

Laser-Induced Crosslinking Polymerization of Acrylic Photoresists

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ABSTRACT: Multifunctional acrylate photoresists have been polymerized within milliseconds by laser irradiation to produce an insoluble polymer network. The polymerization reaction and the insolubilization process were both followed quantitatively by infrared spectroscopy. The most sensitive system consisted of a morpholino-ketone photoinitiator, a triacrylate monomer, and an amino-polyester tetra-acrylate oligomer. An energy as low as 0.1 mJ cm^{-2} proved to be sufficient to achieve insolubilization of a $36 \mu\text{m}$ thick film upon exposure to a Kr^+ laser beam (337 nm) in an inert atmosphere. These highly photosensitive materials are well suited for the manufacturing of printed circuit boards by a laser direct imaging technology. Dry acrylate photoresists were found to be less sensitive than wet photoresists because of severe mobility restrictions in the solid state. A similar drop in photosensitivity was observed when wet acrylate photoresists were exposed to the 488 nm emission of an argon ion laser because of the lower efficiency in radical production of visible photoinitiators. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 833–844, 1997

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INTRODUCTION

Laser-assisted processing of polymers is one of the most efficient methods to induce ultrafast chemical reactions in photosensitive materials.¹ For example, the polymerization of multifunctional acrylic monomers was shown to proceed extensively within milliseconds as a result of the large number of initiating species generated by the intense illumination.^{2,3,4} This advanced technology is becoming increasingly popular and has found a large variety of industrial applications because of the distinct features of these powerful sources of coherent radiation. The spatial coherence of the laser emission provides a great directivity so that

the laser beam can be focused down to a micronic spot, and it can be used to induce reactions at a very long distance as well. The temporal coherence of the laser emission, which occurs at a well-defined wavelength, reduces the extent of undesirable secondary reactions induced by polychromatic radiation. The large power output that is concentrated in the narrow beam leads to high light intensities, thus increasing the overall rate of the photochemical process considered drastically.

A short exposure to an argon ion laser beam, tuned to its emission line at 351.1 nm, proved to be sufficient to induce the cross-linking polymerization of multiacrylate monomers and produce an insoluble polymer network in the illuminated areas.⁵ The relief image obtained after solvent development can serve in the fabrication of printing plates or printed circuit boards (PCBs) by a photolithographic process. By using continuous wave

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lasers emitting in the ultraviolet (UV) or visible range, high-resolution relief images have been drawn directly onto photosensitive plates at writing speeds up to 100 m/s⁶. Laser direct imaging (LDI) offers the advantage of generating a pattern in photoresist without the use of a mask, thus eliminating a number of costly process steps and providing greater flexibility in the manufacture of PCBs.

Since our earlier work on laser-induced curing, which demonstrated that acrylate resins can be polymerized quasi-instantly by UV laser irradiation,^{6,7} several applications of this technology have appeared in various industrial sectors, in particular, in stereolithography,⁸ holography,⁹ optoelectronics,¹⁰ and microlithography.¹¹⁻¹⁴ In the latter application, and more specifically for the manufacture of PCBs by the LDI technology, the sensitivity of these acrylic photoresists was still not high enough to meet the imposed specifications, which require operation at very high writing speeds (up to 1000 m/s) to make the process economically feasible. From the power of the modulated laser beam arising from the plotter (40 mW) and the spot size (20 μm), the energy received by the photoresist upon laser scanning was calculated to be 0.2 mJ cm⁻². Such a low energy, which corresponds to a 0.1 s exposure to UV sunlight, had to be sufficient to achieve an extensive insolubilization and obtain a sharp relief image after development. To meet this challenge, it was necessary to call on chemical amplification, i.e., a chain reaction initiated by photo-generated species, and also to combine highly reactive monomers with the most efficient photoinitiators. We report here on the performance of some newly developed acrylic photoresists that proved to be extremely reactive under laser exposure and particularly well suited for LDI application.

EXPERIMENTAL

Materials

All the photoresist formulations contained two basic components: (1) a photoinitiator, which must effectively absorb the laser photons and split readily into highly reactive free radicals; and (2) a telechelic acrylate polymer or oligomer, which will undergo a fast radical-induced polymerization to generate a strongly cross-linked and insol-

uble polymer. In liquid formulations (wet photoresists), a multifunctional acrylate monomer, acting as reactive diluent, was added to reduce the formulation viscosity.

Aromatic ketones (Irgacure 651 and Irgacure 369 from CIBA) were chosen as UV photoinitiators because of their high initiation efficiency. The following different types of visible photoinitiators were used in consideration of their good performance upon laser irradiation at 488 nm: eosine (Aldrich), a chloromethyl-triazine (Hoechst), and an aryltitanocene (Irgacure 784 from CIBA). The dry photoresists examined in this study were made of the following multiacrylate polymers, all from UCB: polystyrene-maleate diacrylate, epoxy-novolac pentaacrylate, epoxy-novolac octaacrylate, and tetrabromo-phenoxy-diacrylate. For the wet photoresists, the following acrylate monomers and oligomers were selected on the basis of previous studies, which showed the high reactivity of these compounds in laser-curable resins^{4,15}: hydroxypropylacrylate (HPA), hexanediol diacrylate (HDDA), a polyester tetra-acrylate (Ebecryl 80), or hexaacrylate (Ebecryl 830) (all compounds from UCB) and an oxazolidone acrylate (Acticryl CL-959 from SNPE). The chemical formulas of the major compounds used in this study are given in Figure 1.

Irradiation

Two types of continuous wave (CW) lasers were used to induce the crosslinking polymerization: a krypton ion laser (emission line at 337.4 nm) and an argon ion laser (emission line at 488 nm), both from Spectra Physics. Some experiments were also performed with polychromatic light from either a medium pressure mercury lamp (maximum emission at 365 nm) or a halogen lamp (main emission at 470 nm). The photoresist was coated onto a BaF₂ crystal as a uniform 36 μm thick film and exposed to the laser beam for a given time, typically between 10 and 500 ms, by means of an electronic shutter. Irradiations were carried out either in the presence of air or in a pure nitrogen atmosphere by using a specially designed photoreactor equipped with quartz windows.

Figure 2 shows a schematic representation of the laser scanner device developed by Philips.¹⁶ As the optical efficiency of the laser plotter is only 0.1, the power (P) available to perform the direct imaging was 40 mW by using a Kr⁺ or Ar⁺ laser emitting 400 mW continuously in the UV region.

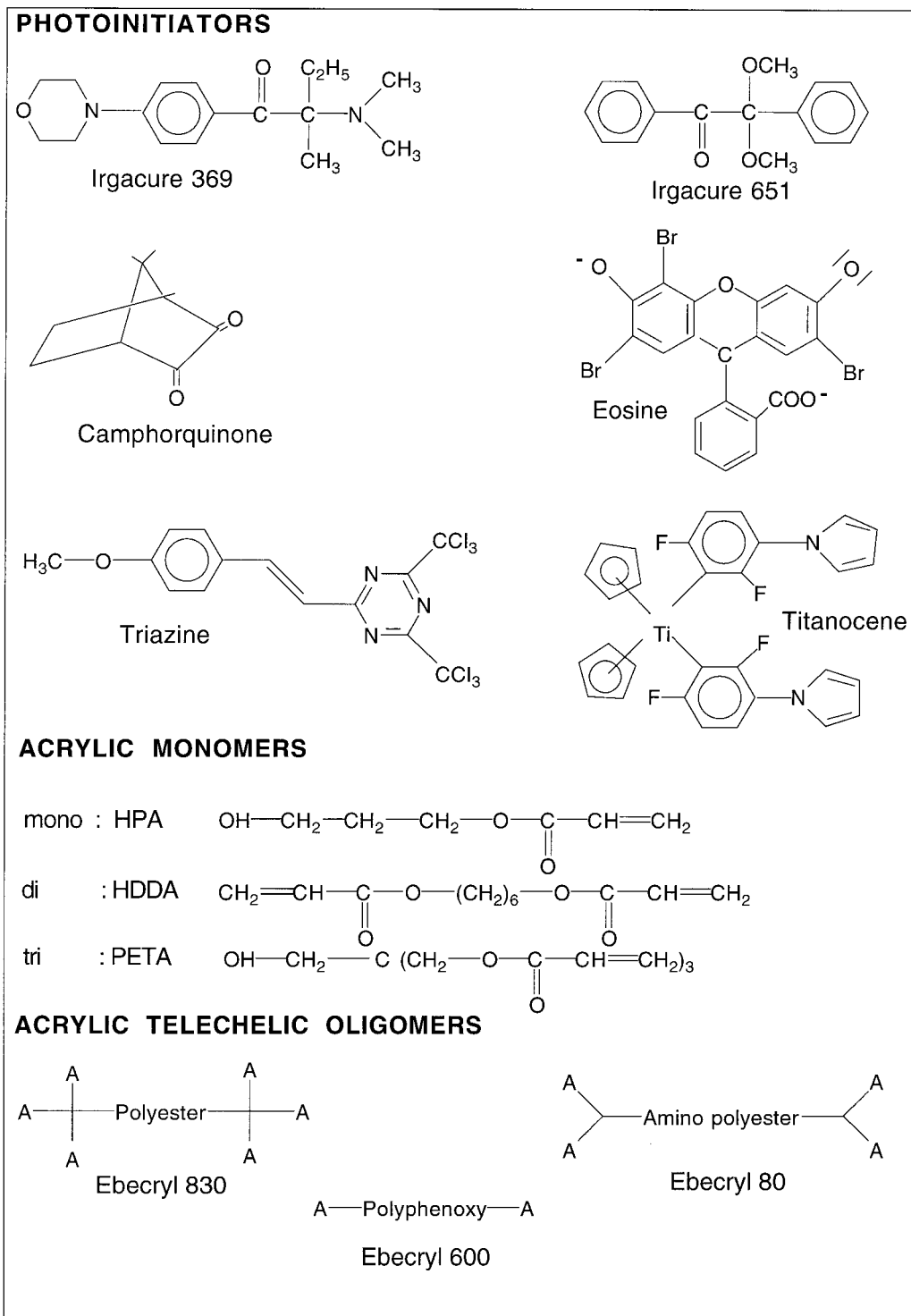


Figure 1 Chemical formulas of the photoinitiators and monomers used in the study.

Based on a spot size (l) of $20 \mu\text{m}$ and on a scanning rate (r) of 1000 m/s , the photoresist sensitivity (S) was calculated to be 0.2 mJ cm^{-2} ($S = P/r$

$\times l$). This energy must be sufficient to achieve nearly complete insolubilization of the photoresist.

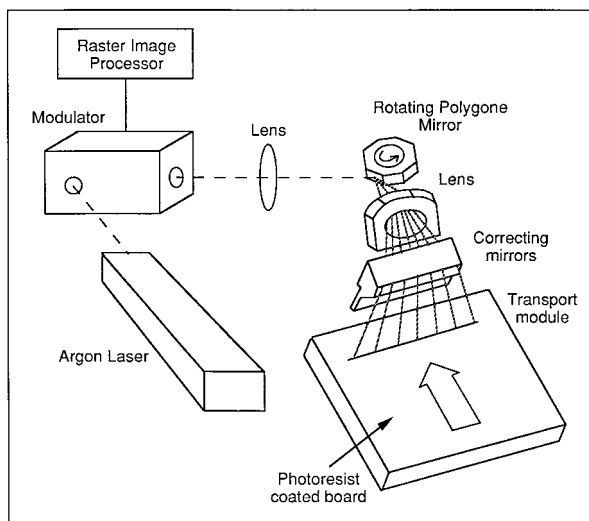


Figure 2 Laser scanner for direct imaging of printed circuit boards.

Analysis

The extent of the polymerization reaction and of the insolubilization process was evaluated by infrared (IR) spectroscopy, by monitoring the changes of the acrylate double bond at 1645 cm^{-1} and of the CH_2 absorption at 2900 cm^{-1} before and after UV irradiation, followed by development in alkaline (Na_2CO_3) solution. Figure 3 shows typical insolubilization and polymerization profiles obtained upon Kr^+ laser exposure of an acrylate photoresist. The following kinetic parameters were determined from these curves: (1) the sensitivity (S), in mJ cm^{-2} , was obtained by extrapolation of the insolubilization curve up to a normalized thickness of 1, reached for an exposure time t_s , by using the equation $S = I \times t_s$, where I is the incident light intensity (highly sensitive photoresists will exhibit low S values); (2) the contrast (γ), usually determined from the slope of the insolubilization curve plotted in a semilog scale, which was simply calculated from the equation $\gamma = [\log(S/I \cdot t_o)]^{-1}$; and (3) the degree of conversion (C_s) reached at time t_s , i.e., the percentage of acrylate double bonds that must have polymerized in order to get an insoluble polymer.

In some experiments, conversion versus time profiles were directly recorded by real-time infrared (RTIR) spectroscopy.¹⁷ The IR detection wavenumber was set at 812 cm^{-1} , where acrylic photoresists exhibit a distinct absorbance peak ($\text{CH}_2 = \text{CH}$ twisting). The sample was exposed simultaneously to the laser beam, which induces the

crosslinking polymerization, and the IR analyzing beam, which monitors *in situ* the amount of unreacted acrylate double bonds. This technique gives a quantitative evaluation of the photoresist reactivity, thus allowing a rapid selection of the most photosensitive formulations.

UV CURING OF DRY ACRYLIC PHOTORESISTS

Most of the photoresists used in imaging applications consist of dry or laminated films that can be stored and are more convenient to handle than wet films. The main drawback of the dry film technology is that photochemical reactions develop less efficiently in the solid state than in liquids, thus leading to a severe drop of the sensitivity. The reactivity of different types of acrylate functionalized polymers has been evaluated, using Irgacure 369 (1 wt %) as photoinitiator.

Figure 4 shows the polymerization profiles recorded by RTIR spectroscopy upon UV exposure of four dry acrylic photoresists in the presence of air. The most reactive system consists of an aromatic polyether diacrylate bearing bromine atoms. This type of substituent is known to accelerate the UV curing of acrylic resins by generating additional initiating radicals upon photolysis. Total insolubilization was found to occur when 8% of the acrylate double bonds had polymerized. For the tetrabromo-phenoxy-diacrylate, it was achieved when the sample had received an energy

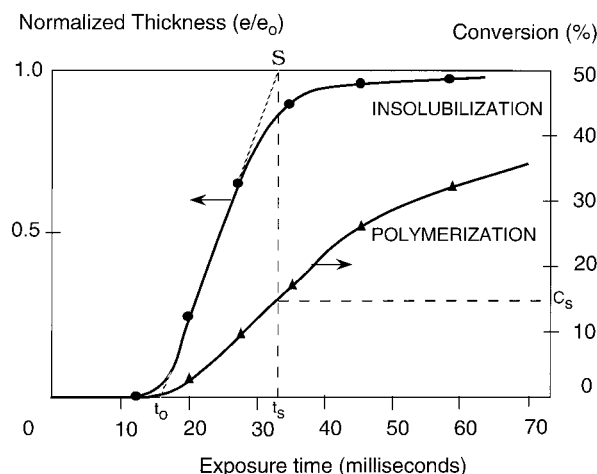


Figure 3 Polymerization and insolubilization profiles of an acrylic photoresist exposed to a UV-laser beam, determined by infrared spectroscopy.

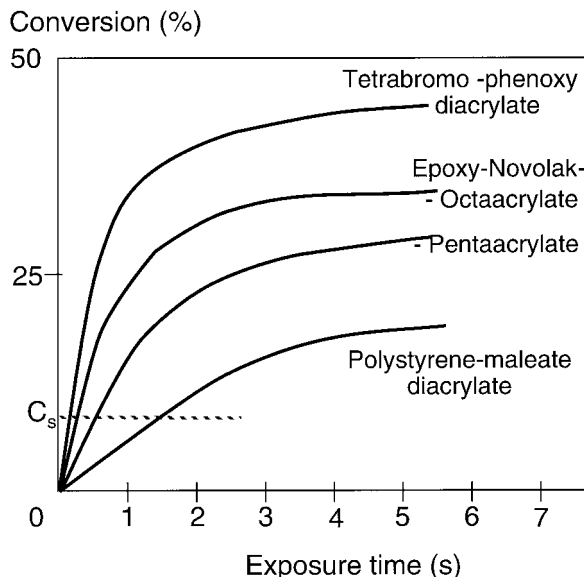


Figure 4 Conversion versus time profiles recorded by RTIR spectroscopy for various dry acrylic photoresists exposed to UV radiation. Photoinitiator: [Irgacure 369] = 1 wt %. Light intensity: 60 mW cm^{-2} , C_s ----: conversion of insoluble polymer.

of 10 mJ cm^{-2} . This value of the sensitivity S is much too large and precludes any use of this photoresist for the considered LDI application.

The presence in the film of some residual solvent, which acts as plasticizer, was found to substantially increase the rate and extent of the crosslinking reaction, as shown by the polymerization profile represented in Figure 5. A similar but more pronounced effect was observed by adding small amounts (5%) of an oxazolidone-acrylate (Acticryl CL-959), a monomer known for its great reactivity,¹⁸ which will act both as plasticizer and crosslinking agent. The polymerization rate was further increased by laminating the photoresist with a transparent polyethylene film to prevent the diffusion of atmospheric oxygen (Fig. 5). The S value of this dry acrylate photoresist (1 mJ cm^{-2}) is 10 times lower than that of the original phenoxy-acrylate, but it is still five times too high to meet the requested LDI specifications.

UV CURING OF WET ACRYLIC PHOTORESISTS

A typical UV-curable liquid resin contains three basic components: a radical-type photoinitiator, a multiacrylate telechelic oligomer, and an acrylate

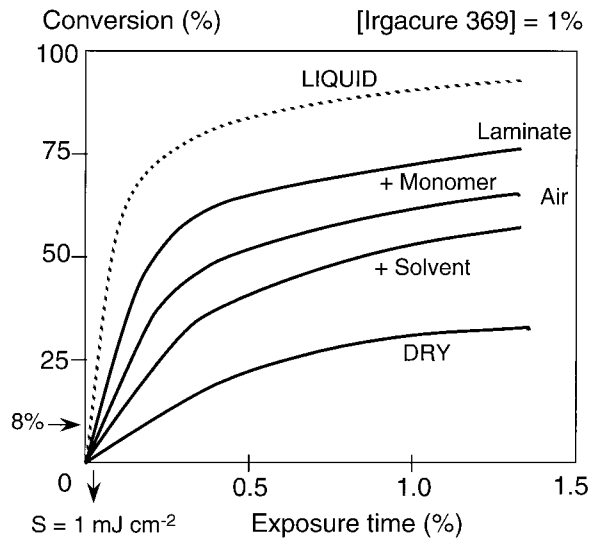


Figure 5 Polymerization profiles recorded by RTIR spectroscopy for a solid polyether acrylate film exposed to UV light. Photoinitiator = [Irgacure 369]: 1 wt %; monomer: [Acticryl CL-959] = 5%, light intensity: 60 mW cm^{-2} . ----: Ebecryl 80 + Acticryl CL-959.

monomer acting as reactive diluent. Several formulations containing different kinds of acrylate monomers and oligomers have been studied in order to find a photoresist that would meet the sensitivity specifications, i.e., with a S value of 0.2 mJ cm^{-2} or less.

Figure 6 shows the insolubilization profiles ob-

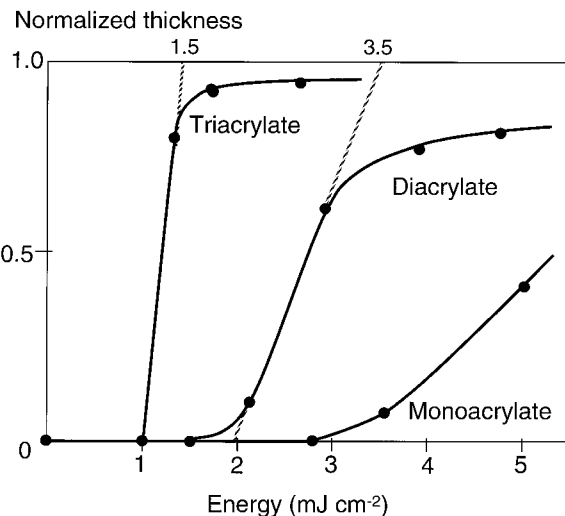


Figure 6 Influence of the monomer used as reactive diluent on the insolubilization of a wet acrylic photoresist upon UV-exposure. Telechelic oligomer: amino-polyester tetra-acrylate (Ebecryl 80); photoinitiator: [Irgacure 651] = 5 wt %; light intensity: 60 mW cm^{-2} .

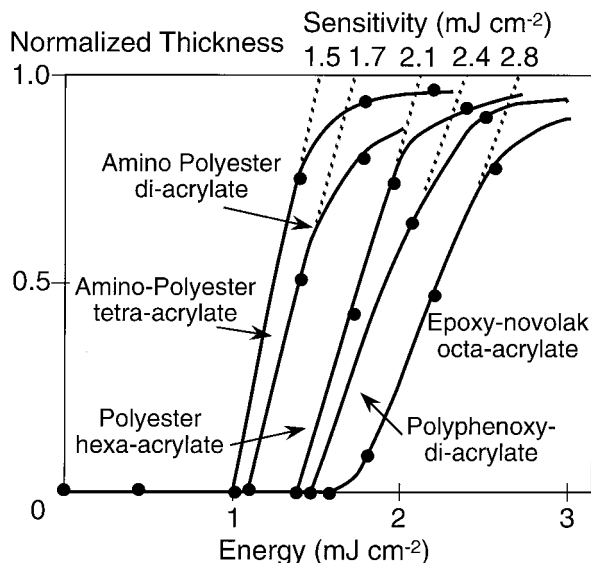


Figure 7 Influence of the telechelic oligomer on the insolubilization of a wet acrylic photoresist upon UV exposure. Monomer: pentaerythritol triacrylate; photoinitiator: [Irgacure 651] = 5 wt %; light-intensity: 60 mW cm⁻².

tained upon UV exposure in the presence of air of three formulations containing an amino-polyester tetra-acrylate (Ebecryl 80) as telechelic oligomer and dimethoxyphenylacetophenone (Irgacure 651) as photoinitiator. The acrylate monomer added to reduce the formulation viscosity (in a 1 : 1 weight

ratio) was a monofunctional (HPA), difunctional (HDDA), or trifunctional (PETA) compound. As expected, the fastest insolubilization was achieved by using the triacrylate monomer, with a S value of 1.5 mJ cm⁻², compared to 3.5 for the diacrylate and 8.0 for the monoacrylate.

In a second step, the chemical structure of the telechelic oligomer chain was varied to optimize the photoresist formulation. The effect on the sensitivity was found to be less pronounced than that of the monomer functionality, with S values ranging from 1.5 to 2.8 mJ cm⁻², as shown in Figure 7. The kinetic parameters of the various photoresists studied are summarized in Table I. The high value of the contrast ($\gamma > 3$) is a prerequisite to obtain sharp edge relief images. The most sensitive photoresist, which has the lowest S value, is that based on an amino-polyester tetra-acrylate and on pentaerythritol triacrylate. A 1 : 1 mixture by weight of these two compounds was found to give the best result with respect to sensitivity, contrast, and viscosity and was thus used for further studies. It should be noticed that its sensitivity (1.5 mJ cm⁻²) is still far away from the 0.2 mJ cm⁻² target.

Insolubilization was achieved when between 11 and 19% of the original amount of acrylate double bonds had polymerized, as shown by the intense peak at 810 cm⁻¹ found in the IR spectrum of the insoluble film. Even if the lightly cross-linked

Table I Performance Analysis of Wet Acrylic UV-Photoresists

Functionalized Prepolymer	Sensitivity (mJ cm ⁻²)	Contrast γ	Conversion C_s (%)
Photoinitiator: [Irgacure 651] = 1%			
Epoxy-novolak octa-acrylate	2.8	3.4	11
Chlorinated polyester tri-acrylate	2.4	4.3	14
Polyphenoxy di-acrylate	2.4	4.4	16
Polyether tetra-acrylate	2.2	3.2	12
Polyester hexa-acrylate	2.1	4.5	17
Amino polyester di-acrylate	1.7	5.7	18
Amino polyester tetra-acrylate	1.5	5.7	19
Functionalized Prepolymer	Sensitivity (mJ cm ⁻²)	Contrast γ	Conversion C_s (%)
Photoinitiator: [Irgacure 369] = 1%			
Amino polyester tetraacrylate			
in air	0.4	3	15
in nitrogen	0.11	4	9

Monomer [PETA] = 50%, Light-intensity: 40 mW cm⁻²; atmosphere : air

polymers have high molecular weight, these low C_s value would only amount to 40 to 75% of the multifunctional monomers and oligomers. Based on these results, one can conclude that the polymer film obtained after laser exposure followed by development in an alkaline aqueous solution contains a substantial amount of trapped monomer, which cannot be extracted by this poor solvent. When organic solvents, like chloroform, were used as developing media, a much higher monomer conversion had to be reached to achieve total insolubilization: 40% for a triacrylate and 65% for a diacrylate.¹⁹ Moreover, when photoresist samples, irradiated at the minimum dose required to achieve total insolubilization in alkaline solution (i.e., the sensitivity value) were further treated in chloroform, they were found to remain insoluble in a proportion of only 30 to 50%. As chloroform is a much better solvent of these acrylic polymers than an aqueous solution of CO_3Na_2 , it is capable of extracting the unreacted monomer, which remained trapped in the cross-linked polymer after alkaline development. For photoresist applications, the important feature is the etching resistance; it can be achieved even with a lightly cross-linked polymer containing relatively large amounts of unreacted monomer, as long as the thickness of the insoluble film remains high enough (here 35 μm) to ensure an efficient

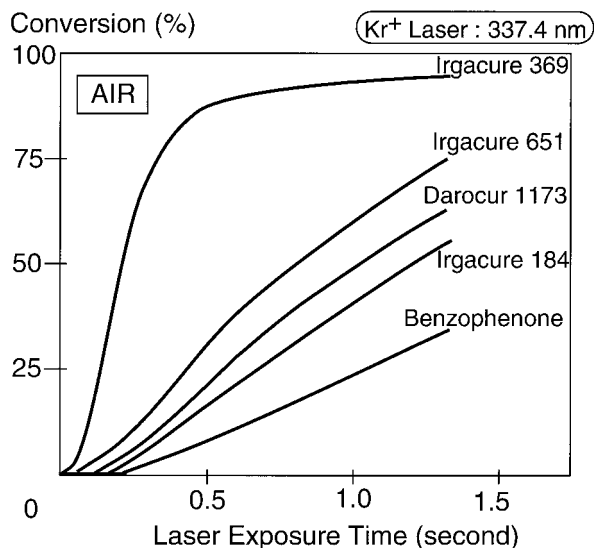


Figure 8 Influence of the photoinitiator on the polymerization kinetics of an amino-polyester tetra-acrylate photoresist exposed to a Kr^+ laser beam. [Photoinitiator] = 2 wt %.

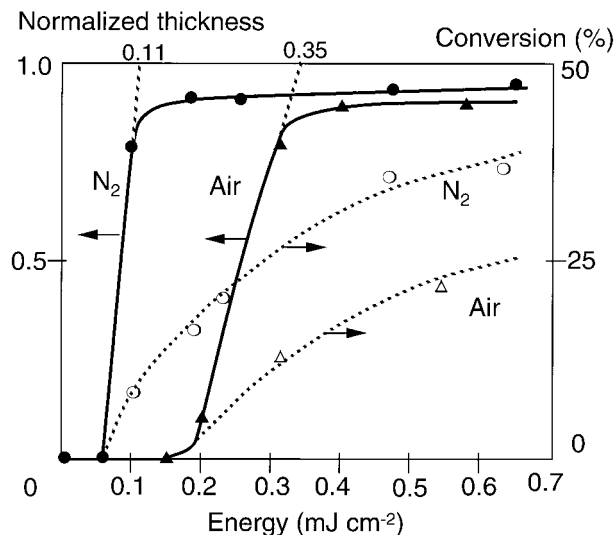


Figure 9 Influence of atmospheric oxygen on the photosensitivity of a wet acrylic photoresist. Amino-polyester tetra-acrylate (50 wt %), pentaerythritol triacrylate (49 wt %), Irgacure 369 (1 wt %); light intensity: 60 mW cm^{-2} .

protection of the imaged areas during the chemical treatment.

A great increase in sensitivity was achieved by replacing the benzilketal photoinitiator (Irgacure 651) by an α -amino alkylphenone (Irgacure 369). This photoinitiator, which exhibits a much stronger absorption at 337 nm, the emission line of the Kr^+ laser, was previously shown to be a very efficient generator of initiating radicals in laser-induced polymerization of acrylic resins.¹⁰ The superior performance of Irgacure 369 appears clearly in Figure 8, which shows the polymerization profiles recorded by RTIR for the amino-polyester tetra-acrylate photoresist containing different types of commercial photoinitiators. Replacing Irgacure 651 by Irgacure 369 leads to a substantial drop of the S value, from 1.5 to 0.4 mJ cm^{-2} , while the contrast remained good ($\gamma = 3$). Further improvement was obtained by performing the UV exposure in an inert atmosphere (Fig. 9). Indeed, atmospheric oxygen is known to have a strong inhibition effect on radical-induced polymerization, particularly for thin liquid film.²⁰ With the PETA + Ebecryl 80 photoresist, the sensitivity dropped to a remarkably low value of 0.11 mJ cm^{-2} , with formation of a well-contrasted relief image ($\gamma = 4$).

In this O_2 -free system, only 9% of the acrylate double bonds had to polymerize in order to get

complete insolubilization compared to 15% in the presence of air. This is probably due to the fact that longer polymer chains are formed in the absence of a radical scavenger like oxygen. The quantum yield of polymerization, which corresponds to the number of acrylate double bonds polymerized per photon absorbed, was calculated to be on the order of $30,000 \text{ mol einstein}^{-1}$. This value is in good agreement with previous evaluations²¹ and clearly shows the great efficiency of the chemical amplification in such acrylate photoresists. It is primarily due to an important dark polymerization process, which develops extensively after the short laser exposure, in O_2 -free media.

RTIR spectroscopy proved to be a technique particularly well suited to quantifying the post-polymerization as it simply requires continuing the monitoring of the variation of the acrylate double bond content once the light has been switched off. Figure 10 shows the conversion versus time curve recorded during and after a 50 ms exposure of the Ebecryl 80/PETA photoresist in a nitrogen atmosphere, in comparison to that recorded upon continuous irradiation (dashed curve). Nearly 90% of the cross-linked polymer was found to be formed in the dark just after the UV exposure. Such an important post-polymerization was already observed in similar laser-curable

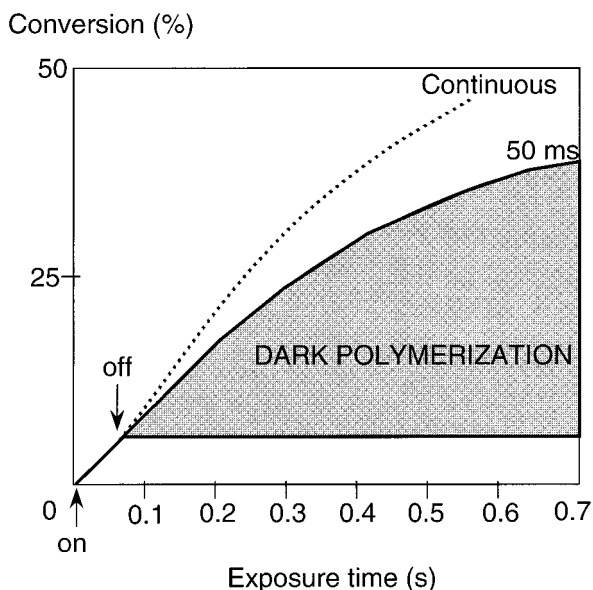


Figure 10 Importance of the dark polymerization in a wet acrylic photoresist exposed to UV radiation in an inert atmosphere ($I = 60 \text{ mW cm}^{-2}$).

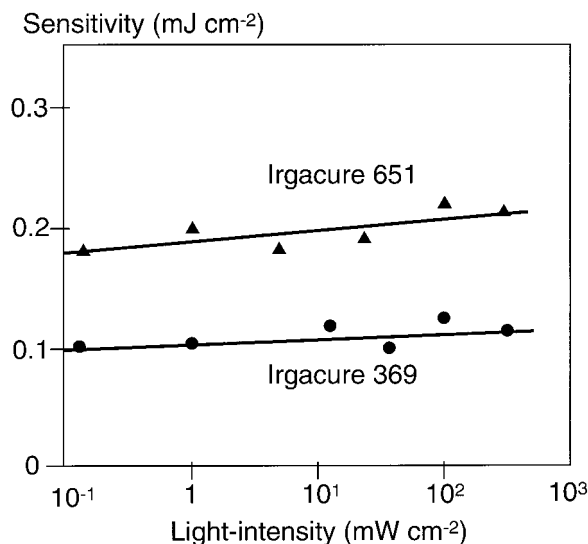


Figure 11 Influence of the light intensity on the sensitivity of a wet acrylic photoresist exposed to UV radiation.

acrylic photoresists.^{4,15} It was attributed to both a high value of the propagation rate constant ($k_p \sim 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$) and a relatively low value of the termination rate constant ($k_t \sim 5 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$).²²

Most of the studies reported so far have been performed at a light intensity of 60 mW cm^{-2} . For LDI applications, it is a prerequisite that the energy required for the insolubilization be independent on the light intensity (reciprocity law) because the patterning is to be carried out with an intense and sharply focused laser beam. The influence of the light intensity on the photoresist sensitivity was therefore studied over a four-decade range. It can be seen in Figure 11 that the S value remains essentially constant when the light intensity was varied from 0.1 to 300 mW cm^{-2} . Additional polymerization experiments have been carried out by using a pulsed nitrogen laser emitting at 337.1 nm . During the 10 ns wide flash, the light intensity rises up to 10^5 W cm^{-2} . An S value of 0.2 mJ cm^{-2} was measured for the formulation containing Irgacure 369 as photoinitiator, which means that the reciprocity law remains valid, even under very intense illumination. The extent of the polymerization process appears to be directly proportional to the amount of photons delivered during the short laser exposure, most probably because bimolecular radical termination is unlikely to occur under these nonsteady state conditions. Indeed, we calculated that each

initiating radical formed after a 0.5 mJ cm^{-2} exposure will be surrounded by as many as 120,000 acrylate double bonds. Therefore, it has little chance to encounter another radical during its short lifetime as R^* or P^* radical and is most likely to become trapped in the tight tridimensional polymer network formed.²³

The UV-curable liquid photoresist developed in this study and which is based on an amino-polyester tetra-acrylate, a pentaerythritol triacrylate, and a morpholinoketone photoinitiator exhibits the high photosensitivity required to perform a patterning by laser scanning at a speed of 1000 m/s.

VISIBLE LIGHT CURING OF WET ACRYLIC PHOTORESISTS

As most continuous wave lasers have their main emission lines in the visible range, there has been a growing demand in laser imaging for photoresists that would be sensitive to radiation above 400 nm. Different types of visible photoinitiators have been developed for LDI applications,²⁴ but their initiation efficiency was found to be substantially less than for UV-absorbing photoinitiators.

When camphorquinone was associated to a hydrogen donor like methyldiethanolamine (MDEA), which is a widely used photoinitiator system for the curing with the visible light, the acrylic resin (Ebecryl 80/Acticryl CL-959 in a 4 : 1 ratio) was

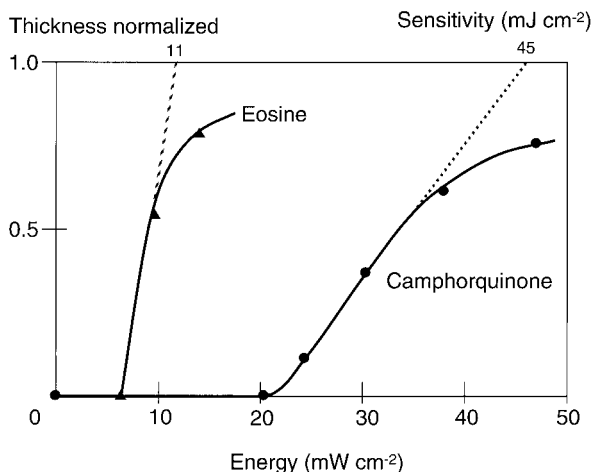


Figure 12 Insolubilization profiles of a wet acrylic photoresist exposed to visible radiation. Ebecryl 80/Acticryl CL-959 (4/1), eosine (1 wt %) or camphorquinone (5 wt %). [MDEA] = 10%. Argon ion laser (488 nm); light intensity: 60 mW cm^{-2} .

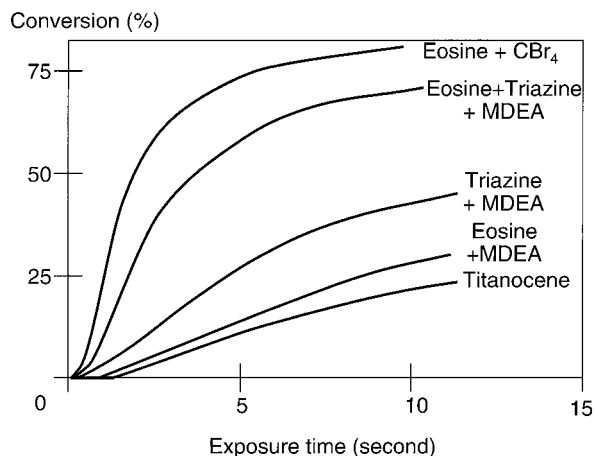


Figure 13 Influence of the photoinitiator on the polymerization profile of a wet acrylic photoresist exposed to visible radiation. [Titanocene] = 0.5 wt %, [triazine] = 0.5%, [eosine] = 1 wt %, [CBr_4] = 1 wt %, [MDEA] = 10%. Ebecryl 80/Acticryl CL-959 (4/1). $I = 14 \text{ mW cm}^{-2}$.

found to polymerize at a slow pace upon exposure to the 488 nm emission of the Ar^+ laser. The sensitivity value, determined from the insolubilization profiles shown in Figure 12, was as high as 45 mJ cm^{-2} . The initiation efficiency was much improved when camphorquinone was replaced by a xanthenic dye, like eosine. At a concentration of 1%, the S value dropped to 11 mJ cm^{-2} . Similar results were obtained with two newly developed compounds that absorb in the 450–500 nm range: a fluorinated diaryltitanocene²⁴ (Irgacure 784) and a chloromethyl substituted triazine²⁵ (CST).

Further improvement was achieved by combining these photoinitiators, in particular with the eosine + CST mixture, as shown by the RTIR polymerization profiles represented in Figure 13. The synergistic effect of this combination is clearly apparent in Figure 14, which shows a five-fold increase of the rate of polymerization for the mixture 0.5% eosine + 0.25% CST. The polymerization rate was further increased by the addition of small amounts of CBr_4 (1%), a compound known to favor the singlet-triplet intersystem crossing process by its heavy atom effect and to increase the yield of free radicals.

The most efficient photoinitiator system consists of a mixture of eosine (1%), Irgacure 784 (0.5%), CST (0.5%) and CBr_4 (1%). Insolubilization experiments carried out on the same acrylic resin (Ebecryl 80 + Acticryl CL-959) exposed to visible light, in the presence of air, have fully con-

firmed the conclusions of our RTIR study. The S value was found to drop from 11 mJ cm^{-2} for eosine to 1.8 mJ cm^{-2} for the compositions containing the four photoinitiators, as shown in Figure 15. This value is close to that obtained upon UV laser irradiation in the presence of air of the Irgacure-651-based photoresist ($S = 1.5 \text{ mJ cm}^{-2}$). The polymerization of the visible light-sensitive formulation appears to be less affected by the presence of air than the UV-sensitive one, probably because of a fast consumption of the oxygen dissolved in the resin by the radicals generated upon photolysis of the initiator mixture. Indeed, only a slight sensitivity improvement was achieved by performing the laser exposure in an O_2 -free environment: $S = 1.3 \text{ mJ cm}^{-2}$. Although this visible sensitive photoresist does not meet the LDI specifications, it should be noticed that the lesser sensitivity of visible photoresists can be partly compensated by the higher power output available with CW lasers tuned to their visible emission lines.

The performances of the different types of acrylic photoresists developed in this study are summarized in Figure 16.

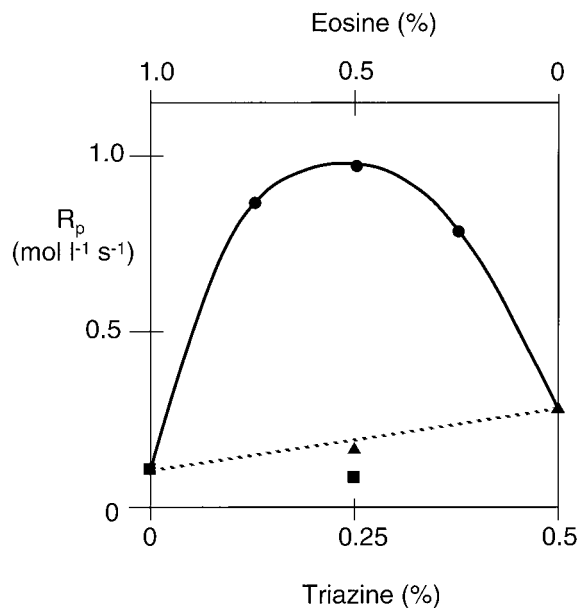


Figure 14 Synergistic effect of the eosine/triazine combination on the rate of polymerization (R_p) of a wet acrylic photoresist exposed to visible light in the presence of air. (■) eosine + MDEA; (▲) triazine + MDEA; (●) eosine + triazine + MDEA. $I = 14 \text{ mW cm}^{-2}$. $[\text{MDEA}] = 10 \text{ wt } \%$.

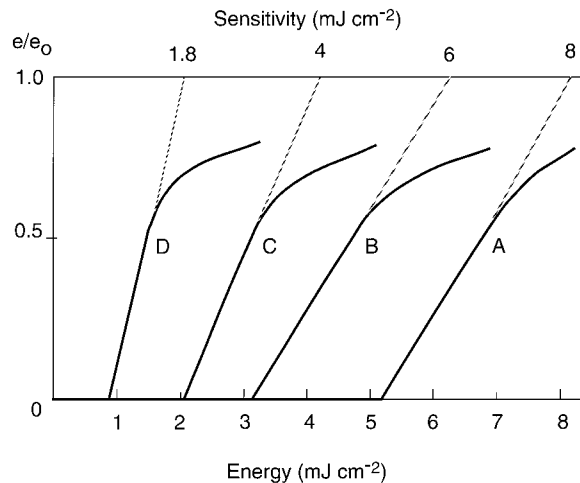


Figure 15 Influence of the photoinitiator system on the insolubilization profile of an acrylic photoresist (Ebecryl 80/Acticryl CL-959) exposed to the 488 nm Ar^+ laser emission in the presence of air. ($I = 60 \text{ mW cm}^{-2}$).

Formulation	Titanocene %	Triazine %	Eosine %	CBr_4 %
A	0.5	0.5	—	—
B	0.5	0.5	—	1
C	0.5	0.5	0.5	—
D	0.5	0.5	0.5	1

APPLICATIONS OF LASER-CURABLE RESINS

The laser-curable acrylic resins presented in this study have been principally developed for the manufacture of printed circuit boards by an LDI process. Because of their high sensitivity to UV or visible radiation, these resins are likely to find interesting applications in some other industrial sectors,^{1,26} which are shown schematically in Figure 17.

Photolithography

The high-definition relief images needed for the manufacture of microcircuits or printing plates can be readily generated via the laser-induced curing of negative photoresists. Pulsed lasers are used mainly as projection light sources for the irradiation of entire wafers or printed circuit boards. The LDI technology offers the combined advantages of elimination of the use of costly

masks, greater flexibility in the production of microcircuits with sharper lines, and fewer defects.

Optoelectronics

LDI technology can also serve to produce optical guides to follow complex patterns.¹⁰ The use of fluorinated acrylate monomers leads to high transparency and, following curing, the ability to withstand prolonged exposure to intense laser beams. Optical designs of micronic dimensions can thus be drawn at high speeds on photosensitive plates by means of a computerized laser beam.

Stereolithography

One of the most remarkable features of laser-induced curing is that it enables the quasi-instantaneous transformation of a liquid resin into a solid material selectively in the areas exposed to the laser beam.⁸ Three-dimensional solid objects can be created by scanning the surface of a photocurable resin with a laser to form a thin, solid pattern and building the model up step-by-step by adding one layer over another. Since it obviates the need for moulds, machine dies, and cutting tools, stereolithographic technology has proven to be of considerable interest to various industrial sectors for the rapid prototyping of solid objects.

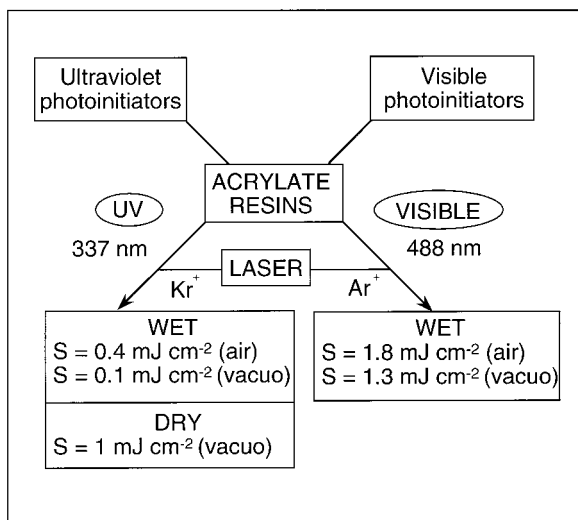


Figure 16 Performance of acrylic photoresists for laser direct imaging applications.

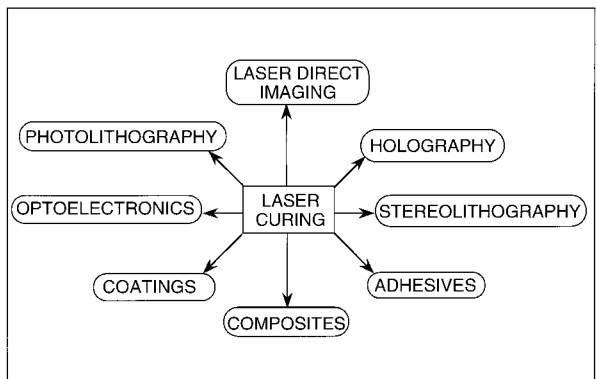


Figure 17 Various sectors of applications of laser-curable systems.

Holography

Laser-sensitive polymers are finding increasing use as recording media for the production of three-dimensional pictures or for holographic interferometric measurement of small deformations of objects subjected to stress.⁹ The laser-induced polymerization causes a change in the refractive index, as a result of the shrinkage accompanying the change from liquid to solid phase. The main advantage of photopolymer holography is that it requires no solvent development and exhibits a wide range of spectral sensitivity, from the deep UV region to near-IR.

Coatings of Optical Fibers

UV lasers appear to be particularly well suited to the achievement of ultrafast hardening of photocurable formulations employed as either low-modulus primers or hard, resistant topcoats to protect the surface of optical fibers. The use of CW lasers leads to a substantial increase of the line speed, while it decreases the overall dimension of the UV oven at the same time.

Laser Curing of Dental Composites

The use of lasers instead of conventional light sources speeds up the hardening process while simultaneously increasing penetration into the composite formulation. Because of safety regulations, only visible radiation can be used to induce the curing reaction, and the acrylic monomers had to be replaced by methacrylic monomers.

Laser Curing of Adhesives

Two pieces of an assembly can be bound together by laser irradiation, provided that at least one of the two components is transparent to the laser beam. The bonding operation can be performed to order and over a great distance (e.g., on a satellite) by simply firing the laser. The liquid resin, acting originally as a lubricant, is thus transformed instantly into a strongly adhesive solid material.

CONCLUSION

Laser curing is a relatively new technology, which has found its major applications in high-tech industrial sectors. The growing interest in laser-induced polymerization processes is largely attributable to the development of high-performance photoinitiators with absorption profiles well matched to the emission lines of commercial lasers, and of highly reactive monomers and prepolymers, capable of generating quasi-instantly polymeric materials with specific, tailor-made properties on curing.

Negative working acrylate photoresists have been developed to produce printed circuit boards by a LDI technology. These resins undergo a rapid insolubilization upon laser irradiation and were found to exhibit an outstanding photosensitivity in the near UV region, with a chemical amplification factor of 50,000. Writing speeds up to 1000 m/s become thus achievable by using the UV emission lines of CW lasers. The LDI technology offers a number of advantages, such as sharper and well-defined lines, fewer defects, rapid prototyping, and small production runs. The laser sensitive photoresists developed in this work are expected to find industrial applications in other sectors than microlithography, in particular, in optoelectronics, holography, and stereolithography.

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