [66, 67].

In a PPM layer based on the photoinitiating system eosin–thienoethanolamine, holograms were recorded by pulse laser light (532 nm) with DE = 60% and a photoinduced refractive index change of $\Delta n = 2.8 \times 10^{-3}$ [68]. The photosensitivity appeared to be the same as that with continuous lasers. The introduction of *N*,*N*'-methylenebisacrylamide into the PPM permitted an increase in DE to 85% [69].

The addition of *N*,*N*'-dihydroxyethylenebisacrylamide as a cross-linking agent to an acrylamide PPM led to an increase in the photosensitivity and DE. In a layer of 100 μm thickness, holograms with DE = 70% were recorded at an exposure of E = 5 mJ cm^{-2} and a spatial frequency of R = 1000 mm^{-1} [70, 71]. Unfortunately, the introduction of this additional component prevents crystallization of polyacrylamide and, therefore, does not permit prolonged storage of holograms [72].

To develop PVA-based PPMs, copolymerization of acrylamide with 2-hydroxyethyl methacrylate was used [66]. Holograms with DE = 70% were obtained in a layer of 110 μm thickness at an exposure of E = 65 mJ cm^{-2}. The introduction of the second monomer permitted an increase in the thickness of the recording layer and, hence, its information capacity. In 150-μm layers containing PVA, Erythrosine B, triethanolamine, acrylamide, and *N*,*N*'-methylenebisacrylamide at optimum concentrations, holograms with DE = 55% were recorded at an exposure of E = 60 mJ cm^{-2} and a resolution of R = 2750 mm^{-1} [73, 74]. It was found that triethanolamine had a strong effect on the photopolymerization process at the initiation stage, whereas diphenyliodohexafluorophosphate introduced additionally into this material had an effect at the propagation step of the photopolymerization process [75]. The angular disagreement at the Bragg angle was found to depend strongly on the recording angle [76]. This disagreement increases with an increase in the angle between the object and the reference beams. This is the result of shrinkage of the photopolymerized layer.

To prepare acrylate PPMs, poly(vinyl acetate) [76], poly(vinylpyrrolidone) [77], poly(isophthalate esters) [78, 79], and fullerene [80] were used as polymeric binders.

To decrease the shrinkage of a photopolymer layer, a hybrid organic–inorganic matrix was used instead of PVA, which was prepared by the synthesis of *N*-vinylpyrrolidone and triethoxyvinylsilane copolymer followed by hydrolytic condensation of the copolymer with a tetraethoxysilane presol [81]. At the stage of mixing the pre-sol and the copolymer, the photopolymer components of the composition were additionally introduced, which consisted of a mixture of acrylamide and acryloylmorpholine (monomers), bisacryloylpiperazine (crosslinking monomer), triethanolamine and mercaptomethyltriazole (initiators), and Methylene Blue (photosensitizer). In these media having a thickness of 0.46 mm, holograms with DE = 80% were recorded at exposures of E = 300 mJ cm^{-2}. The shrinkage of the recording medium was at most 0.7%. The angular selectivity of transmitting holograms reached 0.17%, which provided recording of more than 100 holograms on the same area of the medium. Such an amount of holograms is sufficient for realization of 3D optical memory with an information capacity of 1 TB.

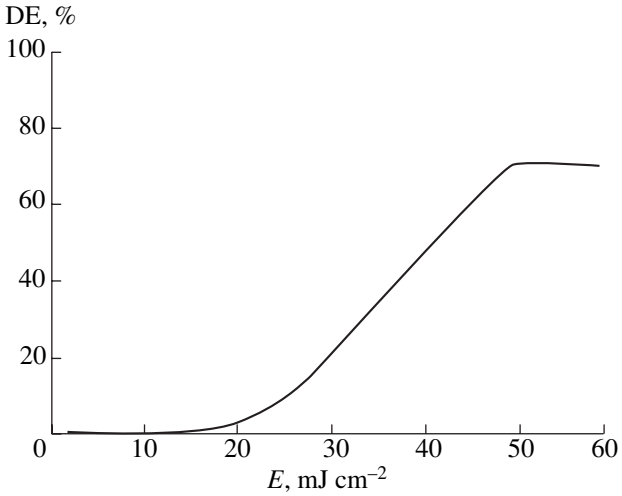


Fig. 5. Characteristic curve for a 0.8-mm thick PPM based on PVA and acrylamide.

Progress in studies on the development of thick-layer PPMs of this type [82] led to the preparation of samples 1 mm in thickness [83–85]. A new process for the fabrication of recording layers with the use of a solution containing PVA (13.3 wt %), acrylamide (0.34 mol l^{-1}), and triethanolamine (0.15 mol l^{-1}) with maximum viscosity was employed for this purpose [70, 86]. The hologram recording mechanism in such media was studied [87]. Holograms with DE = 70% at E = 50 mJ cm^{-2} (Fig. 5) and high angular selectivity were recorded in the obtained samples (Fig. 6) [83]. In relation to the creation of nonshrinkable recording media, hybrid sol–gel PPMs based on acrylamides are of particular importance [88–91]. In such media, holograms with DE = 95% at an exposure of E = 0.5 J cm^{-2} and an angular selectivity of $\Delta\theta = 0.0967°$ were recorded [90]. To record holograms with DE = 60% in a layer of 1.1 mm thickness, an exposure of E = 0.139 J cm^{-2} was required [91]. Figure 7 shows restoring of nine holograms recorded in the layer at angular multiplication [91]. In thin layers (113 μm) of the same PPM, holo-

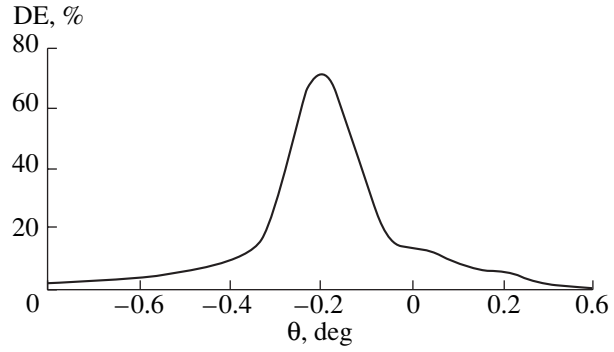


Fig. 6. Angular sensitivity of the 0.8-mm thick PPM based on PVA and acrylamide.

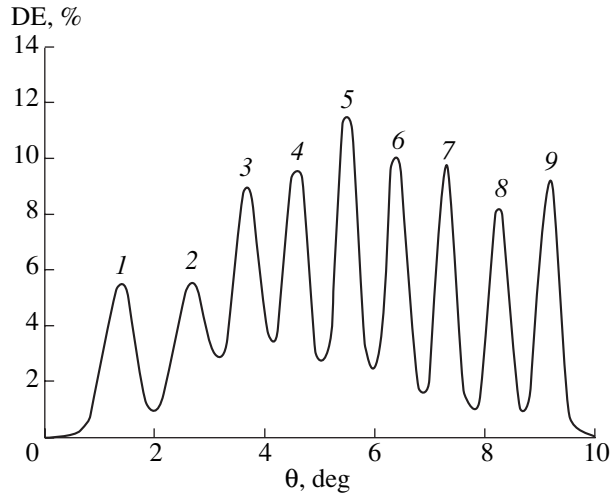


Fig. 7. Diffraction efficiency for holograms recorded at different angles in PPM in silicate porous glass 1.1 mm thick based on acrylamide, *N*,*N*'-methylenebisacrylamide, triethanolamine, and Eosin Yellow.

grams with DE = 80% were recorded at an exposure of $E = 0.01$ J cm^{-2}.

In acrylamide PPMs, up to 30 holograms were recorded in the same area of the recording layer with a resolution of $R = 1500$ mm^{-1} [92]. In PPM layers, holograms were recorded with a spatial resolution of $R = 6380$ mm^{-1} but a low DE value (0.015%) [93].

In the course of development of thick-layer acrylamide recording media, a variety of theoretical studies were performed. It was shown that the PPM thickness determines the hologram recording conditions [94]. It was found that the optical and physical thicknesses of PPM do not coincide [95, 96]; the effect of the introduction of an additional crosslinking monomer on characteristics of the medium was examined [97]; and the dependence of the photopolymerization rate on the activating light intensity [98], the concentration of components [99, 100], the period of the grating recorded [101], the exposure [102], and mutual interference of recorded holograms [103] was revealed. The monomer diffusion constants were determined [104]. A model was developed that explained the effects of thickness, light intensity, and refractive index on the PPM characteristics [105].

At present, PPMs with joint radical and cationic photopolymerization are finding progressively increasing application in holography. Vinyl esters in mixtures with halogenated protic acids are most often used as monomers for cationic photopolymerization. In the photopolymerization process, polymers with characteristics of elastic polyurethanes and epoxy polymers are obtained due to interpenetration of polymer networks. The media based on double photopolymerization with the use of a liquid epoxide resin with an amine hardener and a photopolymerizable vinyl monomer provide a steep photoinduced change in the refractive index of PPM containing *N*-vinylcarbazole and *N*-vinyl-2-pyrrolidone. A characteristic feature of cationic photopolymerization is its continuation after cessation of exposure to light (Fig. 8) [16]. As a result, the photosensitivity of such PPMs increases.

Photopolymerizable materials with different photopolymerization mechanism can be used to manufacture the recording medium itself. Initially, cationic photopolymerization to form holograms is effected by coherent light, and then the holograms are enhanced using radical polymerization. Recording holograms is possible by radical polymerization followed by their enhancement by the cationic photopolymerization process.

A comparative study of the Du Pont PPM [106] and the material based on epoxide and acrylate monomers [107] showed that in the latter case, DE = 55% and did not change upon storage of holograms, thus making it possible to restore the image without changes over a long time [107]. This is achieved at the expense of spontaneous polymerization of the epoxide monomer for 24 h at 45–50°C. In such media, holograms were obtained by photopolymerization of the acrylic monomer. The difference between the polymer and monomer refractive indexes was $\Delta n = n_{pol} - n_{mon} = 1.572–1.412 = 0.16$.

Holograms in a PPM based on a mixture of an acrylic monomer and a bisphenol epoxy medium, and diaryliodonium salt sensitized by 3-ketocoumarin and irradiated with Ar^+ laser light (514.5 nm) were recorded at exposures of $E = 60–150$ mJ cm^{-2} [108].

Photopolymerizable materials based on epoxyacrylate oligomer of bisphenol A, divinyl ether, and a photoinitiating system containing Rose Bengal were proposed for hologram recording [109]. Silicon-containing epoxides were used to prepare a PPM with improved properties [110].

New prospects for creation of 3D holographic memory are offered by two-photon recording of holograms in any area of an epoxide PPM containing Epotek-21 resin as a polymeric binder, dipentaerythritol pentacrylate (monomer), and dimethylketal (photoinitiator)

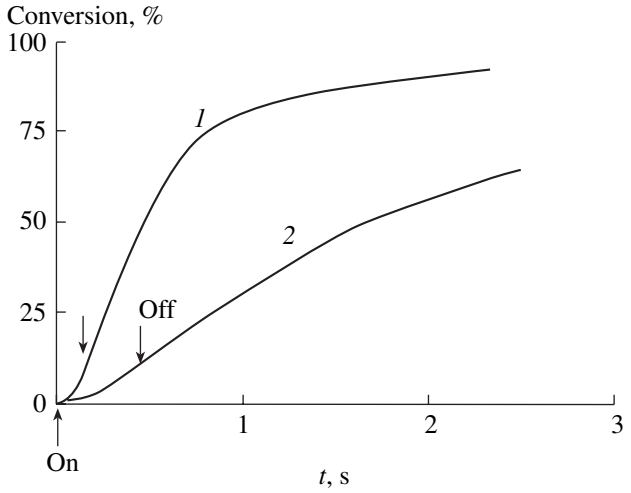


Fig. 8. Photopolymerization after switching on and dark polymerization after switching off laser light (at short exposure) in PPM based on (*1*) cycloaliphatic diepoxy and (*2*) divinyl ether in triethylene glycol containing the diaryliodonium salt–isopropylthioxanthone photoinitiating system.

[36]. The starting composition was characterized by a refractive index of $n = 1.4885$, which increased to $n = 1.5279$ after photopolymerization. The measured value of DE reached 3.5%.

RESULTS OF APPLICATION OF PHOTOPOLYMERIZABLE MATERIALS IN HOLOGRAPHIC OPTICAL DISKS

Three types of holographic recording media were developed on the basis of photopolymerizable compositions that had been proposed for the fabrication of 3D holographic optical disks:

(1) The recording media of the HRF series (HRF-150, HRF-800) designed by Du Pont (USA) containing aromatic or aliphatic acrylate monomers in cellulose acetate butyrate [111]. In such media, holograms were recorded with DE = 100% at exposures to $E = 3$ mJ cm^{-2}. It was shown that, in a 100-μm layer, information could be recorded with a density of 10 b μm^{-2} (6.5 Gb in.$^{-2}$). Optical disks with a thick photosensitive recording layer ensure an information capacity of 40 GB and the reading speed of 50 MB s^{-1} [112], with the angular selectivity being $\Delta\theta = 0.09°$.

(2) The recording medium DHR-128 developed by Polaroid (USA) based on poly-*N*-vinylpyrrolidone polymer matrix containing a mixture of lithium acrylate, acrylic acid, bisacrylamide, and Methylene Blue [113, 114]. This medium provides recording holograms with DE = 80–95% at exposures to $E = 5$ mJ cm^{-2}; moreover, not only scalar but also polarization holograms [115].

(3) The recording medium HMD-120 offered by Aprilis (USA) [116] was created on the basis of organosilicon monomers participating in cationic photopolymerization and acrylate monomers polymerized by the radical mechanism. This medium differs from the media considered above in that the photosensitive layer experience a low shrinkage during hologram writing. This ensures the manufacture of holographic ODs 120 mm in diameter with a information capacity of 200 GB and an information reading speed of 200 MB s^{-1}.

CONCLUSIONS

The analysis of the state of the art of the development of photopolymerizable recording media shows that a PPM of the type HMD-120 (Aprilis, USA), which has been designed to date, meets the requirements for application in 3D holographic ODs and, thus, there is hope that it will be commercialized. However, further enhancement of the information capacity, photosensitivity, and angular selectivity and lowering the noise characteristics demands improvement of photopolymerizable recording media.

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