Photopolymerization of Multifunctional Monomers in Condensed Phase

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INTRODUCTION

Photosensitive resins that polymerize readily under ultraviolet (UV) radiation have found many industrial applications,[1] going from the photoresists used in the fabrication of microelectronic devices and video discs to the photocurable coatings which proved to be very efficient for protecting the surface of all kinds of materials. These systems often consist of multifunctional acrylic monomers which rapidly yield strongly crosslinked and insoluble polymer networks when they are exposed to UV light in the presence of a photoinitiator. The time scale was found to be in the millisecond range when high-intensity mercury lamps[2] were employed as excitation sources and to drop into the microsecond range by using focused laser beams.[3,4]

The kinetics of this crosslinking polymerization have been studied extensively by various analytical methods such as differential scanning calorimetry,[5-7] infrared (IR) spectroscopy,[2,8,9] laser nephelometry,[10,11] dilatometry,[12] refractometry.[13] Among these techniques, only IR spectroscopy allows a direct and precise evaluation of both the polymerization quantum yield (ϕ_p) and the amount of residual unsaturation in the cured polymer. ϕ_p values as large as 8000 acrylic double bonds polymerized per photon absorbed were thus measured for diacrylates exposed to high-intensity UV sources[2] or to laser beams[14]; it shows that the chain reaction can develop very extensively in such multifunctional monomers irradiated in condensed phase, despite the extremely large rates of initiation that were expected to favor termination reactions. Indeed, large concentrations of radicals are created within a very short time in samples exposed to intense UV radiation; this should greatly favor bimolecular terminating interactions of polymer radicals over chain propagation, thus leading to low molecular weight polymers.

In the conventional mechanism of photopolymerization, the kinetic chain length (k.c.l) is known to depend on the reciprocal square root of the light intensity (I) and will thus decrease as I is increased:

$$\left.\begin{array}{ll}\text{rate of initiation:} & r_i \sim I \\ \text{rate of polymerization:} & R_p \sim I^{0.5}\end{array}\right\} \quad \text{k.c.l} = \frac{R_p}{r_i} \sim I^{-0.5}$$

This relationship was found to hold true for monofunctional monomers like

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methyl methacrylate[15] that hardly polymerize under intense UV irradiation or for multifunctional monomer, irradiated in solution.[11] It was yet shown to be no more valid for the photopolymerization of pure multifunctional acrylates where a close to first-order relationship was observed between R_p and I, and kinetic chain lengths as large as 100,000 mol/radical were measured upon intense UV or laser excitation.[14]

This result implies that multifunctional monomers do polymerize in condensed phase by a different mechanism, at least as far as it regards the termination step which must involve only one reactive species, rather than the conventional bimolecular dismutation and combination reactions of polymer radicals. Various explanations have been put forward to account for this unusual kinetic law, in particular a progressive isolation of the polymer radicals in the network under formation.[5,14,16] Early studies on the photopolymerization of vinyl polymers have shown that free radical may remain occluded in polymers prepared heterogeneously[17] or in crosslinked polymers obtained from difunctional monomers.[18] We present here some new evidence, based on postpolymerization investigations by IR and ESR spectroscopy measurements, that strongly argues in favor of this explanation by demonstrating the presence of trapped radicals in UV-curved acrylic coatings.

EXPERIMENTAL

Material

The photosensitive resin contained three main components:

1. A photoinitiator which absorbs UV radiation in the 250–370 nm range and splits rapidly into radical fragments that by reacting with the acrylic double bond will initiate the polymerization;
2. A difunctional oligomer that will constitute, after polymerization, the backbone of the polymer network;
3. A diacrylic monomer that acts as a diluent but also participates to the polymerization process and will therefore be incorporated into the network.

As photoinitiator we selected 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651) and 1-benzoyl-cyclohexanol (Irgacure 184), both from CIBA-GEIGY, because of their high initiation efficiencies. Two types of oligomers were used in these experiments (i) an epoxy-diacrylate compound derived from the glycidyl ether of *bis*-phenol A with a molecular weight of 500 (Ebecryl 605 from UCB) and (ii) a diacrylate aliphatic polyurethane with a molecular weight of ~ 1200 (Actilane 20 from SNPE). The reactive diluent common to all the formulations was a diacrylate monomer, hexanediol diacrylate (HDDA from UCB) which permits lowering the viscosity to ~ 200 m Pa s^{-1}. Typical formulations contained equal parts of oligomer and of diluent and the photoinitiator at a concentration of 1 to 5%.

Irradiation

For the IR kinetic investigation of the photopolymerization, the formulation was applied as a uniform layer of about 10 μm thickness on a sodium chloride disk by means of a calibrated wire wound applicator. Samples were exposed to the radiation of a middle pressure mercury lamp (MAZDA UV 8200), equiped with a semielliptical reflector, that has a power output comparable to that of the UV sources used in the industrial UV-curing equipments (80 W per linear centimeter). The intensity of the UV light received by the sample was 1.0×10^{-6} einstein s^{-1} cm^{-2} or 6×10^{17} photons s^{-1} cm^{-2}. A camera shutter was used to select precise exposure times in the range 1/400 of a second to a few seconds. In order to avoid the strong inhibition effect of atmospheric oxygen on the photopolymerization,[19] samples were exposed to UV light in a sealed reactor equipped with quartz windows, that was evacuated and saturated with pure nitrogen prior to irradiation.

Because the reaction develops very fast with such a high-intensity mercury lamp when operating in a nitrogen atmosphere (70% conversion within 1/400 of a second of exposure), a less intense light source was also used. It consists of a fluorescent lamp that emits in the 280 to 360 nm wavelength range, with a maximum emission at 313 nm; this wavelength just corresponds to the $n\pi^*$ transition of the photoinitiator that was shown[15] to be the most efficient in generating radical fragments by the Norrish type I scission process. The light intensity at the sample position was measured by actinometry and found to be 4×10^{-9} einstein s^{-1} cm^{-2}.

Some experiments have also been carried out in the presence of air by using laminates consisting of two polyethylene films separated by a layer of resin of 10 μm thickness. This technique was found to greatly reduce the diffusion of atmospheric oxygen into the photosensitive material but it did not suppress the induction period observed at the beginning of the irradiation that is due to the oxygen already dissolved in the formulation.

Analysis

The extent of the polymerization process was evaluated quantitatively by IR spectrscopy (Perkin Elmer spectrophotometer, model 580 B) by monitoring the decrease upon irradiation of the sharp peak centered at 810 cm^{-1} which corresponds to the twisting vibration of the acrylic $CH_2{=}CH$ bond. This method presents the main advantage over DSC analysis of allowing a direct and precise measurement of the actual degree of conversion. The number of acrylate groups that have polymerized (N) was calculated from the value of the initial acrylate concentration of the formulation $[M]_0$ which is typically in the order of 7 mol/L and from the ratio of the absorbance at 810 cm^{-1} before and after exposure to UV light, $(A_{810})_0$ and $(A_{810})_t$, respectively, by using the equation:

$$N = [M]_0 \left[1 - \frac{(A_{810})_t}{(A_{810})_0} \right]$$

The effect of the temperature on the postpolymerization that develops in the dark after UV irradiation, was evaluated by monitoring the changes in the IR absorption at 810 cm^{-1} that occur upon heating of the sample in the dark at a given temperature, up to 80°C.

ESR measurements were carried out at room temperature using a BRUKER ER 420 spectrometer operating in the X band at a frequency of 9.6 GHz and employing a field modulation frequency of 100 kHz. Absence of saturation was ensured by using a microwave power in the range 0.1 to 1.0 mW to obtain the ESR spectra; saturation was found to occur at power levels above 2 mW. The ESR spectra were recorded just after the UV irradiation and the decrease of the signal with time was followed at room temperature in the dark.

KINETIC STUDY OF THE PHOTOPOLYMERIZATION

The O_2-free epoxy-acrylate resin was found to polymerize extremely fast when exposed to the UV radiation of a high-intensity middle pressure mercury lamp, leading to a completely insoluble crosslinked network within 2.5 ms of exposure. The degree of conversion (τ) was calculated to be 70%, which corresponds to an overall rate of polymerization (R_p) of 2×10^3 mol/L. Measurements of the incident light intensity (I_0) and of the fraction of UV light absorbed by the sample (f) allow us to evaluate the polymerization quantum yield (ϕ_p), i.e., the number of acrylate double bonds that have polymerized after absorption of one photon, by using the equation:

$$\phi_p(\text{mole einstein}^{-1}) = \frac{R_p}{I_a} = \frac{[M]_0(\text{mol/L})\tau(\%)e(\mu\text{m})}{10^7 f(\%)t(\text{s})I_0(\text{einstein s}^{-1}\,\text{cm}^{-2})}$$

where e is the thickness of the sample and t the duration of the UV exposure.

The extremely high value found for ϕ_p, 10,000 mole einstein^{-1}, fully confirms our previous finding[2] and demonstrates again the efficiency of the light-induced polymerization in pure multifunctional acrylates, in spite of the very large initiation rate (in the order of 10^{22} radicals/L · s). By taking into account that, with DMPA as photoinitiator, *only one initiating radical is formed per* 10 *photons absorbed*,[15] it can be inferred from the ϕ_p value that the kinetic chain length of the polymerization is in the order of 100,000 acrylate functions polymerized or crosslinks formed per initiating radical. It corresponds to a calculated average molecular weight of primary chains of ~ 2×10^7 for the polymer network, a value quite similar to the one obtained in our study of the laser-induced polymerization of acrylic photoresists.[14]

In order to follow more precisely the early stages of the polymerization, a less intense UV source was used that consisted of a fluorescent lamp, emitting in the 280–360 nm wavelength range, with an intensity of 4×10^{-9} einstein s/cm^{-2} at the sample position. The polymerization takes then a few seconds to be completed; it can be stopped at any time in order to be able to follow conveniently the postpolymerization effect as a function of the crosslink density, even at low conversions.

Figure 1 shows typical kinetic curves that were obtained by plotting the degree of conversion, calculated from IR measurements, as a function of the duration of the exposure to the mercury source or to the fluorescent lamp. It is interesting to note that we do not observe the rate acceleration which is common in bulk polymerizations due to diffusional restrictions of the macroradicals. The crosslinking develops very rapidly just from the start because of the gel effect that is expected to occur already in the early stages of the irradiation.[20]

In the later stages, the reactions rate drops because of severe diffusional restrictions in the solid matrix and the conversion reaches an upper limit

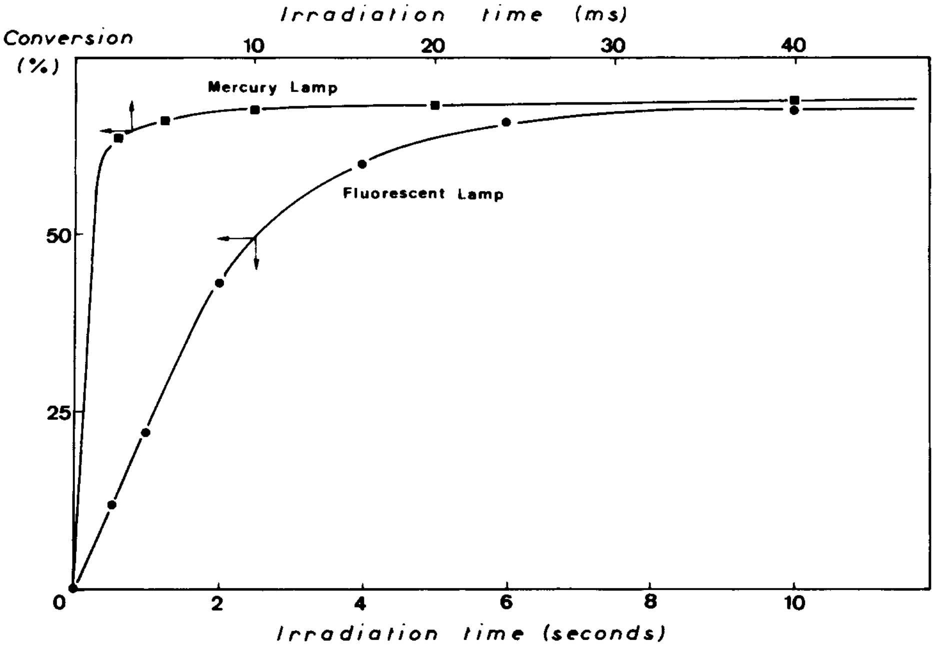


Fig. 1. Kinetics of the photopolymerization of an epoxy-diacrylate film exposed to a middle pressure mercury lamp (■) or to a fluorescent lamp (●) in a N_2 atmosphere. Film thickness: 30 μm; light-intensity: 1×10^{-6} einstein s^{-1} cm^{-2} (■) and 4×10^{-9} einstein s^{-1} cm^{-2} (●).

value that depends on the T_g of the fully cured polymer. In the heavily irradiated epoxy-acrylate sample, it thus remains a certain amount of residual unsaturations (~ 15%) that can no more react because of the vitrification of the network. The chemical reaction is then quenched and a maximum conversion is obtained when T_g becomes equal to the reaction temperature.[21] This is not the case for the more flexible polyurethane network where the T_g of the fully reacted system ($T_{g\infty}$) is still below ambient. Since the reaction temperature is thus always above $T_{g\infty}$, no quenching of the chemical reaction occurs and close to 100% conversions can be reached,[2] which corresponds to a crosslink concentration as high as 7 mol/L.

DARK POLYMERIZATION

When the UV-irradiated sample was stored in the dark, at room temperature, in a nitrogen atmosphere, the polymerization of the remaining acrylic unsaturations was found to proceed slowly for several days, in agreement with previous observations on similar systems.[6] This postpolymerization process develops quite efficiently, even in partly polymerized samples which are still liquid and well before the gel point is reached; for example, the degree of conversion of a sample irradiated for 1 second increased from 22% just after UV exposure to 26% after 7 hours of storage at 25°C.

The occurrence of this dark reaction suggests that some relatively stable reactive species are still present in the polymer network, well after the UV irradiation. They can apparently promote some additional polymerization

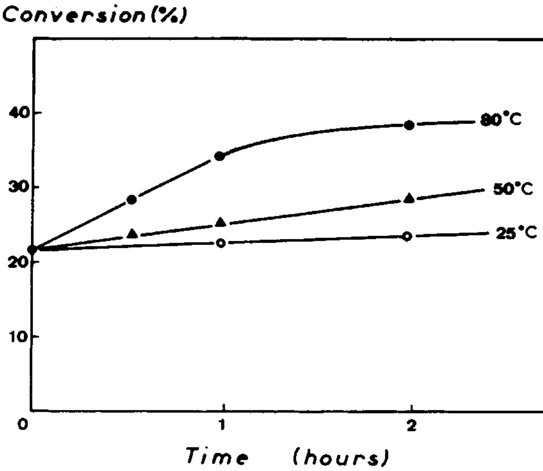


Fig. 2. Effect of the temperature on the dark postpolymerization of a photocrosslinked epoxy-acrylate network.[23]

which develops slowly at 25°C, but is greatly accelerated by moderate heating. The thermal treatment is expected to increase the segmental mobility of the network and therefore to enhance the reaction of the trapped radicals with the remaining acrylic double bonds. By raising the temperature to 50°C, the additional double bond conversion ($\Delta\tau$) was measured to be 6% after 5 hours of heating. At 80°C, the effect was more pronounced since τ increased from 22% after UV irradiation at 25°C to 38% after only 2 hours of heating in the dark. Further heating yields no significant additional polymerization, thus indicating that essentially all of the trapped radicals have disappeared at that temperature. Figure 2 shows the kinetics of this dark reaction at different temperatures for an epoxy-acrylate resin photopolymerized at 22% conversion. That UV generated species are responsible for the observed postpolymerization is demonstrated by the fact that no polymer formation could be detected in nonirradiated samples submitted to the same treatment even after several hours of heating at 80°C in the dark.

It should be mentioned that after storing the irradiated sample in the dark at 25°C and in a N_2 atmosphere for 7 hours, one still observes a substantial postpolymerization effect upon thermal treatment at 80°C (Fig. 3). The conversion increment upon heating appears to be essentially the same whether the thermal treatment was performed just after the irradiation ($\Delta\tau = 13\%$) or after 7 hours of storage at room temperature ($\Delta\tau = 12\%$). It demonstrates that the active radicals involved in the polymerization are quite stable at room temperature in the absence of oxygen. A similar postpolymerization effect was observed for polyurethane-acrylate networks where the degree of conversion was found to increase from 22 to 45% within 3 hours of dark heating at 80°C.

The dependence of the dark reaction efficiency on the extent of the polymerization and thus on the crosslink density of the network was evaluated on samples irradiated for various durations and heated at 80°C for 1 hour. Figure 4 shows the kinetics of the polymerization of an epoxy-diacrylate exposed to UV radiation and to subsequent heating in the absence of oxygen. The additional polymerization appears to be more important in the early

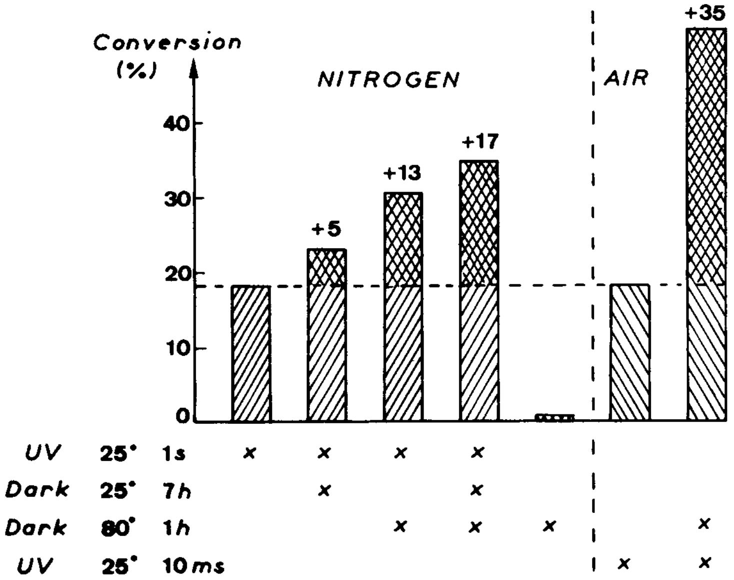


Fig. 3. Influence of the atmosphere on the dark polymerization at 80°C of an epoxy-diacrylate monomer preirradiated to 22% conversion.

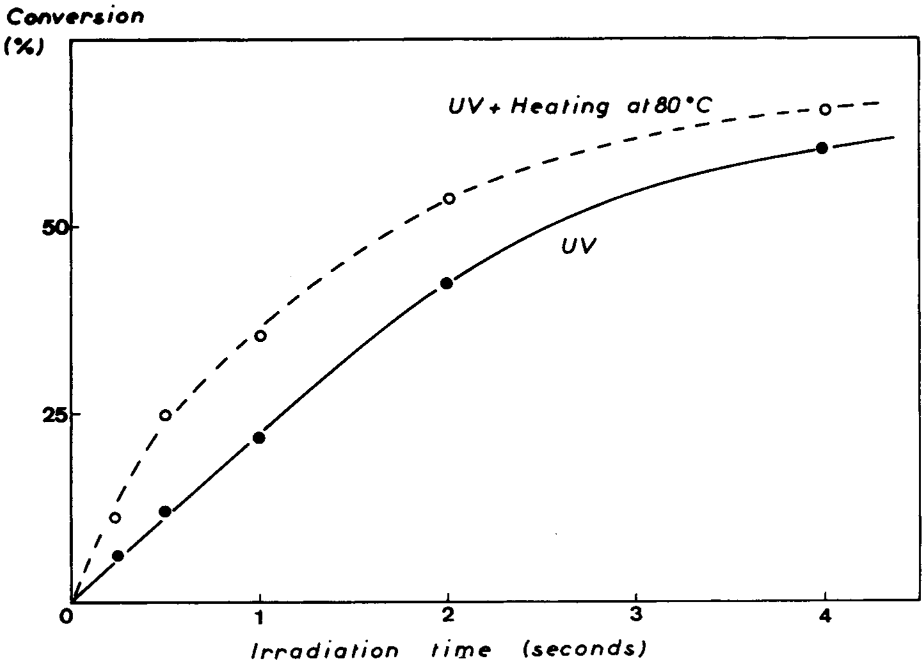


Fig. 4. Kinetics of the photopolymerization of an epoxy-diacrylate film exposed to a fluorescent lamp (●) and subsequently to dark heating at 80°C for 1 hour (—O—).

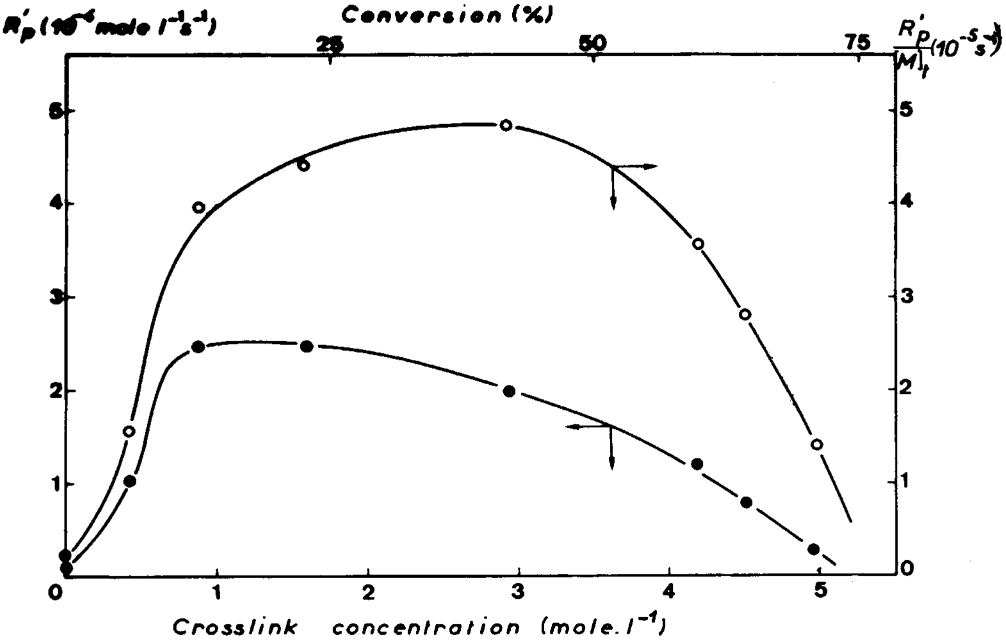


Fig. 5. Dependance of the rate of the dark polymerization (R'_p) at 80°C in N_2 on the crosslink concentration of the pre-irradiated diacrylate monomer. $[M]_t$: concentration of remaining acrylic double bonds in the photocrosslinked sample.

stages of the reaction, $\Delta\tau \approx 13\%$ in the 10 to 30% conversion range, than later on when the network becomes highly crosslinked ($\Delta\tau = 6\%$ at a conversion of 60%). This means that, as soon as the polymerization of the diacrylate starts, crosslinked radicals are being formed and become trapped in the microgel particles; moderate heating will restore some of their mobility and therefore of their reactivity toward the surrounding monomer molecules. At high conversion, two factors will work together to reduce the extent of the dark reaction: (i) the vitrification of the polymer which reduces the segmental mobility of the network, even at 80°C, and (ii) the lower concentration of the unreacted acrylic double bonds.

This is clearly illustrated by Figure 5 (curve a) which shows the variation of the rate of polymerization, R'_p, of the dark process at 80°C with increasing concentration of the crosslinks formed in the irradiated sample. The crosslink concentration of the network after exposure time t was calculated from the initial acrylate concentration of the formulation, $[M_0]$, and the degree of conversion, τ, at time t, assuming that each acrylic double bond consumed has generated a three branches crosslink. The rate equation can be formally written as:

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

where $[M]_t$ is the concentration of the unreacted acrylic double bonds after the UV irradiation and $[P^\cdot]$ the concentration of the radicals trapped in the polymer network. Figure 5 also shows the variation of the ratio $R'_p/[M]_t$ which is directly related to the concentration of trapped radicals (curve b). This ratio appears to increase rapidly in the early stages of the photopolymerization (0 to 10% conversion) due to the build up of polymer radicals which are occluded in microgel particles; it remains fairly constant up to a crosslink concentration of ~ 3.5 mol/L, i.e., when 50% of the acrylate double bonds have polymerized. The decrease of $R_p/[M]_t$ that is observed later on in more strongly photocrosslinked polymers is likely to result from a decrease of the rate constant of propagation in the ever more rigid matrix, as shown by Tryson and Shultz[5] in their study of the photopolymerization of pure diacrylate monomers.

EFFECT OF OXYGEN

It is well known that molecular oxygen strongly inhibits radical-induced photopolymerizations by scavenging the free radicals, with formation of hydroperoxide groups. Therefore, a possible contribution of these hydroperoxides to the initiation of the dark reaction at 80°C can not a priori be excluded; it seems yet very unlikely to occur in the present case since the whole experimental procedure was carried out in a carefully N_2-saturated atmosphere.

It should be mentioned that, when the sample was exposed to the fluorescent source in the presence of air, no polymerization was detected in the time scale investigated (1 to 20 s). Under those conditions, the oxygen dissolved in the resin cannot be consumed rapidly enough to offset the arrival of atmospheric oxygen that diffuses steadily into the film. It is then necessary to rise the light intensity by at least a factor of 100 in order to reduce the relative importance of the diffusion parameter. By using the high-intensity mercury source, it was thus possible to consume within a few milliseconds the oxygen dissolved in the film and to reach the low O_2 concentrations (in the order of 10^{-6} mol/L)[19] that are needed to allow the monomer to compete successfully with O_2 for the scavenging of the initiator radicals.

An additional polymerization was again observed upon heating such samples in the dark and in the presence of air; the conversion increment $\Delta\tau$ was even larger than in the experiment carried out in the absence of oxygen (Fig. 3). This effect can be attributed to the hydroperoxide groups that are formed by O_2 scavenging of the initiator radicals and further reaction of the peroxy radicals, according to the chain reaction scheme shown on Figure 6. Each polymer radical can thus produce several hydroperoxide groups which, by thermolysis, will then generate alkoxy and hydroxy radicals. Both of these

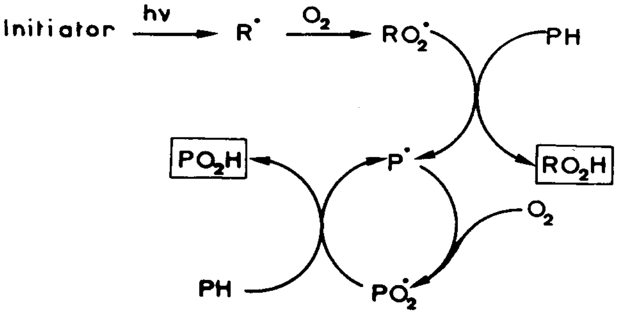
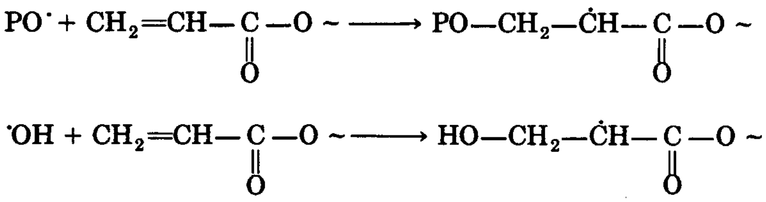


Fig. 6. Reaction scheme of the chain peroxidation in the photopolymerization of acrylic monomers in the presence of air.

species are known to be reactive toward the acrylic double bond and can therefore induce some additional polymerization:

$$PO_2H \xrightarrow{\text{heat}} PO^{\bullet} + {}^{\bullet}OH$$



$$PO^{\bullet} + CH_2{=}CH-\underset{\underset{O}{\|}}{C}-O\sim \longrightarrow PO-CH_2-\dot{C}H-\underset{\underset{O}{\|}}{C}-O\sim$$

$${}^{\bullet}OH + CH_2{=}CH-\underset{\underset{O}{\|}}{C}-O\sim \longrightarrow HO-CH_2-\dot{C}H-\underset{\underset{O}{\|}}{C}-O\sim$$

The substantial postpolymerization observed upon heating samples irradiated in the presence of air is thus expected to result from two major effects: (i) a further growing of the polymer radicals in the matrix that recovers some segmental mobility through heating and (ii) the initiation of new polymer chains by the alcoxy radicals formed by thermolysis of hydroperoxide groups. Experiments carried out in the presence of a decomposer of hydroperoxides indicate an almost equal contribution of these two factors in the observed dark polymerization process.

DETECTION OF TRAPPED RADICALS BY ESR SPECTROSCOPY

ESR spectroscopy analysis of the irradiated samples has provided direct evidence of the presence of long-living radicals in the photocrosslinked polymer. After a short exposure to the fluorescent source, the N_2-saturated sample exhibits an intense ESR signal which remains stable at room temperature. Such a radical occlusion has already been observed by ESR spectroscopy in crosslinked polymers, prepared by photopolymerization of multifunctional acrylic monomers.[6,22,23] The spectrum obtained from the trapped radicals consists of a well resolved triplet (Fig. 7) with a g value close to that of the pitch ($g = 2.0028$) and a hyperfine splitting of 24 Gauss. The hyperfine structure arising from the spread of the unpaired electron distribution over neighboring hydrogen atoms indicates a coupling of the electron with 2 protons. It can be assigned to the $\sim \underset{\underset{\text{COOR}}{|}}{\text{CH}}-\dot{\text{C}}\text{H}_3$ radical which contains one set of two equivalent protons,[24] assuming random orientation of the molecules and a negligible contribution of the hydrogen on the β carbon. It should be mentioned that identical spectra were observed with both the epoxy-acrylate and the polyurethane-acrylate networks, thus confirming that the radical is indeed located on the acrylic function.

When considering the accessibility of the initiating and propagating radicals to the acrylic double bond, one would expect the radicals to be formed to have the following structure: $\sim \text{CH}_2-\underset{\underset{\text{COOR}}{|}}{\dot{\text{C}}\text{H}}$ This would lead either to a doublet or to a quartet ESR signal, depending

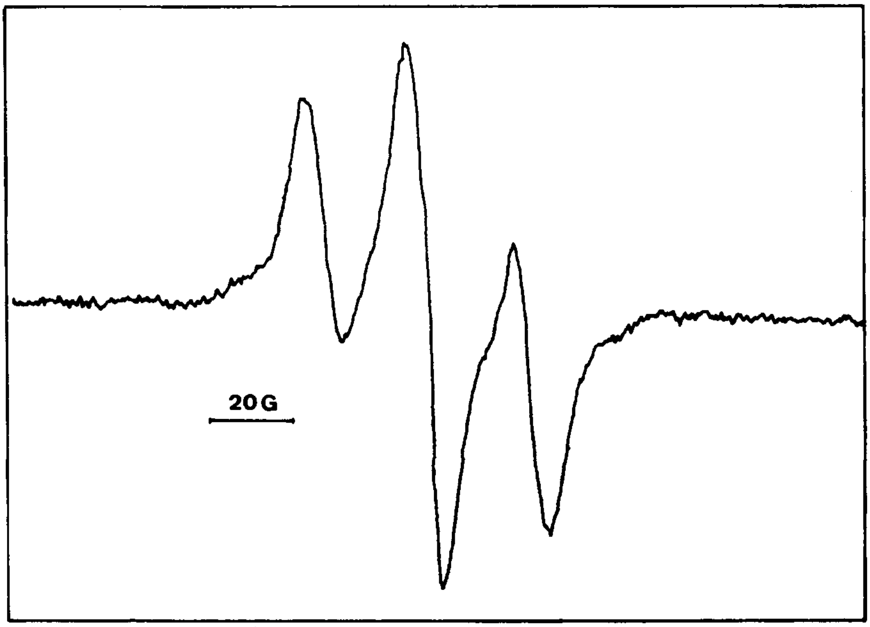


Fig. 7. ESR spectrum of a photocrosslinked polyurethane-acrylate network after 3 hours of storage in air at 25°C.

whether the unpaired electron interacts with none or both of the protons attached to the β carbon. It is still possible for a triplet structure to arise in this case if the rotation about the C_α—C_β bond is restricted and if the unpaired electron interacts with only one of the protons attached to the β carbon. No evidence of such an effect has yet been obtained so far. Tertiary alkyl radicals that are known to be formed in the photolysis of acrylate polymers[25,26] may also contribute to the ESR signal, but probably to a small extent in consideration of the very short UV exposure; 0.1 second at the middle pressure mercury lamp or 10 seconds in the sunlight were already enough to obtain an intense signal, which corresponds to an absorbed dose as low as 5×10^{-8} einstein.

When the irradiated sample was stored in the dark at room temperature and in the presence of air, the intensity of the signal was found to decrease slowly according to a neat exponential law (Fig. 8); it was reduced to 50% of its original value after about 12 hours of storage. The shape of the triplet signal did not basically change with time, thus precluding any transfer reaction of the polymer radicals. For samples that were heavily irradiated and therefore exhibit a high crosslink density, the radical decay appears to be substantially slower, with a lifetime value of about 100 hours.

The concentration of trapped radicals was evaluated using pitch as a standard; it was found to be as high as 6×10^9 radicals/L for the polyurethane-diacrylate formulation exposed to sunlight during 30 seconds in a N_2 atmosphere. In the case of the photopolymerization of dimethacrylate monomers, 30 minutes of UV irradiation were necessary to reach comparable concentrations of trapped radicals.[22]

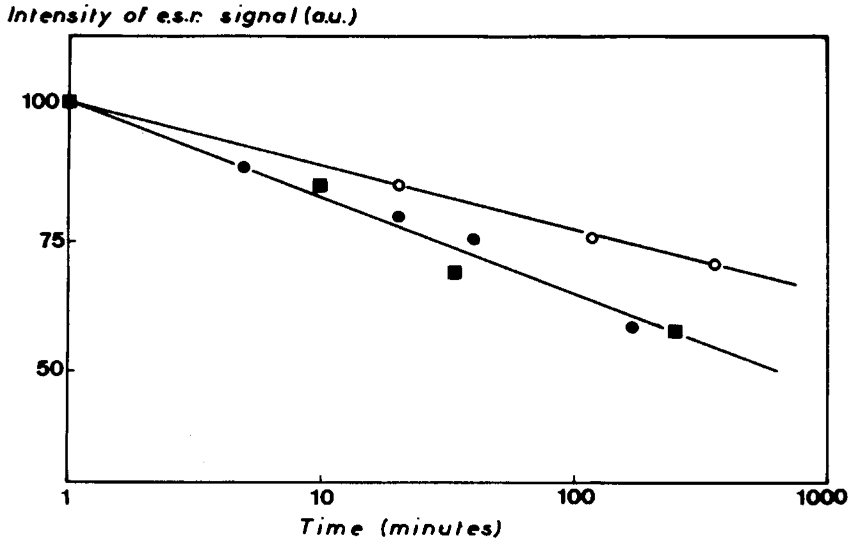


Fig. 8. Decay of the ESR signal in photocrosslinked epoxy-acrylate (o) and polyurethane-acrylate (●, ■) networks.

A new feature observed in this work is that high concentrations of trapped radicals were found in the polyurethane-acrylate network which is much more flexible than the glassy epoxy-acrylate polymer; it means that, even in an elastomeric polymer where the network chains retain some segmental mobility, the macroradicals are being trapped in the crosslinked matrix. This conclusion is in quite good agreement with our previous observations which showed the dark reaction to proceed already very efficiently in partly polymerized samples that are far away from vitrification.

MECHANISM OF THE POLYMERIZATION OF MULTIFUNCTIONAL ACRYLATES

Our previous kinetic studies of the UV-[2] and laser-[27] induced polymerization of multiacrylic monomers, have shown that the rate of polymerization was related to the light intensity by the equation $R_p = kI^{0.85}$ that remained valid over 8 decades. In order to account for this close to first-order kinetic law, it was assumed[14] that the termination of the growing polymer chains occurs by two basically different processes: (i) the usual bimolecular interaction of polymer radicals through dismutation and/or combination, and (ii) a specific termination reaction involving only one polymer radical. Among the various reactions considered, radical isolation was thought to be most feasible.

Based on the assumption that termination occurs by both mono- and bimolecular pathways, the rate of polymerization can be expressed at a first approximate as the sum of two terms which are proportional to the light intensity (I_a) and to its square root, respectively (Table I):

$$R_p = \alpha \frac{k_p}{k_t'}[M_0]\phi_i I_a + (1-\alpha)\frac{k_p}{2k_t^{1/2}}[M]_0 \phi_i^{1/2} I_a^{1/2}$$

TABLE I
Influence of the Termination Process on the Relationship Between the Rate of Polymerization (R_p) and the Light Intensity (I_a)

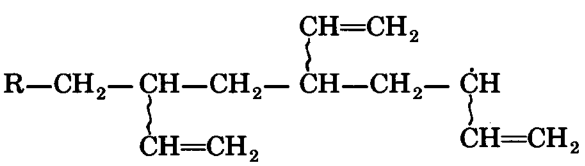
Termination	Bimolecular	Unimolecular
Reaction	$P_m^{\cdot} + P_n^{\cdot} \rightarrow$ polymer	$P_x^{\cdot} \rightarrow$ occlusion
Rate of initiation	$R_i = \phi_i I_a$	$r_i = \phi_i I_a$
Rate of termination	$k_t[P^{\cdot}]^2 \sim I_a$	$k_t'[P^{\cdot}] \sim I_a$
Rate of polymerization	$(k_p/k_t^{0.5})[M]_0\phi_i^{0.5}I_a^{0.5}$	$(k_p/k_t')[M]_0\phi_i I_a$
Overall rate of polymerization: $R_p = (1 - \alpha)I_a^{0.5} + \alpha I_a$		

Here α is a coefficient, between 0 and 1, that reflects the relative contribution of the unimolecular pathway in the termination step, i.e., the probability of polymer radicals to become occluded in the crosslinked network. From the kinetic law obtained between R_p and I_a, the coefficient α was evaluated to be ~ 0.8 for epoxy-acrylate networks photopolymerized in the 30–50% conversion range; it indicates that radical isolation prevails over bimolecular termination in such systems by a ratio of 4 to 1.

The experimental results presented here provide some direct evidence in favor of a termination process occurring mainly through radical trapping and causing eventually the polymerization to stop. It must be remained that, in a crosslinked system undergoing polymerization, the diffusional restrictions upon the macroradical chain end are so severe that the radical termination process is actually controlled by the movement of the chain end.[28,29] We are therefore considering that the two postulated termination pathways are likely to involve two types of acrylic radicals which will basically differ only by their molecular mobility:

(i) linear macroradicals where neither of the pendant acrylic double bonds has yet reacted and which thus conserve some reptation mobility:

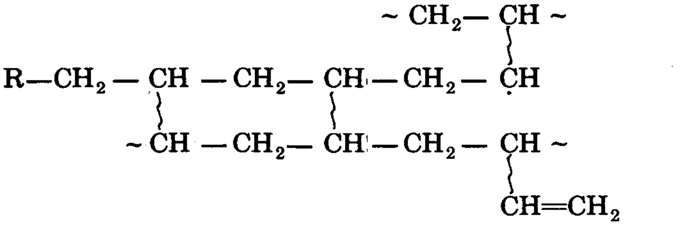
type I radical:



$$\mathrm{R{-}CH_2{-}\underset{\displaystyle CH{=}CH_2}{CH}{-}CH_2{-}\overset{\displaystyle CH{=}CH_2}{CH}{-}CH_2{-}\underset{\displaystyle CH{=}CH_2}{\dot{C}H}}$$

(ii) crosslinked macroradicals that are already attached to the network and can therefore not move freely anymore; they result from a radical attack of one of the many terminal double bonds of type I radical:

type II radical:



$$\begin{array}{ccccccccc} & & & & & & & & \sim CH_2{-}CH\sim \\ & & & & & & & & | \\ R{-}CH_2 & - & CH & -CH_2- & CH & -CH_2- & & & \dot{C}H \\ & & | & & | & & & & \\ & \sim & CH & -CH_2- & CH & -CH_2- & & & CH\sim \\ & & & & & & & & | \\ & & & & & & & & CH{=}CH_2 \end{array}$$

Type I radicals are expected to further propagate the polymerization, either by reaction of the radical chain end with a monomer molecule or by the attack of one of the several pendant acrylic double bonds by an initiator radical, thus generating type II radicals. They can also participate to the conventional bimolecular termination reactions that will involve either another type I radical or an initiator radical ($R^{\cdot}$). Although they are less likely to occur, terminating interactions of type II radicals with type I radicals or with the initiator radicals cannot be excluded, in particular in the early stages of the photopolymerization.

Bimolecular terminations:

$$\left.\begin{array}{ll} \text{radical I} + \text{radical I} & \rightarrow \\ \text{radical I} + R^{\cdot} & \rightarrow \\ \text{radical II} + \text{radical I} & \rightarrow \\ \text{radical II} + R^{\cdot} & \rightarrow \end{array}\right\} \begin{array}{l} \text{dismutation and} \\ \text{combination} \end{array}$$

The fate of type II radicals will depend primarily of the diffusion restrictions existing in the chain end area. In a freely moving environment, macroradicals will continue to grow, as long as monomer molecules can pass close by to the entrapped radical chain end and be scavenged. By contrast, if steric hindrance prevents free access to the macroradical chain end, the polymer chain will stop growing and type II radicals will stay alive, occluded in the crosslinked network. In either case, type II radicals are unlikely to come close together and participate significantly to the bimolecular termination pathway because they are already fixed to the network and have lost their diffusion mobility.

It must be emphasized that one of the major difficulties in trying to elucidate the basic mechanism of the free-radical polymerization of bulk multifunctional monomers is that the diffusion coefficient of the radicals actually varied with the crosslink density so that the overall termination rate constant changes continually during the polymerization.[5] The relative importance of the two termination pathways should therefore depend on the extent of the crosslinking. Unimolecular termination by radical II trapping was thus expected to play a predominant role at high conversions, once a tightly crosslinked network has been formed. Actually, it can already occur in the early stages of the polymerization, as soon as some crosslinks appear and microgel particles are build up,[20] as shown by our postpolymerization experiments at low conversion. The substantial additional polymerization observed upon heating at 80°C (Fig. 4) indeed demonstrates that stable radicals are present in the liquid resin polymerized at only 5% conversion, probably as occlusions in some highly crosslinked particles where mobility restrictions already exist. The presence of insoluble polymer was indeed detected at this low degree of conversion.

On the other side, bimolecular termination may still proceed well beyond the gel point, as shown by the close to first-order kinetic law that is even observed in the later stages of the reaction. It suggests that regions of high mobility, containing the linear type I macroradicals, can persist at conversions above 50%. The presence of such spatial inhomogeneities in the photopolymerization of diacrylate monomers in condensed phase was recently postulated by Kloosterboer et al.[30] who used a percolation model in order to account for local structure variations and trapping of radicals. It should be emphasized that it is this first-order termination process that allows the polymerization to develop so extensively at very high rates of initiation, therefore enabling one to reach extremely large speeds of cure, a prerequisite for using such systems for industrial applications.

Finally, a remarkable feature revealed by our ESR investigation is that the observed spectrum of the trapped radicals is not the expected $—^{\cdot}CH—$ doublet but has clearly a triplet hyperfine structure that could be assigned to the $—^{\cdot}CH_2$ radical. The formation of this type of radical is rather surprising since it implies that, by contrast with the polymerization mechanism generally assumed for acrylic monomers, the chain propagation would occur here primarily by a radical attack on the most substituted carbon of the acrylate double bond. The reasons of this unusual behavior are still unclear. Further experiments are in progress to confirm such an unexpected finding and establish a possible relationship between this Markolnikov process and a matrix effect that would affect the usual steric hindrance rules.

CONCLUSION

Infrared spectrophotometry has revealed as a very convenient analytical method to follow quantitatively the kinetics of the photopolymerization of multiacrylic monomers in a very broad range of conversion and to evaluate the effect of moderate heating on the amount of residual unsaturations in the crosslinked polymer. As a result of this study, it should be apparent that diffusional restrictions play a decisive role in the propagation step as well as in the reaction of termination of the growing polymer chains that is primarily due to an occlusion of the macroradicals in the network under formation. Three major arguments can be put forward in favor of such a radical trapping process:

1. The close to first-order kinetic law between the rate of polymerization and the rate of initiation
2. The additional polymerization observed by moderate heating in the dark
3. The detection by ESR spectroscopy of fairly stable radicals occluded in the polymer network

Such a radical isolation phenomenon is expected to take place in any multifunctional monomer undergoing crosslinking-polymerization in condensed phase and is not limited to glassy polymer networks. It was shown to occur both in elastomeric polyurethane-acrylate networks and in viscous liquid systems at low conversions, as soon as some microgel particles appear. As a result of this termination process which involves only one polymer radical, the rate of polymerization increases almost linearly with the light intensity. The chain reaction can therefore develop quite extensively in those systems, even at very large initiation rates, thus allowing multiacrylic monomers to be polymerized extremely fast with still high quantum yields.

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