Effect of Cationic Photoinitiator on the Polymerization Kinetics of Vinyl Ether Monomers

Tran Nhung Hien Phuong, Pham Thi Kim Hue, Luu Bach Hiep, Hoang Thi Kieu Nguyen*

Hanoi University of science and technology, Hanoi, Vietnam

ABSTRACT

In this study, the performance of a new triarylsulfonium photoinitiators in the initiation of cationic polymerization of vinyl monomers was investigated by infrared spectroscopy (IR). The photoinitiator exhibit absorption characteristics compatible with the emission characteristics of medium pressure mercury lamps, which are the main sources of UV light in the industry. The experimental results indicate that the photoinitiator is most effective at a concentration of 1%. At the investigated conditions, the maximal conversion degree is 77.8% and the polymerization rate is 0.56 s^{-1}. The curing process is even faster than the corresponding free-radical photopolymerization of acrylic monomers

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

I. INTRODUCTION

UV light-induced polymerization reactions has been continuously growing 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 usable monomers. However, free radical polymerization has an inherent disadvantage: oxygen inhibits their polymerization. To overcome this inhibition, cationic polymerization, the alternative curing mechanism [4, 5] has been developed. 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. They have a general structure that consists of an organic cationic moiety with a positive charge on a heteroatom and a counter anion. The cationic portion of the salt plays the role of the light absorber. The structure of the cation controls the UV-absorption characteristics: the photosensitivity, quantum yield, whether the compound can be photosensitized, and the ultimate thermal stability of the salt [3]. This is the reason for the fact that the iodonium cations are critical to the photoinitiator performance. 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 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 energy at about 365 nm and only a fraction in the absorption range of commercial iodonium photoinitiators (Fig. 1). 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].

On the other hand, it is the nature of the anion that determines the strength of the acid formed during photolysis and its corresponding initiation efficiency. The nature of the anion also determines the character of the propagating ion pair. This has a direct impact on the kinetics of polymerization and whether terminations can occur. The larger the negatively charged anion, the more loosely it is bound and the more active the propagating cationic species is in the polymerization. The order of reactivity is as follows: $SbF_6^- > AsF_6^- > PF_6^- > BF_6^-$ [5].

In the case of monomers used in cationic photopolymerization, different types have been proposed and reported in the literature, mainly epoxides, vinyl ethers, and propenyl ethers [3]. Among that vinyl ethers are attractive since their photopolymerization is rather fast and photocuring rates are in many cases faster than for the corresponding free-radical photopolymerization of acrylic monomers [6]. Furthermore, vinyl ethers show the advantages of high diluting power and low toxicity []. To develop the UV polymerization of vinyl monomers, several new iodonium photoinitiators were proposed [5, 8, 9]. However, most studies are focusing on the performance of new materials. The fundamental investigation of the material reaction and kinetics are comparatively limited.

Therefore, in this study, the photopolymerization kinetics were studied for a modern composition of a new cationic photoinitiator and a divinyl ether monomer. The effect of photoinitiator concentration 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_6 50% in propylene carbonate) was supplied by Sigma-Aldrich. The chemical structures of the materials are shown in Fig. 1

Triarylsulfonium hexafluoro-photphatse salt   Triethylene glycol divinyl ether
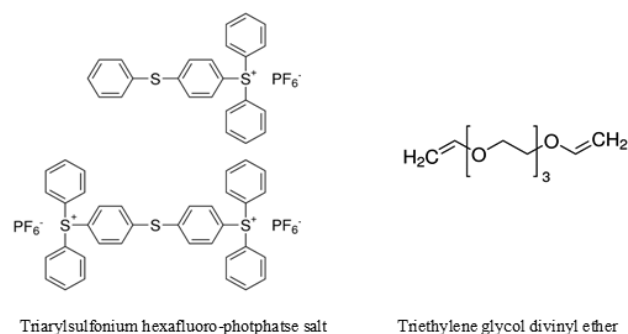
Figure 1: Chemical structures of the used compositions

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 handle roller. The thicknesses of the investigated films were about 20 g/m^2 (equivalent to about 10 μm).

Medium pressure mercury UV lamp (250 W) arranged at the distance from the cured sample so that

the light intensities used in all four experiments was constant at 10 mW.cm^{-2}.

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^3·mol^{-1}·cm^{-1}].

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^{-1}, stretching vibration at 1610 – 1640 cm^{-1}) by a baseline method [10]. The degree of conversion (X) and relative polymerization rate (R_p) were calculated from the well-known equation (1) [11]

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

where $A_{0(\lambda)}$ and $A_{t(\lambda)}$ is the absorbance of monomer's C=C bonds measured at the chosen wavelength (810 cm^{-1}) before and after the exposure to UV light for the time t, respectively

The relative polymerization rate R_p was calculated from the following equation

$$R_p = \frac{dX}{dt} \qquad (2)$$

where X is the conversion degree of monomer's C=C bonds, at the exposure time t. The values of maximum conversion X_{max} and maximum polymerization rate R_P were obtained from the plots of X and R_P vs. time in the initial stage of curing.

III. RESULTS AND DISCUSSION

A. Absorption characteristics of the photoinitiators

The comparison of emission spectrums (of the used light source) to that of the UV absorbance spectrum of the initiator is mentioned in Fig. 2. The initiator shows the peak of absorb light at 334 nm. Meanwhile, the light source emits the energy maximum (nearly 100%) at λ = 365 nm. The extinction coefficient of the initiator at 365 nm is at the level of 46% of that at the peak maximum located at max = 334 nm. The second of most intense emission bands of the lamp almost overlaps the absorbance range of the initiator. Hence, it can be supposed that the light source is the efficient light source for our studied polymeric system.
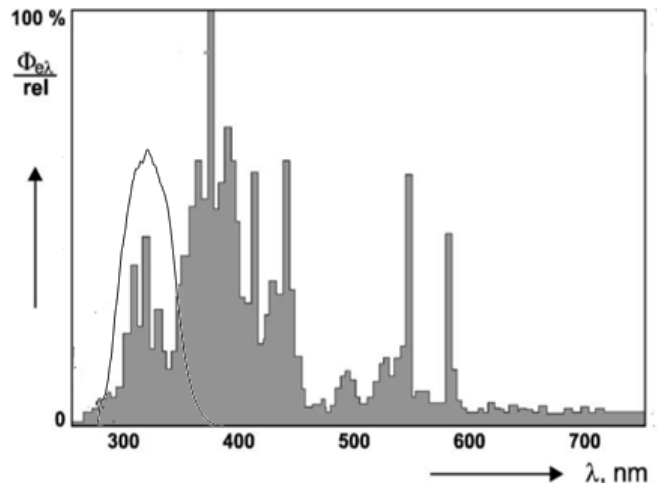

Figure 2: Emission spectrum of metal halogen mercury lamp vs. UV absorbance spectrum of initiator TAS-PF6

B. Effect of the photoinitiator concentration on the curing process

In this investigation series, the concentration of photoinitiator varied in the range of 0.5 – 3% wt. according to the mass of Triethylene glycol divinyl ether monomer. All the samples were cured at the same polymerization conditions. The experimental data are given in Table 1. The curing process kinetics was withdrawn from the IR spectrum of the composition irradiated with time (Fig.3) 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 for a typical sample in Fig. 4.

TABLE I

EFFECT OF INITIATOR CONCENTRATION ON KINETICS OF THE POLYMERIZATION

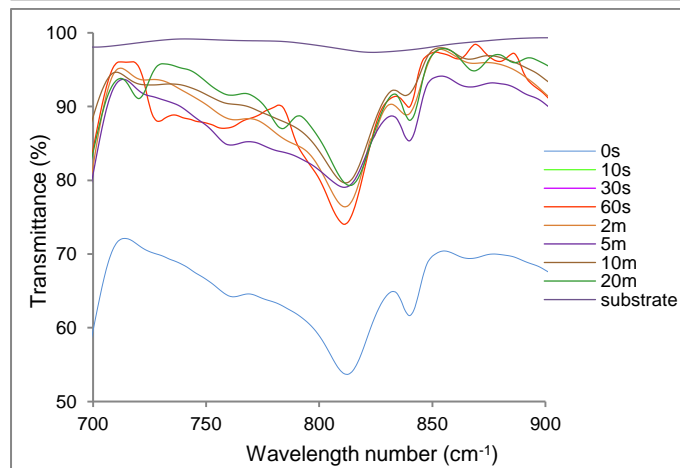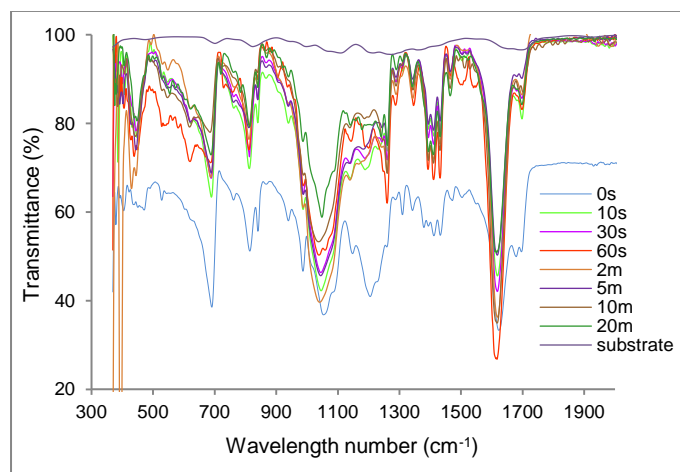| Sample	Initiator concentration (%)	X_{max}(%)	R_p (s^{-1})
1	0.5	75.6	0.47
2	1	77.8	0.56
3	2	69.0	0.34
4	3	63.8	0.33

Figure 3: IR spectrum of monomer TEGDVE (initiator 2%) during irradiation

The amount of initiator has a significant influence on the curing of divinyl ether. The maximal conversion degree is reached at the initiator concentration of 1% wt. (X_{max} = 76%). As the photoinitiator concentration is enhanced from 1% wt. to 3% wt. the decrease of

the double bond conversion as well as the rate of polymerization is observed (Fig. 5 and Fig. 6). A similar phenomenon was reported by Viera Jancovicová et al.[10] for the free radical polymerization of acrylate monomers. Probably the higher concentration of the initiator exhibits high absorption at its absorptions maximum at 334 nm, and the initiator acts as an internal filter. This internal filtration effect (decreased penetration of UV light) can give rise to a concentration gradient between the surface and bottom layer of irradiated film [10]. Additionally, local high concentration of initiator radicals can simultaneously promote radical recombination, and hence consumption of initiator inside reaction not leading to a polymerization. In another study of Haifaa Mokbel for the polymerization of TEGDVE monomer that was initiated by (7-ethoxy-4 methyl coumarin-3-yl) phenyl iodonium hexafluorophosphate (P3C-P), the increase of the conversion with increasing initiator concentration from 1 to 3% was learned. It can be seen that the difference between the two initiators is in the cationic part. The P3C-P initiator has an extinction coefficient (at 365 nm) much higher than the initiator studied here [5]. So that it becomes more effective at high concentrations under this light source.
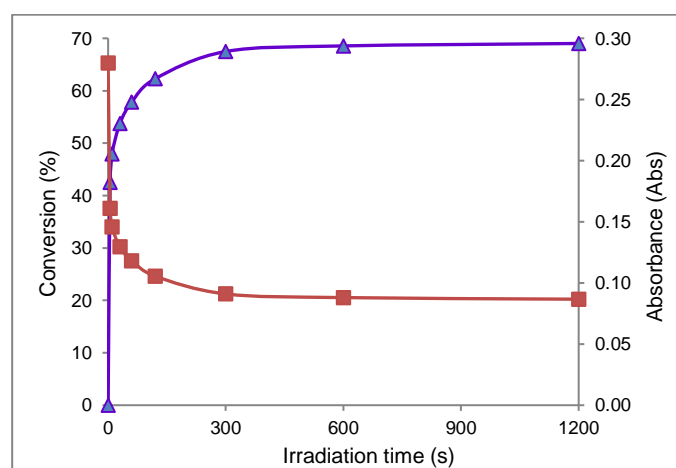

Figure 4: Effect of irradiation time on the conversion degree and the absorbance at 810 cm^{-1} of TEGDVE (initiator 2%)

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 1. The rate of polymerization, R_p, is influenced by photoinitiator concentration. Similar to the conversion, the polymerization rate also gets the maximal value at the initiator concentration of 1%. For quantitative comparison with the performance of new other photoinitiators, such as P3C-P, P3C-Sb, or P6C-Sb, the polymerization rate of TEGDVE with TAS-PF₆ initiator is much higher [5, 8]. The curing process is even faster than the corresponding free-radical photopolymerization of acrylic monomers [10,12].
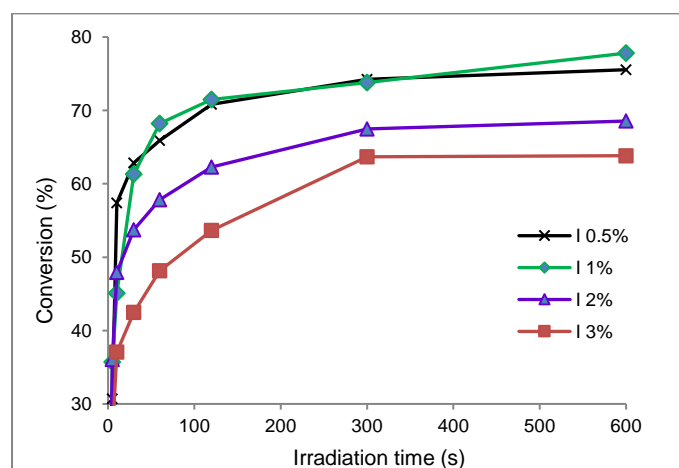

Figure 5: Effect of irradiation time on the UV-curing of TEGDVE with various initiator concentrations
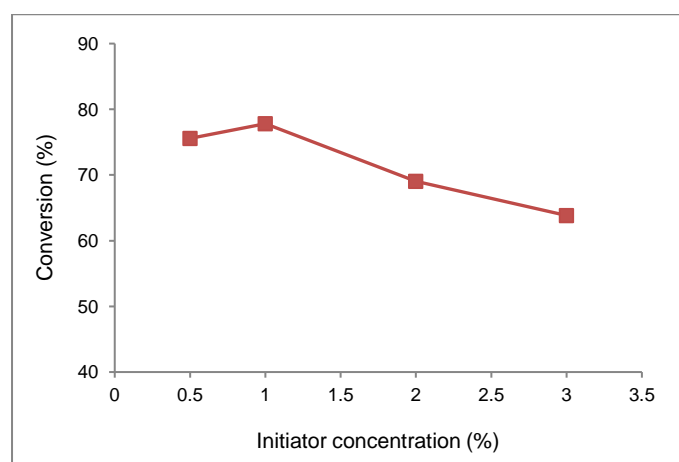
Figure 6: Conversion degree is plotted as a function of initiator concentration

IV. CONCLUSION

The UV-polymerization process of Triethylene glycol divinyl ether with various cationic initiator concentrations of Triarylsulfonium hexafluoro-phosphate salt was studied by IR spectroscopy. The conversion degree and the polymerization rate are significantly affected by initiator concentration. The optimal polymerization is archived at a concentration of 1%. The polymerization rate is much faster than other commercial initiators. The studied polymeric system is effective with industrial light sources.

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