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A Fluorinated Photoinitiator for Surface Oxygen Inhibition Resistance

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Supporting Information

ABSTRACT: A novel photoinitiator called 2-methyl-2benzoylethanolpentadecafluorooctanote (1173-F) was synthesized and characterized. 1173-F is an efficient photoinitiator for free radical photopolymerization in the presence of oxygen and has ability of moving to the surface. The oxygen inhibition of the photopolymerization surface could be decreased because the large amount of photoinitiator at the top to be consumed by oxygen. UV absorption spectroscopy, X-ray photoelectron spectroscopy, gel permeation chromatography, and EDS-line mapping were used to prove the migratory of 1173-F in



monomers. Real time FTIR analysis was taken to investigate the ability of 1173-F to overcome oxygen inhibition.

■ INTRODUCTION

Many products are produced via photopolymerization due to its excellent characteristics as it is economic, environmental friendly, energy saving, efficient, enabling, and rapid.^{1–3} It is widely used in many regions including coatings, adhesives, dental resins, ink, paints, and microelectronics.^{1–7} Free radical photopolymerization dominates most of the interest and industrial applications due to its high quantum efficiency and reactivity.¹ It is reported that the initiation rate is independently dictated by the photoinitiator and the light intensity.⁸ The generation of reactive species is due to a photoinitiator absorbing the incident light and cleaving into initiating radicals.⁹

However, there are still many limitations of free radical photopolymerization, such as oxygen inhibition, volume shrinkage, light shielding. $^{9-12}$ The existent oxygen can terminate the polymerization or consume the photoinitiator by reacting with initiating radicals and growing polymer radicals to form peroxy radicals.¹¹ The peroxy radicals are stable that cannot reinitiate the polymerization. The effect of oxygen inhibition results in an induction period, the slowing down of the reaction, poor double bond conversion. When the sample is open to air, the conversion of polymerization is low, especially at the top of the film. The top layer remains "tacky" due to the oxygen inhibition.^{9,12,13} O'Brien et al. studied the impact of oxygen on photopolymerization kinetics and polymer structure, indicating sample thickness, initiation rate and oxygen concentration result photopolymerization kinetics, respectively.⁸ Several methods have been proposed to reduce the oxygen inhibition. Some traditional strategies such as using high intensity light or high cure dosage, blowing inert atmosphere, adding additives have been developed.¹³⁻¹⁵ Higashi et al.¹⁶reported an alternating copolymer of alkyl sorbates was cured by photopolymerization with oxygen. Balta et al.¹⁷

reported a thioxanthone-anthracene (TX-A) photoinitiator, which is an efficient photoinitiator for free radical polymerization of both acrylate and styrene monomers in the presence of air. El-Roz et al.¹⁸ use silanes, germanes, and stannanes R_3XH as co-initiators and additives to overcome the oxygen inhibition.

Oxygen inhibition could be reduced by increasing the photoinitiator concentration on the surface but high concentration of photoinitiator would lead a result of light shielding and volume shrinkage. We want to find such a photoinitiator which have more content on the surface layer to be consumed by oxygen and low content in the bulk to initiate monomers. Fluorinated polymers were widely used due to the excellent properties such as low surface energy.¹⁹ It was reported that the addition of 1-1.5 wt % of fluorine could reduce the surface energy from 45 to 20-30 mN/m.20,21 Novel polyurethanes were prepared with fluorinated side chains attached to hard blocks. The surface of fluorinated polyurethanes was nonpolar due to migration of fluorinated side chains to the surface.²² Ravenstein et al. reported low surface energy polymeric films from fluorinated blocked isocyanates. The fluorinated species would migrate toward the air interface to minimize the interfacial energy.²³ It was reported that oligoesters end-capped with a perfluoroalkyl group was cured with a liquid polyisocyanate cross-linker by self-stratification to prepare environmentally friendly coating system and low surface energy films. The fluorine level at the surface was many times higher than that in the bulk.^{20,24} Photoinitiator containing fluorine atom was synthesized to prepare surface active coatings

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before^{25,26} but related oxygen inhibition resistance was not reported.

In this paper, we combine the advantage of fluorine molecular and 2-hydroxy-2-methylpropiophenone (1173), making a fluorinated photoinitiator for free radical photopolymerization, which could overcome oxygen inhibition efficiently without any co-initiators or additives. This photoinitiator has ability of migratory that result in aggregation of photoinitiator on the top surface. Monomer with this photoinitiator has high conversion of double bond with the presence of air, as shown in Figure 1.

EXPERIMENTAL DETAILS

Materials. 2-Hydroxy-2-methylpropiophenone (1173) was purchased from Changzhou Runtec Chemical Ltd. Pentadecafluorooctanoyl chloride (PFOC) was purchased from Alfa Aesar. Triethylamine (TEA), methylene dichloride, ethyl acetate, petroleum ether, and acetonitrile were purchased from Sinopharm Group Chemical Reagent Co. (Beijing, China). The monomers used in this paper were hexamethylene diacrylate(HDDA) and methyl methacrylate (MMA) given by Sartomer. All reagents were used as received without further purification.

Synthesis of 2-Methyl-2-benzoylethanolpentadecafluorooctanote (1173-F). First, 1.64 g (0.01 mol) 2-hydroxy-2-methylpropiophenone (1173), 1.012 g (0.01 mol) triethylamine (TEA), and 30 mL methylene dichloride (CH₂Cl₂) were added into a 100 mL roundbottom flask and stirred at room temperature by using magnetic stirring. Mixture of 4.325 g (0.01 mol) of PFOC and 20 mL of CH₂Cl₂ was dropped into the stirred solution in an ice water bath. The reaction was monitored by infrared spectroscopy. When the characteristic peaks of hydroxyl group (OH, 3465.2 cm⁻¹) was disappeared and carbonyl group (C=O, 1773.8 cm⁻¹) was generated, the reaction was stopped. The primary product was purified by silica gel column chromatography with ethyl acetate and petroleum ether as elution (1:10 v/v). ¹H NMR and ¹⁹F NMR characterizations were used to observe the chemical structure of final product. The reaction of synthesis is shown in Scheme 1.

Photopolymerization. The polymerization kinetics was investigated by real time FTIR. For the sample without oxygen penetration experiment, a solution of HDDA and initiator was placed in a sealed mold made from glass slides and spacers with 10 mm in diameter and 1.2 mm in thickness. The solution was irradiated by a medium-pressure mercury lamp with incident light intensity of 10 mW/cm² (EXFO S1000-IB, Photonic Solutions Inc., Canada). The light intensity on the surface of sample was detected by a UV light radiometer (Beijing Normal University, China). The double bond conversion of HDDA was monitored by near FTIR spectroscopy. The absorbance change of peak area from 6100 to 6250 cm⁻¹ was related to the consumption of monomers. For the sample with oxygen, the monomers and initiator with different concentrations was put into a glass container with 10 mm in length, 10 mm in width, 1.2 mm in

height, and the top surface was exposed to the air. The conversion of monomers with presence of oxygen was investigated by real time FTIR with the same conditions above.

The monomer investigated in the SEM EDS-line mapping was HDDA. The sample was placed in a mold with 10 mm in length, 10 mm in width, and 3 mm in height. The light intensity was 40 mW/cm² and the sample was opening to air. The monomer used in GPC analysis was MMA and the monomer used in XPS test was HDDA. Both of the monomers were put into a glass tube with a diameter of 4 mm and height of 10 cm. The monomer was irradiated by a high-pressure mercury lamp with incident light intensity of 40 mW/cm² (FP-108EX–S1-B, Commonwealth Corporation, Taiwan). The UV light was a plane light source to guarantee the equal light intensity on each layer. The glass tube was fixed vertically on a turntable with a rotate speed of 5 r/min, in order to uniform irradiation of different location.

Surface Migratory Property. UV Spectrophotometer. A solution of photoinitiator $(3.25 \times 10^{-6} \text{ mol})$ in acetonitrile (25 mL) was prepared to study the concentration change of 1173-F. The solution was placed into a quartz cell with 10 mm in length, 10 mm in width and 12 mm in height. A black sheet with a $1 \times 1 \text{ mm}^2$ hole was placed in front of the UV light of the UV spectrophotometer. The UV light region was controlled in $1 \times 1 \text{ mm}^2$ by the black sheet. The thickness of layer observed was 1 mm. The absorbance of top layer and the bottom layer was investigated respectively by moving the position of the quartz cell, as shown in Figure 7A. According to the Lambert formula: $A = \varepsilon cL$, where A is the absorbance of the initiator, ε is the initiator molar absorptivity, c is the initiator concentration, and L is optical distance. The value of A could be measured by UV absorption spectroscopy directly.

GPC, XPS, EDS-Line Mapping. The polymer rod initiated by 1173-F was cut into many sheets. Five segments from top to bottom were investigated by GPC and eight segments from top to bottom were observed by XPS. The distribution of fluorine atoms in a polymer transect initiated by 1173-F was constantly observed by the EDS-line mapping with transverse direction and vertical direction, respectively.

Characterization. The chemical structure of 1173-F was investigated by FTIR (Thermo Electro Corporation, Waltham, MA), ¹H NMR, and ¹⁹F NMR (Bruker AV400 unity spectrometer operated at 400 MHz with CDCl₃ as solvent at 23 °C). The photo absorption and photoinitiator dissociation were studied by UV absorption spectroscopy (U-3010, Hitachi High-Technologies Corporation, Tokyo, Japan). The photochemical reactivity was observed by Electron Paramagnetic Resonance (EPR, Bruker ESP300E, Germany) and laser flash photolysis experiments (355 nm, LP920, Edinburgh Instruments Ltd., England). Real time infrared spectroscopy (RTIR, Thermo Electro Corporation, Waltham, MA) was used to analysis kinetics of photopolymerization. The migration of 1173-F was studied by X-ray photoelectron spectroscopy (XPS, Thermo Electron Corporation, Escalab 250, Germany), gel permeation chromatography (GPC, Waters 1515, USA), UV Spectrophotometer (Hitachi High-

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Technologies Corporation, Tokyo, Japan) and mapping energy dispersive spectroscopy (SEM EDS line mapping, Zeiss Supra 55, Germany).

RESULTS AND DISCUSSION

Synthesis and Photochemical Reactivity. 2-Methyl-2benzoylethanolpentadecafluorooctanote (1173-F) was prepared







Figure 3. Absorption spectra of 1173 (dashed line) and 1173-F (solid line) in acetonitrile solution with the same concentration (5 \times 10⁻⁵ mol/L) at 23 °C.

by reacting the OH of 1173 with the COCl of PFOC. The peak of hydroxyl (3645.2 cm⁻¹) disappeared after fluorination; instead a new peak of carbonyl group was shown at 1773.8 cm⁻¹ (Figure 2). The change of peak at 1000 cm⁻¹ to 1300 cm⁻¹ was due to the stretching vibration of fluorine atom. ¹H NMR and ¹⁹F NMR were used to monitor the chemical structure of 1173-F. ¹H NMR (δ , 400 MHz, ppm): 7.945– 7.413 (5H, Ar–H), 1.849 (6H, C(CH₃)₂); ¹⁹F NMR (δ , 400 MHz, ppm): -80.774, -117.757, -121.535, -121.969, -121.969, -122.703, -126.091. (Figure S1, Supporting Information) The UV absorption spectroscopy of 1173 and 1173-F were demonstrated in Figure 3. It could be found that 1173-F had the same UV absorption peak as 1173 at 245 and 280 nm. According to the Lambert formula: $A = \varepsilon cL$ and the L



Figure 4. EPR spectrum of 1173 (A) and 1173-F (B). Photoinitiator was initiated by 355 nm laser in nitrogen saturated acetonitrile solutions at 23 $^\circ$ C.



Figure 5. Polymerization kinetics of HDDA with photoinitiator: (a) 1173 with oxygen, (b) 1173 without oxygen, and (c) 1173-F, with oxygen. All the concentration of photoinitiator is 0.305 mmol/100 g. The intensity of UV light is 10 mW/cm².

is 1 cm, the calculated ε of 1173-F is 1040.41 L/(mol·cm). Initiated by 355 nm laser, the photoinitiator could produce radicals. The radical signal was detected by adding dimethylpyridine *N*-oxide (DMPO) as radical scavenger, as shown in Figure 4. The EPR spectra of radicals produced by 1173 and 1173-F were similar and both had 12 lines, which indicated the cleavage mechanism of 1173-F was the same as 1173. Since the triplet lifetime of 1173-F was shorter than the instrument response, an indirect method of triplet quenching was used to study the triplet lifetime by adding naphthalene.²⁷ The triple lifetime of 1173-F was 13 ns (Figure 2S, Supporting Information). The rate of photoinitiator dissociation (R_d) was calculated according to the following equation:

$$R_d = \frac{-\delta[\mathrm{PI}]}{\delta t} = -\left(\frac{[\mathrm{PI}]}{Ab_0}\right) \frac{\delta[\mathrm{PI}]}{\delta t} \tag{1}$$

where Ab_0 is the absorbance of 1173 and 1173-F at 245 nm before exposure to the UV light. The R_d of 1173-F was 1.46 × 10^{-7} molL⁻¹s⁻¹ and R_d of 1173 was 2.11 × 10^{-7} molL⁻¹s⁻¹.

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Figure 6. (A) XPS spectrum of HDDA with photoinitiator 1173-F (5 wt %). (B) Fluorine content of different layers. No. 1 is the top layer and no. 8 is the bottom layer.

Table 1. GPC Data for Different Layers Based on Polymerization of MMA

layer	M _n (1173- F)	M _w (1173- F)	D(1173- F)	<i>M</i> _n (1173)	<i>M</i> _w (1173)	D(1173)
1	7544	26 012	3.4	14 836	40 076	2.7
2	24 457	39 392	1.6	13 348	42 580	3.2
3	79 696	113 643	1.4	13 203	40 849	3.1
4	100 839	249 292	2.5	12 650	38 541	3.0
5	107 870	338 510	3.1	13 457	39 255	2.9

(Figure 3S, Supporting Information) The quantum yield was related to the dissociation rate of photoinitiator according to the equation below:²⁸

$$R_d = I_0 \varphi \varepsilon[I] l = \varphi I_a \tag{2}$$

where I_0 is the intensity of incident light, φ is quantum yield for production of radicals, ε is molar absorption of photoinitiator, [I] is the initiator concentration, *l* is the path length and I_a is absorbed intensity. According to eq2, the quantum yield of 1173-F was similar to 1173 due to the uniform magnitude order of dissociation rate in the same conditions.

Photopolymerization Kinetic. As shown in Figure 5, the monomers were initiated by 1173 and 1173-F, respectively. Because of the oxygen inhibition of free radical photopolymerization, conversions of HDDA with 1173 were different when the system was with or without oxygen. It was clear that the oxygen inhibited the polymerization at the first 50 s and finally got a conversion of 45% (Figure 5a), compared to the polymerization without oxygen that the conversion got to 75% in 1 min and to 90% finally (Figure 5b). However, it was found that the conversion of HDDA with 1173-F in air (Figure 5c) was higher than HDDA with 1173 in the absence of oxygen. The conversion of HDDA with 1173-F reached to more than 90% though in the condition of opening to air and the polymerization started at the very beginning. The results indicated that the photoinitiator 1173-F had good ability to overcome the oxygen inhibition. It was initially inferred to the fluorine group that contributed to the oxygen inhibition resistance. Because of the low surface tension and low surface energy of fluorine atoms, the photoinitiator containing fluorine tended to move to the surface and gathered on the top. This movement caused high photoinitiator concentration on the top to consume the oxygen and prevented the further penetration of oxygen. The polymerization rate of monomer with 1173-F



Figure 7. (A) Scheme of photoinitiator concentration in different layers by UV spectrophotometer. (B) Concentration of 1173 and 1173-F in acetonitrile solution. All the initial concentration is 1.3×10^{-4} mol/L.

was slower than that of 1173 due to the low concentration of initiator in the bulk.

Surface Migratory of 1173-F. The migratory aptitude was further supported by XPS tests with the monomer HDDA and initiator 1173-F (5 wt %). As shown the integrated spectra Figure 6A, the peak at 689.08 eV represented of fluorine. Because the only source of F in this system is 1173-F, the content of photoinitiator all through the sample could be tracked by F signal. It could be found that the fluorine atom

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Figure 8. EDS-line mapping of HDDA with photoinitiator 1173-F, 5% wt: (A) SEM graph of polymer with 3 mm in thickness, (B) vertical direction from top to bottom, (C) transverse direction of the top layer, and (D) transverse direction of the bottom layer.



Figure 9. Polymerization kinetics of HDDA with different photoinitiator: (1) 1173, 0.305 mmol/100 g, (2) 1173, 0.1525 mmol/100 g and 1173-F, 0.1525 mmol/100 g, and (3) 1173-F, 0.305 mmol/100 g. The intensity of UV light is 10 mW/cm². All samples were investigated without oxygen.

content in the first layer was 1.53%, while the fluorine atom content in the eighth layer was only 0.05%, as shown in Figure 6B. No signal for fluorine element could be detected when running XPS to the very bottom layer of the sample. The distribution of F element through the sample indicated that the initiator containing fluorine had a good migratory ability leading the aggregation of the initiator to the surface. The



Figure 10. Polymerization kinetics of HDDA with different photoinitiator: (1) 1173, 0.305 mmol/100 g, (2) 1173, 0.1525 mmol/100 g and 1173-F, 0.1525 mmol/100 g, and (3) 1173-F, 0.305 mmol/100 g. The intensity of UV light is 40 mW/cm². All samples were investigated without oxygen.

gradient distribution was attributed to the low surface tension and the resulted movement of the fluorine atoms.

Another proof showing the migratory of 1173-F was the resultant molecular weight of polymer. Because of gradient distribution of 1173-F, the surface layer had more initiator than the bottom layer. As known to us, the molecular weight was closely related to the content of initiator. The higher of photoinitiator concentration, the lower the molecular weight is.

Table 2. Molar Ratio of 1173 and 1173-F in HDDA^a

1173/1173-F	1173/10 ⁻⁴ mol	1173-F/10 ⁻⁴ mol	total/10 ⁻⁴ mol	total/g
1173	3.05	0	3.05	0.05
4/1	2.44	0.61	3.05	0.074
0.11	1.525	1.525	3.05	0.11
1/4	0.61	2.44	3.05	0.147
a				

^{*a*}Above HDDA = 100 g. The concentration of PI is 3.05×10^{-4} mol in 100 g monomer.



Figure 11. Conversion of HDDA with varying molor ratio of 1173 and 1173-F. The intensity of UV light is 10 mW/cm^2 . All the samples are open to air.

The data from GPC was accordance well with the result from XPS, shown in Table 1. The molecular weights of the top layers were much lower than the bottom layers and increasing gradually, contrasting with the distribution of F in the system. However, the molecular weight of sample with 1173 has a uniform value from top to bottom.

In order to investigate the migration behaviors of the 1173-F, the distribution of concentration of 1173-F in the acetonitrile solution were characterized by the UV spectrophotometer. According to Figure 7, the concentration of top solution increased while the concentration of bottom solution decreased. Compared to 1173-F, the concentration of 1173 had no change all the time. The change of concentration occurred simultaneously both in top and bottom. Because of Brownian Motion, not all the 1173-F molecules could aggregate on the surface. But it was found that the concentration of the bottom was stable and the concentration of the top still increased. It might be explained that most fluorine atoms in different layers had the trend to move to the top surface with different rate. The fluorine atoms in the bottom had advantage to compete in the migratory due to attraction of low surface energy. Although the concentration of the top changed at the very beginning, it could increased because of more and more fluorine atoms moving to the top until the saturation state.

The surface migratory was investigated constantly by the EDS-line mapping, as shown in Figure 8. The height of *Y* axis indicated the intensity of fluorine signal. It was found that the amount of fluorine decreased along with the EDS-line from the top to bottom in Figure 8B. Parts C and D of Figure 8 show the amount of fluorine atom along with transverse direction on the top and bottom, respectively. It was found that the content of fluorine atom tended to be the same in the same layer. The

fluorine on the top was more than that in the bottom. The trend of migration accorded with the results of XPS. Some fluorine atoms detected in the bottom were due to the molecular diffusion and Brownian motion.

Oxygen Inhibition. To further investigate the properties of photopolymerization with 1173-F, polymerization kinetics were used to investigate both in the presence of oxygen and absence of oxygen. As shown in Figure 9, all the monomers were irradiated without oxygen and the intensity of light was 10 mW/cm². All the samples with different photoinitiator had same molar concentration, 0.305 mmol/100 g of HDDA. It was found that the induction period of 1173-F was longer probably due to the lower concentration of initiator in the bulk and the inhomogenous photopolymerization, as show in Figure 9c. After adding 1173 to 1173-F (n(1173)/n(1173-F) = 1/1), the induction period of mixed photoinitiator decreased and the conversion was higher, as shown in Figure 9b. The molar concentration of photoinitiator in Figure 10 was the same as Figure 9 and the intensity of light was 40 mW/cm². But the conversion of double bond became higher due to increase of light intensity. In Figure 10, the induction period of 1173-F (Figure 10c) was decreased but was still longer than 1173 (Figure 10a). It was speculated that the inhomogenous distribution of 1173-F prevented fast polymerization of low layer. Subsequently the mixture of 1173 and 1173-F was used to initiate monomer in the presence of air. All the samples had an equal molar concentration with different ratio, as shown in Table 2. According to Figure 11, it was found that the conversion increased obviously when the ratio of 1173/1173-F was 1/4 and its induction period was less than other ratios. The results indicated that the existence of 1173-F could decrease the oxygen inhibition effect. Moreover there was a requirement of content of 1173-F to overcome the oxygen inhibition. Low concentration of 1173-F could not satisfy the consumption of oxygen on the surface.

CONCLUSION

A fluorinated photoinitiator promoted a method to overcome oxygen inhibition due to its excellent migratory. The results indicated that this fluorinated photoinitiator had better qualities in surface photopolymerization than traditional photoinitiator and could decrease oxygen inhibition effectively without any other additives or co-initiators. It dramatically increased the final conversion of HDDA to 90% with oxygen in a condition of a low light intensity and thin sample. The surface migratory was confirmed by XPS, EDS-line mapping, GPC and UV spectrophotometer. This method of relating the migratory was especially attractive to be utilized in oxygen inhibition resistance since it was simple and valid.

ASSOCIATED CONTENT

S Supporting Information

¹H NMR and ¹⁹F NMR spectra of final product, triplet time of 1173-F by flash laser photolysis, and dissociation rate of 1173 and 1173-F by UV-abs spectroscopy. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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