

Manufacture of moulded articles by photopolymerisation under visible or near ultraviolet lights

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ABSTRACT.

The manufacture of moulded articles by a photopolymerisation reaction under visible or near ultraviolet light is described. The use of diketones as photoinitiators for the radical polymerization of an acrylate matrix is reported. The efficiency of various diketones/additives formulations is investigated, compared to other photoinitiating systems and discussed. Very high polymerized thicknesses can be obtained. This photopolymerizable formulation is suitable for the production of ophthalmic lenses.

INTRODUCTION.

Photopolymerization reactions in the Radiation Curing area are usually initiated through a radical reaction upon a UV light exposure and very often encountered in the formation of thin films (typically 2-100 μm) [1]. These reactions can be also carried out by using photoinitiating systems sensitive to visible lights because of some specific advantages required in particular applications [2].

Due to the penetration of light, the photopolymerization of thick films remains difficult and only few systems have been designed to meet this challenge (e.g. in the coating area - 100-300 μm heavily pigmented films of paint [3] – or in the fabrication of 1-10 mm transparent objects [4].

In the present paper, we will describe the manufacture of a thick clear moulded object, using a visible light irradiation of an acrylate matrix. This procedure allows the further possibility to incorporate UV absorbing additives in the formulation.

EXPERIMENTAL.

Several formulations are used : I ("laboratory" formulation: Table 1), II ("representative" formulation of a commercial product: Table 2) and III (CR426 which is a commercial mixture, from PPG, based on D121).

Table 1 : The formulation I (w/w %)

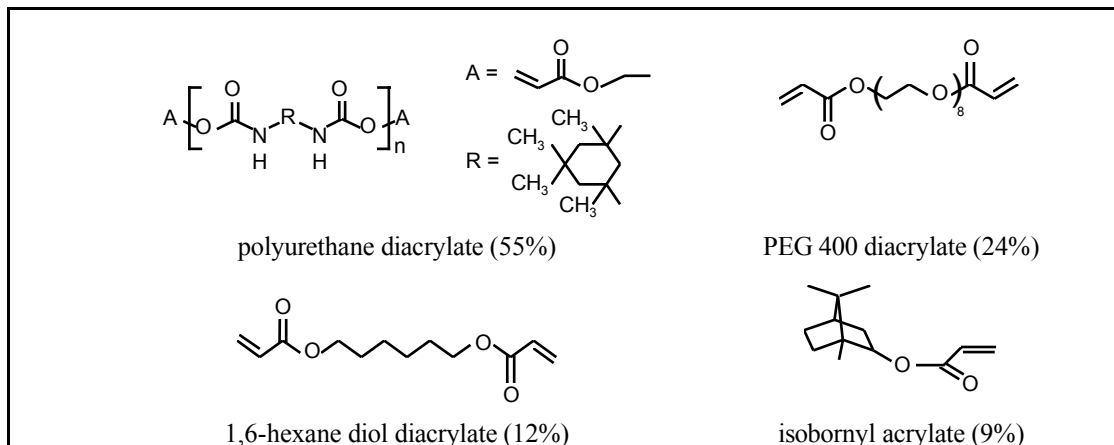
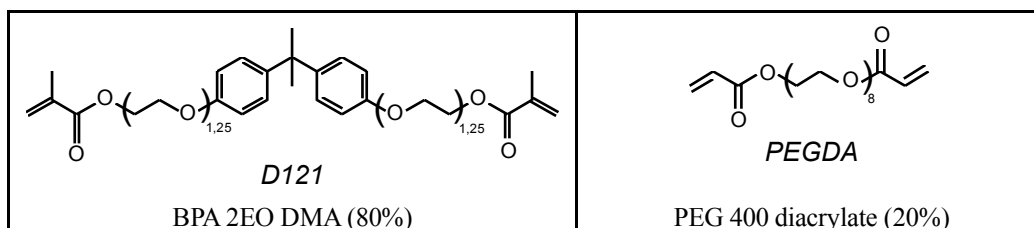


Table 2 : The formulation II (% are in w/w)

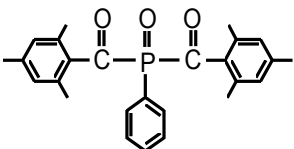
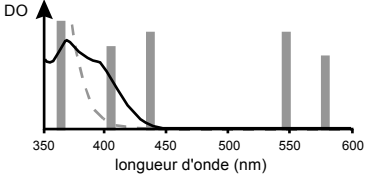
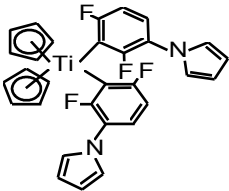
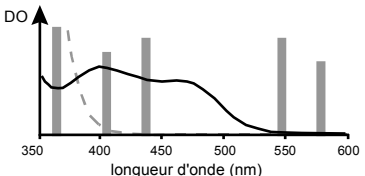
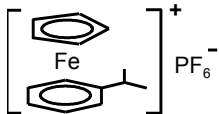
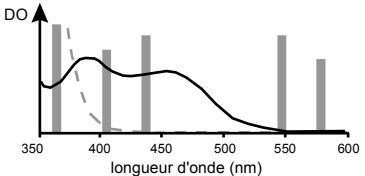
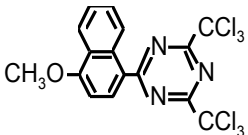
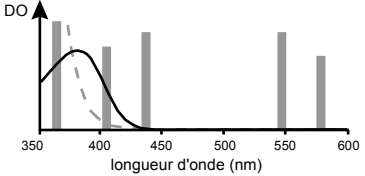
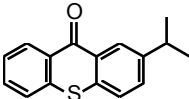
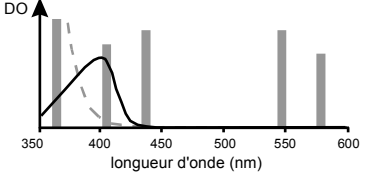
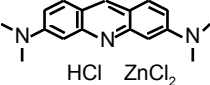
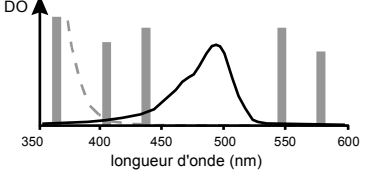
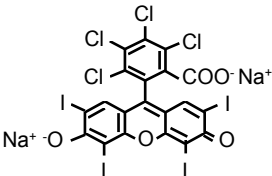
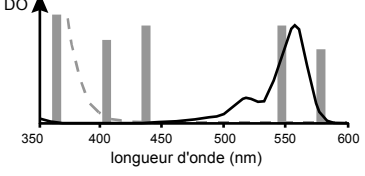


A preliminary screening was done with a first set of photoinitiators (Table 3). The formula of the α -di-ketones selected in a second step are reported in Table 4. These tables show the good matching between the absorption spectra and the emission spectrum of the mercury lamp (HBO 350W). The light is filtered at 380nm (F390 filter) or 410nm (F420 filter). For example, the intensity at the sample is 350mW/cm² when using light at $\lambda > 380$ nm.

The polymerization is carried out under argon (Figure 1) either in a cell (1 cm diameter) where various thicknesses can be selected (up to 10 cm) or in a cupel allowing to get samples having a 4 cm x 4 cm surface and 5.5 mm thick. The quality of the polymerized sample is first evaluated by the tack free test.

The extent of the polymerization is followed in thin films through real time FTIR spectroscopy: these experiments are obviously not really representative of what happens in thick films but they give a first insight in the relative ability of the different formulations to polymerize.

Table 3 : Names, formula and absorption spectra of the photoinitiators in acetonitrile. Emission of the Hg lamp are superimposed on the absorption spectra (gray lines).

Photoinitiators	Abbreviation	Formula	Absorption spectrum
Irgacure® 819	I819		
Irgacure® 784	I784		
Irgacure® 261	I261		
2-(4'-methoxy-1'-naphtyl)- 4,6-bis(trichloromethyl)- 1,3,5-triazine	TB		
isopropylthioxanthone	ITX		
acridine orange	AO		
Rose Bengal	RB		

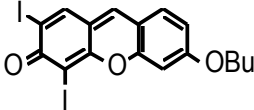
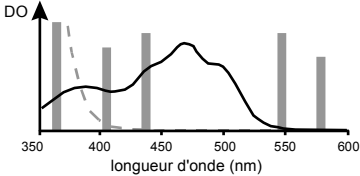
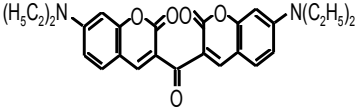
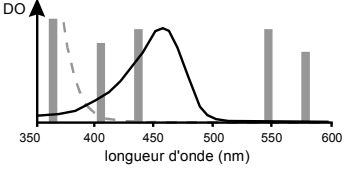
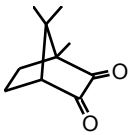
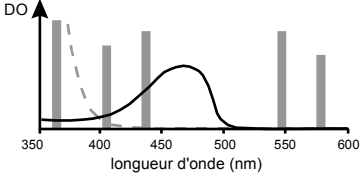
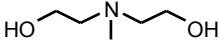
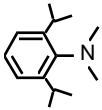
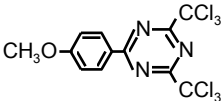
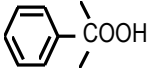
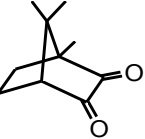
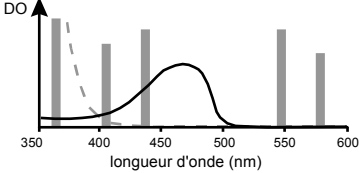
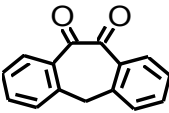
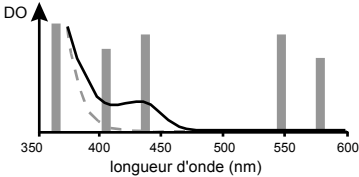
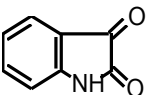
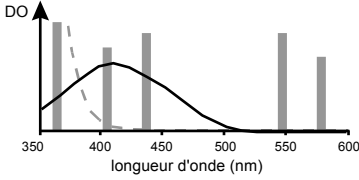
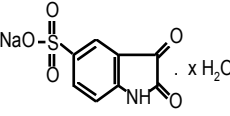
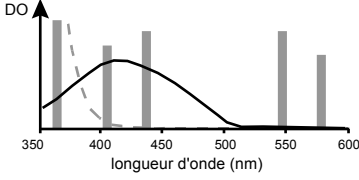
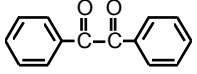
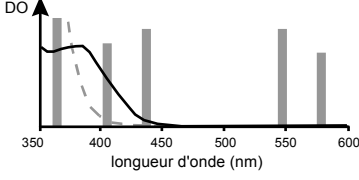
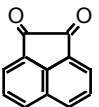
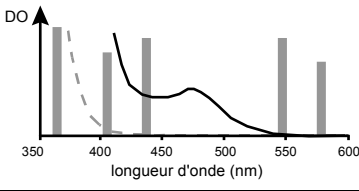
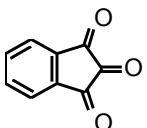
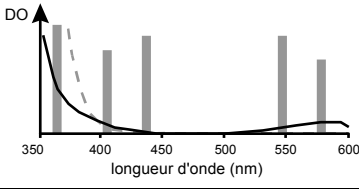
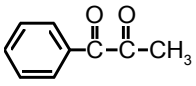
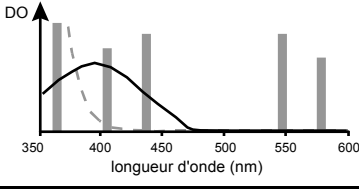
3-butoxy-5,7-diiodo-6-fluorone	HNu470		
3,3'-carbonyl-bis(7-diethylaminocoumarine)	CetCou		
camphorquinone	CQ		
Co-initiators			
<i>N</i> -methyldiethanolamine	MDEA		
<i>N,N</i> -dimethyl-2,6-diisopropylaniline	DiDMA		
2-(4'-methoxyphenyl)-4,6-bis(trichloromethyl)-1,3,5-triazine	TA		
Cumene hydroperoxide	HdC		

Table 4: Absorption spectra of the α -di-ketones in acetonitrile.

camphorquinone	CQ		
5 <i>H</i> -dibenzo[<i>a,d</i>]cyclohepten-10,11-dione	Su		

isatin	Is		
5-isatinsulfonic acid	IsA		
benzil	BZ		
acenaphthenequinone	ANQ		
Trione derivative	Tr		
1-phenyl-1,2-propanedione	PPD		

RESULTS.

Screening of the selected photoinitiators

The photoinitiating systems reported in Table 4 are able to cure the formulation I on the overall 7 mm thickness (Table 5). Samples remain slightly colored after polymerization. The best systems are I784 / HdC and CQ. Good results are also obtained when using the formulations I and III.

As expected [4], I819 yields uncolored samples. Further experiments show that the addition of HdC (0.05%) to CQ (0.2%) in the formulation II also leads to an uncolored cured sample. Complementary experiments on the effect of HdC in the formulations II and III suggest that the coloration is dependent on the matrix. We then decide to focus our attention on the α -di-ketone family.

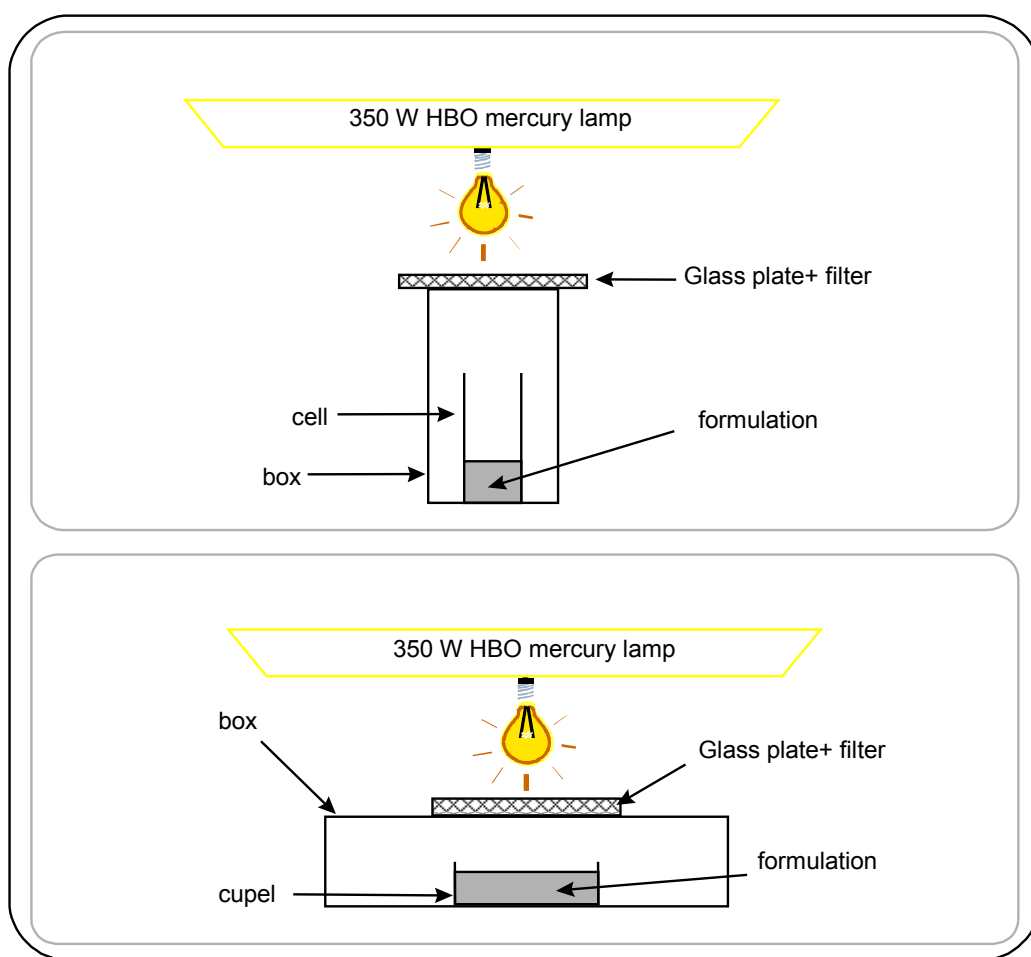


Figure 1. Schematic representation of the sample irradiation (top: in the cell; bottom: in the cupel).

Table 5: The photoinitiating systems that work well. Cell (thickness ~ 7 mm) - 30 min irradiation – after argon bubbling i radiation > 380 nm.

Photoinitiating systems	% w/w
I819	0.08
I784	0.04
I784 / HdC	0.06 / 0.06
I261 / HdC	0.1 / 0.1
RB / MDEA / TA	0.01 / 0.25 / 0.03
AO / MDEA / TA	0.02 / 0.4 / 0.05
CetCou / MDEA	0.01 / 2.5
HNu470 / MDEA	0.02 / 0.4
HNu470 / DiDMA	0.02 / 0.4
TB	0.1
ITX / MDEA	0.04 / 0.5
CQ	0.2

The α -diketones as photoinitiators

The compounds listed in Table 4, except Is and IsA, can efficiently initiate the polymerization of the formulations II and III (Table 6). Concerning the absence of coloration in the formulation III, the best systems are I819, Su and Su/HdC.

These three systems still correctly work upon irradiation at $\lambda > 410\text{nm}$; due to their absorption, Su should remain efficient even at $\lambda > 440\text{ nm}$ contrary to I819 which can no longer absorb.

Table 6 : Photopolymerization of the formulation III in the presence of the α -di-ketones – See the legend of Table 5 for the experimental conditions.

Photoinitiating systems	% w/w	polymerization
CQ / HdC	0.05 / 0.2	yes*
Is	0.1	no
IsA	0.1	no
BZ	0.1	gelification
BZ / HdC	0.05 / 0.2	gelification
PPD	0.1	yes*

Photoinitiating systems	% w/w	polymerization
PPD / HdC	0.05 / 0.2	gelification
Su	0.1	yes
Su	0.05	yes*
Su / HdC	0.05 / 0.2	yes*
ANQ	0.1	yes
Tr	0.1	yes*

* residuel monomer on the surface in contact with air

Several (hydro) peroxides have been selected (Table 7). The effect of these compounds when combined with CQ (chosen as a representative of the di-ketones) as well as the performance of (hydro) peroxide/photoinitiator couples have been studied.

The use of the photoinitiating systems defined in Table 8 leads to an efficient polymerization. I819, CQ/BeP and to a lesser extent Su and Su/BeP yield uncolored samples.

Table 7 : Studied (hydro) peroxides.

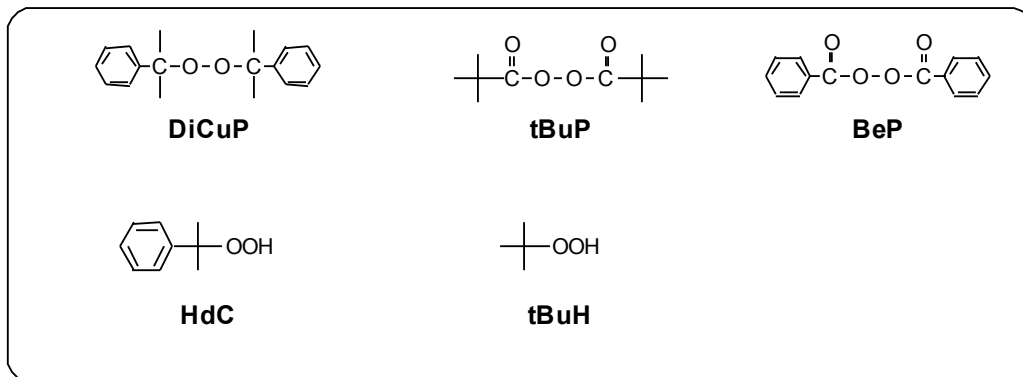


Table 8: The various (hydro) peroxides/ CQ couples. Formulation III. See legend of Table 5 for the experimental conditions. *: [CQ] = 0.2% w/w - **: [ROOH or ROOR] = 0.4% w/w

CQ*	I819 (0.1)
CQ + HdC**	CQ (0.05)
CQ + tBuH	CQ / BeP (0.05 / 0.2)
CQ + DiCuP	Su (0.05)
CQ + tBuP	Su / BeP (0.05 / 0.2)
CQ + BeP	

A kinetic approach of the photopolymerization of thin films

Typical photopolymerization profiles are displayed in Figure 2: they show that fast rates of polymerization as well as high % conversion are attained. The performances of I819 and CQ/BeP are quite similar.

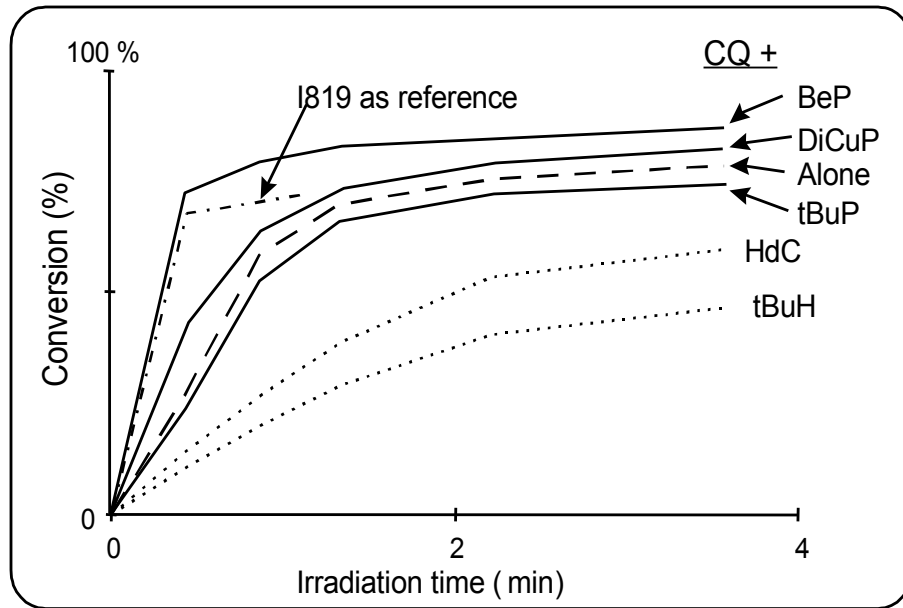


Figure 2 : Effect of peroxides (—) (0.4%) and hydroperoxides (...) (0.4%) when CQ (0.2%) is used as a photoinitiator. Formulation II. I819 (0.1%) is used as a reference- In laminate - $\lambda_{\text{irradiation}} > 380 \text{ nm}$ - 50 μm thin film.

Photopolymerization in the cupels

The curing in cupels allows to see how it is possible to prepare and to explore the properties of large and thick polymerized samples.

A good polymerization is achieved with the selected I819 and CQ/BeP based systems. For these samples, the residual coloration RC after photopolymerization has been calculated (table 9) using the expression:

$$RC = OD(\lambda = 420\text{nm}) - OD(\lambda = 680\text{nm})$$

ΔRC expresses the difference in the residual coloration immediately after 3 weeks of exposure to the day light at room temperature.

Photopolymerization of high thickness samples

Cylindric samples (1 cm diameter) of the formulation III having a thickness up to 8 cm can be polymerized using I819 (as known) but also CQ/BeP (0.05%/0.2%) upon a 30 mn exposure to the mercury lamp.

Table 9 : Residual coloration. See text. See legend of Table 5.

Photoinitiating system	% w/w	Formulation	RC	Δ RC
I819	0.1	II	0.08	0
		III	0.02	0
CQ	0.05	II	0.03	0.06
		III	0.03	0.02
CQ / HdC	0.05 / 0.2	II	0.02	0.01
		III	0.02	0.02
CQ / BeP	0.05 / 0.2	II	-	-
		III	0.03	0.02
Su	0.05	II	0.08	0.03
		III	0.02	0.01

CONCLUSION

The present study shows that α - di-ketones/(hydro) peroxides combinations are efficient photoinitiating systems for the photopolymerization of acrylate formulations under long wavelength irradiation.

The properties of the cured polymer sample suggest that they can be used for the manufacture of molded objects usable as lenses or glasses. The interest of α - di-ketones lies on the fact that they exhibit a very suitable absorption in the near visible part of the spectrum; they absorb at longer wavelength than I819. This property allows to incorporate additives (such as UV absorbers or photochromes) in the formulation without having any problem with the inherent strong absorption of these compounds in the UV. Moreover, the tunability of the absorption can be achieved using an adequate substitution on the starting compounds. Therefore, these α - di-ketones based systems appear as a very good alternative [5] to I819 which has been already designed, in the patent literature, for such an ophtalmic application [6].

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