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Photoinitiated polymerization of a dimethacrylate oligomer: 1. Influence of photoinitiator concentration, temperature and light intensity

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The photoinitiated polymerization of dimethacrylate oligomer with 2,2-dimethyl-2-hydroxy acetophenone (Darocur 1173) as radical photoinitiator was studied by using isothermal photocalorimetry. The effect of temperature, light intensity and photoinitiator concentration on reaction was investigated. The maximum conversion was obtained at temperature near 90°C. This temperature is above the glass transition temperature of the resulting material and below the thermal polymerization temperature of the reacting system. Above 90°C, thermal polymerization interferes on photocalorimetric measures. Assuming that glass transition temperature of the final polymer and conversion are connected, we have estimated thermal conversion. A maximum conversion was obtained for a photoinitiator concentration of 1% (w/w) and for the highest light intensity studied (2.7 $\mathrm{mW\,cm^{-2}}$). © 1997 Elsevier Science Ltd.

(Keywords: photoinitiator concentration; light intensity; dimethacrylate oligomer)

INTRODUCTION

The photoinitiated polymerization of multifunctional monomers leads to highly crosslinked networks which induce particular behaviours as regards kinetic reaction. Several parameters influence this kinetic such as temperature, photoinitiator concentration, light intensity, polymerizable function concentration, and material thickness. The liquid–solid transition increases the viscosity and characteristic phenomena appear[1,2]: autoacceleration at the beginning of polymerization[3,4], limited conversion of polymerizable functions[5–7], propagation and termination reactions controlled by diffusion[8,9], and volume shrinkage[10,11].

The photoinitiated polymerization exhibits the advantage of leading to high reaction rates [12]. These high rates and the resulting exothermic effect of the reaction can be the cause of defects in the final material. These heterogeneities alter greatly the physical properties of ultimate products and particularly the optic properties which is a great problem for the design of a thick and optically perfect material.

In this work, the photoinitiated polymerization of a dimethacrylate oligomer with 2,2-dimethyl-2-hydroxyacetophenone was studied by using photocalorimetry. The effect of temperature, photoinitiator concentration and light intensity on reaction was investigated in order to optimize the experimental conditions of the reaction and to control the homogeneity of the tridimensional crosslinked polymer network performed.

EXPERIMENTAL

Materials

Figure 1 shows the chemical formulas of the reactants used. The average number of oxyethyl units in the dimethacrylate oligomer (Akzo, $M = 575\,\mathrm{g\,mol^{-1}}$) was determined by ^{1}H n.m.r. analysis and was found to be equal to 4.8.

The photoinitiator 2,2-dimethyl-2-hydroxyacetophenone was dissolved in the oligomer under stirring at room temperature for 3 h in the range 0.5–1.5% (w/w) of Darocur 1173.

Sample preparation

About 2 mg of mixture was laid down over a polyethylene (PE) film (0.1 mm) covering the bottom of an aluminium d.s.c. pan in order to lead to a maximum spreading out of the monomer as a thin and plane layer. Indeed, without PE film, an hemispherical drop is obtained and optical disturbances can confuse the experimental data. It is noteworthy that the presence of PE film does not modify our measurements when the

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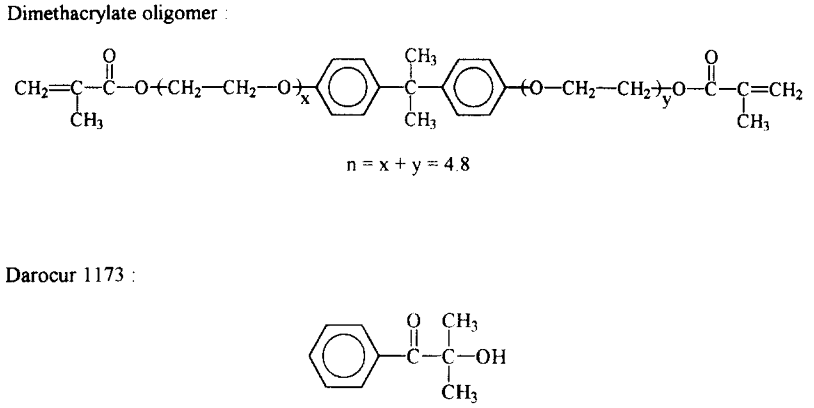

Figure 1 Chemical formulas of reactants

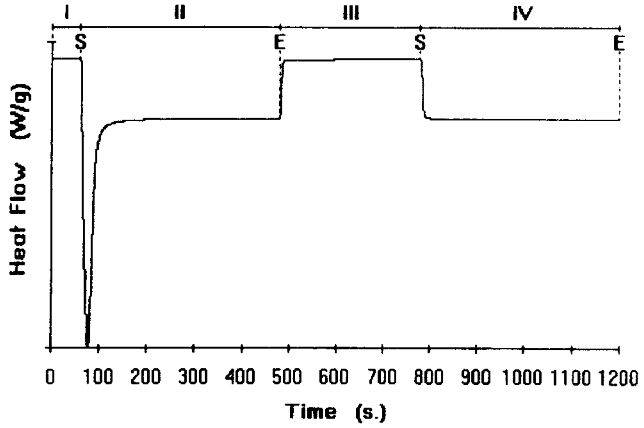

Figure 2 Typical thermogram of photoinitiated polymerization. I and III: baseline without u.v. radiation; II: polymerization exothermic peak; IV: new irradiation after the end of polymerization; S: start of irradiation; E: end of irradiation

experimental temperature is above the PE melting point due to a further thermal stabilization of 5 min before irradiation, as previously mentioned. Moreover, a modelization of heat transfer, by using experimental conversion curves and a heat equation, shows *a posteriori* that, in our case, isothermal conditions are always respected[13].

After irradiation, the thin polymer films are brittle and d.m.a. measurements are very critical. Thus, for convenience sake, 40 mg samples were prepared, without PE film, for d.m.a. analysis. Obviously, we previously verified that the results obtained with 2 and 40 mg samples were identical.

Measurement

The photocalorimeter used is a d.s.c. (DSC 7 Perkin Elmer) topped by an irradiation unit with two quartz windows.

The optical part of the calorimeter includes the following elements:

(a) a light source at a distance of 15 cm from the sample: Hg vapour lamp 100 W (Osram, HBO 100 W/2) fitted with an optical alignment device. A maximum u.v. radiation intensity of 2.7 mW cm^{-2} was measured at the sample level by using a radiometer at 365 nm;
(b) a filter removing i.r. radiations;
(c) neutral filters to modulate the light intensity; and
(d) a manual shutter to control the irradiation time.

Heat flow vs. time was recorded in isothermal mode during the polymerization reaction.

Figure 2 shows a typical thermogram. Before irradiation, each sample was placed in the d.s.c. furnace for 5 min under nitrogen ($\leq$5 ppm O_2) to remove residual oxygen and to allow temperature stabilization (*Figure 2*, Part I). Then the sample was irradiated for 7 min always under inert atmosphere: S point (starting irradiation) to E point (end of irradiation) in *Figure 2*, part II. In order to suppress the shift of the baseline due to a differential absorption between sample and reference, a new irradiation is performed when initial baseline is reached (parts III and IV). The final thermogram (*Figure 3*) is obtained by subtracting part IV from part II.

Conversion was calculated from the overall heat evolved at $t(\Delta H_t)$ corresponding to the dark area in *Figure 3*

$$C = \frac{\Delta H_t}{\Delta H_0^{\text{theor}}} \times 100 \qquad (1)$$

where $\Delta H_0^{\text{theor}}$ is the theoretical heat evolved for complete conversion. Thus, for our dimethacrylate oligomer, a value of $\Delta H_0^{\text{theor}} = -190\,\text{J g}^{-1}$ was used from $\Delta H_{\text{theor}} = -13.1\,\text{kcal mol}^{-1}$ for a methacrylate double bond[14]. Moreover, the polymerization rate was directly connected to the heat flow according to

$$R_p = \frac{dC}{dt} = \frac{dH/dt}{\Delta H_0^{\text{theor}}}$$

Photocrosslinked samples were analysed by d.m.a. (DMA 7 Perkin–Elmer) in compression mode between two parallel plates with a 3 mm diameter probe at 1 Hz frequency and 5°C min^{-1} heating rate. The dynamic and static forces applied were respectively 1200 and 1400 mN. The glass transition temperature T_g was determined at the onset of the storage modulus which is the beginning of the α mechanical transition.

RESULTS AND DISCUSSION

Influence of the temperature

Influence of the temperature on reaction was studied with a photoinitiator concentration of 0.15% (w/w). The light intensity of the u.v. radiation was 2.7 mW cm^{-2}. Ultimate conversion (*Figure 4*) and glass transition temperature T_g (*Figure 5*) were measured for temperature in

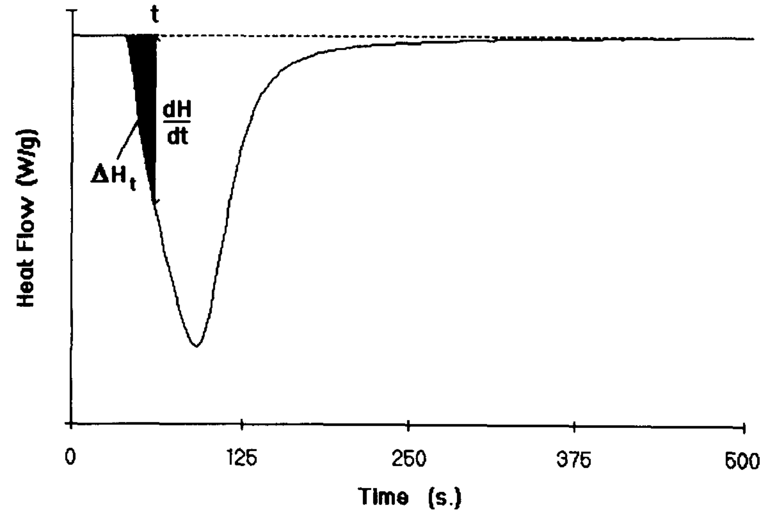

Figure 3 Schematic d.s.c. thermogram after baseline correction

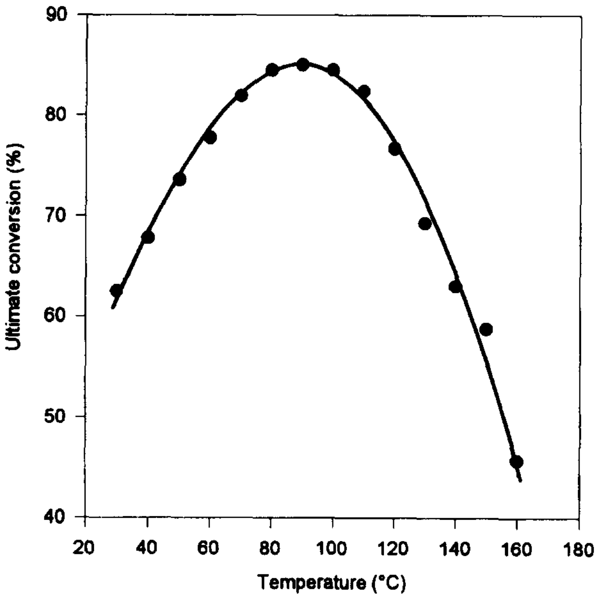

Figure 4 Ultimate conversion vs. temperature for light intensity $I_0 = 2.7\,\mathrm{mW\,cm^{-2}}$

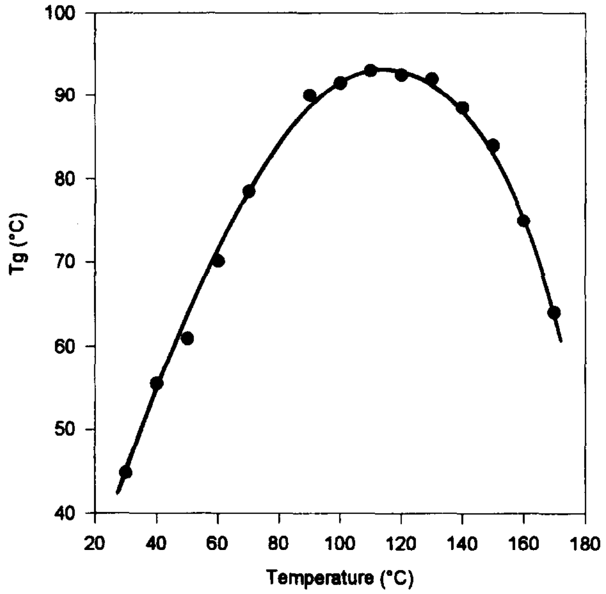

Figure 5 T_g vs. temperature for light intensity $I_0 = 2.7\,\mathrm{mW\,cm^{-2}}$

the range 30–160°C. These two plots show a maximum at 90–100°C.

Conversion vs. time was plotted in *Figure 6* for temperatures below 90°C. At the beginning of the reaction, the initial slopes of conversion plots (R_{pi}) slightly increase with temperature.

If initiation rate is higher than photoinitiator dissociation rate, steady-state assumption leads to

$$R_{pi} = -\frac{d[M]_0}{dt} = k_p[M]_0\left(\frac{\phi\epsilon I_0[A]_0}{k_t}\right)^{1/2} \qquad (2)$$

where ϕ is the quantum yield, ϵ is the photoinitiator molar extinction coefficient, I_0 is the light intensity of the u.v. radiation, and $[A]_0$ is the photoinitiator concentration.

Expressing the rate constants k_p and k_t by their Arrhenius law, it follows that

$$\ln R_{pi} = \ln\left(\frac{A_p}{A_t^{1/2}}\right) + \ln\left(\phi\epsilon I_0[A]_0^{1/2}[M]_0\right) - \frac{E_R}{RT} \qquad (3)$$

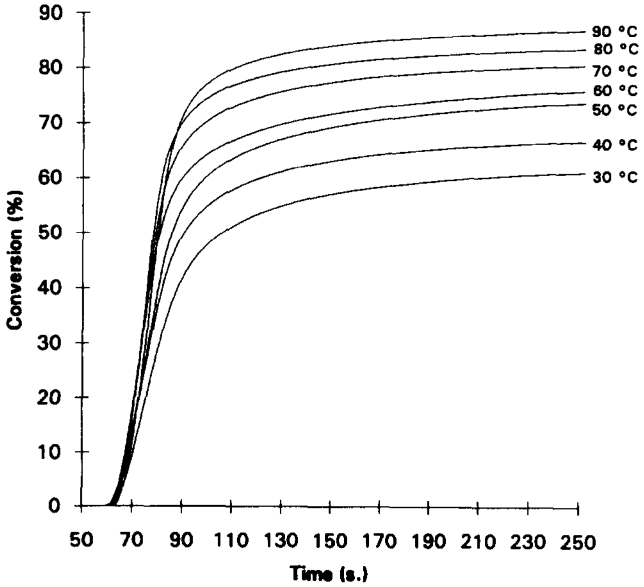

Figure 6 Conversion vs. time for temperature below 90°C

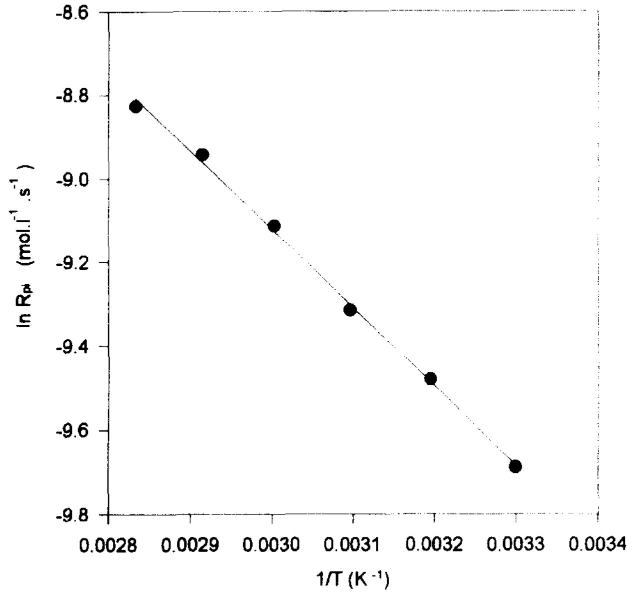

Figure 7 Ln R_{pi} vs. $1/T$ for temperature below 90°C

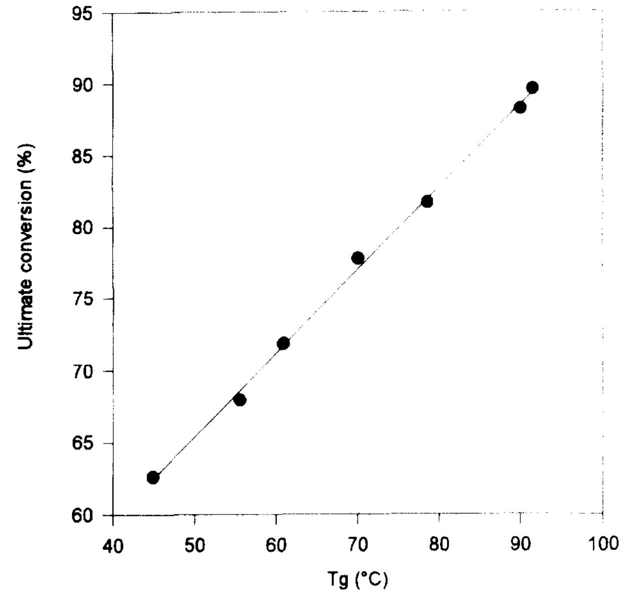

Figure 8 T_g vs. ultimate conversion for temperature below 90°C

with

$$E_R = E_p - \frac{E_t}{2}$$

The slope of the plot ln R_{pi} vs. $1/T$ (*Figure 7*) enables us to calculate the apparent activation energy E_R of the reaction for temperatures lower than 90°C. E_R was found to be equal to $15.5\,\mathrm{kJ\,mol^{-1}}$. This low value is similar to the one reported for methyl methacrylate ($17.1\,\mathrm{kJ\,mol^{-1}}$)[15] and justifies the slight variation of initial rates with increasing temperature.

We also notice in *Figures 5* and *6* that conversion increases with temperature. Although gelation decreases the mobility and the diffusion of the reactive species and leads to a progressive rate deceleration, the reaction completely stops when the glass transition temperature of the crosslinked material is reached (glassy state).

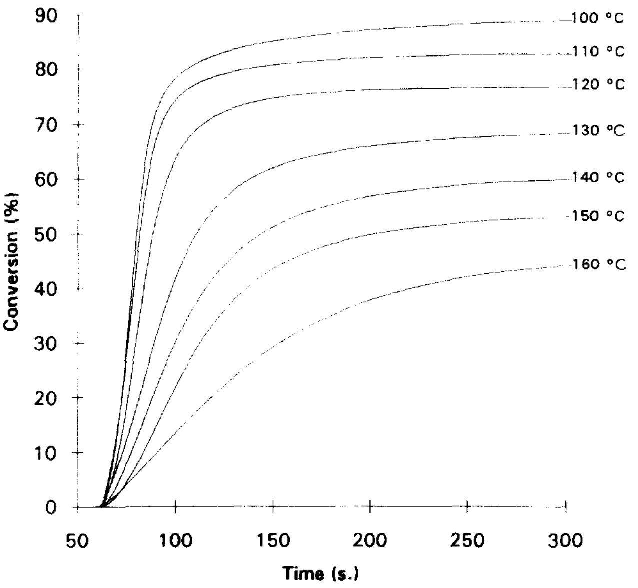

Figure 9 Conversion vs. time for temperature above 90°C

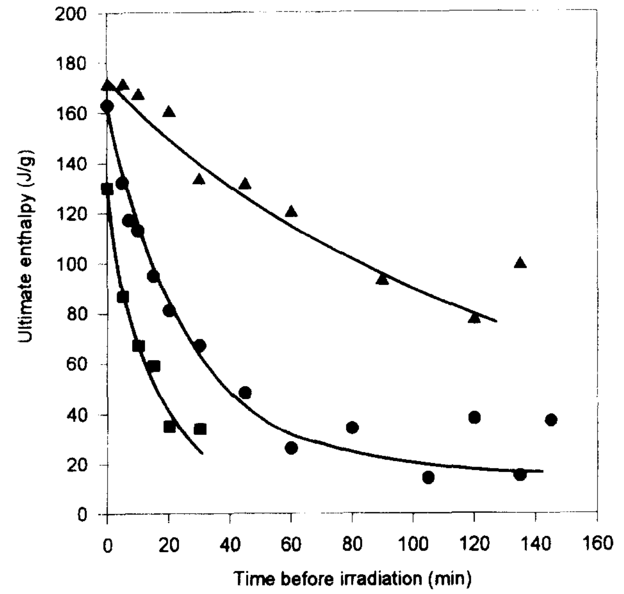

Figure 10 Remaining enthalpy vs. increasing time before irradiation at different reaction temperatures: (▲) 100°C, (●) 130°C, (■) 160°C

It is noteworthy that we obtain a linear relation between T_g and conversion of crosslinked materials for temperatures below 90°C (*Figure 8*)

$$C = 36.5 + 0.58T_g \qquad (4)$$

From equation (4) we can expect, for example, a 25°C variation for T_g when the conversion varies by only 14.5%.

Conversion vs. time for temperatures above 90°C is plotted in *Figure 9*. We notice that initial reaction rate and ultimate conversion decrease when temperature increases though T_g, which decreases, is lower than the reaction temperature (see *Figure 5*).

In that case, it is not possible to put forward the glassy state as a limiting factor. In earlier papers[16], this phenomenon was explained either by evaporation of

Table 1 Experimental and calculated conversions above 90°C

T (°C)	100	110	120	130	140	150	160
T_g^a (°C)	91.5	93.0	92.5	92.0	88.5	84.0	75.0
C_o^b (%)	88.7	90.3	89.8	89.8	87.7	85.1	79.8
C_{ph}^a (%)	88.7	82.4	76.7	69.3	60.4	53.6	44.1
C_{th}^b (%)	0	7.9	13.1	20.5	27.3	31.5	35.7

[a] Experimental values
[b] Calculated values

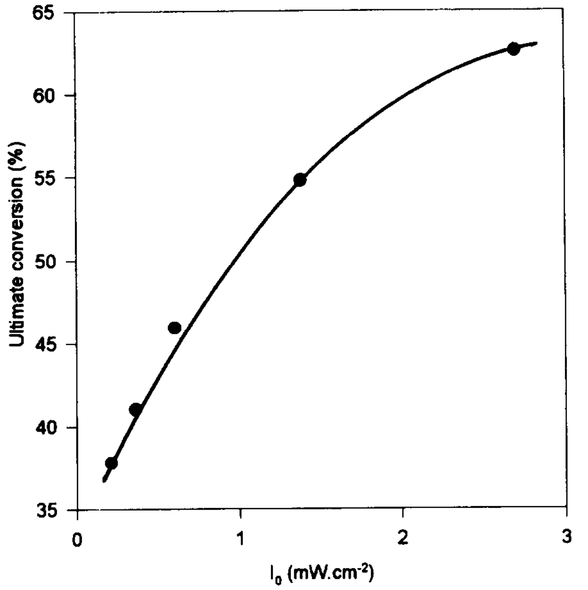

Figure 11 Ultimate conversion vs. light intensity at 30°C

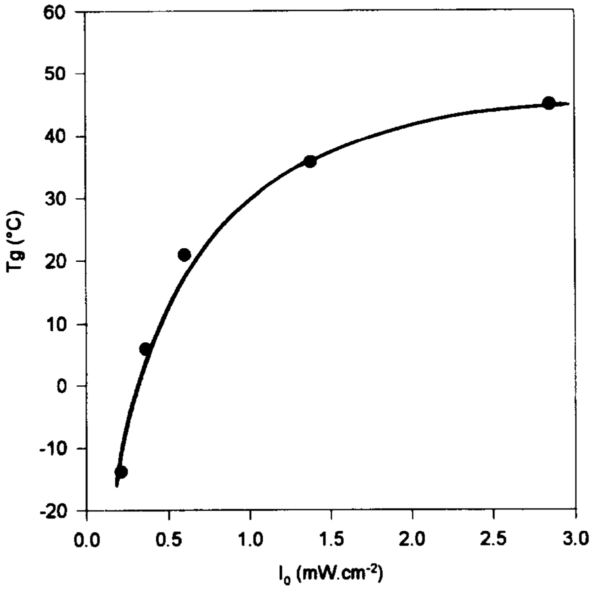

Figure 12 T_g vs. light intensity at 30°C

reactants or existence of a ceiling temperature or photoinitiator degradation. Our interpretation is directly connected to our experimental conditions. In our case, before irradiation, the sample stays at the reaction temperature for 5 min and a thermal polymerization occurs when the temperature is high enough. To strengthen this assumption, ultimate enthalpy was followed with increasing time, at reaction temperature, before irradiation (*Figure 10*). The higher the temperature and time, the more the remaining enthalpy decreases in agreement with an increase of a previous thermal polymerization.

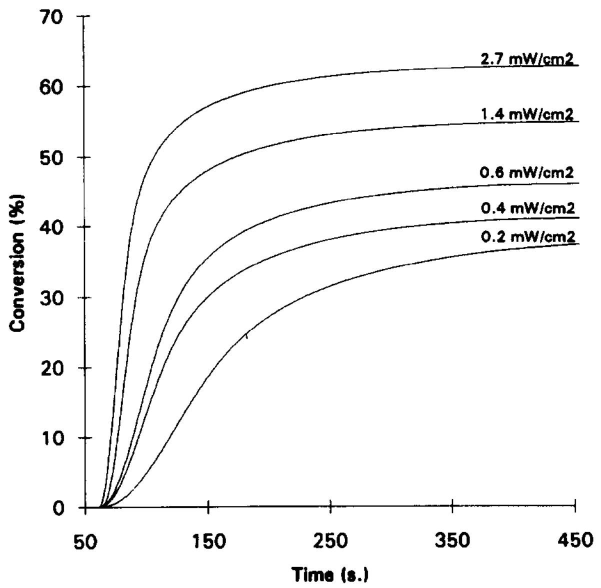

Figure 13 Conversion vs. time for different light intensities at 30°C

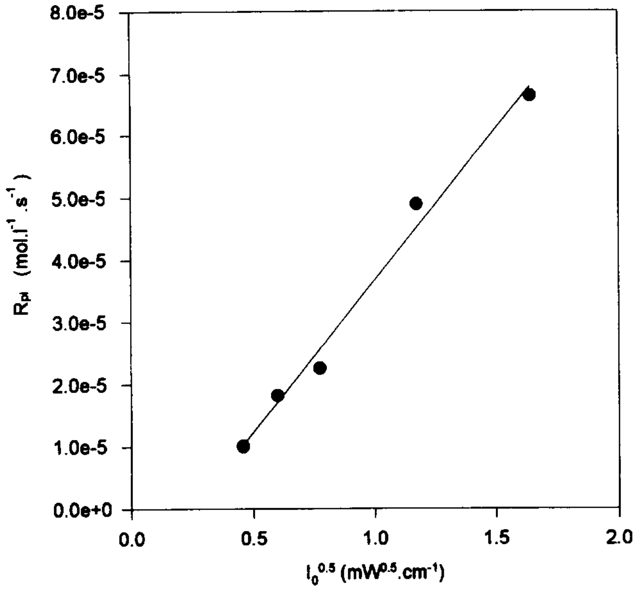

Figure 14 R_{pi} vs. $I_0^{1/2}$ according to relation (2)

According to T_g values, we can assert that conversion never reaches 100%. In fact, the existence of thermal polymerization before irradiation interferes with the system firstly by consuming methacrylate functions which decreases initial rate and secondly by shrinkage of the sample which decreases its initial free volume and therefore resulting conversion.

Photoinitiated polymerization conversion (C_{ph}) and T_g are experimentally measured. If we assume that, whatever the rate of crosslinking, T_g is the same at an equivalent conversion, equation (4) allows us to estimate an overall conversion (C_o) as the sum of thermal conversion (C_{th}) and C_{ph}. Thus,

$$C_o = C_{th} + C_{ph} = 36.5 + 0.58T_g$$

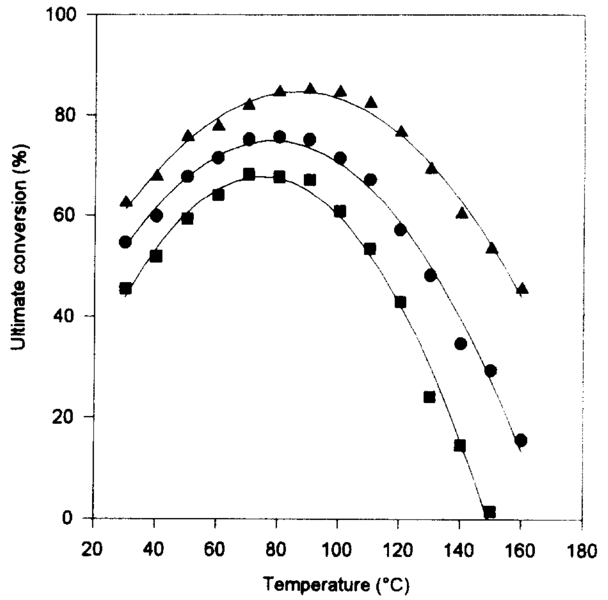

Figure 15 Ultimate enthalpy vs. temperature for different light intensities: (▲) 2.7 mW cm^{-2}; (●) 1.3 mW cm^{-2}; (■) 0.6 mW cm^{-2}

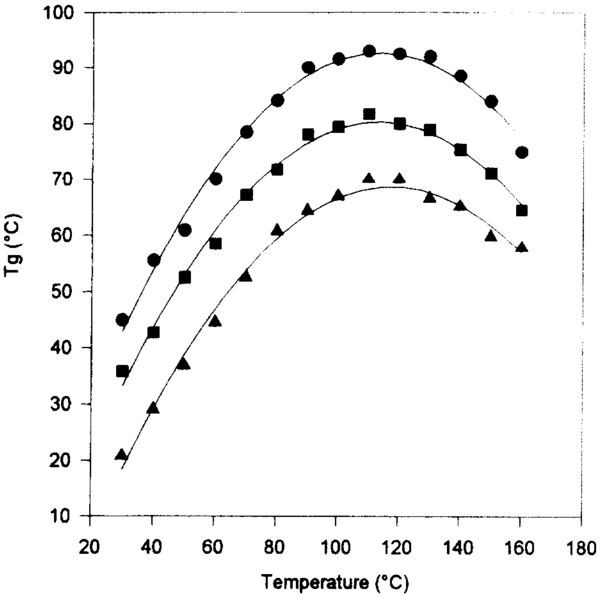

Figure 16 T_g vs. temperature for different light intensities: (●) 2.7 mW cm^{-2}; (■) 1.3 mW cm^{-2}; (▲) 0.6 mW cm^{-2}

i.e.

$$C_{th} = 36.5 + 0.58T_g - C_{ph} \quad (5)$$

The results for C_{th}, calculated using equation (5), are reported in *Table 1* for temperatures in the range 100–160°C.

We observe an increase of thermal conversion to the detriment of photoinitiated polymerization conversion with increasing temperature.

Influence of light intensity

Influence of light intensity was studied with a photoinitiator concentration of 0.15% (w/w). Firstly, the study was carried out at 30°C with light intensity in the range 0.2–2.7 mW cm^{-2}. We observe that ultimate conversion and T_g increase with light intensity (*Figures 11* and *12*).

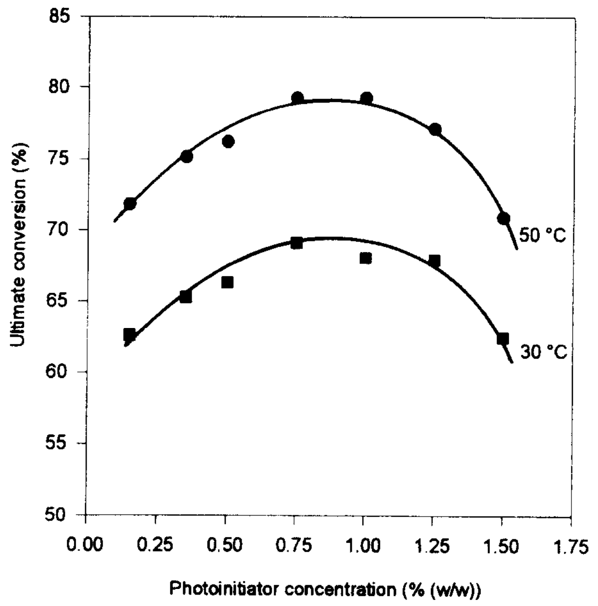

Figure 17 Ultimate conversion vs. photoinitiator concentration at 30 and 50°C

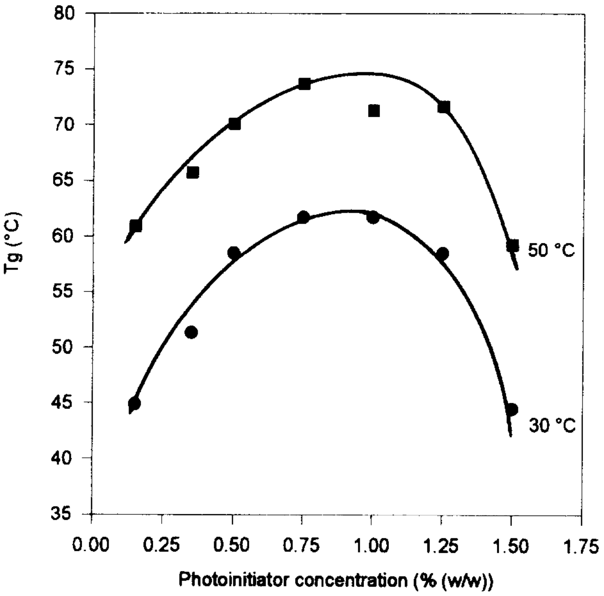

Figure 18 T_g vs. photoinitiator concentration at 30 and 50°C

Conversion vs. time plots (*Figure 13*) show clearly that polymerization rates increase with light intensity. In agreement with equation (2), the initial slopes of the curves (R_{pi}) are proportional to $I_0^{1/2}$ (*Figure 14*).

In case of photoinitiated polymerization, initiation rate is very high. Thus, crosslinking systems cannot be in volumic equilibrium because volume shrinkage rate is much slower than chemical reaction rate. This difference generates a temporary excess of free volume which increases the mobility of the residual double bonds and allows us to reach higher conversion than for systems in volumic equilibrium. So, the higher the light intensity, the higher the polymerization rate and the more important the free volume excess which leads to higher conversions.

Curves with similar trends are obtained for ultimate conversion and T_g plots when temperature varies in the range 30–160°C (*Figures 15* and *16*).

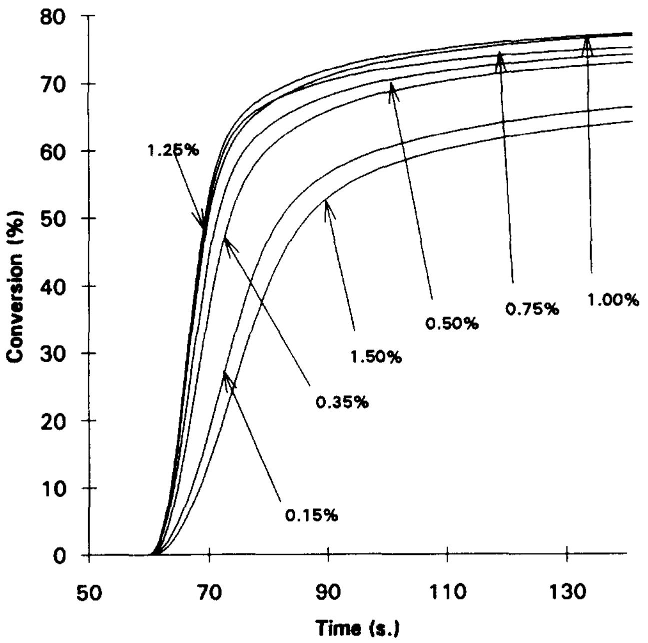

Figure 19 Conversion vs. time for different photoinitiator concentration at 50°C

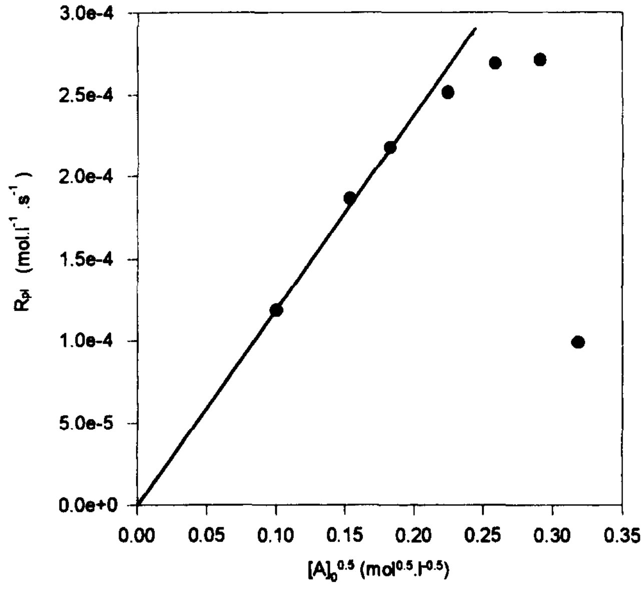

Figure 20 R_{pi} vs. $[A]_0^{1/2}$ at 50°C

Nevertheless, *Figure 15* shows a slight shift of the maximum conversion with light intensity. It should be noted that the lower the light intensity, the longer the reaction time takes to reach the maximum and the smaller the excess of free volume. Thus, conversion decreases sooner.

Influence of photoinitiator concentration

The influence of photoinitiator concentration was studied at 30 and 50°C. The light intensity was 2.7 mW cm^{-2} and photoinitiator concentration varied in the range 0.15–1.5% (w/w). Conversion (*Figure 17*) and T_g (*Figure 18*) vs. photoinitiator concentration have the same trend whatever the temperature and show a maximum for about 1% (w/w) of Darocur 1173.

Likewise, conversion vs. time (e.g. at 50°C, *Figure 19*) shows a maximum initial rate for 1% (w/w) Darocur 1173.

According to equation (2), when $[A]_0$ increases, the polymerization rate R_p must increase. Moreover, according to the theory of free volume, if R_p increases, the conversion must also increase. In fact, this result assumes that the different terms of equation (2) are constant. However, it is reasonable to think that the quantum yield ϕ connected to the photoinitiator efficiency can decrease when $[A]_0$ increases. In fact, in steady-state assumption, ϕ corresponds not only to the light dissociation efficiency of initiator but also to competition between the reaction of the primary radical $A^\bullet$ with a double bond during the initiation, whose rate is proportional to $[A^\bullet][M]_0$, and the coupling of these two primary radicals which is proportional to $[A^\bullet]^2$. So, the more $[A^\bullet]$ increases, the more ϕ must decrease. Thus, the increase of $[A]_0$ and the decrease of ϕ could be responsible for the maximum observed for R_p. To these arguments one can add that the coupling of $A^\bullet$ and $M^\bullet$, which is not taken into account as termination reaction in classical steady-state relation, must have great importance when A_0 is high and must unavoidably lead to a decrease in rate and conversion. The plots R_{pi} vs. $[A]_0^{1/2}$ at 50°C (*Figure 20*), show clearly the limitation of relation (2) with a deviation from the linearity when photoinitiator increases.

CONCLUSIONS

From this study, we have emphasized that photocalorimetry is a good method to follow for photoinitiated polymerization. For the dimethacrylate oligomer studied, a maximum conversion is obtained for a temperature near 90°C, a photoinitiator concentration of 1% (w/w) and for the highest light intensity studied (2.7 mW cm^{-2}). Nevertheless, this result is directly connected to our experimental conditions which require to keep samples at reaction temperatures for 5 min before irradiation, period during which thermal polymerization occurs and interferes on photocalorimetric measures.

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