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# Taking Lithography to the Third Dimension

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**Abstract.** Stereolithography is a new technology which allows the rapid building of plastic models directly from CAD data. The photopolymers needed for this process are developed at Ciba's research center in Marly by a project team from the Polymers Division and the corporate Materials Research. The stereolithography process is described as well as the requirements for the photosensitive monomer formulations. Two types of stereolithography resins have been developed so far: acrylate mixtures which polymerize by a radical mechanism and epoxy-based formulations which are cured cationically. The acrylate resins polymerize very rapidly and several formulations with different mechanical properties are available. Cationic resins are a development of the past two years. They are less photosensitive than the acrylates, but have other advantages, such as low viscosity, high green strength and very high dimensional accuracy. With these resins, parts can be built which can be used directly as patterns for the investment casting process.

## 1. Introduction

About 10 years ago, a new technology began to develop which allows the rapid building of three-dimensional models directly from CAD data. It was called stereolithography by its inventor Charles Hull [1]. In 1986, he and his partner Ray Freed founded the company 3D Systems (which is now located in Valencia, California) in order to commercialize this technology, which combines computer-aided design (CAD), laser technology, and photopolymer chemistry.

Ciba-Geigy, which is also a major stockholder of 3D Systems (ca. 35%), became involved in the chemical part of the business, when 3D Systems looked for a partner for the development of the photopolymers needed for the stereolithography process. The research center in Marly was especially suited for the development of such products, because a polymer research group and laser specialists were working under the same roof on several projects for the Polymers Division and for the corporate Materials Research department. An interdisciplinary project team with sci-

entists from both sections was created in 1988 in order to develop materials for stereolithography and to investigate the basic principles of the process.

A cooperation agreement with 3D Systems regulates the close collaboration of the two companies. The stereolithography (SL) resins developed by the Ciba team are distributed exclusively by 3D Systems. This cooperation has been very successful, and stereolithography is still the leader in the quickly developing market for rapid prototyping techniques.

## 2. The Stereolithography Process

In the stereolithography apparatus (SLA), a computer-controlled laser beam is used to polymerize a liquid photosensitive monomer formulation layer by layer, according to data of a 3D representation of the object in a CAD system (Fig. 1). The part is built on a platform, which, at the beginning, is immersed in the resin one-layer thickness under the surface of the resin. When the first layer (the cross section of the bottom of the object) has been 'drawn' by the laser, the platform is moved down one-layer thickness so that the liquid resin can flow over the first layer of the part. The laser then draws the second layer, and so on. When the construction of the part is finished, the platform with the part moves over the surface of the resin to drain from unreacted liquid resin. After a cleaning procedure, the part is post-cured under UV lamps to assure complete cure of the resin [2].

Until now, 3D Systems has commercialized two families of SLA: one with a He/Cd laser which emits UV light at a wavelength of 325 nm and a vat for the resin of the dimensions 25 x 25 x 25 cm and another one with a powerful Ar/UV laser (300–700 mW, wavelengths 351 and 364 nm) and a vat of the dimensions 50 x 50 cm and selectable depths up to 60 cm.

## 3. Requirements of Materials for Stereolithography

The main requirement for an SL resin is a very fast polymerization, which is confined to the area the laser has exposed.

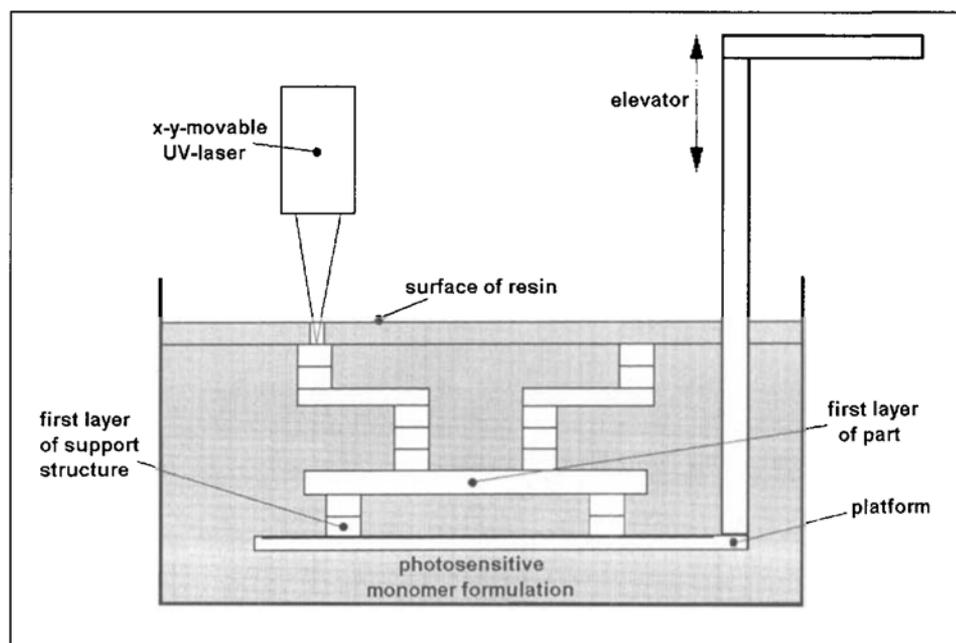


Fig. 1. Schematic representation of the stereolithography process

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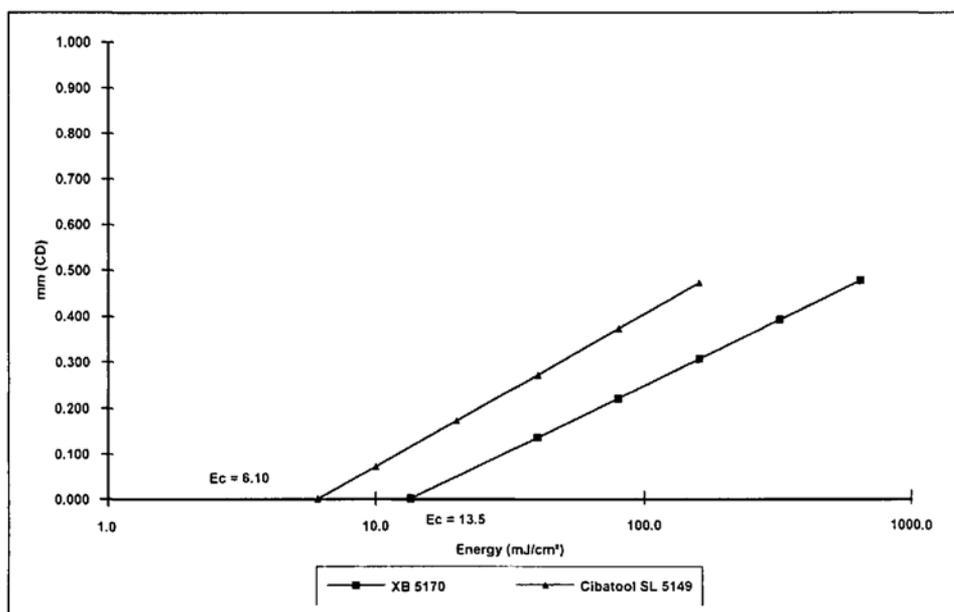


Fig. 2. Cure depth (CD) vs. incident He/Cd-laser energy for Cibatool SL 5149 and 5170

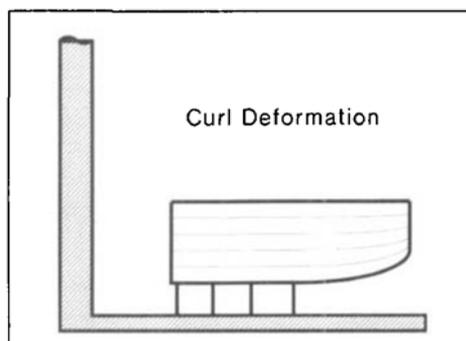


Fig. 3. Schematic side view of part building leading to curl

A continuing polymerization beyond the limits of the cross-section, the laser has drawn would lead to inaccurate dimensions of the part, to rough surfaces and other defaults in the part. The thickness of the layer is given by the amount of liquid which has been recoated on the part. On layers that start an overhang or bridge, the laser beam shines right down into the resin pool, attenuated essentially by the initiator absorption. In practice, the polymerization does not proceed beyond a limited depth where the laser intensity is below a threshold value. A certain energy, the so-called critical energy, is needed to reach the gel point, where actual solid material is formed. It becomes attached to the previous layer, when the cure depth is higher than the layer thickness.

The evaluation of the photosensitivity of an SL resin can be effected by passing the laser beam with a certain intensity and velocity over the resin surface, thus obtaining a polymer string with a certain cure depth  $d$ . A plot of  $d$  vs.  $\ln$  of the incident energy gives a straight line, the photosensitivity curve (Fig. 2) [3].

Another very important property which has to be tuned for SL resins is viscosity. The process of lowering the platform and letting liquid resin flow over the laser-cured surface of the part requires resins with relatively low viscosity (100–3000 mPas) and good wetting behavior.

When the building process is finished, the laser-cured part must have sufficient strength (so-called green strength) so that it will not distort before or during the final post-cure. At the gel point, the material has no mechanical strength. Therefore, the crucial parameter for gaining strength is the energy in excess over the critical energy which is being absorbed in the upper part of the polymer string [3].

Due to shrinkage of the material during the polymerization process a special type of distortion, the so-called curl, can occur. At an unsupported cantilever of the part, the first layer is free to shrink without

inducing distortion stress. The second and successive layers are each bonded to the layers below. If there is shrinkage after these upper layers are fixed to the layers below, a bending moment is introduced which can cause upward curl of the unsupported ends of the layers (Fig. 3). There are several factors which influence curl, e.g. polymerization rate, conversion at the gel point, total volume shrinkage, over-cure, temperature, but the phenomenon is still not fully understood [2].

Finally, the mechanical properties of an SL resin after post-cure have to be considered. Parts that are only used as models for visualization and concept studies are less demanding than parts that are used for functional tests or patterns for casting processes. Depending on the final application, resins with different properties have to be developed.

## 4. Resins for Stereolithography

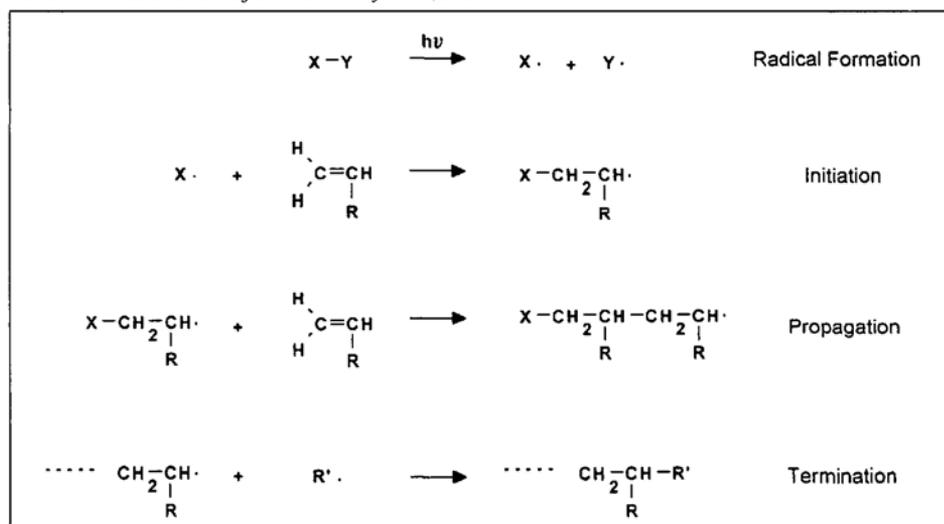
### 4.1. Radically Polymerizable Resins

A suitable class of monomers which can be formulated with a radical photoinitiator to fulfill the requirements outlined above are acrylates and methacrylates. A lot of mono- to polyfunctional monomers or oligomers are commercially available, because they are widely used in UV-curable coatings, adhesives or inks.

(Meth-)acrylates polymerize by a radical mechanism. The three essential steps of the polymerization are shown in Scheme 1.

By a photochemical process, free radicals ( $R'$ ) are formed from the photoinitiator. These radicals react with a monomer  $M$  to initiate a chain reaction. In the propagation step, the addition of a monomer to a macroradical ( $M_n^*$ ) results in a larger

Scheme 1. Mechanism of Radical Polymerization



macroradical. Chain termination may occur by recombination or disproportionation. SL Resins which contain a high concentration of polyfunctional monomers form a cross-linked gel at very low degrees of conversion. The polymerization rate decreases as the viscosity increases (*Tromsdorff* effect). Radicals can be trapped in the gel (occlusion) and the conversion of such highly cross-linked polymers never reaches 100% [4].

Some examples for (meth-)acrylate monomers which are used in SL formulations are shown in Fig. 4.

The first resin, called *Cibatool SL 5081-1*, was a quite brittle material. SL models from this resin were not suitable for functional tests. It was, however, found that they could be used as patterns for the fabrication of silicone rubber molds. From these molds, up to 20–50 copies of the model could be made in polyurethane or wax. Resins with higher impact resistance and very good building properties have been developed soon after (*Cibatool SL 5143*, *Cibatool SL 5149*). As two families of SL machines with two different lasers are available from *3D Systems*, different resins exist for the SLA 250 and for the SLA 500.

Table 1 shows some properties of the commercially available *Cibatool SL* resins.

**4.2. Cationically Polymerizable Resins**

Photoinitiated cationic polymerization of e.g. epoxides has become possible with the development of photoinitiators which generate strong *Brønsted* acids upon irradiation (e.g. triarylsulfonium or diaryliodonium salts) [5]. Some industrial applications for coatings are known, and the question arose if such systems could also be used for SL. First tests with epoxides

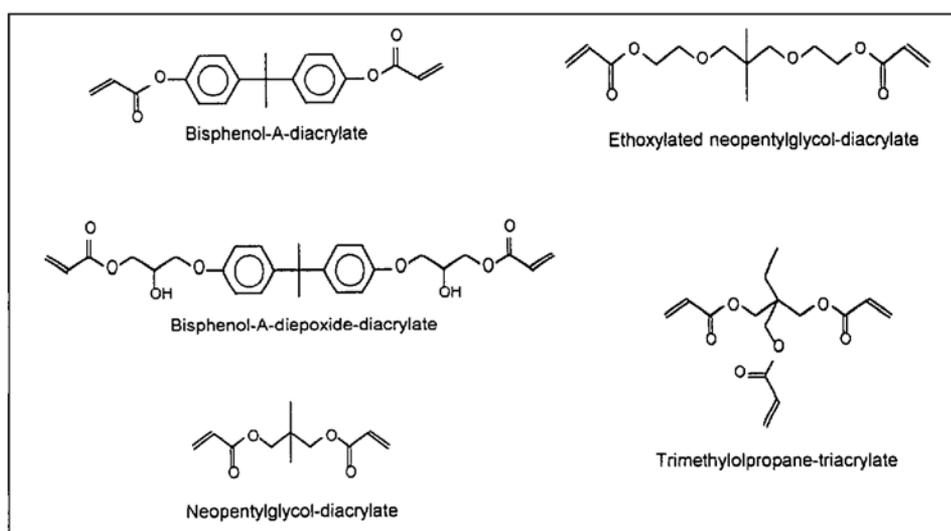
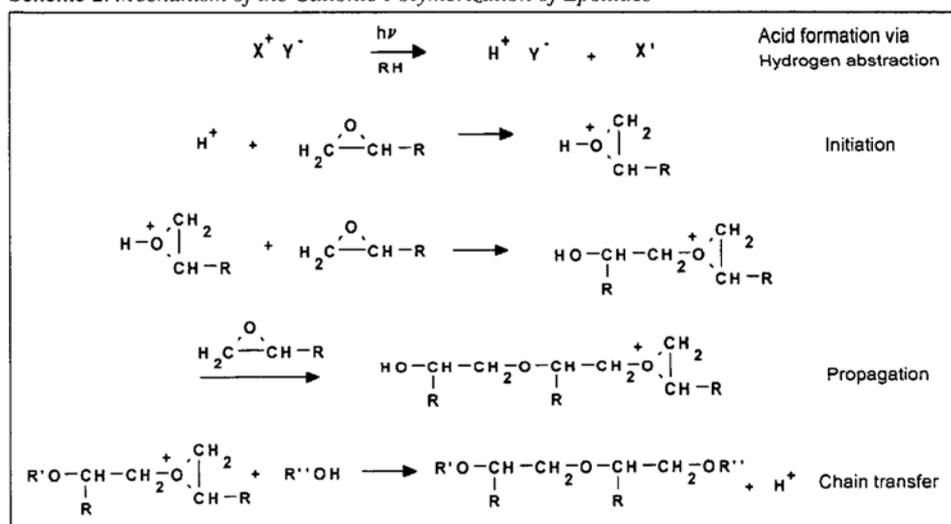


Fig. 4. Di- and trifunctional acrylates

Scheme 2. Mechanism of the Cationic Polymerization of Epoxides



showed that the polymerization rate was lower than for acrylates, but low curl values and interesting mechanical properties could be obtained.

The mechanism of the cationic polymerization of epoxides is outlined in Scheme

2. The photoinitiator yields a proton by H-abstraction from another molecule via a radical cation as intermediate [5]. The proton reacts then with an epoxide to give an oxonium-ion, to which another monomer adds under ring opening and forma-

Table 1. Acrylate Resins for Stereolithography

	SLA 250			SLA 500	
	<i>Cibatool SL 5081-1</i>	<i>Cibatool SL 5143</i>	<i>Cibatool SL 5149</i>	<i>Cibatool SL 5131</i>	<i>Cibatool SL 5154</i>
Viscosity @ 35° [mPas]	1130	1160	1100	1280	1200
$E_{crit.}$ [mJ/cm <sup>2</sup> ]	6.6	4.5	7.3	8	4.5
$D_p$ [slope of photosensitivity curve]	7.3	6	5.6	7.5	5.5
T-Mod. green [N/mm <sup>2</sup> ]	200	110	110	250	130
Tensile modulus [N/mm <sup>2</sup> ]	2500–3500	800–1100	1100–1200	3000–4000	800–1200
Elongation at break [%]	2–3	20	10	3	10
Impact resistance [kJ/m <sup>2</sup> ]		40	25	4	20
Hardness [shore D]	85–90	75	75–80	85–90	75–80
$T_g$ (generally broad) [°C]	150	80	83	150	83

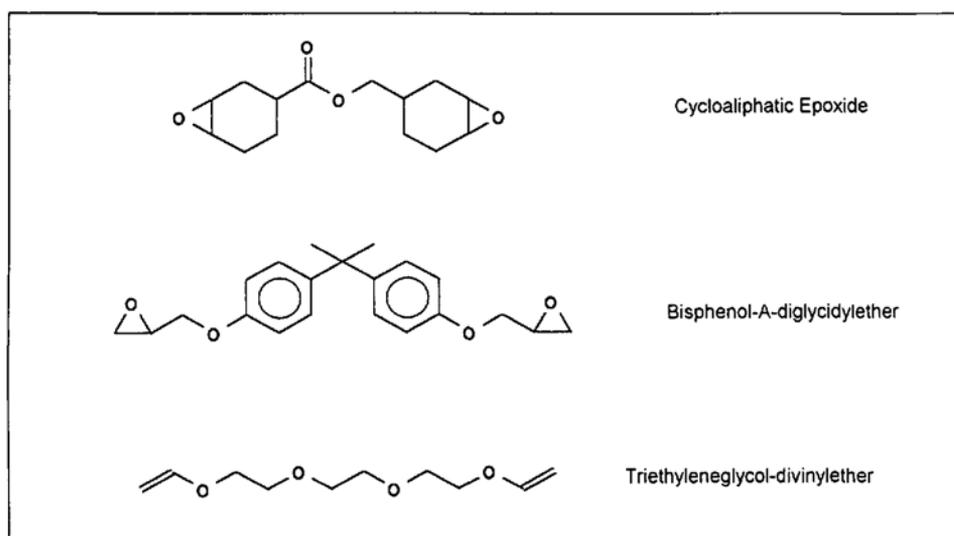


Fig. 5. Cationically polymerizable monomers

Table 2. Epoxy Based Resins for Stereolithography

	SLA 250 <i>Cibatool SL 5170</i>	SLA 500 <i>Cibatool SL 5180</i>
Visc. @ 30° [mPas]	180	187
$E_{crit.}$ [mJ/cm <sup>2</sup> ]	13.5	16.2
$D_p$ [slope of photosensitivity curve]	4.8	5.2
T-mod. green [N/mm <sup>2</sup> ]	ca. 900 <sup>a)</sup>	ca. 600
T-mod. cured [N/mm <sup>2</sup> ]	2500	2500
Elongation [%]	10–12	9–11
Impact [kJ/m <sup>2</sup> ]	~30	27–47
$T_g$ (°) [broad trans.]	90	87

<sup>a)</sup> Flex modulus.

tion of a new oxonium ion. Termination occurs primarily as a result of impurities in the resin. Bases of all kinds can terminate or inhibit cationic polymerization. Alcohols act as chain-transfer agents. Some examples of cationically polymerizable monomers are shown in Fig. 5.

The result of our development work are the new resins *Cibatool SL 5170* for the SLA 250 and *5180* for the SLA 500. Their properties are listed in Table 2. They have a higher critical energy, *i.e.*, a lower photospeed than the acrylate resins, but much lower shrinkage and curl values. Their green strength is 5–8 times higher than that of the acrylate resins.

With these resins, part accuracy has much improved and is now comparable to other conventional techniques of model building by *e.g.*, numerical controlled milling of plastics or aluminium.

Because of these characteristics, *i.e.*, low viscosity, high accuracy, high green

strength, and high tensile modulus after curing, the resin is especially suited for a new application of SL parts, namely as patterns for investment casting. By this technique, a ceramic mold is normally made from a wax pattern which is then burned out and used for the fabrication of a metal part. A part made from the new SL resins *Cibatool SL 5170* and *5180* can be used directly as pattern for investment casting, thus considerably shortening the time from design to the final metal part.

## 5. Outlook

Since the birth of stereolithography, a lot of other rapid prototyping technologies have developed, some of which are also based on photochemistry, others work by deposition of thermoplasts or sintered materials [6]. The *3D Systems* SL process is still the market leader, and over 450 SL

machines have been installed world-wide in large automotive and aerospace companies, as well as in small service bureaus, research institutes or even hospitals. The quality of SL parts has greatly improved during the last years due to machine, software and resin-improvements.

In the future, it will become more and more important to produce functional parts directly by or with the aid of stereolithography. A beginning is the replication with silicone molds and also the investment casting from SL patterns. Another development will be aimed at the direct fabrication of molds *e.g.* for injection molding of thermoplasts. Special materials for other applications will also be needed. Thus, a resin for medical applications, (*e.g.* for operation planning) is in development.

It is a fascinating task to work at the cutting edge of a new technology. The practical development of resins has been supported by the investigation of the fundamental processes from the beginning of the project, but there is still a long way to go to understand all the different aspects of stereolithography.

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