



Synthesis and exploration of triazine ultraviolet absorbers with surface enrichment property



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ABSTRACT

To improve the distribution of ultraviolet absorbers (UVAs) on coating surface, novel fluorinated triazine UVAs with surface enrichment property were developed. The structure of these compounds was characterized by FT-IR, ¹H NMR, ¹³C NMR and HRMS. UV-Vis spectroscopy results indicate that these new UVAs possess an outstanding UV absorption ability, as verified by quantum calculation. Contact angle measurements show that PVC coating mixed with these novel UVAs exhibit excellent hydrophobicity and oleophobicity. Attenuated total reflection Fourier-transform infrared spectroscopy and X-ray photoelectron spectroscopy suggest that the surface enrichment ability of these modified UVAs are improved almost four times.

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1. Introduction

With the depletion of stratospheric ozone layers, an increasing amount of ultraviolet radiation reaches the surface of the earth.¹ However, excessive solar ultraviolet radiation presents serious threats to human health.² The high energy of UV radiation leads to the photo-degradation of organic materials, sunburn and acceleration of aging, among others.³ The damage is cumulative, irreversible, and presently a major concern.⁴ Various UVAs have recently been reported to protect humans and materials from UV radiation emitted by the sun.⁵ Gigantic intramolecular hydrogen bridges have been found in these UVAs. The intramolecular hydrogen bonds can absorb and convert ultraviolet radiation into harmless heat, fluorescence, or phosphorescence without chemical damage.⁶ Consequently, UVAs have been widely used to protect materials from UV radiation emitted by the sun.

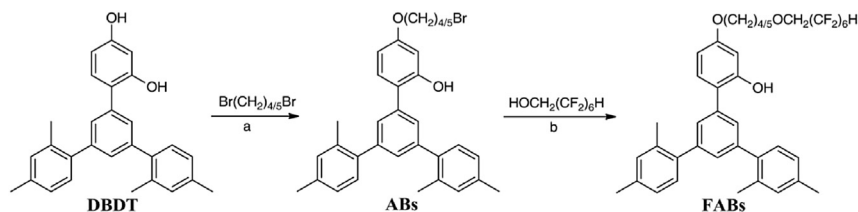
However, most polymer materials containing UVAs are still susceptible to photo-aging when exposed to sunlight for an extended time.⁷ This effect could be attributed to the low utilization efficiency of UVAs, owing to their low distribution on surfaces of materials.^{3b,8} Thus, a study on the type of UVAs with

surface enrichment property can be useful. Under normal conditions, when blending materials contact with air, low surface energy components usually migrate to the material-air interface and aggregate on the surface to reach a steady state.⁹ Thus, a hypothesis was proposed that UVAs with low surface energy can spontaneously be enriched on the surface of materials. The introduction of fluorine elements to materials has currently been applied to decrease the surface energy of materials.¹⁰ Fluorinated materials are characterized by weak intermolecular interactions and low surface energies owing to the high ionization energy and low polarisability of the fluorine atom.¹¹ In addition, the fluorinated components can presumably be enriched on the surface of blending materials. Zheng et al. synthesized fluorinated hyperbranched polyurethane and found that these hyperbranched polyurethanes can be enriched on the surface of materials.^{3b} In addition, Zhu et al. successfully synthesized fluorinated polyesters. The results of X-ray photoelectron spectroscopy (XPS) indicated that the F/C molar ratio on the surface was considerably higher than that in the bulk of the materials because of the surface enrichment of fluoroalkyl groups.^{9a} Prompted by these studies, we proposed the preparation of a series of fluorinated UVAs to solve the problem of traditional UVAs with low distribution on the surfaces of materials.

In the present study, we designed and synthesized a series of novel fluorinated triazine ultraviolet absorbers (FABs) from 4-(4,6-bis(2,4-dimethylphenyl)-1,3,5-triazin-2-yl)benzene-1,3-diol

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Scheme 1. Reagents and conditions: (a) K_2CO_3 , 18-crown-6, acetone, 50°C , 2 h; (b) K_2CO_3 , 18-crown-6, acetone, 50°C , 4 h.

(DBDT). Experiments indicated an improvement in the ultraviolet absorption of FABS. In addition, the surface enrichment property of FABS is improved almost four times, thereby increasing their utilization efficiency in materials. Thus, the type of FABS is economical and environment-friendly, which may set a development direction for UV absorbers.

2. Result and discussion

2.1. Synthesis and characterization

The FABS were synthesized via a series of simple chemical reactions (Scheme 1). The compound DBDT is difficult to be modified because of its high steric hindrance. Thus, DBDT was treated with dibromoalkane in the presence of 18-crown-6 to give intermediates (ABs) in 77% yield after chromatography on silica gel. In addition, the reaction of perfluorocarbon chain with ABs was impeded by low reactivity. Therefore, linear fluorocarbon alcohols were selected as the fluorine segment. Finally, the target products (FABS) were obtained by the ABs reaction with fluoroalcohol under mild conditions in 69% yield after purification by chromatography.

The structure of these synthesized compounds was identified by ^1H & ^{13}C NMR spectra. The ^1H NMR spectra of these compounds are illustrated in Fig. 1 (a) and the NMR spectra of DBDT are shown in Fig. 1S (supplementary information). It can be seen from these spectra that the structure of phenol hydroxy is confirmed by the distinct double peaks at 8.49 ppm. The aromatic proton signals are dispersed between 6.23 and 8.25 ppm. The characteristic peaks at 2.74 and 2.40 ppm belong to the methyl. Compared to ABs ($n = 4$), ABs ($n = 5$) has an additional peak at 1.64 ppm due to its extra methylene. Moreover, the chemical shift of methylene of ABs appears at upfield relative to that of FABS. This may be attributed to the fact that the $-\text{Br}$ of ABs was substituted by $-\text{OCH}_2-$, which

weakened the electron supplying capacity. Finally, the nonet peaks of $-\text{CF}_2\text{H}$ appears at 6.20–6.88 ppm in the spectra of FABS. The ^{13}C NMR spectra are given in Fig. 1 (b). The signals of methyl are found at 21.37 and 29.37 ppm. The peaks at 180–90 ppm are assigned to carbon atoms of the aromatic nucleus. There is an additional peak at 72.45 ppm due to the methylene of FABS. In summary, these results clearly indicate that the desired products (FABS) were successfully synthesized.

The FT-IR spectra of these compounds are shown in Fig. 2 and the FT-IR spectra of DBDT are shown in Fig. 2S (supplementary information). The peaks at 3632 cm^{-1} and 1201 cm^{-1} are related to the stretching vibration of phenolic hydroxyl (Ar-OH). The methyl groups are confirmed by their stretching vibrations and C-H scissoring vibration at 2963 and 1381 cm^{-1} , respectively. The signals of methylene appear at 2922 and 2885 cm^{-1} . The peaks at 1259 cm^{-1} and 1228 cm^{-1} are assigned to aryl ether (Ar-O-C), indicating the para-hydroxyl of DBDT was substituted by alkoxy. The peak at 1042 cm^{-1} is assigned to C-F. In addition, there is a strong absorption band at 1141 cm^{-1} , which is attributed to the characteristic signal of aliphatic ether (C-O-C). Above all, the results of FT-IR spectra further prove that the FABS were successfully synthesized.

2.2. UV absorption

The UV-Vis spectra of DBDT and FABS are illustrated in Fig. 3. These compounds show high absorption in the region of 315–400 nm (ultraviolet A) and 275–315 nm (ultraviolet B). By contrast, these compounds exhibit low absorption in the visible region. These results suggest that these compounds exhibit good ultraviolet absorption and visible light transmission. In addition, the ultraviolet absorption of these modified FABS is stronger than DBDT, which is attributed to the increase of electron density of the conjugate system.¹² The maximum absorption peaks (λ^a_{max}) and molar absorptance (ϵ_b) of the FABS are listed in Table 1. An

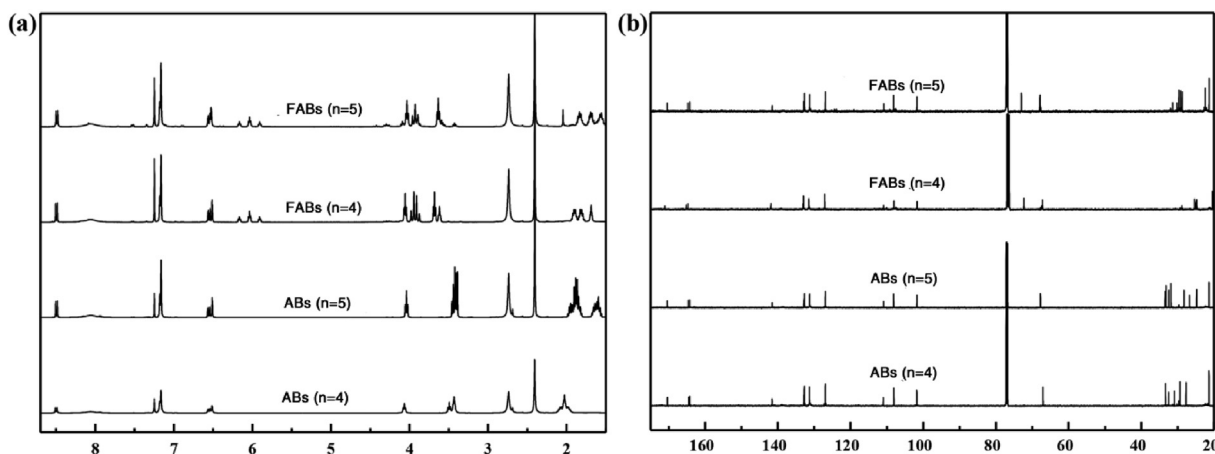


Fig. 1. ^1H NMR (a) & ^{13}C NMR (b) spectra of ABs and FABS.

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