Synthesis and application of new *S*-benzoheterocycle thiobenzoates photoinitiators

Ziren Zhao[1] · Chen Wang[1] · Feng Liu[1] · Bianxiang Zhang[1]

Abstract

A series of free radical photoinitiators with thioester bonds were synthesized by the nucleophilic substitution reaction of acyl chloride and thiol or thiophenol. These compounds could be efficiently obtained under mild reaction conditions and were fully characterized by ^{1}H NMR, ^{13}C NMR and high-resolution mass spectrometry. This kind of compounds exhibited a strong ultraviolet–visible light absorption spectrum with an extended absorption around 330 nm in DMSO. Moreover, these compounds were utilized as free radical photoinitiators in ultraviolet curing and the resulting films exhibited comparable mechanical properties in comparison with commercially available photoinitiators, such as 1-hydroxycyclohexyl phenyl ketone (Irgacure 184) and benzophenone. We also proposed a probable photoinitiated polymerization mechanism for *S*-benzoheterocycle thiobenzoates as photoinitiators.

Keywords UV-curing film · Free radical photoinitiator · Thioester

Introduction

The ultraviolet (UV)-curing technology is a safe, green and friendly environmental technology [1–3]. Generally, the photopolymerization system is composed of a resin (oligomer), an active diluent (monomer), triethanolamine (auxiliary agent) and photoinitiator [4, 5]. It is worth noting that the photoinitiator plays an important role in the system as it determines the photopolymerization speed and affects the polymer properties, such as odor, yellowing and migration. Photoinitiators can be divided

✉ Bianxiang Zhang
zbxthh@sxu.edu.cn

Feng Liu
liufeng112@sxu.edu.cn

1   School of Chemistry and Chemical Engineering, Shanxi University, Taiyuan 030006, China

into cationic photoinitiators and free radical photoinitiators according to the photochemical mechanisms [6, 7]. Nowadays, BP and Irgacure 184 are the most commonly used free radical photoinitiators owing to their low cost and good solubility. However, owing to its small molecular weight, BP can easily migrate out of the polymer network and cause yellowing. These problems limit their applications in food and pharmaceutical packaging. On the other hand, Irgacure 184 whose maximum absorption wavelength is around 250 nm does not match the emission wavelength of high-pressure mercury lamp. To make them more widely used, there are two ways to improve their optical activity: One is to add the sensitizers, and the other is to extend conjugated degree [8, 9]. Therefore, developing long wavelength absorbed photoinitiators with low mobility and low benzene release is a growing area of interest for academic research and industrial applications [10, 11].

Historically, sulfur-containing materials have received significant interest both in academy and industry, optical lens materials [12], mucoadhesive materials [13], drug delivery systems [14], self-assembled monolayers (SAMs) [15–17] and thiol-containing biomolecules [18]. Thioesters are one of the most represented *S*-contained functional materials [19, 20]. Tomioka et al. [21] first reported the use of thioester-based materials as efficient photoinitiators. However, the short light absorption wavelength of *S*-phenyl thiobenzoate limited their practical applications. Herein, we designed and synthesized a series of *S*-benzoheterocycle thiobenzoates, which can be efficiently obtained by the nucleophilic substitution reaction of acyl chloride and thiol or thiophenol. The *S*-benzoheterocycle thiobenzoates exhibit a strong ultraviolet–visible light absorption with an extended absorption around 330 nm in DMSO. Moreover, these compounds can be applied as efficient photoinitiators with high photoactivity in a thiol/vinyl carbonate formulation.

Experimental section

Materials

Unless otherwise stated, all chemicals were obtained from commercial suppliers and used without further purification. 1,6-Hexanediol diacrylate (HDDA) and polyurethane modified acrylate resin (UV 2100) were purchased from Sanmu chemical co., Ltd. 1-Hydroxycyclohexyl phenyl ketone (Irgacure 184) and BP were obtained from Beijing Yingli Technology co., Ltd (Scheme 1).
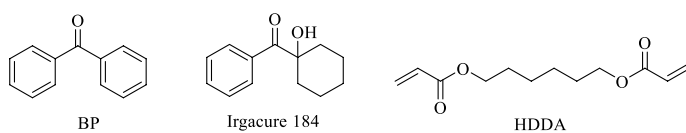
Scheme 1 Chemical structures and abbreviations of the materials used in the polymerization

Instrumentation

^{1}H NMR and ^{13}C NMR spectra were recorded in CDCl$_3$ with a Bruker AVANCE III 600 MHz spectrometer. High-resolution mass spectra were obtained on a Thermo Scientific Q Exactive mass spectrometer. UV–Vis absorption spectra were recorded in DMSO (1×10^{-5} M) on a Hitachi UH-5300 UV spectrophotometer (Hitachi High-Technologies, Tokyo, Japan). The cured films were performed on a UV-Curing machine (ZB-T150-UV1000), and the hardness of films was recorded by a portable pencil scratch hardness tester (QHQ-A).

Synthesis

The substitution reaction of acyl chloride and mercapto reagent was carried out under mild conditions, and the general procedure is as follows: Acyl chloride (2.0 mmol), mercapto reagent (1.0 mmol) and base (2.0 mmol) were dissolved in THF. The reaction mixture was stirred at 60 °C for 12 h. After cooling to room temperature, the precipitates were filtered off. The crude products were purified by silica gel chromatography using dichloromethane and petroleum ether as the eluent to afford compound **3**.

S-(1-benzoyl-6-methoxy-1H-benzo[d]imidazol-2-yl) benzothioate 3e Pale yellow crystals (75%), mp: 152–156 °C. ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.97–7.90 (m, ArH, 4H), 7.66 (dd, J = 16.3, 7.5 Hz, ArH, 2H), 7.55–7.48 (m, ArH, 4H), 7.33 (dd, J = 10.6, 5.7 Hz, ArH, 1H), 6.92 (d, J = 2.4 Hz, ArH, 1H), 6.88 (dd, J = 8.9, 2.4 Hz, ArH, 1H), 3.85–3.79 (m, -OCH$_3$,3H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 170.15, 169.00, 168.92, 157.91, 134.62, 134.38, 132.48, 132.31, 132.26, 130.72, 130.63, 128.93, 128.83, 125.41, 112.85, 112.10, 97.07, 77.25, 77.04, 76.83, 55.98. HRMS (ESI) m/z: calcd for C$_{22}$H$_{16}$N$_2$O$_3$S: 389.0915, found: 389.0950.

S-(6-methoxy-1-(4-methylbenzoyl)-1H-benzo[d]imidazol-2-yl) 4-methylbenzothioate 3f Pale yellow crystals (76%), mp: 239–241 °C. ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.85 (dd, J = 10.6, 8.3 Hz, ArH, 4H), 7.32 (t, J = 7.4 Hz, ArH, 4H), 7.27–7.24 (d, J = 8.7 Hz, ArH, 1H), 6.86 (dt, J = 8.7, 2.2 Hz, ArH, 2H), 3.81 (s, OCH$_3$, 3H), 2.50–2.40 (d, J = 3.1 Hz, CH$_3$, 6H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 169.87, 168.66, 168.58, 157.79, 146.18, 145.90, 132.35, 131.08, 131.00, 129.73, 129.63, 129.58, 129.44, 125.57, 112.60, 111.95, 96.86, 55.97, 21.99, 21.97. HRMS (ESI) m/z: calcd for C$_{24}$H$_{20}$N$_2$O$_3$S{[M + H]$^+$}: 417.1195, found: 417.1262.

S-(6-nitro-1H-benzo[d]imidazol-2-yl) benzothioate 3g Colorless oil liquid (62%), ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.22–8.17 (m, ArH, 3H), 7.71 (t, J = 7.5 Hz, ArH, 2H), 7.56 (t, J = 7.9 Hz, ArH, 4H).

S, S′-(thiobis(4,1-phenylene)) dibenzothioate 3h White Crystals (81%), mp: 112–114 °C. ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.05 (t, J = 8.6 Hz, ArH, 2H), 7.64 (t, J = 7.3 Hz, ArH, 1H), 7.49 (d, ArH, 6H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 189.86, 137.24, 136.47, 135.78, 133.83, 131.52, 128.82, 127.5, 126.45, 77.26, 77.05, 76.83.

S, S'-(thiobis(4,1-phenylene)) bis(4-methylbenzothioate) 3i White crystals (71%), mp: 147–149 °C. ^{1}H NMR (600 MHz, CDCl$_3$) δ 2.50 (s, CH$_3$, 3H), 7.28–7.30 (m, ArH, 2H), 7.43–7.49(m, ArH, 4H)), 7.91–7.93 (m, ArH, 2H). ^{13}C NMR (75 MHz, CDCl$_3$) δ: 22.7, 77.5, 77.9, 78.3, 127.5, 128.5, 130.3, 132.4, 134.8, 136.7, 138.0, 145.7, 190.3; HRMS (ESI) m/z: calcd for C$_{28}$H$_{22}$O$_2$S$_3$: 487.0815, found 487.0852.

The preparation of cured films

The polymeric formulation is composed of 45 wt% monomer (HDDA), 50 wt% polyurethane modified acrylate resin (UV 2100), 2 wt% triethanolamine and 3 wt% photoinitiator. The photoinitiator and HDDA were mixed at room temperature under stirring, and then, triethanolamine and resin were successively added. A thin layer (ca. 75 um) of the resulting mixture was coated on the pre-cleaned glass substrates and exposed to UV irradiation for a certain time to afford cured films.

The gel content was determined by solvent extraction method. The cured films baked at 50 °C for 3 h and weighed M1. After soaking in acetone solution for 24 h, the filtrated solids were dried and weighted M2. The gel content was calculated by the equation:

$$\text{Gel content } (\%) = M2/M1 \times 100\%.$$

Results and discussion

Optimization of the reaction conditions

Firstly, taking the reaction of 2-mercapto imidazole (**1a**) and benzoyl chloride (**2a**) as an example, we carefully studied the reaction conditions, including the reaction solvent, temperature, time and base. All the detailed results are summarized in Table 1. Initial

Table 1 Optimization of the reaction conditions
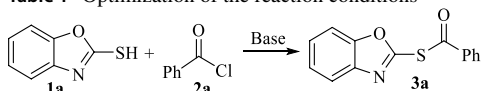
Entry	Temp (°C)	Time (h)	Solvent	Base	Yield (%)
1	r.t	6	DMF	NaOH	35
2	60	6	DMF	NaOH	43
3	60	12	DMF	NaOH	52
4	60	24	DMF	NaOH	53
5	80	12	DMF	NaOH	55
6	60	12	DMF	K$_2$CO$_3$	52
7	60	12	DMF	Et$_3$N	60
8	60	12	THF	NaOH	65
9	60	12	THF	K$_2$CO$_3$	67
10	60	12	THF	Et$_3$N	75

investigations focused on the reaction of **1a** with 2.0 equiv of **2a** in the presence of NaOH (2.0 equiv) as base in DMF at room temperature for 6 h. It was found that the expected product 2-phenylthiobenzimidazole **3a** was obtained in a low isolated yield (35%) (Table 1, entry 1). Further investigations revealed that the most efficient temperature was 60 °C (Table 1, entries 1–5). In addition, when the reaction time was increased from 6 h to 12 h, the yield of the product **3a** increased from 43 to 52%. To further optimize the reaction conditions, various bases and solvents were examined (Table 1, entries 6–10). Finally, **3a** can be obtained with a high yield of 75% in THF at 60 °C for 12 h in the presence of Et$_3$N as base (Table 1, entry 10).

With the optimized conditions in hand, we further examined the scope of the substrates for the reaction of 2-mercaptoheterocycles (**1b–1h**) with chloride (**2a–2b**) (Table 2).

Table 2 Synthesis of thioester compounds

entry	sulfhydryl compound 1	aryl chloride 2	product 3 (%)	λ_{abs} (nm)	ε (L·mol^{-1}·cm^{-1})
1	**1b**	**2b**	**3b** (61%)	305	3.93×10^4
2	**1c**	**2a**	**3c** (65%)	306	7.56×10^4
3	**1d**	**2a**	**3d** (78%)	311	7.38×10^4
4	**1e**	**2a**	**3e** (75%)	323	7.31×10^4
5	**1e**	**2b**	**3f** (76%)	311	7.39×10^4
6	**1f**	**2a**	**3g** (62%)	309	7.45×10^4
7	**1g**	**2a**	**3h** (81%)	265	7.58×10^4
8	**1g**	**2b**	**3i** (71%)	266	7.84×10^4
9	**1h**	**2a**	**3j** (98%)	258	5.18×10^4

As shown in Table 2, the reactions of acyl chlorides with 2-mercaptobenzoxa-zole and 2-mercaptobenzothiazole exhibited moderate yields (< 70%), compared to 2-mercaptobenzimidazole (78%, Table 2, entries 1–3). In addition, we found that methoxy-substituted 2-mercaptobenzimidazole gave the disubstituted products in high yields (> 70%), while 2-mercaptobenzimidazole with an electron-withdrawing group (nitro) on the benzene ring only gave *S*-benzimidazole thiobenzoate, which may ascribe to the activation of the N–H bond by the methoxy group (Table 2, entries 4–5). On the other hand, we also synthesized other thioester compounds from the corresponding substrates (Table 2, entries 7–9). Note that the reaction of 4-methoxybenzenethiol and benzoyl chloride gave the corresponding product S-(4-methoxyphenyl) benzothioate (**3j**) with the highest isolated yield of 98%.

UV–Vis absorption studies

Figure 1 depicts the UV absorption spectra of compounds **3** in DMSO solution. These spectra were measured at an identical molar concentration (1×10^{-5} M), so that a direct comparison of absorbance could be made. As shown in Fig. 1, compounds **3** exhibit stronger ultraviolet absorption intensity due to the introduction of benzoheterocycles and sulfur atoms in comparison with **BP**, and the maximum absorption wavelength has a significant redshift.

Compared with **BP**, it can be seen that **3a**, **3c** and **3d** possess higher ultraviolet absorption intensity and redshift of maximum absorption wavelength due to the introduction of benzoheterocycles. In addition, the absorption wavelengths of compounds **3** with different benzoheterocycles are quite different. When connected with benzoxazole, compound **3a** presents the most significant red-shifted absorption spectrum with a maximum peak at 325 nm. As shown in Fig. 1b, the absorption wavelength of compounds **3e** and **3f** has a strong redshift with the increase in carbonyl structure and benzene ring, which is attributed to $n–\pi^*$ or $\pi–\pi^*$ electron transition. As shown in Fig. 1c, compounds **3h**, **3i** and **3j** have better ultraviolet absorption properties than **BP** due to the introduction of sulfur atoms. The chemical structures and absorption spectra of **3h** and **3i** are similar. Compared with **BP**, **3j** exhibited stronger light absorption intensity and red-shifted spectrum due to the formation of n-π^* transition between heteroatoms and benzene ring structure, which leads to the enhancement of the conjugation degree.

Photopolymerization studies

To evaluate the photopolymerization properties, all the synthesized thioester compounds were utilized as free radical photoinitiators in polyurethane modified acrylate resin (UV 2100) and the activated monomer hexane-1,6-diyl diacrylate (HDDA) with triethanolamine as additive. The experiments of UV-curable surface coating were realized under commercially available UV-lamp (main peak at 365 nm) illumination. All the mechanical properties of the cured film are summarized in Table 3.

As shown in Table 3, compounds **3a**, **3b**, **3c**, **3e**, **3h**, **3j** have been transformed into smooth and transparent films, indicating that they can be used as efficient radical

Fig. 1 Absorption spectra of compounds 3 and BP
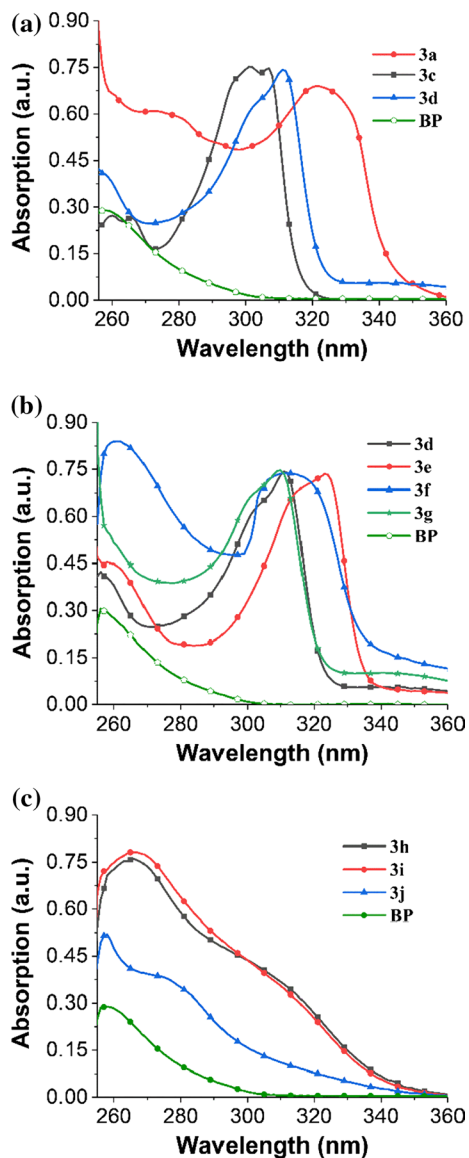
photoinitiators in the ultraviolet curing system. Moreover, we found that compounds **3e**, **3f**, **3h** and **3i** need shorter curing time to transform into films. Compared with **BP** and Irgacure **184**, all the UV-cured coating films show better adhesion. We also found that some films (**3e**, **3f**, **3g** and **3h**) exhibited a better pencil hardness. Gel content is an important parameter of photoinitiators, and **3e** and **3h** give the highest gel content. Accordingly, compounds **3e** and **3h** are the most efficient photoinitiators, which may ascribe to the introduction of multi-ketone segments in the chemical structures.

**Table 3** Properties of UV-curable films

Entry	Photoinitiators	Gloss	Curing time[a] (s)	Adhesion[b]	Pencil hardness	Gel content (%)
1	**3a**	Smooth and transparent	20	0	4H	95.6
2	**3b**	Smooth and transparent	20	0	4H	94.3
3	**3c**	Smooth and transparent	25	0	4H	93.6
4	**3d**	Smooth and translucent	20	0	4H	90.1
5	**3e**	Smooth and transparent	15	0	5H	97.8
6	**3f**	Smooth and translucent	15	0	5H	97.2
7	**3g**	Frosted and translucent	30	0	5H	92.3
8	**3h**	Smooth and transparent	15	0	5H	97.8
9	**3i**	Smooth and translucent	15	0	4H	97.7
10	**3j**	Smooth and transparent	20	0	4H	96.3
11	Irgacure **184**	Smooth and transparent	20	1	4H	96.8
12	**BP**	Smooth and transparent	25	1	4H	96.7

[a]The curing time of the UV-curing coating was measured by the finger contact method

[b]The determination of curing film adhesion by the grid method. The levels are classified into 0–5, level 0 is the best, and level 5 is the worst

Photoinitiation mechanism

Generally, the free radical photoinitiators [22–24] can be divided into pyrolytic free radical photoinitiators and hydrogen-scavenging free radical photoinitiators. Tomioka et al. considered that homolytic α-cleavage of C-S bond in *S*-phenyl thiobenzoates is the initiation mechanism of photopolymerization under UV irradiation. [21, 25–27] However, we found that the resulting films without triethanolamine as additive needed repeated UV-lamp illumination under the same curing conditions. Thus, as shown in Scheme 2, we took the compound **3a** as a model molecular and proposed the possible photoinitiation mechanism [28–32]. Under UV illumination, the sensitized **3a** and the coinitiator triethanolamine can form an exciplex, and then, two radical sources are produced through a photoinduced electron transfer process. Both of them can participate in the following polymerization, thus accelerating the curing process.
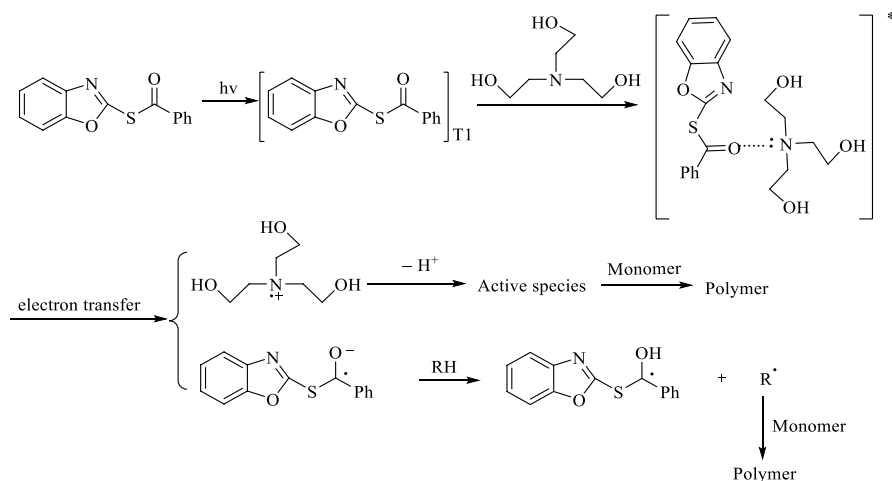
Scheme 2 Possible mechanism of polymerization

Conclusion

A series of *S*-benzoheterocycle thiobenzoate photoinitiators have been synthesized, and their chemical structures were characterized by ^{1}H NMR and ^{13}C NMR, and high-resolution mass spectrometry (HRMS). By introducing the benzoheterocycle into the backbone, *S*-benzoheterocycle thiobenzoate photoinitiators exhibited strong and red-shifted ultraviolet–visible light absorption spectrum. Moreover, these compounds could be utilized as efficient free radical photoinitiators. They exhibited excellent photoinitiating activity. The resulting films possessed comparable/better mechanical properties in comparison with BP and Irgacure 184, implying potential applications in industrial production.

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