

# Effect of UV-curing conditions on the cationic polymerization kinetics of vinyl ether monomers

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## ABSTRACT

In this study, the performance of a new triarylsulfonium photoinitiator in the initiation of cationic polymerization of vinyl monomers was investigated by infrared spectroscopy (IR). The effect of the emission spectrum of light sources on the kinetics of the curing process was examined. The results indicate that the light source characterized by a total overlap of its emission spectrum with the photoinitiator absorption spectrum is the best system for effective cure. In the case of smaller overlap of spectrums, the conversion degree and the rate are lower. Nevertheless, it is easy to regulate by extending the energy of the emitted light. At the UVB light source, the maximal conversion degree is 71.8%, with the polymerization rate of  $1.68 \text{ s}^{-1}$ , which is faster than the corresponding free-radical photopolymerization of acrylic monomers.

**Keywords:** Cationic Initiator, Polymerization, UV-Curing, Divinyl Ether

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## I. INTRODUCTION

UV light-induced polymerization reactions have been continuously growing in interest in different fields, from protective coatings to printing inks, microelectronics, and smart materials for additive manufacturing [1- 3].

During a UV-curing process, radical or cationic species are generated by the interaction of UV light with a suitable photoinitiator. Free radical polymerization currently dominates because of its low cost and the ease of design afforded by a wide selection of functional monomers. However, free radical polymerization has an inherent disadvantage: oxygen inhibits polymerization. An alternative curing mechanism [4, 5] has been developed to overcome this

inhibition, cationic polymerization. In addition, the cationic polymerization has been effectively demonstrated for vinyl ethers (VEs) which are interested in sustainability demands [6, 7]. In this polymerization, cationic photoinitiator onium salts (iodonium I or sulfonium II) represent the most widely used classes of photoinitiators [5, 6]. Properties such as thermal stability and inactivity toward polymerizable monomers at ambient temperature render these salts particularly suitable for photocurable formulations. However, all of the iodonium photoinitiators used in the industry exhibit similar absorption characteristics, with the absorption maximum in the range 220—280 nm [5]. This characteristic creates a technological problem because there are no economical and simultaneously enough powerful light sources that would emit UV light in that range. In the photocurable

coatings industry, medium pressure mercury lamps are used, which emit most of the energy at about 365 nm and only a fraction in the absorption range of commercial iodonium photoinitiators. Hence, there is a mismatch between the absorption characteristics of the commercial photoinitiators and the emission characteristics of the light sources, which lowers the photopolymerization rate [5].

In this study, photopolymerization kinetics were studied for a modern composition of a new cationic photoinitiator and a divinyl ether monomer to develop the applications of UV polymerization. The effect of UV-curing conditions on the curing process was also investigated.

## II. EXPERIMENTAL

### A. Materials

Triethylene glycol divinyl ether (TEGDVE, from Sigma Aldrich) and 3,4-epoxy cyclohexyl methyl 3,4-epoxycyclohexanecarboxylate (CADE, Sigma Aldrich) were applied as model monomers. The photoinitiator Triarylsulfonium hexafluoro-phosphate salt (TAS-PF<sub>6</sub> 50% in propylene carbonate) was supplied by Sigma-Aldrich. The chemical structures of the materials are shown in Fig. 1

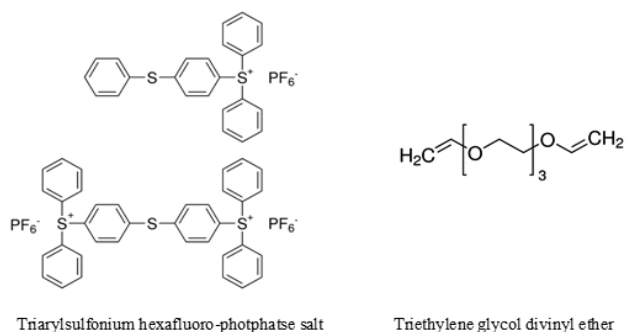


Figure 1: Chemical structures of the used compositions

### B. Curing process

The compositions were prepared by dissolution of the photoinitiator in TEGDVE monomer in such proportions as to obtain the concentrations in the

range of 0.5 – 3% wt. The solutions were prepared in glass vials made of dark glass and were applied immediately after preparation as follows.

The defined sample volume (according to layer thickness) was spread on the same area of a polyester film (white-back) by a handled roller. The thicknesses of the investigated films were about 20 g/m<sup>2</sup> (equivalent to about 10 μm).

The samples were exposed and cured by two UV light sources: a medium pressure mercury lamp (25 W) and a UVB-led lamp (9W). The light sources were arranged at a distance from the cured sample so that the light intensities used in all experiments were constant at 1 mW.cm<sup>-2</sup>. The emission spectrums of two sources are presented in Fig.2.

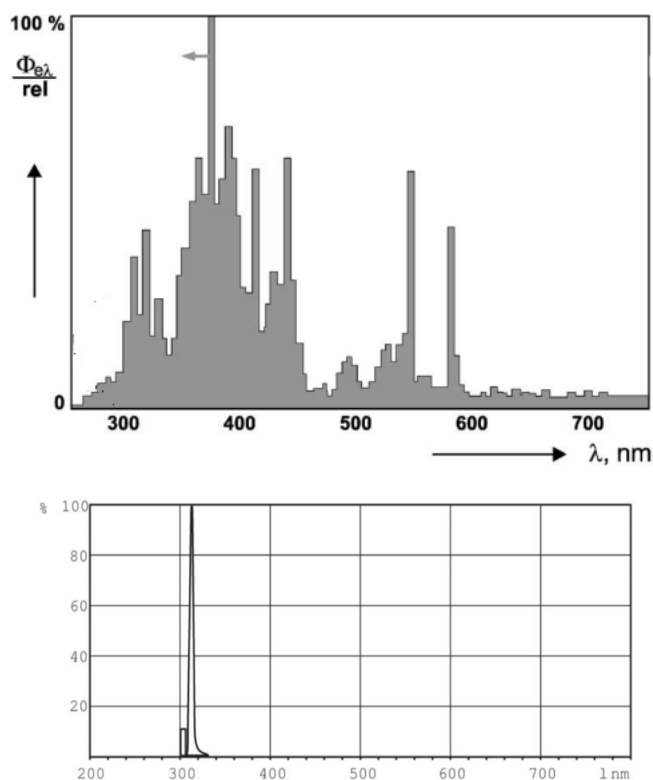


Figure 3: Emission spectrum of mercury lamp (above) and UVB lamp (below)

### C. Absorption measurement

Absorption spectra of the photoinitiators were recorded in methanol, using Agilent 8453 UV/VIS and

a quartz cuvette with a 1.0 cm optical path. For relative comparisons, the absorbance data was converted into extinction coefficient data, expressed in classical units [dm<sup>3</sup>.mol<sup>-1</sup>.cm<sup>-1</sup>].

**D. Polymerization kinetics measurement**

The curing process was evaluated by IR spectroscopy (Spectrophotometer IR Affinity – 1S of Shimadzu) based on the transmittance measurements.

The degree of conversion in the cured film was determined according to the amount of monomer double bond (twisting vibration at 810 cm<sup>-1</sup>, stretching vibration at 1610 – 1640 cm<sup>-1</sup>) by a baseline method [10]. The degree of conversion (*X*) and relative polymerization rate (*R<sub>p</sub>*) were calculated from the well-known equation (1) [11]

$$X = 1 - \frac{A_{t(\lambda)}}{A_{0(\lambda)}} \tag{1}$$

where *A<sub>0(λ)</sub>* and *A<sub>t(λ)</sub>* is the absorbance of monomer’s C=C bonds measured at the chosen wavelength (810 cm<sup>-1</sup>) before and after the exposure to UV light for the time *t*, respectively

The relative polymerization rate *R<sub>p</sub>* was calculated from the following equation

$$R_p = \frac{dX}{dt} \tag{2}$$

where *X* is the conversion degree of monomer’s C=C bonds, at the exposure time *t*. The values of maximum conversion *X<sub>max</sub>* and maximum polymerization rate *R<sub>p</sub>* were obtained from the plots of *X* and *R<sub>p</sub>* vs. time in the initial stage of curing.

**III. RESULTS AND DISCUSSION**

**A. Absorption characteristics of the photoinitiator and spectral contribution of light sources**

As observed in Fig.3, the initiator shows the peak of absorbed light at 334 nm. Meanwhile, the light sources

emits the energy maximum (nearly 100%) at λ = 365 nm (source 1) and λ = 311 nm (source 2). The extinction coefficients of the initiator at 365 nm and 311 nm are 0.46 and 0.90, respectively.

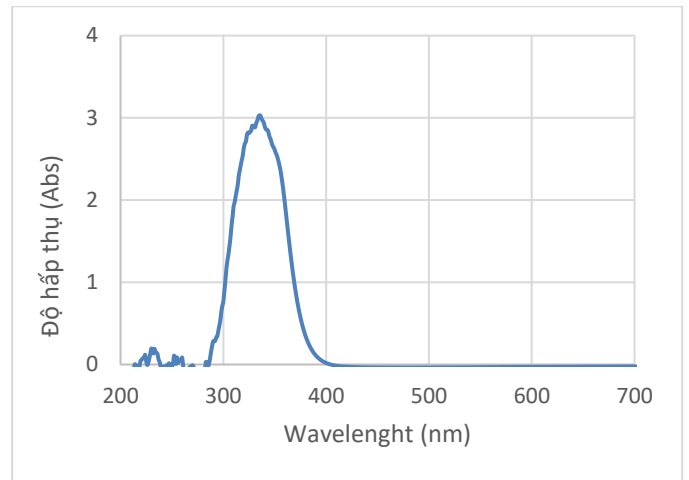


Figure 3: Absorbance spectrum of the initiator

TABLE I

The extinction coefficients of the initiator

	λ <sub>max</sub> (nm)	Extinction (mol <sup>-1</sup> .cm <sup>-1</sup> )	Extinction ratio
Initiator	334	4102	
Mercury lamp	365	1888	0.46
UVB lamp	311	3673	0.90

**B. Effect of light sources on the curing process**

The IR spectrums of the samples exposed at two light sources are presented in Fig.4. The curing process kinetics that was withdrawn from the IR spectrum of the composition irradiated with time is reported in Table II. The conversion degree was calculated according to equation (1) basing on a decrease of the absorbance intensity of C=C band vibrations at 810 wavenumbers. The conversion degree as a function of time is presented in Fig. 5.

TABLE II

EFFECT OF INITIATOR CONCENTRATION ON KINETICS OF THE POLYMERIZATION

Sample	Light source	X <sub>max</sub> (%)	R <sub>p</sub> (s <sup>-1</sup> )
1	Mercury lamp	51.2	1.04
2	UVB lamp	71.8	1.68

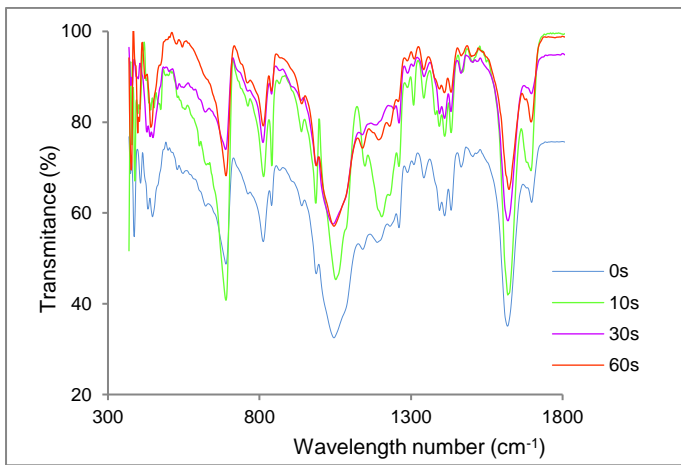
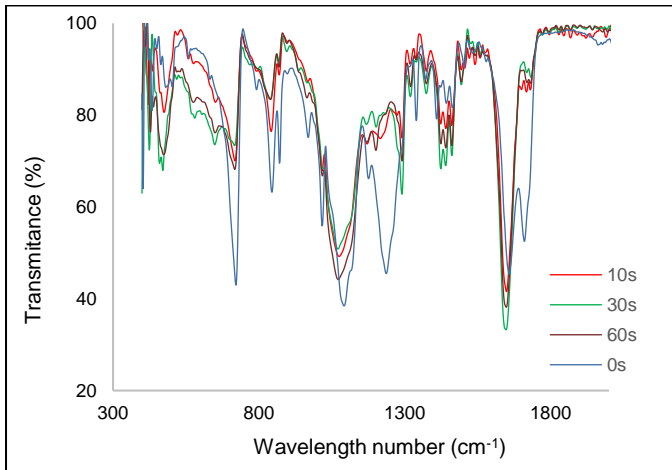


Figure 3: IR spectrum of monomer TEGDVE (initiator 2%) during irradiation under the mercury lamp (above) and UVB lamp (below)

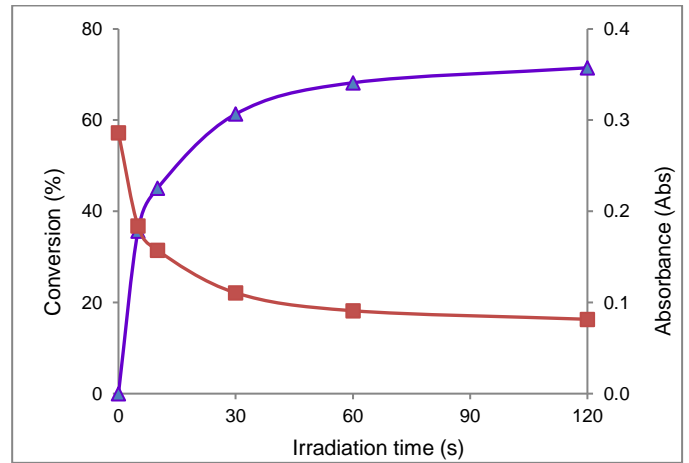
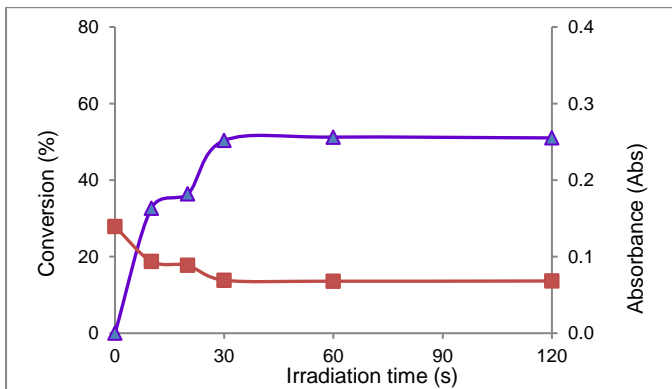


Figure 4: Conversion degree and absorbance at 810 cm<sup>-1</sup> are plotted as a function of irradiation time of the mercury lamp (above) and UVB lamp (below)

The spectral contribution of light source has a significant influence on the curing process. The maximal conversion degree is 71.8 % under the irradiation of UVB lamp, a half higher than that under the mercury lamp (51.2 %). A similar phenomenon was reported by J. Kindernay et al.[8] for the free radical polymerization of acrylate monomers. This result can be explained by the spectral characterizations of the sources. As mentioned above, the extinction coefficient of initiator at the maximal energy of the UVB lamp is twice higher than at the mercury lamp. Hence the energy, effectively usable for UV curing, of the UVB lamp is much higher.

If the slopes ( $dX/dt$ ) of the kinetic profiles, obtained right after the polymerization start, can be used as quantitative indicators of the polymerization rates, the rates of polymerizations at various initiator concentrations are reported in Table II. The rate of polymerization,  $R_p$ , is influenced by light source spectrum. The curing process is faster under the UVB lamp. For quantitative comparison with the performance of the corresponding free-radical photopolymerization of acrylic monomers [9, 10], the polymerization rate of TEGDVE with TAS-PF<sub>6</sub> initiator under both light sources is much higher.

#### IV. CONCLUSION

The UV-polymerization process of Triethylene glycol divinyl ether with Triarylsulfonium hexafluorophosphate salt initiator was studied by IR spectroscopy. The conversion degree and the polymerization rate are significantly affected by the spectral contribution of light sources. It is found that the light source characterized by a full overlap of its emission spectrum with the photoinitiator absorption spectrum is the best system used for an effective cure. In the case of smaller overlap of spectrums, the conversion degree and the rate are lower. Nevertheless, it is easy to regulate by extending the energy of the emitted light.

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