

# Kinetics of Acrylic Films Photopolymerization Through Analysis of the Thermal Curve

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**ABSTRACT:** Kinetic curves of polymerization were obtained through a photocalorimetric device that allows thermal measurements on flat films of controlled thickness of oligomers based on bis-phenol-A-diglycidyl-ether diacrylate. The temperature of the film was monitored during the ultraviolet irradiation under controlled conditions and the resulting thermal curve was processed by a suitable thermokinetic model based on the balance between the internal energy generation and the heat flow at the surfaces. The kinetic behavior of the acrylic group polymerization agrees with the kinetics followed by Fourier transform infrared analysis and fulfills the kinetic behavior expected for a photopolymerization process under steady state conditions. The proposed technique should be a suitable method to study in real time the reactivity of ultraviolet crosslinkable films in different condition of process. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 458–463, 2000

**Key words:** acrylic films; UV curing; kinetics; thermal curve; photocalorimetry

## INTRODUCTION

Ultraviolet (UV)-induced polymerization allows a transformation of liquid monomers into solid polymers through reactions that are very fast, even at room temperature. In the same way, liquid multifunctional oligomers, layered on a solid substrate, originate polymeric networks with interesting properties for technological applications. Photopolymerization of functionalized oligomers is widely applied to obtain thin films with controlled mechanical properties for coatings, adhesives, electronics, and graphic arts.<sup>1</sup> Photopolymerizable films have been proposed as optical devices for diffraction elements manufacture.<sup>2</sup>

Monomers or oligomers suitable for use in UV photopolymerization processes are mainly based

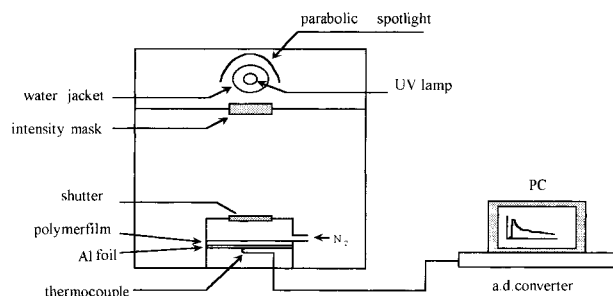
on acrylic functionality. The reaction occurs through a chain mechanism induced by the presence of a photoinitiator that absorbs the UV radiation and originates the primary radicals that start the crosslinking reaction.

Many experimental techniques have been proposed to follow the kinetics of the photopolymerization process.<sup>3</sup> These are based on the measurement of the viscosity or on the spectroscopic, thermal, or dilatometric properties that change during the crosslinking process. Some techniques have been proposed to obtain the kinetic curve in real time.<sup>4</sup>

An important parameter, for property control in applications of photoreactive resins, is the thickness of the film. The reaction rate in the inner layers of the film can be modified by light absorption in the external layers and the mean reaction rate can change with the thickness of the film. Moreover, the double bond (d.b.) conversion in a crosslinking system is limited by gel formation or by the glass transition temperature ( $T_g$ ) of the crosslinked network. In the case of glassy

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**Figure 1** Scheme of the apparatus to record the thermal curve during the photopolymerization.

networks, the high increase of temperature of thicker films during photopolymerization can allow the final d.b. conversion to increase because of the higher chain mobility.

Reported herein are the results obtained with a calorimetric device that allows the film temperature acquisition during the photopolymerization reaction. The device was specifically designed to analyze the kinetic behavior of a layer of resin in the real conditions adopted in the industrial UV curing processes.

The recorded thermal curve, processed through a suitable thermokinetic model, allows one to obtain, in real time, the kinetics of d.b. conversion for a film of resin of controlled thickness supported on a metallic foil.

## EXPERIMENTAL

### Materials

The monomer used for the curing experiment was the bis-phenol-A-diglycidyl-ether diacrylate (BGEDA; UCB, Belgium). Tripropylen-glycol diacrylate (TPGDA; UCB) was added to the monomer in a 25:75 weight ratio to obtain a liquid of a suitable viscosity to be layered in uniform thickness with a wire wound applicator. The photoinitiator 2,2-dimethoxy-2-phenyl acetophenone (DMPA; Ciba-Geigy) was added to the mixture before the UV treatment.

### Thermal Curves Recording

The scheme of the experimental apparatus is shown in Figure 1. The UV irradiation of the sample was performed using a 500 W Hg medium pressure lamp (Helios Italquartz) equipped with a water jacket to screen infrared radiation. The intensity and dose of the UV radiations were con-

trolled with an optical mask and a mechanical shutter, respectively. The measurement of the energy power on the film was made using a UV light meter Goldilux manufactured by Oriel.

The reactive resin film was coated on Al foil and settled in a cell fluxed with inert gas ( $N_2$ ). The Al surface was put into contact with Fe and Cu-Ni wires in two close points and the thermoelectric voltage, amplified and calibrated by an electronic circuit, was stored in a data logger at a sampling rate of 10 Hz.

### Evaluation of the Convective Heat Transfer Coefficient

After the thermal curve was recorded, a complete reaction of d.b. was assured by further UV irradiation. Then, and in the same conditions as those adopted for recording the thermal curve, the Al foil was submitted to a fast electrical heating (Joule effect) and the temperature decrease of the Al film was recorded. In these conditions, the layers of polymer and Al can be considered isothermal and the cooling curve can be analyzed through an equation that takes into account the heat transfer by convection at the surfaces:

$$T - T_a = (T_o - T_a) \exp(-hSt/mC_{p,m})$$

where  $T$  is the temperature of the film at the time  $t$ ,  $T_a$  the surrounding inert gas temperature,  $T_o$  the initial temperature of the analyzed cooling curve,  $S$  the area of the film surface, and  $m$  its mass.

The value of  $C_{p,m}$ , the specific heat of the system constituted by the two layers, was obtained as

$$C_{p,m} = C_{p,pol} + C_{p,Al}(\rho_{Al}s_{Al}/\rho_{pol}s_{pol})$$

From these equations the coefficient of convection,  $h$ , was evaluated as the slope of the plot of  $\ln[(T_o - T_a)/(T - T_a)]$  as a function of  $[St/(mC_{p,m})]$ .

### Characterization of the Polymeric Film

The thickness of the films was evaluated using a QuaNix 7500 coating thickness gauge manufactured by Automation Nix GmbH, Koln. The density of the materials was determined by hydrostatic method.

The mean density,  $\rho_m$ , of the composite film, polymer of thickness  $s_{pol}$  layered and Al foil of thickness  $s_{Al}$ , was evaluated as:

$$\rho_m = (\rho_{pol} s_{pol} + \rho_{Al} s_{Al}) / (s_{pol} + s_{Al})$$

Differential scanning calorimetry (DSC) measurements were performed on a Mettler DSC 20 instrument.

Infrared analysis was performed using a Fourier transform infrared (FTIR) ATI Mattson Genesis Instrument. Thin films of resin were layered on a KBr disk and the stretching band at  $1636\text{ cm}^{-1}$ , with reference to the aromatic ring band at  $1510\text{ cm}^{-1}$ , was used for quantitative determination of the acrylic d.b.s.

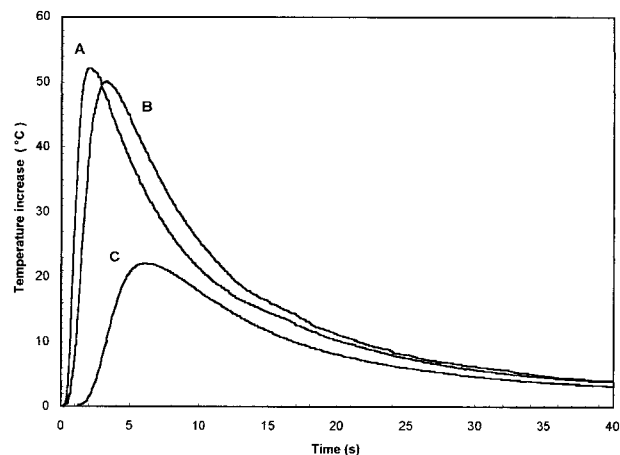
The enthalpy for the BGEDA/TPGDA polymerization reaction was evaluated through DSC analysis by adding a thermal initiator to the mixture (benzoyl peroxide). With heating rates in the range of  $2\text{--}20^\circ\text{C min}^{-1}$  and a final temperature of  $270^\circ\text{C}$ , an exothermal peak of  $340\text{ J/g}$  ( $\text{SD} \pm 1.57$ ) was evaluated. This value was taken as the polymerization heat of the mixture as the FTIR analysis of the crosslinked material did not show any bands of residual d.b.s.

## RESULTS AND DISCUSSION

The shape of the thermal curves collected during UV irradiation of films of the BGEDA/TPGDA mixture depends on different factors: UV intensity, film thickness, photoinitiator concentration, and purge gas flow. Some curves obtained at different irradiation power at constant photoinitiator concentration are reported in Figure 2. The value of the peak temperature depends on the reaction rate: as UV intensity or DMPA concentration increases, the value of the peak temperature of the thermal curve increases.

To obtain the kinetics of d.b. conversion, the thermal curves must be processed by modeling the heat transfer during the photopolymerization process. Some simplifications can be introduced into the mathematical description of the system. The main assumption is to consider the two-layer film, polymer and Al, as an isothermal system during the polymerization.

The thermal behavior during the photopolymerization of a layer of acrylic resin supported on Al foil has been evaluated with a thermokinetic model that takes into account the thermal conduction in the two different phases and the thermal convection at the surfaces. As we reported in a previous article,<sup>5</sup> the resulting equations can be solved only by means of a numerical method.



**Figure 2** Thermal curves for the BGEDA/TPGDA (75:25 w/w) mixture submitted to photopolymerization at different UV irradiation powers. Films thickness ( $\mu\text{m}$ ): Al = 30; Polymer: A = 51, B = 70, C = 65. UV intensity ( $\text{mW cm}^{-2}$ ): A = 2.76, B = 0.92, C = 0.28. DMPA (w/w): 0.04.

The results obtained by solving the thermokinetic equations through a finite difference approximation method, show that a  $10\text{--}200\text{ }\mu\text{m}$  acrylic film, with a convective coefficient corresponding to still or slowly flowing surrounding gas ( $10\text{--}20\text{ J m}^{-2}\text{ s}^{-1}\text{ K}^{-1}$ ), has a difference of temperature of some tenth of degrees between core and surface during the photopolymerization process. That means the assumption that the polymer film is thermally homogeneous, i.e., the temperature of each point is dependent on the time but independent of the distance from the surfaces of the films, can be taken in consideration without appreciable influence on the results. This allows a remarkable simplification of the mathematical treatment of the experimental data.

Another simplification, which arises from the high value of the ratio area/thickness of the polymeric film, is to consider the heat flux as one-dimensional, neglecting the border effect. In our system, the thermal curves obtained under identical experimental conditions did not show significant differences when performed on polymeric films with a length/thickness ratio higher than  $4 \times 10^2$ .

Under the above mentioned assumptions the films, during the photopolymerization process, can be considered an isothermal body with internal generation of heat, mainly due to the reaction, and heat dissipation by convection at the surfaces. The heat generation term can be attributed

either to the enthalpy of the d.b.s polymerization ( $\Phi_R$ ) or to the physical absorption of radiations ( $\Phi_\lambda$ ).

The thermal energy balance for the total volume  $V$  of the film gives:

$$\Phi_R + \Phi_\lambda = \rho_m V c_{p,m} dT/dt + 2Ah(T - T_a)$$

where the right term is the sum of the heat storage due to the temperature increase of the films ( $\rho_m$ , mean density;  $c_{p,m}$ , mean specific heat) and of the heat flux due to the convection at the surfaces ( $A$ , surface area;  $h$ , convection coefficient;  $T$ , film temperature;  $T_a$ , surrounding inert gas temperature).

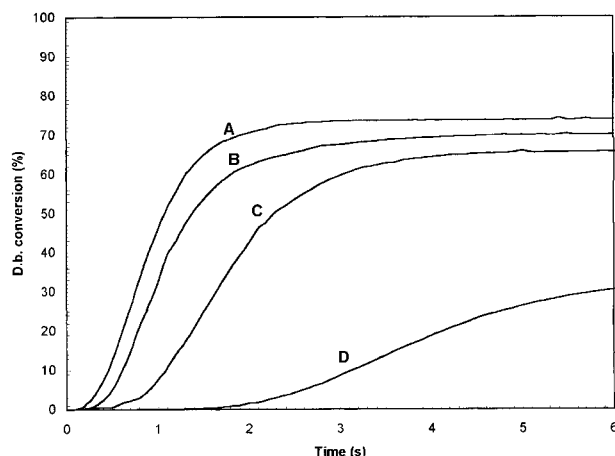
The heat absorbed by lamp irradiation,  $\Phi_\lambda$ , was evaluated by using the same expression with the term  $\Phi_R = 0$ , that is, by recording the thermal curve after the reaction was over (full crosslinking).

The energy balance per volume unit can be expressed as:

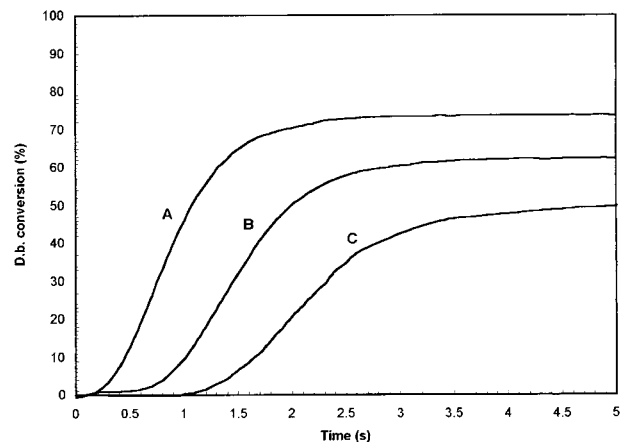
$$(\Phi_R)_V = \rho_m c_{p,m} dT/dt + 2h(T - T_a)/s$$

where  $s$  is the sum of the polymer and the Al thickness.

This last equation can be integrated to obtain the heat  $Q_R$  released by the reaction at the time  $t$ . If the thermal curve is obtained by acquisition of  $i$  ( $=$  time/frequency) temperature values, a suitable expression to evaluate  $Q_R$  is:



**Figure 3** Kinetics of d.b. conversion at different values of UV intensity. Films thickness ( $\mu\text{m}$ ): Al = 30; Polymer: A = 51, B = 55, C = 70, D = 65. UV intensity ( $\text{mW cm}^{-2}$ ): A = 2.76, B = 1.84, C = 0.92, D = 0.28. DMPA (w/w): 0.04.



**Figure 4** Kinetics of d.b. conversion with different concentrations of photoinitiator. Films thickness ( $\mu\text{m}$ ): Al = 30; Polymer: A = 51, B = 55, C = 70. Conc of DMPA (w/w): A = 0.04, B = 0.02, C = 0.01. UV intensity:  $2.76 \text{ mW cm}^{-2}$ .

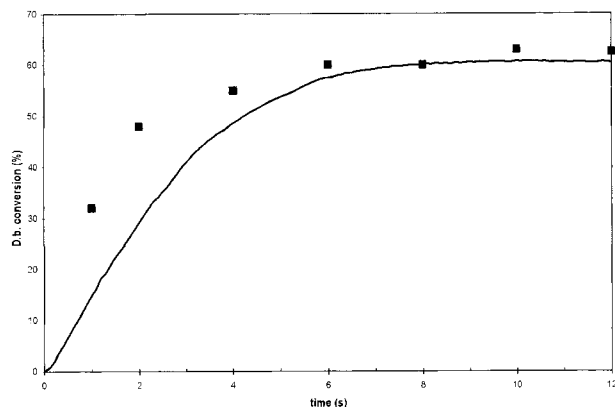
$$Q_R = \rho_m c_{p,m} (\Delta T)_i + (2h/s) \sum_i (\Delta T)_i$$

In this form the heat that can be evaluated easily from the temperature data stored in the thermal curve and the d.b. conversion can be obtained as  $\eta = Q_R/Q_R^\circ$ , where  $Q_R^\circ$  is the enthalpy of polymerization

Some kinetics of d.b. conversion, obtained applying the above mentioned equations to thermal curves of photopolymerization at different UV irradiation intensities, are reported in Figure 3. It is evident from this figure that as the UV intensity increases there is a decrease of the time corresponding to the induction period of the polymerization and a decrease of the residual uncured d.b.s. As can be seen from Figure 4, similar behavior is shown for systems cured under a constant value of UV intensity but containing different concentrations of photoinitiator.

In any case, the decrease of the induction period is due to the increase of the rate of production of radicals and to a faster removal of the oxygen, or other inhibiting molecules, dissolved in the resin film. As soon as these molecules are removed, the polymerization starts and, in a few seconds, the maximum polymerization rate is achieved.

The kinetics evaluated through the analysis of the thermal curves has been compared with the kinetics obtained by infrared spectroscopy. The extent of the reaction was determined by evaluation of the d.b. absorption band at  $1630 \text{ cm}^{-1}$  after



**Figure 5** Kinetics of photopolymerization by FTIR measurements (■) and by thermal curve analysis (full line). UV intensity:  $4.5 \text{ mW cm}^{-2}$ ; film thickness:  $33 \mu\text{m}$ ; DMPA (w/w): 0.04.

the sample was submitted to the UV irradiation for a fixed time.

The results, an example of which is reported in Figure 5, show that higher values of conversion are obtained by the spectroscopic analysis, with a relative higher discrepancy at the lower level of d.b. conversion. The difference between the two kinetics can be explained by taking into account the effect due to the postpolymerization that occurs when the irradiation is over. As has been reported through the study of kinetics of photopolymerization with a real time experimental procedure,<sup>6</sup> the relative extent of this phenomenon is higher at lower conversion as a consequence of the higher chain mobility. The FTIR data clearly show the advancement of the reaction due to the radicals trapped into the network after partial UV curing.

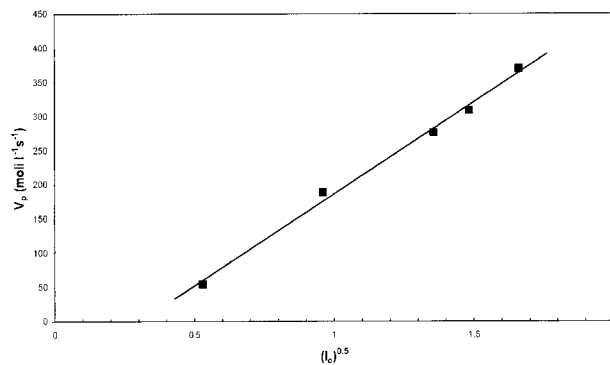
The rate of polymerization,  $R_p$ , can be evaluated from the slope of the curves (d.b. conversion) versus time. Taking into account that the initial concentration of d.b.s  $[\text{d.b.}]_0$ , and their concentration at the time  $t$  [d.b.], are related:

$$[\text{d.b.}] = [\text{d.b.}]_0(1 - \eta)$$

the rate of polymerization can be evaluated as:

$$R_p = d[\text{d.b.}]/dt = -[\text{d.b.}]_0 d\eta/dt$$

The general equation of photopolymerization under steady state conditions, applied to the process in thin film, can be expressed as<sup>3</sup>:



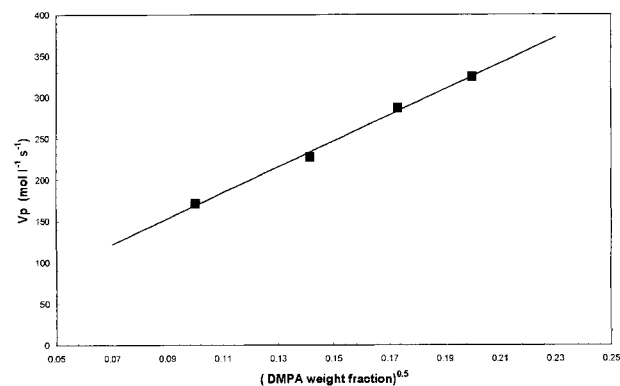
**Figure 6** Dependence of the rate of photopolymerization (d.b. conversion: 15%) on the square root of UV intensity. DMPA (w/w): 0.04.

$$R_p = K(I_0[\text{DMPA}])^{0.5}[\text{d.b.}]$$

At constant d.b. concentration, i.e., in our system at a fixed value of d.b. conversion, the rate of polymerization results linearly dependent on the square root of the UV intensity and on the square root of the photoinitiator concentration.

This behavior could be unexpected because during a polymerization time of the order of some seconds a steady state concentration of radicals should not be reached. However, similar behavior was recently reported<sup>7</sup> by using a real time technique to follow photopolymerization at higher reaction rate, where a process occurring under non-steady conditions can be supposed.

The data reported in Figures 6 and 7, where the values of the rate of photopolymerization at a fixed conversion are plotted against the square root of the UV intensity or photoinitiator concen-



**Figure 7** Dependence of the rate of photopolymerization (d.b. conversion: 15%) on the square root of the concentration of the photoinitiator (DMPA). UV intensity:  $2.76 \text{ mW cm}^{-2}$ .



tration respectively, show agreement of the experimental data with the above mentioned equation.

In the studied system these conditions are verified at low conversion, where the initial induction period and the final gelification of the system have negligible effects on the reaction.

## CONCLUSIONS

The analysis of the thermal curve appears to be a suitable method of studying the kinetics of photopolymerization of acrylic films, supported on a flat surface, in real time. The acquisition of the thermal curve and the evaluation of thermokinetic parameters can be performed with a simple experimental set that is suitable for use in real conditions. The results, obtained by considering a homogeneous distribution of temperature across the film, are in agreement with the kinetic behavior expected under steady state conditions. The proposed technique appears to be suitable for application to studies on the reactivity of UV

crosslinkable resins under different process conditions.

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