

# Photopolymers as a powerful tool in modern technology

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**Abstract:** Light does not only provide the ultimate energy for nature's biological processes, it is also serving modern technology. Efficient and accurate photo-imaging spanning from submicron photolithography to three-dimensional stereolithography requires specially tuned photopolymers as functional materials. Classical photopolymers, combination approaches and tailor-made solutions to technological problems will be described.

## Introduction

Highly diversified chemical and pharmaceutical companies are owing much of their commercial success to light and its action on biological and technical systems (1). *Agriculture* would not exist without photosynthesis (and as humans are herbivorous - we would not exist either). Specific molecules whose beneficial functional response depends on light are used today as crop protection agents. For example, photobleaching herbicides for selective use in corn dramatically reduce the carotenoid biosynthesis in susceptible plant species, thus eliminating the plant's internal protection shield against  $^1\text{O}_2$ -attack to chlorophyll (2). Weeds may selectively be bleached, which, in turn, allows their selective decay in the corn fields. - In *medicine*, photodynamic therapy is a novel treatment modality for malignant tumors. The underlying principle consists in the selective accumulation of an exogenous photosensitizer in cancerous tissues, followed by its selective irradiation. The therapeutic effect, i.e. necrosis of diseased tissue, results from the local action of  $^1\text{O}_2$  (3). - Parallel *chemical synthesis* of a highly diverse set of products (up to 250000 per  $\text{cm}^2$ ) became possible by a technology that harnesses photolithography, solid-state chemistry and photo-labile protecting groups (4). - In *industrial segments* the interaction of light not only offers a basis for many desired effects such as dyeing, pigmenting and optical brightening; light also enables imaging within a wide span of applications (microelectronics, printed wiring board industry, information storage, display technologies, textile and printing industry). In this segment our contribution will focus on modern functional materials for lithographic applications.

The use of light for preparation of polymers with desired properties is well known. As early as in 1913, *Klatte* (5) converted 50 tons (!) of vinylchloroacetate into polyvinylchloroacetate by sunlight irradiation in 5 liters glass bottles. This truly remarkable process was apparently exercised until 1929 for preparation of 'Mowilith G', used, among other things, for insulation of electric devices. In the 1960's, *Wichterle's* pioneering discovery of shape-controlled polymerisation of hydroxyethyl-methacrylate opened the door for soft hydrophilic contact lenses (6). His process, which can in principle use radical photoinitiators, also serves today's manufacture of contact lenses (7).

## A classification of photopolymer systems for modern technologies

Photopolymer applications are well documented topics in the literature (8). We will rather focus on synthetic, mechanistic and material science issues of the underlying chemistry. One can distinguish between three levels of approaches to photopolymer systems (Table 1).

TABLE 1. Principal photopolymer systems.

Photopolymer concept	Main features	Applications
<b>Classical:</b>		
Acrylate/radical photoinitiator	Light penetration, photospeed	Resists, Stereolithography
Epoxide/cationic photoinitiator	Low reaction shrinkage	Solder masks, Stereolithography
Novolak/Diazoquinone	Photosolubilisation	Photoresists for microelectronics
<b>Combination systems:</b>		
Acrylated polyimide precursors	Photocrosslinking followed by thermal cure	Permanent layers in microelectronics
Epoxide/Acrylate hybrids	Combination of photospeed and low shrinkage	Stereolithography
<b>New photopolymers:</b>		
Auto-photosensitive polyimides	Direct photocrosslinking of a soluble, fully imidized system	Permanent layers in microelectronics
Dimethylmaleic imide containing photopolymers	[2+2] photo-cycloaddition as photocrosslinking reaction	Textile printing, cartographic use
Photo-terpolymers	Chemically amplified photosolubilisation	Positive deep-UV microresists

*Classical photopolymers* represent an important pillar in today's coating and imaging markets. Polymerisation of acrylic and epoxy monomers or prepolymers by photoactivated radical or cationic species is a standard concept which grants high photosensitivity, easy handling and good final properties of the cured resin (9). Figure 1 depicts three main components of a formulation used in three-dimensional stereolithography (10), a technique employed to sequentially build-up structures through a layer-by-layer laser induced photopolymerisation of liquid resins.

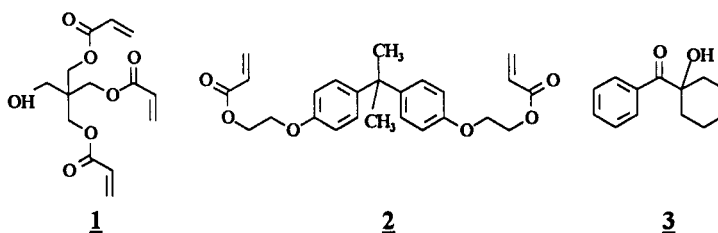


Fig. 1 Components of an acrylic photopolymer formulation for three-dimensional stereolithography (11).

1-Hydroxy-cyclohexyl-phenyl-ketone **3** (12) is a highly efficient non-yellowing UV curing agent used to initiate the photopolymerisation of unsaturated systems such as acrylates **1** and **2**. Exposure of **3** to UV light produces radicals in high efficiency (13).

The traditional stronghold of Ciba-Geigy in the polymer field is epoxy resins. The fact that cationic sulfonium salt initiators are able to yield Brønsted acids under irradiation (14) renders them an obvious tool for epoxy-based photosystems. However, the application demand for higher light sensitivity, improved light absorption in the visible region, better storage stability and less corrosion led us to the design of novel organometallic Lewis acid precursors: ( $\eta^6$ -cumene)( $\eta^5$ -cyclopentadiene) iron(II) hexafluorophosphate **4** liberates a powerful Lewis acid **5** upon irradiation just by losing the uncharged arene ligand (see Fig. 2).

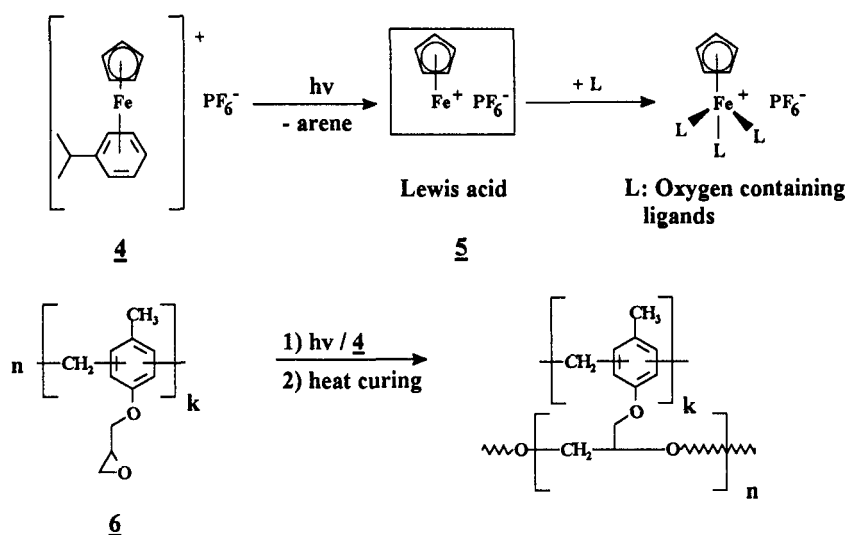


Fig. 2 Photochemistry and application of organometallic Lewis acid precursor **4**.

This Lewis acid **5** undergoes complexation preferentially with oxygen-containing ligands such as the epoxy group (15). A short heat treatment (100°C for 5 minutes) cleaves the so activated epoxy ring and starts polymerisation. As a practical consequence, multifunctional novolac-epoxy compounds **6** crosslink efficiently upon irradiation in the presence of less than 2% of **4** (16). These negative working photopolymers retain the outstanding electrical, physical and mechanical properties of the epoxy resins. Such a system is available under the name of PROBIMER™ 61 for use as high-resolution insulation and solder mask in the printed wiring board manufacture (17).

In order to fully exploit the vast potential photopolymer systems can offer, *combination systems* have been designed to eliminate certain shortcomings associated with single monomer/initiator systems such as the considerable reaction shrink of pure acrylate formulations or the low photosensitivity of pure epoxy resins. At the same time the synergy between different monomers, prepolymers and photoinitiators may produce an over-proportional gain in performance. A hybrid approach to an improved stereolithographic resin contains an acrylate/radical photoinitiator subsystem (as depicted in Fig. 1), an epoxy formulation with the liquid resins **7** and **8** and the cationic photoinitiator **9** (Fig. 3). After irradiation epoxy and acrylate photopolymer segments form an interpenetrating network.

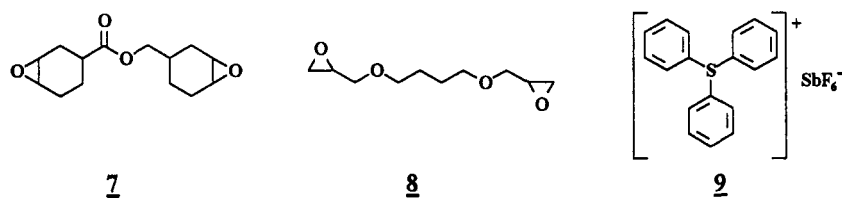


Fig. 3 Epoxy/cationic photoinitiator subsystem used in hybrid approach.

An on-line laser-interferometric method (11) allows one to monitor the reaction shrink of these photosensitive resins directly. The acrylate photopolymer (**1**, **2** and **3**) rapidly reaches its total reaction shrink of 6.2%, whereas the epoxy system (**7**, **8** and **9**) exhibits a slow shrinkage to a considerably lower final value of 3.5%. Because the most prominent part of shrinkage is occurring after gelation, which translates into curl and warpage of the final product, it is of applicatory importance that the acrylate/epoxy hybrid formulation, despite its acrylate-like fast initial photoresponse to light, is shrinking slowly and only 5% overall (11).

The combination approach is of special benefit also to microelectronic manufacturing processes. Permanent polymer layers in microelectronics devices have to withstand high temperatures, steep heat gradients and stress build-up. Polyimides are today's widely accepted materials in the manufacture of

integrated circuits and multilayer interconnections [18]. Classical microstructuring of polyimide layers proceeds via a two-step technique: a non-photosensitive polyimide layer is deposited on the silicon wafer and covered by a photosensitive polymer layer. This photoresist can be patterned by a photolithographic procedure and will act as a pattern transfer mask to the polyimide. The image is transferred into the polyimide by an etching process. The novel approach combines the photosensitivity of the photocrosslinkable acrylate group with the required thermal stability of the polyimide structure into a single precursor macromolecule 10. The final, insoluble polyimide 11 will be generated by thermal elimination of the residual (photo-crosslinked) acrylate side group after the imaging step (Fig. 4). This system is available under the tradename of PROBIMIDE 300™(19).

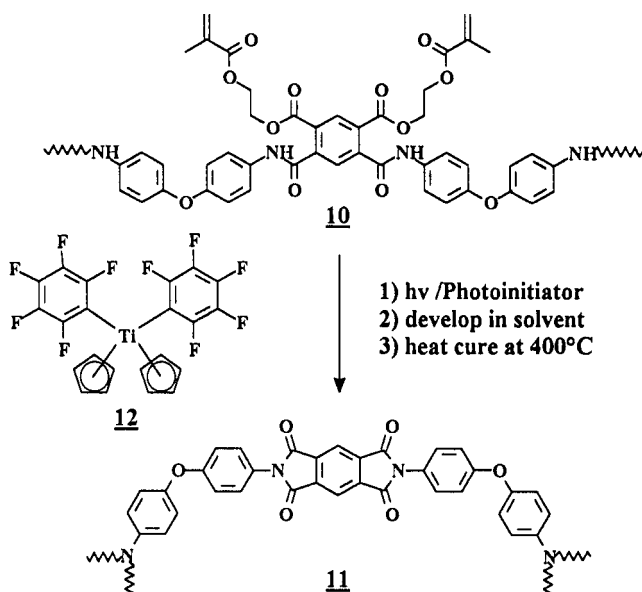


Fig. 4 Processing steps of polyamide ester polyimide precursor 10.

The titanocene photoinitiator 12 presents a technological breakthrough due to its long wavelength absorption and bleaching capability allowing the photoimaging of polyimide layers of more than 100  $\mu\text{m}$  thickness. Light-sensitive titanocene(IV)-complexes have been described and extensively studied (20). However, the oxygen and moisture sensitivity prevented their practical use as photoinitiators. Surprisingly, fluorinated aryl ligands rendered compound 12 stable to oxygen, moisture, acid and heat, while keeping its remarkable photosensitivity alive (21). During flash-photolysis of a dry benzene solution of 12 at room temperature, a blue intermediate was formed (with a quantum yield of unity), to which a mono-hapto-cyclopentadienyl-structure 13 has been assigned (22). Trapping experiments of 12 with 2,2,6,6-tetramethyl-piperidine-1-N-oxide led to the isolation of a pentafluoromethyl-substituted cyclopentadiene 14 and a titanium-fragment 15 which had reacted with two radical scavengers (23) (Fig. 5).

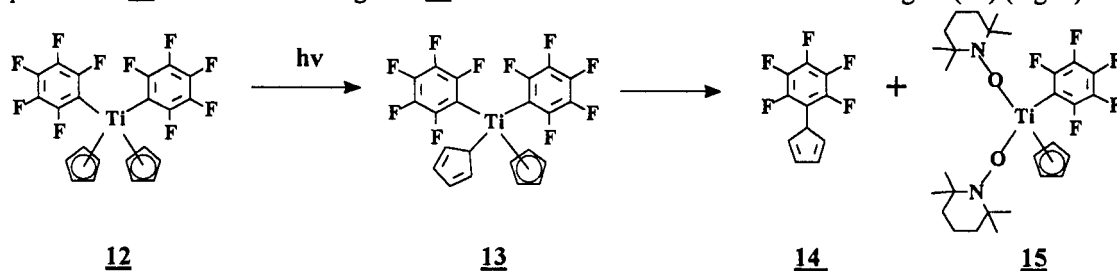


Fig. 5 Photochemistry of titanium(IV) complex 12.

**New photopolymers** consist neither of different monomers (see, e.g., Fig. 3), nor contain thermolabile auxiliary groups (like in 10), but assemble all necessary moieties already in a single macromolecule.

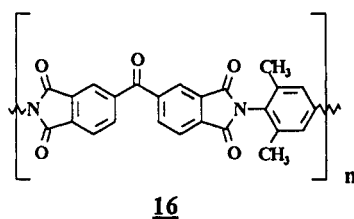


Fig. 6 Typical structure of fully imidized, soluble, auto-photosensitive polyimide.

For example, Fig. 6 depicts a fully imidized, soluble, auto-photosensitive polyimide **16** (24), where

- the *benzophenone* moiety acts as the light-absorbing chromophore,
- the *polyimide* backbone grants for thermal stability (up to 400°C),
- the *alkyl* substituents allow tuning of the solubility and the glass transition temperature and at the same time act as  $\alpha$ -benzylic hydrogen donors to the excited carbonyl groups.

The radicals so produced crosslink the polyimide chains forming an insoluble layer. This negatively acting photopolymer is used as permanent layer in microelectronics application and is available under its tradename PROBIMIDE 400™ (25).

Microphotoresists used for structuring submicron features into the silicon wafer are predominantly positive tone systems. Photosolubilisation of the polymeric layer is achieved by a photoinduced change of matrix polarity. Thus, the exposed areas become hydrophilic and can be washed away by an aqueous base developer which leaves the hydrophobic non-exposed parts untouched. Whereas classical systems rely on the photochemistry of naphtho-diazoquinones embedded in a novolak matrix and yielding indene carboxylic acid (26), deep-UV resists are based on chemical amplification (8b). The polymer matrix consists of a polymer bearing hydroxyl groups which are protected: tert.-butyloxy-carbonyl protected 4-hydroxy-styrene is a typical example. By the help of a photogenerated acid the deprotection of the hydroxyl groups takes place just in the areas exposed to light, thus rendering them soluble to the dilute base developer. In order to obtain steep, thermally stable profiles by a straightforward projection imaging process, severe criteria have to be met by a practical photopolymer system. Those include high accuracy and contrast, sub-micron resolution capability, low thermal flow of the structures up to 130°C and a smart distinction between high dose exposure light and low dose scattered light. The latter is due to the fact that resolution is approaching the wavelength of the incident light. Therefore diffraction effects are imposed by optical laws (27). A smart resist will literally have to neglect light below a certain level dose, but should promptly react when a threshold of light energy has been passed. Our photo-terpolymer **17** (see Fig. 7) embraces different building blocks fulfilling selective tasks simultaneously in a single polymer sequence (28).

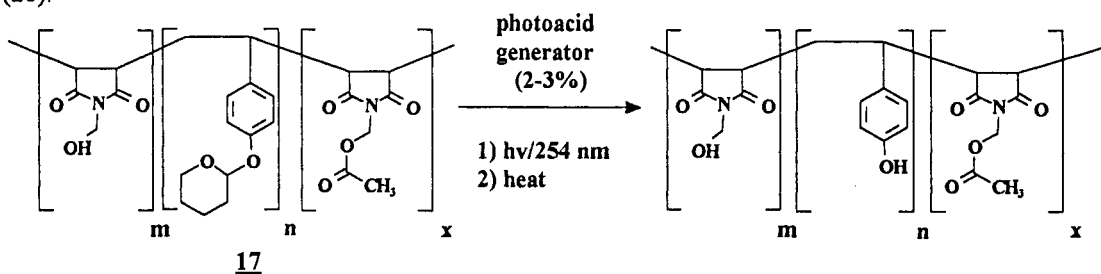


Fig. 7 Photosensitive terpolymer approach and its photochemical deprotection.

The dihydropyrane modified 4-hydroxy-styrene block in **17** stands for the photosolubilising action, whereas the N-hydroxymethyl-maleic imide component adds thermal stability and its acetylated counterpart contributes to the development of the deprotected zones.

## Outlook

What will the future bring? Modern technology requirements call for tailor-made photopolymers with high

latency, either well defined linear or explicitly non-linear response to incident light, higher resolution in optical lithography and inherent end properties of the cured material such as high thermal stability, low reaction shrink and special mechanical and electrical properties.

How can we design such new photopolymer principles? A first successful attempt has been achieved in our laboratories starting almost 20 years ago. With the generous help of serendipity we were able to develop a superb negative working polymeric film for cartographic purposes. Namely, in a broad connection with the chemistry of imides for weed control, a reaction of maleic anhydride with 2-aminopyridine in acetic acid was attempted. Instead of the expected imide of maleic acid, the imide of the dimethylmaleic acid was isolated. Its hydrolysis afforded dimethylmaleic anhydride **18** in 75% yield (29). The systematic study of the detailed mechanism of this originally mysterious decarboxylative dimerisation rendered the catalytic, one-pot preparation of **18** feasible. Thus, the door was opened for industrial utilisation of this compound which features two very specific properties: first, the pronounced ability to undergo [2+2] cycloaddition under UV-irradiation and, second, the reluctance of its sterically hindered double bond to participate in radical or cationic polymerisation. The latter property allows an easy homo- or co-polymerization of acrylic monomers **19** to afford linear, soluble polymers **20** with pendant dimethylmaleimidyl-groups. UV-exposure of **20** in the presence of a photosensitizer such as thioxanthenes yields crosslinked, insoluble polymers of type **21** (30) (see Fig. 8).

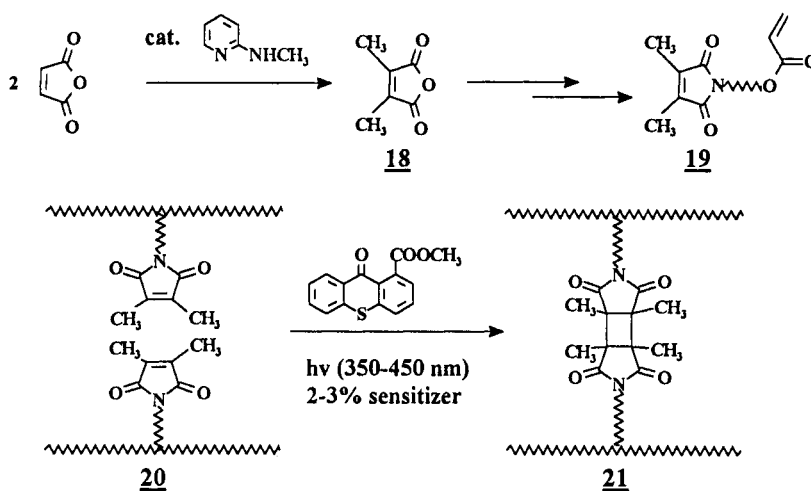


Fig. 8 Synthesis of dimethylmaleic anhydride and its photochemical utilisation.

A wide structural variety of tailor-made photopolymers is achievable using this approach. For example, a co-monomer methacrylic acid provides groups for subsequent dyeing by basic dyes as well as for the development of thin layers by a low-alkaline water. Applied on a supporting film or aluminium sheet, such photopolymer coatings of 2-3  $\mu\text{m}$  thickness exhibit excellent resolution, dimensional stability and, especially noteworthy, no oxygen inhibition effects on photocrosslinking. They find use in photolithographic applications (30).

*In summary, a prerequisite for new multifunctional photopolymers in electronics, stereolithography, coating and tooling is a photoreactive principle whose activity is not affected by the other building blocks bearing different functionalities. Decoupling of the different functions leading to intrinsic photosensitivity or to special mechanical, electrical or other physical properties leads to real tailor-made photopolymer systems needed for tomorrow's technologies.*

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