
An aqueous photopolymer for classroom holography

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Abstract: An aqueous photopolymer possessing good photosensitivity for recording holograms in red laser light is described. This development follows the author's earlier discovery of the enhancing effects of an acid-base amine combination used as a free-radical producing co-initiator with methylene blue dye to polymerise suitable monomers. The system also works with green laser light using the dye safranin-O. After exposure, the image develops in water. With this photopolymer, individual students in a classroom can use small cheap red laser pointers with their collimating lenses cut off to make simple Denisyuk holograms under subdued lighting. As the polymer is water-based, its preparation in a school lab is feasible.

Keywords: aqueous photopolymer, classroom holography, methylene blue, safranin-O, amine co-initiators

1 INTRODUCTION

In recent years, the situation for amateur holographers and college science teachers has changed dramatically. Whereas at one time the cheapest laser cost hundreds of pounds, today a small red laser diode capable of recording a single-beam reflection hologram now costs less than a 4 × 5 inch silver-halide glass plate. Furthermore, to avoid the expense of buying proprietary holographic plates, amateurs can coat their own glass with silver halide gelatin emulsion¹ or a silver-free system such as methylene blue (MB) dichromated gelatin (DCG).² Both these systems require chemical solutions for developing the image, and for safety reasons, students may not be in a position to use such chemicals. This paper offers an alternative by employing a photopolymer using only water for the development process. The chemicals used to make the photopolymer coating are neither expensive nor particularly toxic, and the water used can be safely disposed of down the sink, as it contains only harmless biodegradable substances.

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1.1 New photopolymers

A remarkable hydrophobic photopolymer requiring no post-exposure chemical processing has been produced for some time by DuPont. Now a new and even more remarkable panchromatic photopolymer is apparently about to be made available from Bayer MaterialScience. The DuPont material has been successfully used for some while as an anticounterfeiting aid, for example, to make special reflection holograms for German passports and on computer components as brand protection aids. However, the unexposed DuPont material has long been unavailable for general usage for security reasons. Early discussions on the possibility of obtaining high diffraction efficiency (DE) in the DuPont material without any chemical treatment to develop the image³ have been useful in developing the very different hydrophilic system described here. The DuPont system apparently relies on diffusion mechanisms during and after the exposure step so that the final holographic grating structure has a relatively high refractive index (RI) in the exposed fringes and relatively low RI in the unexposed fringes (which are hereafter referred to respectively as 'light' and 'dark' fringes). There may be several causes underlying such diffusion mechanisms; but it is clear that when a monomer is converted to a polymer, there is usually a reduction in volume,

especially if the polymer is substantially cross-linked. This means that material from outside the polymerising light fringe migrates into it to replace the volume lost in the polymerisation process, and this leads to yet more monomer travelling into the fringe. This diffusion process appears not to disturb the spatial integrity of the fringe structure during the exposure, presumably because the process takes place equally on each side of the growing fringe.

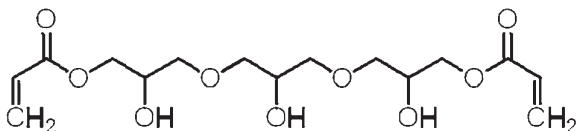
2 PRELIMINARY RESEARCH

It is difficult to produce the required high RI difference between 'light' and 'dark' fringes needed when restricted to a water-based photopolymer system. This is basically because a high concentration of monomer held in a supporting polymer is needed. This has two purposes: to achieve a good rate of photopolymerisation through a free-radical chain reaction process, and to obtain an adequate DE through having a high concentration of polymerised monomer in the 'light' fringes. In particular, a high concentration of cross-linking monomer, i.e. one with at least two sets of carbon-carbon double bonds (C=C), can be especially helpful in enabling the system to form a polymerised dense three-dimensional structure with considerable shrinkage, so that the diffusion mechanism referred to above can occur between the 'light' and 'dark' fringes. In hydrophobic systems, one can use monomers with aromatic structures (i.e. molecular structures containing π -electron rings), and/or attach heavy bromine atoms, to raise the RI of the polymerised monomers. However, up to now the author has not discovered any hydrophilic cross-linking monomers to match the RI differences obtainable in hydrophobic grating systems. In addition, the hydrophilic monomers must not contain heavy atoms such as bromine, or they would lose water solubility. From the very limited number of water-soluble cross-linking substances having a double set of C=C bonds that were available, none had significant aromatic character. Heavy metal compounds such as (say) barium or zinc diacrylates were also ruled out, as they would have undermined the ethylenediaminetetraacetic acid (EDTA)/amine system (see below) that was needed in order to obtain adequate photosensitivity.

2.1 Photobleaching of dyes co-initiated by amines

The key starting point for developing a water-based photopolymer was the extraordinarily rapid bleaching

reaction of the dye MB to red light occurring under the right conditions in the presence of certain amines. This reaction has long been known, as has the fact that this bleaching reaction can initiate the production of free radicals that can cause a range of monomers to polymerise in a chain reaction process.⁴ This reaction is special in the case of MB and its thiazine relatives, because red light has less intrinsic energy for breaking chemical bonds than blue or violet light. For polymerising with blue laser light, there are many more types of free-radical generators available. The rates of photobleaching in the late 1980s had already been investigated by Blyth² with a view to improving the photosensitivity to red laser light of DCG using MB. In that work, two factors which greatly helped to speed up the MB photobleaching reaction were found, but both of these were contrary to the requirements of the DCG project and it was thus not possible at the time to make use of them; but now these two factors could be employed to make a photosensitive water-based photopolymer able to record holograms with low-power red lasers. The first had appeared in early papers on the relative ability of various amine systems to increase the photobleaching rate of MB. In particular, the 1976 paper of Kayser and Young⁵ gave a list of amines with the relative reaction speeds. Heading the list was triethyleamine (DABCO). Earlier work had shown that acid EDTA in a neutralised state could also co-initiate photobleaching with dyes.⁴ It was thus possible to obtain the fastest dye bleaching rate of MB by first neutralising EDTA with DABCO. Apparently, the use of cationic and anionic amines in combination seems to have a synergistic effect. This enhanced effect could not be used in the MB/DCG experiments because both EDTA and DABCO are powerful sequestering agents which will hinder chromium-III from forming complexes with the gelatin in DCG.² The second factor was that in those earlier experiments to find the fastest photobleaching reactions, the best results came using polyvinyl alcohol (PVA) as the carrier film. When the same reactants were used with gelatin films, the speed of the reaction was substantially lower. The reason for this difference was not clear. A clue might be in the fact that the speed of photobleaching was also less in polyacrylamide films. Both polyacrylamide and gelatin have amino or amide groups fundamental to their structures, whereas PVAs contain no such groups. It is also of interest to note that where gelatin is used as the carrier for the photoreduction of MB (measured as



1 Glycerol 1,3-diglycerolate diacrylate (GDD)

photobleaching with respect to exposure energy), the authors of this paper⁶ conclude with the following statement: ‘...we can conclude that the EDTA does not favor photoreduction and that in large quantities it interferes with the process. These results imply that gelatin by itself can reduce the excited dye’. So combining anionic EDTA with cationic DABCO is perhaps a useful step forward. Another cationic amine that works equally well with EDTA is N,N,N',N'-tetramethyl ethylenediamine (TEMED). This amine is commonly used in labs as a co-initiator for preparing polyacrylamide gels for electrophoresis. It is, however, volatile and has a fishy smell (fortunately absent in DABCO).

2.2 Probable mechanisms behind the achievement of high DE

In my photopolymer formulation, the diffusion mechanism may indeed have been working during exposure, but the newly formed polymer in the ‘light’ fringes has achieved an RI value that is apparently close to that of the carrier polymer PVA, which finishes as the main constituent in the ‘dark’ fringes [this includes the diethylene glycol (digol); it also acts as a humectant and plasticiser and probably also as a monomer diffusing aid]. This means that after exposure the hologram’s DE is very low and the image is virtually invisible, even though the diffusion mechanism may well have allowed the polymerising monomer to concentrate in the ‘light’ fringes. However, if the hologram is given a brief exposure to strong diffuse white light and then placed in a small black tray of water, a remarkable transformation occurs: over several minutes, the hologram develops to give a bright image under a spotlight (Fig. 2; a video demonstration of the development effect can be seen in the video demonstration that can be seen in the middle section of the demonstration to be found at http://rivervalley.tv/media/conferences/isdh2009/0301-Jeff_Blyth/).

2.3 The effects of water

The water causes the ‘dark’ fringes to swell so that their RI falls towards the value for water (1.33),



2 Original object

whereas in the ‘light’ fringes, the concentration of more rigidly cross-linked polymer prevents much swelling. This effect greatly enhances the fringe contrast and thus the DE. Without the white light exposure before the water immersion, the post-development replay wavelengths are longer; this may be preferable when using a 532 nm laser. However, the time needed for development becomes longer (see Section 3). For the students, this image development process can be exciting to watch. To successfully replay under water, the diffracted replay wavelengths need to be around the middle of the human colour vision sensitivity range. The formulation thus needs to compensate the swelling of the polymer by the shrinkage caused by the loss of water-soluble constituents and by the polymerisation process itself. The holograms are capable of lasting under water for months, provided that the glass has been pre-treated with silanated PVA (see Section 3). If the hologram is now taken out of the water and dried the image vanishes, it can take many hours to return after placing it back in water. This is not necessarily bad news: holographers have long been familiar with the struggle to keep DCG holograms totally sealed, to exclude moisture at all costs; but here is a hologram that can be displayed indefinitely in a fish tank.

3 MATERIALS AND METHODS

3.1 Classroom holography set-up

Little red diode laser pointers may be cheap, but they are capable of recording holograms up to 3 cm in diameter in this photopolymer with exposure times of



3 Developing image in water

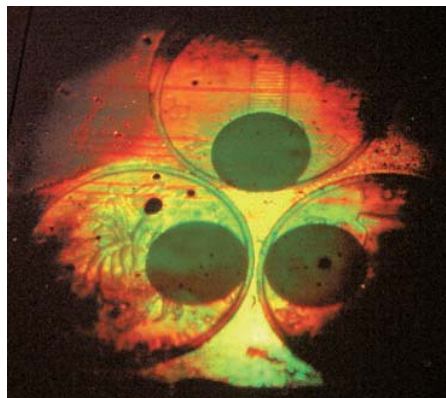
a minute or so. As supplied, the collimating lens is built into the head assembly and needs to be sawn off with a junior hacksaw (Figs. 5 and 6), after which the beam is seen to be spread out into a long ellipse. It is then no longer hazardous in any way. The small cells supplied with the laser do not have sufficient staying power to give either a steady light output or a constant wavelength. For a classroom demonstration, it is advisable to connect the diode to a more reliable power source such as a 4.5 V dry battery, using small crocodile clips (Figs. 7 and 8). It is important to get the polarity right: in these lasers the case, is the positive terminal. The hologram can be displayed in a small black tray of water. The development takes place over a 5-min period (Figs. 3 and 4). A class of students could each have their own laser pointer prepared in this fashion for making individual small Denisyuk holograms. Note that a settling time of around 5 min is necessary for both the laser and the subject matter before making the exposure, because if the fringes move during the exposure, the resulting image will be weak or even absent.

3.2 Photopolymers and solvents

Two types of polyvinyl PVA, obtainable from Kuraray Europe GmbH Division PVA-PVB D-65926 Frankfurt am Main, were used. Mowiol 3-85 was used as the main supporting polymer in the formulations given below (Table 1). Type R-1130, which contains some silane

Table 1 Formulation of GD-1

Methylenebisacrylamide	0.11 g
Methanol	6.0 ml
GDD 50% (w/w) in methanol	2.1 ml
Diethylene glycol ('digol')	0.34 ml
PVA (3-85) 30% solution	10.0 ml
DABCO/EDTA solution	0.46 ml
1% MB	0.22 ml



4 Hologram viewed nearly perpendicularly

groups, was used as an effective means of bonding the photopolymer to glass when required for making holograms with a longer life. The other chemicals used in the formulations are all available from the Sigma-Aldrich Chemical Co. The triethylenediamine (DABCO) was obtained from Fisher Scientific (Thermo Acros Organics, Fair Lawn, NJ, USA).

3.3 Preparation of stock solution of 30% (w/w) PVA type Mowiol 3-85

Cold de-ionised water (DI) of 70 ml was poured into a 250 ml beaker, and vigorously stirred mechanically while exactly 30.0 g of Mowiol 3-85 granules were poured in. After about a minute, the stirrer was stopped briefly, and an indelible black marker pen was used to mark the level of the PVA/DI mixture. The beaker was then placed in a cold water bath on a heater and the bath was heated with constant stirring until the temperature reached about 90°C. The PVA grains took some 20–30 min to dissolve completely at a temperature of 80–90°C. The beaker was then removed and inspected to see if any traces of undissolved PVA grains remained in the bubble filled solution. Then, after allowing the bubbles to drift to the surface, the level of the liquid was checked to see if significant evaporation of the DI had occurred, and the beaker contents topped up with DI to the black mark as necessary. The 30% (w/w) solution was then poured into a bottle and stoppered.

3.4 Preparation of DABCO/EDTA stock solution

Twenty grams of EDTA was stirred into 100 ml of DI as a part slurry (important note: this must be the acid EDTA and not a sodium salt). This acid slurry solution was then constantly stirred and with the aid



5 Disassembly of economical laser pointer

of a pH meter brought to about pH 7.5–8.0 by slowly adding increments of DABCO powder. The amount of DABCO required was roughly 25 g. With this treatment, the solution becomes clear and appears to keep indefinitely in a sealed bottle. It contains roughly 15% DABCO/EDTA salt solution.

3.5 Preparation of stock dye solutions

3.5.1 For red wavelengths

A 1% (w/w) solution of MB is used in a 1:1 (w/w) solution of methanol and water (note: the methanol/water mix is here by weight, not volume).

3.5.2 For green sensitivity at 532 nm

A 0.5% solution of safranin-O is used (Aldrich cat. no. S8884) in the above solution instead of the 1% MB.

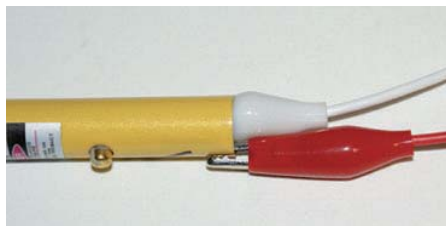
3.6 Preparation of 50% (w/w) glycerol 1,3-diglycerolate diacrylate (GDD) in methanol

Fifty grams of 50 of GDD was dissolved in 50 g of methanol. This solution has a low viscosity.

It is noteworthy that with three –OH groups along the molecule (Fig. 1), one would expect this monomer to have a much better solubility in water than it actually has. This is probably caused by strong internal hydrogen bonding which is folding the



6 Cutting the collimating lens off laser pointer



7 Attachment of insulated crocodile clips

molecule up on itself. It has a very high viscosity but a low volatility and low toxicity.

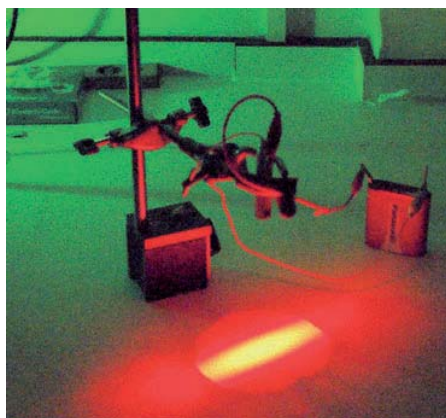
The preparation was made initially as two separate parts:

3.6.1 Part A

Take 10.0 g of stock 30% PVA solution and pour it into a 30 ml dark brown bottle. Then stir in 0.46 g of stock DABCO/EDTA solution.

3.6.2 Part B

In a separate bottle which can be made of clear glass, take 0.11 g methylenebisacrylamide (MBA) and add 3 g methanol, stirring the mixture until all the MBA has dissolved (note: there may be traces of polymerised impurity in the MBA as supplied; this will not dissolve. It should just be allowed to settle). Now add 2.1 g of stock GDD solution, followed by 0.34 g of diethylene glycol. Pour the contents of the part B bottle into the part A bottle, excluding any bits of solid impurity. Rinse the part B bottle with 3 g of methanol, and pour this into part A, again leaving behind any remaining solid matter. At this point, the alcoholic layer in bottle A will be sitting on top of the aqueous PVA layer. These two layers are not very



8 Attachment of leads to 4.5 V battery

compatible and it is now necessary to combine them with vigorous hand stirring. Take care to sweep away all the PVA solution sticking to the walls and bottom of the bottle. This can take a full 2 min. Finally, inspect the contents to ensure that the solution is completely homogeneous. It is now ready for sensitisation.

3.7 Dye sensitisation

For He–Ne lasers, about 0.22 ml of stock MB solution is mixed. For laser diodes operating between 660 and 670 nm, this quantity may need to be less, say, 0.16 ml of stock MB solution. This is much affected by the thickness of the coating required for reflection holograms. After mixing, the contents will contain many air bubbles; so before coating unless there is access to a small centrifuge, the solution should be left to settle for some hours.

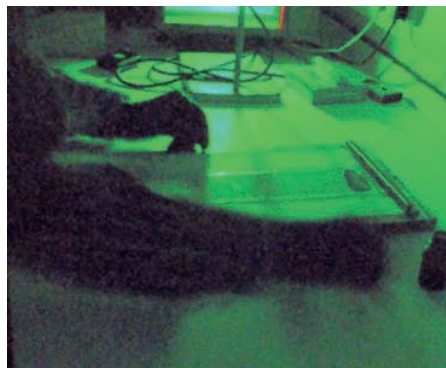
Note: Since this formulation will have some shrinkage in pure water, this can be quite suitable for red lasers. But after initially using water to develop, the green laser image will shift to the blue. Ways to deal with this are: (1) make the coating quite dry using a hairdryer for several minutes at about 35°C (albeit with some loss of photosensitivity); or (2) avoid the initial exposure to white light: place the hologram in a water bath under a green safelight without examining the image first. After a minute, shine a spotlight on it while it is in the water bath (see below).

3.8 Method of coating PVA solutions

When compared with gelatin solutions, PVA solutions have a very high surface tension; this causes them to reticulate on glass surfaces. To get round this problem, it was necessary to use a sufficient concentration of PVA in water to produce a viscosity in the solution resembling that of golden syrup. Methanol (or methanol solutions of the formulations above) was then gradually added up to nearly the maximum that could be tolerated without the PVA beginning to precipitate out. This enabled a smooth film to be coated onto glass. Then, to prevent reticulation occurring as the alcohol evaporated, a warm blast of air from a hair-dryer was used briefly to dry it rapidly to a touch dry state.

3.9 Coating GD-1 under safelighting

For initial trial purposes, a crude coating method was used, namely, dropping about 0.5 ml of solution onto



9 Mayer bar spreading of PVA mix

one of two 5×7 cm glass slides, squeezing them together and then sliding them apart. The slides were then placed flat and treated with a hair-dryer as described above. Subsequent trials used a Mayer bar on clean glass microscope slides butted together with the help of sticky tape along the sides and edges, on a sheet of A4 paper (Fig. 9). The high surface tension of PVA prevents liquid from leaking between the joins in the few seconds it takes to draw down the liquid. The appropriate bar is close wound with 8 turns/cm. Immediately after the draw-down, a hair-dryer on a warm full blow setting was swept over the slide from a height of about 5 cm for about 10 s (Fig. 10), to flatten out any residual bar lines. The hair dryer was then clamped above the coated glasses at a height which would not cause the temperature to exceed 35–40°C for about 1 min on the blown surface (this coating should not be over-heated: it should feel rubbery, not sticky). The coating was then left to equilibrate overnight in a dark room.

3.10 Photosensitivity: extent of drying and the ‘fluid fringe’ effect

If the coating is dampish rather than bone-dry, the bleaching rate by red light is faster, and the effective photosensitivity is a maximum. Measurements have shown it to be some 7 mJ cm⁻² in terms of the energy needed to form a photographic image. For holography, however, if the coating is too damp, the fringe structure as it grows during the laser exposure may finish up losing its spatial integrity. This may be termed the ‘fluid fringe’ effect. It usually results in a bright holographic image along the edges where the plate has dried sufficiently to maintain spatial integrity, but a blank area bearing no image in the



10 Rapid drying of PVA mix on slides

centre of the plate. It is recommended that the drying time be adequate to allow the coating to reach equilibrium in an atmosphere of 60% relative humidity.

3.11 Effect of exposure to white blight after the laser exposure

The quickest development in water took place when the exposed hologram was first given an exposure to a bright white diffuse light source for about 30 s. However, it was found that if the laser-exposed plate was put straight into water without first exposing it to white light, the replayed image would be redder and would take longer to develop. After the first minute in the water under a safelight, a bright spotlight can be turned on to watch the development progress. So if using the safranine-O dye system for 532 nm lasers, it may be best not to examine the hologram before the water immersion step.

3.12 Pre-subbing glass

This process may be necessary to prevent the coating from separating from the glass support in making permanently wet holograms. The procedure is used to give a thin coating to clean glass. For this purpose, approximately 10 g of R-1130 was slowly poured into 100 ml of cold DI with constant stirring, and immersed in a water-bath. The bath temperature was then slowly raised to about 90°C. The PVA was completely dissolved after about 20 min. It was then allowed to cool to about 40°C, and an equal volume of a solution of 3:1 (v/v) methanol/water was then added and stirred (it was necessary to get all the PVA first into an all-water solution before adding methanol, and the methanol itself needed to contain a substantial amount of water to prevent precipitation

of this high molecular weight PVA. The methanol was itself needed to reduce the surface tension).

After drying, the coating does not usually become detached from an untreated support when the plate is put into water after exposure. However, to be sure of this the glass can be 'pre-subbed' with the stock PVA R-1130 solution made as described above. As only a very thin coating is necessary, a finely wound Mayer bar or even a smooth straight rod is adequate. Immediately after the draw-down, a blast from a hair-dryer set to maximum heat about 5 cm above the glass is needed to raise the temperature of the glass to about 100°C for about 30 s, in order to obtain good bonding.

4 CONCLUSION

This method of providing holographic images using inexpensive equipment and materials of low toxicity lends itself well to the teaching of students of all ages, providing a hands-on introduction to the principles of optical interference and diffraction.

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