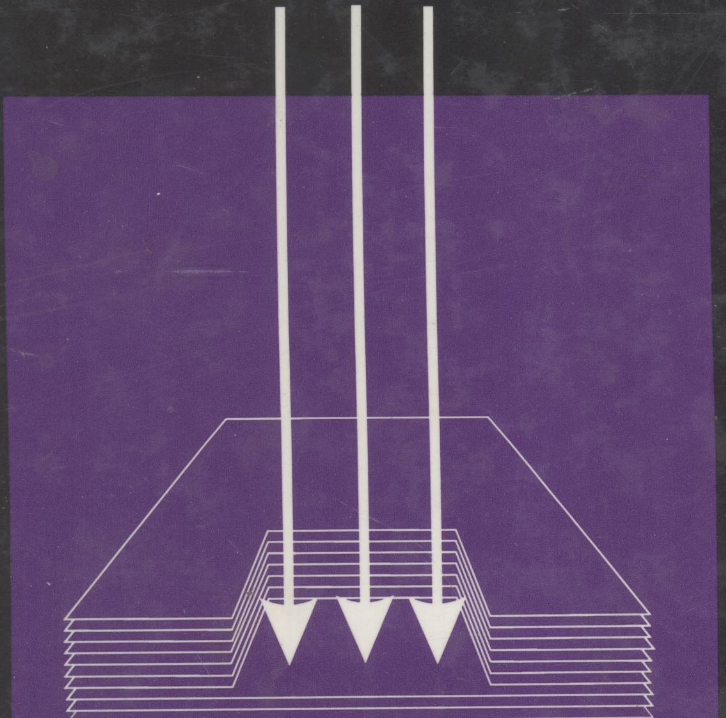
PHOTOCHEMISTRY AND POLYMERIC SYSTEMS



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Photochemistry and Polymeric Systems

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Photochemistry and Polymeric Systems

Preface

The papers collected in this volume were given at the Faraday and Industrial Divisions' Symposium "Light on Polymers - Photochemistry and Advanced Materials" and the Industrial Division's half-day symposium on Photography at the Royal Society of Chemistry's Autumn meeting held in Dublin in September 1992. The organisers' aim was to bring together a number of leading researchers, both chemists and physicists, from academia and industry, in order to consider the fundamental scientific principles and the technological applications of the physical and chemical effects of light on monomers, polymers and polymer-based composites. We have grouped the papers under the following main headings; Radiation curing; Photoablation; Photoluminescence of Polymers; Electro-optics and Nonlinear optics; Photochromism and Photoimaging; Photography. However a primary objective of such an interdisciplinary meeting was to highlight links between these topics and we trust that this is still apparent in these proceedings.

The last two decades has seen dramatic advances in the application of photochemistry to materials' preparation (e.g. for integrated circuits, surface modification, data storage). Such developments and prospects for the future are reviewed by Ledwith (Pilkington,UK), and illustrated by applications in digital optical recording, fibre optics based chemical sensors, stereolithography, and holography. Most such systems involve radiation curing of acrylates using free radical initiators. The development of new photo-initiators (e.g. for work at short u.v. wavelengths) and a detailed mechanistic study with the well-known Irgacure^{R} 907 initiator using photo-DSC and CIDNP are discussed by Davidson (University of Kent). Other methods for monitoring photocuring processes of acrylates are described in the papers by Decker (CNRS Mulhouse) (using pulsed laser methods with UV or IR monitoring) and by Pethrick (University of Strathclyde) (using viscosity/gel time measurements). Decker also describes the properties of new high performance acrylate monomers.

Another approach to polymeric materials processing is the use of high intensity u.v. lasers to photoablate the materials. In his review of this topic, Srinivasan (UV Tech, U.S.A.), who pioneered much of the work in this area, details some methods for rapidly probing the process. As he points out there is still a lot to learn about the primary processes of photoablation. Of particular interest is whether the ablation is caused by (multiphoton) photochemistry or by thermolysis due to the uv-light-generated heat. A detailed study of the photoablation of polyetheretherketone (PEEK) and polyethyleneterephthalate (PET) is given by Oldershaw (University of Hull) . It is shown that, at least for XeCl laser photoablation of PET, the photothermal mechanism is most important. An interesting application of photoablation [reported by Blau (Trinity College Dublin)] is the formation of waveguides in conjugated polymers.

Photophysical methods have been used for many years to probe the properties of polymers and the continually improving methodology of time-resolved fluorescence methods continues to provide new insights about molecular order and motion as discussed by Phillips (Imperial College London) in his article. Applications to the photoresist polyester PPDA, vinyl aromatic polymers and to surface effects in polydiacetylene are reported. Pethrick (University of Strathclyde) discusses the use of fluorescence methods to probe the nature of the structures responsible for the formation of gels and crystals in isotactic polystyrene.

The optimisation of optical nonlinearities in polymeric systems continues to be an area for close collaboration involving physicists, chemists and electronics specialists. Williams (Eastman Kodak,USA) discusses the design and characterisation of polymers for second order nonlinear optical (NLO) applications. Orientational and relaxational effect in poled polymers containing push-pull chromophores (such as 4-amino-4'-sulphone-azobenzenes) have been studied, using a technique which simultaneously measures second harmonic signal intensity and thermally stimulated discharge current. The same group also report that Langmuir-Blodgett films from suitably derivatised polymers containing similar chromophores exhibit large second order NLO susceptibilities. Blau (Trinity College Dublin) has concentrated on third order NLO phenomena in conjugated polymers such as polydiacetylenes and polythiophenes. Using laser induced grating methods it is shown that these materials have switching times in the picosecond range, which suggest their application in all-optical switching devices, although stability problems still remain to be addressed. Cross et al. (University of Durham) have also studied third order NLO processes but in polymer matrices containing quantum-confined microcrystals of 1:1 TCNQ salts. The convenience of the thin film format of these samples suggests their use for waveguiding. The research reported by Bradley (University of Cambridge) is a striking example of how device physics and macromolecular engineering have been combined. He describes work on the electro-luminescence of poly(p-phenylene vinylene) [PPV], where applications as light emitting diodes and large flat panel displays can be envisaged. Colour tuning has been achieved by judicious choice of PPV-copolymers with appropriate energy gaps, and devices can now be operated with threshold voltages as low as 4V and at 2% efficiency.

The ability to reversibly switch between differently coloured states makes photochromics of interest for a number of applications ranging from digital devices to sunglasses. Crano (PPG Industries, USA) summarises the results of a long-range research project, aimed at the production of plastic organic photochromic prescription eyewear. This necessitated the development of fast-reversing, photochemically-sensitive spiroxazines with long-term stability. Heller (Univerity of Cardiff) describes the preparation of fatigue-resistant photochromic fulgides for digital optical recording. In particular his group, by suitable molecular engineering approaches, has developed systems operating at near infra-red laser diode wavelengths. Crowded helical fulgides, which exhibit optical activity and hence offer the possibility of polarisation-selective readout, are also reported. Irie (Kyushu University, Japan) has addressed some similar problems but from a different perspective and with heteroatomic diarylethenes. Long wavlength (680 nm) absorbing species with excellent fatigue resistance have been prepared and non-destructive optical readout has been achieved using a thermal threshold for the photochromic reaction in conjunction with an optically-induced thermal-biasing technique. A quite different approach to photochromic systems is that described by Hampp exploiting the photochemical properties of mutated bacteriorhodopsins (BR). Genetic, as opposed to molecular, manipulation has been used to produce customised BR variants with optimised polarisation, absorption, refractive index and excited state lifetime properties. Two applications already demonstrated for these biomaterials are in holography and real-time optical correlators for pattern recognition.

Fatigue in organic layered photoconductors, which is responsible for the diminished performance of most photocopiers, is an interesting problem in applied photochemistry described by Pacansky (IBM, Almaden, USA). Two major reasons for light-induced fatigue were identified. First the photochemical isomerisation of the hydrazone which is the active component of the charge transport layer. Computational methods were used to assist in designing molecules so as to minimise the photoisomerisation but maintain high efficiency hole transfer. The second major photochemical reaction was due to photo-induced electron transfer between the hydrazone and chlorodiazine blue, a component of the charge generating layer. In this case also computational methods proved invaluable in helping to elucidate the mechanism.

The four papers on Photographic Chemistry illustrate different aspects of the subject. Sahyun (3M, USA) discusses recent advances in our understanding of photographic development. The kinetics of growth of the silver(0) from the latent image can now be mathematically modelled, which should prove very useful for the design of improved photographic emulsions. Fyson (Kodak, UK) describes the changes in chemistry required to reduce the processing time for colour negative films from one hour to 7.5 minutes. This was achieved principally by working at higher temperatures - a course that was only possible by raising the "aqueous melting point" of the gelatin. The papers by Ware (University of Manchester) and Patel (3M, UK) deal with alternatives to silver-based processes. Ware reviews the history and chemistry of the photographic printing methods based on iron polycarboxylates and platinum, palladium or gold. The prints so produced can be of exceptionally high quality. For many purposes photographic processes not involving noble metals are of interest, despite their generally much lower sensitivity than the silver process. Patel outlines methods based on photo-induced electron transfer between oxonol dyes and diphenyliodonium salts. Using a combination of 4-oxonols good colour separation is obtained yielding full colour images.

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During the past two decades there has been a huge increase in the nature and reaction type, wavelengths of light employed, and practical applications of photochemically induced molecular transformations leading to enhancement of both specific and general material properties.

Established commercial technologies include lithography for integrated circuit manufacture[1], from which the entire field continues to derive much stimulus, and equally important ultra violet/visible light curing processes in which wholly reactive liquid or solid precursors are converted to appropriate solids with designed mechanical, chemical and surface properties[2].

For both lithography and more general applications of radiation curing there is a choice between radiation induced molecular step transformations (i.e. one chemical transformation per photon utilised) or radiation induced chain polymerisations which may proceed via free radical or cationic propagating species. Examples include printing and all types of surface coatings, sealants and adhesives, laminates, dental treatments and three dimensional solid imaging. More recent developments utilising rather similar photochemical and molecular principles include holographic imaging[3], surface modification procedures[4], alignment in liquid crystal displays[5], variable light transmission[6], and photovoltaic energy sources[7].

A number of these areas are covered by the proceedings of the Symposium (reported elsewhere in this volume) and the purpose of this presentation is to provide a general perspective on major developments which have occurred over the last twenty years or so and to provide an introduction to the more detailed discussions of specific aspects which follow.

Photoinitiation (Photocure) by Free Radical Processes

In free radical photocure systems the overall requirement is to initiate free radical polymerisation and/or crosslinking by a light induced process. Leaving aside the rather obvious complications which could arise from internal conversions between photochemically excited singlet and triplet states and the possibilities of quenching (including oxygen quenching) and sensitisation, there are essentially three major ways of generating free radical intermediates from a photochemically excited species:

1. Homolytic Cleavage

$$\mathrm{A-B^{*}} \longrightarrow \mathrm{A\bullet + B\bullet}$$

2. Hydrogen Abstraction

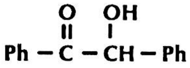
$$\mathrm{A^{*} + RH} \longrightarrow \mathrm{AH\bullet + R\bullet}$$

3. Electron Transfer

$$\text{(a)}\quad \mathrm{A^{*} + DH} \longrightarrow \mathrm{(A^{\bullet -}\ DH^{\bullet +})} \longrightarrow \mathrm{AH\bullet + D\bullet}$$

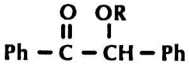
$$\text{(b)}\quad \mathrm{(A^{+})^{*} + X^{-}} \longrightarrow \mathrm{A\bullet + X\bullet}$$

Homolytic cleavage leading to formation of free radicals has been known longest and is manifest in the use of benzoin and its alkyl ethers in photoinitiation. Related molecules such as hydroxyalkylketones, dialkoxyacetophenones and benzoylphosphine oxides[8] are also utilised and in every case, simple alpha cleavage generates a benzoyl radical and a more reactive radical derived from the appropriate molecular skeleton.



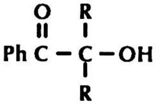
$$\mathrm{Ph-\overset{\overset{O}{\|}}{C}-\overset{\overset{OH}{|}}{CH}-Ph}$$

benzoin



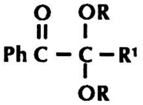
$$\mathrm{Ph-\overset{\overset{O}{\|}}{C}-\overset{\overset{OR}{|}}{CH}-Ph}$$

benzoin alkyl ether



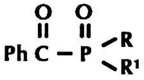
$$\mathrm{Ph\overset{\overset{O}{\|}}{C}-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{C}}-OH}$$

hydroxyalkyl ketones



$$\mathrm{Ph\overset{\overset{O}{\|}}{C}-\underset{\underset{OR}{|}}{\overset{\overset{OR}{|}}{C}}-R^{1}}$$

dialkoxyacetophenones

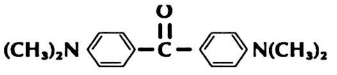


$$\mathrm{Ph\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{P}{<}^{R}_{R^{1}}}$$

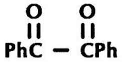
benzoylphosphine oxides

A useful survey of quantitative aspects of the use of u.v. initiators, and some indication of newer molecular structures, has been given by Fouassier[9].

Hydrogen abstraction from organic molecules by photochemically excited ketones such as benzophenone is one of the best known reactions in molecular photochemistry. However it is not commonly employed for photoinitiation except when used in conjunction with an electron donor such as an amine or an amino-substituted benzophenone like Michlers Ketone. Electron transfer processes are prevalent in reactions between donor molecules (such as amines) and aromatic ketones which have lowest lying singlet states with π,π^* character. Intersystem crossing to reactive n,π^* triplet states then provides a mechanism for radical formation. An additional feature of such systems is the relatively strong absorption at wavelengths greater than 400 nm which facilitates light induced curing in pigmented systems. Typical examples of ketones participating in photoinduced electron transfer processes are indicated below.

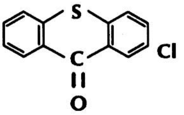


Michlers ketone

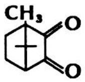


$\mathrm{PhC(=O)-C(=O)Ph}$

benzil

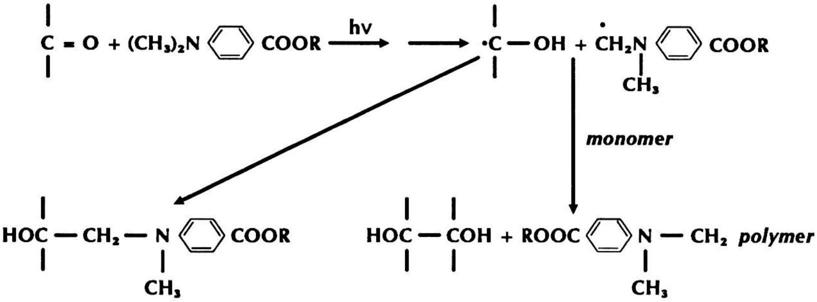


2 - chlorothioxanthone



camphorquinone

Whilst many tertiary amine-type donor molecules may be employed with these and related carbonyl compounds, a particularly convenient amine donor class is that comprising the alkyl esters of 4-dimethylamino benzoic acid the reactions of which may be taken as representative of many ketone/amine combinations.



There are abundant examples of use of many of these ketone and ketone/amine systems in u.v./visible light cure but it is perhaps worth noting the rapid growth in the use of visible light (i.e. wavelengths longer than 400 nm) as a convenient cure mechanism for a variety of dental repairs[10]. Camphorquinone has appropriate light absorption properties and is frequently employed as the ketone component. Many amines may be used but it is especially convenient to include (2-dimethylaminoethyl) methacrylate in the particle filled acrylic resin system. Excellent wear and cosmetic properties are obtained and highly convenient and efficiently focused light sources have been especially designed for the dentist and patient's convenience. Polymerisable single paste, composite, dental cement fillings have been under development and application for a considerable time and use of visible light curing affords maximum convenience - not least because the dentist can stop the cure at any point by removing the light source. This provides for optimised manipulation of the composite paste cement in order to ensure complete, and relatively defect free, filling of cavities and other features as well as effective bonding to the cavity walls.

Photoinitiation by Cationic Processes

Accompanying the widely diverging technologies involving photochemically induced free radical polymerisation, there has been a concurrent awakening of interest in the rather more limited applicability of photochemically induced cationic polymerisations. The potential value of this type of photocure was first elaborated by Crivello[11] and a wide ranging review of appropriate kinetics and mechanisms has been published very recently[12]. Important aspects are covered by Davidson in these proceedings. In outline the process requires direct excitation (u.v. source) or sensitised decomposition (u.v. or visible light) of di-aryliodonium or tri-arylsulphonium salts. Detailed photodecomposition mechanisms vary with the particular system employed but it is widely assumed that formation of protonic acid is an indirect product of photolysis. Provided that the counter ion of the initial onium salt is relatively stable (i.e. non-nucleophilic), the resultant protonic acid will be a good initiator for cationic polymerisation of epoxides and alkyl vinyl ethers e.g.

$$Ph_2I^+X^- \xrightarrow{h\nu} (Ph_2I^+)^*X^- \begin{array}{l} \nearrow PhI + Ph^+ + X^- \\ \searrow Ph\cdot + PhI^{+\cdot} + X^- \end{array}$$

$$Ph^+ + PhI \longrightarrow Ph\text{-}PhI + H^+$$

$$H^+(\text{or } Ph^+) + \textit{monomer} \longrightarrow \textit{polymer}$$

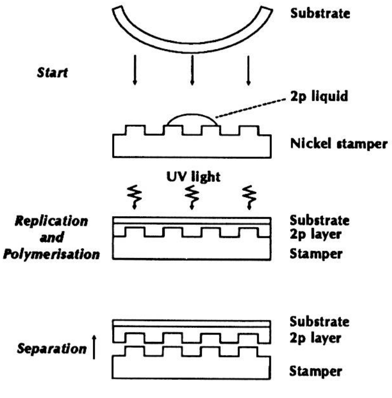
$$X^- + SbF_6^-, PF_6^- \text{ etc.}$$

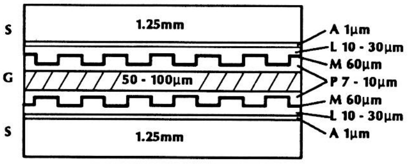
The examples noted below serve only to illustrate the scope of current commercially important materials technologies which may be derived from photocure systems or from the basic photochemistry associated with the corresponding photoinitiation process.

Digital Optical Recording and Laser Vision Video Discs

An important application of light curing technology, developed by the Philips Company, is required in the manufacturing process for optical data storage (archival) and the more generally applicable video disc recording media[13]. The process is commonly referred to as the '2p process' (from photopolymerisation) and is based on u.v. light initiated curing of multifunctional acrylic monomers, the development and performance of which has been described by Kloosterboer[14].

2p Process (Philips)





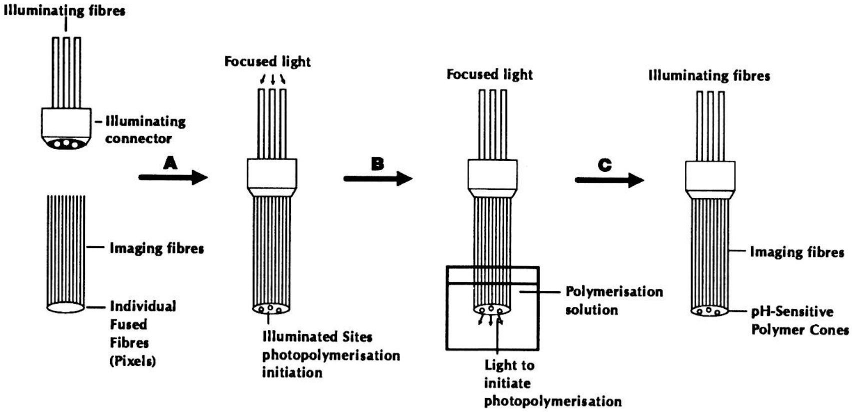
Configuration of a double-sided LaserVision disc.
The hole at the centre is not shown.
S - transparent substrate
A - primer layer
L - laquer with picture and sound information in the form of pits.
M - mirror coating
G - adhesive layer

A brief outline of the process for replicating video discs is shown in the figure and, as indicated, the substrate can be any material provided it is transparent to the wavelengths of light required for initiation of cure. For video discs it is normal to use plastic substrates (e.g. polymethylmethacrylate) whereas for archival storage, which requires larger disc sizes, it is commonplace to use glass. The master mould plate is usually made of metal and following the indicated photocuring of liquid monomer between mould and substrate, the formatted 2p layer is given a laser light read-out reflective metal coating and a further protective polymer layer. Typical disc dimensions and organisation of a finished disc are given in the figure and the information is recorded as a spiral track of small pits about 0.12 microns deep and 0.4 microns wide. The length of the pits and the minimum separation vary between 0.5 and 2.0 microns.

Fibre Optic Based Chemical Sensors

An important objective in clinical medicine is the continuous, *in situ* measurement of concentrations of blood solutes such as pH, CO_2 and O_2. Most multi-analyte sensors developed for *in situ* monitoring consist of several sensors aggregated into a bundle and this is not ideal where sensor size is an important factor. A recent technique, shown schematically in the figure, utilises localised photopolymerisation of appropriate dye indicators on the face of an imaging optical fibre[15]. It is convenient, by this means, to locate and interrogate several different units on a compact multi-analyte fibre optic chemical sensor system.

Sensor Fabrication

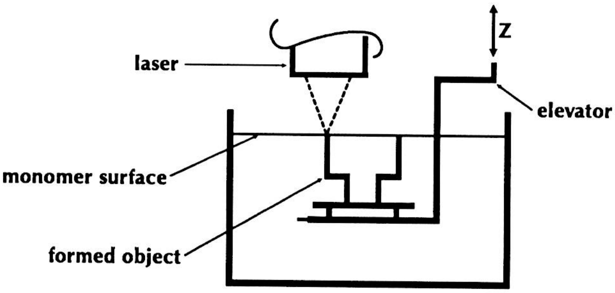


Although the development is at a very early stage, this technique holds great promise and it should be possible to generate micron sized sensing regions. Typically a short length of imaging fibre was attached, by means of a fibre connector, to the distal end of the illuminating fibres which, in turn, direct light to the proximal end of a discrete number of individual pixels that comprise the imaging fibre. It is this readily controlled activation of pixels which determines the areas of the distal face functioning as initiation sites for photopolymerisation of the dye/polymer solution. Illumination fibres are about 125 microns in diameter and the imaging fibres are suspended in a solution of acryloyl fluorescein, 2-hydroxyethylmethacrylate, methylene bisacrylamide and benzoin ethyl ether. The resulting photocure yields cones of polymer entrapped dye at the end of the imaging fibre which may be varied in area and height by adjusting the illuminating light source focus and the time of exposure.

Stereolithography (Photochemical Machining)

Stereolithography is a new technology linking the power of computer graphics to the rapid formation of a solid, shaped object. Patented originally by Hull[16], stereolithography converts CAD/CAM/CAE generated solid or surface model data to a three-dimensional real part synthesised, via photopolymerisation, from a photosensitive monomer such as an acrylate. Cured by a laser beam directed across an x,y surface, a liquid monomer mix is converted to a solid plastic object, point by point, layer by layer, with quality in all three dimensions x, y and z determined by the properties (especially densities) of the monomer/polymer components.

Schematic Representation of the Stereolithography Apparatus

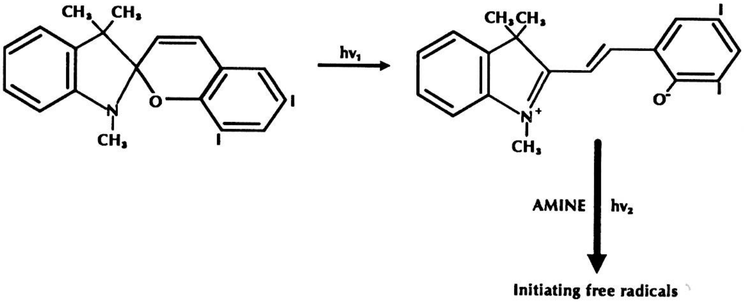


Stereolithography is simple in concept[17] and it provides great economies for the design lab as well as for the modelling process. It also provides previously unrecognised challenges for the polymer photochemist, for it is entirely a laser-initiated technology, and the polymerisation reactions take place to depths below a finitely thin surface layer. Currently, modelled parts made by stereolithography are generally on the order of 3″ to 6″ on a side. The goal is to make much larger parts and to make them faster and truer. If stereolithography is ever to play a role in manufacturing, parts must be synthesised from widely usable plastics like epoxies and polyurethanes and not just from the rather brittle crosslinking acrylic systems. One of the monomers widely used in stereolithography is bis-phenol-A-diacrylate.

Minimisation of cure shrinkage is one of the greatest challenges in stereolithography resin development. Even the best of the pure acrylates shrink 6-8% in volume when fully converted to polymer from monomer. Most direct laser-initiated photocures are not complete and there always remain unreacted olefinic centres in the polymer. After the laser initiated photopolymerisation there is opportunity for additional radical chemistry to occur in the photopolymer which can change the overall mechanical properties and shape of the formed polymer. In the best case today, a maximum deviation of 0.015″ over 10″ is achieved. But as part geometry changes, and part sizes increase, there is even less tolerance for shrink in the formed photopolymer.

There are many putative no-shrink monomer systems which may or may not have application in stereolithography. Among these are the very large number of ring opening polymerisation systems reported by Bailey[18] and the thio/norbornene systems reported by Jacobine[19]. Both are said to minimise shrink. However stereolithography also requires a rapid photochemical curing step, and many resins fail on this count. Clearly, the development of resin systems amenable to rapid photopolymer formation is an important step in advancing stereolithography.

For laser induced polymerisation it is necessary to work with visible light absorbing initiator systems and these can be free radical or cationic in nature. Lee and Neckers[20] have recently reported a most interesting two photon initiator system based on photochromic spiropyrans. The latter form intensely coloured merocyanine dyes on exposure to u.v. irradiation which, in the presence of N-phenylglycine, may then be selectively activated to produce initiating free radicals with a helium/neon laser at 632 nm. It is convenient to use a helium/cadmium laser at 324 nm for the first photon.



Photochemistry at the intersection of two laser beams is an obvious way of improving the quality of solid parts produced by stereolithography.

Holographic Optical Elements

Holographic techniques allow a wide range of devices to be made from 3 dimensional photographs to specialised optical elements[3]. An important practical application of holographic optical elements is as wavelength selective mirrors for the combiner plates of Head-Up-Displays (HUDs). In an aircraft head-up-display (HUD), information is displayed on a cathode ray tube. This can be navigational aids, weapon aiming markers, or a picture of the outside terrain produced by forward looking infra