Polymer 40 (1999) 6313–6320

polymer

Photoinitiated polymerization of a dimethacrylate oligomer
Part 3. Postpolymerization study

L. Lecamp[a], B. Youssef[a], C. Bunel[a,*], P. Lebaudy[b]

[a]Laboratoire de Matériaux Macromoléculaires, Institut National des Sciences Appliquées de Rouen, Place E. Blondel, BP 08, 76131 Mont Saint Aignan Cédex, France
[b]Laboratoire d'Etude et de Caractérisation des Composés Amorphes et des Polymères, Université de Rouen, Place E. Blondel, 76821 Mont Saint Aignan Cédex, France

Received 8 December 1998; received in revised form 19 January 1999; accepted 19 January 1999

Abstract

The effects of the presence of trapped radicals after UV irradiation were studied on a dimethacrylate oligomer. The postpolymerization reaction was characterized by differential scanning calorimetry and dynamic mechanical analysis. The photopolymerization was realized with 2,2-dimethyl-2-hydroxyacetophenone (Darocur 1173) as radical photoinitiator by using isothermal photocalorimetry. The postpolymerization was clearly shown in the isothermal mode and under N_2 atmosphere by following the variation of the glass transition temperature of the samples. The influence of crosslinking density, O_2 and thermal postcure were investigated. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Dimethacrylate oligomer; Photoinitiated reaction; Trapped radicals

1. Introduction

For about 20 years, photoinitiated reactions have been used in several applications in thin layers (microlithography [1], microelectronics [2], lacquers and varnishes for surface treatment [3], protective coatings [4], printing inks [5], and antiadhesive support [6]), as well as in thick layers (dental stratification [7], stereolithography [8]). The usage of this technology and the progress in the development of resins and curing systems have contributed towards its high and fast development. The rate of the process is one of the main advantages of the UV curing which leads to highly crosslinked materials. It is known that photopolymerization reactions have particular behaviours, such as autoacceleration [9–12], incomplete functional group conversion [13–16], unequal functional group reactivity [15,17,18], and temporary free volume excess [19,20]. UV cured samples are also characterized by the existence of free radicals trapped within the material [20–22]. As a result of the rapid gelation and vitrification of the network during photopolymerization, the diffusivity of the reactive species is highly reduced. A lot of radicals cannot react immediately by propagation or termination. Moreover, trapped radicals present certain implications with respect to the long-term properties of the material. Indeed, they still stay efficient towards the unreacted functional groups, and are later responsible for the existence of a slow postpolymerization reaction. This reaction cannot be measured in real time, but has been the subject of many works. Thus, it was shown that trapped radicals are present when the reaction temperature is low. In the case of densely crosslinked di(meth)acrylates, under free O_2 atmosphere and at room temperature, Zhu et al. [23–26] have shown that the lifetime of these free radicals can reach several days or months and depends mainly on the crosslinking density, the storage temperature and the atmosphere. Marino et al. [27] have observed this reaction on photopolymerized unsaturated polyester samples after several days in the dark. Other studies have shown that this reaction is highly accelerated by moderate heating [15,20,28–30]. Indeed, heating increases the segmental mobility of the network and thus, favours the reaction between the present radicals and the surrounding unreacted functional groups. Finally, at room temperature, the postpolymerization is less important in the presence of O_2. Indeed, free radicals can react with diffusing O_2 molecules to form peroxy radicals and hydroperoxides [31]. Kloosterboer et al. [29] have shown that, according to differential scanning calorimetry (DSC) analysis, dimethacrylate samples heated under N_2 atmosphere immediately after

---

* Corresponding author. Tel.: + 33-02-35-52-84-46; fax: + 33-02-35-52-84-46.

0032-3861/99/$ - see front matter
PII: S0032-3861(99)00042-7

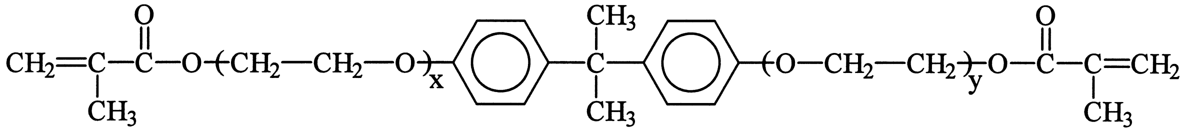
photopolymerization exhibit an exothermic effect, whereas heating these samples after one night under free air gives no detectable exothermic effect. Decker et al. [32] have observed a postpolymerization at room temperature for polyurethane or epoxyacrylate samples which were photopolymerized under laser. This post polymerization lasts 30 s under N_2 atmosphere and only 2 s under air.

While the property requirements for the final material vary widely and depend on the particular application, the long term performance and stability of the material are important issues. Such issues are strongly dependent on the polymer structure and changes that occur in the polymer structure with time. In previous articles [33,34], the photopolymerization of a dimethacrylate oligomer in the presence of 2,2-dimethyl-2-hydroxyacetophenone (Darocur 1173) as radical photoinitiator was studied. The influence of different experimental parameters (temperature, light intensity, photoinitiator concentration) and a kinetic study was investigated. In this work, we are interested in the postpolymerization reaction of this same system. Two techniques were mainly used to perform this study: DSC and dynamic mechanical analysis (DMA). First, the existence of the postpolymerization reaction was demonstrated and quantified. The effect of crosslinking density, O_2 and thermal postcure on the postpolymerization was then investigated.

2. Experimental part

2.1. Materials

The chemical formula of the reactant used is the following:



$$CH_2{=}\underset{CH_3}{\underset{|}{C}}-\overset{O}{\overset{\|}{C}}-O\!-\!(CH_2-CH_2-O)_x-C_6H_4-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-C_6H_4-(O-CH_2-CH_2)_y-O-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{C}}{=}CH_2$$

$$n = x + y = 4.8$$

The average number of oxyethyl units in the dimethacrylate oligomer (Akzo, $M = 575\ \mathrm{g\ mol^{-1}}$) was determined by ^{1}H NMR analysis and was found to be equal to 4.8.

The photoinitiator, 2,2-dimethyl-2-hydroxyacetophenone, was dissolved in the oligomer while stirring at room temperature for 3 h at approximately 0.15% (w/w), i.e. $10^{-2}\ \mathrm{mol\ l^{-1}}$ Darocur 1173 concentration.

2.2. Measurement

The photocrosslinking and postpolymerization reactions were carried out in a differential scanning calorimeter (DSC 7 Perkin–Elmer) which included an irradiation unit. Heat flow versus time was recorded in isothermal mode under N_2 atmosphere. The optical part of the calorimeter, the sample preparation, the treatment of the thermogram and the computation of conversion and reaction rate are described elsewhere [33]. The UV radiation intensity was measured at the sample level by a radiometer at 365 nm and was $2.7\ \mathrm{mW\ cm^{-2}}$.

Photocrosslinked samples were analysed by DSC (DSC 7 Perkin–Elmer) under N_2 atmosphere at a heating rate of $20°\mathrm{C\ min^{-1}}$. The glass transition temperature T_g was determined at $0.5\Delta C_p$.

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

3. Results and discussion

3.1. Measurement of the postpolymerization reaction

Our main objective was to show clearly and to measure the dark polymerization. With this objective, the samples were subjected to the following treatments at 30°C or 50°C under N_2 atmosphere:

- first, an UV irradiation for 6 s, monitored in the DSC, leading to a measured photocrosslinking enthalpy ΔH_1 which is roughly a constant whatever the applied experimental process;
- then, a variable dark period during which the reaction enthalpy is ΔH_{dark}. Unfortunately, this enthalpy is almost unknown because the postpolymerization rate drops rapidly and cannot be measured by DSC on the overall dark period;
- at last, a second UV irradiation of 7 min to complete the polymerization leading to a variable photocrosslinking enthalpy ΔH_2.

The overall polymerization enthalpy ΔH_T is then given by:

$$\Delta H_T = \Delta H_1 + \Delta H_{\mathrm{dark}} + \Delta H_2. \tag{1}$$

In a previous work [33], a linear relationship (2) between

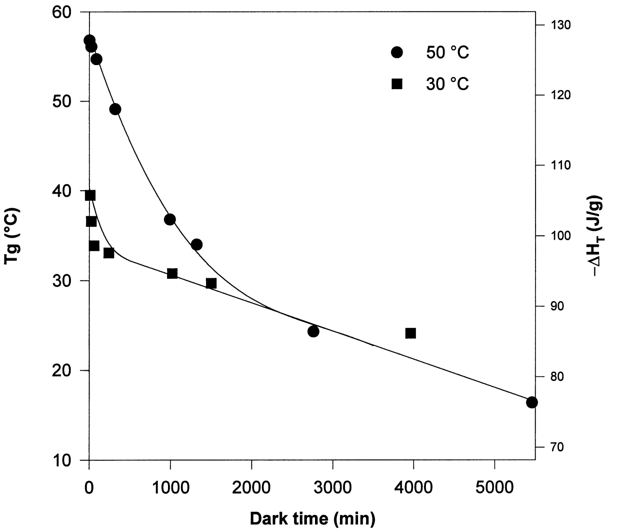


Fig. 1. T_g (or $-\Delta H_T$) versus dark time at 30°C (■) and 50°C (●).

conversion C (%) and glass transition temperature T_g (°C) was found on the overall conversion range:

$$C = 29.2 + 0.67\ T_g \tag{2}$$

with

$$C = \frac{\Delta H_T}{\Delta H_0^{\text{theor}}} \times 100$$

leads to

$$\Delta H_T = \frac{\Delta H_0^{\text{theor}}}{100}(29.2 + 0.67\ T_g), \tag{3}$$

where $\Delta H_0^{\text{theor}}$ is the theoretical enthalpy (-13.1 kcal mol^{-1} per methacrylate double bond [30], i.e. -190 J g^{-1} for our dimethacrylate oligomer). Using this relationship and the glass transition temperature T_g of the samples, ΔH_T can be estimated. In our experimental conditions, T_g is assumed to be similar to mechanical transition T_α measured by DMA. Therefore, the knowledge of ΔH_1, ΔH_2 and ΔH_T allows us to calculate ΔH_{dark}.

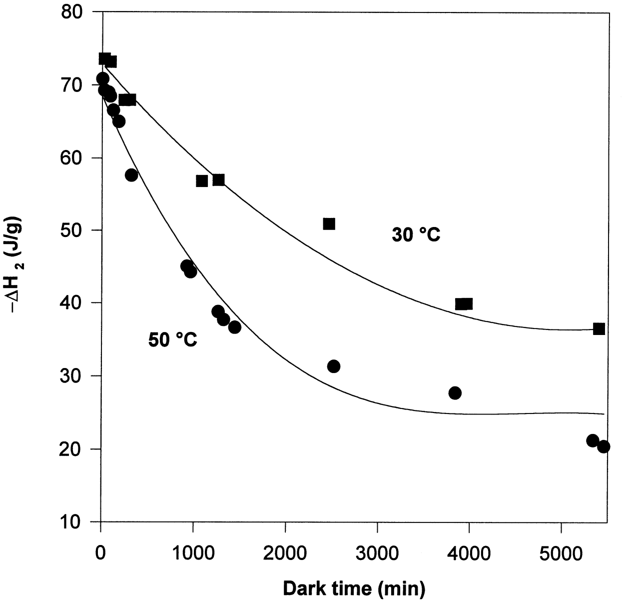


Fig. 2. $-\Delta H_2$ versus dark time at 30°C (■) and 50°C (●).

Fig. 1 shows the glass transition temperature T_g, measured by DMA, at the end of the polymerization process (or $-\Delta H_T$ according to Eq. (3)) as a function of the dark time. Likewise, the photocrosslinking enthalpy $-\Delta H_2$ as a function of the dark time is shown in Fig. 2. The variation of $-\Delta H_{\text{dark}}$, calculated according to (1), is shown in Fig. 3.

For a better understanding, we chose to discuss the figures in the reverse order. Fig. 3 reveals that postpolymerization is very fast during the first few minutes after the irradiation shutting and faster at the higher reaction temperature. At 50°C, a plateau is reached after 300 min of darkness. At 30°C, ΔH_{dark} seems also to tend towards this same value, but is much slower. This limit corresponds in fact to a global conversion of about 35% at the end of the dark period ($\Delta H_1 + \Delta H_{\text{dark}}$). This value is usually reached when the gelation occurred [35]. Close to gelification, the radical diffusion towards the unreacted double bonds is highly reduced and the postpolymerization greatly decreases until it stops after 300 min at 50°C. Moreover, at the beginning of the second irradiation, the amount of residual double bonds as well as the reactive species diffusion are lower for long dark periods. Thus, the resulting enthalpy ΔH_2 decreases as a function of the dark time (Fig. 2). It is surprising that the decrease in ΔH_2 is continuous at 50°C, while ΔH_{dark} becomes constant after 300 min of darkness. Indeed, as there is no further consumption of double bonds during this period of stability, ΔH_2 would also have to become a constant. This evolution can be related to a reorganization of the network (volume shrinkage, chain relaxation) during the dark period, leading to a decrease in the residual double bonds accessibility, and then to a decrease in ΔH_2.

We can also notice that, at 30°C, ΔH_2 is always higher than at 50°C for a same dark time. Indeed, at 30°C, the amount of residual double bonds is greater at the end of the dark period. Thus, when the second photochemical reaction starts, the state of the sample is further away from the gelation at 30°C than at 50°C. Therefore, the photoinitiated reaction rates are higher at 30°C and according to the free volume theory (higher rates lead to higher conversions), higher conversions are obtained.

Finally, Fig. 1 shows that the glass transition temperature decreases when the dark time increases. The two curves plotted at 30°C and 50°C intersect after about 2000 min of darkness. Two antagonistic factors can explain this evolution. The first is a temperature effect, and the second is the residual amount of double bonds before the second irradiation. Thus, because the reaction rates and then the conversions increase with temperature, consequently, T_g (50°C) must be higher than T_g (30°C). This was observed during the first dark hours. Nevertheless, as the dark period

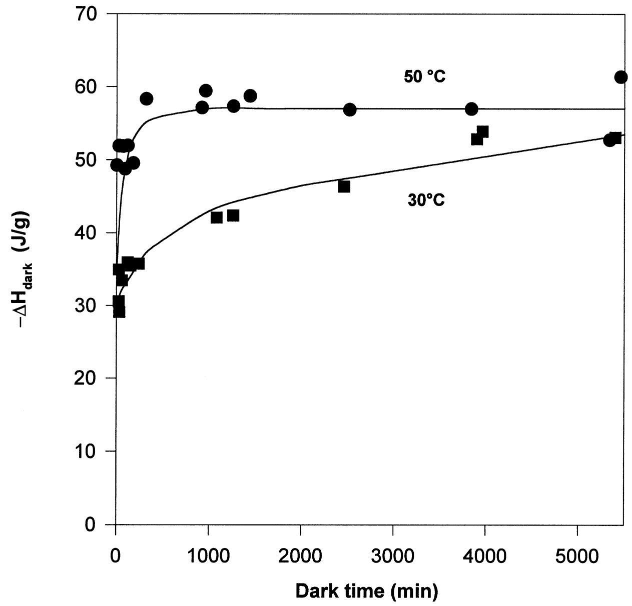


Fig. 3. $-\Delta H_{\text{dark}}$ versus dark time at 30°C (■) and 50°C (●).

increases, the residual amount of double bonds is logically lower at 50°C than at 30°C. Then, at the beginning of the second irradiation, the rate of the reaction will be higher at 30°C than at 50°C, leading to a higher conversion at 30°C. Thus, the combination of these two antagonistic effects for dark time greater than 2000 min leads to similar conversion and glass transition temperatures at 30°C and 50°C.

3.2. Effect of the crosslinking density

Samples were subjected to the following treatment at 50°C under N_2 atmosphere:

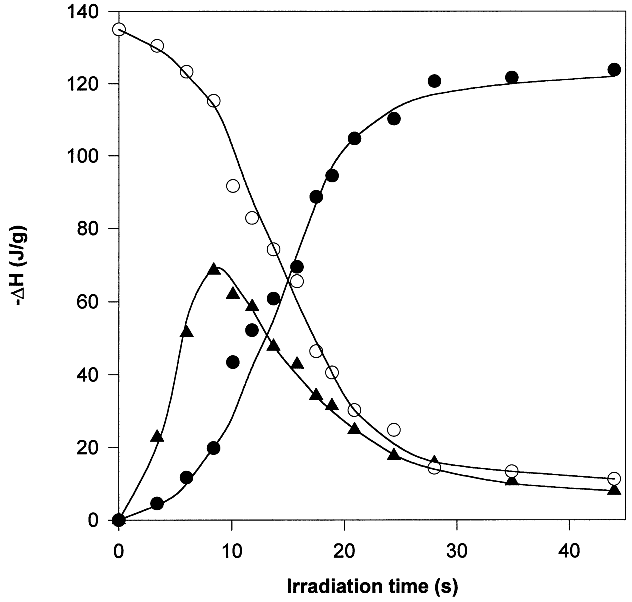


Fig. 4. $-\Delta H_1$ (●), $-\Delta H_{\text{dark}}$ (▲) and $(135 + \Delta H_1)$ (○) versus irradiation time at 50°C.

- a first irradiation of few seconds giving a photocrosslinking enthalpy ΔH_1;
- then, a short dark period of 5 min in order to obtain a measurable enthalpy ΔH_{dark};
- at last, a second UV irradiation of 7 min to complete the overall polymerization and giving a photocrosslinking enthalpy ΔH_2.

The overall polymerization enthalpy is given again by Eq. (1). Here, ΔH_1, ΔH_{dark} and ΔH_2 were measured by DSC. Experiments have shown that, whatever the first irradiation time, the overall enthalpy ΔH_T is relatively constant and equal to $-135\ \text{J g}^{-1}$. This value corresponds to the maximum photocrosslinking enthalpy which is obtained at 50°C under continuous irradiation.

$-\Delta H_1$ and $-\Delta H_{\text{dark}}$ are plotted as a function of the first irradiation time in Fig. 4.

A third curve $(135 + \Delta H_1)$ which represents what remains to be polymerized at the end of the first irradiation is also plotted. We can notice that, for irradiation times higher than 8.4 s (top of the $-\Delta H_{\text{dark}}$ curve), the $-\Delta H_{\text{dark}}$ curve follows the $(135 + \Delta H_1)$ curve. These two curves tend to merge at higher irradiation times. Indeed, after irradiation, what reacts in the dark corresponds to the available residual double bonds. Hence, the longer the irradiation time, the more important the amount of double bonds consumed and the lower the dark reaction.

The relative dark conversion of the postpolymerization is plotted as a function of photopolymerization conversion in Fig. 5, after computation as follows:

$$C_{\text{dark}}^{\text{relative}} = \frac{-\Delta H_{\text{dark}}}{135 + \Delta H_1} \times 100. \tag{4}$$

When the photochemical conversion reaches about 15%,

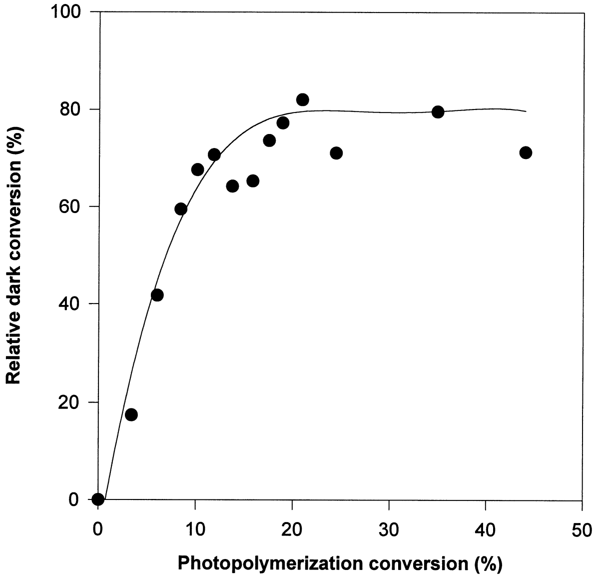


Fig. 5. Relative dark conversion versus photopolymerization conversion at 50°C.

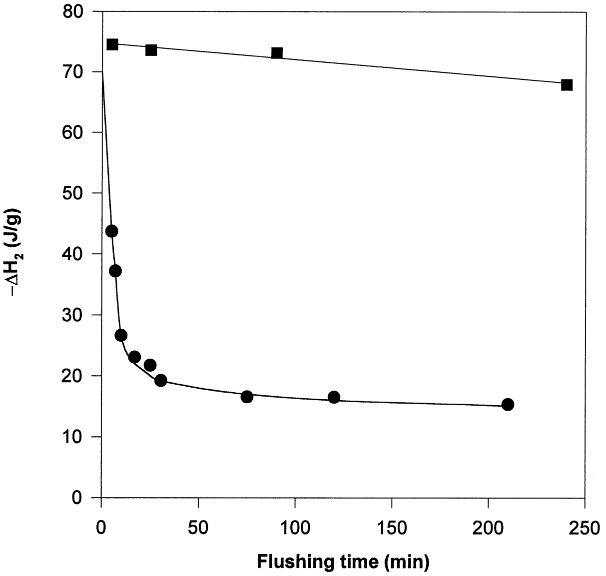


Fig. 6. $-\Delta H_2$ versus O_2 (●) or N_2 (■) flushing time at 30°C.

80% of the residual double bonds are consumed after 5 min of darkness.

3.3. Effect of oxygen

A first series of experiments was performed to evaluate the O_2 efficiency. Samples were subjected to the following treatment at 30°C or 50°C:

- a first UV irradiation of 6 s under N_2 (ΔH_1);
- then, an O_2 flushing for *t* min;
- at last, a second UV irradiation of 7 min under N_2 to complete the polymerization (ΔH_2).

Figs. 6 and 7 show the variation of $-\Delta H_2$ as a function of the O_2 flushing time. As expected, the longer the flushing time, the lower the $-\Delta H_2$. At 30°C, $-\Delta H_2$ decreases very quickly during the first flushing minutes and reaches a plateau after 1 h under O_2. Moreover, the diffusion of O_2 is easier when the sample temperature is higher. Thus, at 50°C, the O_2 effect is so fast that the drop of $-\Delta H_2$ cannot be observed at the beginning of the O_2 flushing. $-\Delta H_2$ reaches a plateau which is lower when the reaction temperature is higher, but not equal to 0. Indeed, at the end of the dark period, there are still photoinitiators and double bonds. The second irradiation step restarts the photoinitiator decomposition. At first, the primary radicals react with O_2 dissolved within the material. Then, when all O_2 is consumed, the primary radicals initiate the polymerization again and a small reaction is monitored. Moreover, when the reaction temperature increases, the amount of O_2 dissolved within the material increases and, by contrast, the residual amount of double bonds, at the beginning of the second irradiation, decreases. Thus, the resulting photochemical conversion corresponding to $-\Delta H_2$ is lower at 50°C than at 30°C.

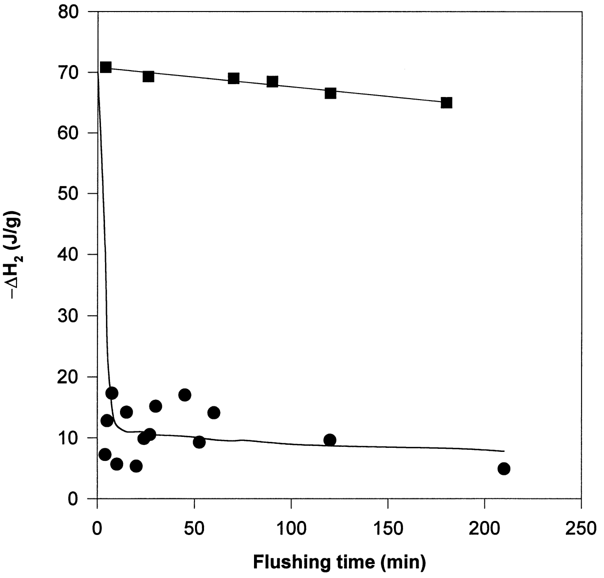


Fig. 7. $-\Delta H_2$ versus O_2 (●) or N_2 (■) flushing time at 50°C.

For high conversion, it is very difficult to observe the glass transition temperature T_g by using the DSC measurements, owing to the low value of ΔC_p. On the contrary, at low conversion (<55%), a curve ΔC_p versus conversion is available (Fig. 8). Thus, we have chosen to follow the variation of ΔC_p to characterize the effect of O_2 on the postpolymerization of samples which were irradiated during 6 s at 30°C or 50°C, and then stored in the dark at the same temperature either under N_2 or O_2 atmosphere as a function of the flushing time (Figs. 9 and 10).

Figs. 9 and 10 show the very good efficiency of O_2 in freezing the postpolymerization. Under N_2 and at 30°C, the dark reaction progresses very quickly during the first hours and then stabilizes. At 50°C, the postpolymerization reaction is faster and also reaches a plateau.

After 6 s of UV irradiation and 4 min of postpolymerization, the conversion is about 26% at 30°C and 30% at 50°C. Using Fig. 9, the conversion of postpolymerization increases by about 22% at 30°C against 15% at 50°C after 20 h of darkness. Many antagonistic factors must be taken into account to explain this observation. During the 6 s of irradiation, an increase in the reaction temperature favours the mobility of the reactive species, increases the polymerization rate, and then the conversion. For these reasons, one can think that the postpolymerization conversion could also be enhanced with higher temperature. On the contrary, owing to higher conversion, at the beginning of the postpolymerization, the residual amount of double bonds is lower and the resulting higher crosslinking density can rapidly drop the mobility of the species and decrease the rate. The result is a decrease in the dark conversion at 50°C with respect to 30°C, and we may assume that the amount of double bonds and the crosslinking density are the major parameters.

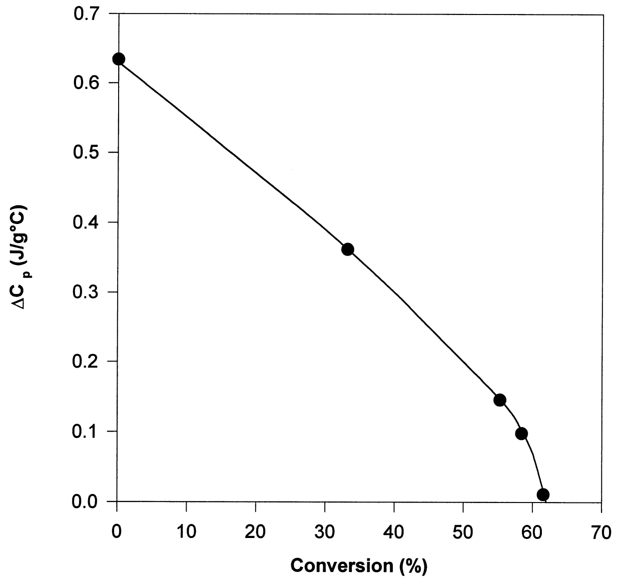


Fig. 8. ΔC_p versus conversion at 50°C.

3.4. *Effect of a thermal postcuring*

Several samples were irradiated at 30°C for 5 min and then heated at 2°C min^{-1} in the DSC oven, under N_2 atmosphere, at temperature ranging from 40°C to 90°C. If no exothermic effect was detected by DSC during the heating, measurements of mechanical properties clearly show the effect of the postpolymerization on T_g during the postcuring.

We report the values of T_g at the end of the postcuring versus the ultimate postcuring temperature in Fig. 11. We can notice an important increase in T_g which is related to the reaction of the free radicals. Nevertheless, these T_g do not reach the values obtained when the samples were irradiated 7 min at the corresponding postcure temperature.

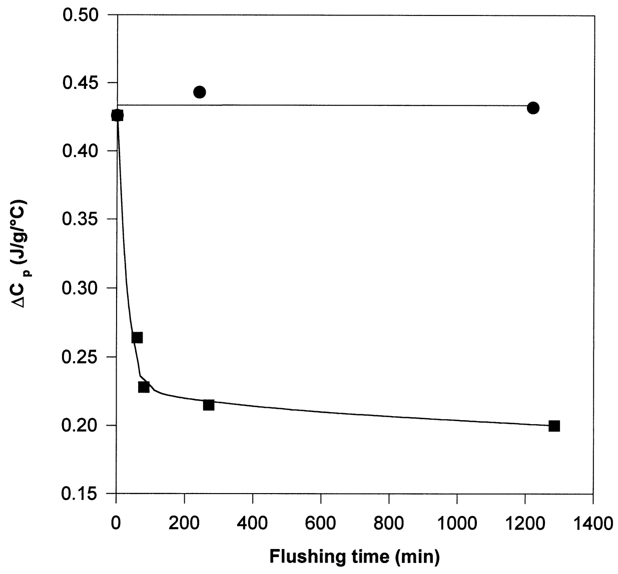


Fig. 9. ΔC_p versus O_2 (●) or N_2 (■) flushing time at 30°C.

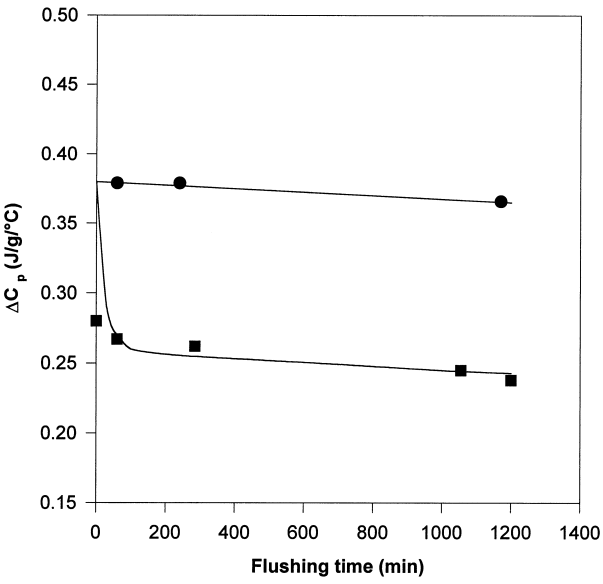


Fig. 10. ΔC_p versus O_2 (●) or N_2 (■) flushing time at 50°C.

The influence of several parameters, such as irradiation time, time interval between irradiation shutting and heating, heating rate and duration at ultimate temperature, on T_g were investigated and the results are given in Table 1.

Experiment 1 is given as reference. Experiments 3 and 5 exhibit that the value of T_g is not really influenced by the duration at ultimate temperature or by the irradiation time. In contrast, as the increase in the heating rate highly decreases the reaction time (time to reach 90°C: 3 min at 20°C min^{-1} against 30 min at 2°C min^{-1}), the value of T_g decreases when the heating rate increases (Experiment 2).

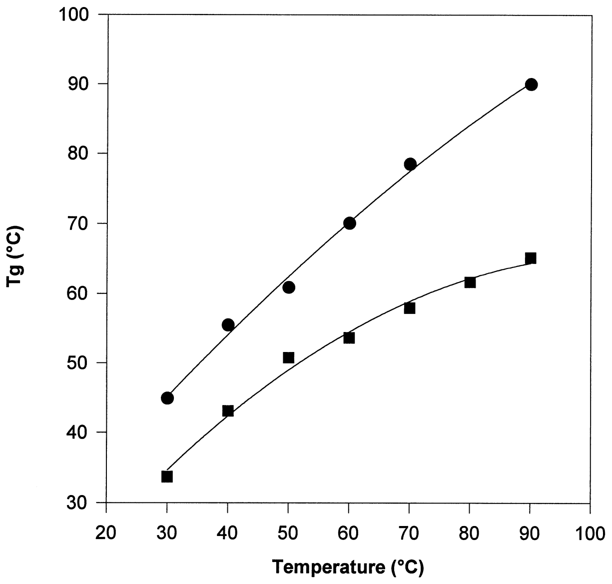


Fig. 11. T_g versus ultimate reaction temperature: (■) photopolymerization at 30°C and thermal postcuring from 30°C to ultimate reaction temperature (2°C min^{-1}); (●) photopolymerization during 7 min at the corresponding temperature.

Table 1
Influence of several parameters on postpolymerization during thermal postcuring

No.	Irradiation time at 30°C (min)	Time between irradiation and heating (min)	Heating rate (°C min^{-1})	Time at 90°C (min)	T_g (°C)
1	5	0	2	5	65.2
2	5	0	20	5	60.8
3	5	0	2	0	64.4
4	5	5	2	5	56.5
5	14	0	2	5	63.5

By increasing the dark duration before heating (Experiment 4), a previous postpolymerization reaction can occur. In this case, we observe a lower value of T_g. As mentioned before, among the antagonistic effects, the decrease of the residual amount of double bonds and the increase of crosslinking density before the thermal postcuring reaction, explain the experimental result.

To confirm this assumption, further experiments were carried out. Samples were submitted to a first UV irradiation of 11.8 s at 30°C followed by t min of darkness at 30°C. Finally, the samples were heated to 60°C at 2°C min^{-1}. The overall process was performed under N_2 atmosphere. The glass transition temperature of the final material was measured by DMA.

Fig. 12 reveals a decrease in T_g as a function of the dark duration at 30°C. These results are in good agreement with those previously described, i.e. when the dark period increases, the residual amount of double bonds before the thermal postcuring decreases, and the ultimate conversion and the corresponding T_g also decreases.

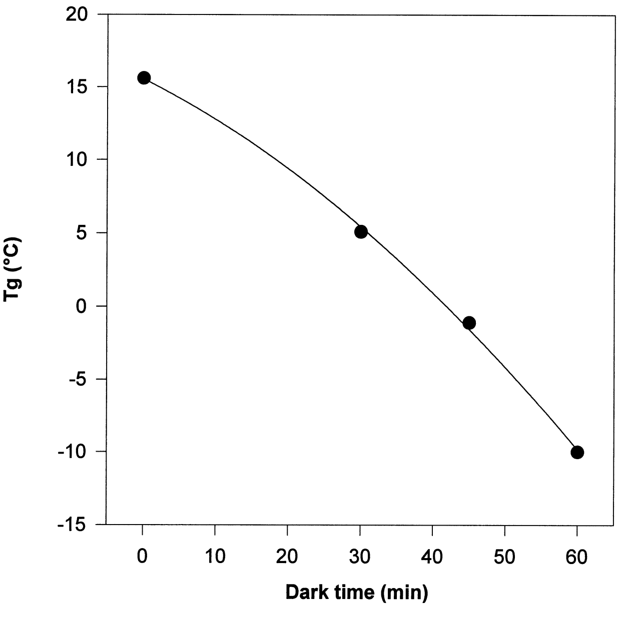


Fig. 12. T_g versus dark time after thermal postcuring at 60°C.

4. Conclusion

The presence of trapped radicals is characteristic of UV irradiated samples. The resulting postpolymerization has been investigated. A first study has shown clearly this postpolymerization on weakly photocrosslinked samples. This reaction is important and fast when the storage temperature in the dark is high. Thus, experimental results show that, for samples which were irradiated during 6 s at 50°C, and then stored in the dark under N_2 atmosphere during 300 min, the dark reaction can participate in half to the overall conversion of the material. Nevertheless, this reaction is highly slowed down close to the gelification because of the decrease of the mobility of the radicals.

Moreover, the relative importance of the dark conversion has been studied as a function of the crosslinking density. It appears that 80% of the residual double bonds are able to postpolymerize by shutting the UV irradiation at 50°C after about 15 s.

We have also shown that O_2 highly reduces the postpolymerization. The decay is faster as the O_2 diffusion is easier when the sample temperature is higher.

At last, we have observed the effect of a thermal postcuring on the postpolymerization. The dark conversion also increases by heating as the mobility of the reactive species is enhanced.

References

[1] De Forest WS. Photoresist: materials and process. New York: MacGraw Hill, 1979.
[2] Burga RA. RadTech Europe Conf Proc, 425, Lyon (France), 1997.
[3] Eranian A. Eur. COMETT, Le Mans (France), 1995.
[4] Finter J, Frischinger I, Haug T, Marton R. RadTech Europe Conf Proc, 489, Lyon (France), 1997.
[5] Pappas SP. UV curing: science and technology, vol. 1. Stamford: Technology Marketing, 1978 vol. 2, 1985.
[6] Crivello JV, Eckberg RP. US Patent 4617238 (General Electric), 1986.
[7] Abadie MJM, Parfait A, Rouby M. Eur Polym J 1994;30(3):399.
[8] Fouassier JP, Rabek JF. Lasers in polymer science and technology. Boca Raton, FL: CRC Press, 1990.
[9] Allen P, Simon G, Williams D, Williams E. Macromolecules 1989;22:809.
[10] Cook WD. Polymer 1992;33:2152.
[11] Broer DJ, Mol GN, Challa G. Polymer 1991;32(6):690.

[12] Kloosterboer JG, Lijten GFCM, Boots HMJ. Makromol Chem Makromol Symp 1989;24:223.

[13] Doornkamp AT, Tan YY. Polym Commun 1990;31:362.

[14] Anseth KS, Newman SM, Bowman CN. Adv Polym Sci 1995;122:177.

[15] Kloosterboer JG. Adv Polym Sci 1988;84:1.

[16] Allen P, Bennet D, Hagias S, Hounslow A, Ross G, Simon G, Williams D, Williams E. Eur Polym J 1989;25:785.

[17] Kloosterboer JG, van de Hei GMM, Boots HMJ. Polym Commun 1984;25:354.

[18] Bowman CN, Peppas NA. Chem Engng Sci 1992;47:1411.

[19] Bowman CN, Peppas NA. Macromolecules 1991;24:1914.

[20] Kloosterboer JG, van de Hei GMM, Gossink RG, Dortant GCM. Polym Commun 1984;25:322.

[21] Selli E, Oliva C, Termignone G. J Chem Soc Faraday Trans 1994;90:1967.

[22] Selli E, Oliva C. Macromol Chem Phys 1995;196:4129.

[23] Zhu S, Tian Y, Hamielec AE, Eaton DR. Polymer 1990;31:154.

[24] Zhu S, Tian Y, Hamielec AE, Eaton DR. Polymer 1990;31:1726.

[25] Zhu S, Tian Y, Hamielec AE, Eaton DR. Macromolecules 1990;23:1144.

[26] Tian Y, Zhu S, Hamielec AE, Fulton DB, Eaton DR. Polymer 1992;33:384.

[27] Marino T, Long OL, Neckers DC. Ind Engng Chem Res 1995;34:4549.

[28] Nicolais L, Apicella A, Grimaldi P. J Appl Polym Sci 1987;33:2077.

[29] Kloosterboer JG, Lijten GFCM. Polymer 1987;28:1149.

[30] Anseth KS, Bowman CN, Peppas NA. Polym Bull 1993;31:229.

[31] Decker C, Moussa K. J Appl Polym Sci 1987;34:1603.

[32] Decker C, Moussa K. Eur Polym J 1990;26(4):393.

[33] Lecamp L, Youssef B, Bunel C, Lebaudy P. Polymer 1997;38(25):6089.

[34] Lecamp L, Youssef B, Bunel C, Lebaudy P. Polymer 1999;40(6):1403.

[35] Anseth KS, Wang CM, Bowman CN. Polymer 1994;35:3243.