Studies on Synthesis and Properties of PAGs Containing Thienyl Group^a

Wen-Guang Wang, Mei-Li WANG and Jia-Ling PU^b; Lab. of Printing & Packaging Material and Technology, Beijing Institute of Graphic Communication, NO.25, Xinghua, Beilu, Huangcun, Daxing, Beijing 102600, China

Abstract

Photo-acid Generator, which could decompose and generate a kind of acid under external excitation (for example, light, heat, radial, plasma), can be widely used in many fields, such as resist, computer to plate, polymerization and special indicator. The components containing PAG and acid-sensitive polymer, providing with potential high chemical amplification, are more and more regarded as the imaging materials. At the same time, it is of much significance to explore the relationship between PAG's structure and performance (especially with acid-forming performance) in order to farther design and synthesize more excellent PAGs. In this thesis 3 new PAGs containing thienyl group have been designed and synthesized. Their structures have been confirmed by IR, ¹HNMR. Our interesting has been focused on evaluations about their DSC, UV-vis absorption, thermal-stabilization and photolysis under exposure in CH₃CN solution at 405 nm.

Introduction

More and more powerful purple laser resource, whose energy is from hundreds of milliwatts even to integral watts, makes purple laser computer-to-plate (CTP) in printing field come true. Studies of imaging materials and components based on this kind of system are more and more fantastic [1]. Imaging materials containing photo-acid generator (PAG) and photosensitive polymers are playing an important role in modern printing technology [2].

PAG could undergo photo-chemically bond cleavage reactions to produce acid, and the acid can be easily controlled by external conditions (for example, light, heat, radial, plasma), thus PAG can be widely used in many fields, such as photo-resist, CTP. polymerization and special indicator. The components containing PAG and acid-sensitive polymer, providing with potential high chemical amplification, are more and more regarded as the imaging systems based on acid induced or catalyzed reactions. Seeking excellent PAGs sensitive to light at 405 nm is necessary to purple laser imaging system. It is of much significance to explore the relationship between PAG's structure and performance (especially with acid-forming performance) in order to further design and synthesize more excellent PAGs. A series of triazinyl compounds have also synthesized in our lab and some selected excellent PAGs were found with high quantum yields of acid-forming [3]. According to our previous researching results an interesting conclusion that triazinyl PAGs with strong donating-electron group at the end of their molecules could give high quantum yields of photo-acid-forming could be come to. Toshikage A. had reported a kind of excellent purple laser PAG which was a kind of sulfonyloxyimino ester containing thienyl group [4] to result in a series of treatises [5] and patents [6] in

imaging system. In this paper 3 novel triazinyl compounds containing thienyl group were designed and synthesized, their photo-acid-forming properties in solution were also emphatically studied to be expected to be sensitive to light at 405 nm in order to explore excellent PAGs for purple laser printing technology.

Experimental

Melting points were tested by NETZSCH DSC200PC Differential Scanning Calorimeter. The thermal stability was figured on a NETZSCH TG209C Thermo-gravimetric Analyzer. ¹HNMR spectra were obtained on FT-80A spectrometer, chemical shifts were reported in δ units downfield from internal Me₄Si. IR spectra were reported in KBr films on a SHIMADZU FTIR-8400 spectrometer. UV spectra were detected by SHIMADZU UV-2101PC spectrometer. The exposing equipment was CHG-200 UV radiation system produced by Normal University of Beijing in China. Monochromic light at 405 nm was acquired by Monochromic filter.

THF and ether was dried over refluxing with sodium, n-BuLi was prepared by n-BuBr and Li, 2-methyl-4,6-bis(trichloromethyl)-s-triazine was prepared according to the literature [7]. 2-formaldehyde thiophene [8] and 2, 5-diformaldehyde thiophene [9] were synthesized from thiophene with n-BuLi. Other reagents and solvents were used directly without further purification. The reaction was carried out according to Scheme 1.



Scheme 1 Chemical Structures of MTMA, PTMA and CTMA

Synthesis of 3-(5-formylthiophen-2-yl)-2-phenylacrylonitrile (S1) [10]

A 100ml three-neck flask was fitted with a mechanical stirrer and a pressure-equalizing side tube. Under the protection of nitrogen, 2, 5-diformaldehyde thiophene (1.4 g, 10 mmol) was dissolved in 50ml of ethanol while stirring. Then 2-phenylacetonitrile (1.2 g, 10 mmol) was added. After mixing uniformity, the sodium ethoxide (0.068 g, 1 mmol) in ethanol (10 ml) was added dropwise with vigorous stirring. TLC was used to tail the reaction. After the reaction completed, a lot of yellow solid was produced. After filtration, pure yellow solid (1.0 g) was obtained. $R_f = 0.6$ (ethyl acetate: petroleum ether = 1: 2 v/v), yield: 40%; melting point:177.6 °C(DSC peak). ¹HNMR(CDCl₃): δ 9.99 (s, 1H, -C<u>HO</u>), 7.80-7.85(m, 2H), 7.69-7.71(d, 2H), 7.64(s, 1H), 7.47-7.49(d, 3H). IR(KBr, cm⁻¹): 3055.5, 2210.3(-C=N), 1652.9(-C=O), 1496.7, 1436.9, 1218.9, 1055.0, 920.0, 896.8, 806.2, 748.3, 678.9, 513.0.

Synthesis of 2, 5-di-(2-(4, 6-bis(trichloromethyl)-1,3,5-triazin-2-yl)-vinyl)thiophen (PAG1)

0.35 g (2.5 mmol) 2,5-diformaldehyde thiophene was added to the solution of 1.73 g (5.26 mmol) of 2,4-bis(trichloromethyl)-6-methyl-1,3,5-triazine in 50ml of ethanol. The resulting mixture was stirred uniformity. Then 0.21g (2.5 mmol) piperidine and 0.15 g (2.5 mmol) acetic acid were added to the mixture. Then the reaction mixture was kept stirring under heating at 40°C. At the end of reaction a lot yellow solid was obtained. The yellow solid was purified by column chromatography on silica gel with a 2:1 mixture of petroleum ether and dichloromethane to afford 0.6g of pure solid. yield: 30%; melting point: 257.9°C (DSC peak), ¹HNMR (CDCl₃): δ 8.523-8.562(d, 2H), 7.494(s, 2H), 7.184-7.223(d, 2H). IR (KBr, cm⁻¹): 1618.2C=N), 1541.0, 1392.5, 1334.6, 1234.4, 972.1, 821.6, 804.3, 769.5, 698.2(C-Cl), 671.2, 640.3.

Synthesis of 2-(3,5-bis(trichloromethyl)styryl)thiophene (PAG2)

2.016 g (18 mmol) 2-formaldehyde thiophene was added to the solution of 4.935 g (15 mmol) of 2,4-bis(trichloromethyl)-6-methyl-1,3,5-triazine in 50ml of ethanol. The resulting mixture was stirred uniformity. Then 0.7 g (8.2 mmol) piperidine and 0.5 g (8.2 mmol) acetic acid were added to the mixture. Then the reaction mixture was kept stirring for 1h under heating at 40 °C. While the reaction completed, a lot yellow solid was obtained. After filtration, pure yellow solid (3.1g) was acquired. yield: 50%; melting point: 157.9 °C (DSC peak), ¹HNMR(CDCl₃) : δ 8.58-8.62(d, 1H), 7.55-7.56(d, 1H), 7.49(s, 1H), 7.11-7.16(t, 2H). IR(KBr, cm⁻¹): 1618.2(C=N), 1541.0, 1517.9, 1394.4, 1355.9, 1334.6, 1288.4, 972.1, 829.3, 769.5, 696.3(C-Cl).

Synthesis of (3-(5-(2-(4,6-bis(trichloromethyl)-1,3,5-triazin-2-yl)vinyl)thiophen-2-yl)-2-phenylacrylonitrile (PAG3)

1.205 g (5 mmol) 3-(5-formylthiophen-2-yl)-2-phenylacrylonitrile (S1) was added to the solution of 1.81 g (5.5 mmol) of 2,4-bis(trichloromethyl)-6-methyl-1,3,5-triazine in 50 ml of ethanol. The resulting mixture was stirred uniformity. Then 0.3 g (3.5 mmol) piperidine and 0.214 g (3.5 mmol) acetic acid were added to the mixture. Then the reaction mixture was kept stirring under heating at 40°C. At the end of reaction a lot yellow solid was obtained. The orange solid was purified by column chromatography on silica gel with a 2:1 mixture of petroleum ether and dichloromethane to afford 1.5g of pure solid. Yield: 54%; melting point: 214.1 °C (DSC peak), ¹HNMR(CDCl₃) : δ 8.538-8.577(d, 1H,), 7.697-7.701 (d, 2H), 7.636-7.651(t, 2H,), 7.423-7.5(m, 4H), 7.231-7.27(d, 1H). IR (KBr, cm⁻¹): 1612.4(C=N), 1500.5, 1452.3, 1400.3, 1332.7, 1288.4, 1230.5, 1064.6, 972.1, 815.8, 765.7, 698.2 (C-Cl), 671.2, 648.0

Photolysis

The results are based on the change of the UV absorption of a kind of PAG in acetonitrile solution upon exposure to 405 nm monochromatic light. A distinctive absorption at maximum peak decreased following increasing exposure time. The change clearly indicated that PAGs are photo-chemically conversion to other species.

Results and Discussion

Fig. 1 shows UV absorption of PAG1, PAG2 and PAG3. Maximum absorption peaks of PAG1 and PAG3 are shifted to 423 and 430 nm due to their enlarged conjugation chain length. Because their strong absorptions are extended into 405 nm, they are more satisfactory than PAG2 ($\lambda_{max} = 369.5$ nm).



Fig. 1 UV-Vis spectra of PAG1, PAG2 and PAG3



Fig. 2 Thermo-decomposition of PAG1, PAG2 and PAG3

Fig. 2 shows decomposition temperatures of PAG1, PAG2 and PAG3 from TG. Their T_ds are 265.9, 190 and 221.9 $^\circ \rm C$ respectively. The data show they all are stable below 160 $^\circ \rm C$ at least.

Quantum yields of photolysis (Φ_d) of PAG1~PAG3 and other 3 PAGs from the literature [4] in acetonitrile at 405 nm were determined and listed in Table 1.

MATA, T TWA, CTWA III acetonitine at 403 min			
	compound	Light intensity (w/cm ²)	Φ_d (%)
	PAG1	1.034*10 ⁻⁴	5.7
	PAG2	1.034*10 ⁻⁴	18
	PAG3	1.034*10 ⁻⁴	3.5
	MTMA	no data	15 [1]
	PTMA	no data	13 [1]
	CTMA	no data	12 [1]

Table 1 Quantum yields of photolysis (Φ_d) of PAG1 \sim PAG3 and MATA_PTMA_CTMA in acetonitrile at 405 nm

According to Tsuchiya's literature [4], a series of compounds, (5-alkylsulfonyloxyimino-5H-thiophen-2-ylidene)-2-methylphenylacetonitriles (Fig. 3 methyl: MTMA; propyl: PTMA; camphor: CTMA) exhibit enough solubility, red-shifted UV absorption (λ_{max} : 405 nm), good thermal stability up to 140 °C and effective acid generation in terms of quantum yield in an acetonitrile solution (Table 3) and high sensitive in negative tone and positive tone CA resist formulations with g-line exposure. Because 6 PAGs in Table 1 have similar structures, 3 new PAGs should be expected to have high quantum yields. In fact quantum yield of only PAG2 among 3 new PAGs is much higher (up to 18%) than those of PAG1 and PAG2 and as high as that of MTMA and its analog.



Fig. 3 Chemical Structures of MTMA, PTMA and CTMA

Compared with high quantum yield of photolysis of PAG2, those of PAG1 and hopeful PAG3 are relatively low very much and disappointing. Our previous research data about quantum yields of photolysis of different substituted triazinyl PAGs showed that existing donating-electron group at the end of molecular structures could result in increasing quantum yield of photolysis of triazinyl PAGs and on the contrary strong withdrawing-electron group make quantum yield of the PAG decrease. In fact the structures of PAG1 and PAG3 contain withdrawing-electron groups, the results of low quantum yields of PAG1 and PAG3 maybe are in agreement on our previous opinion. From Table 1 the analogs like MTMA have high quantum yields, though PAG3 is similar in structure to MTMA, the evaluated PAG3 should exhibited at least equivalent quantum yield to that of MTMA. But in fact its quantum yield of photolysis apparently is less than that of MTMA. It should contribute to their differences in the type of their chemical structures and the mechanism of acid-forming, it is known that PAG3 belongs to triazinyl derivative while MTMA to sulfonyloxyimino ester. Maybe just the differences in chemical types result in their differences of mechanisms of photolysis. Further studies on acid-forming upon exposure at 405 nm and performance on imaging are in progress.

Conclusions

3 novel triazinyl derivatives based on thiophene were synthesized, their quantum yields of photolysis as photo-acid generator showed PAG2 have excellent upon exposure at 405 nm, and an attempt was made to explain why quantum yield of PAG3 was unexpectedly low.

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Author Biography

Wang Wen-Guang received his B. S. degree in Organic Chemistry from Nankai University (Tianjin, China) in 1991 and a Ph. D. in Organic Chemistry from the Institute of Chemistry, Chinese Academy of Science in 1994. Then he worked as scholar at Chinese University of Hong Kong. He has been working at Beijing Institute of Graphic Communication Science 1996. His interesting was focused on organic information recording materials, especially organic photoconductive and computer-to-plate