Macromolecules **1990,** *23,* 5217-5220

Real-Time Monitoring of Polymerization Quantum Yields

Christian Decker

Laboratoire de Photochimie Générale, CNRS, Ecole Nationale Supérieure de Chimie, 3, rue A. Werner, 68200 Mulhouse, France

Received March 7, 1990; Revised Manuscript Received May 21, 1990

ABSTRACT: Real-time infrared (RTIR) spectroscopy was used to study the polymerization kinetics of a polyurethane–diacrylate photoresist exposed to UV radiation or to a Kr^+ laser beam. The conversion versus time curves recorded allow the polymerization rate, R_p, to be determined at any stage of the reaction. Variation of the polymerization quantum yield, ϕ_p, upon exposure was monitored in real time from the ratio of R_p to the absorbed light intensity. The effect of atmospheric oxygen on ϕ_p is substantial and was quantified. In O_2-free systems, ϕ_p reached its maximum value after 130 ms of exposure and a conversion of 6%. A sharp drop of the ϕ_p value was observed after 25% conversion; it is attributed to a decrease of the initiation quantum yield, ϕ_i, due to segmental mobility restrictions brought on by gelation. The kinetic chain length of the propagation step was evaluated from the ratio ϕ_p/ϕ_i; it was found to reach its maximum in the early stages of the polymerization, with values on the order of 7000 mol/radical in the presence of air and up to 50 000 mol/radical in N_2-saturated systems.

Introduction

UV irradiation is one of the most efficient methods to induce ultrafast reactions in polymer systems. This technology is widely used in photolithography and in the coating industry to transform, within milliseconds, a liquid monomer film into an insoluble polymer material.[1] A great number of kinetic investigations on photopolymerization and UV curing have been reported,[2-20] but there are only a few data available on the quantum yield of the polymerization[5,21-23] (ϕ_p). This quantity, which is defined as the number of monomer functions that have reacted per photon absorbed, is of great significance since it provides basic information about the intrinsic efficiency of the polymerization and its kinetic chain length, which cannot be determined otherwise in cross-linked polymers. We report here a novel analytical method, based on IR spectroscopy, which permits instant evaluation of ϕ_p for light-induced polymerizations that occur within a fraction of a second, continuously throughout the course of the reaction.

Basic Principle of Quantum Yield Evaluation

The overall quantum yield of a light-induced polymerization can be calculated from the ratio of the rate of polymerization (R_p) to the flux of photons absorbed by the sample (I_a). The basic idea is to monitor in real time both of these quantities during the photopolymerization and thus be able to evaluate ϕ_p at any stage of the reaction.

The photopolymerizable resin consisted of three components: (1) a photoinitiator ((2,2-dimethoxyphenyl)-acetophenone from CIBA-GEIGY), which decomposes rapidly upon UV irradiation to yield very reactive free radicals;[24] (2) a polyurethane–diacrylate oligomer (Actilane 20 from SNPE), which will constitute the frame of the tridimensional network; (3) an acrylic monomer, which acts as reactive diluent; an oxazolidone monoacrylate (Acticryl CL 960 from SNPE) was selected because of its high reactivity.[20]

The formulation contained up to 5% (w/w) of photoinitiator and equal amounts of monomer and oligomer. A 25-μm-thick film was coated onto a polyethylene sheet, which is transparent to both the UV radiation in the selected wavelength range (280–360 nm) and the IR radiation in the 800-cm^{-1} region. Samples were exposed for a few seconds to the filtered emission (313 nm) of a medium-pressure mercury lamp, in the presence of air or pure nitrogen, leading to a highly cross-linked and totally insoluble polymer.

The polymerization profile was recorded by using real-time infrared (RTIR) photospectroscopy, a technique that permits us to determine in a single run the important kinetic parameters, for polymerizations that develop in the millisecond time scale.[25] The monomer sample was exposed simultaneously to the polymerizing UV beam and to the analyzing IR beam. The resulting drop of the IR absorbance at 812 cm^{-1} of the acrylic function was monitored continuously on a transient memory recorder (Schlumberger SI 8200), which has a response time of 0.4 ms. From the slope of the kinetic curve thus recorded (Figure 1), R_p values can be determined at any time, from the very beginning of the reaction to completion.

The flux of photons at the sample position (I_0) was measured by actinometry[26] or by radiometry (International Light Radiometer 390). Its value was typically on the order of 10^{-8} einstein cm^{-2} s^{-1} or 6×10^{15} photons cm^{-2} s^{-1}. The fraction of incident light absorbed by the sample was determined by monitoring with a photocell the photon flux transmitted by the monomer film coated onto a transparent polyethylene sheet (I_1) and by the support alone (I_2). The number of photons absorbed by the monomer per second (I_a) was then calculated from the equation

$$I_a\ (\text{einstein L}^{-1}\ \text{s}^{-1}) = I_0\ (\text{einstein cm}^{-2}\ \text{s}^{-1}) \times \frac{I_2 - I_1}{I_2} \times \frac{10^3}{l_{\text{cm}}}$$

where l is the thickness of the monomer film. The slow decrease of I_a during the polymerization, due to the photolysis of the initiator, was followed continuously by recording the photon flux transmitted by the irradiated sample (Figure 1). Combining the two real-time kinetic analyses allows the polymerization quantum yield to be evaluated at any stage of the reaction, simply from the ratio R_p/I_a.

Results and Discussion

Polymerization Kinetic Profile. Typical conversion versus time curves recorded by RTIR spectroscopy are shown in Figure 2, for a polyurethane–diacrylate photoresist exposed to UV radiation. In the presence of air, the sigmoid character of the kinetic profile was attributed to

0024-9297/90/2223-5217$02.50/0 © 1990 American Chemical Society

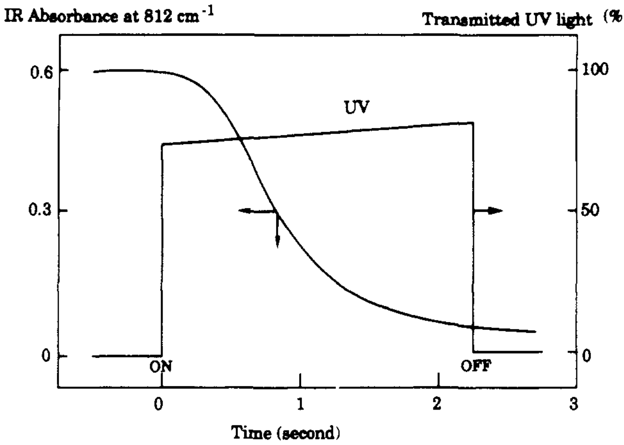


Figure 1. Real-time monitoring of the IR absorbance of the acrylic double bond and of the transmitted UV light, during the polymerization of a polyurethane–diacrylate photoresist. Film thickness: 25 μm. Incident light intensity: $I_0 = 4 \times 10^{-8}$ einstein s^{-1} cm^{-2}.

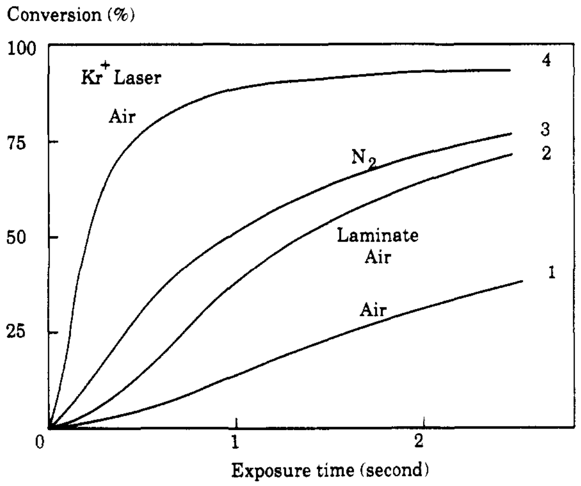


Figure 2. Polymerization profiles recorded by RTIR spectroscopy for a polyurethane–diacrylate photoresist exposed to the radiation of a mercury lamp ($I_0 = 10^{-8}$ einstein s^{-1} cm^{-2}) in the presence of air (curve 1), as laminate (curve 2), or in the presence of N_2 (curve 3) or of a krypton ion laser emitting at 337.4 nm (curve 4; $I_0 = 2 \times 10^{-7}$ einstein s^{-1} cm^{-2}).

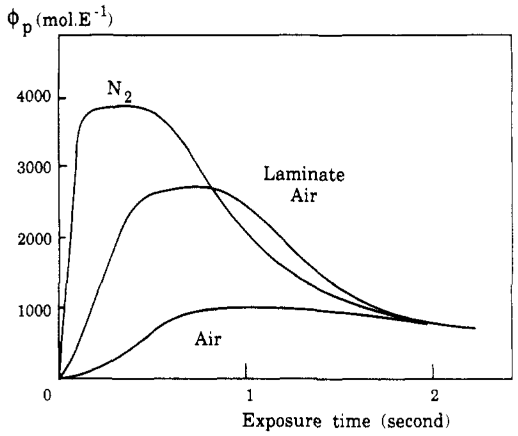
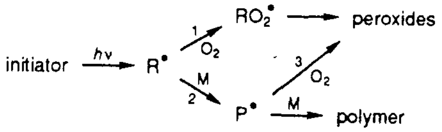


Figure 3. Variation of the polymerization quantum yield (ϕ_p) upon UV exposure of a polyurethane–diacrylate photoresist ($I_0 = 10^{-8}$ einstein s^{-1} cm^{-2}).

Scheme I



two major factors: (i) the induction period is due to the strong inhibition effect of O_2 on radical-induced polymerization,[27] since it disappears almost completely in O_2-free systems; (ii) the rate decrease observed after 30% conversion results mainly from the gelation of the irradiated medium, with its related mobility restrictions. Ultimately, the reaction stops because of a lack of reactant mobility, leading to the occlusion of the radicals in the cross-linked polymer.[2] The polymerization rate is drastically increased when the sample is exposed to the intense UV emission at 337.4 nm of a krypton ion laser, 50% conversion being reached within less than 0.2 s (Figure 2). For irradiations carried out in a nitrogen atmosphere, the induction period was greatly reduced and the polymerization developed much faster, with again a marked rate decrease at higher conversions. A similar but less pronounced effect was found by covering the sample with a transparent polyethylene film (laminate), which prevents diffusion of atmospheric oxygen during the photopolymerization (Figure 2).

R_p values were obtained directly from the first derivative of the RTIR curve recorded, $(R_p) = [A]_0 \times \mathrm{d(conversion)}/\mathrm{d}t$, where $[A]_0$ is the acrylate concentration of the unirradiated resin. Calculation of the ratio of $(R_p)_t$ and $(I_a)_t$, both quantities that are monitored in real time during the reaction, leads finally to the value of ϕ_p. As pointed out by one of the reviewers, in order to know how many monomer units are polymerized by a radical formed at time t, we must actually look at the rate at some time $t + \Delta t$. The error introduced on ϕ_p by our mode of calculation appears yet to be of minor importance in the present case, since ϕ_p exhibits a rather weak dependence on time. If this is no longer true, RTIR spectroscopy still permits us to evaluate instantly ϕ_p, simply by monitoring the ratio $(R_p)_{t+\Delta t}/(I_a)_t$, for the selected value of Δt.

Polymerization Quantum Yield. Figure 3 shows how the overall polymerization quantum yield varies with the exposure time, for a polyurethane–diacrylate photoresist irradiated in the presence of air or in pure nitrogen. In O_2-free systems, it takes about 130 ms of UV exposure and a conversion of 6% before the polymerization reaches its maximum efficiency, each photon absorbed inducing the polymerization of 4000 acrylic functions. This result is in good agreement with our recent study[28] of the polymerization of the same photoresist irradiated under identical conditions, which showed the radical concentration to increase during the first 150 ms of exposure, until it leveled to a constant value when steady-state conditions were attained. When an Ar^+ laser was used as the radiation source, this exposure time was shortened down to only 30 ms,[29] as expected from the related increase of the initiation rate.

In the presence of air, ϕ_p reaches its maximum value only after 0.8 s, because of an efficient scavenging of the initiator radicals by the oxygen dissolved in the sample (reaction 1, Scheme I). It was recently shown[30] that the O_2 concentration has to drop by more than 2 orders of magnitude before the monomer can compete efficiently with O_2 for the scavenging of the initiating radicals and thus make the polymerization start (reaction 2). The maximum value of ϕ_p is still much lower (1000 mol einstein^{-1}) than in the N_2-saturated polymerization, since atmospheric oxygen is diffusing continuously into the sample, thus slowing down the polymerization (reaction 3). This effect can be reduced to a large extent, either by shortening the exposure time through an increase of the light intensity[30] or by covering the sample with a polyethylene film. With such laminates, ϕ_p reaches then values close to that observed in N_2-saturated films (Figure 3).

For all the systems examined, the polymerization quantum yield started to drop when about one-quarter of the acrylic functions had polymerized. Various factors can be put forward to account for this effect, by consideration of the quantum yield equation:

$$\phi_p = \frac{k_p}{(2k_t)^{0.5}}[M]I_a^{\,0.5}\phi_i^{\,0.5}$$

The rate constants k_p and k_t were both found to decrease as the conversion rises above 25%, but the ratio $k_p/k_t^{0.5}$ was much less affected and remained nearly constant up to 50% conversion.[28] During the polymerization, the light intensity absorbed by the sample decreases slowly with the irradiation time (Figure 1), due to the photolysis of the initiator, which makes ϕ_p rise accordingly. It thus appears that the drop of ϕ_p above 25% conversion is most likely due to a decrease of the initiation quantum yield ϕ_i. Indeed, as polymerization develops, with its growing segmental mobility restrictions, the radical pairs generated by photocleavage of the initiator will have more tendency to recombine than to diffuse apart and initiate new polymer chains. Such an effect was already shown to occur in the light-induced polymerization of bulk poly(methyl methacrylate).[31,32] It is expected to be even more pronounced for difunctional monomers, which generate a polymer network.

Kinetic Chain Length. Since the polymerization of multifunctional monomers leads to highly cross-linked insoluble polymers, with infinite molecular weight, it is usually not possible to determine the kinetic chain length (kcl) of the propagation step. One of the distinct advantages of UV initiation is to afford such evaluation from quantum yield measurements, since kcl = R_p/r_i = ϕ_p/ϕ_i. By taking ϕ_i = 0.4 radical/photon for the photoinitiator used,[33] kcl values were calculated to be on the order of 2000 and 10 000 acrylate groups polymerized per initiating radical, for air- and N_2-saturated systems, respectively.

It should be emphasized that the real kcl values are actually much larger, since the polymer chains continue to grow after UV exposure,[25] before they terminate by radical recombination, chain transfer, radical trapping,[2] or scavenging by O_2.[30] This postpolymerization was found to be particularly important in the early stages of the reaction and in air-free systems, where it may account for up to 80% of the total polymer formed.[28,29] Figure 4 shows the variation of kcl with conversion, calculated by taking into account the dark polymerization, for a polyurethane–acrylate photoresist irradiated in the presence of air or pure N_2.

The high kcl values obtained, up to 50 000 mol/radical in N_2, demonstrate how effectively the chain reaction can develop in difunctional monomers irradiated in bulk, even at large initiation rates ($r_i = \phi_i I_a = 10^{-3}$ initiating radical $L^{-1}\ s^{-1}$). This is mainly due to a rather inefficient termination process, with a k_t value 3 orders of magnitude less[28] than that in the bulk polymerization of methyl methacrylate.[13] The low k_t value, together with a high k_p value ($6 \times 10^3\ mol^{-1}\ L\ s^{-1}$ [28] compared to $3 \times 10^2\ mol^{-1}\ L\ s^{-1}$ for PMMA[13]), are the main reasons why multiacrylic monomers polymerize so fast under exposure to intense UV radiation[21] or laser beams.[29] As expected in such a radical-induced process, polymerization proceeds less extensively in the presence of oxygen, making the maximum kcl value drop to 7000 mol/radical.

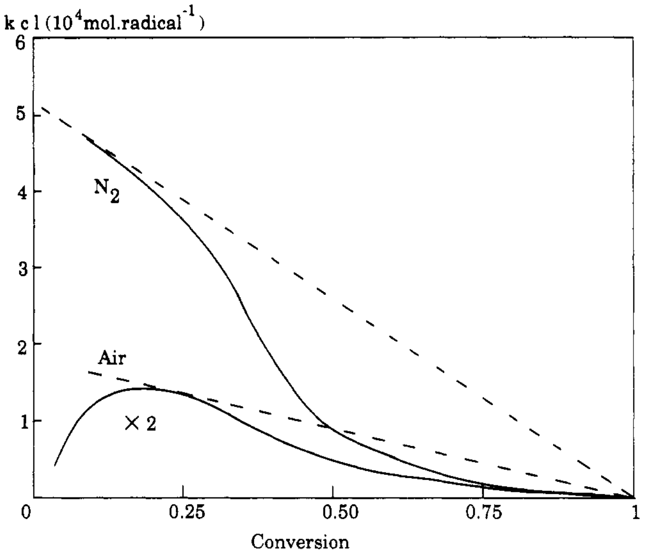


Figure 4. Dependence of the kinetic chain length (kcl) upon conversion during the light-induced polymerization of a polyurethane–diacrylate film.

In most polymerizations, the kinetic chain length decreases linearly with conversion (x), due to the consumption of the monomers:

$$\text{kcl} = \frac{k_p}{(2k_t)^{0.5}}(1 - x)[M]_0 r_i^{-0.5}$$

The faster than linear decrease of kcl observed at conversion above 25% (Figure 4) reflects the importance of gelation in those cross-linking polymerizations. When the segmental mobility is reduced, it prevents ultimately the polymer chains from further growing, leading to the trapping of the reactive radicals in the tight polymer network formed.[32]

Conclusion

The time-resolved kinetic analysis, which was used here to evaluate the polymerization quantum yield of multiacrylates, can be applied to any system undergoing chemical modifications that can be monitored by IR spectroscopy. It was found to be particularly well suited to the study of the photopolymerization of other acrylic and vinyl monomers, as well as the ring-opening polymerization of epoxy compounds.[35] This novel technique should prove very valuable to the determination in real time of the kinetic parameters of ultrafast reactions induced by radiation in polymer systems and to the assessment of the effect of chemical and physical factors on the quantum efficiency of such processes.

References and Notes

(1) Roffey, C. G. *Photopolymerization of Surface Coatings*; Wiley Interscience: Chichester, U.K., 1982.
(2) Bamford, C. H.; Jenkins, A. D.; Symons, M.; Townsend, M. *J. Polym. Sci.* **1959**, *34*, 181.
(3) McGinniss, V.; Provder, T.; Kuo, C.; Gallopo, A. *Macromolecules* **1978**, *11*, 393 and 405.
(4) Tryson, G. R.; Schultz, A. R. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 2059.
(5) Reiser, A.; Egerton, P. *Macromolecules* **1979**, *12*, 670.
(6) Egerton, P.; Reiser, A.; Shaw, W.; Wagner, H. M. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 3315.
(7) Decker, C.; Fizet, M. *Makromol. Chem., Rapid Commun.* **1980**, *1*, 637.
(8) Decker, C. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2451.
(9) Pemberton, D. R.; Johnson, A. F. *Polymer* **1984**, *25*, 529.

(10) Hoyle, C. E.; Hensel, R. D.; Grubb, M. B. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 1865.
(11) Olaj, O. F.; Bitai, I.; Gleixner, G. *Makromol. Chem.* **1985**, *186*, 2560.
(12) Olaj, O. F.; Bitai, I.; Hinkelmann, F. *Makromol. Chem.* **1987**, *188*, 1689.
(13) Olaj, O. F.; Schnöll-Bitai, I. *Eur. Polym. J.* **1989**, *25*, 635.
(14) Olaj, O. F.; Kremminger, P.; Schnöll-Bitai, I. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 771; *Eur. Polym. J.* **1989**, *25*, 535.
(15) Buback, M.; Schweer, J. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 145 and 699.
(16) Timpe, H.; Strehmel, B.; Schiller, K.; Stevens, S. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 749.
(17) Hoyle, C. E.; Keel, M.; Kim, K. *Polymer* **1988**, *29*, 18.
(18) Hoyle, C. E.; Chang, C. H.; Trapp, M. A. *Macromolecules* **1989**, *22*, 3607.
(19) Hoyle, C. E.; Trapp, M. A.; Chang, C. H.; Lathant, D. D.; McLaughlin, K. W. *Macromolecules* **1989**, *22*, 3866.
(20) Decker, C.; Moussa, K. *Polym. Mater. Sci. Eng.* **1989**, *60*, 547.
(21) Decker, C.; Bendaikha, T. *Eur. Polym. J.* **1984**, *20*, 753.
(22) Decker, C. *ACS Symp. Series* **1984**, *266*, 207.
(23) Decker, C.; Moussa, K. *J. Polym. Sci., Polym. Lett. Ed.* **1989**, *27*, 347.
(24) Kirchmayr, R.; Berner, G., Hüsler, R.; Rist, G. *Farbe + Lack* **1982**, *88*, 910.
(25) Decker, C.; Moussa, K. *Makromol. Chem.* **1988**, *189*, 2381.
(26) Hatchard, G.; Parker, C. *Proc. R. Soc. London* **1956**, *A235*, 518.
(27) Decker, C.; Faure, J.; Fizet, M.; Rychla, L. *Photogr. Sci. Eng.* **1979**, *23*, 137.
(28) Decker, C.; Moussa, K. *Eur. Polym. J.* **1990**, *26*, 393.
(29) Decker, C.; Moussa, K. *Macromolecules* **1989**, *22*, 4455.
(30) Decker, C.; Jenkins, A. *Macromolecules* **1985**, *18*, 1241.
(31) Hwang, D.; Cohen, C. *Macromolecules* **1984**, *17*, 2890.
(32) Sack, R.; Schulz, G. V.; Meyerhoff, G. *Macromolecules* **1988**, *21*, 3345.
(33) Gronenboom, J.; Hageman, H.; Overeem, T.; Weber, A. *Makromol. Chem.* **1982**, *183*, 281.
(34) Decker, C.; Moussa, K. *J. Appl. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 739.
(35) Decker, C.; Moussa, K. *J. Polym. Sci., Polym. Chem. Ed.*, in press.