



# Ultraviolet light absorber with low surface energy: synthesis and characterization



Yuanpeng Liang<sup>a</sup>, Bin Xiang<sup>a,\*</sup>, Chao Liu<sup>a</sup>, Xiangdong Zhou<sup>b</sup>, Dan Wang<sup>a</sup>, Shan Song<sup>a</sup>, Genghua Bai<sup>a</sup>, Qi An<sup>a</sup>, Quehong Huang<sup>a</sup>, Shujun Chen<sup>a</sup>, Xuefeng Wei<sup>c</sup>

<sup>a</sup> College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, PR China

<sup>b</sup> Department of Medicinal Chemistry, College of Pharmacy, Third Military Medical University, Chongqing 400038, PR China

<sup>c</sup> Chongqing Sanxia Paints Company Limited, Chongqing 402260, PR China

## ARTICLE INFO

### Article history:

Received 10 April 2014

Received in revised form 26 June 2014

Accepted 2 July 2014

Available online 7 July 2014

### Keywords:

Low surface energy

Ultraviolet light absorber

DFT

TD DFT

XPS

Contact angle

## ABSTRACT

Novel fluorine-containing ultraviolet absorbers (FBPs) with low surface energy were successfully synthesized based on 2,4-dihydroxy benzophenone (BP-1), and their structures were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, FTIR, and HRMS. UV absorption of FBPs was studied in 10<sup>-4</sup> M dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), which demonstrated the superior UV absorption capability of FBPs (ca.  $\epsilon=1.7\times 10^4$  to  $2.2\times 10^4$  at  $\lambda_{\max}$ ) over the matrix ( $\epsilon=1.7\times 10^4$  at  $\lambda_{\max}$ ). Quantum chemistry calculation was performed to investigate the stable structure and UV electronic absorption bands of FBPs. The surface chemistry information of high-chlorinated polyethylene (HCPE) coating films embedded with ultraviolet absorbers (UVAs) was given by X-ray photoelectron spectroscopy (XPS) and contact angle measurement. The results show that the surface enrichment capability of FBPs is remarkably better than traditional UVAs (including BP-1, BP-3, BP-12) because of the low surface energy properties of FBPs.

© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

It is widely known that UV light (wavelengths between 280 nm and 400 nm) is a major contributor to photo-degradation of polymers, skin aging, and eye diseases.<sup>1</sup> In order to protect polymer materials against the damage of UV light and extend their service life, ultraviolet absorber (UVA) is an extremely effective and convenient additive in practice.<sup>2</sup> Currently, benzophenones, benzotriazoles (Fig. 1), and other *o*-hydroxy aromatic compounds are

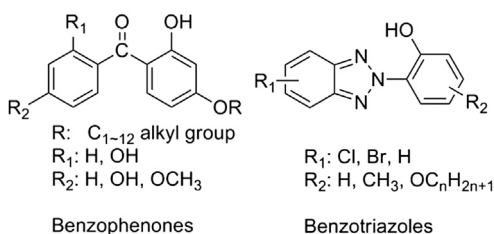


Fig. 1. Molecular structures of benzophenones, benzotriazoles type UVAs.

most representative in the ultraviolet absorber family.<sup>1a,2g,3</sup> Intra-molecular hydrogen bond (IMHB) chelate ring can form in these ultraviolet absorbers, which is the structural basis for energy dissipation. During the reversible keto–enol tautomerism cycle, fast excited state intramolecular proton transfer (ESIPT)<sup>1e,2a,4</sup> (Fig. 2) effectively converts excitation energy into harmless heat, fluorescence, or phosphorescence without chemical damage.<sup>5</sup>

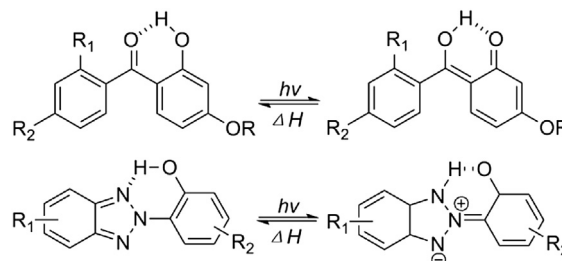


Fig. 2. ESIPT of *o*-hydroxy aromatic UVAs.

Various UVAs have been prepared and studied in many fields to satisfy practical needs. The ideal UVAs should be highly effective in the absorption band of UV light (280–400 nm) as well as transparent for visible light.<sup>2d,6</sup> UVAs with square wave type absorption

\* Corresponding author. Tel./fax: +86 23 65102531; e-mail address: xiangbin@cqu.edu.cn (B. Xiang).

peak were desired for this purpose, however, there are not any applications reported yet. Detail experiments have demonstrated that UVAs in polymer products present a gradient rather than even distribution, which makes the concentration of UVAs in the external surface significantly lower than in the bulk.<sup>7</sup> This is one reason that polymers added with UVAs still degraded rapidly once exposed to the environment. A solution for this problem is that the enrichment of UVA nearby the surface of polymer would effectively protect the inner layers in the bulk from the ultraviolet damage, which extends the service life of polymers.

Herein, we report the successful synthesis of a series of fluorine-containing benzophenone UV absorbers (FBPs) based on 2,4-dihydroxy benzophenone (BP-1). The purpose of this paper is to obtain UVAs with surface enrichment property and testify their related performances. We believe this work will offer a direction for future design and modification of UVA.

## 2. Result and discussion

### 2.1. Syntheses

UVAs containing benzophenone structure have been frequently employed as polymer additives due to their simple structure and high efficiency in ultraviolet protection.<sup>8</sup> The optimization of alkyl group in UVA molecules can improve their compatibility and photostability within the polymer matrix. For this purpose, 2,4-dihydroxy benzophenone (BP-1), 2-hydroxy-4-methoxybenzophenone (BP-3), and 2-hydroxy-4-*n*-octoxybenzophenone (BP-12) (Fig. 3) are most widely applied. Besides, BP-1 is mainly used as chemical intermediate to synthesize other UVAs due to its low molecular weight and easy extraction and volatilization from the polymer matrix. As a result, BP-1 was used as the parent molecule in our work.

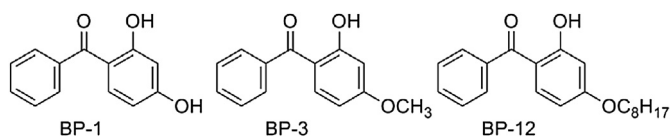
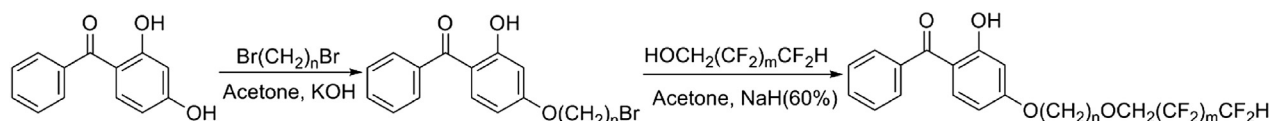


Fig. 3. Molecular structures of BP-1, BP-3, and BP-12.

It is known that perfluorocarbon has low surface energy, but its low polarizability also brings poor miscibility and inferior chemical reactivity in hydrocarbon solvent,<sup>9</sup> which makes it difficult to graft fluorocarbon into the BP-1 molecule directly. To partially solve this problem, linear fluorocarbon alcohol was applied as the fluorine segment.

It is necessary to couple a linker between linear fluorocarbon alcohol and benzophenone for the introduction of fluorine-containing group. Because the chemical activity of primary brominated alkyls are superior over chlorinated alkyls in the coupling reaction,<sup>10</sup> the primary dibromoalkanes ( $\text{Br}(\text{CH}_2)_n\text{Br}$ ) were employed as intermediate linkers in this paper. A series of intermediates (bromo-benzophenones, BrBPs) were prepared through the O-alkylation reaction under a mild condition followed by reaction with linear fluorinated alcohol ( $\text{HOCH}_2(\text{CF}_2)_m\text{CF}_2\text{H}$ ). Finally the desired products (fluorine-containing benzophenones, FBPs) were successfully synthesized. The reaction process is shown in Scheme 1.



Scheme 1. Synthetic route ( $n=2, 3, 4, 5, 6$ ;  $m=3, 5$ ).

### 2.2. Structural characterization

**2.2.1. NMR spectroscopy.** The  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR spectra of typical 12FBP ( $n=3$ ) are shown in Fig. 4. The NMR spectra of BrBPs and other FBPs are given in Fig. SI-1–10 (Supplementary data).

Compared to BrBPs, the most significant change in the  $^1\text{H}$  NMR spectra of FBPs is a nonet at ca. 6.2–5.9 ppm and a triplet at ca. 4.0 ppm. The characteristic peaks of the end hydrogen atom of fluorocarbon chain ( $-\text{CF}_2\text{H}$ ) might be split into a nonet since  $^1\text{H}$  is coupled with  $^{19}\text{F}$  on the same geminal carbon and other remote carbon atoms. Meanwhile, its characteristic peaks ought to appear at lower field due to the electron-withdrawing effect of fluorine atom. Accordingly, the nonet at ca. 6.2–5.9 ppm refers to the  $-\text{CF}_2\text{H}$  and the triplet at ca. 4.0 ppm is assigned to the methylene of fluorocarbon chain ( $-\text{CH}_2-(\text{CF}_2)_m-$ ). From the  $^{13}\text{C}$  NMR spectra of FBPs, it can be found that the carbon signals of aliphatic methylene of BrBPs are also present. Different from the BrBPs, the  $^{13}\text{C}$  NMR spectra of FBPs generate a group of very weak signals at ca. 111.4–107.2 ppm, two triplet signals at ca. 105.3–104.7 ppm, and ca. 68.3–67.4 ppm. These weak signals at ca. 111.4–107.2 ppm should belong to the carbon signals of fluorocarbon chain due to carbon coupled with fluorine. It is difficult to accurately assign a specific peak for difluoromethylene ( $-\text{CF}_2-$ ), but the above analysis show that the fluorine-containing segment exists in FBPs. In addition, according to the ' $n+1$ ' splitting rules and the influence of electronegativity, it may be deduced that the triplet at ca. 105.3–104.7 ppm and the triplet at ca. 68.6–67.4 ppm are attributed to the end carbon atom and the methylene of fluorocarbon chain, respectively.

In summary, the NMR spectra of FBPs show that the fluorine-containing segment has been grafted in BP-1 molecule by intermediate linkers and the target products (fluorine-containing benzophenones, FBPs) are successfully obtained.

**2.2.2. FTIR spectroscopy.** Fig. 5 shows the FTIR spectra of BP-1 and typical BrBP ( $n=3$ ), 12FBP ( $n=3$ ). In the spectrum of BP-1, the broad smooth strong band at  $3185\text{ cm}^{-1}$  and the peak at  $1280\text{ cm}^{-1}$  are related to the stretching vibration of phenolic hydroxyl group ( $\text{Ar}-\text{OH}$ ) while the peak at  $1321\text{ cm}^{-1}$  refers to the deformation vibration of  $\text{Ar}-\text{OH}$ . The weak peak at  $3064\text{ cm}^{-1}$  is the stretching vibration of the methyne ( $-\text{CH}-$ ) of benzene ring and the signals at  $1450$ – $1600\text{ cm}^{-1}$  are the skeletal vibration of benzene ring. Additionally, the peaks at  $781$  and  $700\text{ cm}^{-1}$  further demonstrate the asymmetric tri-substitute and mono-substitute of benzene, respectively. However, on account of conjugation effect from benzene ring, the characteristic signal of carbonyl ( $\text{C}=\text{O}$ ) is shifted to  $1629\text{ cm}^{-1}$  from ordinary values (ca.  $1730$ – $1700\text{ cm}^{-1}$ ).

Compared with BP-1, it can be found that the broad smooth strong band of BrBP at  $3185\text{ cm}^{-1}$  moved to a higher wavenumber  $3443\text{ cm}^{-1}$ , which might be resulted from the tautomeric interconversion of keto–enol. This means that the structures of BrBPs mainly display enol form while BP-1 presents keto form. The disappearance of signals at  $1321$ ,  $1280\text{ cm}^{-1}$  suggests the *para*-hydroxyl of BP-1 is substituted by other groups. Another difference between BrBPs and BP-1 is the appearance of stretching vibration signals of aliphatic methylene ( $-\text{CH}_2-$ ) at ca.  $2973$ ,  $2935$ ,  $2876\text{ cm}^{-1}$  and the aryl ether ( $\text{Ar}-\text{O}-\text{C}$ ) at ca.  $1256$ ,  $1224\text{ cm}^{-1}$ , indicating that the *para*-hydroxyl of BP-1 is replaced by alkoxy. The

Download English Version:

<https://daneshyari.com/en/article/5216882>

Download Persian Version:

<https://daneshyari.com/article/5216882>

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