

Effect of spatial conformation of a photoinitiator on photoinitiating activity

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Abstract

A series of the derivatives of benzophenone such as 2,2'-thiobis(2,1-phenylene)-bis(phenylmethanone) and methylthio benzophenones were synthesized. The inhibition effect of alkyl sulfide substituent at the ortho-position of benzophenone to photopolymerization was discussed basically. The steric effect affects the maximum UV absorption wavelength and molecular molar absorption intensity..

Keywords Photoinitiator, Benzophenone, Steric effect, Conjugation, Inhibition

1. Introduction

The free radical photoinitiators used for UV curing systems are normally divided into hydrogen abstraction type and alpha cleavage type. The typical hydrogen abstraction type photoinitiator is benzophenone (BP) where the hydrogen atoms can be replaced by substituents, such as alkyl, halogen, oxygen, sulfur, nitrogen or other heteroatoms. The substituents, such as alkyl, halogen, usually affect the UV absorption wavelength, and distinctly the molar absorption intensity of a photoinitiator. Moreover, the different position of the same substituent results in big difference on the melting point of isomer. For example, the melting point of 4-methyl-benzophenone is 57 °C, while that of 2-methyl-benzophenone is -18 °C, which is lower 75 °C than that of 4-methyl-benzophenone. The substituents such as oxygen, sulfur, nitrogen usually at the para-position of acyl group make the red shift of absorption wavelength obviously. The compound containing sulfur atom is one of the most important photoinitiators^[1,2,3]. The methylthio substituent at the para-position of carbonyl will affect the red shift of absorption wavelength and the activity of a photoinitiator. The maximum absorption wavelength of 4-mehtylthio benzophenone is 318 nm, making a red shift of 68 nm, compared with that of benzophenone. The maximum absorption wavelength of 2-mehtylthio benzophenone is 247nm, make a little blue shift of 3 nm. As described in the literature^[4], 2-mehtylthio benzophenone showed weaker photoreactivity than 4-mehtylthio benzophenone^[5]. However, according to the results in our study, 2-mehtylthio benzophenone even can't act as a photoinitiator because it has no photoreactivity. On the contrary, 2-mehtylthio benzophenone possesses inhibiting effect to photopolymerization.

2. Experimental

2.1 Synthesis of sample N7

2-Chloro benzophenone (40g) and sodium methyl mercaptide (48g) were mixed and stirred at 70 °C for 24 h, subsequently added 200 ml of dichloroethane. Then the solution was washed with 50 ml of deionized water and concentrated in vacuo, obtaining 47 g yellow oil. Finally the oil was distilled under reduced pressure to collect the fraction, named N7, at 170 °C (34.6 g) as a pale yellow product with the purity of 97.6% and the yield of 82%.

2.2 Synthesis of sample N15

The synthesis process of N15 was similar with that for N7 except for that 2-chloro benzophenone was replaced with 2-chloro-4'-phenyl benzophenone. The obtained crude product was recrystallized by ethanol to give N15 as a pale yellow crystal with purity of 98.5% and the yield of 80%.

2.3 Synthesis of sample N10

2-Chloro benzophenone, DMSO as a solvent, sodium sulfide, and copper powder as a catalyst were mixed in a high-pressure reaction vessel, and stirred for 24 h. Then 100 ml of 10% sodium hydroxide solution and 50 ml of dichloroethane were added to the above reaction solution, and washed and concentrated in vacuo, obtaining a taupe oil. Finally, the oil was purified by column chromatography to give a pale yellow powder (6.4g) with the purity of 98.78% and the melting point of 91-93 °C. The structure of product was identified by elemental analysis.

2.4 Synthesis of sample N8

The Friedel–Crafts reaction of benzoyl chloride with thioanisole in the presence of anhydrous aluminum chloride gave the crude product, which recrystallized by ethanol, obtaining N8 as a white crystal with the purity of 99%, and the yield of 85%.

2.5 Analytical instruments

- 1) Shimadzu HPLC LC-10AT
- 2) Micro melting point apparatus XT-5
- 3) NMR instrument Bruker AR 300
- 4) Element analysis instrument Vario EL
- 5) UV-Vis spectrophotometer UV1100 (Beijing Rayleigh)

2.6 Photoactivity evaluation

The formulations used for photoactivity evaluation are listed in Table 1.

Table 1: Formula used for photoactivity evaluation

Formula	A	B	C	D	E	F	G	Manufacturer
EB600	26	26	26	26	26	26	26	Cytec
EO-TMPTA	70	70	70	70	70	70	70	Tianjin tianjiao
EDB*1	1	1	1	1	1	1	1	IFC

N8	3				3	3	IHT
N7	1	3				0.1	IHT
N15			3				IHT
N10				3			IHT
ITX					3		Tianjin JiuRi

*1 Ethyl-4-dimethyl amino benzoate

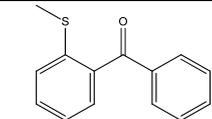
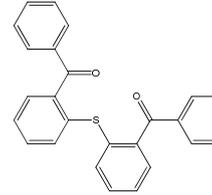
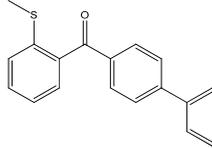
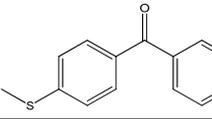
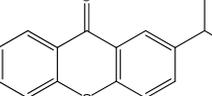
UV curing

The formulation was coated on a microscope slide with a coil bar spreader, then exposed to a medium pressure mercury (2000 W) with a distance of 13 cm to the sample, and the band conveyer speed of 4 m min⁻¹. The photoactivity of photoinitiators were determined by the hardness and touch free time of the cured surface. Y was labeled as the good hardness and dryness indicated high photoactivity, while R was labeled as the contrary status, Y⁻ was labeled as the poorer hardness and dryness than that of Y labeled.

3. Results and discussion

The results for the photoactivity are listed in Table 2.

Table 2. Photoactivity results.

Sample	Molecular structure	λ_{\max} nm	Melting point	H ¹ -NMR	Element analysis result %			Photo-activity
			°C	δ CH ₃	C	H	S	
N7		247	Liquid	2.422	73.65	5.30	14.04	R
N10		247	91~93	—	79.16	4.60	8.13	R
N15		294	79~82	2.447	78.91	5.30	10.53	R
N8		311	77~78	2.540	73.60	5.31	14.0	Y
ITX		380	74~76	—	—	—	—	Y
N7+N8	Formula A							Y ⁻
	Formula G							Y

The electron-attracting character of carbonyl on the ortho-position normally make the hydrogen atoms of methyl on the ortho-position shift to the low-energy field. The chemical shifts of hydrogen atoms of methyl at 2, 6, 4 position of 2,4,6-trimethylbenzoic acid are 2.42, 2.42 and 2.30 respectively. On the contrary, the chemical shift of hydrogen atom of methyl at ortho-position of N7 is 2.42 while the chemical shift of the hydrogen atom of methyl at para-position of N8 is 2.54. As a result, besides the electron-attracting character of carbonyl, there must be some other factors which make the circumstance of s-methyl filled with more electrons, and lead to the chemical shift of hydrogen atoms of methyl on N7 move to higher-energy field.

When there has no substitute on both benzene rings of benzophenone, the rings can rotate freely, resulting the stable conformation with the least energy. The absorption spectrum is only brought by benzoyl and not by another benzene ring. When a alkoxy or alkylthio group at the para-position of benzophenone, the enhanced conjugation effect makes a significant red-shift of the maximum absorption wavelength. Whereas, as the substitute is located at the ortho-position, there has no such effect. The maximum absorption wavelength of methoxy or methylthio benzophenone has very little difference with the methyl. This can be explained to be the steric effect of the ortho-position substitute. The benzene ring rotates only in a limited angle and the two benzene rings can only stand at positions which keep their plane cross angle larger than 45° [6], so that the conjugation effect is poor than benzophenone itself. As a result, there has no red-shift but has 5 nm of blue-shift in the absorption wavelength. It is demonstrated by the ^1H NMR data of higher-energy field, the methylthio substituent, affected by the electron clouds of another benzene ring, stands on the top of the ring plane not the lateral of the ring plane. But in the ITX case, because the rigid fused ring connection of its structure makes a hyperplane conjugated system [7], the absorption wavelength shift from 250 nm to 380 nm.

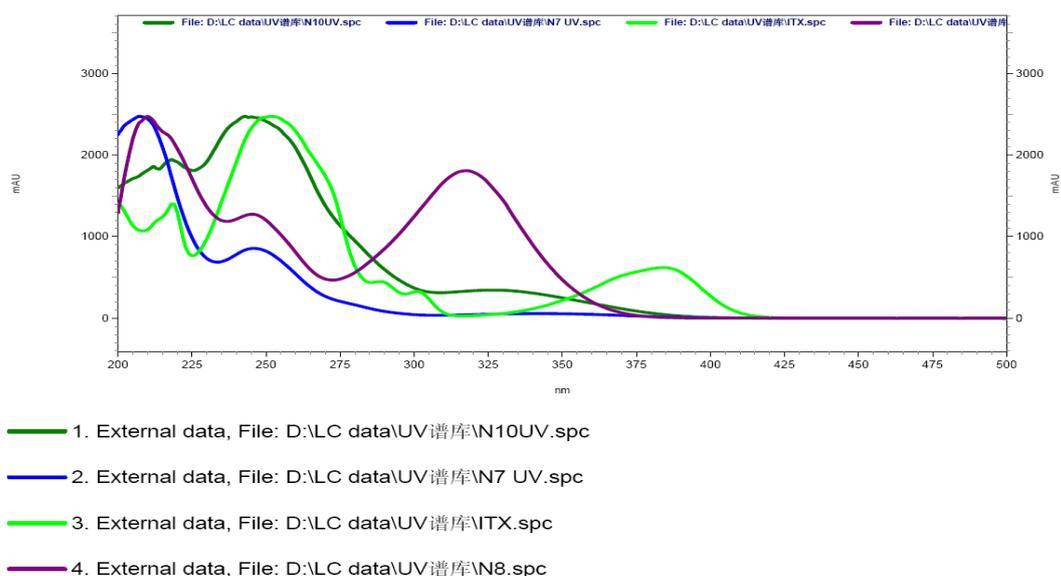


Figure 1. UV-vis spectra of the samples N7, N10 and ITX

In the study of activity of radicals, unlike others ortho-substituted benzophenone, the ortho-sulfide benzophenone show inhibition effect, either alkyl sulfide (N7、N15) or aryl sulfide (N10). Therefore, the inhibition effect of sulfur atom at the ortho-position of carbonyl can be explained by a special inhibition mechanism. Compared the structure and performance of N10 with that of ITX, we could find that the sulfur atom at the ortho-position of carbonyl in both structures, and the rigid fused ring connection of ITX makes a hyperplane conjugated system and a longer absorption wavelength which lead to a good light-induced radical initiation activity. But because of the flexible structures of N7 and N10, there is a possible configure of which the sulfur atom and the oxygen atom of carbonyl are nearer to each other with a estimated distance of 0.2 nm, almost the distance of a single bond. This distance leads to the formation of a stronger local conjugation effect and lost of a larger conjugation effect. Especially when the excited carbonyl abstracts hydrogen, the sulfur atom is so near to oxygen and the hydrogen attached to it (Six-membered ring conformation, the distance is 0.15nm, nearly the distance of a S-H single bond) that the intramolecular energy transfer occurs more easily, which resulting in the lost of excitation energy and the lack of the expected intermolecular energy transfer. Therefore, the excitation of radical can't occur finally. While in the rigid structure of ITX, the estimated distance between the sulfur atom and the oxygen atom fixed by the fused ring is 0.42 nm, and the distance would be not smaller than 0.42 nm when hydrogen abstraction happened. The intramolecular energy transfer can't occur with this distance, so the radical can be excited normally.

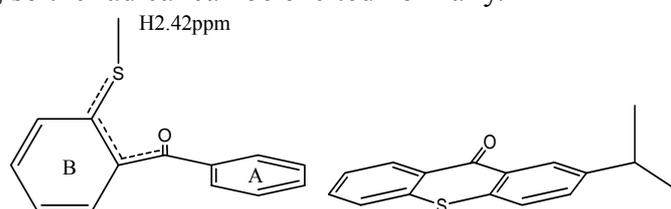


Fig.2 Three-dimensional diagram of the molecular conformation.

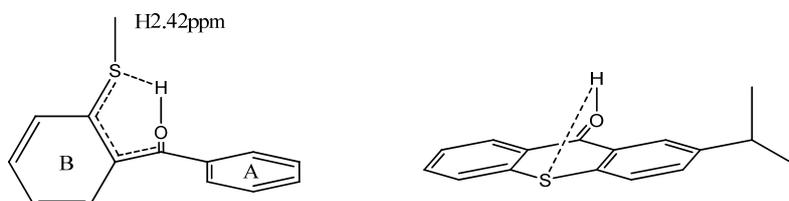


Fig.3 Active hydrogen atom and sulfur atom distance diagram.

4. Conclusion

A series of the derivatives of benzophenone, such as 2,2'-thiobis(2,1-phenylene)bis(phenylmethanone) and methylthio benzophenones were synthesized. The inhibition effect of alkyl sulfide substituent at the ortho-position of benzophenone to photopolymerization was discussed basically.

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