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PHOTOINITIATED CROSSLINKING POLYMERISATION

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1. INTRODUCTION

Highly crosslinked polymers are readily synthesised by photoinitiated polymerisation of multifunctional monomers and telechelic polymers. The main advantage of using UV radiation to initiate the chain reaction lies in the very high polymerisation rates that can be reached under intense illumination, so that the liquid to solid phase change takes place within a fraction of a second. Another distinct feature of light-induced reactions is that the polymerisation will occur only in the illuminated areas, thus allowing complex relief patterns to be produced after solvent development.

The photoinitiated polymerisation of multifunctional monomers, or UV-radiation curing, has found a large number of applications in various industrial sectors. This technology is now commonly utilised to perform the ultrafast drying of protective coatings, varnishes, printing inks and adhesives, and to produce the high-definition images required in the manufacture of microcircuits and printing plates. Besides its great speed and spatial resolution, radiation curing presents a number of other advantages, in particular ambient temperature operation, solvent-free formulations, low energy consumption and the production of polymer materials having tailor-made properties.

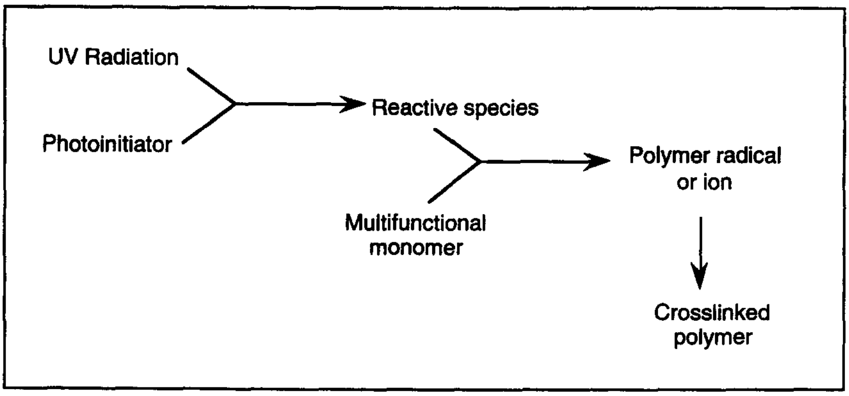
Most of the research efforts devoted to photocuring have been centred on the development of very efficient photoinitiators and of highly reactive monomers and telechelic oligomers or polymers. The subject has been extensively covered in several textbooks and comprehensive review articles.[1–14] A large variety of high performance compounds are now commercially available,[15–18] thus allowing the polymer chemist to design a formulation that will meet the cure speed and product property specifications required for the considered application. Acrylate-based resins, which polymerise by a radical mechanism, have been thoroughly investigated as they are by far the most widely used UV-curable systems, because of their great reactivity. Photoinitiated cationic polymerisation, mainly of epoxides and vinyl ethers, has recently experienced a renewed interest for some specific applications, in consideration of its distinct features, namely its insensitivity toward oxygen and its living character providing a substantial dark polymerisation.

The kinetics of photoinitiated crosslinking polymerisation has been extensively studied over the years,[19–29] mainly by calorimetric analysis, a technique which is hampered by its poor time resolution (a few seconds) and thus requires operation at low light intensities for real-time monitoring. This explains why only a few kinetic studies have been reported on photocuring reactions performed under conditions similar to those commonly found in industrial applications, namely thin films exposed to intense UV radiation in the presence of air.[30–35]

In this review article, the progress recently made regarding the kinetics of ultrafast photocuring processes will first be outlined, with special emphasis being given to the evaluation of the important kinetic parameters that govern the chain reaction (quantum yields and rate constants). The performance of some newly developed photoinitiators and monomers will then be discussed in terms of efficiency, reactivity, polymerisation mechanism and properties of the cured polymer. Various novel systems based on this advanced technology will also be described, such as hybrid resins, which undergo simultaneously radical and cationic polymerisation to produce quasi-instantly interpenetrating polymer networks, and photocrosslinking of functionalised polymers in the solid state. The main characteristics of laser-curable photoresists will finally be discussed, in consideration of the growing use of such systems for specific applications, such as stereolithography, holography and laser direct imaging. Throughout this review, special attention will be given to the basic chemistry involved in photo-crosslinking polymerisation, because the final properties of the UV-cured polymers will depend primarily on a good understanding and control of the manifold reactions occurring during such ultrafast molecule to material transformations.

2. BASIC PRINCIPLES

UV curing is typically a process that transforms a multifunctional monomer into a crosslinked polymer by a chain reaction initiated by reactive species (free radicals or ions), which are generated by UV irradiation. Most monomers do not produce initiating species with sufficiently high yields when they are exposed to UV light, so that a photoinitiator must be added to the formulation. Once initiated, the chain reaction will develop very much like in a conventional thermal polymerisation, except for the much larger rates of initiation that can be reached by intense illumination. The overall process can be represented schematically as follows



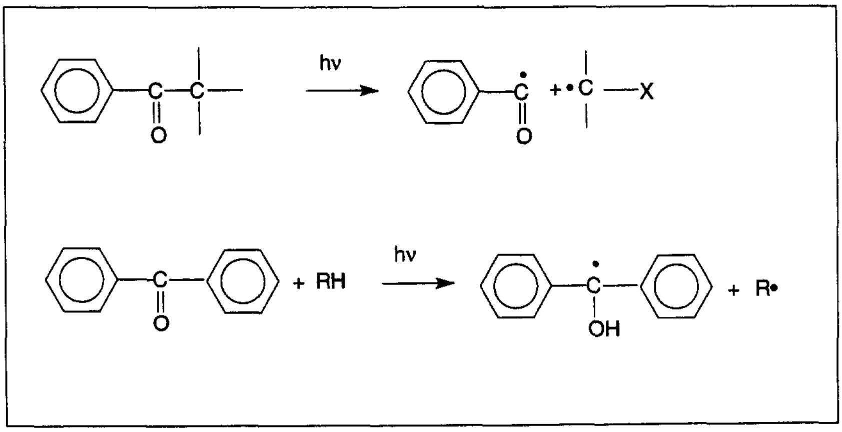
There are two major classes of UV-curable resins, which differ basically by their polymerisation mechanism:

photoinitiated radical polymerisation of multifunctional monomers, mainly acrylates or unsaturated polyesters;
photoinitiated cationic polymerisation of multifunctional epoxides and vinyl ethers.

The various types of photoinitiators and monomers currently employed in UV-curing applications will now be described briefly.

2.1. *Photoinitiated radical polymerisation*

Free radicals are readily produced upon UV irradiation of aromatic carbonyl compounds, either by homolytic cleavage of C–C bonds, or by hydrogen abstraction from a H-donor molecule



The benzoyl radical was shown to be the major initiating species, while the other radical fragment may also contribute to the initiation.[36] The ketyl radical generated upon photolysis of benzophenone is essentially inactive toward vinyl double bonds, so that initiation occurs here through the H-donor radical, usually an α-amino alkyl radical, since tertiary amines are typically employed as co-initiators.

An efficient photoinitiator must exhibit a large absorption in the emission range of the light source and generate initiating species with the highest possible quantum yields. A great number of photoinitiators have been developed for UV-curing applications. Their photolysis mechanisms and performances have been extensively studied,[36–42] and have been recently reviewed in an excellent textbook.[15] Typical examples of radical-type photoinitiators are given in Fig. 1.

There are three main classes of UV-curable resins that polymerise by a radical mechanism.

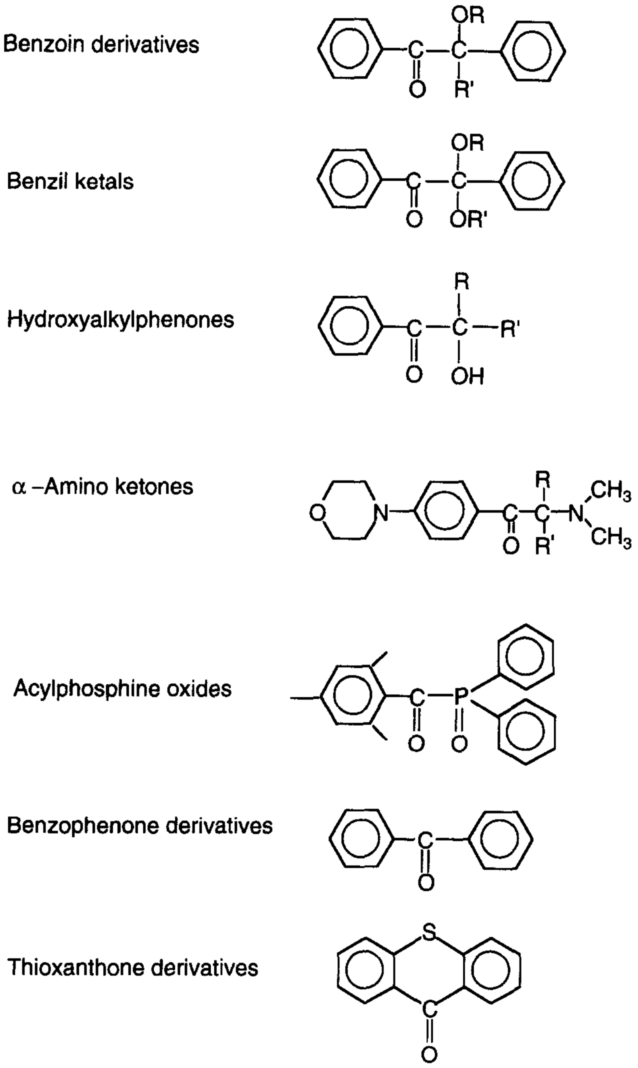
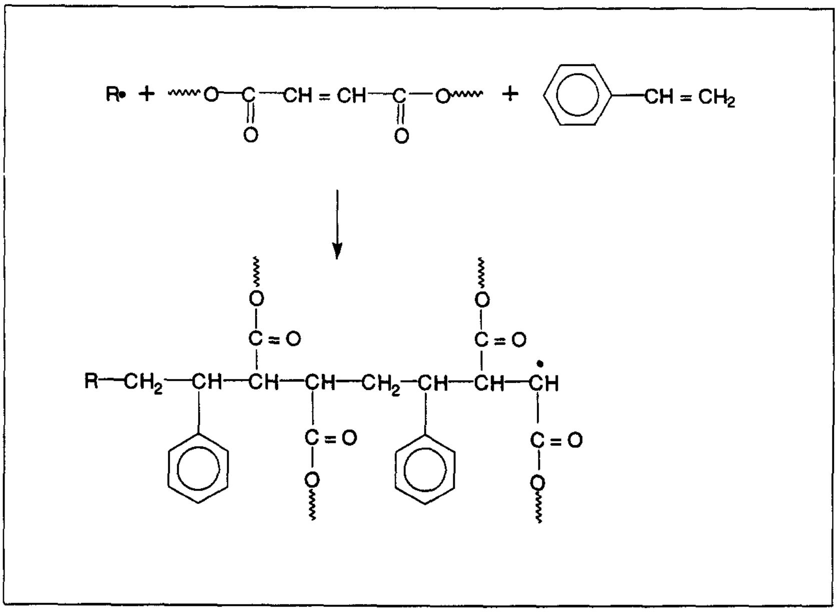


Fig. 1. Different types of radical photoinitiators used in UV-radiation curing.

2.1.1. *Unsaturated polyester/styrene*

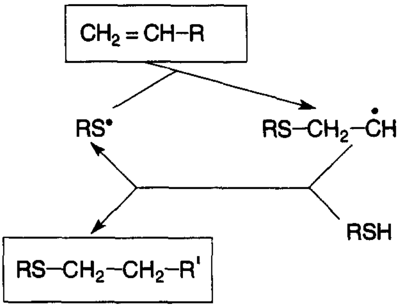
One of the first UV-curable resins to be used in large scale applications consisted of a mixture of styrene and an unsaturated polyester containing fumaric or maleic structures.[43,44] When exposed to UV radiation in the presence of a radical photoinitiator (PI), this system undergoes a direct addition copolymerisation with the formation of an insoluble crosslinked polymer.



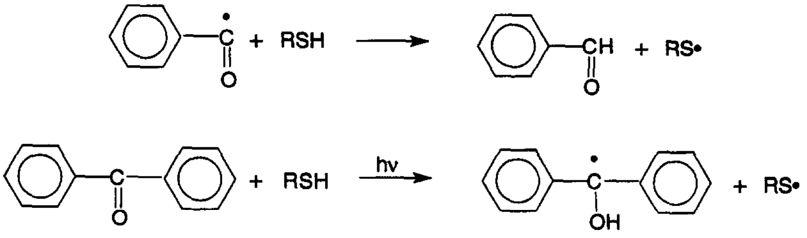
Although this system shows inferior performance compared to acrylic resins, in terms of cure speed and product properties, it is still widely used, mainly in the wood finishing industry, because of its low cost.

2.1.2. *Thiol-polyene*

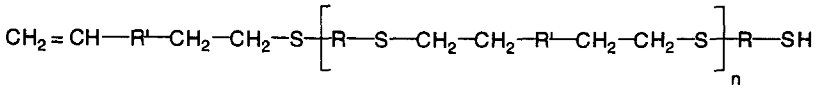
The thiol-ene polymerisation proceeds by a step growth addition reaction that is initiated and propagated by the thiyl radical (RS·) through an efficient chain transfer process.[45]



The thiyl radical can be readily generated by UV radiation of a thiol in the presence of either one of the two types of radical photoinitiators.



A chain reaction will develop only if both the thiol and the olefinic compound contain at least two reactive functions, e.g. a diene plus a dithiol:

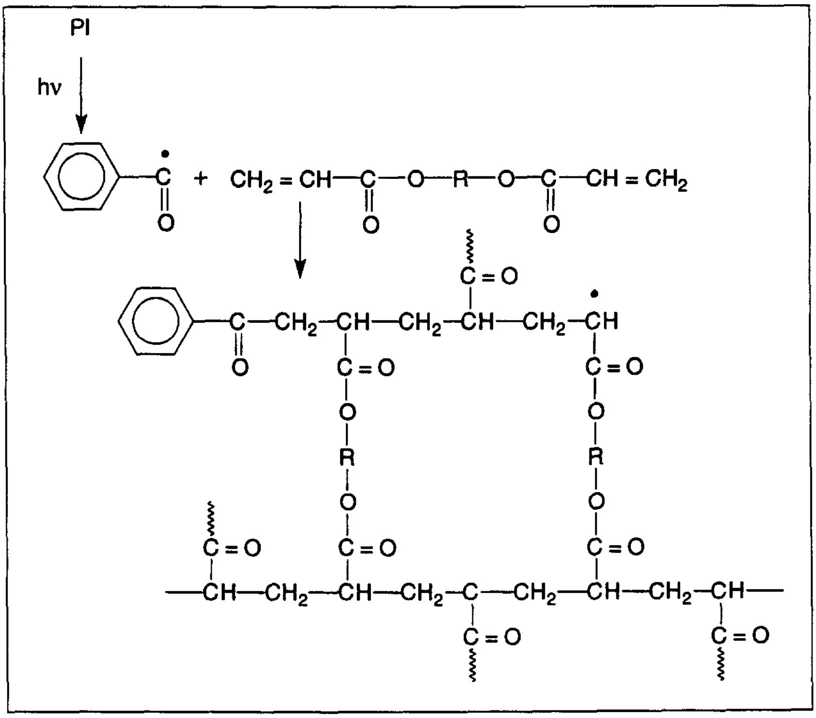


$$CH_2=CH-R'-CH_2-CH_2-S-\left[R-S-CH_2-CH_2-R'-CH_2-CH_2-S\right]_n-R-SH$$

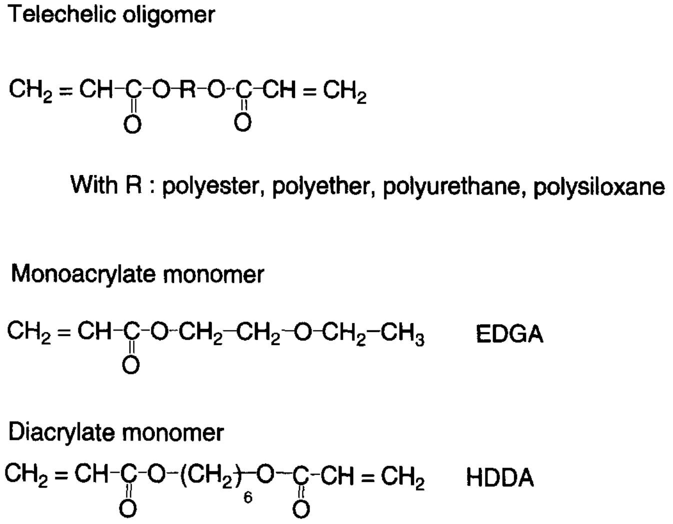
Crosslinked polymers will be formed by combination either of a polyene with a dithiol, or of a diene with a polythiol, such as $C(RSH)_4$. The thiol-ene system has been used in a number of specific UV-curing applications, mainly as protective coatings, adhesives and photoresists.[46–48] The main limitations to its industrial development lie in its relatively high cost and the unpleasant odour of sulfur-containing products.

2.1.3. *Acrylate monomers*

Acrylates are known to be among the most reactive monomers polymerising by a free-radical mechanism. This feature, together with the remarkable chemical, optical and mechanical properties of the polymers obtained, account for the great commercial success of acrylate-based UV-curable resins. It also explains why the photoinitiated polymerisation of multifunctional acrylate monomers and oligomers has been so thoroughly investigated, mainly from the kinetic and mechanistic points of view.[9,10,22,30,32,33,35,49–55] For a diacrylate monomer irradiated in the presence of a photocleavable aromatic ketone, the basic process can be represented as shown in Scheme. 1.



Scheme 1. Photoinitiated crosslinking polymerisation of a diacrylate monomer.



$$CH_2=CH-\underset{\underset{O}{\|}}{C}-O-R-O-\underset{\underset{O}{\|}}{C}-CH=CH_2$$

$$CH_2=CH-\underset{\underset{O}{\|}}{C}-O-CH_2-CH_2-O-CH_2-CH_3$$

$$CH_2=CH-\underset{\underset{O}{\|}}{C}-O-(CH_2)_6-O-\underset{\underset{O}{\|}}{C}-CH=CH_2$$

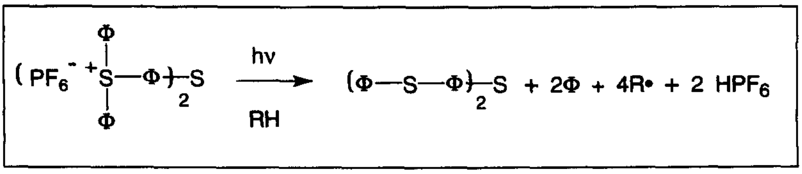
Fig. 2. Different types of acrylate compounds used in UV-curable resins.

Different types of structures (R) can be used for the telechelic polymer or oligomer backbone, such as polyurethanes, polyesters, polyethers and polysiloxanes (Fig. 2). The final properties of UV-cured acrylate polymers depend primarly on the chemical structure of the functionalised oligomer. Low-modulus elastomers are generally obtained with aliphatic compounds, whereas hard and glassy materials are formed when aromatic stuctures are introduced into the polymer chain.

The great reactivity of acrylate monomers, together with the large choice of acrylate-functionalised oligomers, have afforded these radical-type systems a leading position in UV-curing applications. The high viscosity of the prepolymers often necessitates the addition of low molecular weight monomers, which will act as reactive diluents (Fig. 2). Because of their high crosslink densities, such photocured polymers exhibit a great resistance to chemicals, heat and radiation, and show well-designed physical properties depending on the length and chemical structure of the crosslink segments.

2.2. *Photoinitiated cationic polymerisation*

Protonic acids are readily generated by photolysis of onium salts in the presence of a hydrogen donor molecule.[8,16,23,26,56,57] The most efficient photoinitiators contain diaryliodonium or triarylsulfonium cations and fluorinated anions, such as BF_4^-, PF_6^-, AsF_6^- or SbF_6^-. The photolysis reaction, which produces both Brönsted acids and free radicals, can be formally written as follows for sulfonium salts:



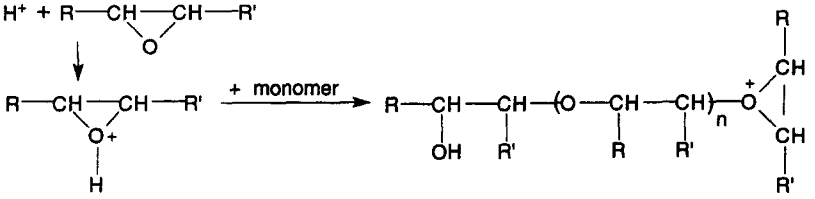
$$(PF_6^-\;{}^+\underset{\Phi}{\underset{|}{\overset{\Phi}{\overset{|}{S}}}}-\Phi)_2\!-S \xrightarrow[RH]{h\nu} (\Phi-S-\Phi)_2\!-S + 2\Phi + 4R^\bullet + 2\,HPF_6$$

The two distinct features of photoinitiated cationic polymerisation are its lack of sensitivity toward atmospheric oxygen and its living character, due to the fact that the propagating polymer cations are not reacting among themselves. By contrast to radical-initiated polymerisation, the chain reaction will continue to proceed effectively after UV exposure.[58]

Photoinitiated cationic polymerisation is being increasingly used to cure multifunctional monomers that are inactive towards radical species, in particular epoxides and vinyl ethers. UV-curable hybrid systems, made of a mixture of monomers that polymerise by different mechanisms, offer a promising route to the ultrafast production of interpenetrating polymer networks.

2.2.1. *Epoxides*

The ring-opening polymerisation of epoxides proceeds efficiently in the presence of a photogenerated protonic acid, with oxonium ions as the reactive species, to ultimately produce a polyether.[8,23,58–62]



With difunctional epoxides, the chain reaction develops in three dimensions to form a tightly crosslinked polymer, as shown in Fig. 3 for a typical aliphatic dicycloepoxide. Termination occurs by chain transfer to give inactive species, or by reaction with nucleophilic impurities, in particular, traces of water. The rate of polymerisation of difunctional epoxides is one order of magnitude lower than that of diacrylate monomers, most probably because of a lower propagation rate constant.[63]

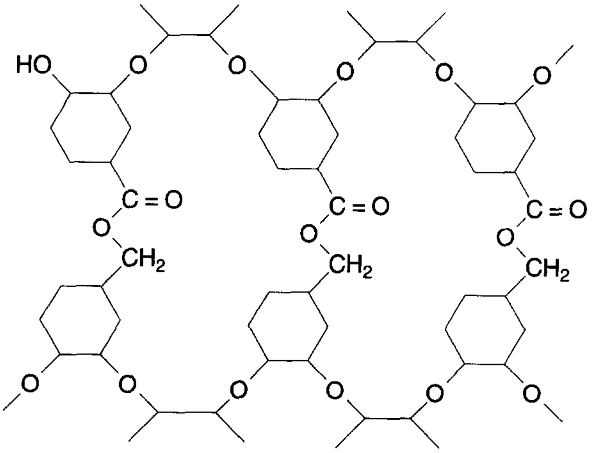


Fig. 3. Structure of the polymer network obtained upon UV curing of a dicycloaliphatic epoxide.

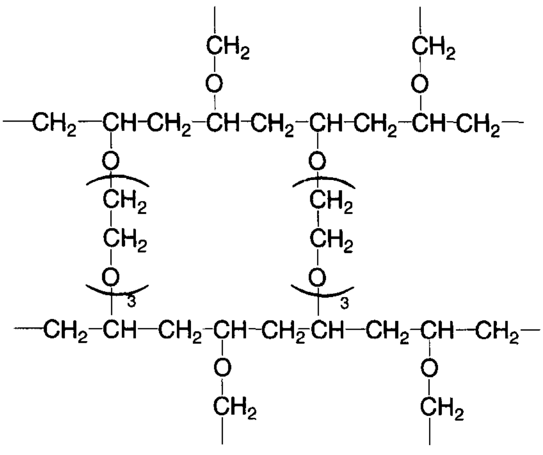
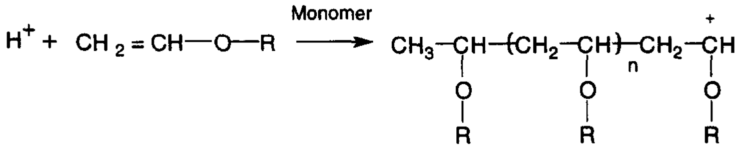


Fig. 4. Structure of a polymer network obtained upon UV curing of the divinyl ether of triethyleneglycol (DVE-3).

2.2.2. *Vinyl ethers*

Vinyl ethers (VE) do not homopolymerise in the presence of free-radical initiators because of their electron-rich double bonds, but they do undergo a very fast cationic polymerisation in the presence of protonic acids:



$$H^+ + CH_2{=}CH{-}O{-}R \xrightarrow{\text{Monomer}} CH_3{-}\underset{\underset{R}{|}}{\underset{O}{|}}{CH}{-}(CH_2{-}\underset{\underset{R}{|}}{\underset{O}{|}}{CH})_n{-}CH_2{-}\underset{\underset{R}{|}}{\underset{O}{|}}{\overset{+}{C}H}$$

Three-dimensional polymer networks are created by UV irradiation of VE-terminated telechelic oligomers containing typically ether (Fig. 4), ester, urethane or siloxane structures. The performances of vinyl ethers in UV-curable resins have been thoroughly evaluated[64–69] and the subject has been recently covered in a comprehensive review.[70] Vinyl ethers offer the advantage of undergoing a fast and complete polymerisation to yield polymer materials showing excellent solvent resistance and tailor-made properties, depending on the chemical structure of the crosslinking segments.

2.2.3. *Hybrid systems*

By taking monomers that polymerise by different mechanisms, e.g. radically for the acrylate and cationically for the vinyl ether, two interpenetrating polymer networks (IPN) having contrasting properties can be produced within a few seconds under intense illumination.[64,68] Besides the vinyl ether/acrylate combination,[67,71,72] different types of UV-curable hybrid systems have been developed in recent years, in particular vinyl ether/epoxide,[65,73] vinyl ether/unsaturated ester [68,74–76] epoxide/acrylate[73,77,78] (for a review, see Ref. 79). It should be mentioned that in some systems, like the vinyl ether/

acrylate mixture, copolymerisation can occur, thus leading to a chemical bonding of the two networks. The major advantage of hybrid systems lies in their superior combination of properties, which can be achieved by selecting properly the two components and by adjusting their relative proportions.

2.3. *Applications of UV-curable systems*

Photocuring technology has found major applications in various industrial sectors where it has outclassed other processing techniques because of its distinct advantages, namely an ultrafast polymerisation of solvent-free formulations occurring selectively in the illuminated areas. Its most successful applications are in the graphic arts,[80] where UV curing is used both in the pre-press part of the operation to produce printing plates,[81] as well as in the printing process itself where the use of fast-drying UV-curable inks has provided a substantial increase in the line speed. It intervenes also in the last step when an overprint varnish is to be applied in order to obtain a high quality glossy image. The UV technology offers an alternate compliance strategy to the problem of volatile organic compounds, while it reduces at the same time the total energy consumption of the process.

UV-curable varnishes are commonly used to obtain highly resistant coatings, well-suited for protecting essentially any substrate: wood, plastics, metals, glass, optical fibers, leather, paper, fabrics, etc.[80] The viscoelastic properties of the cured coating must be specially designed to fit the characteristics of the substrate. Hard and scratch resistant coatings based on aromatic polyethers and polyesters are used for the surface protection of rigid substrates, such as metals or organic glasses, whereas low-modulus polyurethane elastomers showing a good abrasion and impact resistance are needed to protect flexible supports.

In the field of adhesives, radiation curing has found two main sectors of applications: (i) to bond together two pieces of an assembly (laminate), thus acting as a quick-setting glue,[82] and (ii) to produce pressure sensitive adhesives and release coatings.[83,84] The reasons for using photoinitiation, rather than a thermal treatment of solvent-based adhesives are essentially the same as for the other UV-curable systems, and include pollution control, economic gains and enhanced performance.

In microelectronics, UV-curable resins serve not only as photoresists in the imaging step, but also as fast-drying adhesives, sealants and protective coatings.[10] Conventional exposure tools require the fabrication of patterns on glass or film photomasks that will serve in the manufacture of printed circuit boards or integrated circuits by a photolithographic process.[9] Alternatively, a computer controlled scanning laser can be used to define a pattern directly on the photosensitive film.[85,86] This maskless technology, laser direct imaging, offers a means to produce boards with finer geometries and fewer defects at higher yields.[87]

Other promising applications of photo- and laser-induced polymerisation include the creation of 3D solid objects by laser stereolithography,[88] the recording of holograms by a development-free process,[89] the production of optical guides of micronic dimensions,[90,91] the ultrafast curing of dental composites [92] or reinforced plastics,[93] and the manufacture of optical discs [94] and aspherical lenses.[95] The main areas of today's end uses of UV-radiation curing are summarised in Table 1.

Table 1. Current applications of UV-curable systems

Graphic arts	Printing inks
	Overprint varnishes
	Printing plates
Coatings	Wood finishing
	Floor covering
	Organic glasses
	Metals
	Leather, fabrics
	Optical fibers
Electronics	Printed circuits
	Patterning (video disk)
	Sealants (encapsulation)
	Conformal coatings
Adhesives	Pressure sensitive adhesives
	Glass laminates
	Release coatings
	Quick-setting glues
Miscellaneous	Hologram recording media
	Optical wave guides
	Stereolithography
	Dental composite materials

3. POLYMERISATION KINETICS

3.1. *Basic processes*

The bulk polymerisation of multifunctional monomers is a complex process which exhibits a number of anomalous behaviours with respect to the reaction kinetics:[10,96]

An autodeceleration in the initial stage because of mobility restrictions of the radical species in the polymer network under formation. This will affect mainly the termination step which will become diffusion controlled, thus leading to an increase in the radical concentration and hence in the polymerisation rate.

An autodeceleration, generally observed in the later stage when the propagation reaction also becomes diffusion controlled. The decreased mobility of the propagating radical and of the functional groups leads to a slowing down of the polymerisation, which ultimately stops before completion due to vitrification. The UV-cured polymer will therefore contain a certain number of functional groups that have not polymerised, as well as trapped radicals.[24,97,98]

A termination process controlled by reaction diffusion,[99,100] and not by segmental diffusion as in linear polymerisation. In crosslinking polymerisation, most polymeric radicals are bound to the 3D network and have a limited mobility so that the radical site will move mainly by reacting with neighbouring functional groups until it combines with another radical. When these conditions are reached, the termination rate constant becomes proportional to the propagation rate constant.

The formation of structural heterogeneities, which leads to microgels.[101] They are resulting from the fast polymerisation of the pendent double bonds which are in large concentrations in the vicinity of the radical site.[10] Kinetic gelation models have shown

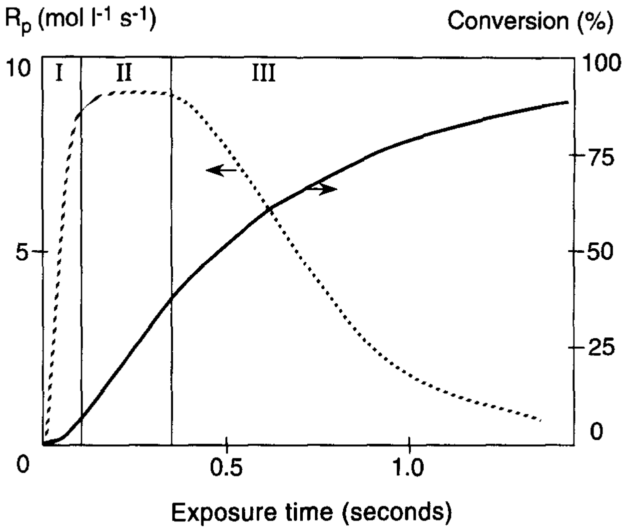


Fig. 5. Conversion-versus-time profile recorded by RTIR spectroscopy upon UV curing of a polyurethane acrylate. Dashed line: rate profile. Light intensity: 30 mW cm^{-2}.

the effects of the reaction behaviour on the network microstructure and on the material properties.[102]

The physical effect of volume shrinkage on the polymerisation kinetics, which leads to higher final degrees of conversion at large reaction rates.[98] At the high initiation rate provided by UV irradiation, the polymerising system cannot maintain its volume equilibrum, as volume shrinkage occurs in a much longer timescale than the chemical reaction. The time lag between conversion and shrinkage generates a temporary excess of free volume that increases the mobility of unreacted double bonds, thus allowing higher degrees of conversion to be reached than in volume equilibrium systems.[10]

3.2. *Kinetic profiles*

The three stages of the curing process can be recognised on a kinetic profile such as that represented in Fig. 5. It shows a typical conversion versus time curve recorded by real-time infrared (RTIR) spectroscopy for a photocurable polyurethane-acrylate resin exposed to the UV radiation from a medium pressure mercury lamp in the absence of air. The method used to study the kinetics of such ultrafast polymerisation reactions has already been described.[103,104] The sample was exposed simultaneously to the UV beam, which induces the polymerisation, and to the analysing IR beam, which monitors continuously the drop of the absorbance of the reactive group. The spectrophotometer was operated in the absorbance mode, and the detection wavelength set at 812 cm^{-1} where acrylate monomers show a distinct and sharp peak ($CH_2 = CH$ twisting). Because the IR absorbance is proportional to the monomer concentration, conversion (τ) versus time profiles are then directly displayed on the PC screen.

The three steps of the curing process become more apparent when the rate of polymerisation (R_p) is plotted as a function of the exposure time (Fig. 5). The value of R_p is easily

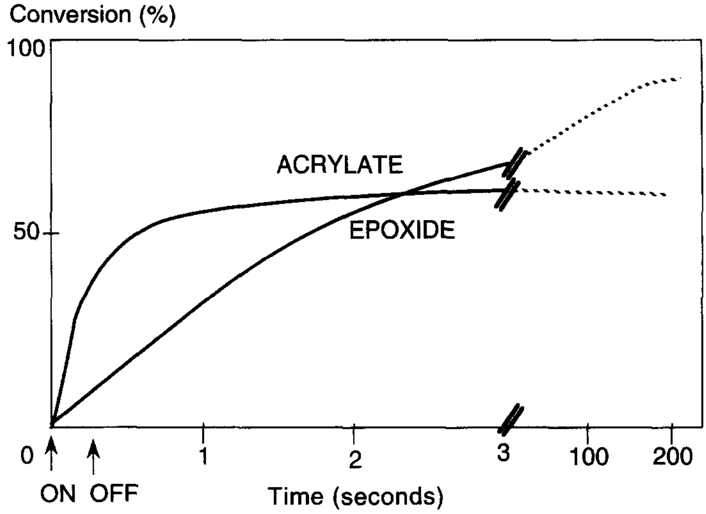


Fig. 6. Polymerisation profiles of a polyurethane-acrylate and of an epoxidised rubber exposed to intense UV radiation during 100 and 300 ms, respectively. Light intensity: 400 mW cm^{-2}.

calculated at any time from the slope of the RTIR curve ($d\tau/dt$) and the initial acrylate double bond concentration $[A]_0$:

$$R_p = [A]_0 \times (d\tau/dt)$$

Autoacceleration occurs at the very beginning of the irradiation because of the rapid increase in viscosity until about 5% conversion when the reaction reaches its maximum value $(R_p)_{max}$. It is followed by a period where the polymerisation develops at a sustained pace during 0.3 s (about 30% conversion), the time after which autodeceleration starts to take place when propagation becomes diffusion controlled. Ultimately, vitrification leads to a complete stop of the curing process at about 90% conversion. There remains in the crosslinked polymer a certain amount of unreacted acrylate double bonds, which may ultimately affect the longterm properties of the UV-cured material.

3.3. *Post-polymerisation*

RTIR spectroscopy was shown to be a technique particularly well suited to studying the dark polymerisation that occurs just after the UV light has been switched off.[105] While such post-polymerisation is easily detected in photoinitiated cationic polymerisation due its living character,[58] it is more difficult to observe in photoinitiated radical polymerisation because of the fast terminating interactions of the propagating radical species.

Figure 6 shows the polymerisation profiles recorded by RTIR spectroscopy after a short UV exposure of an acrylate and an epoxide-based resin. It can be seen that most of the dark polymerisation develops within the first second, just after the 200 ms exposure, for the acrylate sample, whereas it continues to proceed for several minutes in the case of the epoxy monomer, up to a near total consumption of the oxiranne ring. The relative importance of the post-polymerisation in acrylate resins was shown to increase steadily with decreasing degree of conversion, measured just at the end of the UV irradiation.[106] For very short but intense exposures, as much as 90% of the polymerisation is actually taking place in the dark, a value which reaches 100% for pulsed laser-induced polymerisation.[32]

The initial rate of the dark polymerisation (R'_p) is directly related to the concentration of radicals $[P\cdot]$ which are present at the end of the UV exposure:

$$R'_p = k_p[M]_t[P\cdot]$$

where $[M]_t$ is the concentration of acrylic double bonds that have not polymerised after irradiation time t. As the propagation rate constant k_p of these acrylic monomers was shown to remain essentially constant for degrees of conversion up to 30%,[107] the radical concentration can be evaluated from the ratio $R'_p/[M]_t$. This ratio was found to increase rapidly with irradiation time and to level off to a constant value after about 30 ms in O_2-free systems[106] and 70 ms in the presence of air.[53] The radicals are then expected to have reached their stationary concentrations ($d[P\cdot]/dt = 0$), where the rate of termination equals the rate of initiation.

3.4. *Kinetic chain length*

Because the polymerisation of multifunctional monomers leads to highly crosslinked insoluble polymers with infinite molecular weight, it is usually not posible to determine the kinetic chain length (kcl) of the propagation step. One of the distinct advantages of photoinitiation is to afford such an evaluation from quantum yield measurements. The quantum yield of a photochemical reaction is defined as the number of molecules transformed per photon absorbed. In photoinitiated polymerisation, two quantum yields are to be considered:

the initiation quantum yield: $\Phi_i = r_i/I_a$

the polymerisation quantum yield: $\Phi_p = R_p/I_a$where r_i is the rate of initiation, R_p the rate of polymerisation and I_a the absorbed light intensity (in photon $L^{-1}\ s^{-1}$). The kinetic chain length can be evaluated from the ratio R_p/r_i, and thus from the ratio Φ_p/Φ_i. By taking $\Phi_i = 0.4$ radical/photon for the photoinitiator used in this study (dimethoxyphenylacetophenone),[108] kcl values were calculated to be on the order of 2000 and 10,000 acrylate groups polymerised per initiating radical, for air- and nitrogen-saturated systems, respectively.[109]

When taking into account the dark polymerisation that proceeds substantially in the polyurethane-acrylate photoresist tested, the kcl value was found to increase up to 50,000 mol/radical for the O_2-free samples.[109] This very large value clearly demonstrates how effectively the chain reaction can develop in such diacrylate monomers irradiated in bulk, even at large initiation rates ($r_i = \Phi_i I_a = 10^{-3}$ radical $L^{-1}\ s^{-1}$). It is mainly due to a rather inefficient termination process, together with an extensive propagation step (see next section).

3.5. ***Propagation and termination rate constants***

Photoinitiation is a useful process for determining kinetic rate constants of free-radical polymerisations.[110–112] By monitoring the rates of polymerisation during UV exposure and afterwards in the dark, one can evaluate the propagation and termination rate constants (k_p and k_t), two important parameters that control directly the polymerisation process.[22,105]

Under continuous illumination, the rate of polymerisation after a given exposure, $(R_p)_i$, is assumed to obey the following equation, once steady-state conditions are reached:

$$(R_p)_i = \frac{k_p}{(2k_t)^{0.5}}(\Phi_i I_a)^{0.5}[M]_i$$

The ratio $k_p/(2k_t)^{0.5}$ can thus be easily evaluated from measurements of $(R_p)_i$ and of the remaining monomer concentration $[M]_i$, both quantities being determined from the RTIR profile.

Once the light has been switched off, the polymerisation will continue to proceed for some time at a steadily decreasing rate. Under those conditions, the polymer radicals (P·) are expected to disappear by bimolecular reactions, and their concentration will decrease according to a hyperbolic law:

$$-\frac{d[P\cdot]}{dt} = = 2k_t[P\cdot]^2 \text{ or } \frac{1}{[P\cdot]} = 2k_t \times t + \frac{1}{[P\cdot]_i}$$

where $[P\cdot]_i$ is the radical concentration at the end of the exposure. Replacing [P·] by the expression $(R_p)_t/k_p[M]_t$, leads to the following rate equation for the dark reaction:

$$\frac{[M]_t}{(R_p)_t} = \frac{2k_t}{k_p} \times t + \frac{[M]_i}{(R_p)_i}$$

The monomer concentration $[M]_t$ and the rate of polymerisation $(R_p)_t$ after a given exposure and storage in the dark during time t are directly accessible from the RTIR profile recorded after the UV exposure. A plot of the ratio $[M]_t/(R_p)_t$ versus t yields a straight line, which permits one to calculate from its slope the ratio $2k_t/k_p$ and, together with the $k_p/(2k_t)^{0.5}$ ratio, to determine individual values of k_p and k_t.

In the initial stage of polymerisation, the propagation is reaction controlled and the k_p value was found to remain relatively constant, on the order of 10^4 L mol^{-1} s^{-1} for the acrylate system studied.[107] It begins to decrease above 20% conversion once propagation becomes diffusion controlled, due to mobility restrictions. By contrast, termination is initially controlled by radical diffusion so that k_t drops rapidly, down to 10^5 L mol^{-1} s^{-1}, because of the build up of the polymer network.[107] At conversions beyond 20%, k_t was found to be proportional to k_p (Fig. 7), which is a clear indication of a termination mechanism proceeding by reactive diffusion in the photocuring of this polyurethane-acrylate resin. A similar reaction behaviour has been observed for the photopolymerisation of multifunctional methacrylate monomers.[113] When studying photoinitiated crosslinking polymerisation, it is especially important to know the propagation and termination rate constants because their values will not only govern the reaction kinetics but will also effect the overall extent of cure and therefore the final properties of the polymer material produced.

4. NOVEL PHOTOINITIATORS

The photoinitiator (PI) is an integral part of a UV-curable formulation. It plays a key role in so far as it directly affects the polymerisation rate, as well as the cure depth profile. Great

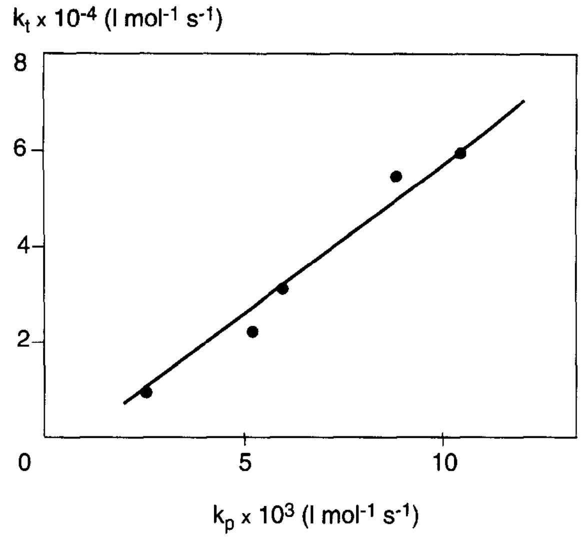


Fig. 7. Linear dependence of the termination rate constant with the propagation rate constant in the photo-initiated crosslinking polymerisation of a polyurethane-acrylate.

progress has been achieved in recent years with the development of ever more efficient photoinitiators, for both radical- and cationic-type polymerisable resins (for a comprehensive review, see Refs 15 and 16). Most of today's research efforts in this area are focused on two important areas:

the development of photoinitiators best suited for the UV curing of pigmented coatings, e.g. printing inks, paints, or lacquers widely used in the graphic arts and the surface protection of materials;

the development of highly sensitive photoinitiators absorbing in the visible range, mainly for imaging and recording applications.

Other related problems of concern have also been recently investigated. These include differential through-cure due to a photoinitiator or pigment screen effect, and the fate of the photoinitiator and its photolysis kinetics. In this respect, it should be mentioned that negative effects due to long-term migrations of residual photoinitiator and other photoproducts can be successfully overcome by the use of copolymerisable photoinitiator systems.[114]

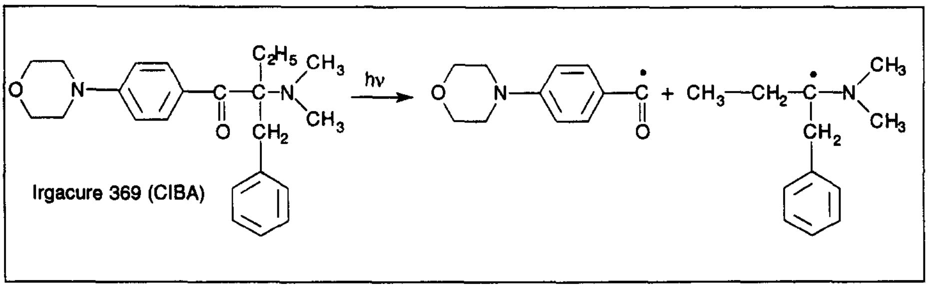
4.1. *Photoinitiators for pigmented systems*

Achieving a fast, deep through-cure in thick pigmented coatings by UV radiation remains one of the greatest challenges in photocuring. Light scattering by the pigment particles will indeed prevent the penetration of photons in the deep-lying layers. An efficient cure can be reached only by working out a good overlap between the absorption spectrum of the photoinitiator (PI), the transmission spectrum of the pigment, and the emission spectrum of the light source.

Among the numerous photoinitiators developed for UV-curable printing inks or lacquers, the best performing ones appear to belong to three major classes of radical-type photoinitiators.

4.1.1. *α-Amino-alkylphenones*

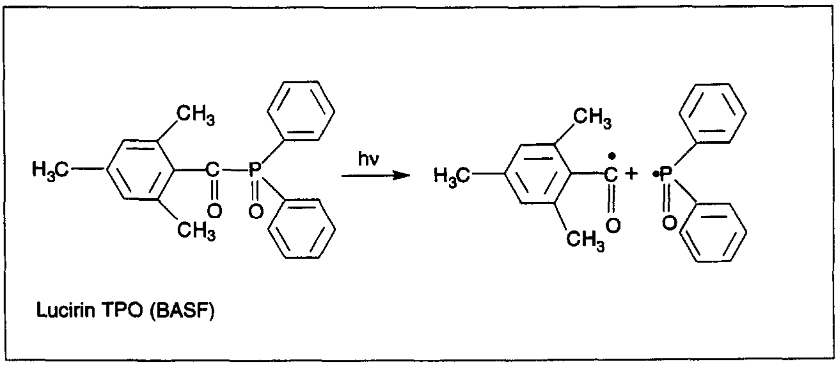
These compounds undergo a rapid photocleavage reaction that generates the highly reactive free radicals needed to initiate the polymerisation process. The greatest cure speeds have been obtained with a morpholino ketone developed by Ciba under the trade name Irgacure 369.[115]



The performance improvement results primarly from an improved absorption of near UV radiation rather than from a higher yield in radical production.[53]

4.1.2. *Acylphosphine oxides*

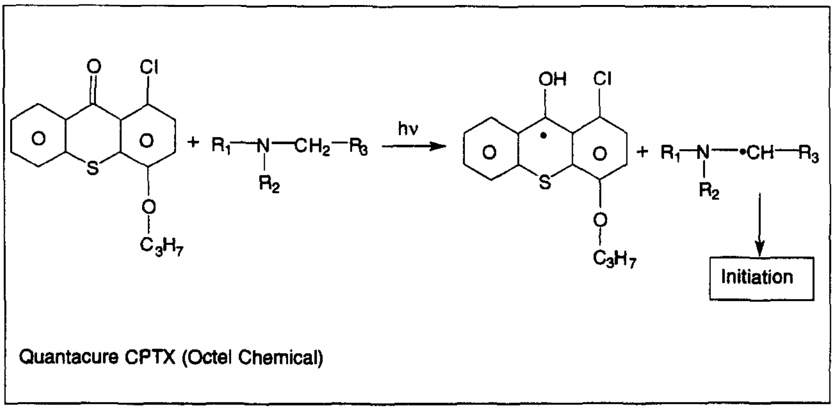
Acylphosphine oxides belong to another class of α-cleavable photoinitiators, that have also proved quite efficient for curing rapidly both clear and pigmented coatings, especially in O_2-free conditions.[116]



Both the benzoyl and the phosphinoyl radicals are reactive[117] and are capable of initiating the polymerisation of acrylates, styrenes, unsaturated polyesters and thiol-polyene systems. Bisacylphosphine oxides (BAPO from Ciba) were found to give superior curing performance in white and coloured UV-curable acrylic lacquers,[118] partly because this photoinitiator can generate up to four free radicals per molecule upon UV exposure.[119]

4.1.3. *Propoxy-substituted thioxanthones*

In the presence of hydrogen donors, such as tertiary amines, the excited states of the 1-chloro-4-isopropoxy-thioxanthone produce very active α-aminoalkyl radicals that will, in turn, initiate the polymerisation of acrylated resins.



Propoxy-substituted thioxanthones can also act as sensitizers, passing on their high triplet energies to a photoinitiator that then produces free radicals. In a blue offset litho ink based on phenoxy acrylates, maximum cure speeds were thus obtained by combining Irgacure 369 with Quantacure CPTX.[120]

The marked increase in the cure speeds provided by these three types of photoinitiators in comparison to a typical hydroxyalkylphenone (Darocur 1173) is illustrated by the polymerisation profiles shown in Fig. 8 for a polyester-acrylate white lacquer. This is due to a larger light absorption in the near-UV range where the mercury lamp has its strongest emission, and where the pigment becomes more transparent. In addition, these

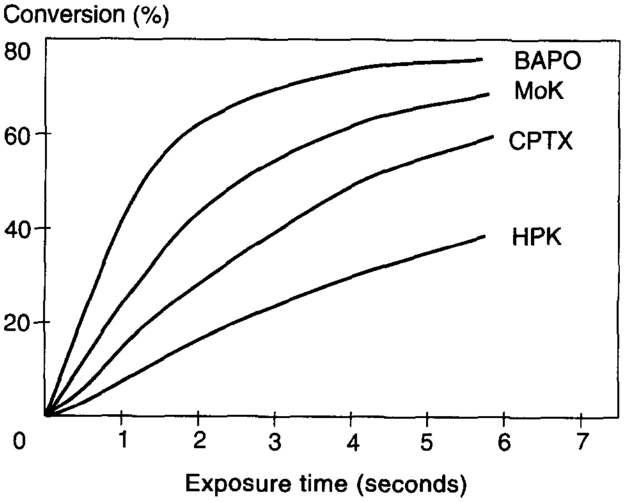


Fig. 8. Influence of the photoinitiator (2%) on the photoinitiated polymerisation of a white polyester-acrylate lacquer. Hydroxyalkylphenone (HPK), chloropropoxythioxanthone (CPTX), morpholino ketone (MoK), bisacylphosphine oxide (BAPO).

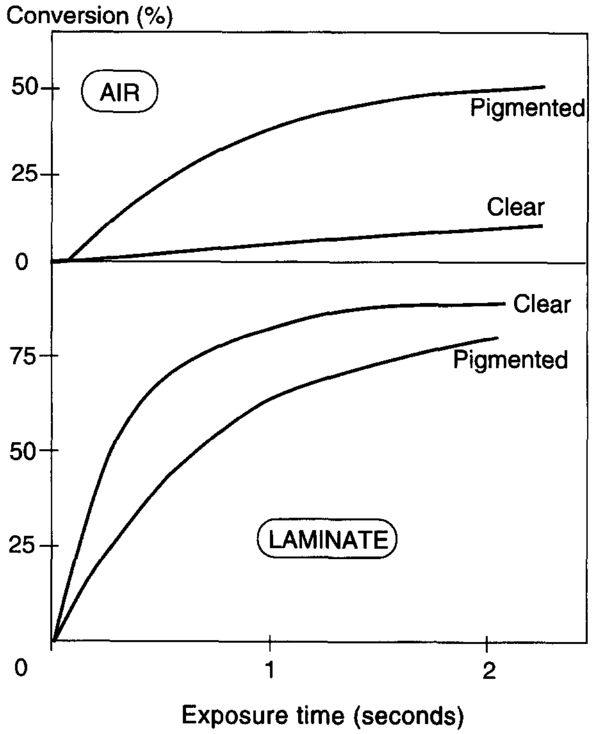


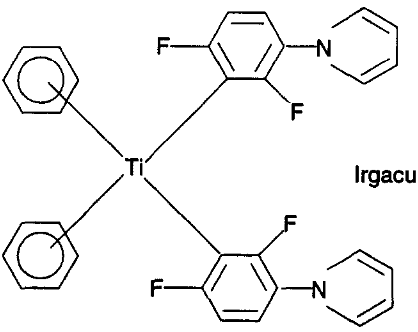
Fig. 9. Conversion versus exposure times for pigmented and clear coatings exposed to air and protected from air (laminate).

photoinitiators undergo a photo-bleaching process, thus allowing UV radiation to penetrate progressively deeper into the sample. Up to 100 μm thick pigmented coatings have thus been photocured within seconds by using either one of these new photoinitiators. In contrast to morpholino ketone and thioxanthone derivatives which yield slightly yellow photoproducts, acylphosphine oxides undergo a fast photolysis that generates non-colored products. By combining BAPO and Darocur 1173, a non-yellowing liquid photoinitiator system has been obtained which has proved to be particularly efficient for curing opaque white lacquers or printing inks.[119]

Oxygen is known to strongly inhibit radical-induced polymerisation by scavenging both the initiating and polymer radicals.[21,121] This effect is particularly pronounced in the UV curing of acrylic coatings and requires intense illumination operations in order to generate an excess of free radicals. For very thin films (< 10 μm), O_2 inhibition was found to be less pronounced in pigmented coatings than in clear coatings,[122] as shown by the polymerisation profiles of Fig. 9. This behaviour can be explained if one considers that the amount of photons absorbed by the highly transparent thin film is too low to produce enough initiating radicals to overcome successfully O_2 inhibition. On the contrary, in the opaque pigmented film most of the incident light is scattered by the pigment particles and will eventually be absorbed by the photoinitiator. A larger amount of free radicals will then be generated and help consume the oxygen dissolved in the resin. An effective way to prevent the diffusion of oxygen into the coating involves covering the sample with a transparent polyethylene film (laminate), as shown in Fig. 9. The screen effect of the pigment on the polymerisation process can thus be quantified. Another solution is to increase the light intensity in order to lower the duration of exposure during which atmospheric oxygen can diffuse into the sample.[121]

4.2. *Visible photoinitiators*

Photopolymerisable systems that can be cured rapidly by visible radiation are required for some specific applications such as direct laser imaging, holography or photopolymerisation colour printing. A large variety of dyes has been tested as initiators or sensitizers,[123] but their industrial use in radiation curing has been restricted so far by their relatively low initiation efficiencies and their poor dark stabilities. High performance visible photoinitiators have been developed in the past few years to overcome these limitations,[15] thus opening new opportunities for visible light curing applications. A fluorinated diaryltitanocene (Irgacure 784 form Ciba) proved to be very effective for initiating the polymerisation of acrylate monomers under visible light exposure.[119] Because of its great photosensitivity and its wide absorption range, up to 500 nm, this photoinitiator is ideally suited for use in the previously-mentioned visible light curing applications, as well as for the curing of UV opaque formulations used in the microelectronic industry and in dental compositions.



Irgacure 784 (CIBA)

Most of the other visible photoinitiator systems consist of an association of a photoreductible organic dye (such as eosin, methylene blue, cyanines, or ketocoumarins) with different types of co-initiators, such as tertiary amines, peroxides, organotin compounds, borate salts, and imidazoles.[15] Synergistic effects can often be observed by combining some of these photoinitiator systems with a chloromethyl substituted triazine,[124] as illustrated by Fig. 10.

The addition of small amounts of carbon tetrabromide was shown to further increase the sensitivity to visible light of such multiacrylate-based photoresists.[86] Deep through-cure of thick samples was readily achieved due to the fast bleaching of the photoinitiator system.

4.3. *Depth of cure*

In contrast to electron beam curing that develops uniformly throughout the irradiated coating, photoinitiated curing follows a surface to depth gradient because of the limited penetration of light in those systems. In a clear formulation, UV radiation is absorbed

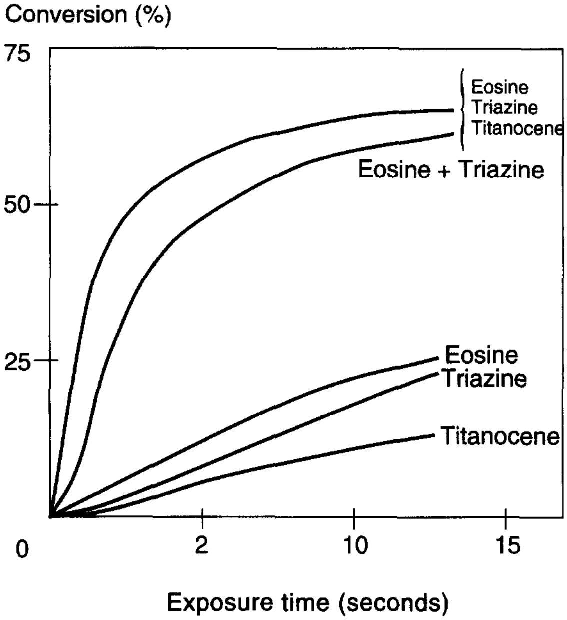


Fig. 10. Influence of the photoinitiator (0.5%) on the polymerisation of a polyester-acrylate resin exposed to visible light. Light intensity: 16 mW cm^{-2}.

mainly by the photoinitiator, so that the cure depth is directly controlled by the PI concentration. For each specific application, the best compromise must be found between cure speed and cure depth, the two extremes being either a uniform but slow deep-through cure for low absorbing coatings, or a rapid but differential through-cure for highly absorbing coatings (at an optical density of 0.5, the bottom layer receives three times less light than the top layer). If the PI photoproducts absorb at shorter wavelengths than the photoinitiator (as it is usually the case) UV radiation can progressively penetrate deeper into clear coats, thus rendering the cure process more uniform.[125] Some photoinitiators (such as phosphine oxides or morpholino ketones) are particularly prone to such photobleaching processes.

The situation is quite different in pigmented coatings where a screen effect leads to a pronounced through-cure differential that persists upon irradiation.[126] This is clearly illustrated by Fig. 11, which shows how the cure distribution profile varies with the exposure time in a 25 μm thick white lacquer film. Here, prolonged irradiation is required in order to obtain sufficient curing at the coating/substrate interface to ensure a good adhesion.

4.4. *Photolysis of the initiator*

Although extensive research efforts have been devoted to the synthesis of photoinitiators and to the understanding of their mechanisms of photolysis, there is scant information about the actual PI disappearance rate during UV-curing operations. This quantity is of prime importance, for it governs the rate of production of initiating species which will in turn determine the rate of polymerisation. A real-time ultraviolet (RTUV) spectroscope was recently used to record the loss profiles of radical and cationic photoinitiators under conditions similar to those used in UV-curing applications.[63] With the morpholino-ketone

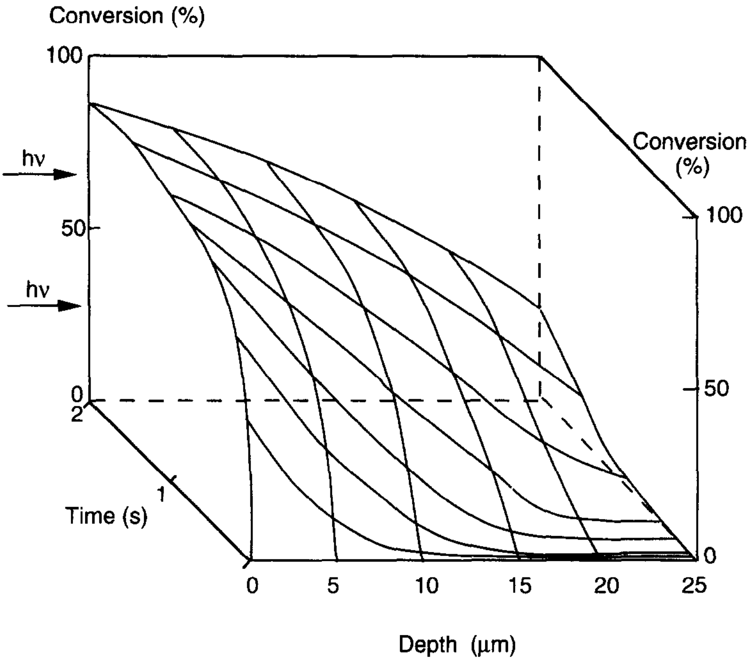


Fig. 11. Time dependence of the cure depth profile in a polyester-acrylate white lacquer exposed to UV radiation in the absence of air. Light intensity: 100 mW cm^{-2}.

PI (Irgacure 369), photobleaching was shown to occur according to an exponential law (Fig. 12), the photolysis rate being at any time proportional to the PI concentration. As expected for a direct photolysis process, the rate constant was found to increase linearly with the light intensity (I_0), the PI lifetime dropping to values below 1 s at high

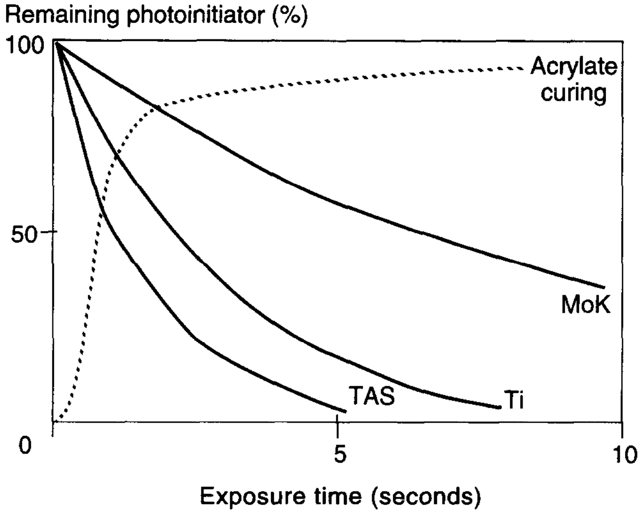


Fig. 12. Decay profiles of different types of photoinitiators in UV-curable formulations. TAS triarylsulfonium PF_6 salt in epoxide; MoK morpholino ketone and Ti: titanocene in acrylate. ——: Polymerisation profile of the diacrylate (TPGDA) + MoK.

I_o values ($\leq$200 mW cm^{-2}). The fluorinated diaryltitanocene (Irgacure 784) was found to undergo a substantially faster photolysis when exposed to visible light of the same intensity (Fig. 12). This result indicates that the lower polymerisation of the acrylate monomer observed with this photoinitiator, in comparison to the morpholino ketone, is mainly due to a lower quantum yield for the production of initiating radicals.

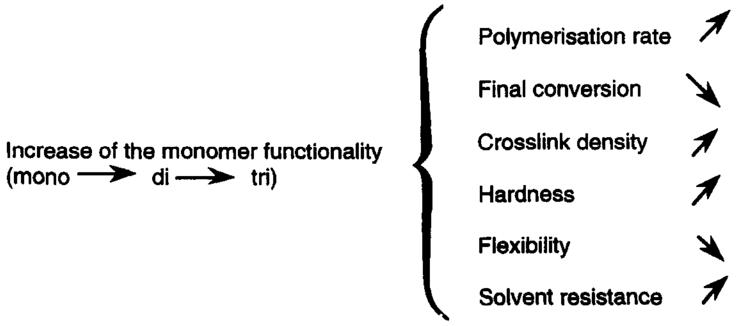
It can be seen in Fig. 12 that the polymerisation of the acrylated resin develops substantially faster than the PI photolysis so that the cured polymer contains a large amount of unreacted photoinitiator. A quite different behaviour was observed in the photoinitiated cationic polymerisation of a cycloaliphatic diepoxide where the triarylsulfonium salt was found to be rapidly photolysed (Fig. 12), thus causing an early stop of the polymerisation.[63] Despite the fast PI photolysis and the related high initiation rate, the cationic polymerisation of the epoxy monomer develops at a slower pace than in acrylic systems because of much shorter kinetic chain lengths.[63] Further progress towards faster cure is thus expected to result from a substantial increase in monomer reactivity rather than in the initiation efficiency.

Real-time UV spectroscopy is a useful method to monitor quantitatively fast photolysis reactions, and thus allows for an accurate evaluation of the photosensitivity of new initiators. When employed in conjunction with real-time IR spectroscopy, it allows one to determine both the amount of residual photoinitiator and the amount of unreacted monomer at any stage in the polymerisation. These two quantities are known to affect the long-term properties of UV-cured polymers.

5. NOVEL ACRYLATE MONOMERS

The basic characteristics of photocured polymers depend primarly on the type of telechelic oligomer employed and on the monomer used as a reactive diluent. The chemical structure and functionality of the oligomer are known to greatly affect thermal stability, chemical and weathering resistance and mechanical properties such as resistance to abrasion, scratching and shock.[127] For example, aliphatic polyurethane chains give highly flexible and soft materials, whereas stiff aromatic polyether or polyester chains yield hard, scratch-resistant coatings.

The monomer used to lower the formulation viscosity also plays a key role, for it acts both on the cure speed and on the polymerisation extent, as well as on the properties of the crosslinked polymer formed.



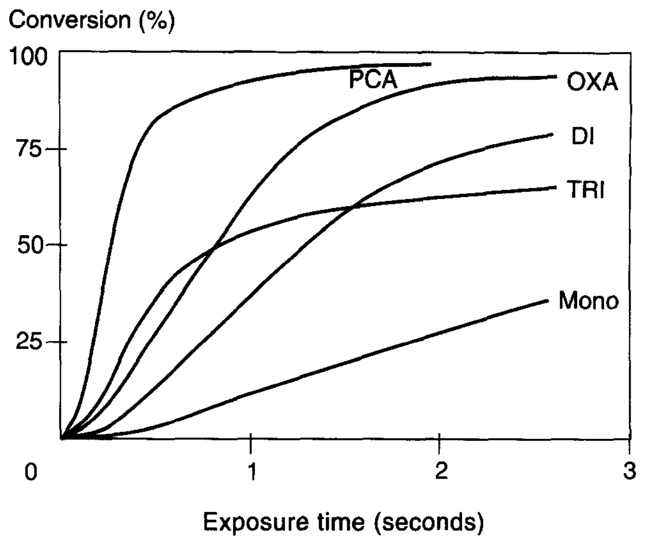


Fig. 13. Influence of the monomer (50%) used as reactive diluent on the polymerisation kinetics of a polyurethane-diacrylate oligomer (Mn = 1300). Monoacrylate: EDGA; diacrylate: TPGDA; triacrylate: TMPTA; OXA: monoacrylate of hydroxyethyl oxazolidone; PCA: monoacrylate of hydroxymethylpropylene carbonate.

An increase in the functionality of the reactive diluent was shown to accelerate the curing process, but at the expense of the overall conversion, thus leading to a polymer that contained a substantial amount of residual unsaturation.[128] The increased crosslink density also makes the cured polymer harder, but less flexible and more brittle.

One of the prime objectives in UV-curing chemistry is to create new monomers that can undergo fast and extensive polymerisation, yielding polymer materials having well-designed properties. In this respect, very promising results have been obtained recently with some novel acrylate monomers containing heterocyclic structures and silicone groups.

5.1. *Acrylates with cyclic structures*

Introducing an oxazolidone function in the structural unit of an acrylate monomer was found to greatly increase its reactivity.[129] The light-induced polymerisation proceeds substantially faster than with conventional mono- or diacrylate monomers, and almost as fast as with the highly reactive triacrylates (Fig. 13). As with other monoacrylates, the reaction occurs extensively to reach close to 100% conversion, in marked contrast with di- and trifunctional monomers where chain mobility restrictions lead to an early stop of the polymerisation. Despite the high rate of initiation caused by the intense illumination, the reaction was shown to proceed with long kinetic chains, each initiating radical being capable of affording the polymerisation of up to 50,000 acrylate double bonds.[106]

Highly reactive monomers have also been obtained by introducing into the monoacrylate structure a cyclic group containing one or two heterocyclic oxygen atoms: oxetane, dioxolane or propylene carbonate (Fig. 14).[130,131] In the presence of a radical-type photoinitiator and under intense illumination, 95% conversion was reached within 200 ms with the formation of a totally insoluble polymer, a rather unexpected feature for

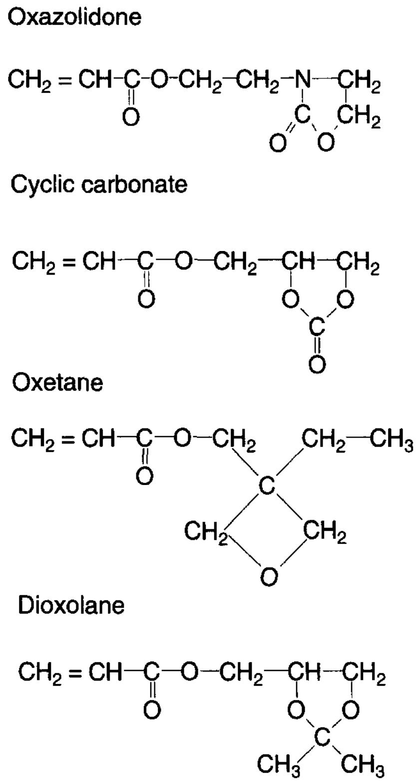


Fig. 14. Formulas of highly reactive novel monoacrylate monomers.

the homopolymerisation of a monoacrylate. The greater reactivity of these novel monomers was attributed to a strong hydrogen-donor character.[14] It will enhance chain-transfer reactions and make these compounds act as crosslinking agents. Moreover, the viscosity increase, due to the building up of a tridimensional polymer network, will favour propagation over termination and thus be a key factor in the observed increase of the monomer reactivity. Indeed, the termination rate constant for monoacrylates containing heterocyclic structures was found to be five times lower when compared to conventional monoacrylate monomers.[107]

All of these monomers have been used as reactive diluents in UV-curable resins based on acrylate functionalised polyurethane polyester and polyether oligomers. Superior curing performances were again observed upon UV exposure, with the formation of highly crosslinked polymers containing a low amount of residual unsaturation (Fig. 13). Another advantage of these monomers is that they impart both hardness and flexibility to UV-cured polymers,[132] which also exhibit good resistance to organic solvents, chemicals and weathering.[133] The main characteristics of this new class of acrylate monomers are summarised in Table 2, and are compared to typical mono-, di- and tri-acrylates.

5.2. *Silicone-acrylates*

Silicone-based polymers have experienced a fast growth during the last decade because of their unique properties, and they are used today in an ever-growing number of

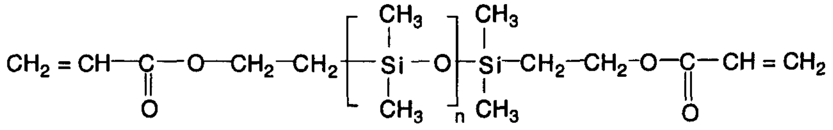
Table 2. Performance analysis of various acrylate monomers in UV-curing of a polyurethane diacrylate resin[131]

Monomer	Reactivity (s^{-1})	Residual unsaturation* (%)	Persoz hardness* (s)	Mandrel flexibility* (mm)
Monoacrylate				
ether (EDGA)	9	2	30	0
oxetane	42	2	50	0
dioxolane	100	4	70	0
oxazolidone	130	3	80	0
cyclic carbonate	125	4	270	0
ether-cyclic carbonate	165	6	100	0
Diacrylate				
ether (HDDA)	25	16	150	2
carbonate	200	14	250	2
Triacrylate (TMPTA)	110	36	270	5

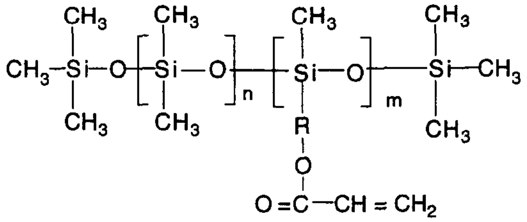
* Tack-free UV-cured film.

applications.[134] Radiation curing has proved to be a particularly efficient technique to produce rapidly crosslinked silicone polymers by photopolymerisation of multifunctional monomers and oligomers containing silicone groups in their structural units (for a comprehensive review on this subject, see Ref. 48).

The rate of polymerisation of phenyl-silicone-based di- and triacrylates was shown to be much greater than that of standard diluents such as hexanediol diacrylate (HDDA), tripropylene glycol diacrylate (TPGDA) and trimethylolpropane triacrylate (TMPTA).[135] This effect is probably due to the presence of the aromatic group, rather than to the presence of the silicone, as purely aliphatic silicone-triacrylates were found to cure significantly slower than TMPTA. An interesting and important feature of the films formed from trifunctional silicone-acrylates is a lack of visible shrinkage upon curing.[135] Most of today's UV-curable acrylated silicones consist of either acrylate end-capped linear polydimethylsiloxanes or of silicone chains containing pendent acrylate groups.[136–140]



$$CH_2=CH-\underset{\displaystyle O}{\overset{\|}{C}}-O-CH_2-CH_2-\left[\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{Si}}-O\right]_n-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{Si}}-CH_2-CH_2-O-\underset{\displaystyle O}{\overset{\|}{C}}-CH=CH_2$$



$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{Si}}-O-\left[\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{Si}}-O\right]_n-\left[\underset{\displaystyle R-O-C(=O)-CH=CH_2}{\overset{\displaystyle CH_3}{Si}}-O\right]_m-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{Si}}-CH_3$$

The versatility of silicone-acrylates in regard to curing, coatability, compatibility and release control make them ideally suited for a variety of applications, in particular for coatings having a desired release level.[140] Some newly developed silicone-acrylates show an outstanding reactivity, with reported line speeds of 600 m/min for both UV and EB

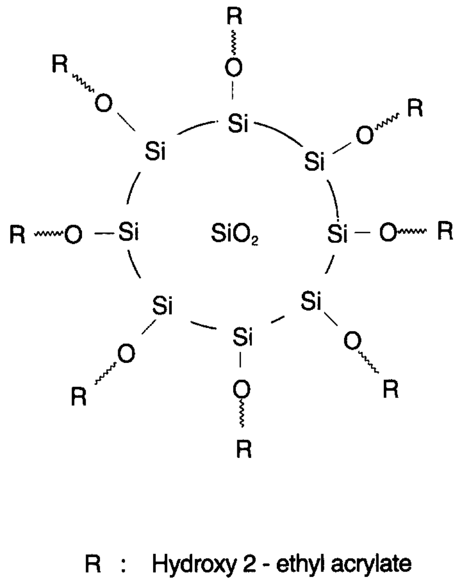


Fig. 15. Structure of an acrylic organosol of silica (Highlink OG-101 from Hoechst). Silica particle size: 10–50 nm. Number of chains 1000–20 000 per particle.

curing in an inert atmosphere.[140] As expected, atmospheric oxygen has a strong inhibition effect on such radical-induced polymerisations,[136] especially in those resins that are highly permeable to oxygen.

Silicone-based polymers are known for their softness, thermal stabilities, insulating qualities, biocompatibilities, high substrate wettabilities and good permeabilities to gases. Such remarkable properties account for the increased use of UV-curable silicone-acrylates in various sectors of applications,[141] in the coating industry for the surface treatments of optical fibers, papers and textiles. They also show good performance as pressure-sensitive adhesives, electronic circuit encapsulents, separation membranes and release coatings.[48]

A new class of functionalised silica organosols has been recently introduced by Hoechst (Highlink OG®). These consist of a colloidal suspension of amorphous silica particles modified at their surfaces 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_2 particles, reaching values up to 40% for 50-nm large particles. The structure of these compounds is illustrated schematically in Fig. 15. 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.

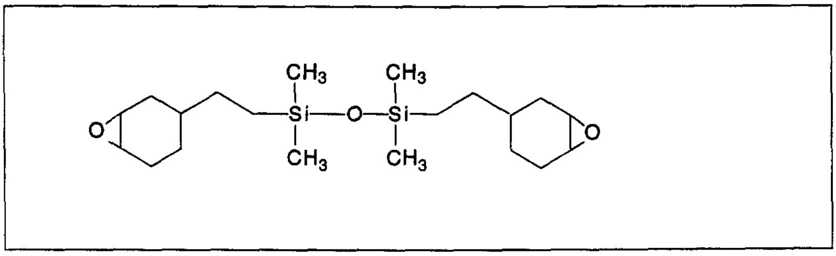
If the grafted organic moiety is terminated by an acrylate function, the organosol will act as a multifunctional crosslinking agent.[142] With the 2-hydroxyethyl acrylate substituent, photocuring was found to develop faster in the silica organosol than in the parent monomer, leading to an insoluble material.[132] A similar approach has been recently used to obtain UV-curable coatings that provide abrasion resistance to a variety of plastic substrates.[143,144] The formulation contained 40% of colloidal silica which was rendered organo-functional with methacryloxypropyltrimethoxysilane and dispersed in a diacrylate monomer (HDDA). Such UV-curable silicone-acrylates are of a great interest for coatings and adhesives applications because they improve markedly the properties of the cured product, in particular the hardness, scratch resistance, thermal stability, weatherability, chemical resistance and adhesion to various substrates.

6. PHOTOINITIATED CATIONIC POLYMERISATION

Photoinitiated cationic polymerisation has not experienced fast growth in UV-curing applications when compared to free-radical polymerisation. This is mainly because of cure speed, product properties and cost considerations, as well as because of the limited choice of photoinitiators and monomers that are commercially available. This situation may change in the future with the appearance of novel, highly reactive monomers containing siloxane groups, the possibility to ''photovulcanize'' quasi-instantly epoxidised rubbers at ambient temperatures, and the renewed interest in vinyl ether monomers.

6.1. *Epoxy-silicone monomers*

The polymerisation of typical dicycloepoxides exposed to UV radiation in the presence of an onium salt proceeds about 10 times slower than that of diacrylate resins.[63] Introducing a dimethyl siloxane group between the two cyclo-epoxide groups was found to increase drastically the reactivity of these monomers.[26,145–148]



In the presence of iodonium or sulfonium salts, the ring-opening polymerisation proceeds as fast as with some diacrylate monomers to yield a strongly crosslinked polyether network (Fig. 16). Epoxy monomers containing cyclic siloxanes rings have also been developed, together with multifunctional epoxy monomers with star or branched structures.[26,145] One of the additional benefits of epoxy-silicones is their ability to increase the cure rate of conventional organic diepoxides when incorporated as a blend.[147]

Copolymerisation with alcohols or polyols was shown to improve the physical properties of the final product, with no loss of cure speed.[149] Novel epoxy-fluorosilicones have recently been synthesized and have been found to combine exceptionally fast UV cure with good solvent resistance.[147] Such highly crosslinked polymers are likely to be used as conformal coatings, as well as for other end uses in the automotive and aerospace industries. The excellent chemical and physical properties of the radiation-cured film (hardness, flexibility, heat resistance) make epoxy-containing silicone monomers highly attractive for applications as coatings, adhesives, inks and composites. Most noteworthy are the very high glass transition temperatures that were obtained for some of the cured polymers, up to 200°C after 5 s of UV irradiation at room temperature, and the related remarkable thermal stabilities of such crosslinked materials.[26]

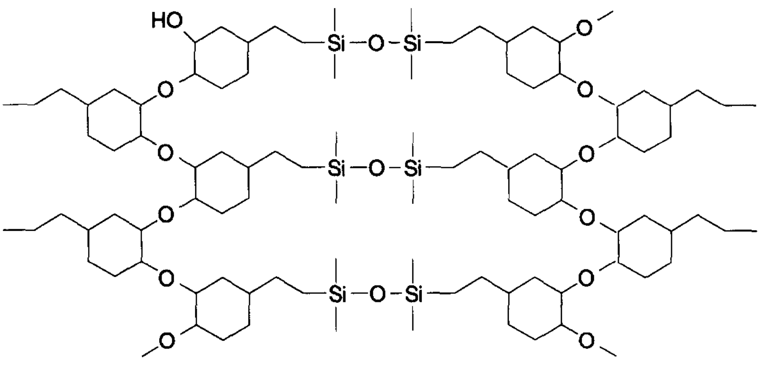


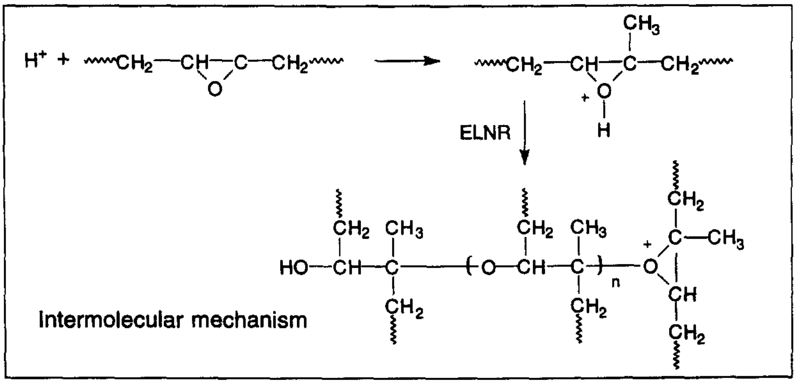
Fig. 16. Structure of the polymer network formed upon photoinitiated cationic polymerisation of a dimethylsiloxane dicycloepoxide monomer.

6.2. *Epoxidised natural rubber*

Tridimensional polymer networks can be readily obtained by photoinitiated polymerisation of functionalised polymers.[150] A typical example is the photocrosslinking of epoxidised polyisobutylene,[151] polyisoprene,[152] or polybutadiene.[152–154] In the case of natural rubber, the isoprene double bonds can be easily epoxidised by treatment with peracetic acid.[155] In the presence of a triarylsulfonium salt, "photovulcanisation" can be achieved within seconds under intense illumination at ambient temperature to yield a polymer combining the elastomeric character of rubbers and the toughness of epoxy polymers.[156] The UV-cured material proved to be both hard and flexible, thus showing good resistance to scratching and shock. Such coatings also exhibit excellent adhesion properties to various substrates, in particular aluminum, steel and glass.[151,153]

6.2.1. *Photocrosslinking of epoxidised polyisoprene*

Photogenerated protonic acids can easily initiate the ring-opening cationic polymerisation of the oxiranne function, with the formation of ether crosslinks between the rubber chain.



For epoxidised liquid natural rubber (ELNR), a good correlation was found to exist between the disappearance of the epoxy group (monitored by its IR absorption at

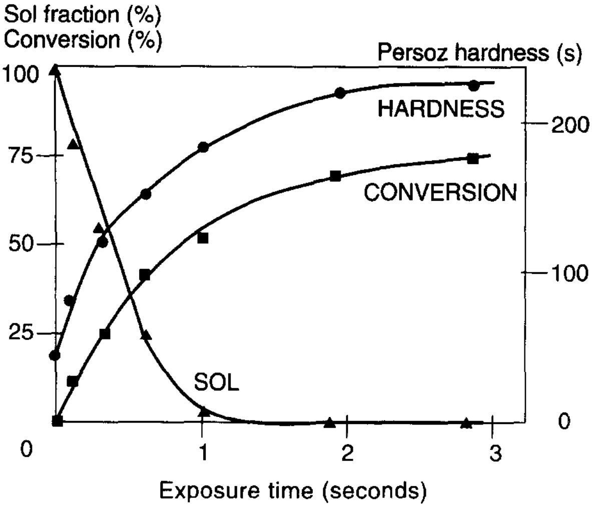
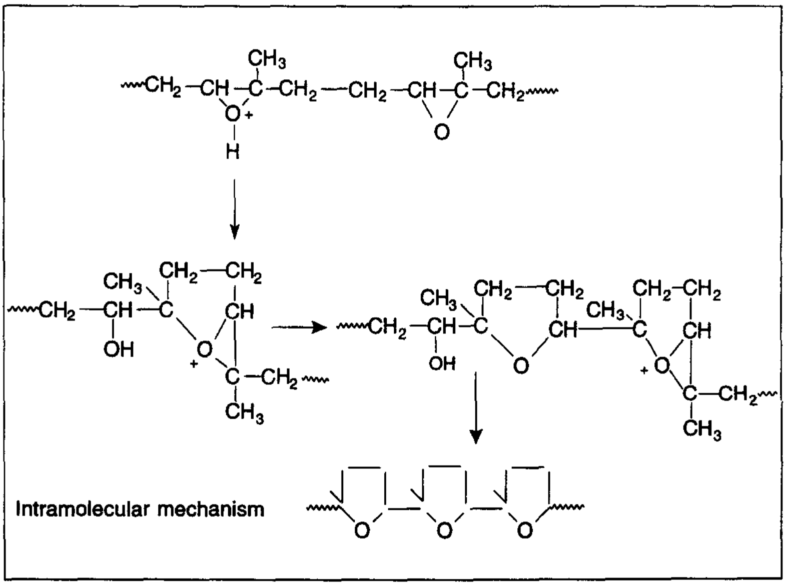


Fig. 17. Photoinitiated crosslinking polymerisation of epoxidised liquid natural. Photoinitiator: triarylsulfonium PF_6 salt (3%) Light intensity: 400 mW cm^{-2}.

877 cm^{-1}) and the formation of the ether group (monitored at 1080 cm^{-1}).[73] Within seconds, insolubilisation occurred and the pendulum hardness increased from 50 to 250 s (Fig. 17).

Complete insolubilisation was only achieved once about 50% of the epoxy groups had polymerised (Fig. 17). Because only a few of the 120 epoxy groups located on the ELNR chain need to react to render the polymer insoluble, this result strongly suggests that the ring-opening polymerisation proceeds also by an intramolecular mechanism involving neighbouring epoxy groups located on the same polymer chain. Such groups have indeed been detected by ^{13}C-NMR spectroscopy in the UV-cured epoxidised rubber,[73] with the formation of tetrahydrofuran structures along the rubber chain.



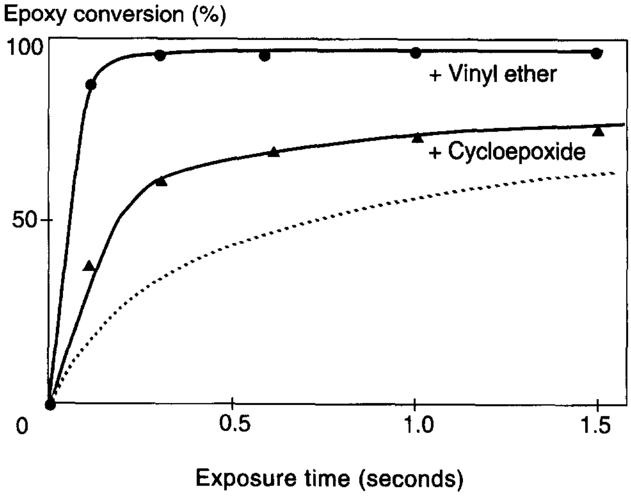
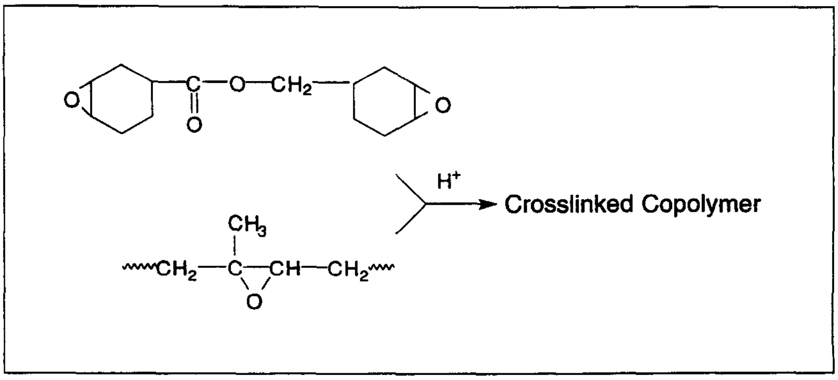


Fig. 18. Influence of difunctional monomer (50%) on the photoinitiated crosslinking polymerisation of epoxidised liquid natural rubber (ELNR). Vinyl ether: DVE-TEG, dicyclo epoxide: DCE photoinitiator: triarylsulfonium PF_6 salt (3%). Light intensity: 400 mW cm^{-2}. —: ELNR without added monomer.

A distinct feature of cationic polymerisation is that the chain carrier oxonium ions do not react among themselves, so that the ring-opening polymerisation will continue to proceed once initiating species are no longer produced, namely just after UV exposure. After a 50 h storage of the sample in the dark, most of the epoxy groups were found to have polymerised.[157]

6.2.2. *Polymerisation of multifunctional monomers in epoxidised rubber*

The cure speed of epoxidised rubber can be substantially enhanced by the addition of a monomer that will act as a reactive plasticiser. The most promising results have been obtained with dicycloepoxide and divinyl ether monomers.[73] The ring-opening polymerisation of the epoxy groups proceeds rapidly when ELNR and a dicycloepoxy monomer were exposed to UV radiation in the presence of a triarylsulfonium salt, as shown in Fig. 18. The two types of epoxy groups follow similar kinetic patterns, but the epoxy rubber reaches higher ultimate conversion (90% after 3 s exposure) than the cycloepoxide (76%), probably because of the intramolecular polymerisation process.



The UV-cured copolymer is totally insoluble in organic solvents and shows a much lower degree of swelling than the UV-cured ELNR, thus indicating that a tight tridimensionnal polymer network has been formed. As a result, such coatings are very hard and resistant to scratching, which makes them particularly well suited for the protection of organic glasses and plastic materials.

The plasticising effect of the highly fluid divinyl ether of diethyleneglycol is more pronounced than that of the viscous dicycloepoxide, thus making the rubber epoxy group polymerise six times faster than in the unplasticised film (90% conversion after 0.1 s), as shown by Fig. 18. The highly reactive vinyl ether monomer was found to polymerise about half as fast as the epoxy group which is expected to undergo a very effective polymerisation along the rubber chain. An interpenetrating polymer network is thus being formed, very much like in the photoinitiated cationic polymerisation of blends of multifunctional vinyl ether and epoxide monomers.[65] The photocured IPN is soft and easily scratchable, but it exhibits good resistance to impact. Such low-modulus polymers may be best used for the fabrication of safety glasses or fast-drying adhesives as they show a good adhesion on metallic and plastic supports.

6.3. *Vinyl ether monomers*

Today's growing concern for environmental issues within the radiation-curing industry has led to the development of non-acrylate formulations that should be more friendly for both the manufacturer and the end user. In this respect, vinyl ethers appear as an attractive alternative because these monomers combine low toxicities and low odour with great reactivity, while also being excellent viscosity reducers. Several reports have appeared in the past few years on radiation-curable vinyl ether-based resins containing either divinyl ether diluents or vinyl ether-functionalised esters, urethanes, ethers, or siloxanes.[64–70]

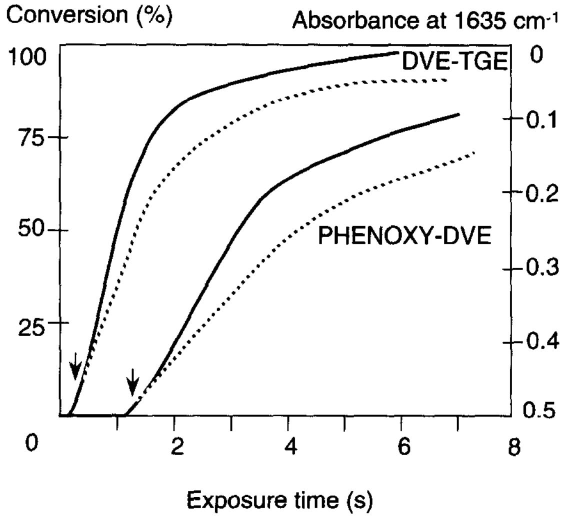
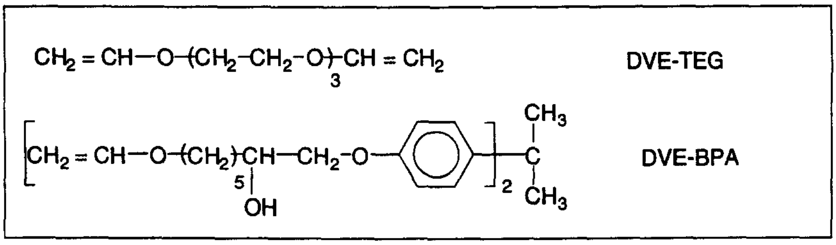


Fig. 19. Photoinitiated cationic polymerisation of divinyl ether monomers. Kinetic profiles recorded by RTIR spectroscopy.[Triarylsuifonium PF_6 salt] = 3%. Light intensity: 500 mW cm^{-2}. —: Dark polymerisation after a short UV exposure (↓ end of irradiation).

Vinyl ether monomers are readily polymerised by a cationic mechanism in the presence of photoacid initiators. Figure 19 shows conversion versus time profiles recorded by RTIR spectroscopy for two divinylether derivatives containing triethyleneglycol or bis-phenol A structures that were UV irradiated in the presence of a triarylsulfonium. PF$_6^-$ salt:



After a short induction period due to the presence of an alcaline stabiliser, the polymerisation of DVE-TEG develops rapidly until near total consumption of the monomer, so that the crosslinked polymer contains essentially no residual unsaturation. This is due to the elastomeric character of the polymer formed (low T_g), which provides sufficient molecular mobility to the reactive species to complete the chain process.

The slower and less extensive polymerisation observed with the phenoxy divinylether (DVE-BPA) can be attributed to three main factors: the higher initial viscosity which decreases the propagation rate constant, the less pronounced hydrogen-donor character of DVE-BPA, which reduces to the initiation rate, and the stiffness of the polymer formed, which leads to a premature end of the chain reaction process. The cure speed and final conversion were greatly increased by the addition of DVE-TEG, which acts as a viscosity reducer, a strong H-donor and a reactive plasticiser. With a 50/50 wt mixture, essentially the same polymerisation profile was recorded as in DVE-TEG alone.

In comparison to the radical-induced polymerisation of acrylate systems, the cationic polymerisation of vinyl ether monomers presents two distinct advantages:

It is insensitive to oxygen inhibition, because of the lack of reactivity of the propagating carbocation toward the O_2 molecule. Indeed, identical polymerisation profiles were recorded for samples irradiated in the presence of air and for those covered by a transparent polypropylene film to prevent oxygen diffusion (laminate).

The carbocation species do not react with each other, in contrast to free radicals, and have therefore a longer lifetime. As a result, the polymerisation will continue in the dark, even when initiating species are no longer created. Figure 19 clearly shows how effectively this post-polymerisation develops, once the light has been switched off in the early stages of the reaction.

As the rate of the dark polymerisation R'_p is directly dependent on the concentration $[P^+]$ of the polymer cation, $R'_p = k_p\,[P^+]\,[M]$, one can follow continuously the decay of the cation concentration by monitoring the variation with time of the ratio $R'_p/[M]$, where $[M]$ is the monomer concentration after UV exposure and post-cure during time t. It can be seen from the decay curve observed for DVE-TEG (Fig. 20) that the cation disappears according to a simple exponential law, characteristic of a first order termination process. A semi-log plot of the ratio $R'_p/\,[M]$ versus time yields a straight line, the slope of which corresponds to the decay rate constant k and allows the $[P^+]$ lifetime to be evaluated, assuming that k_p remains

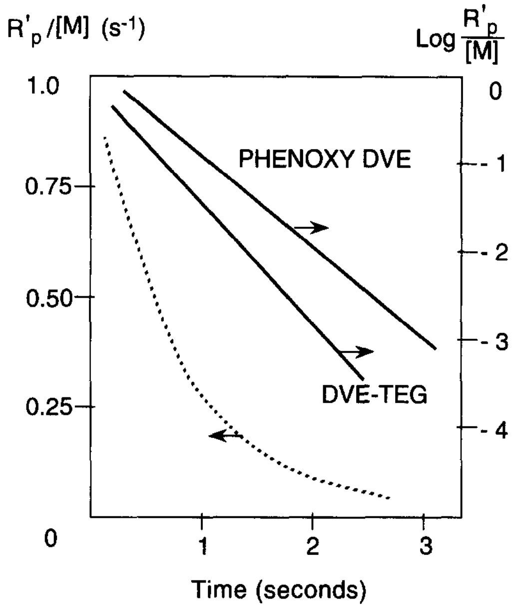


Fig. 20. Decay profiles of the carbocation after UV exposure of divinyl ether monomers.

constant in the conversion range investigated:[158]

$$\mathrm{Log}(k_p[P^+]) = -k \times t$$

For the highly reactive DVE-TEG, a lifetime value of the carbocation as short as 1 s was measured, compared to 5 s for the phenoxy divinylether. High k values (or short lifetimes) reveal the great reactivities of the living polymer cations which undergo termination reactions with impurities and with counter-ions.

From these kinetic data, the quantum yield of polymerisation can be evaluated by taking the ratio of the amount of vinyl ether groups polymerised to the amount of photons absorbed:

$$\Phi_p = \frac{[\mathrm{VE}]_0 \cdot \tau}{I_0 \cdot t \cdot f}$$

where $[\mathrm{VE}]_0$ is the initial vinyl ether concentration, τ the final degree of conversion after exposure time t and f the fraction of incident light (of intensity I_0) which has been absorbed by the sample. This calculation takes into account the dark polymerisation that develops effectively after UV exposure. The large values of Φ_p obtained (10,000 mol/photon for DVE-TEG) indicate that the crosslinking polymerisation develops with long kinetic chains in these difunctional vinyl ethers.

An increase of the initiation rate by altering the light intensity value, leads to a proportional increase of the polymerisation rate (Fig. 21). Such a linear relationship is expected to be found in a chain reaction process where only one propagating species is involved in the termination step, as is the case in cationic polymerisation. A linearity failure was observed above a certain value of the light intensity (50 mW cm^{-2}), the polymerisation rate tending

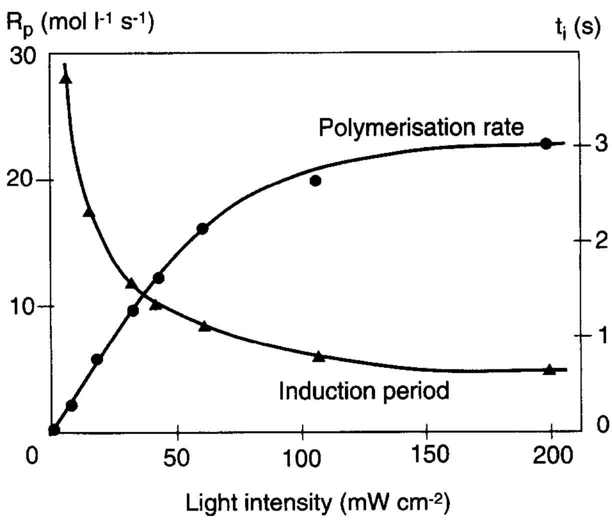


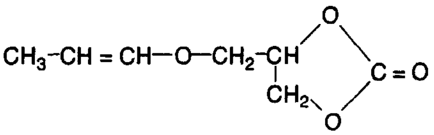
Fig. 21. Light intensity dependence of the polymerisation rate and induction period in photoinitiated cationic polymerisation of a divinyl ether (DVE-TEG + phenoxy DVE). [Triarylsulfonium PF_6 salt] = 3%.

to level off, reaching a maximum value as shown in Fig. 21. One can consider that, under those extreme conditions where a great number of initiating species are generated during a short period of time, the rate-controlling factor is not the initiation rate anymore, but the diffusion rate of the reactive species. From the polymerisation profile recorded by RTIR spectroscopy at such high light intensifies, it is then possible to evaluate the rate at which the polymer chains are actually growing. For the DVE-TEG/DVE-BPA system, its value was found to be on the order of 23 mol l^{-1} s^{-1}.

Figure 21 also shows that the induction period (t_i) decreases with the light intensity, according to a clear hyperbolic law: $t_i = KI^{-1}$. Such a behaviour could be foreseen on the ground that, whatever the initiation rate, a constant amount of photons ($I.f.t_i$) need to be absorbed by the sample in order to generate the amount of protonic acid required to consume the inhibitor.

A combination of vinyl ether monomers and vinyl ether urethane oligomers, along with onium salt catalysts, provides versatile new UV- or EB-curable systems.[159] The curing was reported to proceed at high rates in the presence of oxygen and to produce coatings with desirable physical properties. Highly crosslinked polymers, showing a low degree of swelling, have been recently obtained by photoinitiated cationic polymerisation of vinyl ether/styrene copolymers, a process which develops with long kinetic chains.[160] Similarly, the divinyl ether of bis-phenol A was shown to cure rapidly under UV irradiation to give a tough film having low moisture absorption.[161] It is an excellent candidate for adhesive and UV-coating applications, in particular on epoxy fiberglass.

One of the problems encountered in photoinitiated cationic polymerisations is the poor solubility of the onium salts in the usual monomers. A new reactive diluent has been especially designed for solubilising cationic photoinitiators, in particular arylsulfonium salts: the propenyl ether of propylene carbonate (Rapi-Cure PEPC from International Specialty Products).[162]



This low viscosity monomer proved particularly effective in the UV curing of vinyl ethers, cycloaliphatic epoxy resins and epoxidised natural oils.[162]

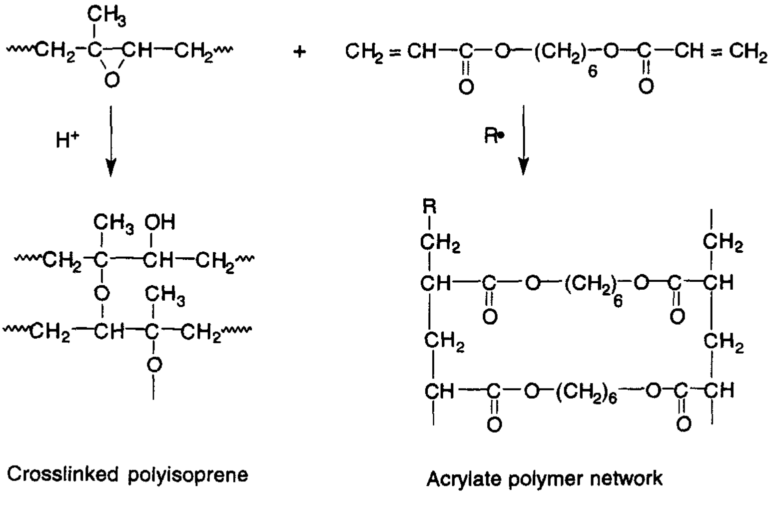
Further progress on photoinitiated cationic polymerisation can be expected to occur in the near future, with the recent development of new vinyl ether functionalised oligomers,[163] and some highly reactive propenyl and butenyl ether monomers.[164-166] This will expand the choice of formulations and help create, through UV curing, high performance polymer materials that are well designed for specific applications.

7. RADICAL AND CATIONIC POLYMERISATIONS

Photoinitiated polymerisation of two multifunctional monomers is one of the most efficient methods to produce rapidly interpenetrating polymer networks (IPN). By taking monomers or telechelic oligomers that polymerise by different mechanisms, e.g. by free radical and by cationic-type reactions, two polymer networks can be created simultaneously but independently from each other. The following examples illustrate the potential of this technology to generate novel IPNs.

7.1. *Acrylates in epoxidised rubbers*

When a diacrylate monomer, like hexanedioldiacrylate, was incorporated into an epoxidised rubber and exposed to UV radiation in the presence of both a radical- and a cationic-type photoinitiator, the crosslinking polymerisation of the two functional groups was found to proceed readily, with the ultimate formation of an IPN.



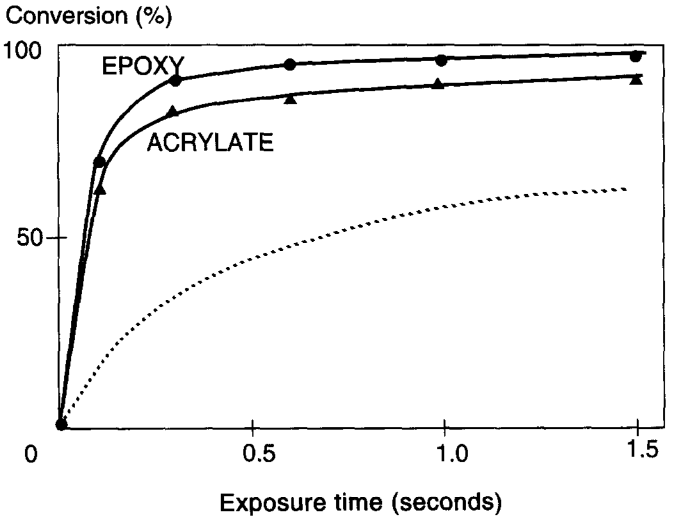


Fig. 22. Photoinitiated polymerisation of a mixture of hexanediol diacrylate and epoxidised liquid natural rubber, in a 2 to 1 weight ratio. Photoinitiator: triarylsulfonium PF_6 salt (1%) + hydroxyalkylphenone (2%). ---: ELNR without added monomer. Light intensity: 400 mW cm^{-2}.

The disappearance of the two reactive groups can be easily monitored by infrared spectroscopy through their distinct absorption peaks at 812 cm^{-1} (acrylate twisting) and 877 cm^{-1} (epoxy ring breathing). Figure 22 shows a typical conversion versus time plot obtained by exposing a 20 μm thick film to intense UV-light (400 mW cm^{-2}). The ring-opening polymerisation of the epoxy group located on the rubber chain proceeds initially as fast as the radical-induced polymerisation of the acrylate double bond. After UV curing, the polymer contains essentially no residual epoxy groups and less than 10% unreacted acrylate unsaturation.

The surprisingly fast polymerisation of the epoxy group of the rubber chain was attributed to both the plasticising effect of the acrylate monomer and to an efficient intramolecular process leading to the formation of tetrahydrofuran structures.[73] The photocured IPN is too stiff to allow for complete polymerisation of the acrylate double bonds, whereas the rubber backbone retains enough mobility so that the polymerisation of neighbouring epoxy groups can proceed along the rubber chain until exhaustion.

The ultrafast polymerisation of both the epoxy and acrylate functions leads to a rapid insolubilisation of the irradiated sample, with nearly 90% insoluble material formed after a 0.1 s exposure (Fig. 23). The two interpenetrating polymer networks, which are formed simultaneously but independently of each other, are tightly crosslinked, as shown by the remarkably low value of the degree of swelling (Fig. 23): 150% after a 0.3 s exposure compared to 1900% for the epoxidised rubber irradiated under the same conditions. Such a short exposure proved also to be sufficient to transform the low modulus polymer blend into a hard and tough polymer material that showed great resistance to abrasion and scratching. The IPN formed thus combines the elastomeric properties of the ether crosslinked rubber and the toughness of the acrylate network.

Because of the great reactivity of this hybrid formulation, the curing process can be induced by simple exposure to sunlight, as shown by Fig. 24. The polymerisation of the

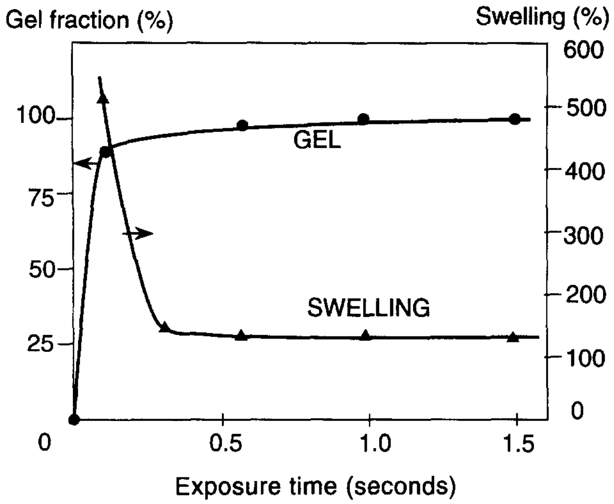


Fig. 23. Insolubilisation and swelling profiles of a 2 to 1 mixture of hexanediol diacrylate and epoxidised liquid natural rubber upon UV exposure. Light intensity: 400 mW cm^{-2}.

acrylate groups was achieved within 3 min, and that of the epoxy groups within 10 min. The slower cure of the epoxide is due to the fact that the triarylsulfonium cationic photoinitiator has a weaker absorption in the range of UV sunlight (300–400 nm) than the phosphine oxide used as the radical photoinitiator.

By reducing the photoinitiator concentration, up to 1 mm thick samples were deep through-cured within 30 min using ambient sunlight. Similar performance has been achieved by Crivello in his study of the cationic photocuring of fibreglass epoxy composites.[167] By using a triacylphosphine oxide as a radical photoinitiator, one can generate successively the two polymer networks.[73] The acrylate monomer will first be polymerised

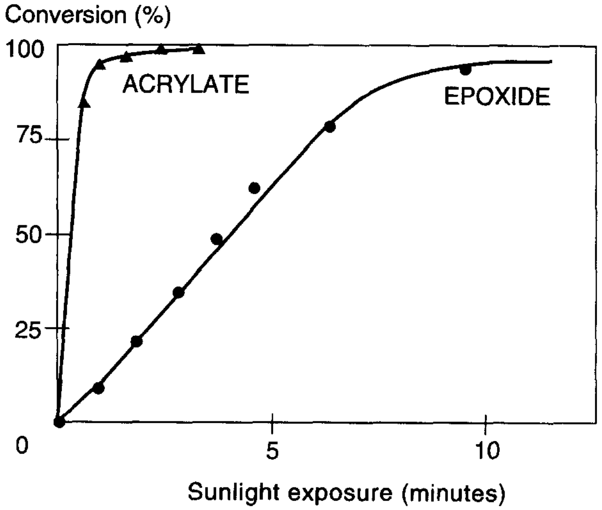


Fig. 24. Crosslinking polymerisation of a 4 to 1 mixture of epoxidised natural rubber and hexanediol diacrylate upon sunlight exposure. Photoinitiator : triarylsulfonium PF_6 salt (4%) + triphenylphosphine oxide (1%).

Table 3. Performance analyses of various rubber-based photocrosslinked polymers. Values after a 3 s exposure at 500 mW cm^{-2}.

System	Network structure	Conversion %		Gel %	Swelling %	Pendulum hardness s	Elongation at break %
		Rubber epoxy	Monomer				
ELNR	Epoxy-homopolymer	100	—	100	800	250	> 100
ELNR + DCE	Epoxy/epoxy copolymer	90	76	93	300	350	> 100
ELNR + DVE	Epoxy/vinyl ether copolymer	100	80	50	500	75	> 100
ELNR + HDDA*	Epoxy/acrylate interpenetrating polymer networks	100	93	100	130	320	40

*The same performance was reached after a 1 s exposure.

by an irradiation at long wavelengths (365 nm) to form a semi-IPN, and the rubber epoxy in a second step by a short exposure to the full emission of the mercury lamp. With this radical/cationic hybrid system, one can thus achieve a quasi-instant transformation of a semi-IPN into a true IPN selectively in the illuminated area. Such a two step UV-curable dry photoresist might be valuable for some specific applications, in particular in laser imaging by using successively a UV/argon ion laser (364 nm) and a helium/cadmium laser (325 nm) to create 3D-images.

Tridimensional polymer networks having quite different structures can be readily produced by photoinitiated polymerisation of epoxidised rubbers in the presence of different types of difunctional monomers. Some of the main characteristics of these crosslinked polymers are reported in Table 3, in comparison to those of UV-cured epoxidised natural rubber. The acrylate/rubber hybrid presents the best performance in terms of reactivity and properties, with the formation of transparent and non-coloured films. The overall process is easy to work out, the epoxidised rubber being simply dissolved in the acrylate monomer at 60°C together with the two photoinitiators, and exposed to UV radiation or sunlight in the presence of air. In addition, this hybrid system offers a great latitude in formulation to produce organic materials with tailor-made properties because of the large selections of acrylate monomers currently available.

7.2. *Acrylates and vinyl ethers*

As vinyl ethers (VE) do not undergo homopolymerisation in the presence of free radicals, one would expect to generate IPNs by UV irradiation of a mixture of vinyl ether and acrylate monomers in the presence of both cationic and radical photoinitiators. Indeed, the vinyl ether radical, which is inactive towards the electron-rich VE double bond, is capable of reacting with the electron poor acrylate double bond in systems of this kind.

7.2.1. *Radical photoinitiators*

Figure 25 shows typical polymerisation profiles recorded by RTIR spectroscopy upon UV exposure of a mixture of DVE-TEG and a polyester acrylate (Ebecryl 80 from UCB), in

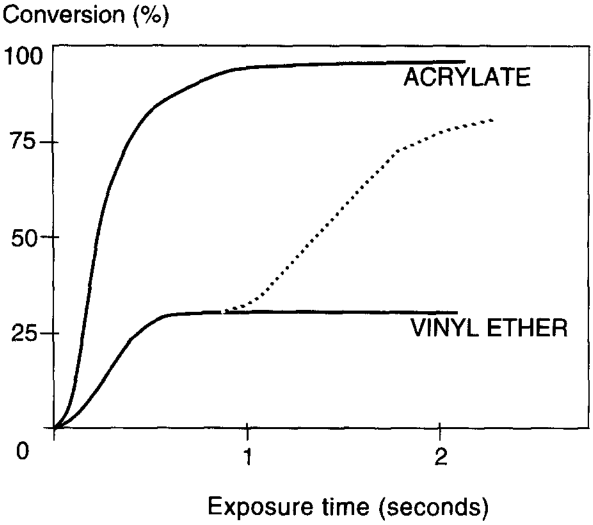


Fig. 25. Photoinitiated polymerisation of a 1 to 1 mixture of a divinylether (DVE-TEG) and a polyester-acrylate, monitored by RTIR spectroscopy. Photoinitiator: [triarylsulfonium PF_6 salt] = 2%. .....: vinyl ether polymerisation profile upon addition of a radical photoinitiator. Light intensity: 50 mW cm^{-2}.

the presence of a radical photoinitiator (1% of Darocur 1173). The acrylate oligomer was found to polymerise three times faster than the vinyl ether, reaching a high final conversion (> 90%). By contrast, the DVE-TEG polymerisation stopped after 0.5 s at only 30% conversion. The cure limitation of the vinyl ether monomer was attributed to the fast consumption of the acrylate double bonds, which are therefore no longer available for reaction with VE radicals. From the observed effect of the monomer feed composition on the polymerisation rate of each monomer and on the composition of the crosslinked polymers (Fig. 26), it was concluded that acrylate radicals are twice as reactive towards the acrylate double bond as they are toward the vinyl ether double bond.[68]

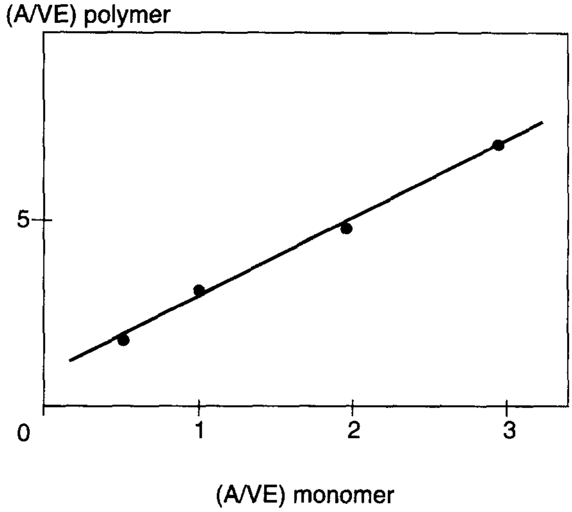


Fig. 26. Influence of the monomer feed ratio on the composition of the copolymer in the photoinitiated radical polymerisation of an acrylate (A) and vinyl ether (VE) mixture.

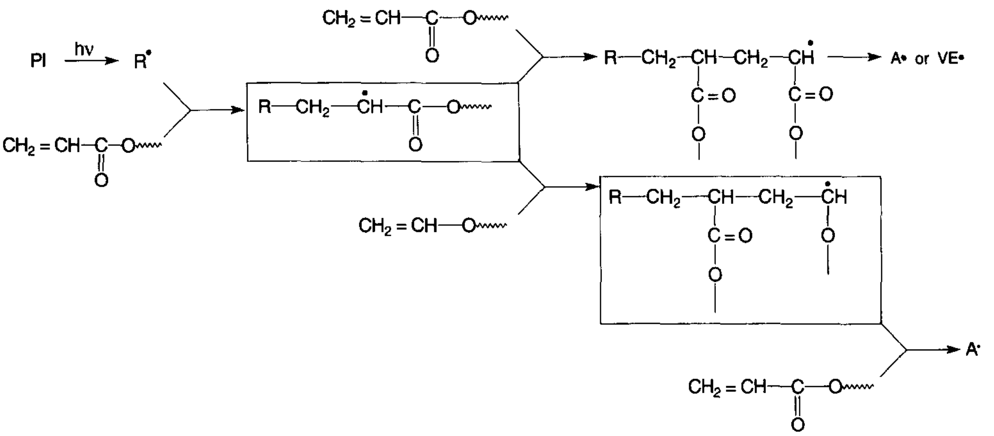
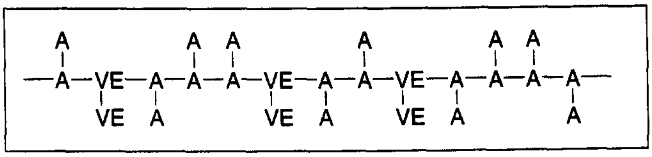


Fig. 27. Photoinitiated copolymerisation of a vinyl ether/acrylate hybrid system.

All of the kinetic results point to a copolymerisation mechanism involving cross-propagation by the vinyl ether and acrylate radicals, together with a homopolymerisation of the acrylate moiety as represented schematically in Fig. 27. A crosslinked copolymer will thus be formed where vinyl ether units are isolated. For a stoichiometric monomer feed composition (acrylate/vinyl ether = 1), the copolymer will contain three times more acrylate than VE units with the following type of sequence for the growing chain:



$$\begin{array}{cccccccccccccc}
 & \text{A} & & & \text{A} & \text{A} & & & \text{A} & & & \text{A} & \text{A} & \\
 & | & & & | & | & & & | & & & | & | & \\
— & \text{A}— & \text{VE}— & \text{A}— & \text{A}— & \text{A}— & \text{VE}— & \text{A}— & \text{A}— & \text{VE}— & \text{A}— & \text{A}— & \text{A}— & \text{A}— \\
 & & | & | & & & | & | & & | & | & & & | \\
 & & \text{VE} & \text{A} & & & \text{VE} & \text{A} & & \text{VE} & \text{A} & & & \text{A}
\end{array}$$

As a result, the photocured polymer will contain large amounts of unreacted vinyl ether double bonds (up to 70% of the original amount), as shown on Fig. 28. Because this will affect the long-term properties of the polymer, it is necessary to achieve a more extensive polymerisation of the VE monomers, which can be done by adding a cationic photoinitiator to the formulation.

7.2.2. *Cationic photoinitiators*

The DVE-TEG/polyester hybrid was found to undergo a fast and extensive polymerisation involving two types of functional groups when it was UV irradiated in the presence of both radical- and a cationic-type photoinitiators (Fig. 25). The polymerisation of DVE-TEG proceeds according to a typical two step profile, the fast but limited radical-induced copolymerisation being followed by the cationic-initiated crosslinking polymerisation of the remaining divinyl ether monomer. The 1 s induction period observed is due to the nucleophilic stabiliser present in DVE-TEG, and can be shortened by reducing the amount of this compound.

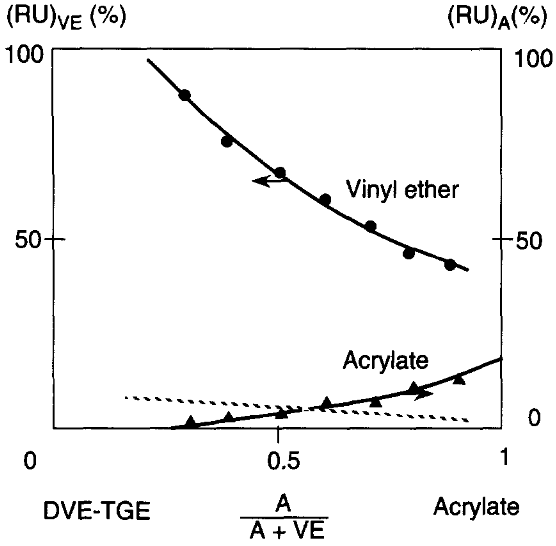
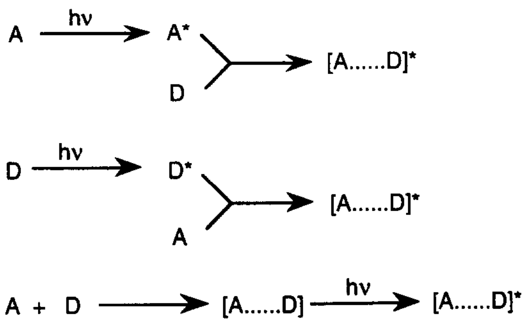


Fig. 28. Influence of the monomer feed ratio on the amount of residual unsaturation in the UV-cured vinyl ether/acrylate copolymer. Photoinitiator: [hydroxyalkylphenonel = 2%; - - - - : with added triarylsulfonium salt (2%).

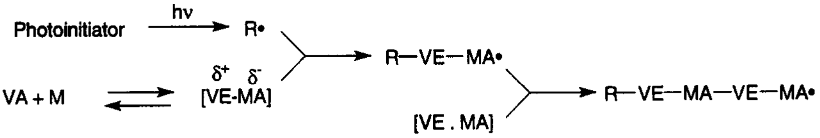
The slower cationic polymerisation of the VE units in the hybrid system, as compared to the neat DVE-TEG (Fig. 19), was attributed to the early formation of the acrylate/VE copolymer network and the related mobility restriction of the reactive species. The chain reaction continues to proceed after the UV exposure until near exhaustion of the vinyl ether monomer, so that the photocured material contains essentially no unreacted VE double bonds and less than 10% residual acrylate unsaturation (Fig. 28). The final product consists of two interpenetrating polymer networks: (i) a vinyl ether/acrylate crosslinked copolymer with isolated VE units whose composition can be varied by acting on the monomer feed ratio, and (ii) a tridimensional vinyl ether polymer network. Different types of IPNs showing well contrasted properties have been produced by using VE functionalised telechelic polymers instead of DVE-TEG and by changing the chemical structure of the acrylated oligomer chain (polyurethane, polyether, polyphenoxy, polysiloxane).

7.3. *Vinyl ether/unsaturated ester hybrids*

Vinyl ether monomers have been shown to undergo a radical-initiated copolymerisation with unsaturated esters, such as maleates,[74–76] or with maleimides,[168] to generate alternating copolymers. The mechanisms for copolymerisation reactions via charge transfer (CT) or donor/acceptor (DA) complexes have been thoroughly investigated.[169–172] The formation of an excited state complex (DA*) can take place from an excited state donor or acceptor that will associate to the ground state A or D, or by the direct excitation of the ground state complex:



The fastest polymerisation rate and highest final conversion were observed for the stoichiometric composition by using hydroxy-alkylphenones as photoinitiators.[68] From the observed linear variation of R_p with the product of the two monomer concentrations, it was concluded that the polymerisation proceeds by a mechanism where the propagation step involves the reaction of a polymer radical with a ground state donor/acceptor complex:[68]



Polymerisation rate

$$R_p = \frac{k_p}{2\,k_t^{0.5}} (\Phi_i\, I_{abs})^{0.5}\; K\,[VE]\,.\,[MA]$$

$$\text{with } K = \frac{[VE-MA]}{[VE]\,.\,[MA]}$$

The fact that polymerisation was found to occur even in the absence of added photoinitiator, by direct excitation of the donor/acceptor complex, was taken as further evidence in favour of such a mechanism. A number of other photoinitiator-free formulations were shown to undergo copolymerisation by direct photolysis of donor/acceptor complexes.[168] Depending on the strength of the complex, which can be controlled by the choice of the acceptor and donor monomers, one can favour the free-radical polymerisation process.[172] In this respect, one should mention the remarkable performance of the combination of hexylimaleimide with cyclohexane dimethanoldivinylether that proved particularly reactive, undergoing a fast and extensive polymerisation upon UV irradiation even in the presence of air.[168] Such VE-based photocurable resins appear as attractive alternatives to replace widely used acrylate-based resins as they combine great reactivities, low odours and low irritancies of the formulation, together with the faculty of generating highly crosslinked polymers presenting the desired properties for the considered application.

One of the critical problems encountered in the photoinduced polymerisation of donor/acceptor complexes lies in the final monomer conversion which usually levels off at about 80% under stoichiometric conditions (Fig. 29). The remaining double bonds are reactive

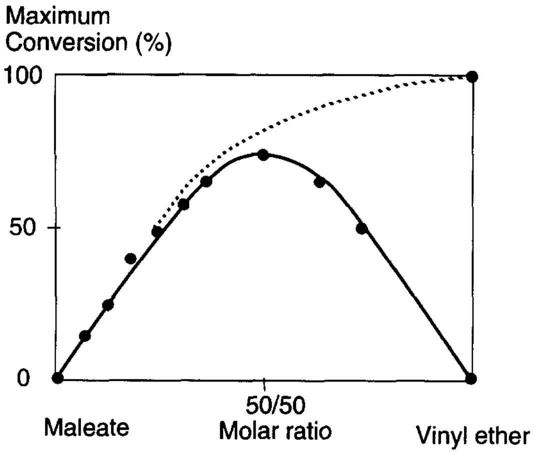


Fig. 29. Influence of the monomer feed ratio on the maximum conversion in the UV curing of a divinylether/dimaleate mixture. Photoinitiator: [hydroxyalkylphenone] = 2%; - - - -: remaining vinyl ether with added triarylsulfonium salt (2%).

sites that are likely to undergo unwanted oxidation or degradation reactions upon storage or during outdoor applications, thus affecting the long-term properties of the photocured polymer. One possible way to overcome this difficulty is by increasing the vinyl ether content of the formulation and by introducing a cationic photoinitiator, together with a radical photoinitiator, in order to polymerise the VE in excess. Overall conversion values superior to 95% have thus been obtained (Fig. 29). The photocured polymer is then comprised of two IPNs, a radical type VE/maleate crosslinked copolymer and cationic type VE homopolymer network.

Another efficient way to reduce the residual unsaturation content of the final product is by the addition of an acrylate monomer which will copolymerise with the vinyl ether and increase both the polymerisation rate and the final conversion. In such vinyl ether/maleate/acrylate hybrid systems, three polymer networks will be formed simultaneously by a purely radical process: (i) an alternate VE/maleate copolymer, (ii) a VE/acrylate copolymer with isolated VE units, and (iii) the acrylate crosslinked homopolymer. The three networks are chemically bound together because of the bivalent contribution of both the vinyl ether and the acrylate monomer. VE/maleate monomer mixtures were recently used as reactive diluents in combination with acrylate oligomers to reduce formulation viscosities and to obtain UV-curable resins having a low odour and low irritancy.[173]

8. PHOTOINITIATED POLYMERISATION IN THE SOLID STATE

Semi-interpenetrating polymer networks can be readily prepared by light-induced polymerisation of multifunctional monomers dispersed in a linear polymer matrix. This type of photopolymer has recently attracted the attention of polymer chemists, for it permits one to create rapidly new organic materials having tailor-made properties which cannot be achieved with a single polymer alone.[174] In a solid medium, with its related molecular mobility restrictions, the chain reaction develops usually at a slower pace and less extensively than for liquid monomers.[175] The great advantage of the UV technology is to allow a

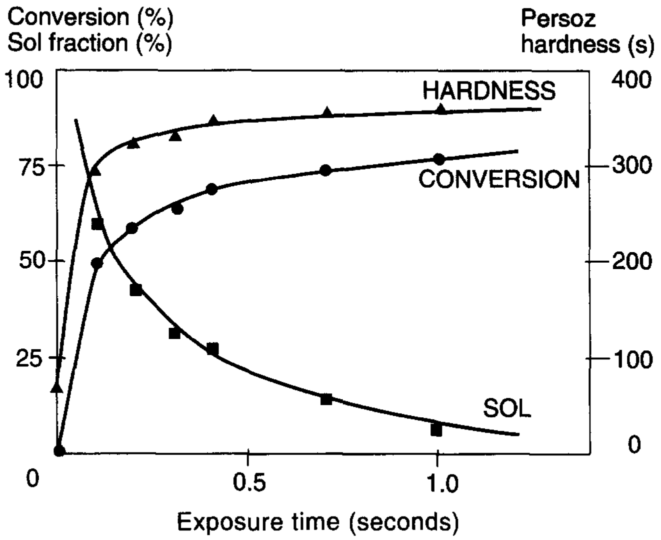


Fig. 30. Photoinitiated polymerisation of a triacrylate monomer (TMPTA) in a PVC matrix. Light intensity: 400 mW cm^{-2}.

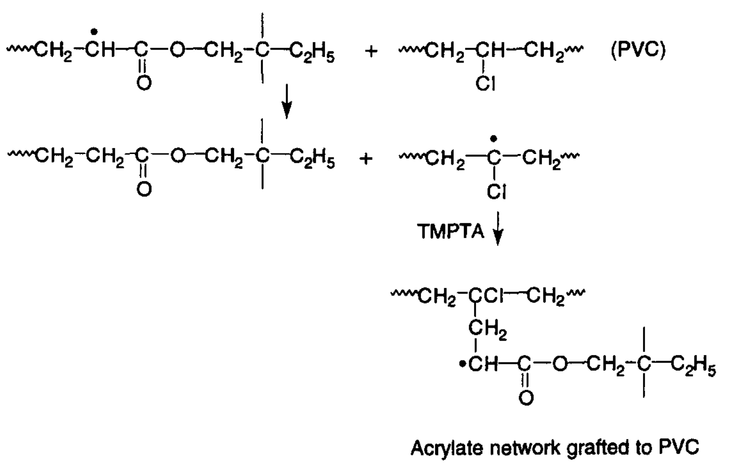
relatively fast curing to be achieved because of the great initiation rate provided by the intense illumination.

Several reports have appeared in recent years on the UV curing of vinyl, epoxy and acrylic monomers in a polymer matrix.[176–183] The compatibility of the monomer with the polymer was shown to be a key factor, as it strongly affects both the polymerisation kinetics and the optical and mechanical properties of the semi-IPN formed. With multifunctional acrylic esters dispersed in various binders, phase separation was found to occur during photopolymerisation, leading to non-transparent films.[179,180]

Clear coatings were obtained by UV curing of a triacrylate monomer (TMPTA) dispersed in poly(vinyl chloride) (PVC), poly(methyl methacrylate) (PMMA), or aliphatic polyurethanes.[184,185] The polymerisation kinetics was studied quantitatively by monitoring acrylate conversion, the insolubilisation and the hardness increase of the irradiated samples.

Figure 30 shows some typical kinetic profiles for a 50/50 TMPTA/PVC blend exposed to UV radiation in the presence of air, by using an hydroxy-alkylphenone photoinitiator. It can be seen that, after only 0.1 s, half of the acrylate double bonds of TMPTA have already polymerised, while 40% of the sample has become insoluble. At the same time the elastomeric PVC, plasticised by the triacrylate monomer, has been transformed into a high-modulus and very hard material (Persoz hardness = 350 s, compared to 400 s for mineral glass). Such a photoforming process has the advantage over thermoforming for allowing moulding to be performed at ambient temperatures in a very short time by simple exposure to UV radiation or even sunlight.

Further irradiation leads to a slower but steady increase of the degree of conversion and of the gel fraction, which levels off after about 2 s exposure at 80 and 95%, respectively. The fact that more than 50% (the original binder content) of the photocured sample was found to become insoluble was taken as a strong argument in favour of a grafting process, probably through a chain transfer reaction.



This result is in good agreement with previous studies on the photoinitiated polymerisation of an acrylate resin coated onto a PVC substrate that had already provided conclusive evidence in favour of such a chemical grafting, which leads to improved adhesion.[186] DSC experiments have fully confirmed this conclusion in showing that a large fraction of the PVC binder is bonded to the acrylate polymer network. The glass transition temperature of the UV-cured TMPTA/PVC semi-IPN was found to be about 130°C, between that of PVC (80°C) and that of poly(TMPTA) (150°C).[14]

Similar results have been obtained by exposing TMPTA to UV radiation in a PMMA matrix.[185] Here again, the unexpectedly high degrees of conversion (75%) and of insolubilisation (93%) were explained on the basis of an efficient chain transfer reaction involving the labile hydrogens of the PMMA chains.

The same UV technology has been used to produce a true IPN by polymerisation of a multifunctional monomer that has been introduced into a pre-swollen polymer network.[185] Because TMPTA generates upon polymerisation a hard and glassy polymer, an elastomeric material was used for the pre-existing polymer network. It was rapidly produced by UV-curing of a liquid urethane diacrylate oligomer. A short irradiation (0.5 s) of the TMPTA swollen urethane polymer induces the polymerisation of the triacrylate monomer and generates the second IPN. Owing to its method of preparation, the final product consists of an entanglement of two very different polymer networks, one composed of elastomeric polyurethane chains and the other of stiff TMPTA crosslinking segments. As a result, the acrylate-reinforced polyurethane film was found to be hard and flexible at the same time, and resistant to scratching, abrasion and shock.

9. LASER-INDUCED CROSSLINKING POLYMERISATION

Processing by laser is becoming increasingly popular as an advanced technology. This is due to the distinct features of these powerful sources of coherent radiation and, also, to the recent development of high-performance, low-cost lasers with longer lifetimes. By using lasers that emit in the UV or visible region, ultrafast photochemical reactions can be carried out in well-defined areas. Thus, multifunctional monomers, such as those used in UV-curable resins, have been polymerised quasi-instantaneously to produce highly crosslinked polymeric materials[53,54,58,86,91,121,122,128,187–200] (for a recent survey on laser curing and imaging see Ref. 200).

The most promising applications of laser-induced curing are to be found in sectors where ultrafast cure must be achieved on demand in localised areas. Examples include micro-lithography, holography, three-dimensional imaging and certain coating applications.

9.1. *Basic aspects of laser-induced curing*

One of the great advantages of radiation curing is the rapidity of the curing process, with extensive crosslinking usually being achieved within a single second. In the continuing search for higher cure rates, lasers appear to represent the ultimate light source to provide quasi-instantaneous polymerisation and allow operation at extremely high line speeds.

In addition to their great power output, lasers offer a number of other advantages which make them very attractive for curing applications. A laser emits light coherently, which means that all the photons possess exactly the same energy and are travelling in the same direction, with their waves in phase with each other. The spatial coherence of the laser emission is responsible for the great directivity of the beam that can be focused down to a tiny spot of micronic dimensions. Such a sharp focus enables the generation of high resolution patterns, either by scanning a photosensitive material with a modulated beam or by using an X–Y direct writing device.

Another consequence of the collimated light beam is that the light intensity does not increase with increasing distance from the laser. This enables uniform illumination of large, non-planar objects at a distance, by scanning evenly with the laser beam. The temporal coherence of the laser emission, which occurs at a precise wavelength, reduces undesirable secondary reactions induced by polychromatic radiation, whilst allowing for accurate control of the depth cure.

Finally, the speed of generation of the reactive species not only leads to high rates of cure, but also reduces susceptibility to oxygen inhibition as a result of the ultrashort exposure. The performance characteristics and advantages of laser-induced curing are summarised in Fig. 31.

9.2. *Types of laser-curable resins*

The types of photosensitive resins used in laser-curing applications are essentially the same as those commonly employed in UV-curable formulations. The key component is the photoinitiator, which must absorb the monochromatic laser emission. Laser-curable resin systems contain two basic components:

a photoinitiator, which generates reactive free radicals or ions, and
a multifunctional monomer, which, on polymerisation, produces a highly crosslinked and insoluble polymer network.

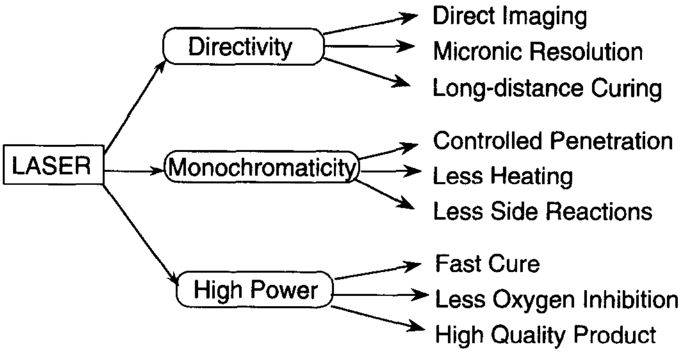


Fig. 31. Performance characteristics of laser-induced curing.

Of the various types of photocurable resins available, acrylate-based systems have become the most widely employed due to both their high reactivity and the extensive range of commercial monomers and pre-polymers that can be obtained. It is no surprise, therefore, that the potential for laser technology in quasi-instantaneous curing has been evaluated first on acrylate-based photoresists.[187,188] Other laser-induced photoreactions, which can serve to generate crosslinked polymer matrices, include the addition of multifunctional thiols to polyenes, and the cationic polymerisation of multifunctional epoxides and vinyl ether monomers.

One of the great advantages of using lasers as light sources is that the decrease in curing rate, as chain propagation becomes increasingly hindered during solidification, can be compensated for by the higher rate of initiation afforded by the intense laser irradiation. Semi-interpenetrating networks have been produced within milliseconds by exposing triacrylate monomers in a polymer matrix to a UV-laser beam.[201]

9.3. *Reaction kinetics*

In order to obtain a better understanding of the curing mechanisms, some knowledge of the fundamental kinetic parameters that govern such ultrafast processes is essential. In particular, the rate constants for the propagation and termination reactions (k_p and k_t, respectively), as well as the kinetic chain length of the polymerisation, are important. These quantities can be best determined from the cure profile obtained by monitoring in real time the consumption of the reactive functional groups (observed through the disappearance of the appropriate infrared absorption bands). Figure 32 shows a typical conversion-versus-time curve, recorded for a polyurethane acrylate photoresist exposed to a krypton ion laser beam. From such a curve, it is possible to determine the precise amount of polymer formed at any stage in the reaction and to evaluate the kinetic chain length.

For the most reactive acrylate photoresists studied, it has been determined that each initiating radical is capable of inducing the polymerisation of as many as 50,000 double bonds in oxygen-free systems.[52] Such high efficiencies are the result of both an extensive propagation reaction (high k_p) and a rather inefficient termination step (low k_t), with the latter process being the more strongly affected by the drop in molecular mobility resulting from the change from liquid to solid phase. Crosslinking also leads to insolubilisation,

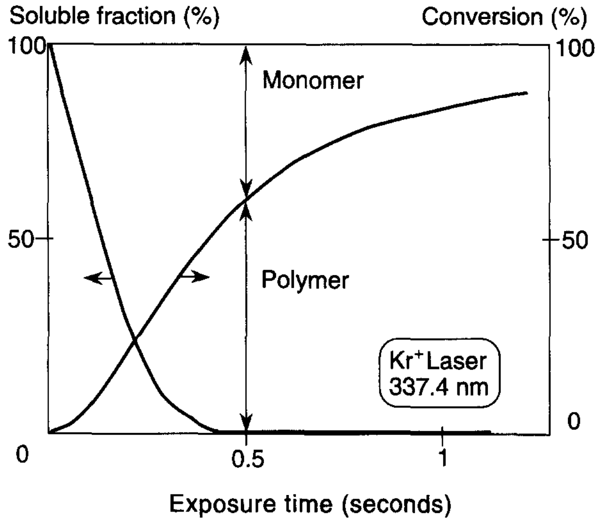


Fig. 32. Polymerisation and insolubilisation of a polyurethane/acrylate photoresist exposed to a 100 mW laser beam.

which is usually achieved at degrees of conversion of 20–60%, depending on the functionality of the monomer and the molecular weight of the prepolymer (Fig. 32). Since insolubilisation occurs only in the exposed areas, high-resolution relief areas are obtained after development in a solvent by scanning the photosensitive sample with a focused laser beam. This scanning can be performed at very high speeds — up to 1000 m/s for acrylate photoresists[86] — because of the great chemical amplification factor.

One of the key observations made by RTIR kinetic studies of laser-induced curing of multifunctional acrylates is that the actual rate of polymerisation reaches an upper limit as the light intensity is greatly increased (Fig. 21). Such saturation effects may reduce the interest and potential for laser curing in industrial applications, particularly for laser direct imaging where the photosensitive plate is exposed to a very intense focused laser beams.

A post-polymerisation study performed at various light intensifies has shown that the dark reaction proceeds much more efficiently after intense illumination.[53] Figure 33 shows the RTIR traces recorded for an acrylate photoresist exposed to the UV emission of a Kr$^+$ laser operated at a power output of either 100 mW cm^{-2} or 1 W cm^{-2}. The same polymerisation profile was observed upon continuous exposure at these two light intensities, thus clearly demonstrating the diffusion-controlled rate limitation effect. When the sample was exposed to a single 30 ms wide laser flash, a different behaviour was observed that depended upon the laser power output. The dark polymerisation was found to develop much more effectively at 1 W cm^{-2} than at 100 mW cm^{-2}, with a kinetic profile close to that recorded for continuous exposure.

It may be noticed that, under intense illumination, most of the polymer is being formed after the laser exposure. These results can be accounted for by considering that a greater number of radicals has been produced during the 1 W cm^{-2} irradiation, thus allowing the dark polymerisation to develop more extensively as expected from the rate equation:

$$R'_p = k_p[P\cdot][M]_t$$

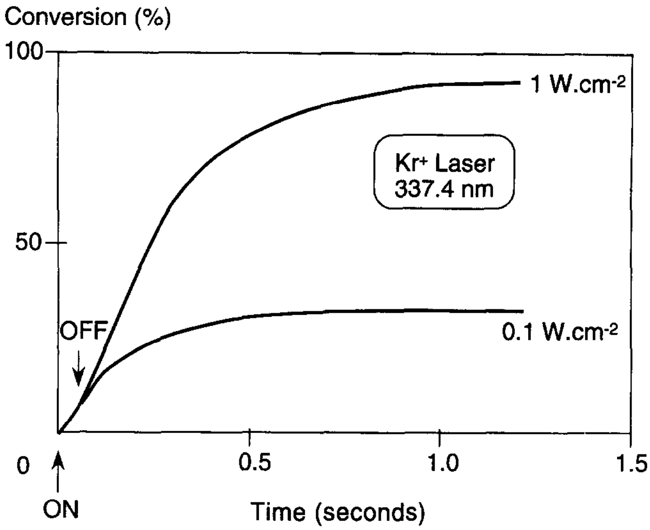


Fig. 33. Influence of the light intensity on the polymerisation of an acrylate photoresist exposed to a Kr^+ laser beam during 50 ms.

A practical consequence of this light intensity effect is that efficient curing can be achieved by a short and intense exposure, such as by fast scanning with a CW laser beam, or by the ultrashort flashes emitted by pulsed lasers.

9.4. *Properties of laser-cured materials*

Laser-cured polymers exhibit essentially the same characteristics as corresponding materials cured by conventional UV radiation. This observation was initially unexpected, since it was believed that high temperatures are reached under laser exposure. In fact, the temperature increase derives mainly from the curing process itself, which has been shown to follow the same kinetic profile at all times, once the light intensity exceeds a value of around 100 mW cm^{-2}.[107] Consequently, a given material cured under varying but, nevertheless, intense irradiation conditions will exhibit the same temperature profile in each case and, thus, similar physico-chemical characteristics. For example, similar polymerisation profiles were recorded by RTIR spectroscopy for a polyurethane/acrylate resin that was exposed to UV radiation either from a mercury lamp (0.3 W cm^{-2}) or from a pulsed nitrogen laser (10^5 W cm^{-2}).[91]

The mechanical properties of laser-cured polymers depend primarly on the chemical structure, functionality and concentration of the individual constituents. Crosslinked polymers containing aliphatic polyurethane chains tend to show strong elastomeric character, with low glass transition temperatures and good impact resistance. Such low-modulus polymers are ideally suited for the protection of surfaces of flexible supports. By contrast, polymer networks containing aromatic polyether or polyester chains are hard and stiff. These materials demonstrate good resistance to chemicals and scratching, and are best suited for topcoating applications. Depending on the particular intended end-use, laser-cured polymers with properties intermediate between these two extremes can be obtained

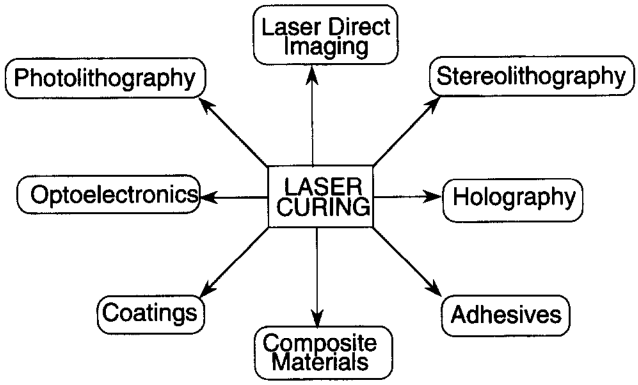


Fig. 34. Applications of laser curing.

by acting on the reactive diluent, and by careful mixing of urethane acrylate and phenoxy acrylate pre-polymers.

9.5. *Applications of laser curing*

Laser-induced polymerisation technology is likely to find its main industrial applications in areas where the high cost of laser operations is outweighted by the distinct advantages of the intensity of the emission (e.g. high cure rates, high imaging resolution, high levels of penetration into organic materials). Major developments of this advanced technology are currently underway in the various industrial application sectors shown on Fig. 34.

9.5.1. *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 circuits boards, whilst continuous lasers are better suited to the direct production of patterns of small size.[202] Laser direct imaging (LDI) technology offers the combined advantages of the elimination of the use of costly masks, greater flexibility in the production of microcircuits with sharper lines and fewer defects.[86,203,204]

9.5.2. *Optoelectronics*

LDI technology can also serve to produce optical waveguides in thin layers of photopolymer films.[205] These devices can act as optical interconnects for information transmission and processing systems. The use of fluorinated acrylate monomers leads to high transparencies and, following curing, to the ability to withstand prolonged exposures to intense laser beams. This is combined with a level of heat-resistance greater than that of poly(methyl methacrylate).[54] Optical designs of micronic dimensions can, thus, be drawn at high speeds on photosensitive plates, by means of a computerised laser beam.[91]

9.5.3. *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.[206] Furthermore, this transformation is limited to those specific areas exposed to the laser beam. A novel technology, known as stereolithography, takes advantage of these features to create three-dimensional solid objects.[207,208] This is achieved 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 dyes and cutting tools, stereolithographic or 3D-imaging technology has proven to be of considerable interest in various industrial sectors for the rapid prototyping of solid objects.[209,210]

9.5.4. *Holography*

Laser-sensitive polymers are finding increasing use as recording media for the production of 3D pictures or for holographic interferometric measurements of small deformations or objects subjected to stress.[211] The laser-induced polymerisation causes a change in the refractive index, as a result of the shrinkage accompanying the change from liquid to solid phase.

The main interest of photopolymer holography is that it requires no solvent development and exhibits a wide range of spectral sensitivity, from the deep-UV region to the near-infrared.

9.5.5. *Miscellaneous applications*

Other applications of laser-induced curing that take advantage of the great power output of lasers are expected to emerge in the near future

9.5.5.1. *Coating of optical fibres by laser-curable resins* – 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.[212]

9.5.5.2. *Laser curing of dental composites* – The use of lasers instead of conventional light sources speeds up the hardening process, whilst simultaneously increasing penetration into the composite formulation.[212,213]

9.5.5.3. *Laser curing of adhesives* – Two pieces of an assembly can be instantly 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. Typically, photocurable structural adhesives are composed of either liquid acrylate resins or functionalised thermoplastic polymers.[214]

Laser curing is a relatively new technology that has found major applications in high-tech industrial sectors. The growing interest in laser-induced polymerisation processes is largely attributable to the unique performances achieved when using intense beams of coherent light.[215] The economic prospects of laser-processing technology will depend primarily upon further advances in the understanding and control of fundamental processes in such ultrafast reactions, together with the development of reliable and low-cost lasers suitable for safe application within the chemical industry.

10. CONCLUSIONS

In this review article, an attempt has been made to give a survey of the present situation in the field of photoinitiated crosslinking polymerisation, without pretending to achieve an exhaustive coverage. The photopolymerisation of multifunctional monomers remains one of the fastest and most efficient methods available to generate three-dimensional polymer networks. Because of its distinct advantages regarding process facility and product quality, radiation curing technology has found major openings in the coating industry and in photolithography.

Significant progress has been achieved in recent years with the development of very efficient photoinitiators and highly reactive monomers and telechelic oligomers capable of generating polymeric materials with specific, tailor-made properties upon curing. The performance of such novel compounds is best assessed by real-time infrared spectroscopy, a technique that allows one to monitor continuously the rapid formation of the polymer on the millisecond timescale. The important kinetic parameters of different types of light-induced polymerisations have thus been determined *in situ* under the same conditions as those used in most industrial applications. Such evaluations, together with mechanistic studies, are necessary for a better understanding and control of the manifold processes involved in ultrafast photocuring reactions.

In consideration of the many advantages that are to be gained by using UV and laser-curable systems, it is anticipated that this advanced technology will continue to expand and attract attention in an ever growing number of industrial sectors.

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