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C. Carré, D. Lougnot. Photopolymers for holographic recording: from standard to self-processing materials. *Journal de Physique III*, 1993, 3 (7), pp.1445-1460. 10.1051/jp3:1993211 . jpa-00249010

HAL Id: jpa-00249010

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Submitted on 4 Feb 2008

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Classification

Physics Abstracts

42.65 — 82.50 — 78.20

Photopolymers for holographic recording : from standard to self-processing materials

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(Received 8 December 1992, revised 8 February 1993, accepted 9 February 1993)

Abstract. — There has been a recent surge of interest in photopolymerizable materials in the field of holographic recording. Such materials exhibiting sensitivity in the UV, visible and near IR domains are now available. They are used for transmission or reflexion holography and generate permanent thick phase gratings. In spite of their poor photosensitivity compared to silver halide emulsions, they are interesting candidates for many holographic applications such as real time interferometry. The direct generation of images with no post-treatment, nor repositioning is their most attractive feature. A recording system which is sensitive in the 450-550 nm range and which is the most advanced version of the materials developed in Mulhouse, is used to exemplify the performances of self-developing polymer layers in the fields of interferometry, optical correlation or HOE.

1. Introduction.

Photopolymerizable materials and photosensitive polymers have been used for recording holograms since the late sixties [1-9]. Over the twenty five following years, the first laboratory experiments which demonstrated the feasibility of the concepts, were followed by a prolonged search for better materials that still seems nowhere near its end. The interest attached to this field is evident from the number of contributions reporting various formulations and processes.

Basically, a holographic recording material is nothing else than an imaging system : the sensitive layer memorizes information as local modifications of the optical properties. Thus, the record contains image and non-image areas whose microscopic optical characteristics are different. In their conventional sense, the words « image recording » refer to any kind of physical or chemical process producing a pattern of optical absorption in the sensitive layer. In the broader and less restrictive sense used here, the word « image » means a spatial change of the optical properties of the recording material, which is able to induce a modification of a light beam passing through the record.

Based on this approach, the holographic imaging process can be associated with a local modulation of either the refractive index or the transmission of the recording material, or both.

Refractive index patterns which modulate the phase of a « reading » laser beam (and not its amplitude) are usually referred to as phase holograms. The main advantage of this type of records is their ability to reconstruct a wavefront without optical absorption, i.e. without attenuation of the amplitude of the incident carrier wave.

A great variety of materials have been used to record phase holograms [10-12]. From a general point of view, the sensitive system should be able to memorize accurately the spatial variations of intensity contained by the pattern arising from the interference between an object and a reference beam of coherent light. In addition, it should lead to perfect wavefront reconstruction, display a sensitivity matched to available lasers, exhibit linear transfer characteristics and not introduce noise into the diffracted beam. Taking everything into account, an ideal material would be relatively inexpensive and indefinitely recyclable. As no recording system is thus far able to meet all these requirements, one has to choose among those available, the material best adapted for a given practical application. Among the major materials exhibiting attractive features, silver halide emulsions, dichromated and dye-sensitized gelatin, ferroelectric crystals and photochromic or photodichroic substances should be mentioned.

A number of organic materials, that can be photoactivated either directly or through a sensitization process, exhibit refractive index changes resulting from polymerization, crosslinking or depolymerization. Despite several shortcomings (poor photosensitivity and low index modulation), polymer-derived materials display some attractive features which offer the holographer the possibility to do away from the typical drawbacks of dichromated gelatin or silver halides for particular applications (complex wet processing, poor shelf-life or environmental instability).

The holographic technologies using polymer recording materials can be divided into four categories :

- *dry formulation* containing a polymeric film-forming binder (substrate), a dissolved monomer and a photoinitiating system ;
- *liquid or highly viscous coating* containing monomers with several reactive functions and an initiating system ;
- *dry film composition* containing crosslinkable, dispersed or grafted structures or unreacted double bonds and an initiating system ;
- *polymer film composition* containing sensitive groups capable of undergoing photomodification (isomerization) or photodegradation (cleavage).

Of these four categories, only 1 and 2 seem to have enjoyed some practical and commercial success.

Several attempts have also been made at extending the sensitivity of photopolymer holographic layers to the far red and even the near infrared. Though promising, the available materials did not open really new perspective in this spectral range. In this context, we have recently introduced new self-processing formulations which exhibits light sensitivity from 600 to more than 850 nm [13] and which were used with success for real time holographic interferometry.

2. Mechanism of hologram formation.

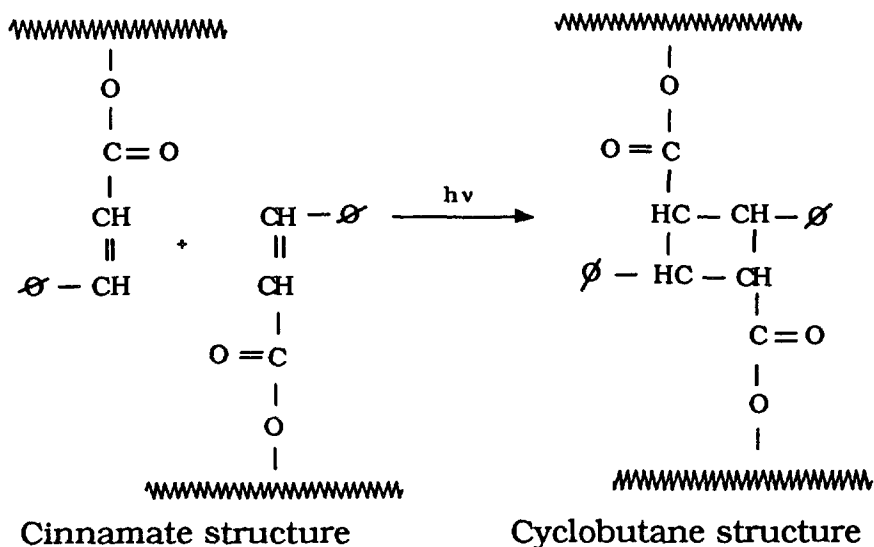
In earlier reviews concerned with organic materials used for holographic recording, three basic ways were listed to induce refractive index changes in a photosensitive material [14, 15] :

- *change the spatial arrangement of the atoms* of one or more components, to modulate spatially their molar refractions and, by way of consequence, the refractive index at the macroscopic scale ;

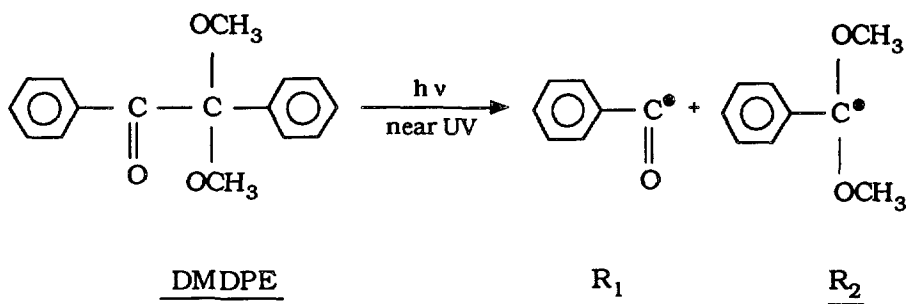
- *change the concentration of various components* of the reactive mixture at the microscopic scale, without changing the overall density of the composition ;
- *change the density of the sample* at the microscopic scale (micron or sub-micron), without changing the macroscopic chemical composition.

A large number of systems illustrating these three different possibilities have been described. Of them, several examples led to practical materials which can compete with dichromated gelatin or silver halide emulsions.

2.1 CHANGE OF MOLECULAR STRUCTURE. — In the systems based on this mechanism, the molecular structure of, at least, one component of the reactive mixture undergoes phototransformation on irradiation. Recording systems in which the change in refractive index is the consequence of a photocyclization to a dimer structure (photolocking) or of the corresponding back reaction, belong to this class of materials [16]. Molecular structures based on the cinnamate function are typical examples of this mechanism [17].



Other systems, in which the local change of refractive index is associated with the grafting of radical fragments generated by the photolysis of a cleavable molecule on a homopolymer or copolymer structure, were studied by Driemeyer. Dimethoxydiphenylethanone is commonly used to photogenerate primary radicals [18, 19].

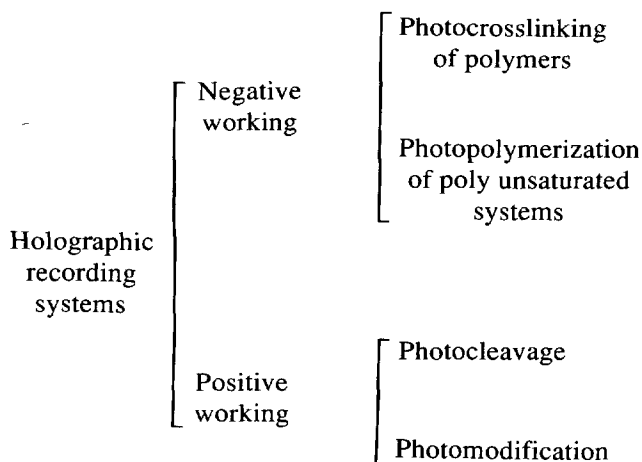


R_1 or R_2 + polymer with reactive groups \rightarrow photomodified polymer.

In order to achieve a good stability of the record, the polymer matrix is hardened by a moderate photocrosslinking in the presence of a reactive diluent.

Since the radical generator DMDPE is moderately volatile at 100 °C, the refractive index patterns can be further « developed » and fixed by simple annealing at 100 °C for some hours. After this treatment, the unreacted DMDPE is removed from the non-light-struck regions and the polymer film becomes insensitive to further irradiation. Maximum refractive index changes of 2.1×10^{-2} were achieved. Other systems have also been reported to undergo important modulation of thickness on holographic exposure [20].

Hologram recording with polymer layers can also be accomplished in a number of ways using a variety of photosensitive materials which, in turn, can produce a variety of recording systems through photoactivation. Basically, all the systems of current use in imaging technology and in which the mechanism of action involves a photoinduced change of the solubility parameters of the exposed area, should be suited for holographic recording. There are two main groups of such photosensitive systems which, in practice, are able to memorize optical information and can be used, after wet treatment, to generate holographic elements : the negative and the positive working films [21].

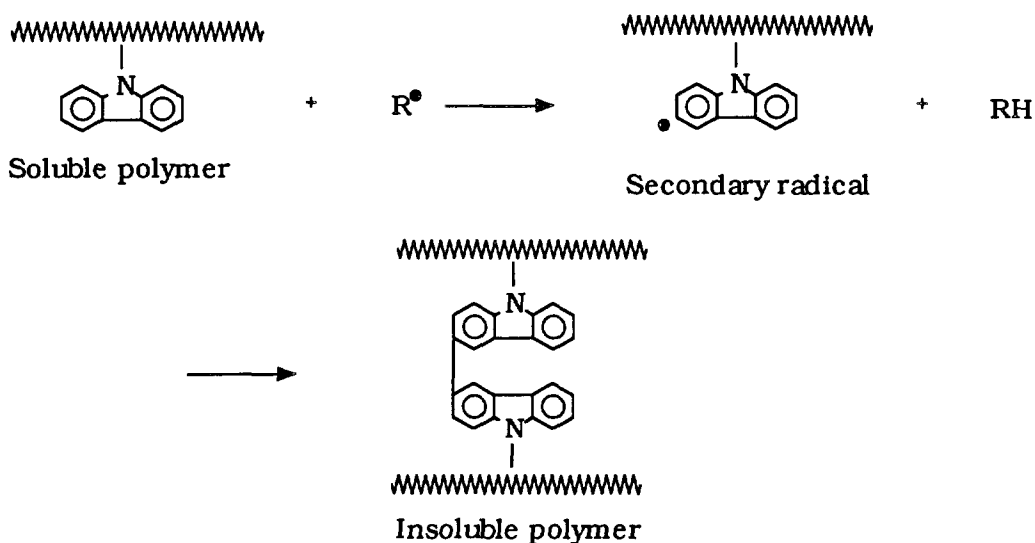


In negative working systems, the light-struck areas are made insoluble by the photoinduced crosslinking process, that generates a tridimensional network. This crosslinking reaction results in a difference in solvent resistance between the exposed areas and the unexposed areas. In the positive working ones, due to photolysis of the functional groups carried by the polymer structure, the degree of polymerization and the molecular weight are reduced in the illuminated areas and, hence, the solubility of these regions increases.

Thus, in those systems, a hologram is obtained by treating the exposed layer with a solvent, so as to form a relief hologram pattern. Further, the holographic characteristics can be improved by subjecting the record to either a swelling treatment in a solvent, in which the material is insoluble but capable of being swollen, or to a contraction treatment in a non-solvent medium or both successively [22-24].

Among the various holographic recording media belonging to this category, the system based on polymer carrying vinylcarbazole pending groups is a representative example [25]. On irradiation by light in the presence of an adequate radical generator, vinyl carbazole undergoes

hydrogen abstraction ; the secondary radicals produced can, then, lead to a locking process which goes along with a change of the solubility parameters.



Another class of recording systems based on the idea of changing the structure at the local scale, has been introduced by Chandross *et al.* [26]. The recording process involves the selective photolysis in the desired pattern of an initiator chemisorbed on the internal surfaces of a porous glass matrix. During this step, the latent image formed corresponds to only small changes in the optical properties of the material. This image is, then, developed by filling the matrix with a suitable monomer mixture and using a uniform optical exposure (i.e. non-holographic) to initiate polymerization. Final modulations of up to 3×10^{-4} have been observed.

2.2 CHANGE OF CONCENTRATION. — Systems in which this way of altering the refractive index within the sample is used to record the holographic information, are based on formulations containing at least two basic components : a photopolymerizable substance, the monomer, and an active polymer substrate, referred to as the binder.

This idea was turned to account in a large number of polymer materials introduced from the early seventies, to create important modulations of the refractive index [27-31]. Several compositions based on this concept, and which can be used both for transmission and reflection recording, were described by du Pont. Although these coated photopolymers appear to be macroscopically homogeneous solids, they are microscopically heterogeneous with viscous, binder-rich and non-viscous, monomer-rich phases. On initiation of the polymerization in regions corresponding to the bright fringes of the interference pattern, the monomer is converted to polymer and additional monomer molecules diffuse to these regions from non-light struck areas. Due to progressive formation of the polymer network, large molecules are prevented from migrating into the recording layer, hence a one-way diffusive process, which only affects the unreacted monomers. The consequence of this process is an expansion of the polymerizing regions, that goes along with an increase in concentration of the monomer-derived polymer and a decrease in binder concentration in the irradiated regions. At the same time, the binder-rich microphases (which are no longer swollen by monomer) contract.

In addition, as polymer is being formed, the solubility of the binder in the monomer is suspected to decrease so that, in the first moments of the photoprocess, at least, there may be some net migration of binder away from the monomer rich microphases. It was also reported that addition of a second monomer or a plasticizer, may increase the refractive index modulation and, by way of consequence, the final diffraction efficiency. The highest modulations were observed with materials containing an aliphatic binder, a liquid aromatic monomer (e.g. phenoxyethylacrylate) and an additional solid aromatic monomer carrying either heavy atoms or polycyclic rings [32, 33].

Quite interestingly, the modulation induced by the photochemical process can be increased by subsequent « backing ». By way of illustration, in the case of a film recording a transmission hologram at 514 nm (du Pont HRF-700), the index modulation was reported to increase by over 250 % to 0.0088, after heating at 100 °C for 30 min with a diffraction efficiency going up from 16 to 77 % [34, 35]. In the case of reflection holograms, the same kind of post-processing procedure leads to efficiencies ranging from 70 to 99.9 % with corresponding index modulations of 0.008 to 0.068 [36].

Another procedure of development of such materials was described and turned to advantage by the Polaroid corporation, to increase the modulation of refractive indexes associated to the spatial modulations of concentration. This procedure involves a swelling of the record in an appropriate solvent. During this incubation, small voids are created in the regions where the photopolymerization induces important internal stress. Refractive index modulations of 0.03 are routinely achieved [37-43].

2.3 CHANGE OF DENSITY. — The third way to induce a modulation of the refractive index in a photosensitive polymer film on holographic exposure, is based on a physical process which leads finally to regions with various segment densities. This process basically involves a migration of monomer molecules in the plane of the interference pattern and normally to the fringes.

During the initial exposure, monomer in light-struck areas polymerizes and, thus, becomes depleted in these regions, whereas its local concentration is not affected in non-light-struck areas. The resulting concentration gradient causes unreacted monomer molecules to diffuse from dark fringes to bright fringes. This diffusion process continues until the hologram is fixed by overall post-exposure (Fig. 1). It can also come to a stop, since the remaining monomers are unable to undergo bimolecular reaction, due to the gelation or vitrification which goes along with crosslinking [44].

Acrylic monomers which are currently used in these recording systems, are known to undergo an important molecular volume decrease when polymerized (up to 20 % in vol.). The local change in refractive index during the polymerization is expected to be related to this observation. This behavior is predicted, at least qualitatively, from the Clausius-Mossotti equation of electrostatics, which indicates that a change in refractive index in a given substance depends only on the initial value of this index and on the fractional change in density.

Another possible explanation of the dependence of the refractive index on the exposing light intensity is that the average molecular weight of the photopolymer (in the case of a linear polymer) or the average length of the crosslinks (in a three-dimensional system) depends on the stationary free-radical concentration, which in turn, depends on the irradiance. Since free radicals both terminate and initiate the polymerization process, stronger irradiance would lead to higher concentrations of radicals and shorter macromolecules.

With this approach, polymers made up of smaller macromolecules should lead to the denser structures, that is consistent with the observed dependence of the refractive index on the irradiance [45-47]. Such a behavior is effectively observed in the case of pentaerythritol

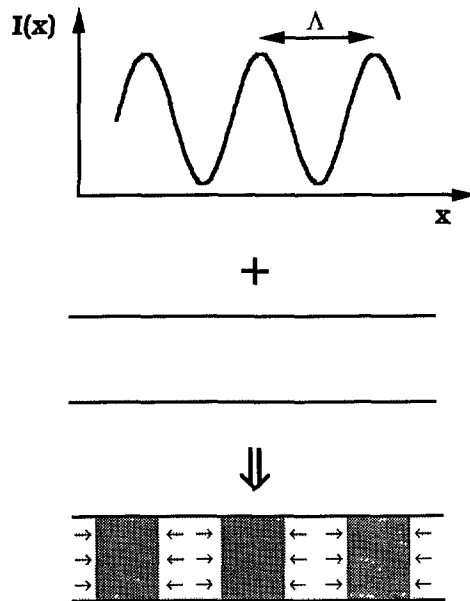


Fig. 1. — Schematic cross section of a phase grating engraved in a polymer material by a photoprocess involving local change of segment density (The horizontal arrows materialize the diffusion flow).

triacrylate (PETIA), a trifunctional monomer base, which is in current use in holographic recording systems.

A property of these systems opening up interesting possibilities, in their unusual termination process. When the polyfunctional bases used to crosslink a polymerizable medium are thoroughly converted, the network reaches such a degree of entanglement that the bimolecular reaction between the living macroradicals and the unreacted sites becomes impossible. The termination is said to occur through occlusion and, as a matter of fact, the photoreaction comes to a standstill. Although uncompletely converted, the monomer sites cannot undergo a photochemical bimolecular reaction and hence a completely inactive stage, which is reached without post-illumination. Some characteristics of these materials are shown in table I [48].

Such systems, which lend themselves to spectral sensitization, were described by several authors. Due to their very attractive features — complete absence of wet processing, high flexibility of the formulation, high diffraction efficiency, insensitivity of the record to environmental factors — these materials are held in high repute by holographers. They are considered as excellent recording media for research laboratory experiments, and more especially for real time interferometry [49-51].

3. The materials available.

A great number of holographic recording materials based on photopolymers are now available. Depending on the specific application which is foreseen, they show a great variety of physicochemical and optical characteristics. In order to help the holographers in their search for more adapted recording systems and to make up their mind about photopolymers, tables I and II gather a few pieces of information about the systems mentioned in the literature.

Table I. — *Characteristics of the photopolymer recording media for holography.*

Spectral range of sensitivity	320 - 855 nm	- no panchromatic system available. - generally, sensitivity range ~ 150 to 200 nm for a given material.
Type of modulation	Phase - refractive index and/or thickness.	
Thickness	Few μm - few hundreds.	- radical polymers for thin layers. - cationic for thick ones.
Sensitivity (photospeed)	With processing few mJ/cm^2 to few tens.	- subsequent processing.
Holographic sensitivity	UV systems: 0.01 to 0.1 m^2/J Visible : 10 to 100 cm^2/J . Near-IR : 1 to 5 cm^2/J .	Measures the initial rate of building up to the record.
Spatial frequencies covered	Few hundreds to 3500 lines/mm. Typ. 1000 lines/mm.	Some mentions of systems with up to 6500 lines/mm, but not technical information available.
S/N ratio	10 to 300	Depends on the system and on η_{max} .
Index modulation	10^{-3} to 0.06 Typ. 0.003 to 0.008 without processing	Depends on the post-treatment.
Diffraction efficiency	Few percents to 99.99 %	Depends on the range of sensitivity and on the treatment.
Angular bandwidth	Fraction of degree to few deg. without processing. Up to few tens after processing.	Narrow viewing angle compared to DCG Can be an advantage for specific applications.
Shelf-life storage	- unilluminated films: minimum one year. - holographic records: several years at RT.	Resistance to atmospheric agents depends on conditioning
Others	Possibility to record several holograms in the same layer by adequate control of the exposures.	Applications in interferometry

4. Holographic applications using a self-processing polymer material sensitive in the 450-550 nm range.

The photopolymerizable material referred to as B in table II which exhibits sensitive in the blue green range has been described in details elsewhere [49-53]. Its optimization has been performed using holographic spectroscopy associated to analytical techniques such as time resolved absorption laser spectroscopy, UV-visible or IR spectroscopy and NMR.

Table II. — Characteristics of the self-processing systems developed in Mulhouse.

Reference of system	A	B	C	D
Spectral range covered (nm)	300-400	450-550	550-700	650-850
Holographic sensitivity S (cm ² /J)	100-500	10-50	30-60	1-2
η_{\max} (%)	15	75	50	30
Refractive index modulation	/	$3-5 \times 10^{-3}$	$1-2 \times 10^{-3}$	/
Energetic sensitivity (mJ/cm ²)	50	300	50	600

This recording material contains a monomer base (a mixture of acrylic esters of pentaerythritol and of the Michael adduct of pentaerythritoltriacylate with acrylic acid), a sensitizer dye (an eosin derivative), and a cosensitizer (methyl diethanolamine) [54]. This material is embedded between two glass slides and the thickness of the recording layer is defined by a metal foil spacer in order to obtain a thickness of about 50 μm .

The conditioning of this layer involves a preillumination by an appropriated UV source, the object of which is to seal the edges of the recording layer together with the glass slides and to increase the viscosity of the material by creating a three-dimensional network. Such a structure is propitious to the microsineresis process which takes place during the building up of the record.

4.1 CHARACTERIZATION OF THE RECORDING MATERIAL. — Its spectral sensitivity (from 450 to 550 nm with a maximum at 530 nm) fits perfectly the lines of Ar⁺ and frequency doubled YAG lasers.

The recording layers are of a very simple use. The pre-treatment is necessary for applications such as Fourier holograms storage. In that case, the diameter of the record is smaller than 1 mm. Since the mobility of the active species is decreased owing the presence of some long polymer chains in the medium, the final degree of conversion and the grating efficiency are lower. In return, the periphery of the hologram is not damaged by the shrinkage of the polymer. Afterwards, the recording plates can be stored in black envelopes at room temperature for more than 1 year. They are immediately ready for holographic experiments.

Transmission and reflection thick phase gratings are recorded *in situ* during exposure. Maximum efficiencies exceeding 75 % are readily obtained for transmission holograms. Optimum imagewise exposure is typically 300 mJ/cm². Experimental results for writing power densities varying from 0.07 to 230 mW/cm² show that the higher the incident power density, the faster the building up of the grating. When the power density is too weak, the maximum diffraction efficiency remains quite low. Transmission holograms were recorded with 40 $\mu\text{m}/\text{cm}^2$ in the reference beam, 5 $\mu\text{W}/\text{cm}^2$ in the object beam and a 7 min exposure. In spite of the low diffraction efficiency (ca. 5 %), the result was interesting for applications in

real time interferometry when the size of the object beam becomes very large. As a general rule, a power density of 1 to 6 mW/cm² is preferred.

The resolution power extends up to 3 000 lines/mm when no special precaution is taken. The major part of the loss of resolution is due to Fresnel reflections at the different interfaces, in particular at the glass-air interface. They introduce spurious reflected beams which partially destroy the grating. The use of an experimental set-up with prisms and index matching with an appropriate liquid (Fig. 3) allows the spatial resolution be extended up to 4 000 lines/mm. Orthoxylene whose refractive index is very close to that of Pyrex® glass is perfectly suited for this purpose. In this experiment, the two incident beams overlap at the polymer layer with an interference angle of 45° the fringe spacing is then 0.24 μm. With such a set up, it becomes possible to use the polymerizable layer for reflection hologram recording. The experimental results are summarized in table III.

Another interesting feature of this material is to allow multiple holographic storage with the possibility of testing each record by direct visualization of the images at each step of the operation. It is possible to record sequentially at least five successive holograms with a diffraction efficiency around 10 % in the same polymerizable layer without loss of the spatial resolution (Fig. 2). Because of the high degree of angular selectivity, a rotation of 4° between the records is enough to eliminate intermodulation. Since the species involved in the initiation mechanism are progressively consumed as the holograms build up, the incident intensities and exposure times must be determined so as to take into account the degree of conversion of the components of the recording mixture and reach complete exhaustion at the end of the last

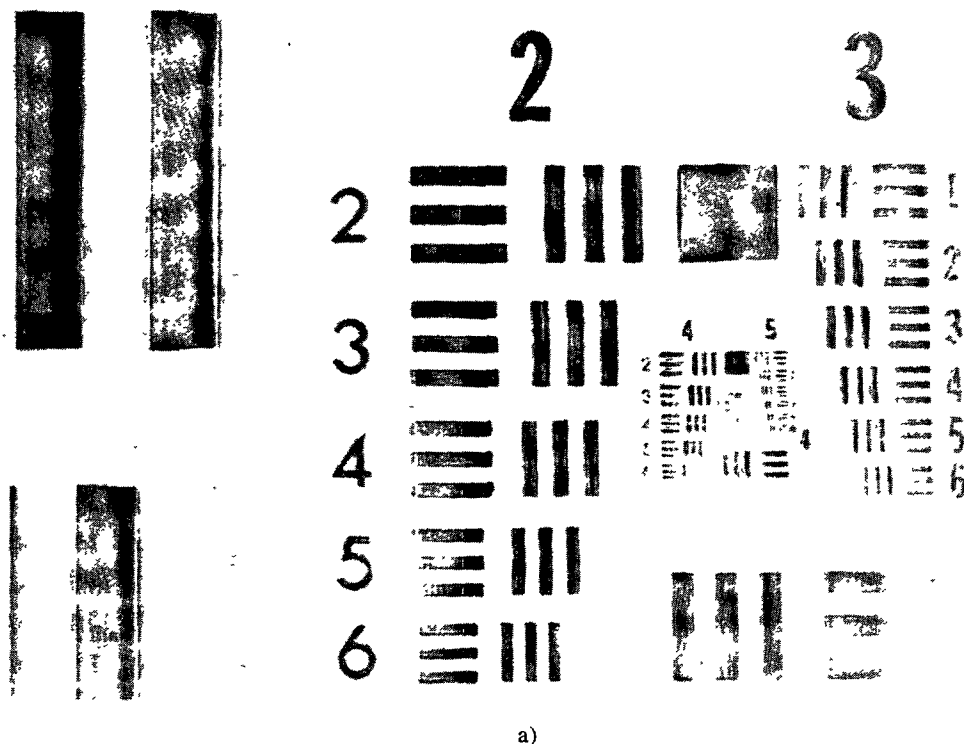


Fig. 2. — Multiple storage of holograms in a same photopolymerizable layer (spatial frequency = 1 450 lines/mm): a) first record (reference intensity = 1.1 mW/cm², object intensity = 0.25 mW/cm² and exposure time = 40 s), b) fourth record (reference intensity = 1.1 mW/cm², object intensity = 1.2 mW/cm² and exposure time = 300 s).

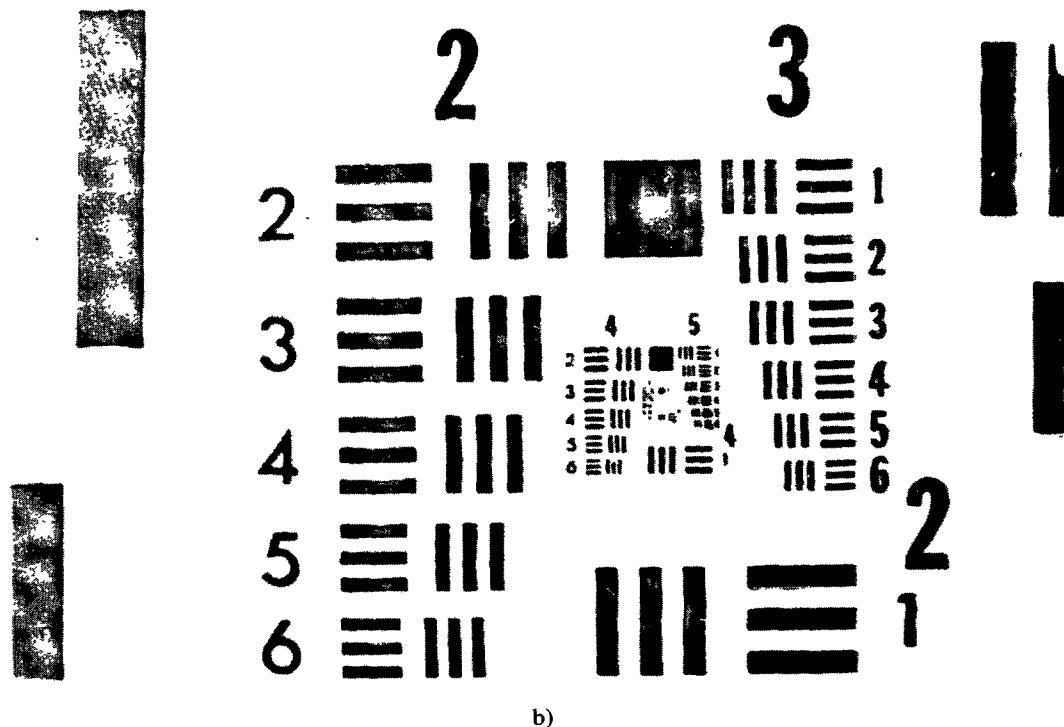


Fig. 2 (continued).

Table III. — Values of η for $\theta = 45^\circ$ and $\Lambda = 0.24 \mu\text{m}$.

	classical set-up	set-up with prisms and index matching
transmission holography	3 %	30 %
reflection holography	< 1 %	14 %

imagewise exposure. The different records can be inspected immediately after holographic illumination with a reading intensity lower than $5 \mu\text{W}/\text{cm}^2$.

4.2 APPLICATIONS. — Several applications are now under development in close collaboration with industrial or university partners. Since the features of the polymerizable material (chemical composition, method of conditioning) are very flexible, they can be adapted so as to meet the requirements of various applications. For instance, the desired diffraction efficiency is not the same for interferometric studies that for holographic optical elements recording. The possibility of a permanent dialogue between chemists (designers) and physicists (users) is, thus, an important key for success.

4.2.1 *Interferometric holography.* — Real time and time average holographic interferometry have been tested successfully [52, 53]. Moreover, it can be used in double exposure

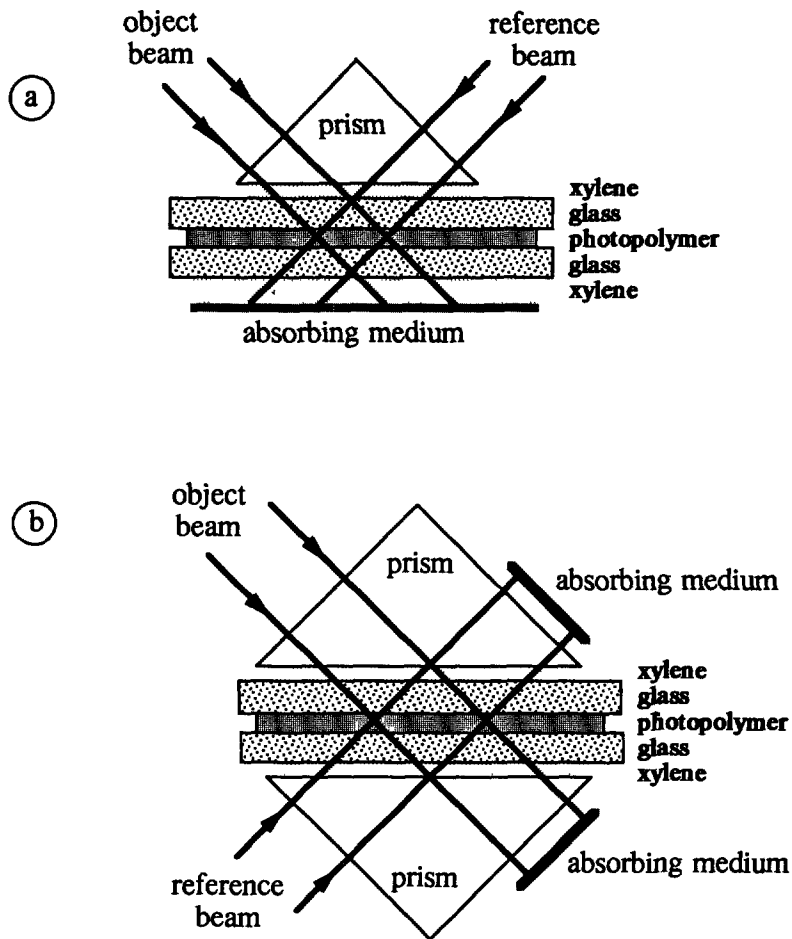


Fig. 3. — Holographic set-up with prisms and index matching used in order to limit the spurious reflections : a) for transmission holography, b) for reflection holography.

interferometry whenever time evolution of the system under investigation is not faster than the time response of the recording material.

Real time holographic interferometry is the field of application where the generation of images *in situ* is an outstanding advantage compared to other holographic materials. Crystal growth experiments [55] using polymer recording materials are carried out in collaboration with the Centre National d'Etudes Spatiales in Toulouse. The recent emergence of small FD YAG lasers with enough power offers new possibilities to instrument designers, particularly for microgravity experiments. The polymer emulsion can also be used in the kinetic study of the concentration gradients associated to electrolysis processes (Fig. 4) or to photopolymerizations.

Studies of the mechanic vibrations of a turbine blade were carried out using real time and time average interferometry or strob holography by the Laboratoire de Physique Générale of the University of Liège [56].

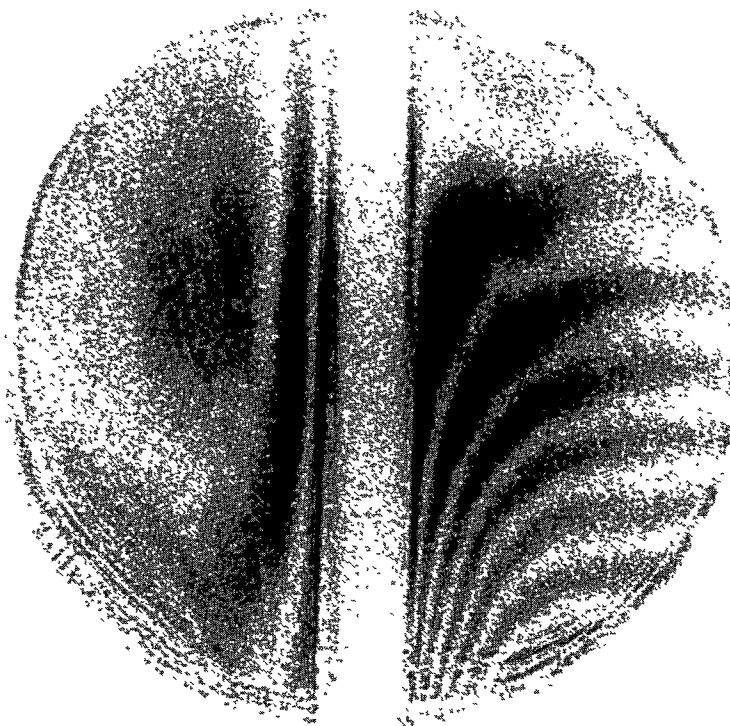


Fig. 4. — Interferometric fringes obtained during electrolysis of a copper sulphate solution, near the cathode.

4.2.2 Holographic optical elements. — Different applications are now under development in this field :

— the duplication on photopolymer of diffractive optical elements in collaboration with the Ecole Nationale Supérieure des Télécommunications de Bretagne, the Centre National d'Etudes des Télécommunications of Lannion [57] and the Laboratoire de Physique Générale of the University of Liège [58] ;

— the fabrication of holographic filters used in optical correlator systems in collaboration with the Laboratoire Central de Recherche of Thomson-CSF [59].

Duplication of Computer Generated Holograms (CGH). — CGHs are traditionally available on silver halide emulsions as amplitude transmission images. The conversion of such thin amplitude holograms to thick phase holograms by duplication on a polymerizable layer allows the diffraction efficiency to be substantially increased.

Different methods are under investigation. The direct contact copy is unsatisfactory for this material. The duplication technique based on the recording of an intermediate hologram seems to be better adapted. This method uses the inverse Fresnel transform of the object or a 4-f set-up imaging the CGH in the plane of the polymer layer. In both cases, the pattern recorded by the holographic plate results from the interference between a reference wavefront and the scattered wavefront from the object. The new CGHs could be implanted in optical computing systems as focusing elements (Fresnel lenses arrays, interconnection matrixes..).

An original application of polymer systems in which the CGH is an off-axis Fresnel lens was presented recently. A 4-f processor is used to filter the object wavefront; all the orders diffracted by the thin binary amplitude hologram are masked except the first one. The set-up with an interference angle of 90° between the two beams is intended to generate polarizing properties: an *E*-polarized wave is not diffracted contrary to an *H*-polarized wave which is diffracted. The choice of the polymer recording system in preference to dichromated gelatin was motivated by swelling effects which occur during the development process of DCG and which alter the Bragg selection. The photopolymer used evades this problem as no post-processing is required. The final polymer element diffracts a wave linearly polarized at more than 99.9 % on illumination with a non-polarized plane wave.

Application to optical correlation. — The reference filter used in optical correlation can be recorded with the photopolymerizable layer. It is produced by interfering a collimated beam with the Fourier transform of the reference object. The sensitive material must be able to record and to reconstitute the wide dynamic range of intensities in the Fourier transform plane (as much as 50 orders of magnitude) and to reach complete insensitivity at the reconstruction wavelength. Moreover, a linear response of the medium is essential. In the case of a non-linear response, the central region of the pattern is properly exposed whereas the low-intensity areas are underexposed and the corresponding high-frequency components are not effectively filtered. On the other hand, if the emulsion is exposed long enough to record the high-frequency components, the central region will be, by far, overexposed. The first experiments using the photopolymer show that it is possible to memorize correctly the incident information with diffraction efficiencies approaching 25 %.

4.2.3 Other studies. — Studies are now under way in the field of microholography. Since this application does not require a high diffraction efficiency, the polymer materials seem to be specially suited for recording Gabor holograms. The emulsion is optimized in order to use an in-line set-up and a FD pulsed YAG laser. The holographic image may be analyzed with an He-Ne laser at 633 nm — a wavelength corresponding to photons which are inactive towards the polymerizable material — insensitivity of the record at the writing wavelength during reconstruction is not necessary. As a consequence, any change in the formulation or in the recording procedure which is likely to improve the initial photospeed of the recording material can be resorted to, even if this change appears to be detrimental to the stabilization of the record. For instance, an increase of the dye concentration or a shortening of the exposure (at constant dose of holographic illumination) are favourable factors.

5. Conclusion.

Due to their very attractive features, which are repeatedly praised up in the technical meetings, heat is now on photopolymer materials. Until recently, most holographic recording media were formulated according to a more or less empirical approach. Several classes of sensitive materials, however, were identified with respect to specific properties or characteristics which are considered to be critical for given applications: low degree of aberrations and high efficiency for holographic optical elements, good holographic characteristics and cheapness for mass display holography or self-processing character for interferometry.

In recent years, an increased interest in the chemical aspects of the recording process opened the door to a new approach to the formulation of photosensitive media, which is first and foremost, based on molecular or macromolecular engineering.

Thus, provided that this approach is not actuated by a desire to oust existing recording materials from their fields of excellence, photopolymer systems can be expected to have a fine future before them. New classes of products exhibiting properties which have been in demand

hitherto, might become available. In addition, very interesting opportunities could appear with holographic experiments carried out on board of automatic spacecrafts where their ability to self-process is a decisive advantage over most conventional materials [55-60].

Finally, it should be kept in mind that the basic idea used for recording a hologram in a polymerizable layer does not only involve a polymerization reaction. Diffusion and energy transport phenomena also play an important part in the building-up of the record. Thus, understanding these physico-chemical processes and quantifying their influence should be of the utmost importance for scientists interested in mechanistic and kinetic investigations on the polymerization of new materials. Such an approach based on chemical and molecular engineering seems to be the most advisable way to identify really new classes of polymer recording materials.

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