Photoinitiated cross-linking of a thiol–methacrylate system

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Abstract

The photoinitiated thiol–ene cross-linking of a dimethacrylate polyether of Bisphenol A and pentaerythritol tetrakis 2-mercaptopropionate was studied in the presence of 2,2-dimethyl-2-hydroxy acetophenone (Darocur 1173). Two complementary techniques were used: photocalorimetry and real-time infrared spectroscopy. In the first part, the kinetic reaction was characterized by a stoichiometric mixture in reactive functions. The influence of temperature, photoinitiator concentration and ultraviolet (UV) light intensity was investigated. The results mainly show that the methacrylate homopolymerization is faster than the thiol–ene addition so that the reaction is usually stopped because of the complete consumption of the methacrylate double bonds. A theoretical approach has allowed us to determine a transfer constant of 0.26. Moreover, an increase in the autoacceleration rate was observed in the presence of the thiol monomer. In the second part, the molar fraction of methacrylate double bonds and thiol functions was changed to determine the effect on the kinetic reaction and the glass transition temperature of the final material. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords*: Thiol–ene; Photocalorimetry; Real-time infrared spectroscopy

1. Introduction

Thiol–ene systems have known a rapid expansion and are particularly useful for the preparation of ultraviolet (UV) curable coatings, adhesives, …, and find wide applications in industry [1]. Indeed, the resulting materials are more flexible and present greater adhesion than those containing only acrylate systems [2].

If it is well established that thiol–ene photoinitiated polymerization only proceeds from a radical step-growth mechanism that propagates by chain transfer, in contrast with acrylate functional systems, a competitive chain propagation can occur. This mechanism can be described as follows:

Initiation

$$\text{Photoinitiator} \xrightarrow{h\nu} A^{\cdot}$$

$$A^{\cdot} + RSH \rightarrow AH + RS^{\cdot}$$
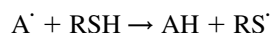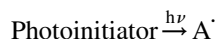
Propagation
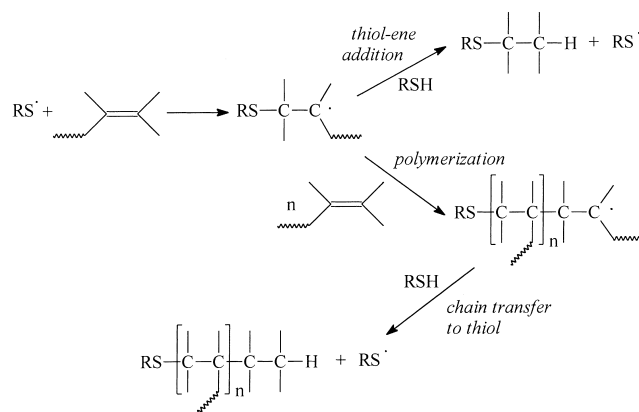
Termination occurs through a bimolecular recombination of any two radicals. It then appears that using multifunctional thiol and ene monomers allows the formation of a three-dimensional cross-linked network. Finally, in relation to the monocomponent acrylate system, the bicomponent thiol–ene system has the advantage of being less sensitive to the inhibitor effect of oxygen [3].

Thiol–ene photoinitiated polymerization has been the subject of many studies but, in most cases, only FTIR spectroscopy was used to characterize UV curing kinetics.

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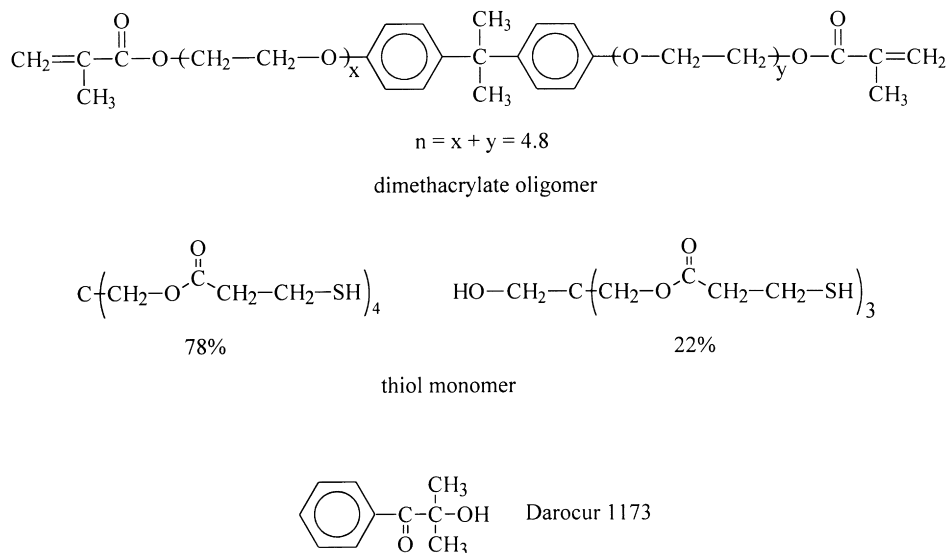 *E-mail address:* claude.bunel@insa-rouen.fr (C. Bunel).

Fig. 1. Chemical formula of the products.

The recent development of the real-time infrared (RTIR) spectroscopy technique has enhanced this supremacy to monitor UV curing [4–7]. Indeed, this technique enables us to monitor the specific changes in chemistry during UV curing by following the decay of the stretching vibrations of the reactive functional groups. Nevertheless, this technique supposes that the reactive group presents an easily located characteristic vibration band. Moreover, there is no control of the reaction temperature as kinetics are highly dependent on this parameter. Differential scanning calorimetry (DSC) is the second technique to monitor UV curing kinetics. The global heat flux evolved by the exothermal reaction is measured with a total control of the temperature but without giving information on the chemistry of this reaction. Perhaps, that is the reason why very few works [8] have used photoDSC to study thiol–ene systems.

In this paper, we propose to study photoinitiated thiol–ene polymerization by combining these two techniques. The two components used are a dimethacrylate polyether of Bisphenol A and pentaerythritol tetrakis 2-mercaptopropionate. Photoinitiated polymerization of the pure dimethacrylate oligomer ($\Delta H_0 = -190$ J/g) has been very well characterized already in previous works [9–12]. These studies were carried out in the presence of Darocur 1173. This radical photoinitiator belongs to the class of the PI_1 photoinitiators. In the presence of hydrogen donors such as thiol monomers, PI_2 photoinitiators are usually used for their great efficiency [2,13–16]. Nonetheless, the Darocur 1173 was kept for the thiol–ene system in order to compare and to understand best the experimental results. Moreover, the efficiency of PI_1 photoinitiators for initiating a thiol–ene reaction has been demonstrated already in another work [17].

The study is divided into two parts. First, the influence of temperature and photoinitiator concentration on the thiol–ene reaction was characterized by using a stoichiometric mixture in thiol and methacrylate functions. Secondly, the mass ratio in the reactive functions was changed. The influence of the thiol or dimethacrylate amount on the reaction kinetics and the glass transition temperature of the photocross-linked material was studied.

2. Experimental part

2.1. Materials

Fig. 1 shows the chemical formula of the reactants used. The average number of oxyethyl units in dimethacrylate oligomer (Akzo, $M = 575$ g/mol) was accurately determined by ^{1}H NMR analysis and found to be equal to 4.8. Pentaerythritol tetrakis 2-mercaptopropionate was purchased from Aldrich and characterized by ^{1}H NMR. In fact, this thiol monomer is a mixture of 78% of the tetrafunctional molecule and 22% of the trifunctional molecule as shown in Fig. 1. The average functionality of the thiol monomer is then 3.8 and the average molar mass is 470 g/mol.

The photoinitiator 2,2-dimethyl-2-hydroxyacetophenone (Ciba Geigy, Darocur 1173) was dissolved in the mixture of these two components under stirring at room temperature under light cover. The Darocur 1173 concentration and the relative amounts of the two other products were changed according to experimental conditions.

2.2. Photocalorimetry

The photocross-linking reactions were carried out in a differential scanning calorimeter (Perkin Elmer DSC 7) topped by an irradiation unit. Heat flow versus time was recorded in isothermal mode under nitrogen atmosphere.

The optical part of the calorimeter, the sample preparation, the treatment of the thermogram and the computation of conversion and reaction rate have been described elsewhere ($\Delta H_0 = -54.7$ kJ/mol per methacrylate double bond) [9]. The UV radiation intensity at 365 nm was 2.7 mW/cm^2 at the sample level.

2.3. Real-time infrared spectroscopy

Photocross-linking reactions were also followed by RTIR spectroscopy (Perkin Elmer FTIR 2000 spectrometer). UV radiation from a 350-W Oriel mercury vapour lamp was introduced into the FTIR spectrometer sample chamber by a flexible light guide so that it did not interfere with the IR beam. The UV radiation intensity was 18.1 mW/cm^2 at the sample level at 365 nm. A set of neutral filters enabled us to modulate the UV light intensity. Samples were sandwiched between two polyethylene films, leading to a photocross-linked film about 10 μm thick. Each of the IR spectra was obtained from the spectrophotometer with a resolution of 8 cm^{-1}. The time between each spectrum was 6 s so that the reaction was followed in real time. The C=C stretching vibrations of the methacrylate functional groups at 1638 cm^{-1} and the S–H stretching vibrations of the thiol functional groups at 2568 cm^{-1} were used to calculate conversions. After correction of the baseline, the conversion of the two functional groups can be calculated by measuring the absorbance at each time of the reaction and determined as follows:

$$\chi_{C=C(t)} = \frac{A_0^{1638} - A_t^{1638}}{A_0^{1638}} \times 100$$

$$and \ \chi_{SH(t)} = \frac{A_0^{2568} - A_t^{2568}}{A_0^{2568}} \times 100$$

where $\chi_{(t)}$ is the conversion of these reactive functions at time t, A_0, the initial absorbance (before UV irradiation) and A_t, the absorbance of the functional groups at time t.

2.4. Dynamic mechanical analysis

Photocross-linked samples were analyzed by dynamic mechanical analysis (DMA 7 Perkin Elmer) in compression mode between two parallel plates with a 1-mm-diameter probe at 1 Hz frequency and 5°C/min heating rate. The dynamic and static forces applied were 1000 and 1200 mN, respectively. The glass transition temperature T_g was determined at the onset of the storage modulus, which was the beginning of the α mechanical transition.

3. Results and discussion

3.1. Influence of the temperature

The influence of the temperature on the reaction was studied for a stoichiometric mixture in thiol and methacrylate functions in the presence of 0.15% (w/w) of Darocur 1173, i.e. a molar concentration of 10^{-2} mol/l of photoinitiator. The photoinitiated reaction was first followed by photocalorimetry in isothermal mode for temperature in the range 30–110°C.

Fig. 2 presents the heat flux versus irradiation time. This tells us about the evolution of the reaction rate since this latter is directly proportional to the height of the exothermic peak. Almost all the curves show a more or less pronounced double peak according to the experimental reaction temperature.

This phenomenon was very recently explained [18–21] by a change in the control of the termination mechanism. In one of our previous papers [10], we determined the relative variations of the propagation and termination kinetic rate constants for pure dimethacrylate. Generally, termination is controlled by polymer diffusion whereas propagation is controlled by small monomer molecule diffusion. At the beginning of the reaction, the diffusivity of the polymer species decreases with the increase in double bond conversion, leading to a drop in k_t. On the other hand, diffusion of the small molecules is not disturbed and k_p remains relatively constant. These evolutions of k_p and k_t generate the autoacceleration related to the Trommsdorff effect, which is observed as soon as the viscosity of the reactional mixture becomes high enough to restrict the segmental movements of the polymer radicals, i.e. as soon as the polymerization reaction starts in the case of viscous multifunctional monomers. As the reaction continues, the environment becomes even more restricted. The propagation reaction and then the termination reaction become diffusion controlled.

Several works [19–21] have shown that adding a solvent or another monomer to the dimethacrylate system leads to a reduction in the viscosity of the system and to a delay in the Trommsdorff effect. This involves an increase in the autoacceleration rate. Thus, at the beginning of the reaction, k_t always decreases because of the limitation of segmental movement, leading to an increase in the radical concentration and then in the propagation rate. Then, because of the lowest initial viscosity of the system, the substantial restriction of segmental movement and hence the gel effect come much later. The resulting effect of this delay is the appearance of a second maximum reaction rate at relatively high conversion.

In our case, the addition of a thiol monomer can play the role of reactive diluent. The DSC thermograms then reveal a double peak. We can also observe a shift of the second peak toward high conversion when the reaction temperature increases up to 70°C. Above 70°C, the second peak appears much earlier as the reaction temperature is high, the effect of the increase in the reaction temperature being compensated by the existence of a thermal polymerization before UV irradiation which increases the viscosity of the initial system. This thermal polymerization is clearly shown in Figs. 3 and 4.

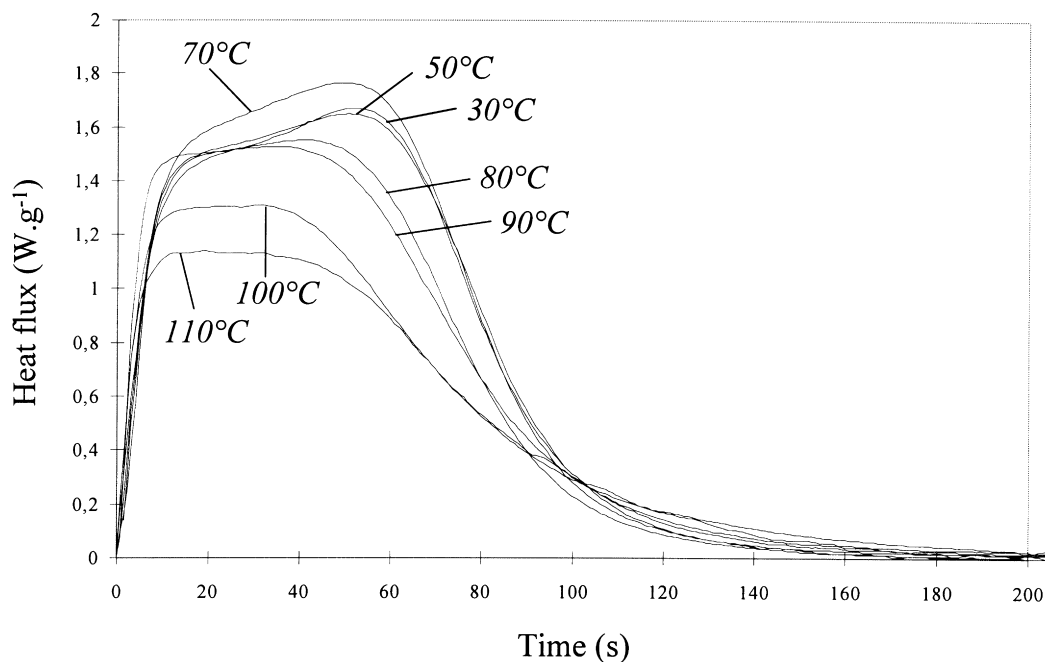As a matter of fact, it is well known that an increase in the

Fig. 2. Heat flux versus time at various temperatures for a stoichiometric mixture in the presence of 0.15% (w/w) of Darocur 1173.

reaction temperature leads to an increase in the reaction rate [8,9,22] and then to a higher reaction yield. In our case, only a slight variation is observed up to 70°C. The reaction enthalpy reaches a maximum of -137 J/g at 70°C. Above this temperature, the amount of evolved heat slowly decreases because of the thermal instability of the mixture. This thermal instability was displayed by changing the

latency time in the DSC apparatus before irradiation. Fig. 4 shows that the ultimate photochemical reaction enthalpy decreases when the latency time before UV irradiation increases. Moreover, the higher the reaction temperature and time are, the faster the photochemical reaction enthalpy decreases in agreement with an increase in a previous thermal polymerization. For experiments collected in Fig. 3,
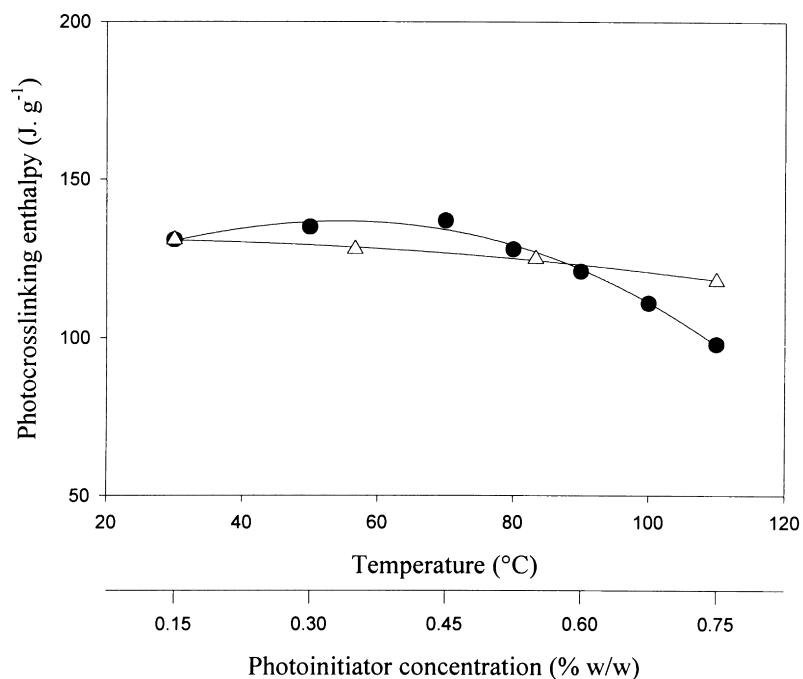

Fig. 3. Absolute value of the photochemical reaction enthalpy versus reaction temperature (●) and photoinitiator concentration (△) for a stoichiometric mixture in the presence of 0.15% (w/w) of Darocur 1173; $I_0 = 2.7$ mW/cm^2 at 365 nm.
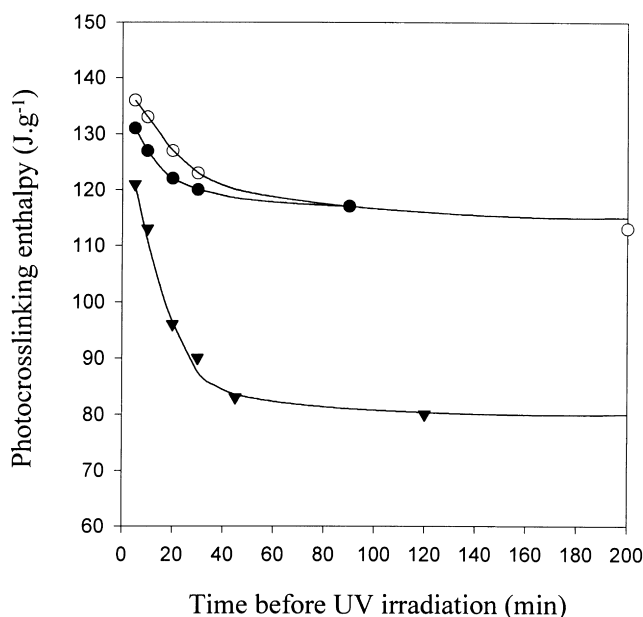
Fig. 4. Absolute value of the photochemical reaction enthalpy versus latency time before UV irradiation at 30 (●), 50 (○) and 90°C (▼).

The thermal stability of the pure dimethacrylate was already studied in a previous paper [9]. A thermal polymerization was also clearly shown for temperatures higher than 100°C. Thus, the presence of the thiol monomer seems to favour the thermal reaction at lower temperature.

The problem of the thermal instability of the thiol–ene system was already described with photoinitiators such as benzoin ether [23]. The authors explain that this poor stability is due to the benzylic hydrogen atom of the photoinitiator. Thus, efficient radicals are produced, even in the absence of light, by a chain reaction which initiates a crosslinking reaction. In our case, Darocur 1173 does not have such a hydrogen atom but a similar phenomenon occurs to lead to a thermal cross-linking without UV light. In another paper [8], a stabilizer (H_3PO_4) was added to benzophenone to avoid this thermal polymerization. In our case, a storage of the reactional mixture in the dark and in the cold (5°C) is enough to prevent this thermal polymerization.

Photocross-linked samples were characterized by dynamic mechanical analysis. It is interesting to note that their T_g is always equal to 20°C whatever the photochemical reaction temperature. In a previous paper [9], we have shown that the photopolymerization stops as soon as the glass transition temperature of the materials reaches the reaction temperature. In the case of the thiol–ene system, the same value of T_g — whatever the temperature — is in agreement with the similar experimental conversion observed. Thus, it is reasonable to think that identical ultimate photocross-linking materials are obtained. Nevertheless, this low value of T_g shows very likely that the reactions are not complete.

samples remain for 5 min in the DSC oven at the reaction temperature before irradiation, in order to reach the thermal equilibrium and to eliminate the inhibiting oxygen by the nitrogen flux. During these 5 min, a thermal polymerization occurs leading to a decrease in the amount of initial reactive functions which reduces the heat flow resulting from photo-induced polymerization, especially above 70°C.
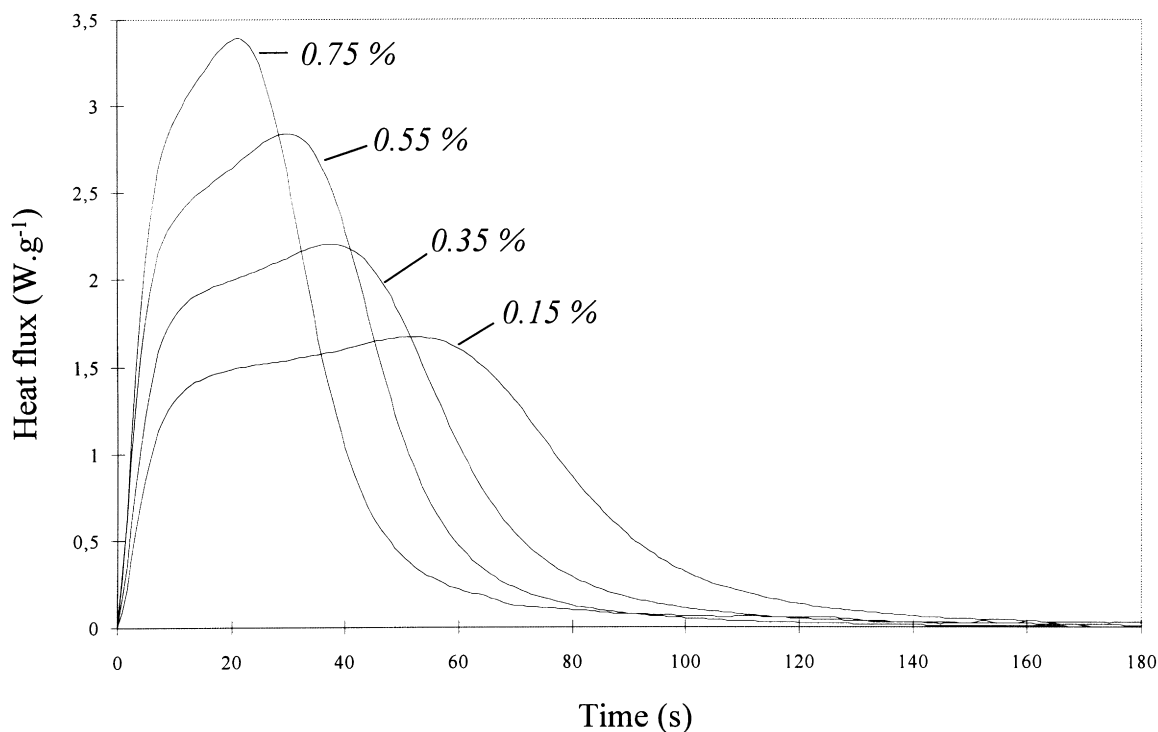

Fig. 5. Heat flux versus time at various Darocur 1173 concentrations for a stoichiometric mixture at 30°C.
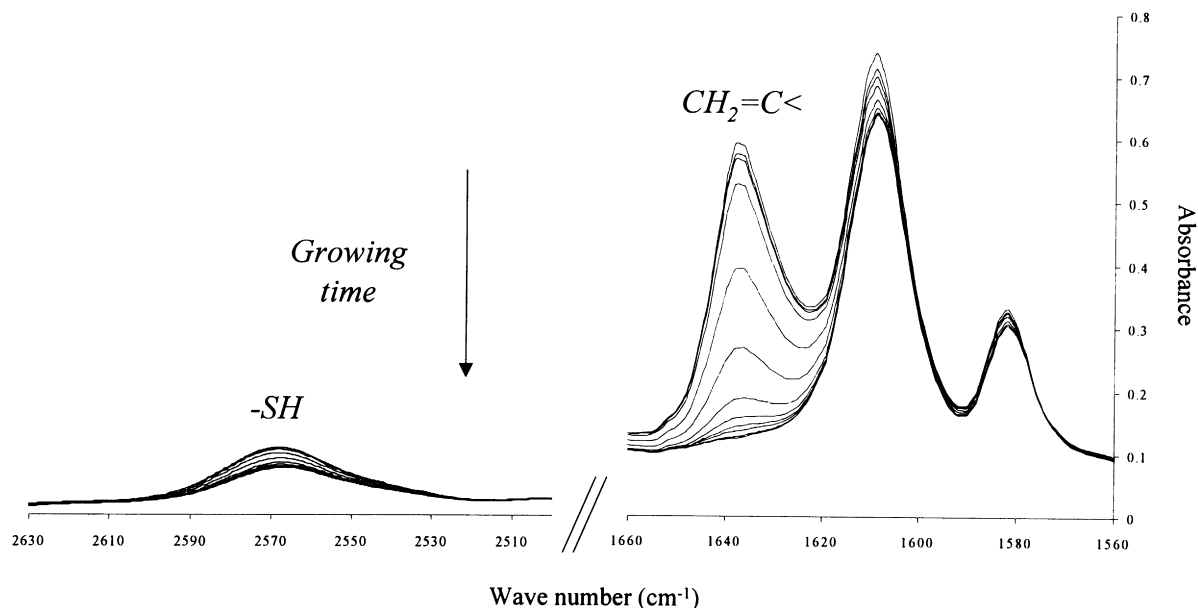
Fig. 6. Decay of the stretching vibration bands of methacrylate double bond at 1638 cm^{-1} and thiol functional group at 2568 cm^{-1} in real-time UV curing. The sample was a stoichiometric mixture with 0.15% (w/w) of Darocur 1173. $I_0 = 18.1$ mW/cm^2 at 365 nm.

3.2. Influence of photoinitiator concentration

The thiol–ene reactions were carried out at 30°C on a stoichiometric mixture by using DSC and RTIR spectroscopy. Fig. 5 shows the variation of the heat flux versus irradiation time by DSC for Darocur 1173 concentration within the range 0.15–0.75% (w/w). For the same reasons as

previously mentioned, the shift of the second peak toward low reaction times is related to the Trommsdorff effect, which appears much earlier as the photoinitiator concentration is high.

Moreover, we can usually observe that the higher the reaction rate, the higher the free volume, leading to a higher ultimate conversion of the material [24,25]. In our case,
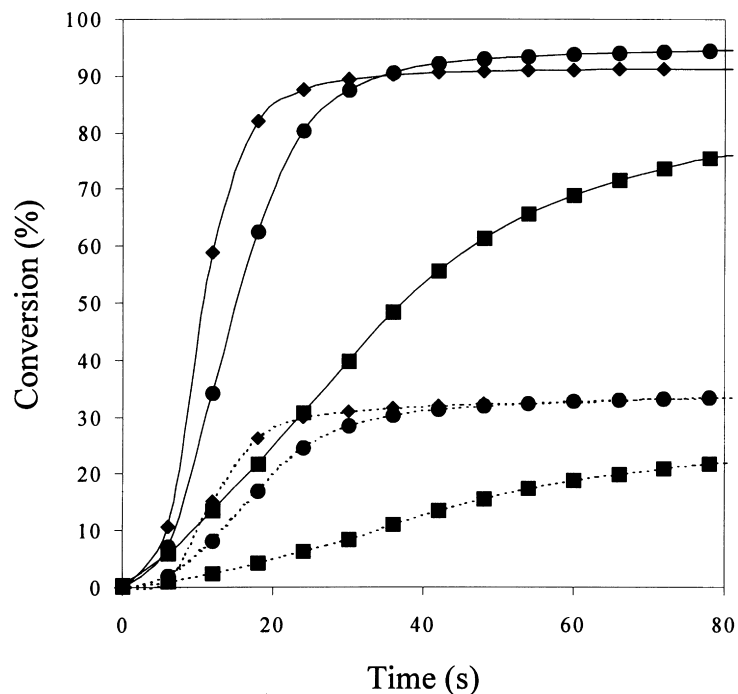

Fig. 7. Double bond (—) and thiol (- - -) conversion versus UV irradiation time obtained from RTIR analysis on a stoichiometric mixture in the presence of 0.15 (●) and 0.75% (◆) (w/w) of Darocur 1173 with $I_0 = 18.1$ mW/cm^2 at 365 nm; and 0.15% (■) (w/w) of Darocur 1173 and $I_0 = 3.7$ mW/cm^2 at 365 nm.

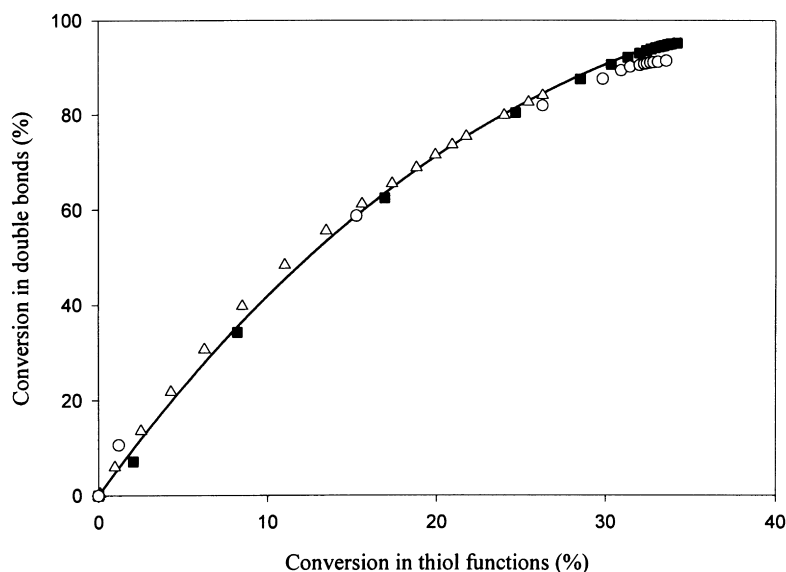Fig. 8. Conversion in double bonds versus conversion in thiol functions. Experimental values: $I_0 = 18.1$ mW/cm^2 at 365 nm with 0.15% (○) and 0.75% (■) (w/w) of Darocur 1173; $I_0 = 3.7$ mW/cm^2 at 365 nm and 0.15% (△) (w/w) of Darocur 1173. Theoretical curve with $C_{tr} = 0.26$ (—).

this law does not seem to be verified since the photocross-linking enthalpy is nearly the same whatever the photo-initiator concentration (Fig. 3). The slight decrease observed is probably also due to a previous thermal polymerization before irradiation, which slightly increases with photo-initiator concentration. Indeed, whereas a mixture with 0.15% of photoinitiator is stable at room temperature during several hours, only 30 min are enough to obtain a totally cross-linked sample without UV light in the presence of 0.75% of Darocur 1173.

The RTIR technique gives complementary information about the reaction although the experimental conditions are not rigorously the same for the two techniques. The decay of the absorption bands of the SH function at 2568 cm^{-1} and the double bond at 1638 cm^{-1} was followed as a function of irradiation time (Fig. 6). The plot of relative conversions in reactive functions versus time for two photo-initiator concentrations is reported in Fig. 7.

It is noteworthy that with $I_0 = 18.1$ mW/cm^2 and 0.15% of photoinitiator, at room temperature, only 34% of the thiol functions was consumed in the addition reaction whereas 95% of the double bonds reacted either in polymerization or in thiol–ene addition. This observation can show that T_g is always the same whatever the experimental conditions because, in all cases, polymerization stops because of the complete consumption of methacrylate double bonds. Moreover, polythiol ($\bar{f} = 3.8$) may be almost considered as a monothiol tranfer agent (statistically, 1.3 functions per monomer have reacted) and a 95% conversion in double bonds leads to an average of methacrylate units per thiol of 2.8.

This faster disappearance of double bonds is contrary to the results often described but in agreement with those of Pelaprat et al. [26]. These authors have determined a trans-fer constant C_{tr} around 0.5 between methyl methacrylate and mercapto 2-ethanol. This means that the transfer rate constant k_{tr} is twice as high as the propagation rate constant k_p. For our system, the thiol–ene photoinitiated cross-linking also proceeds by propagating the methacrylate chain rather than by transfer to the thiol monomer.

In order to quantify the relative importance of homo-polymerization and thiol–ene addition, we have done a computation based on a classical Mayo equation [27]. In our case, it is necessary to allow for consumption of monomer in the transfer reaction [28–31], as shown below:

$$-\frac{d[RSH]}{dt} = k_{tr}[M^\cdot][RSH]$$

$$-\frac{d[M]}{dt} = k_p[M^\cdot][M] + k_i[RS^\cdot][M]$$

and assuming that there is no accumulation of M$^\cdot$ (stationary state):

$$k_{tr}[M^\cdot][RSH] = k_i[RS^\cdot][M]$$

one can write,

$$\frac{d[M]}{d[RSH]} = \frac{k_p}{k_{tr}} \frac{[M]}{[RSH]} + 1$$

or

$$d[M] = \left(\frac{1}{C_{tr}} \frac{[M]}{[RSH]} + 1\right) d[RSH] \qquad \text{with } C_{tr} = \frac{k_{tr}}{k_p}$$

In these conditions, it is possible to obtain C_{tr} by numerical resolution of the following relations:

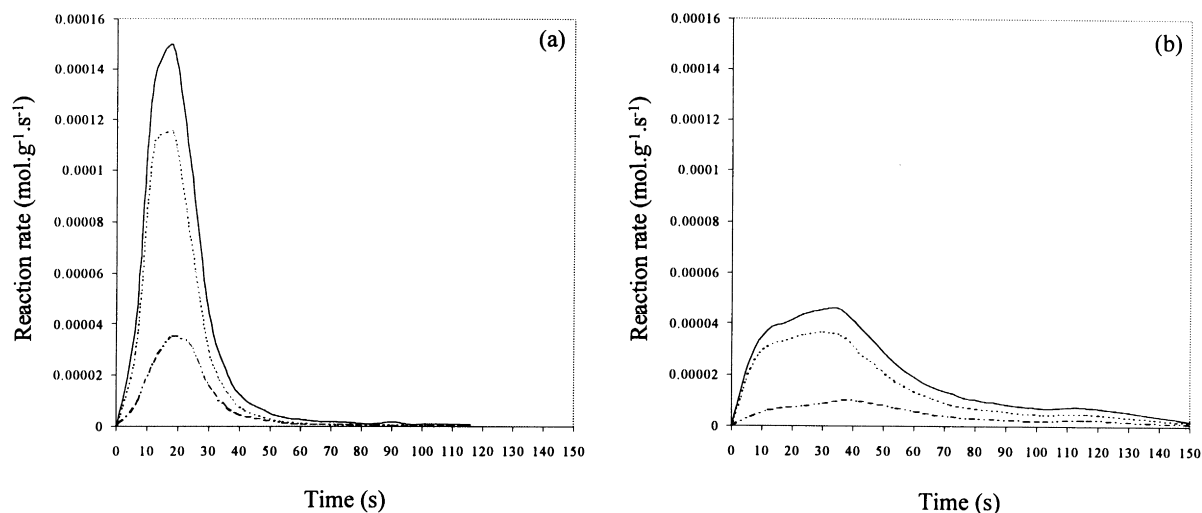$$\Delta[M]_1 = \left(\frac{1}{C_{tr}} \frac{[M]_0}{[RSH]_0} + 1\right) \Delta[RSH]$$

Fig. 9. Reaction rate versus UV irradiation time obtained from RTIR analysis on a stoichiometric mixture in the presence of 0.15% (w/w) of Darocur 1173: (a) $I_0 = 18.1$ mW/cm^2; (b) $I_0 = 3.7$ mW/cm^2 at 365 nm; (—) total reactive functions; (- - -) methacrylate double bond; (- - — - -) thiol function.

and

$$\Delta[M]_{i+1} = \left(\frac{1}{C_{tr}} \frac{[M]_i}{[RSH]_i} + 1\right)\Delta[RSH]$$

with $\Delta[RSH]$ constant and sufficiently small (0.1%),

$$[RSH]_i = [RSH]_0 - i\Delta[RSH]$$
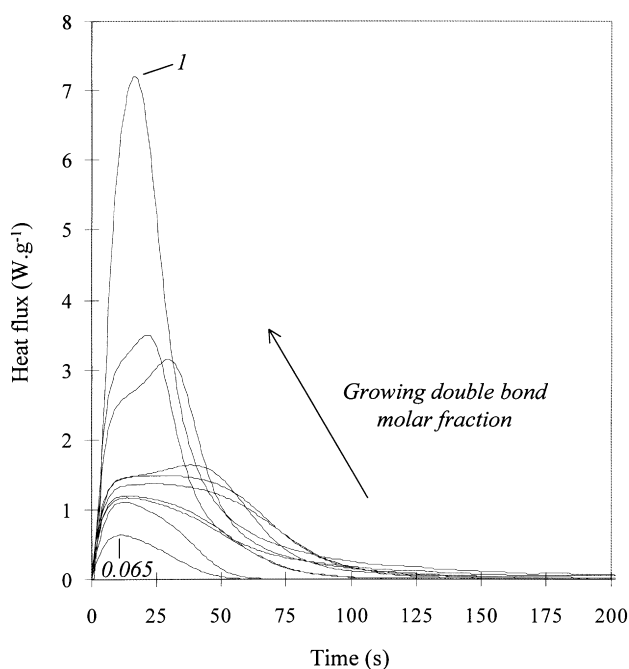
and $[M]_i = [M]_{i-1} - \Delta[M]_i$.

Fig. 10. Heat flux versus time at various double bond molar fractions for a Darocur 1173 concentration of 0.15% (w/w) at 30°C.

Thus, by plotting the resulting conversion in double bond versus conversion in thiol and by comparing with the experimental curves in Fig. 7, we can optimize the value of C_{tr}. One can notice in Fig. 8 that we obtain the same experimental variations whatever the photoinitiator concentration or light intensity and a good fit is obtained for $C_{tr} = 0.26$. Moreover, this computation gives 4.9 methacrylate units per thiol at the beginning of the reaction and 1.3 at 95% with an average value of 3.2, close to the experimental 2.8 mentioned above.

3.3. Influence of light intensity

This evolution can be transposed to the effect of an increase in photoinitiator concentration. Indeed, increasing photoinitiator concentration or UV light intensity produces the same effect since, in both cases, the primary radical amount increases and a higher reaction rate is then observed [22] (Fig. 7). The reaction rate was calculated by derivation and the corresponding curves for each reactive function separately and together were plotted for two different UV light intensity values (Fig. 9). As expected, we well observe a delay in the appearance of the gel effect when the UV light intensity is lower.

3.4. Influence of the relative amounts of thiol and methacrylate functions

The evolution of the heat flux versus irradiation time and the resulting photochemical reaction enthalpy, at 30°C for methacrylate function fraction within the range 0–1 with photoinitiator concentration of 0.15% (w/w), are plotted in Figs. 10 and 11. In case of photopolymerization of pure dimethacrylate oligomer, the gel effect occurs as soon as the reaction starts and so a unique reaction rate maximum is observed (Fig. 10). Then, the higher the thiol fraction is,
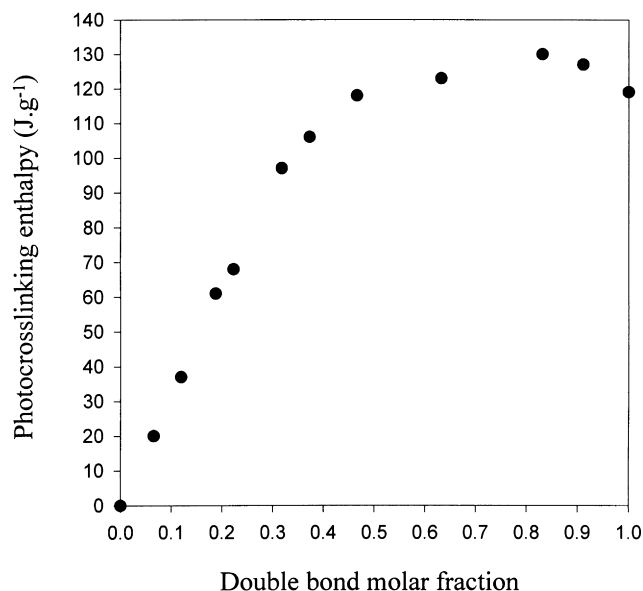
Fig. 11. Absolute value of the photochemical reaction enthalpy versus double bond molar fraction at 30°C in the presence of 0.15% (w/w) of Darocur 1173.

the more the Trommsdorff effect is delayed. A second rate maximum is observed and shifts toward the higher reaction times when the thiol amount increases. When the thiol fraction becomes too high, the system is so diluted that the gel effect becomes less and less important. Thus, the second peak tends to disappear.

The following can be observed from Fig. 11:

i. One can notice that in the absence of dimethacrylate oligomer, no enthalpy was measured under UV radiation.

ii. Enthalpy increases with methacrylate function fractions. For a double bond fraction of 0.065, one might think that, due to the large excess of SH functions, there is only an addition of one SH function on each double bond, which indicates the presence in the medium of dimethacrylate with thiol on each extremity and free unreacted thiol monomers. The RTIR analysis well confirms that only the thiol–ene addition takes place (Fig. 12), SH and double bond functions disappearing at the same time. Moreover, a theoretical average methacrylate unit value of 1.1 per thiol is obtained by using the previous transfer constant.

iii. Finally, the yield for pure dimethacrylate is 62% (-118 J/g) whereas it is 95% under stoichiometric conditions. That is to say that small amounts of thiol promote dimethacrylate polymerization and photocross-linking enthalpy increases to reach a maximum for methacrylate function fractions between 0.6 and 0.8 (Fig. 11).

The T_g of the photocross-linked samples normally shows the same evolution (Fig. 13) as T_g is directly dependent on the conversion of the material. If we assume that at very low concentration of thiol monomer its conversion is complete, one can explain that the highest value of T_g obtained for a methacrylate function fraction of 0.9 leads probably to the best compromise between enhancement of double bond polymerization and decrease in thiol monomer conversion when thiol concentration increases.
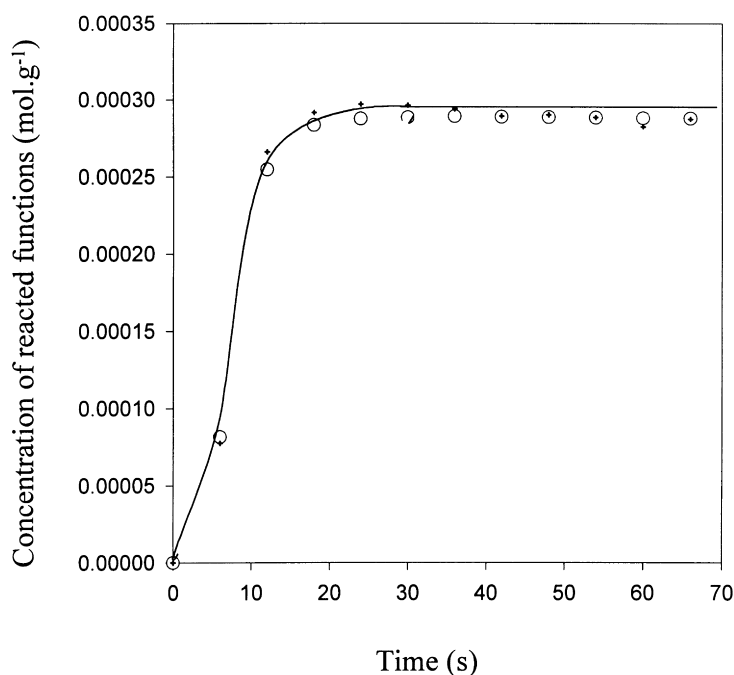

Fig. 12. Double bond (+) and thiol (○) concentration versus UV irradiation time obtained from RTIR analysis for a double bond molar fraction of 0.065. $I_0 = 18.1$ mW/cm^2.
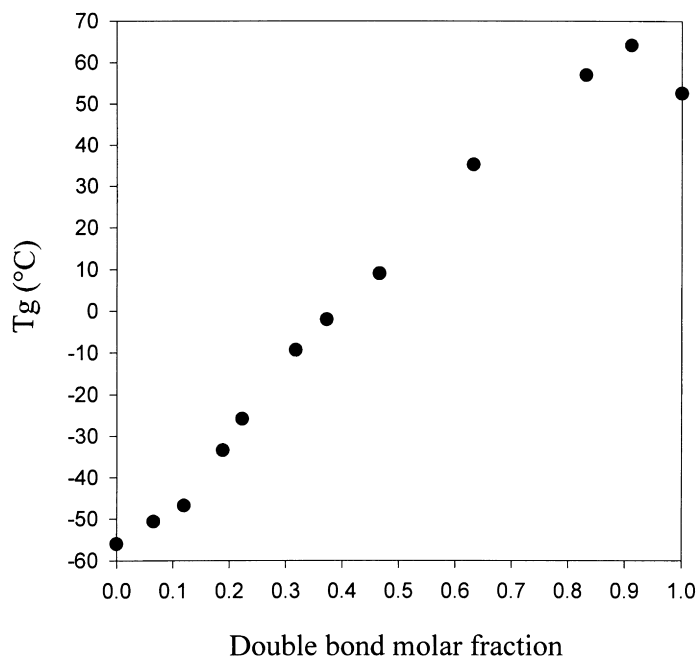
Fig. 13. Glass transition temperature of photocross-linked samples versus double bond molar fraction.

4. Conclusions

This work shows well the complementarity of the DSC and RTIR techniques to characterize photopolymerization kinetics. The main result is that competition between thiol–ene addition and homopolymerization leads to favour the latter. Indeed, RTIR analyses have shown that methacrylate double bonds disappear more quickly than thiol functions when the two reactive functions are in stoichiometric amounts. These results are in agreement with a thiol transfer constant of 0.26. The effect of reaction temperature, photo-initiator concentration, UV light intensity and relative methacrylate–thiol amounts was also investigated. In some experimental conditions, a double peak was observed and was justified by the increase in the autoacceleration rate related to the gel effect. This phenomenon is very sensitive to the composition of the reactional mixture. Finally, the RTIR spectroscopy has revealed that only the thiol–ene addition can be obtained for a very low dimethacrylate proportion in the reactional system.

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