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# Photoinitiated Curing of Multifunctional Monomers

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**Abstract.** Radiation curing is being increasingly used in advanced technology applications, owing to its distinct advantages, mainly its great speed, selective cure and 100% solid formulation. Under intense UV or laser irradiation, the polymerization of multiacrylate monomers was shown to proceed extensively in a fraction of a second. The kinetics of these ultrafast reactions was studied quantitatively by means of the newly developed real-time infrared (RTIR) photo-spectroscopy. From the conversion vs. time curves recorded, the efficiency of some novel photoinitiators and acrylic monomers has been evaluated in UV-curable resins. The crosslinking-polymerization was found to proceed with long kinetic chains, despite the high initiation rate provided by UV or laser irradiation. The actual rate at which polymer chains are growing has been first determined from the polymerization profile recorded upon pulsed laser exposure. The photocured polymers exhibit remarkable mechanical properties, as well as a great resistance to chemicals, heat and radiation. These characteristics, together with the process facility, account for the wide-spread applications of UV curable resins, in particular as protective coatings to improve the weatherability of polymer materials, such as poly(vinyl chloride). Other applications of laser-induced curing are to be found in stereolithography, optoelectronics, holography, and laser direct imaging.

## Introduction

Light-induced polymerization is among the most efficient methods capable to achieve fast and extensive curing of multifunctional monomers [1]. With the highly reactive acrylate systems, the polymerization takes place within a fraction of a second, upon exposure to intense UV radiation or laser beams, thus transforming quasi-instantly the liquid resin into a strongly cross-linked solid polymer [2]. Studying the kinetics of such ultrafast reactions in order to get quantitative information proved to be a real challenge, specially when operating at the great light intensities used in most UV-curing applications.

Besides its rapidity, the photocuring technology presents a number of unique advantages, in particular a low energy consumption, no solvent emission, room temperature operations in the presence of air, and selective cure in the illuminated areas. Moreover, the large variety of multifunctional monomers and oligomers, which are now commercially available, makes it possible to produce polymer materials having tailor-made properties, best suited for the specific end-uses considered.

Due to their distinct characteristics, UV-curable resins are being increasingly employed in various sectors of applications, mainly in the coatings and adhesives industry, in the graphic arts and in

microelectronics. The surface protection of all kinds of materials exposed to an aggressive environment, such as metals, plastics, wood, or fabrics can be readily achieved by means of fast-drying UV-curable varnishes or paints, which exhibit a long lasting resistance owing to their high cross-link density. In photolithography, high-resolution relief images, which are needed for the manufacture of printed circuit boards or printing plates, are being produced by patterning of negative working photoresists, either by UV exposure through a mask or by laser direct imaging.

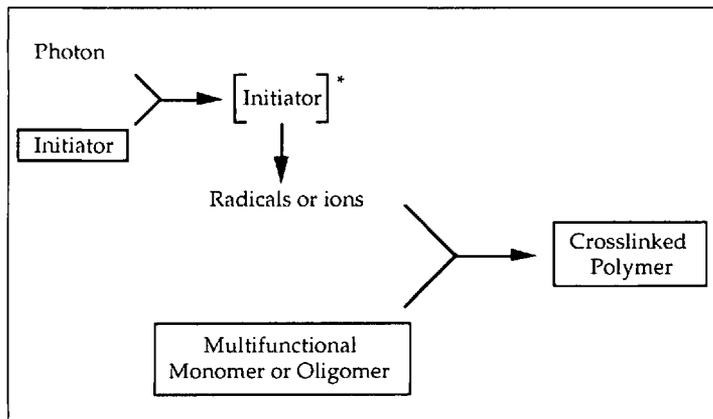
This article will first outline the basic principle of UV-curing of both radical and cationic-type systems. The kinetics of such ultrafast polymerizations induced by intense UV radiation or laser beams will then be discussed, based on the results obtained with a recently developed method of real-time analysis. Some novel applications of UV- or laser-curable resins will finally be described, special emphasis being directed toward the outstanding advantages provided by photoinitiation, in comparison to more conventional methods of curing.

## Basic Principle of UV-Curing

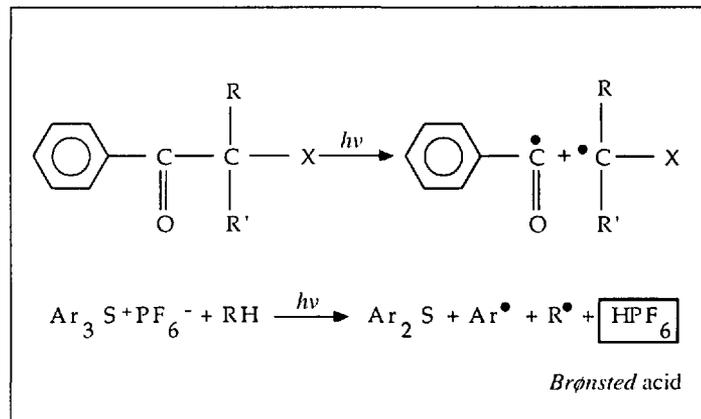
Photocurable resins consist usually of multifunctional monomers and/or oligomers, which generate upon polymerization a tight tridimensional polymer network. Since these monomers do not produce enough initiating species upon UV exposure, it is necessary to introduce a photoinitiator that will absorb effectively the incident radiation and generate free radicals or ions with a high quantum yield. The basic principle of photocuring is represented schematically in *Scheme 1*.

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Scheme 1



Scheme 2



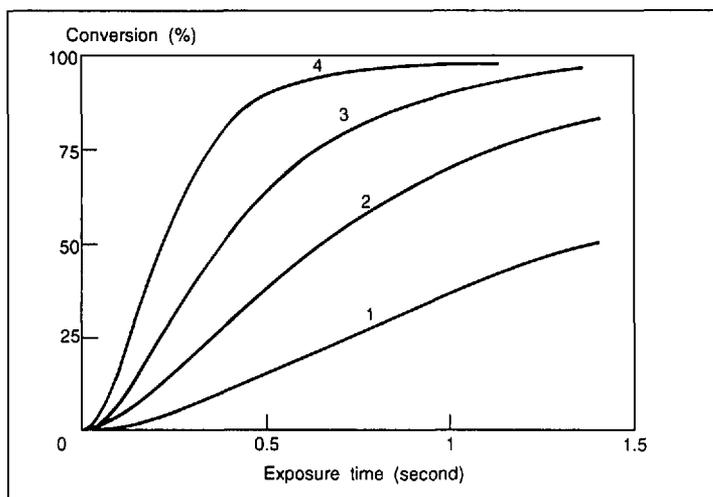


Fig. 1. Polymerization profiles recorded by RTIR photo-spectroscopy for a polyurethane-acrylate resin exposed to UV radiation in the presence of various photoinitiators (1%). 1) Benzophenone + methyl-diethanolamine; 2) hydroxy-phenylketone (*Darocur 1173*); 3) arylphosphine oxide (*Lucirin TPO*); 4) morpholinoketone (*Irgacure 369*).

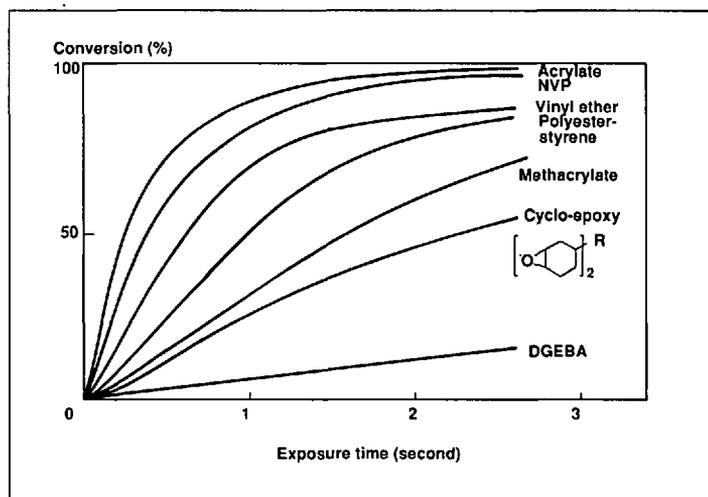


Fig. 2. Polymerization profiles recorded by RTIR photo-spectroscopy for different types of UV-curable systems

There are two major classes of UV-curable resins, depending on the type of initiating species and on the polymerization mechanism:

- photoinitiated radical polymerization of multifunctional acrylates or unsaturated polyesters;
- photoinitiated cationic polymerization of multifunctional epoxides or vinyl ethers.

Initiating species are produced either by photocleavage or H-abstraction of aromatic ketones with formation of reactive free radicals, or by photolysis of onium salts with formation of protonic acids (Scheme 2).

The great reactivity of acrylate monomers, together with the excellent properties of the UV-cured polymers, have given to radical-type systems a predominant position on the radcure market. A large number of acrylate functionalized prepolymers are now available (polyesters, polyethers, polyurethanes, polysiloxanes), and permit the creation of cross-linked polymers having the chemical and physical properties precisely required for a given application. The high viscosity of these prepolymers necessitates the addition of low-molecular weight acrylic monomers, which will act as reactive diluents and are thus incorporated into the polymer network.

### Kinetic Analysis of Photoinitiated Curing

Various analytical methods have been used to study the kinetics of light-induced polymerization of multifunctional monomers. They consist either of discrete measurements of the chemical modifications occurring after a short exposure (IR spec-

troscopy, photoacoustic spectroscopy, gravimetry), or of a continuous monitoring of some physical modifications induced by UV-curing, like the heat evolved (calorimetry, IR radiometry), the shrinkage (dilatometry) or changes in the refractive index (interferometry). A recent critical survey [3] has shown that none of these methods has been able so far to monitor quantitatively and in real time curing reactions that occur within a fraction of a second.

A novel technique, real-time infrared (RTIR) photospectroscopy, has been recently developed for this purpose, and has proven to be the first method capable to record directly conversion vs. time profiles for ultrafast light-induced polymerization processes [4]. Fig. 1 shows some typical kinetic curves obtained by exposing a polyester-acrylate film to intense UV radiation in the presence of various photoinitiators (PI). With the most efficient PI, a morpholino-ketone from *Ciba*, close to 100% conversion was reached within less than 1 s of irradiation.

One of the unique advantages of RTIR photospectroscopy is to allow the important kinetic parameters to be evaluated in a single experiment:

- the induction period ( $t_i$ ), which shows how effectively atmospheric oxygen or inhibitors interfere with the curing process;
- the actual rate of polymerization ( $R_p$ ), which can be determined at any time from the slope of the RTIR curve and the initial monomer concentration  $[M]_0$ :  
$$R_p = [M]_0 \times d(\text{conversion})/dt$$
- the quantum yield of polymerization ( $\Phi_p$ ), which corresponds to the number of functions polymerized per photon absorbed;
- the kinetic chain length (kcl), which

can usually not be determined in cross-linking-polymerization, and is calculated here simply from the ratio of  $\Phi_p$  to the initiation quantum yield  $\Phi_i$ ,

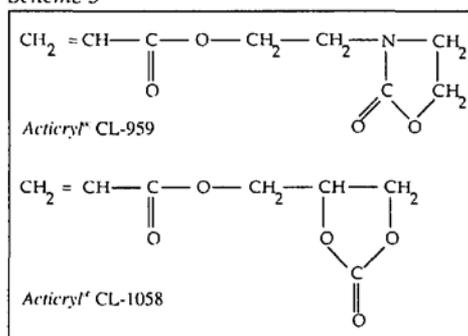
- the photosensitivity ( $S$ ), which is defined as the amount of energy required for total insolubilisation, often achieved at ca. 20% conversion;
- the contrast of the photoresist ( $\gamma$ ), which can be evaluated simply by replottting the kinetic curve on a semi-log scale;
- the residual unsaturation content (RU) of the cured polymer, which can be determined precisely from the IR spectrum of the final product.

All these kinetic parameters need to be known for a correct evaluation of the performance of various UV-curable resins or photoresists, in order to select the most efficient system. RTIR photo-spectroscopy proved to be an analytical method particularly well-suited to determine the effect of chemical and physical parameters on the curing kinetics, such as the light-intensity, the film thickness, the temperature or the ambient atmosphere [5]. It is also a most valuable tool for assessing rapidly the actual efficiency of new photoinitiators (Fig. 1), as well as of monomers or functionalized oligomers. In this respect, the superior reactivity of acrylate-based systems appears clearly from a comparison of the RTIR profiles recorded with different types of UV-curable resins irradiated under the same experimental conditions (Fig. 2).

### New Acrylate Monomers

The basic characteristics of UV-cured polymers depend primarily on the type of functionalized prepolymer and of monomer employed in the resin formulation.

Scheme 3



Both the chemical structure and functionality of the oligomer were shown to determine the thermal stability and chemical resistance, as well as the mechanical properties of the cured product. Aliphatic polyurethane chains give soft, highly flexible materials showing a great impact resistance, whereas aromatic polyester or polyether chains yield hard and stiff coatings showing a great resistance to scratching.

The monomer used to lower the formulation viscosity plays also a key role, by acting on both the polymerization rate and on the cure extent, as well as on the properties of the cross-linked polymer formed. Increasing the monomer functionality was found to accelerate the curing reaction, but also to reduce the final degree of conversion, due to early gelation of the irradiated sample and related mobility restriction of the reactive sites. In addition the greater cross-link density leads to glassy polymer materials which are harder, but also more brittle than monofunctional-type systems.

**Acrylates with Cyclic Structures**

One of the main goals in UV-curing chemistry is to create new monomers that would undergo fast and extensive polymerization, to yield polymer materials having well designed properties. In this respect, very promising results have been

recently obtained by introducing a cyclic carbonate [6], or an oxazolidone [7] group in the structural unit of a monoacrylate (Scheme 3).

The light-induced polymerization was found to occur rapidly up to high conversions, thus leading to a cured polymer containing little residual unsaturation. The remarkable performances of these new monomers (Acticryl from SNPE) are clearly illustrated by the recorded kinetics profiles shown on Fig. 3. Despite the high rate of initiation caused by the intense illumination, the chain reaction was shown to develop extensively, each initiating radical being capable to start the polymerization of up to 50 000 acrylate double bonds, in O<sub>2</sub>-free media. Another advantage of these reactive diluents is to impart both hardness and flexibility to UV-cured polymers (Fig. 4), which in addition exhibit a good resistance to organic solvents, chemicals, and weathering.

**Silicon Acrylates**

Acrylate end-capped poly-dimethylsiloxanes are readily polymerized upon UV irradiation in the presence of a radical photoinitiator to yield tridimensional polymer networks. The versatility and physical properties make them ideally suited for a variety of applications, mainly as pressure-sensitive adhesives, separation membranes and protective coatings for optical fibers, textiles or papers.

A new class of functionalized silica organosols has been recently introduced by Hoechst under the trade name Highlink OG<sup>®</sup>. It consists of a colloidal suspension of amorphous silica particles modified at their surface by a hydrocarbon chain, which makes them compatible with organic media. The silica content of the organosol increases with the size of the spherical SiO<sub>2</sub> particles, reaching values up to 40% for 50-nm large particles. The structure of

these compounds is illustrated schematically by Fig. 5. The number of chains grafted to the silica core depends on the particle size and was calculated to range between 1000 and 20 000 per particle.

If the grafted organic moiety is terminated by an acrylate function, such organosol will act as multifunctional cross-linking agent. With the 2-hydroxyethyl acrylate substituent (Highlink OG 101), photocuring was found to develop much faster in the silica organosol than in the parent monomer, leading to an insoluble material. Such UV-curable silicon acrylates present a great interest for coatings and adhesives applications, due to the marked improvement of the properties of the cured product, in particular the hardness, scratch resistance, thermal stability, weatherability, chemical resistance, and adhesion to various substrates.

**Surface Protection of Materials by UV-Cured Coatings**

One of the most effective methods for improving the surface characteristics of polymer materials and increasing their outdoor durability consists in protecting them with highly resistant coatings [8]. These are usually made of strongly cross-linked polymers containing light-stabilizers or pigment particles. Such clear coats or lacquers can be rapidly produced by photopolymerization of aliphatic multiacrylate monomers. By filtering the most harmful solar radiation and reducing the deleterious effects of moisture and oxygen, UV-cured coatings were found to substantially enhance the resistance to weathering of macromolecular materials, while ameliorating at the same time some of their surface properties, such as gloss, wettability, resistance to scratching, and abrasion.

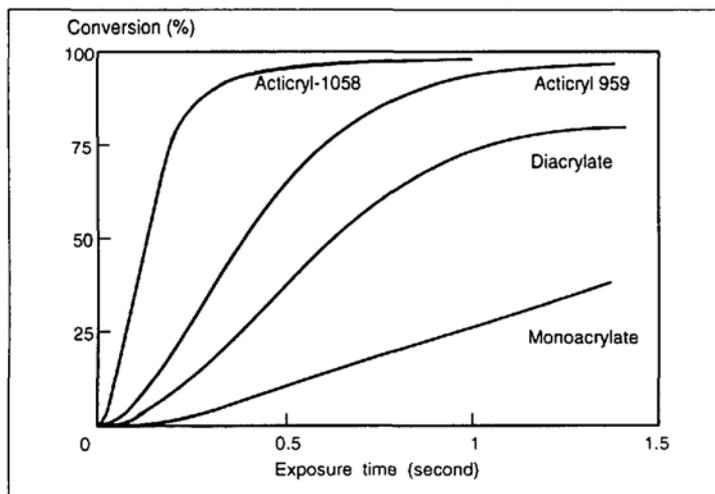


Fig. 3. Influence of the monomer (50%) used as reactive diluent on the cure kinetics of a polyurethane-acrylate photoresist. [Irgacure 651] = 5%.

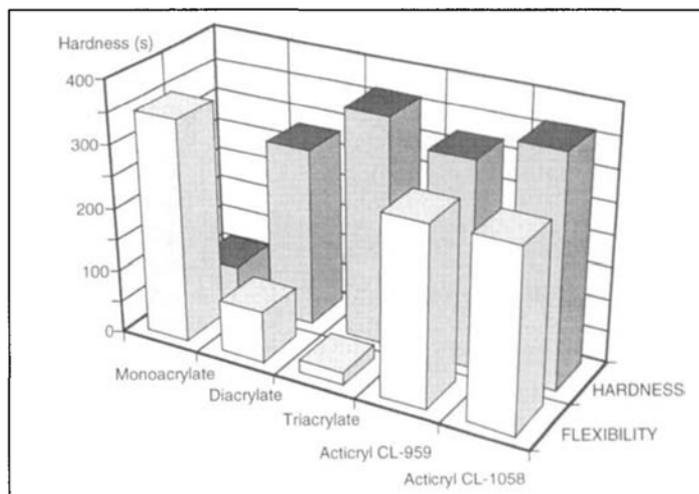


Fig. 4. Influence of the monomer on the flexibility and on the hardness of a UV-cured epoxy-acrylate coating

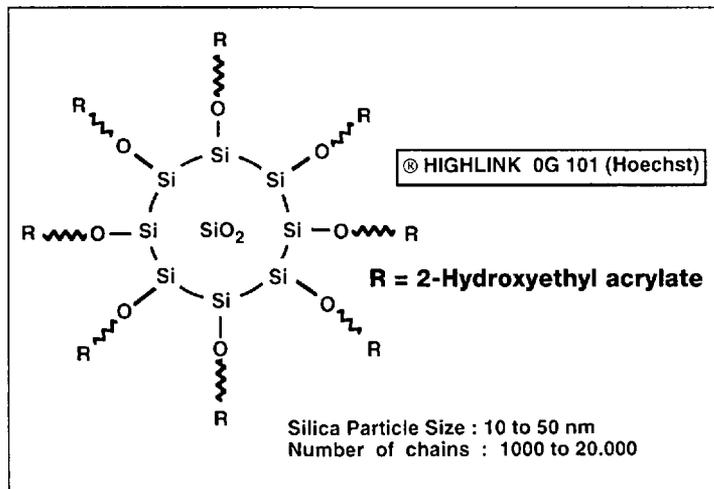


Fig. 5. Structure of an acrylic organosol of silica (Highlink OG 101)

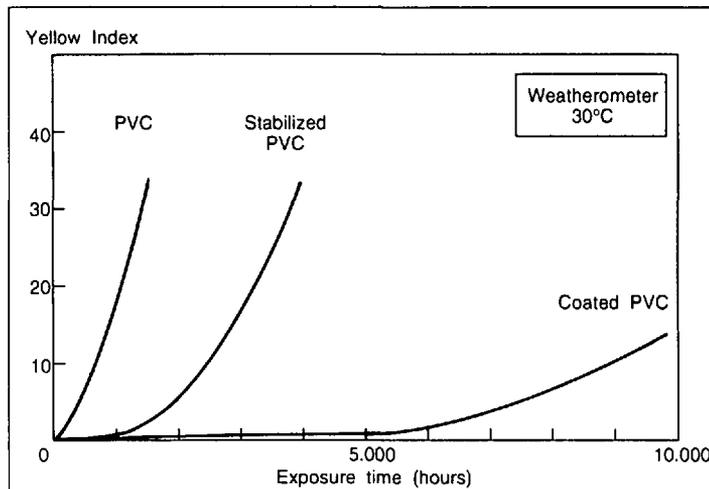


Fig. 6. Photostabilisation of clear PVC by a UV-cured coating containing a UV absorber (1% Tinuvin 900 + 1% Tinuvin 292)

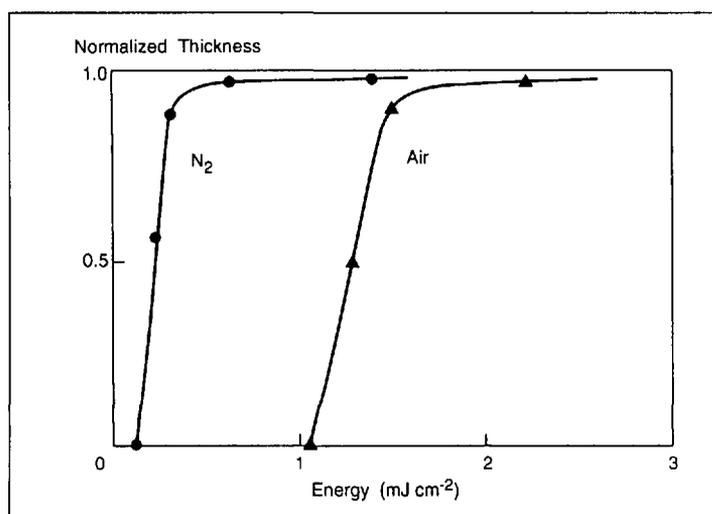


Fig. 7. Insolubilisation profiles of a polyester-acrylate photoresist exposed to the UV emission of an Ar-ion laser

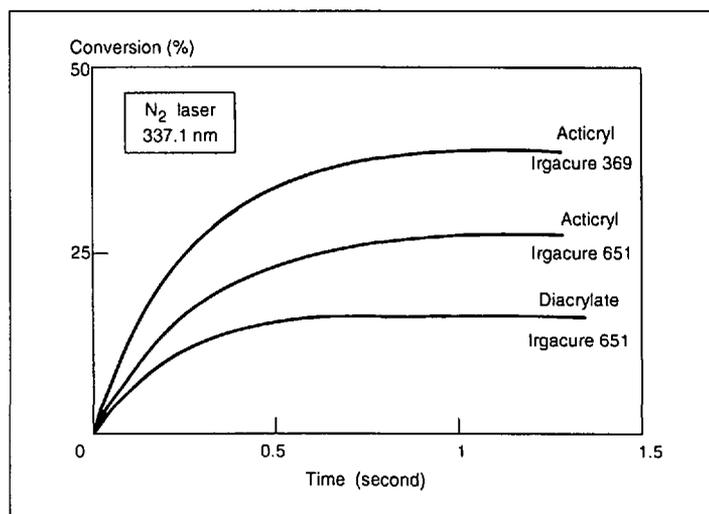


Fig. 8. Post-polymerization profiles recorded by RTIR photo-spectroscopy after pulsed-laser irradiation of a polyurethane-acrylate photoresist, in an inert atmosphere. Pulse duration: 8 ns; Pulse energy: 5 mJ.

The efficiency of this method of photostabilization was best demonstrated in the case of poly(vinyl chloride), a polymer well known for its poor resistance to photodegradation [9]. A well-stabilized commercial PVC glass was found to become colored and brittle after as little as 500 h of accelerated QUV weathering. By simply coating the PVC plate with a 50- $\mu\text{m}$  thick UV-cured film containing some photostabilizers (*Tinuvin 900 + Tinuvin 292* from *Ciba*), the light-fastness was drastically improved, as shown by *Fig. 6*. A similar stabilizing effect was observed by exposing coated clear or pigmented PVC samples in a Weather Ometer for up to 10000 h, or outdoor for several years. This technology was also used to renovate photodegraded PVC materials, first by removing the colored top layer by sanding, and then by applying a UV-cured coating to recover the initial transparency [10]. Other polymer materials have been treated by UV-cured coatings or lacquers in order to increase their resistance to weathering or to chemicals, the best results being ob-

tained with objects made of wood or composite materials [11].

### Laser-Induced Curing

In the continuous search for faster cure rates, one would naturally conclude that lasers should be the ultimate light source that would provide quasi-instant polymerization. Laser-induced radical production offers some remarkable advantages over conventional UV-initiation, that result mainly from the large power output available, the great penetration in organic materials, the narrow bandwidth of the emission and the spatial coherence of the laser beam which can be finely focused.

### Kinetics of Laser Curing

Multifunctional acrylate monomers have been shown to polymerize after a few millisecond exposure to an Ar-ion [12][13] or krypton-ion laser [14] tuned to their continuous emission in the UV range, with formation of a totally insoluble polymer.

*Fig. 7* shows some typical profiles obtained by plotting the normalized thickness of the insoluble polymer against the duration of the laser exposure, in a semi-log scale, for a polyester-acrylate containing 1% *Irgacure 369*. The choice of the photoinitiator is crucial in laser-induced curing since, for optimum efficiency, it is necessary to achieve the best overlap between the PI absorption spectrum and the selected emission line of the laser.

From the insolubilisation profiles of *Fig. 7*, the two important kinetic parameters of a photoresist can be directly evaluated: the sensitivity (*S*), by extrapolation of the straight line to 100% insolubilisation, and the contrast ( $\gamma$ ) from the slope of the linear portion of the curve. With the best-performing system, sensitivity values as low as 0.1  $\text{mJ cm}^{-2}$  have been measured in  $\text{O}_2$ -free media, with formation after solvent development of a sharp relief image having a good contrast ( $\gamma > 3$ ). This negative-working photoresist appears to be well suited for laser direct imaging (LDI) applications, as it would allow writ-

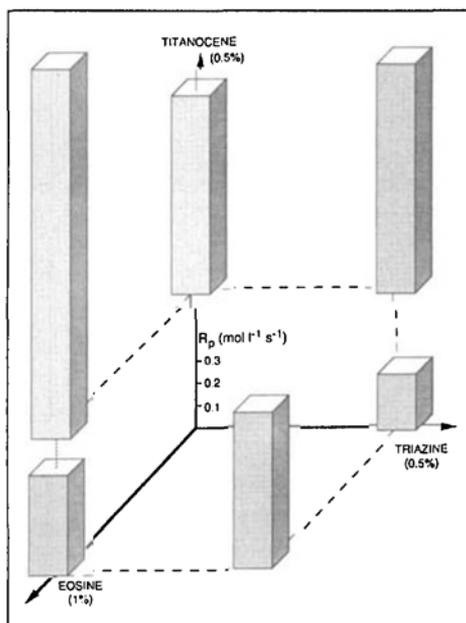


Fig. 9. Influence of the photoinitiator on the rate of polymerization of a polyester-acrylate photoresist exposed to visible radiation in the presence of carbon tetrabromide (1%). Light intensity:  $16 \text{ mW} \cdot \text{cm}^{-2}$ . Atmosphere: air.

ing speeds on the order of 1000 m/s to be reached with a 50-mW focused laser beam.

#### Pulsed Laser Curing

Earlier work has shown that multiacrylate resins can also be cured by means of pulsed lasers emitting an intense flash of UV radiation during a few nanoseconds [15]. Since this is about the time needed to generate the initiating radicals, the polymerization observed under those conditions will develop exclusively in the dark. Consequently, the polymerization profiles recorded by RTIR photospectroscopy (Fig. 8) will accurately reflect the rate at which the polymer chains are actually growing, a quantity which depends primarily on the propagation rate constant ( $k_p$ ), on the number of initiating radicals ( $R^*$ ) generated by the laser flash and on the monomer concentration  $[M]$ :

$$R_p = k_p [R^*] [M]$$

Pulsed-laser irradiation appears thus as a convenient method to compare the reactivity of different UV-curable resins, and assess rapidly the efficiency of new photoinitiators and new monomers.

#### Curing with Visible Lasers

Multiacrylate monomers can also be cured by using visible radiation, but at a much smaller rate than with UV radiation, due to the lower efficiency of visible-type photoinitiators [16]. Fast curing can still be achieved by means of an Ar-ion laser tuned to its emission lines at 488 or 514 nm, thanks to the large power output available. Promising results have been recently obtained by combining different types of visible PI (eosine, a fluorinated diaryli-

tanocene and a chloromethyl substituted triazine), which show some synergistic effect in the presence of small amounts of carbon tetrabromide (Fig. 9). With the eosine + triazine combination, the photoresist sensitivity was found to be similar to that of conventional photoinitiators. Deep through-cure of thick samples was readily achieved, due to the great penetration of the laser beam and to the fast bleaching of the photoinitiator system.

#### Applications of Laser-Induced Curing

Laser-cured acrylic polymers are highly transparent materials which were found to resist quite well to solvents, chemicals, heat and UV or laser irradiation, owing to their high cross-link density. As a result, these organic glasses are ideally suited for the fabrication of optical components and wave guides of micronic dimension, to be used in optoelectronics [17].

In microlithography, multiacrylate photoresists have been employed to generate by laser direct imaging the high-resolution relief patterns needed for the production of printing plates, printed circuits boards or integrated circuits [18]. Another field of application of laser-curing is in stereolithography, where complex 3-D solid objects are created by photopolymerization of successive layers of a liquid acrylic resin, by means of a computer-ordered laser beam [19]. The same kind of resin has been recently used to produce large dimension holograms by a dry process requiring no further treatment after the laser exposure [20].

Laser-induced curing appears thus as a promising new technology which shows a great potential of future growth, due to the distinct advantages of these powerful sources of coherent light, mainly large cure rates, high imaging resolution and great penetration in organic materials.

#### Conclusion

In this article, it has been shown that the curing of multifunctional monomers can be achieved quasi-instantly by UV or laser irradiation to generate tridimensional polymer networks with tailor-made properties. A novel technique, real-time IR photo-spectroscopy, was developed in order to monitor continuously such ultrafast reactions, and evaluate *in situ* the important kinetic parameters, thus allowing the reactivity of photocurable resins to be assessed quantitatively. Significant progress has been achieved in radiation curing chemistry with the appearance of new highly efficient photoinitiators and acrylic monomers that provide fast and complete cure, while improving at the

same time the overall performance of the cross-linked polymer.

Radiation curing has now become a field of recognized importance in various industrial sectors, due to its distinct advantages regarding both process facility and product quality. Particularly impressive is the surface protection achieved by UV-curable coatings which increase markedly the durability of organic materials, as well as their surface characteristics. Laser-induced curing of multifunctional monomers also offers a great potential for specific end-uses requiring ultrafast cure and high-definition patterning. The future of this advanced technology lies in the hands of the polymer chemist and its ability to create materials with well-designed properties providing new opportunities of industrial applications.

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