

Photopolymers and Holograms

Professor Nicholas J. Phillips, Centre for Modern Optics, De Montfort University
LEICESTER. LE1 9BH

Abstract

This short paper addresses some of the characteristics of some of the photopolymers used in holography today. The field is by no means limited to the materials of DuPont or the Polaroid Corporation, but now includes several new materials, some of which are extremely fascinating in what they can achieve.

An introductory view is taken of what we commonly consider to be a photopolymer. and then several specific regimes are discussed culminating in novel polymers that create phase conjugation of incident coherent waves of light.

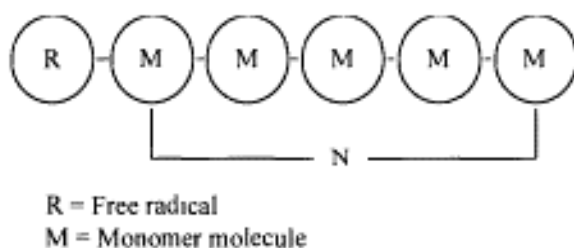
1. Introduction

For many years, holographic scientists have enjoyed the fruits of research into image forming photopolymers from two main sources. The HRF materials from DuPont and the DMP 128 of the Polaroid Corporation have basically played nominally similar roles. Both have produced bright and glitzy holograms that have helped the public appreciation of holography to become more secure. These two materials are very different in the way they are produced and in the way they perform. In general, the diffraction efficiency of reflection holograms is the measure by which these materials are properly judged. In order to achieve high diffraction efficiency there needs to be a high refractive index modulation Δn and the magnitude of this factor is all-important. For the record, Δn values as high as 0.5 for Polaroid and up to about 0.07 for DuPont would be seen as par for the course. This wide difference of factors is reflected in the ability of Polaroid's material to produce very high reflection efficiency in a thin layer (a few microns) whereas we might consider a layer of DuPont material at a thickness of 20 μ m to be an alternative workable regime. The thin hologram (Polaroid) and the thick hologram (DuPont) would as a result have different levels of selectivity and perceived luminance in white light replay.

Polaroid's material when processed has entrapped voids like those of DCG (dichromated gelatin). The process control required in its use is tricky and needs professional standards of care. That is why in general, Polaroid prefer not to let amateur users have access to DMP128, but will certainly process amateur-created samples at their factory in Cambridge. A detailed wet process is required. The DuPont material has an advantage over that of Polaroid in that there is no wet process procedure. One simply exposes the material to light and monomer diffuses so as to create a spatial variation of refractive index. Heating then enhances such diffusion and a form of UV cure is implemented. Such a simple and attractive process is of course limited by the Δn available from diffusion transfer, but such transfer can be augmented by transfer of monomer into the recorded medium from laminated sheets of monomer laced film. Let us now take a look at the underlying physics and chemistry of the photopolymerisation process.

2. Photopolymerisation, the role of free radicals

Photopolymers for holography usually contain a mixture of binders, polymer, monomer, photoinitiators and sensitisers. They are generally chemical mixtures that require some care in handling because of their toxicity. When exposed to light, the photoinitiator enables the formulation of free radicals. These free radicals, denoted by R, then interact with neighbouring monomer molecules



as shown in Fig. 1.

Fig 1. One free radical can cause a change in the outer electronic state of a neighbouring monomer molecule which then offers a bonding opportunity to its neighbouring monomer molecule and so on. In the case cited, **N** such monomer molecules are involved with only *one* free radical. A *long chain* or *polymer* molecule is thus formed.

The dangers of free radicals are thus seen for what they are. In a human biology sense, havoc can be played with a bio-structure with only a few free radicals - so much of biological control in the human body is related to diffusion within or between cells. To interfere with such processes, say by creating large molecules where there should only be small molecules, is of course extremely dangerous. The modern preoccupation with the dangers of free radicals to the human body is well justified. Note that the formation of long chain molecules also depends on the presence of the monomer. In the human body, the whole process depends on what we have eaten as well as what is there already. Thus getting skin cancer needs both sun and a suitable collection of chemicals within the human body.

As the long chain forms (as in Fig. 1), the volume occupied by the long chain is less than the total volume occupied by the original monomer molecules and the associated free radical. Thus *condensation of matter* is another important characteristic of the polymerisation process.

If we look at the model shown in Fig.2 (a), 2 (b), and 2 (c), we see the collapse of the irradiated zone so as to create a thickness change of the layer as monomer becomes polymer.

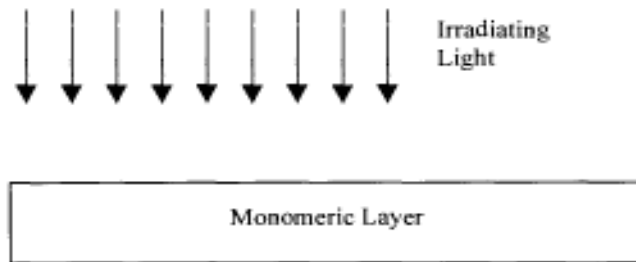


Fig.2 (a). The irradiation of the monomer layer is masked so as to create different levels of irradiation.

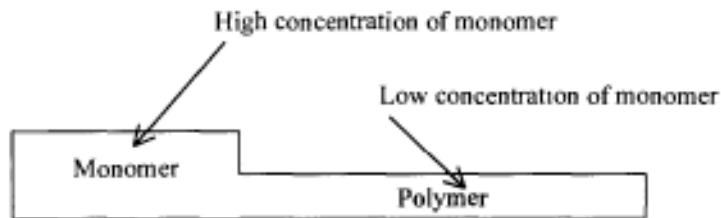


Fig.2 (b). Where the polymer has formed, shrinkage occurs reflecting the effects of molecular condensation.

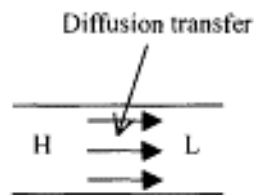


Fig.2 (c). In a layer that has different levels of monomer concentration, the monomer will diffuse from a region of higher concentration H to one of lower concentration L.

These various mechanisms must all be considered when assessing the overall performance of the polymerisable material.

In essence, we can at this stage see that n is dependent on shifting molecules around in a layer or molecular condensation.

Condensation of monomer in materials may also be due to a phase change, e.g. liquid to solid - Fig.3.

A monomeric liquid that starts out as a liquid form may be caused to set solid as a result of polymerisation. Thus the predicted behaviour shown in Fig.2 (c) may result.

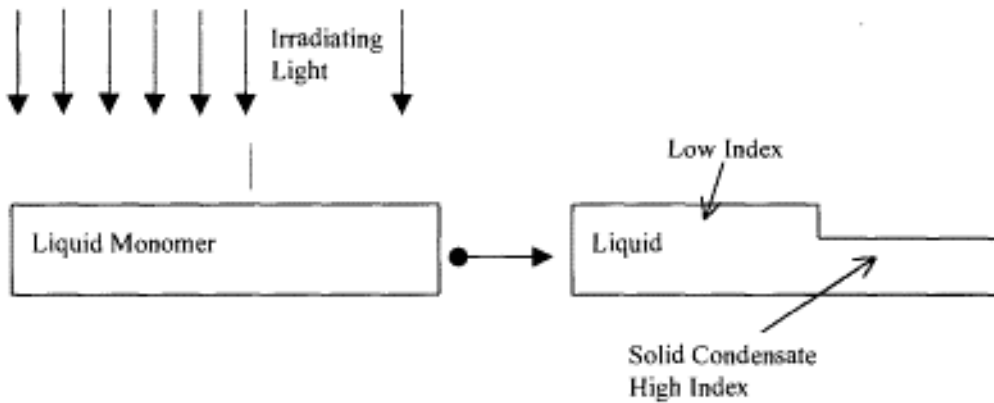


Fig.3. A liquid monomer layer can be caused to condense (solidify).

However, such a system also permits the idea shown in Fig.4. in which a “fixer” is applied to the liquid *uncondensed* region.

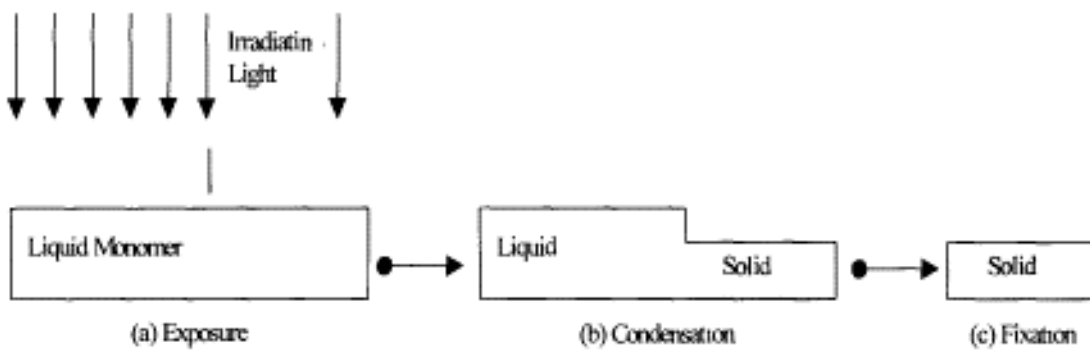


Fig.4. Conversion of liquid to solid followed by fixation.

In step (c) a solvent (usually organic) removes the remaining liquid which then leaves only the solid condensate.

Such a technique is used for example to make optical light guides using masking techniques. The use of the term “fixation” is inspired by the fact that the removal of the unexposed liquid by differential solubility in the organic fixer is similar to the solution of unexposed silver halide by an inorganic fixer. One might ask the question, what would happen if we left the unexposed liquid *in situ* if there was a finite risk of long-term polymerisation and condensation of this part of the structure? Evidently, there might be an overall hardening of the sample shown in stage (b), with the result that the sample of material then becomes spatially uniform, and by hypothesis then:

$$\Delta n = \text{index of solid} - \text{index of solid} \equiv 0.$$

If we close this section by considering the differing values of Δn between DuPont and Polaroid, we then have to consider where this difference comes from. In practice, the Δn for the DuPont material is caused by the diffusion transfer process, which sets a limit on Δn imposed by the molecular density differences attained by the inbuilt collection of molecular species. Attempts to force Δn to higher than expected limits may only come from overheating and hence softening of the polymer matrix. This can often be counter-productive and lead to distortion of the holographic fringes.

On the other hand, the very high values of Δn in the Polaroid material are caused by the formation of voids, very much akin to those in dichromated gelatin in the antinodal (high exposure) areas of the holographic patterns. Such nodes are thought to be air filled ($n = 1$) and as a result, it is easy to see where a value of $\Delta n \approx 0.5$ can come from (the host polymer may have an index $n_{\text{polymer}} \approx 1.5$).

3. The role of oxygen in the polymeric process

Oxygen tends to kill off the process of polymerisation, and thus trapped oxygen within the polymer layer is an important issue. If we take the case of normal DuPont sheet film on a polyester base with a peel-off cover, then as the exposure takes place, entrapped oxygen is “gettered” by the free radical structure created during the exposure. Fig.5.

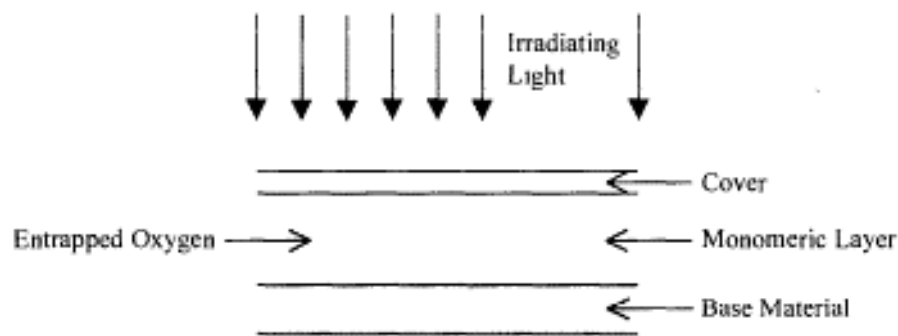


Fig.5. Exposure of the polymer to light uses up entrapped oxygen and allows polymerisation to proceed. It is important that subsequent oxygenation by further penetration is strongly inhibited. Hence the role of the cover sheet, or if removed, the role of an oxygen-opaque contact surface.

Many such anaerobic processes, for example the setting of cyanoacrylate adhesive, exist. In nearly all cases oxygen inhibits the polymerisation reaction.

If attention is not paid to this effect. e.g. by stripping off the cover layer and leaving the monomer layer exposed during optical exposure, then optical sensitivity may be greatly reduced.

4. What's new?

Here we have some very interesting news. A group working under Professor Terence A. King at Manchester University's Schuster Laboratory has discovered a polymer that behaves like a photorefractive crystal (e.g. barium titanate).

We remind the reader that such crystals can also reflect, or more precisely, phase conjugate coherent light, see Fig.6.

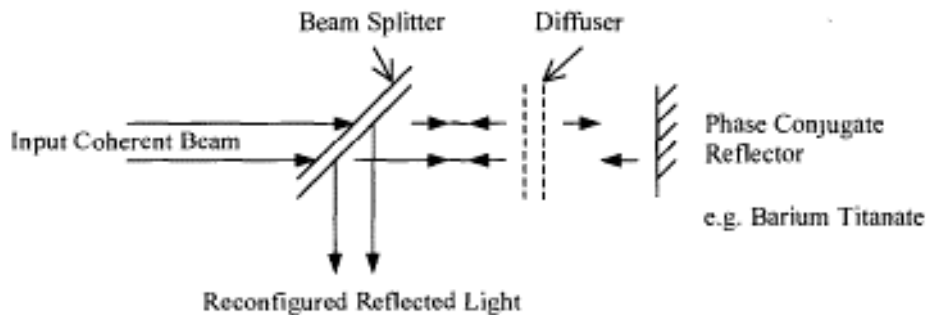


Fig.6. Coherent light passing through a diffuser can be probably retro-reflected by a phase conjugate mirror, thus the action of a diffuser can be time reversed.

Such an effect can be seen dramatically by considering the reflection of a beam of coherent light off the same phase conjugate reflector.

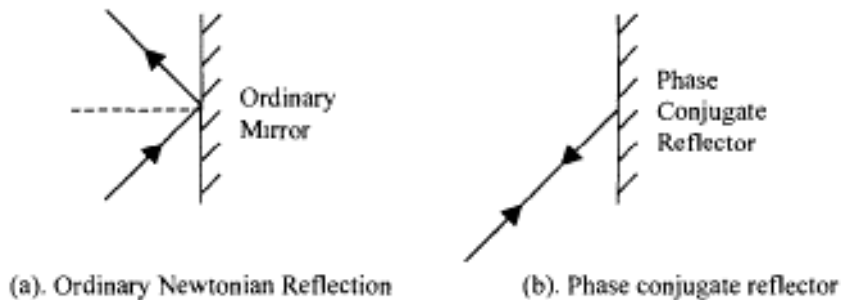


Fig.7. Showing comparison of reflection of a ray of light off an ordinary mirror and off a phase conjugate reflector.

The reflection of an object cannot be seen in a phase conjugate reflector as in an ordinary mirror.

We note that phase conjugation is commonly used in replaying the real image of an ordinary off-axis hologram. Fig.8.

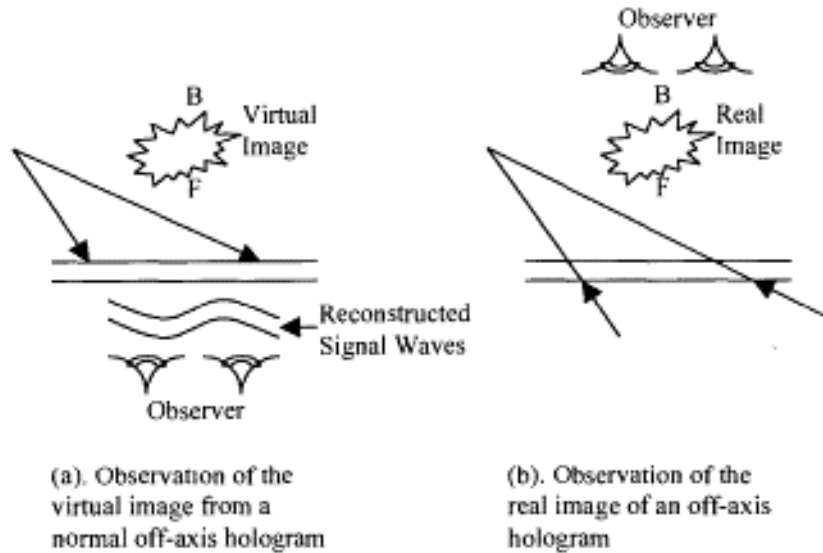


Fig.8. Showing the method of phase conjugation applied to an ordinary off-axis hologram; using conventional convergent optics.

F and B stand for foreground and background of the image respectively.

We note that the essential ingredient of (b) is the time reversal (phase conjugation) of the reference beam. Usually a large lens or an off-axis mirror performs the time reversal process.

Now, out of the blue comes a new polymer that performs the task of the time reversal optical element such as the off-axis mirror.

We consider in Fig.9. the use of a novel layer of polymer which when irradiated appropriately undergoes a non-linear electro-optical transformation to produce a phase conjugation effect.

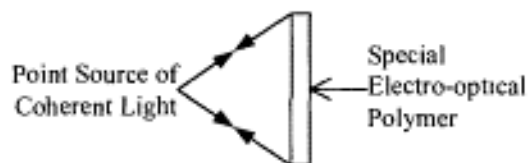


Fig.9. Using the Manchester University electro-optic polymer, coherent light can be retro-reflected from large areas of material.

The actual structure of the polymer layer is as shown in Fig. 10.

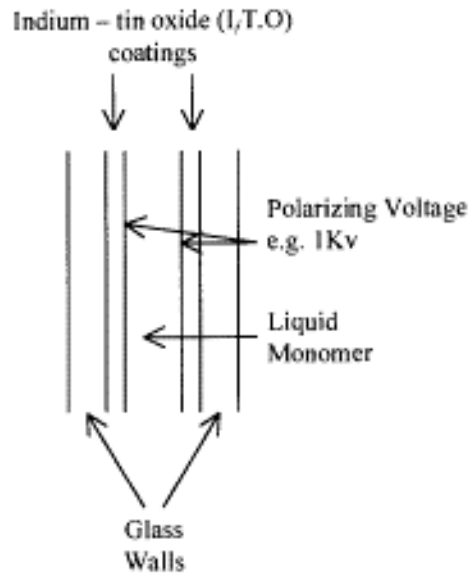


Fig. 10. Showing the structure of the polymer electro-optic layer.

N.B. This type of electro-optic polymer is much more sensitive to light and faster in response than the materials of DuPont or Polaroid. Thus, the formation of a conjugating optical element can take place on a time-scale short by comparison with the imaging forming time-scale of the conventional polymers.

The polymer layer begins as a liquid and sets under the action of the light. During exposure, the material is “polled” by action of the applied voltage and sets hard, locking in the electro-optic properties needed for phase conjugation.

Thus, in effect we have created a flat conjugator or phase conjugate mirror with powered retro-reflective capability - a remarkable and important result.

What is almost beyond expectation is that the optical sensitivity of this novel polymer is much higher than that of the imaging photopolymers. Furthermore, the response time for completion of the polymerisation process is very brief by comparison with, for example, the diffusion times of the DuPont process. Thus, the achievement of the optical phase conjugation effect can take place on a time-scale short by comparison with the forming of the holographic image, and using much lower laser powers.

Evidently, we have the potential to create holograms and associated phase conjugation optics in a unified sense but on widely differing time-scales.

5. Summary

In this short paper, I have jotted down some notes on what I have seen over the years that will be of interest to the holographer.

Polymers are very interesting. They are however, in general, insensitive to light, and can suffer from poor ageing stability and colourfastness. They are not the panacea many people take them to be.

The idea of fixing partially solidified polymer has rarely been explored in the context of modern holography.

The advent of the new phase conjugator material is exciting in that it opens up a whole range of possibilities for the future of phase conjugate optics, combining some of the remarkable capabilities of crystalline conjugators with large areas suitable for the recording of holographic displays.