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## KINETIC STUDY OF ULTRAFAST PHOTOPOLYMERIZATION REACTIONS

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### ABSTRACT

The photopolymerization kinetics of UV-curable polyurethane-acrylate resins has been studied by real-time infrared spectroscopy (RT-IR). From the conversion versus time curves recorded during and after UV exposure, the rate constants of propagation ( $k_p$ ) and termination ( $k_t$ ) reactions were determined at different stages of the curing process. The  $k_p$  value was shown to remain fairly constant at about  $10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ , until 30% conversion, and to decrease later on due to gelation and related molecular mobility restrictions. The increasing viscosity of the medium undergoing polymerization was found to have a stronger effect on the  $k_t$  value, which decreased rapidly from the very beginning of the irradiation. The proportionality of  $k_p$  and  $k_t$  observed above 10% conversion was taken as evidence of a termination process occurring by a reaction diffusion mechanism. The rate of polymerization was found to increase with the light intensity up to an upper limit above which the reaction kinetics is not controlled by the initiation rate but only by the diffusion rate of the reactive species. The temperature profile has also been recorded by RT-IR spectroscopy and shown to correlate well with the cure profile. The increase of the temperature shows the same light intensity dependence as the polymerization rate and levels at a maximum value under very intense illumination.

## INTRODUCTION

The light-induced polymerization of multifunctional monomers is known to be one of the most efficient methods to generate rapidly polymer networks of high crosslink density. It takes generally less than 1 second under intense illumination to pass from the liquid molecule to the solid polymer material. Although UV-radiation curing has now become a well-accepted technology which has found numerous industrial applications, the basic mechanism of crosslinking polymerization is far from being fully understood. A number of kinetic investigations have been reported in recent years on the widely used acrylate monomers [1–9], but the polymerization experiments were generally carried out at low light intensities in a time scale of minutes rather than seconds because of the poor response time of calorimetric analysis [4].

Quantities which must be known to gain deeper insight into the photocuring process are the rate constants of both the propagation reaction ( $k_p$ ) and the termination reaction ( $k_t$ ). Indeed, it is the values of  $k_p$  and  $k_t$  which will govern the kinetics of polymerization, the extent of overall cure and therefore the final properties of the polymer material. The difficulty is that, despite their names, these constants change during the curing reaction due to important viscosity variations brought on by the liquid to solid phase change. The values of  $k_p$  and  $k_t$  were determined by Tryson and Shultz for the bulk photopolymerization of multiacrylate monomers exposed to low intensity UV radiation [5]. Most of the UV-curable resins used in industrial applications are made of a mixture of a telechelic polymer and a multifunctional monomer which acts as a reactive diluent. Polyurethane-acrylates are among the most employed telechelic polymers, mainly to produce fast drying coatings and adhesives, because of their elastomeric character and their great resistance to abrasion, impact, and scratching.

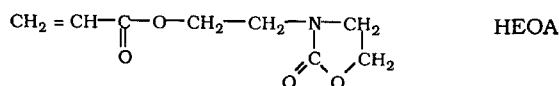
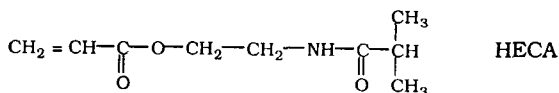
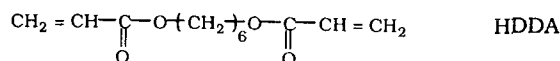
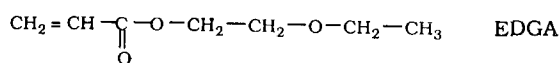
The objective of this work was to evaluate the propagation and termination rate constants in a typical UV-curable polyurethane-acrylate resin exposed to intense UV-radiation, and to quantify their variation as a function of the degree of conversion. This was made possible by following the reaction in real time by means of infrared spectroscopy (RT-IR), a technique which allows conversion versus time profiles to be directly recorded for polymerizations occurring in a fraction of a second [6, 7]. This technique has also the distinct advantage of permitting the actual rate of polymerization ( $R_p$ ) to be determined at any stage of the process. By studying the variation of  $R_p$  with the light intensity, we show that the polymerization rate ultimately reaches an upper limit value once the cure kinetics becomes controlled by the diffusion of the reactive species and not by the initiating rate anymore. This finding has important consequences on the temperature of the sample undergoing polymerization as well as on the ultimate cure extent, quantities which both level off under intense illumination.

## EXPERIMENTAL

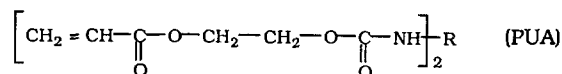
### Materials

Different types of acrylate monomers from SNPE, whose structures are shown on Fig. 1, were copolymerized with an acrylate telechelic polyurethane in order to evaluate the propagation and termination rate constants of such typical UV-curable

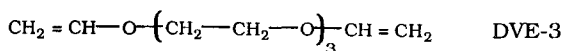
## ACRYLATE MONOMERS



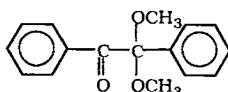
## TELECHELIC POLYURETHANE-ACRYLATE



## VINYL ETHER MONOMER



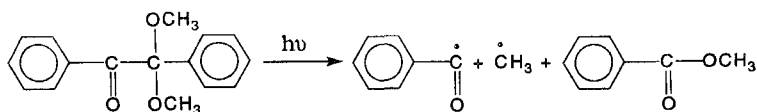
## PHOTOINITIATOR

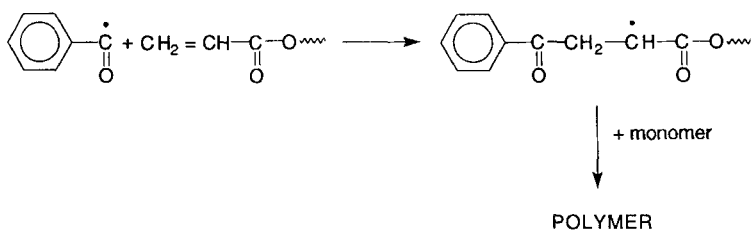


DMPA

FIG. 1. Chemical formulas of the various monomers used.

resins. The light-induced polymerization was performed in a 1/1 mixture of a polyurethane-diacrylate oligomer (Actilane 20 from SNPE) with one of these monomers by using as photoinitiator the dimethoxyphenylacetophenone, DMPA (Irgacure 651 from CIBA), at a concentration of 3% by weight. This compound absorbs UV radiation of wavelength below 365 nm, and by photolysis effectively generates benzoyl and methyl radicals which are highly reactive toward the acrylate double bond.





Some UV-curing experiments were also carried out with a bis-arylphosphine oxide photoinitiator, BAPO, recently developed by CIBA (Irgacure 700), which proved to be even more efficient than DMPA. For the cationically photoinitiated polymerization of the divinyl ether of triethyleneglycol (DVE-3 from ISP), a triaryl-sulfonium salt was used as photoinitiator (Cyracure UVI-6990 from Union Carbide). DVE-3 was also copolymerized with a low molecular weight unsaturated polyester ( $M_w = 2000$ ) containing maleate double bonds.

### Irradiation

The liquid formulation was applied as a uniform film of controlled thickness by a calibrated wire-wound applicator. Films typically of  $25 \mu\text{m}$  thickness were coated on a KBr disk for infrared analysis. Samples were exposed to the radiation of a 200-mW medium pressure mercury lamp (HOYA-SCHOTT HLS-210 U) using a specially designed  $\text{N}_2$ -flushed photocell equipped with  $\text{BaF}_2$  windows. At the sample position, the light-intensity, measured by radiometry, was typically  $20 \text{ mW}\cdot\text{cm}^{-2}$ . It could be varied in the 5 to  $200 \text{ mW}\cdot\text{cm}^{-2}$  range by acting on the UV beam intensity through an iris diaphragm.

### Analysis

The method used to study the kinetics of such ultrafast polymerization reactions, real-time infrared spectroscopy (RT-IR), has already been described [5, 6]. The sample was exposed simultaneously to the UV beam, which induces the polymerization, and to the analyzing IR beam, which monitors the drop of the absorbance of the reactive group. The spectrophotometer was operated in the absorbance mode, and the detection wavelength set either at  $812 \text{ cm}^{-1}$ , where acrylate monomers show a distinct and sharp peak ( $\text{CH}_2=\text{CH}$  twisting), or at  $1628 \text{ cm}^{-1}$  for the vinyl ether monomer ( $\text{CH}_2=\text{CH}$  stretching). The decrease of the sample absorbance upon irradiation was monitored in real time on a transient memory recorder or on a personal computer. Because the IR absorbance is proportional to the monomer concentration, conversion versus time profiles are then directly obtained from the curves recorded.

The same technique was used to record the temperature profile of a sample undergoing photopolymerization. In this case the resin was coated on a polypropylene (PP) sheet and covered by a second polypropylene sheet of  $20 \mu\text{m}$  thickness. The variation of the PP peak at  $843 \text{ cm}^{-1}$  ( $\text{CH}_3$  rock) was monitored by RT-IR spectroscopy upon UV exposure. The intensity of this peak was shown to depend on the temperature, so that the IR absorbance value could be related to a temperature value through a calibration curve.

### BASIC INVESTIGATION OF THE PHOTOPOLYMERIZATION

The bulk polymerization of multifunctional monomers is a complex process which exhibits a number of anomalous behaviors with respect to the reaction kinetics [8, 9]:

An *autoacceleration* 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 of the radical concentration and hence of the polymerization 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 polymerization, which ultimately stops before completion due to vitrification. The UV-cured polymer will therefore contain a certain amount of functional groups which have not polymerized, as well as trapped radicals [10, 11].

A *termination process controlled by reaction diffusion* [12, 13] and not by segmental diffusion as in linear polymerization. Most polymeric radicals in crosslinking polymerization are bound to the 3-D network and have a limited mobility, so that the radical site will move mainly by reacting with neighboring functional groups until it combines with another such 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 [14]. They result from fast polymerization of the pendant double bonds due to their great concentration in the vicinity of the radical site [8]. Kinetic gelation models have shown the effects of the reaction behavior on the network microstructure and on the material properties [15].

The *physical effect of volume shrinkage* on the polymerization kinetics, which leads to higher final degrees of conversion at large reaction rates [11]. At the high initiation rate provided by UV irradiation, the polymerizing system cannot maintain its volume equilibrium because volume shrinkage occurs in a much slower time scale than the chemical reaction. The time lag between conversion and shrinkage generates a temporary excess of free volume which increases the mobility of unreacted double bonds, thus allowing higher degrees of conversion to be reached than in volume equilibrium systems [8].

The three stages of the curing process can be recognized on a kinetic profile such as that represented in Fig. 2, which shows a typical conversion versus time curve recorded by RT-IR spectroscopy for a photocurable polyurethane-acrylate resin exposed to the UV radiation of a medium pressure mercury lamp in the absence of air. The reaction kinetics was followed in real time by monitoring the decreases of the IR absorption at  $812\text{ cm}^{-1}$  of the acrylate double bond. The degree of conversion ( $\tau$ ) is defined as the ratio of the amount of acrylate double bonds which have polymerized after a given exposure to the original acrylate content. The three steps become more apparent when the rate of polymerization ( $R_p$ ) is plotted as a function of the exposure time.  $R_p$  is easily calculated at any time from the slope of the RT-IR curve ( $d\tau/dt$ ) and the initial acrylate double bond concentration  $[A]_0$ :

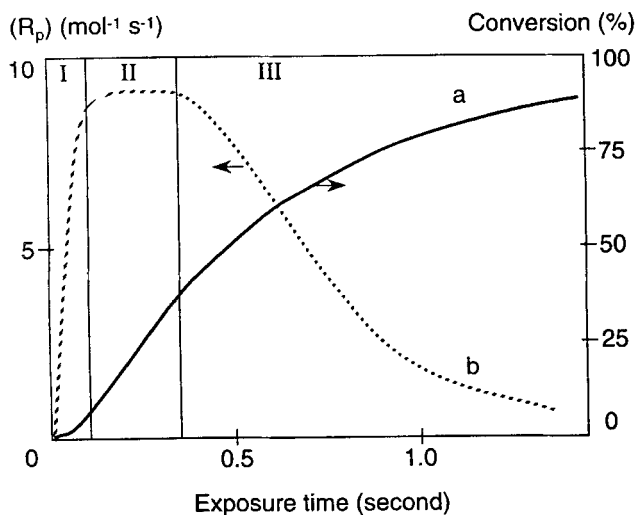


FIG. 2. Photoinitiated polymerization of a polyurethane acrylate resin. Curve a: conversion profile recorded by RT-IR spectroscopy. Curve b: variation of the actual rate of polymerization with exposure time. Light intensity:  $I = 35 \text{ mW} \cdot \text{cm}^{-2}$ .

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

Autoacceleration occurs at the very beginning of irradiation because of the fast increase in viscosity until at about 5% conversion when the reaction reaches its maximum value  $(R_p)_{\text{max}}$ . This is followed by a period where the polymerization develops at a sustained pace for 0.3 second (about 30% conversion), 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.

Both the propagation and termination rate constants are known to play key roles in bulk polymerization because they control the chemical reaction which induces severe changes in viscosity and molecular mobility. Such changes affect the rate constants in turn, so that it is important to know how  $k_p$  and  $k_t$  vary with the extent of cure. While the photopolymerization kinetics of multifunctional acrylic monomers has been thoroughly studied [4, 5, 8, 12], there is only scant information about the rate constants of the copolymerization of such monomers with telechelic polymers, which is the actual process occurring in most UV-curable formulations.

### EVALUATION OF PROPAGATION AND TERMINATION RATE CONSTANTS

The polymerization rate constants  $k_p$  and  $k_t$  were determined in a typical UV-curable polyurethane-acrylate resin by continuously monitoring by RT-IR spectroscopy the variation of the degree of conversion, first during UV exposure and then in the dark when new initiating radicals are no longer created [5, 16].

### Polymerization under UV Exposure (steady-state analysis)

The rate of polymerization is expected to obey the following equation after a given exposure time ( $t_i$ ):

$$(R_p)_{t_i} = \frac{k_p}{(2k_t)^{0.5}} \times [A]_{t_i}(\phi_i I_a)^{0.5} \quad (1)$$

where  $\phi_i$  is the initiation quantum yield,  $I_a$  is the intensity of the light absorbed by the sample, and  $[A]_{t_i}$  is the concentration of the acrylate double bonds remaining after irradiation during time  $t_i$ .

### Dark Polymerization (nonsteady-state analysis)

Once the light has been switched off, the polymerization will continue to proceed for some time at a steadily decreasing rate. The concentration of the polymer radicals will decrease according to a hyperbolic law, assuming bimolecular termination:

$$-d[P^\cdot]/dt = 2k_t[P^\cdot]^2 \quad \text{or} \quad \frac{1}{[P^\cdot]} = 2k_t \times t + \frac{1}{[P^\cdot]_0} \quad (2)$$

where  $[P^\cdot]_0$  is the radical concentration at the end of the exposure:

$$(R_p)_{t_i} = k_p[P^\cdot]_0[A]_{t_i} \quad (3)$$

The polymer radical concentration  $[P^\cdot]$  can also be expressed as a function of the rate of the dark polymerization  $(R_p)_{t_i+t}$  reached at given time  $t$  after the exposure:

$$[P^\cdot] = (R_p)_{t_i+t}/k_p[A]_{t_i+t} \quad (4)$$

By replacing  $[P^\cdot]$  and  $[P^\cdot]_0$  in Eq. (2), one finally obtains the rate equation of the dark reaction:

$$\frac{[A]_{t_i+t}}{(R_p)_{t_i+t}} = \frac{2k_t}{k_p} \times t + \frac{[A]_{t_i}}{(R_p)_{t_i}} \quad (5)$$

All these quantities can be easily determined from the RT-IR profile recorded during and after UV exposure (Fig.3). A plot of the left-hand term of Eq. (5) versus the duration of the dark period ( $t$ ) gives a straight line (Fig. 4). Its slope corresponds to the  $2k_t/k_p$  ratio. Its value was found to drop as the exposure time was increased, which means that gelation has a stronger slowing down effect on the termination step than on the propagation step. Individual values of  $k_p$  and  $k_t$  can then be calculated from the ratios  $k_p/(2k_t)^{0.5}$  and  $2k_t/k_p$  obtained under steady-state and nonsteady-state conditions, respectively.

As pointed out by the reviewer, values of  $k_p$  and  $k_t$  determined by this method actually represent averages over the duration of the dark period because of the significant changes in the reaction medium that will accompany the increase in conversion during this time.

This kinetic approach was used to determine  $k_p$  and  $k_t$  values for a polyurethane-acrylate resin containing, in a 1-to-1 weight ratio, one of the following acrylate monomers as the reactive diluent:



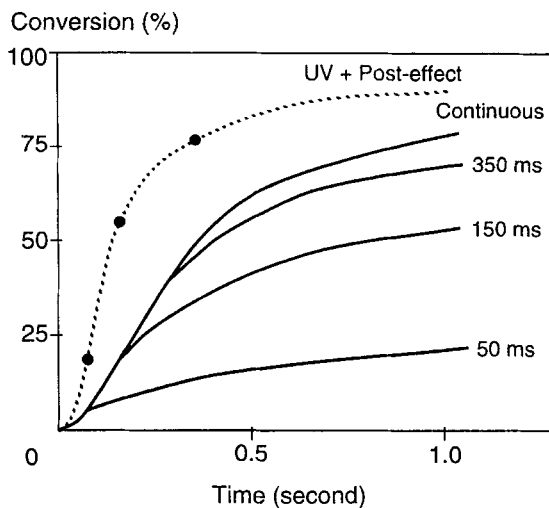


FIG. 3. Polymerization profiles recorded by RT-IR spectroscopy upon UV exposure of a polyurethane acrylate resin during 50 ms, 150 ms, 350 ms, and 1 s (---): overall conversion after UV irradiation and postpolymerization.  $I = 20 \text{ mW} \cdot \text{cm}^{-2}$ .

- EDGA: ethyldiethyleneglycol monoacrylate  
 HDDA: hexanediol diacrylate  
 HEOA: hydroxyethyl-oxazolidone monoacrylate  
 HECA: hydroxyethyl-carbamate monoacrylate

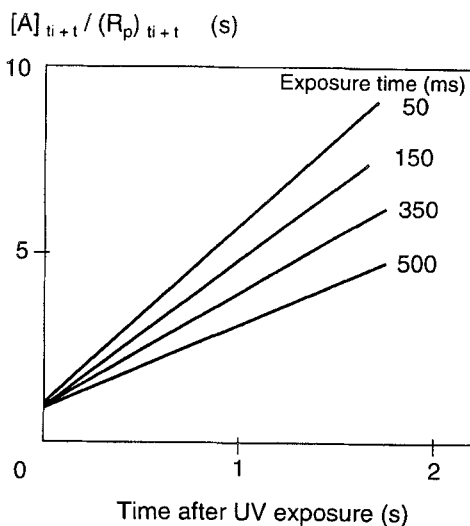


FIG. 4. Determination of the ratio  $k_t/k_p$  by nonsteady-state analysis of a polyurethane-acrylate. Irradiation during 50, 150, 350, and 500 ms.  $I = 20 \text{ mW} \cdot \text{cm}^{-2}$ .

Dimethoxyphenylacetophenone was used as the photoinitiator at a concentration of 3%.

Figure 5 shows the variation of  $k_p$  and  $k_t$  with the extent of the polymerization process. A very similar behavior has been recently observed for acrylate and methacrylate multifunctional monomers [9]. Termination is controlled in the initial stage by radical diffusion, and  $k_t$  drops rapidly because of the build up of the polymer network (for monoacrylate monomers,  $k_t$  is typically on the order of  $10^7 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ ). Increasing double bond conversion decreases the radical diffusivity and, hence, the termination constant. Above 10% conversion the radical diffusivity has become so low that termination occurs through reaction diffusion rather than segmental diffusion. The propagation step is initially reaction-controlled, with a relatively constant value of  $k_p$  on the order of  $10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  for the four systems studied. Above 30% conversion, propagation becomes diffusion-controlled due to the strongly reduced mobility of the acrylate function.

The fact that  $k_t$  was found to be proportional to  $k_p$  for conversions above 10% (Fig. 6) is a clear indication of a termination mechanism proceeding by reactive

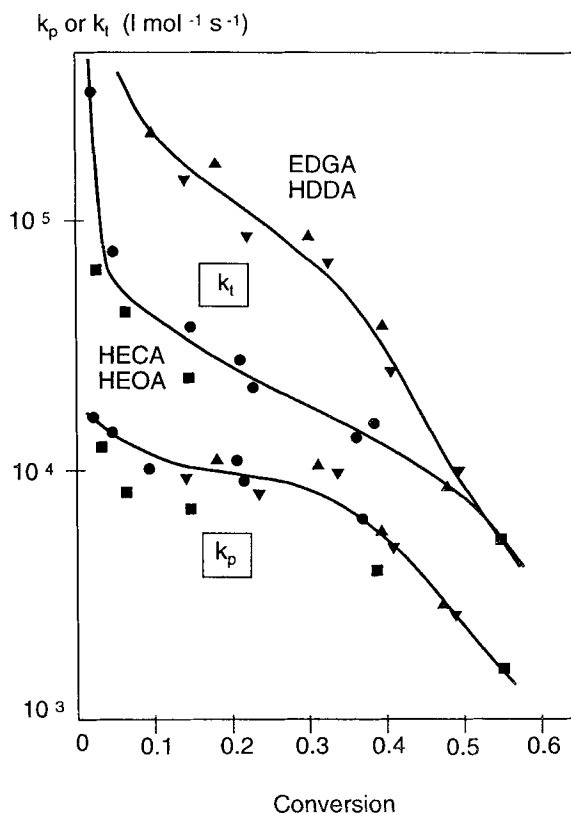


FIG. 5. Variation of the rate constants of propagation ( $k_p$ ) and termination ( $k_t$ ) with the degree of conversion for a UV-curable polyurethane-acrylate containing different types of monomers in a 1/1 ratio. EDGA ( $\nabla$ ), HDDA ( $\blacktriangle$ ), HECA ( $\bullet$ ), HEOA ( $\blacksquare$ ).  $I = 20 \text{ mW} \cdot \text{cm}^{-2}$ .

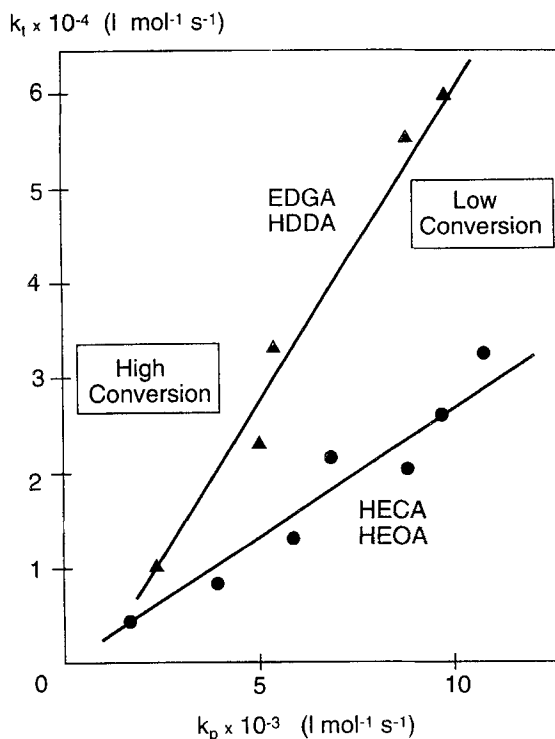


FIG. 6. Linear dependence of the termination rate constant with the propagation rate constant for different UV-curable polyurethane-acrylate formulations.  $I = 20 \text{ mW} \cdot \text{cm}^{-2}$ .

diffusion in the photocuring of these polyurethane-acrylate resins. The large reactivity of the formulations based on HEOA and HECA monomers, which was previously observed [17], appears to be due mainly to a poorly efficient termination process, with  $k_t$  values nearly five times lower than for the HDDA- or EDGA-based formulations (Fig. 5). As a result, the dark polymerization develops much more extensively with these novel acrylate monomers, the degree of conversion rising from 25% just after a short UV exposure up to 75% after a few minutes of storage in the dark, compared to only 36% for the HDDA- and EDGA-based resins (Fig. 7). This behavior bears some analogy with that observed in photoinitiated cationic polymerization [18] where the dark reaction develops extensively after UV exposure up to total monomer consumption in the case of vinyl ethers (Fig. 7).

### INFLUENCE OF THE LIGHT INTENSITY ON THE POLYMERIZATION KINETICS

Both the autoacceleration and autodeceleration processes are kinetically controlled by the photoinitiator concentration, the temperature, and the light intensity. The latter factor has the strongest effect because  $I_0$  can be varied in a very large range, from  $0.1 \text{ mW} \cdot \text{cm}^{-2}$  up to  $1 \text{ W} \cdot \text{cm}^{-2}$  for the high powered mercury lamps

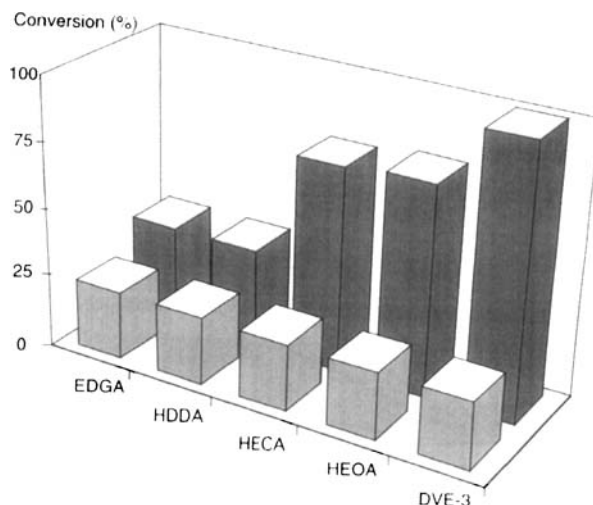


FIG. 7. Importance of dark polymerization for various UV-curable resins irradiated up to 25% conversion.  $I = 20 \text{ mW} \cdot \text{cm}^{-2}$ . Light shading: conversion just at the end of the exposure. Dark shading: conversion after 10 minutes of storage in the dark at ambient temperature.

currently used on industrial UV-curing lines. It was shown previously that the rate of polymerization rises rapidly in the course of the curing process up to a maximum value,  $(R_p)_{\text{max}}$ , and decreases steadily later on (Fig. 2). The objective of this study was to determine the light-intensity dependence of the polymerization rate and of the extent of cure in photosensitive resins.

Figure 8 shows the polymerization profiles recorded by RT-IR spectroscopy for a polyurethane-acrylate resin irradiated at various light intensities. The curing reaction developed both faster and more extensively as  $I_0$  was increased, up to a certain value above which identical RT-IR curves were recorded.  $(R_p)_{\text{max}}$  thus reaches an upper limit value for light intensities superior to  $100 \text{ mW} \cdot \text{cm}^{-2}$  (Fig. 9, Curve a). This saturation effect is not due to some limitation of the RT-IR technique because the response time of IR detection (40 ms) is short enough to allow even faster processes to be monitored (Fig. 8). It thus appears that even with the most reactive formulation exposed to intense UV or laser radiation, the liquid-to-solid phase change will require at least 0.2 second to take place.

The reasons of this rate upper limit are not fully understood, but they are likely to be related to molecular mobility restrictions in viscous systems undergoing gelation [19] [ $(R_p)_{\text{max}}$  is still measured in the early stage of the reaction, typically below 10% conversion]. Indeed, above a certain value of light intensity, when the initiation rate becomes very large, polymerization is not controlled by the rate at which radicals are produced but by the diffusion of the reactive species, which will then become the limiting factor. The RT-IR curve recorded under those conditions will therefore reflect the maximum rate at which the polymer chains can grow. The value of the rate limit,  $(R_p)_{\text{lim}}$ , will depend, among other factors, on the viscosity of the resin. It was found to increase from  $17 \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$  for the viscous polyurethane-acrylate resin to  $22 \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$  for a more fluid diacrylate formulation

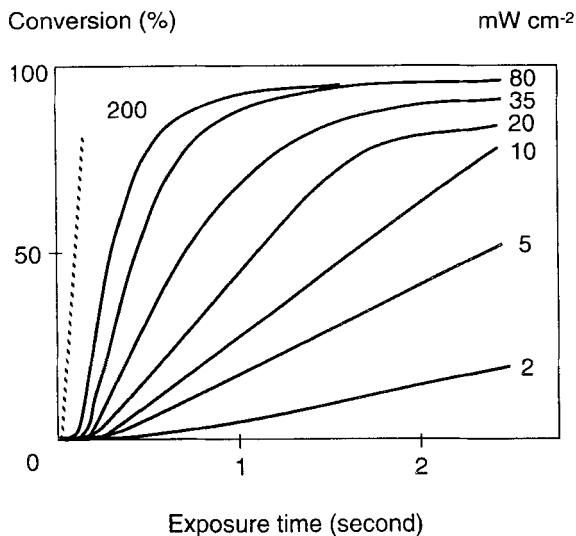


FIG. 8. Influence of the light intensity on the polymerization kinetic profile of a UV-curable polyurethane-acrylate. (---) Response time of the IR detection.

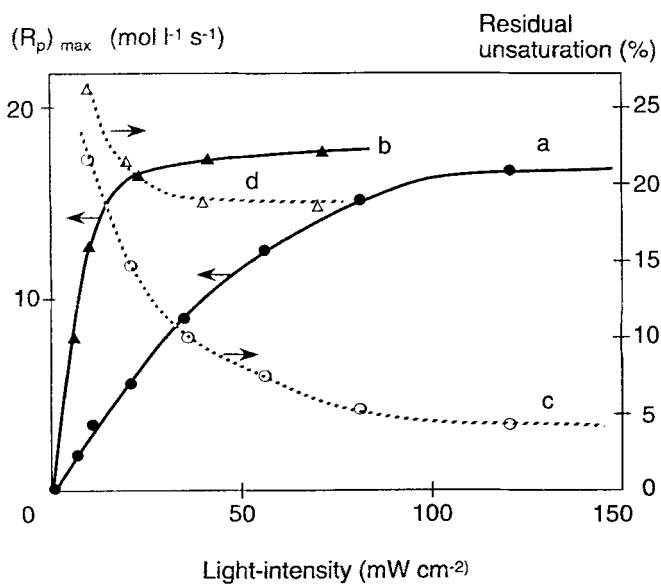


FIG. 9. Light-intensity dependence of the maximum rate of polymerization and of the amount of residual acrylate double bonds in the UV-cured polymer. Polyurethane acrylate + DMPA ( $\bullet$ ,  $\circ$ ); polyether acrylate + BAPO ( $\blacktriangle$ ,  $\triangle$ ).

[19]. In some very reactive UV-curable systems, the rate saturation effect was shown to occur at relatively low light intensities, mainly because of high initiation efficiency. With the bis-acylphosphine oxide (BAPO) recently developed by CIBA,  $(R_p)_{\max}$  was found to reach its upper limit value at an incident light intensity as low as  $30 \text{ mW} \cdot \text{cm}^{-2}$  (Fig. 9, Curve b).

Based on these results, one could reasonably question the opportunity to perform UV-curing under very intense illumination, as is commonly done in most industrial applications. Besides reasons related to surface inhibition by oxygen, there is still a practical interest in operating at high light intensities because the larger amount of radicals generated by intense but short UV exposure will induce a more efficient dark polymerization. This is clearly illustrated by Fig. 10 which shows RT-IR profiles recorded after a 0.1-second exposure at either 50 or  $300 \text{ mW} \cdot \text{cm}^{-2}$ . At the highest intensity the polymerization continued to develop in the dark, almost as fast as upon permanent irradiation, to give a fully cured polymer. This was not the case for the sample irradiated at low light intensity, which required a 0.5-second exposure to reach the same extent of cure.

Very similar results were obtained with vinyl ether-based formulations where  $(R_p)_{\max}$  was also found to level off at about  $20 \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$  when the light intensity was increased above  $100 \text{ mW} \cdot \text{cm}^{-2}$  (Fig. 11). As expected from molecular mobility considerations, the  $(R_p)_{\text{lim}}$  value was higher for the fluid divinylether resin than for the more viscous DVE-3 + unsaturated polyester (UPE) formulation.

An increase of the light intensity leads not only to a faster cure but also to a more extensive cure, so that the final product contains a lower amount of unreacted functional groups (Fig. 9, Curves c and d). This trend can be explained by two factors: 1) an increase of the sample temperature, which provides more mobility and leads to higher ultimate conversion; and 2) a longer time lag between conversion and shrinkage, which generates a greater excess of free volume and thus increases

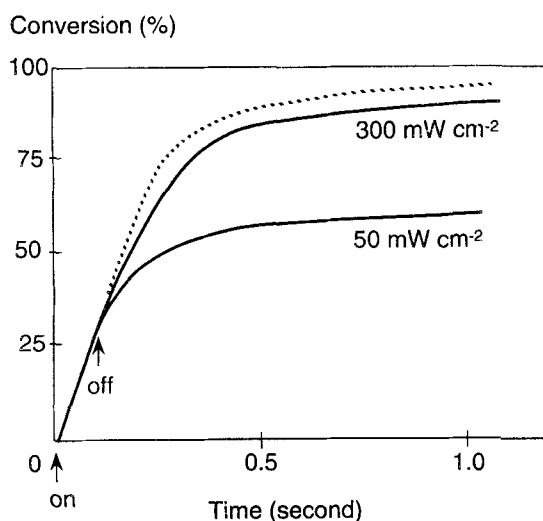


FIG. 10. Influence of the light intensity on the extent of dark polymerization for a polyurethane-acrylate resin exposed to UV radiation during 0.1 second.

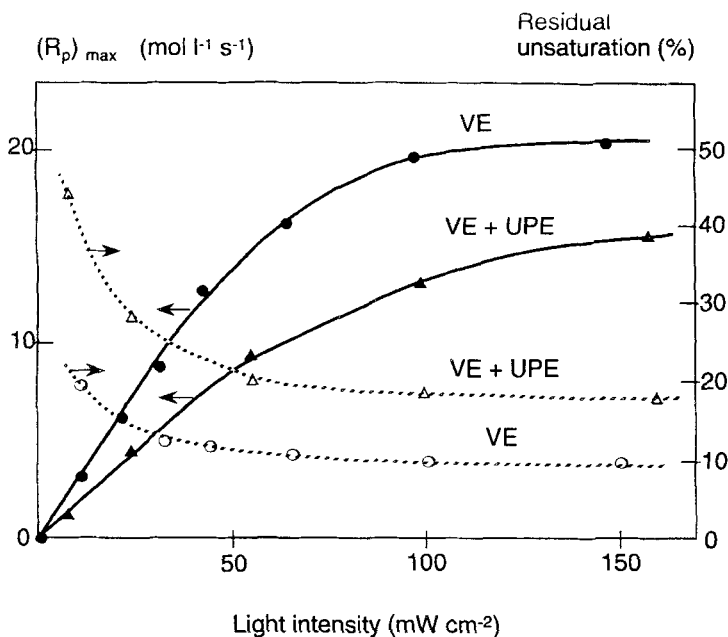


FIG. 11. Light-intensity dependence of the maximum rate of polymerization and of the amount of residual VE double bonds in a UV-cured vinyl ether polymer. Divinylether oligomer + DVE-3 ( $\bullet$ ,  $\circ$ ); unsaturated polyester + DVE-3 ( $\blacktriangle$ ,  $\triangle$ ).

the molecular mobility. Figure 11 shows how the amount of residual unsaturation (RU) in the photocured vinyl ether polymers decreases with increasing light intensity until it levels off at a limiting value for  $I_0 > 100 \text{ mW} \cdot \text{cm}^{-2}$ . The fact that  $(R_p)_{\max}$  and RU were found to reach a plateau at essentially the same light intensity was taken as a strong argument in favor of the above-mentioned explanation. Indeed, the invariance of the polymerization rate above  $(I_0)_{\text{lim}}$  leaves both the temperature increment and the excess free volume unaffected by a further increase of the light intensity (see below).

### TEMPERATURE PROFILES IN PHOTOINITIATED POLYMERIZATION

During the UV-curing process, the heat evolved by exothermic polymerization makes the sample temperature rise, and even more so as the reaction occurs in such a short time scale. The heat flux and temperature increase can be monitored by calorimetric analysis. However, the poor response time of this technique (a couple of seconds) makes it impossible to record the temperature profile of coatings undergoing photocuring within a fraction of a second under intense illumination. Here again, RT-IR spectroscopy proved to be a most valuable technique in that it allowed temperature profiles to be directly recorded for UV-curable resins undergoing ultra-fast polymerization.

A sample of controlled thickness was laminated between two transparent polypropylene films and exposed to UV radiation. The IR peak at  $843 \text{ cm}^{-1}$  of polyprop-

ylene was used as the temperature probe; its intensity was found to decrease linearly with temperature in the 20 to 100°C range. Figure 12 shows the temperature profile recorded as a function of the irradiation time for a polyurethane-acrylate resin. It can be seen that the temperature starts to rise as soon as polymerization begins (same induction period), and that it reaches its maximum value ( $\sim 70^\circ\text{C}$ ) once the reaction starts to slow down because of gelation. The temperature later decreases slowly as air cooling becomes predominant over the small amount of heat evolved at that stage. No significant temperature increase could be detected upon UV exposure of a sample containing no photoinitiator, where polymerization is not proceeding (Fig. 12).

A linear relationship was found to exist between the rate at which the temperature rises and the rate of polymerization (Fig. 13). As expected, the maximum temperature increment increases with both the sample thickness and the light intensity. The temperature value was also found to reach an upper limit for a light intensity which has essentially the same value ( $\sim 50 \text{ mW}\cdot\text{cm}^{-2}$ ) as that observed when monitoring  $(R_p)_{\text{max}}$  and RU, thus leading to a nearly perfect match of the three curves (Fig. 14). As a result of this saturation effect caused by a diffusion-controlled reaction rate, samples which are cured at very high light intensities, either on industrial lines ( $I_0 < 1 \text{ W}\cdot\text{cm}^{-2}$ ) or with powerful lasers [20, 21] ( $I_0 > 1 \text{ W}\cdot\text{cm}^{-2}$ ), will exhibit essentially the same temperature profile as those cured at lower light intensities, as long as  $I_0$  stays above  $(I_0)_{\text{lim}}$ . The UV, visible, and IR radiations are expected to contribute only to a small extent to the temperature increases because of the short exposure (tenths of a second) required for curing. A direct consequence of the rate and temperature saturation effects is that a given material, cured under different but still intense irradiation conditions, will exhibit similar physicochemical characteristics.

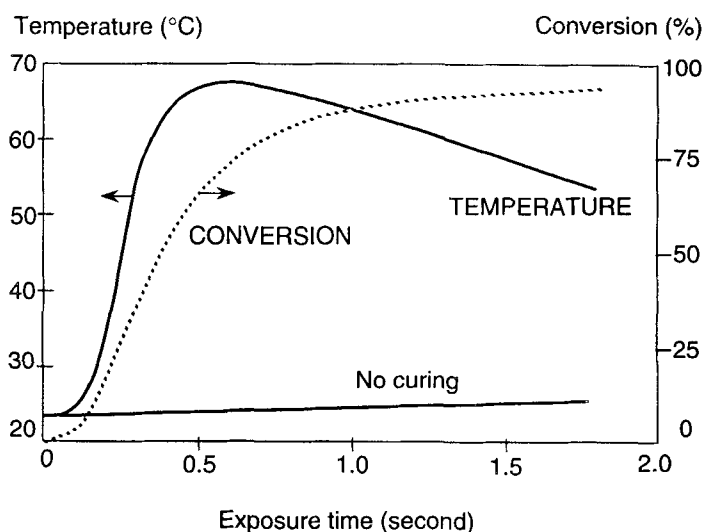


FIG. 12. Temperature profile recorded by RT-IR spectroscopy for a 12- $\mu\text{m}$  thick polyether-acrylate coating exposed to UV radiation. Light intensity:  $12 \text{ mW}\cdot\text{cm}^{-2}$ .



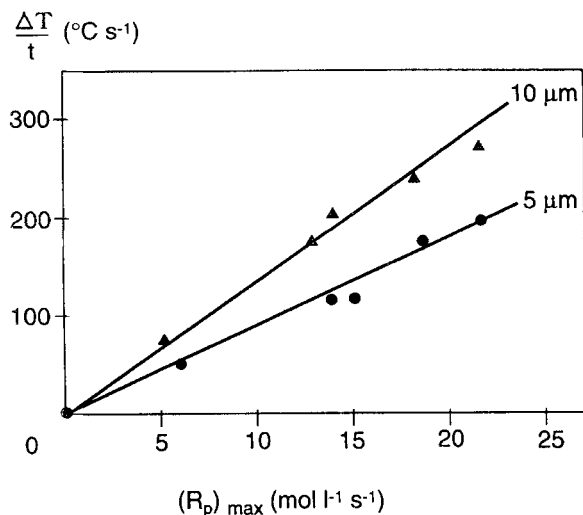


FIG. 13. Variation of the rate of temperature rise with the rate of polymerization in the photocuring of a polyurethane-acrylate resin irradiated at various light intensities.

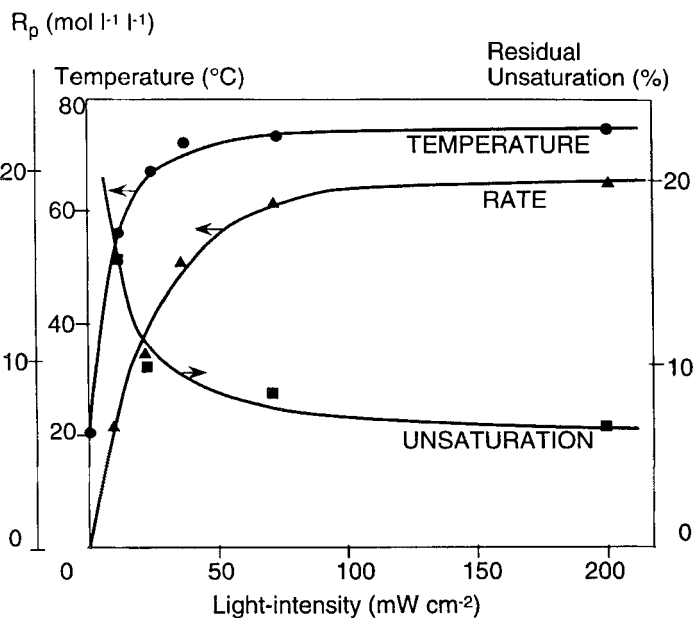


FIG. 14. Influence of the light intensity on the rate of polymerization, the residual unsaturation content, and the sample temperature in the photocuring of a polyurethane-acrylate resin. Film thickness: 12 μm.

## CONCLUSION

UV-radiation curing remains one of the most effective processes to produce quasi-instantly highly crosslinked polymers. The liquid-to-solid phase change obeys a complex kinetics which is primarily governed by the rate constants of the propagation ( $k_p$ ) and termination ( $k_t$ ) reactions. The values of  $k_p$  and  $k_t$  are highly dependent on the molecular mobility, and therefore change markedly in the course of polymerization.

Real-time infrared spectroscopy appears to be the best method to monitor quantitatively such ultrafast polymerizations, both during and after UV exposure, thus allowing a reliable evaluation of the rate constants. The great reactivity of UV-curable acrylate resins results from both a fast propagation reaction (high values of  $k_p$ ) and an inefficient termination process. In multifunctional monomers where molecular mobility restrictions appear in the early stages of polymerization, bimolecular termination is rapidly controlled by reactive diffusion of the propagating radical.

A simple way to increase both the cure speed and the extent of cure is by raising the light intensity ( $I_0$ ). This is true only up to a certain value of  $I_0$ , above which the polymerization follows essentially the same kinetic pattern, the crosslinking process then being controlled only by the diffusion rate of the reactive species. Operating at higher light intensities therefore has little effect on the actual polymerization rate, the ultimate conversion, and the sample temperature. It is still of practical interest to perform curing by a short and intense irradiation because the exceeding large amount of initiating radicals produced will greatly favor the dark polymerization process and help overcome oxygen inhibition. Further kinetic investigations of UV-curable systems are required to better understand the complex mechanism of such crosslinking polymerizations and to put forward some guidelines to help develop more reactive monomers.

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