



A fluorinated compound used as migrated photoinitiator in the presence of air



Yuxuan Zhang^{a, b}, Yong He^{a, b}, Jinliang Yang^{a, b, c}, Xueqin Zhang^{a, b},
Roberta Bongiovanni^{d, **}, Jun Nie^{a, b, *}

^a College of Materials Science and Engineering, State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing, 100029, PR China

^b Beijing Laboratory of Biomedical Materials, Beijing University of Chemical Technology, Beijing, 100029, PR China

^c China Lucky Group Corporation, Baoding, 071054, PR China

^d Department of Applied Sciences and Technology, Politecnico di Torino, Corso Duca Degli Abruzzi-24, 10129, Torino, Italy

ARTICLE INFO

Article history:

Received 14 March 2015

Received in revised form

3 June 2015

Accepted 20 June 2015

Available online 23 June 2015

Keywords:

Fluorinated photoinitiator

Migratory

Oxygen inhibition

Photopolymerization

Photochemistry

ABSTRACT

A fluorinated photoinitiator, namely perfluorooctanoyl acid 2-[4-(2-hydroxy-2-methyl-propionyl)-phenoxy]-ethyl ester (F-2959) was synthesized and characterized. To increase the polymerization rate, fluorine groups were connected to the benzene ring rather than the hydroxyalkyl. Real time FTIR analysis was taken to study the ability of F-2959 to overcome oxygen inhibition. UV–vis absorption spectroscopy, XPS, SEM, and multi-channel thermo detector were used to prove the migration of F-2959 in the formulations. During photopolymerization, the oxygen inhibition could be obviously decreased as the large amount of photoinitiator at the surface could consume oxygen in the air atmosphere. The fluorine compounds gathering on the surface also reduced the surface energy. By using this strategy, the film surface develops a wrinkled pattern with a low surface energy. And the wrinkled pattern may prove very useful in photopolymerization.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Many products were produced via photopolymerization for its excellent characteristics, such as economic, environmental friendly, energy saving, efficient, enabling and fast manufacture [1–3]. Due to its high quantum efficiency, reactivity and economy of raw materials, free radical photopolymerization dominates most of the interests and is widely used in various applications such as coatings, adhesives, dental resins, inks, paints and microelectronics [1–9].

However, there are still many limitations of free radical photopolymerization, such as oxygen inhibition, volume shrinkage and light shielding [10–14]. The existent oxygen can consume the

photoinitiator by reacting with initiating radicals and growing polymer radicals to form less active peroxy radicals are generated or even terminate the polymerization [12]. The effect of oxygen inhibition exists in the whole photopolymerization process and results in the slowing down of the reaction and poor double bond conversion. That means, as soon as the sample exposed to air during the curing period, the conversion of polymerization will decrease immediately, especially at top layer of the sample. Thus the top layer will remain “tacky” [10,13]. For well understanding the impact of oxygen effect in photopolymerization, O’Brien et al. did a series of research and indicated that sample thickness, initiation rate and oxygen concentration would affect photopolymerization kinetics, respectively [9]. The effects of dissolved oxygen on the kinetic constants of propagation and termination were investigated by Ohshima et al. [15] Lots of methods have been proposed to reduce the oxygen inhibition such as using high intensity light or high cure dosage, blowing inert atmosphere and adding additives [14–18]. Higashi et al. [19] studied an alternating copolymer of alkyl sorbates which was cured by photopolymerization with oxygen. Tar et al. [20] reported thioxanthone derivatives can act as efficient photoinitiators for free radical polymerization of both

* Corresponding author. College of Materials Science and Engineering, State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing, 100029, PR China.

** Corresponding author. Department of Applied Sciences and Technology, Politecnico di Torino, Torino, 10129, Italy.

E-mail addresses: roberta.bongiovanni@polito.it (R. Bongiovanni), niejun@mail.buct.edu.cn (J. Nie).

acrylate and styrene monomers in the presence of air. F. Oytun et al. [21] reported glucose and gluconolactone as additives, which is of considerable technical and commercial importance to overwhelm O₂ inhibition. Fluorinated photoinitiators have been cited in patents [22,23] and academic literature [24,25] with the claim that they should tend to collect on the top surface, where oxygen inhibition is most detrimental. Silanes, germanes, stannanes and metallocenes catalysts could be used as co-initiators or additives to overwhelm the oxygen inhibition [26–28].

Oxygen inhibition could also be reduced by increasing the photoinitiator concentration on the surface but high concentration of photoinitiator would also result in high light shielding, more self-quenching and small molecular residual [29,30]. Thus a special kind of photoinitiator needs to be created for selectively enriching the surface layer which would be consumed by oxygen while maintaining a low content in the bulk to initiate monomers. Fluorinated polymers were widely used in a lot of fields due to their low surface energy. The fluorinated species would migrate toward the liquid–air interface to minimize the interfacial energy [31]. It had been reported that the addition of 1–1.5 wt% of fluorinated compounds could reduce the surface energy from 45 to 20–30 mN/m [32,33]. The surface stratification of fluorine was also demonstrated by photocopolymerizing fluorinated monomers and typical difunctional oligomers [34–36]. Among these works fluorinated monomers were used in very low content (maximum 1% wt/), so the bulk properties of the films were unchanged with respect to that obtained by curing the pure hydrogenated monomers. Due to the high surface activity of the fluorinated compounds, they migrated to the film surface in contact with air and enriched the external layer of the films, which made the films become highly hydrophobic. Except the low surface energy compounds, the hydrophobic surfaces could also be produced by the cooperation of binary structures at micro- and nanometer scales [25,37].

In our previous study, a fluorinated photoinitiator (1173F) [24] was reported, in which fluoroalkyl groups were linked with hydroxyalkyl part of 1173 (a commercial photoinitiator) and the low surface energy of fluoroalkyl groups resulted in the gradient distribution of the photoinitiator in formulas. And aggregation of large amount of initiators on the surface layer could overcome oxygen inhibition and maintain a low content in the bulk to initiate monomers. But the initiation rate of 1173F was much lower than 1173 because of the fluorine-containing long carbon chain substitution. As part of our continuous interest in developing higher efficient fluorinated photoinitiators, perfluorooctanoyl acid 2-[4-(2-hydroxy-2-methyl-propionyl)-phenoxy]-ethyl ester (F-2959) is reported here. Because it is well known that the initiation rate of hydroxyalkyl radical is much higher than benzoyl radical [38], fluoroalkyl modification of benzoyl part would lead to less influence to initiation rate than modification to hydroxyalkyl part. So this photoinitiator should exhibit a higher initiation rate and also overcome oxygen inhibition compare to 1173F. In this paper, SEM, UV–vis absorption spectroscopy and multi-channel thermodetector were used to prove that F-2959 has the ability to migrate to the surface which results in enrichment of photoinitiator on the surface. It has been demonstrated that monomer initiated with F-2959 has high conversion of double bond with the presence of air. Moreover, the wrinkled patterns and aggregation of fluorinated photoinitiators can lead to a hydrophobic surface on a hydrophilic polymer.

2. Experimental

2.1. Materials

2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (2959) was received from Changzhou Runtec Chemical Ltd (Jiangsu

China). 2-methyl-2-benzoyl ethanolpentadeca-fluorooctanote (1173-F) was synthesized as our previous work [32]. Pentadeca-fluorooctanoyl chloride (PFOC) was obtained from Alfa Aesar (Massachusetts, USA). Triethylamine, methylene dichloride, ethyl acetate, and acetonitrile were purchased from Sinopharm Group Chemical Reagent Co. (Beijing, China). The monomer used in this study was hexamethylene diacrylate (HDDA) and Poly (ethylene glycol) diacrylate (PEGDA) donated from Sartomer (Warrington, PA, USA) as a gift. All reagents were used as received.

2.2. Synthesis

The synthesis route is outlined in Scheme 1.

A mixture of 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (2.24 g, 0.01 mol), triethylamine (1.01 g, 0.01 mol), and methylene dichloride (80 mL) were added into a 250 mL round-bottom flask equipped with stirrer, dropping funnels and stirred in ice bath. The mixture of PFOC (4.325 g, 0.01 mol) and dichloromethane (40 mL) was added dropwise over 2 h. Then the ice bath was removed and the mixture was stirred for another 3 h. The process of the reaction was monitored by TLC. The reaction mixture was washed by water and dried overnight by anhydrous sodium sulfate. The solvent was evaporated under vacuum and a yellow solid was obtained. The crude product was purified by column chromatography with ethyl acetate and methylene dichloride (1:2 v/v) as eluent to obtain a yellow solid. Yield: 2.82 g (43%).

IR (cm⁻¹): 3485 (O–H stretching), 2919 (C–H stretching), 1773 (C=O, stretching). (Figure S1, Supporting Information).

Q-ToF-MS (*m/z*): calcd for C₂₀H₁₅O₅F₁₅, 620.0680. Found: 621.0751 [M + H]⁺. (Figure S2, Supporting Information).

¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.075–6.960 (4H; Ar–H), 1.636 (6H; C(CH₃)₂), 4.007–4.165 (4H; (CH₂)₂);

¹⁹F NMR (400 MHz, CDCl₃): δ (ppm) –80.785, –118.418, –119.020, –121.609, –122.005, –122.656, –126.129. (Figure S3, Supporting Information).

2.3. Instrumentation

The ACPI-MS experiments were carried out by using a Xevo G2 Q-ToF mass spectrometer (Waters, MA, USA) equipped with an atmospheric pressure chemical ionization interface. The instrument was calibrated with leucine enkephalin in the mass range of 50–1200 amu.

The ¹H and ¹⁹F NMR spectra were carried out on a 400 MHz NMR instrument (Bruker Corporation, Germany) at 298 K with CDCl₃ as solvent and TMS as internal standard.

The UV–vis absorption spectra were recorded on a Hitachi U-3010 UV spectrophotometer (Hitachi High-Technologies Corporation, Tokyo, Japan) at room temperature using acetonitrile as solvent.

The ESR spectra were run on a Jeol JES-FA200 X-band ESR spectrometer (JEOL Ltd., Tokyo, Japan) in acetonitrile at 298 K.

The SEM morphology analysis was carried out on a Hitachi S-4700 scanning electron microscope (Hitachi Company, Japan) at room temperature.

2.4. Photopolymerization kinetics

The real-time Fourier Transform IR (FT-IR) spectrometer (Nicolet 5700) equipped with an MCT/A KBr detector-beam splitter combination was used to monitor the photopolymerization kinetics. The spectrometer was operated in the absorbance mode between 4000 and 7000 cm⁻¹, and the polymerization kinetics were determined by the FT-IR spectrometer working in the rapid mode with an average of 4 scans s⁻¹ collection rate (4 cm⁻¹).

Download English Version:

<https://daneshyari.com/en/article/5180111>

Download Persian Version:

<https://daneshyari.com/article/5180111>

[Daneshyari.com](https://daneshyari.com)