



Test Method

Photopolymerization of hybrid monomers, Part II: Determination of relative quantum efficiency of selected photoinitiators in cationic and free-radical polymerization of hybrid monomers

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ABSTRACT

A method for determination of relative initiation efficiency of free-radical photoinitiators directly in monomers by Fluorescence Probe Technique (FPT) has been expanded into cationic photoinitiators and the use of LEDs instead of monochromatic light sources. The relative initiation efficiency of a series of cationic photoinitiators relative to diphenyliodonium hexafluorophosphate, and a series of free-radical photoinitiators relative to 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651), in cationic and free-radical photopolymerization of 2-(2-vinylxyethoxy)ethyl acrylate (VEEA) and 3,4-epoxycyclohexylmethyl methacrylate (Cyclomer M100) hybrid monomers has been determined. It was found that the initiation efficiency of cationic photoinitiators does not depend on the type of monomer, while the type of monomer affects initiation efficiency of free-radical photoinitiators.

1. Introduction

Initiation quantum efficiency of a photoinitiator in photopolymerization of a monomer is an important parameter, which characterizes photoinitiator performance, and which can be used for optimization of the photoinitiator structure in design of new photoinitiators, or for selection of the best photoinitiator for any particular photocurable system. In a previous paper (i.e., in Part I of this series [1]), we compared the performance of a series of cationic and free-radical photoinitiators in example hybrid monomers and we noticed that, when extinction coefficients of photoinitiators at the irradiation wavelength were very different, the magnitude of the extinction coefficient was the key factor that affected the photopolymerization rate. However, when the light absorption abilities of photoinitiators were similar, the efficiency of generation of initiating species from the photoinitiator became important.

In general, the photoinitiation quantum efficiency (Φ) of a photoinitiator can be defined as the number of polymer chains initiated per photon absorbed within an illuminated volume (equations (1) and (2) for free-radical and cationic photopolymerization, respectively).

$$\Phi = \frac{dn_{M_n^* \text{ generated}}}{dn_{\text{photons absorbed}}} \quad (1)$$

$$\Phi = \frac{dn_{M_n^+ X^- \text{ generated}}}{dn_{\text{photons absorbed}}} \quad (2)$$

Determination of the absolute quantum efficiency (Φ) of a photoinitiator directly in a monomer would be difficult. However, for quantitative comparison of the photoinitiation efficiency of a series of photoinitiators in any particular monomer, relative quantum efficiency of initiation, called shortly relative initiation efficiency, can be used. The relative initiation efficiency (Φ^{rel}) of a photoinitiator (i) is defined as the ratio of its absolute efficiency (Φ_i) to the absolute efficiency of the photoinitiator assumed as a reference (Φ_{ref}) (equation (3)).

$$\Phi_i^{rel} = \frac{\Phi_i}{\Phi_{ref}} \quad (3)$$

The relative initiation efficiency (Φ^{rel}) is a good parameter for comparison of the performance of a series of photoinitiators in the same photocurable composition, because reactivity of the radical or ionic species generated from the photoinitiators may depend on the type of monomer, but the conclusions concerning the effect of photoinitiator

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structure on its performance usually are more general and transferable to other monomers.

A method for determination of the relative initiation efficiency of various free-radical photoinitiators in monomers on the basis of FPT data was described in detail in [2]. In the case of free-radical photoinitiators, the initiation efficiency of a photoinitiator (*i*) relative to a reference photoinitiator (*ref*) is calculated from the ratio of initial rates of photopolymerization ($R_{po(i)}$ and $R_{po(ref)}$) and the absorbances of the photoinitiators (A_i and A_{ref}) in the thin-layer sample, measured at the irradiation wavelength used to induce the photopolymerization process (equation 4)

$$\Phi_i^{rel} = \left(\frac{R_{po(i)}}{R_{po(ref)}} \right)^2 \cdot \frac{1 - 10^{-A_{ref}}}{1 - 10^{-A_i}} \quad (4)$$

As at low monomer conversions the rate of photopolymerization (R_{po}) is proportional to the initial slope (dr/dt) of the kinetic curve obtained by FPT, equation (4) was converted into equation (5), where all of the variables were directly measurable [2], (Note that, to avoid symbol confusion between the reaction rates, labeled with capital "R", and the fluorescence intensity ratios previously labeled also with "R" [1], for the purpose of this paper the ratios are labeled with lower case "r").

$$\Phi_i^{rel} = \frac{\left(\frac{dr}{dt} \right)_{o(i)}^2}{\left(\frac{dr}{dt} \right)_{o(ref)}^2} \cdot \frac{1 - 10^{-A_{ref}}}{1 - 10^{-A_i}} \quad (5)$$

However, it has to be pointed out that equation (5) can be used directly only when a very narrow-bandwidth or monochromatic light is used for irradiation, (which was the case when CM1000 Cure Monitor was used [2]), and only for free-radical photoinitiators. Moreover, for accurate measurements, the fluorescent probe used for determination of the slopes (dr/dt) by FPT should be used at as low concentration as possible, so that its absorbance is negligible compared to the absorbance of the photoinitiators studied (which was possible in the case of highly fluorescent DASB probe [2]).

In the case of cationic photopolymerization, the expression for the relative initiation efficiency of cationic photoinitiators can be expected to be different because of different polymerization mechanisms. Moreover, UV LEDs used for this study are neither monochromatic nor very narrow-bandwidth light sources. Hence, in this paper, the FPT method for measuring the relative initiation efficiency of free-radical photoinitiators [2] has been extended into cationic photoinitiators and the use of LEDs instead of monochromatic light sources. Moreover, a more versatile equation for calculation of the relative initiation efficiency that takes into account also the probe absorbance has been derived and applied for determination of the relative initiation efficiency of a series of free-radical and cationic photoinitiators in example hybrid monomers.

2. Experimental section

2.1. Materials

2-(2-Vinyloxyethoxy)ethyl acrylate (VEEA, from Nippon Shokubai Co. Ltd. - Japan) and 3,4-epoxycyclohexylmethyl methacrylate (Cyclomer M100, from Daicel Corporation - Japan) were applied as the hybrid monomers, while *trans*-2-(2',5'-dimethoxyphenyl)ethenyl-2,3,4,5,6-pentafluorobenzene (25ST), reported by Neckers et al. [3], was applied as a fluorescent probe for study of the photopolymerization kinetics by FPT.

The relative initiation efficiency of the following cationic photoinitiators is reported: (7-methoxy-4-methylcoumarin-3-yl)phenyliodonium hexafluoroantimonate (Sylanto 7M-S) and (7-methoxy-4-methylcoumarin-3-yl)phenyliodonium hexafluorophosphate (Sylanto 7M-P) from Synthos S.A. (Poland), bis(4-*tert*-butylphenyl)iodonium

hexafluorophosphate (Speedcure 938) and 9-[4-(2-hydroxyethoxy)phenyl]thianthrenium hexafluorophosphate (Esacure 1187) from Lambson Ltd. (UK), (4-methylphenyl)[4-(2-methylpropyl)phenyl]iodonium hexafluorophosphate (Irgacure 250) from BASF (Germany), and diphenyliodonium hexafluorophosphate (HIP) from Alfa Aesar (Germany).

Moreover, the efficiency of the following photoinitiators in free-radical polymerization of the hybrid monomers has been evaluated: 1-hydroxycyclohexyl phenyl ketone (Irgacure 184), 1,1'-(methylenebis(4,1-phenylene))bis(2-hydroxy-2-methylpropan-1-one) (Irgacure 127), 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651), phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (Irgacure 819), and (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (Speedcure TPO). All of the free-radical photoinitiators were purchased from BASF (Germany) and were used as received.

Structures of the hybrid monomers, the fluorescent probe, and the photoinitiators studied were shown previously in Part I of this series [1].

2.2. Sample preparation

The photocurable compositions and the thin-layer samples used for measurements were prepared in the same way as described previously [1]. Thickness of the compositions within the thin-layer samples was 0.080 ± 0.002 mm. The 25ST probe concentration was 0.10% by weight in all the compositions. The concentrations of the cationic photoinitiators were adjusted so that the total amount of UV light absorbed by the thin-layer sample (ΔI_{abs}) within the emission range of UV LED did not exceed 50% of initial light intensity (I_o), while the photopolymerization rate was still high enough to be measurable within a reasonable time scale. This corresponded to $1.9 \cdot 10^{-2} \text{ mol dm}^{-3}$ for weakly absorbing photoinitiators (i.e., Speedcure 938, Irgacure 250 and HIP), and $3.7 \cdot 10^{-3} \text{ mol dm}^{-3}$ for the strong absorbers (i.e., Esacure 1187 and the Sylanto photoinitiators). In the case of free-radical photopolymerization, the photoinitiator concentrations were $1.7 \cdot 10^{-3} \text{ mol dm}^{-3}$ for the phosphine oxide-based photoinitiators (i.e., Irgacure 819 and Speedcure TPO), and $1.9 \cdot 10^{-2} \text{ mol dm}^{-3}$ for the other Irgacures.

2.3. Measurements

The constant-temperature cure monitoring system used for the quantitative measurements was the same as that shown in [1]. Fig. 1 shows drawing of the main component of the FPT system, which was specially designed for this study. A Peltier cell was applied as a heat pump to maintain constant temperature of 25 ± 0.1 °C during measurements. Power to the heat pump was supplied from a Thorlabs ITC4020 temperature controller, while a miniature Pt100 thermistor was applied as the temperature sensor. A UV LED emitting at $\lambda_{max} = 320$ nm (UVTOP315-BL-TO39 from Roithner Lasertechnik) was used as the excitation light source. All the other measurement details were the same as those reported previously [1].

3. Results and discussion

3.1. The equations

Equations that describe kinetics of cationic photopolymerization are different from those describing free-radical photopolymerization. The differences and similarities between free-radical and cationic photopolymerization are summarized in Table 1.

The major difference between cationic and free-radical polymerization that affects the polymerization rate is in the termination reaction (equation (8) in Table 1). While the termination of growing macroradicals occurs by a bimolecular reaction (i.e., usually by combination or disproportionation of the radicals), the termination of growing

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