Novel Photosensitizer and Methoxy Styryl Pyridines for Photoradical Initiator System

Xuesong Jiang, Jie Yin, Yasuharu Murakami*, and Makoto Kaji*

Shanghai Jiao Tong University, School of Chemistry and Chemical Technology
800 Dongchuan Road, Shanghai, 200240 China

*Hitachi Chemical Co., Ltd., Research and Development Center,
13-1 Higashi-cho 4-chome, Hitachi-shi, Ibaraki-ken, 317-8555 Japan

Distyryl pyridine (DSP) photosensitizer for HABI photoinitiator systems was newly designed and eleven methoxy DSP (distyrylpyridines)s were synthesized and evaluated. The results showed that 2, 4-dimethoxy DSP (24DMOP-DSP) was the most efficient among studied methoxy DSPs. Compared with coumarin 1 as reference, the photosensitivity for 24DMOP-DSP as photosensitizer was increased by 150%. Potential of DSP as photosensitizer was supported by the mechanism study, such like photobleaching property of 24DMOP-DSP, derived from configuration change of *E* to *Z*, and efficient fluorescence quenching of excited singlet DSP by BCIM.

Keyword: photoresist, photoradical polymerization, distyryl pyridine

1. Introduction

Photopolymerization science and technology have assumed in recent years an increasing relevance in many applications, such as curing of coatings on various materials, adhesives, printing inks, and photoresists [1-3]. This technology is based on the use of photoinitiator systems suited to absorb a light radiation of the appropriate wavelength and to produce primary radical species able to convert a multifunctional monomer into a crosslinked network. Therefore, photoinitiator system plays a very important role in the photopolymerization science and technology. Among the most photoinitiator systems, hexaarylbiimidazole (HABI or Lophine dimer, L2) have been widely used as free radical initiators in photopolymer imaging, such as proof paper, dry film resist etc[4-8]. The application of HABI is based on well-established properties of its photolytic dissociation. Under UV irradiation, the homolysis of the excited singlet HABI produces long-lived 2,4,5-triarylimidazolyl radicals (lophyl radicals, L^*) because of the low C-N bond energy. The triarylimidazolyl radicals can abstract

hydrogen atoms from hydrogen donor (HD) to generate active radicals, and consequently initiate photopolymerizations of acrylate monomers efficiently according to Scheme 1. Alternate path via electron transfer from hydrogen donor to the triarylimidazolyl radicals may occur depending on each system's electronic character.

Scheme 1 Mechanism for photoinitiation

The most widely used HABI derivatives such as BCIM, however, do not possess the satisfied UV absorption property, as their maximum absorption peaks are below 300 nm. Moreover, their extinction coefficients at 365 nm, irradiation

wavelength most widely utilized for photocuring, are very low. Therefore, it is necessary to add photosensitizer (S) into HABI photoinitiator systems, which can absorb UV light around 365 nm efficiently and transfer the energy to HABI. Actually, almost all HABI photoinitiator systems in industrial formulation comprise of photosensitizers such as Micheler's ketone (MK), Eosin Y, and Rose Bengal [4]. These photosensitizers can enhance the performance of HABI photoinitiator systems. Thus, development of efficient photosensitizer is very important to HABI photoinitiator systems in industrial photopolymers, such as dryfilm photoresist, because of requirements from industry such as high sensitivity and high resolution. The efficient photosensitizer should possess two important characters: the first is that photosensitizer can absorb UV light very efficiently and then be excited to the excited state; the other is that the excited state of photosensitizer can transfer its energy to HABI efficiently to produce lophine radicals. For example, as to efficient singlet state's photosensitizer, compound should possess high fluorescence quantum yield, and its fluorescence can be quenched by HABI efficiently.

Scheme 2 Structure and synthesis of methoxy DSPs.

Distyrylpyridine derivatives (DSPs) [9] are a new class of fluorescent molecules which are pyridine derivatives with structurally fixed styryl moieties, and can be synthesized through one-step according to Scheme 2. Structural rigidity of DSPs allows us to expect for them high fluorescence quantum yields. In this context, therefore, we

studied methoxy-DSPs as photosensitizer for HABI photoinitiator systems in electronic related photopolymers. This report described absorption properties, photosensitivity evaluation, photobleaching character and fluorescence decay analyses of synthesized eleven methoxy DSPs.

Though distyryl pyridines should be called as 3, 5-dibenzylidenedicyclopentano [b, e] pyridines, in this report these compounds are called as DSPs for short, such like, 24DMOP-DSP for 3, 5-bis (2, 4-dimethoxybenzylidenedicyclopentano [b, e]), 4-2,4-dimethoxyphenyl pyridine.

2 Experimental

2.1 Syntheses of methoxy DSPs

All methoxy DSPs were synthesized through one-step according to Scheme 2, and confirmed by NMR and FT-IR. Using 24DMOP-DSP as example, the detailed process of synthesis is as following: A mixture of 2,4-dimethoxybenzaldehyde (0.1 mol), cyclopentanone (0.05 mol) and ammonium acetate (0.5 mol) in ethanol (250 mL) with 1 mL of 30% hydrogen peroxide was boiled during 1 hr and left to stand overnight at 20°C. The precipitate was refluxed in 50 mL acetone, and then filtered to get product, which is dried in vacuum at 80°C for 24 h. Melting point: 241-243°C, ¹H NMR (CDCl₃, 400 MHz): δ=7.60 (2H, =CH), 6.6-7.4 (9H, aromatic), 3.65-3.85 (18H, -OCH₃), 2.65-3.0 (8H, -CH₂).

2.2 Measurements

¹H NMR spectra were recorded on a Mercury Plus 400 Hz spectrometer with CDCl₃ as solvent. FT-IR spectra were recorded on a Perkin-Elmer Paragon1000 FTIR spectrometer. The samples were prepared as KBr disc. Elemental analysis was conducted on an Elementar Varioel apparatus. Mass spectra were recorded on an HP5989A mass spectrometer. UV-vis spectra were recorded by Perkin-Elmer Lambda 20 UV-vis spectrophotometer. Fluorescence spectra were recorded by Perkin-Elmer LS50B luminescence spectrophotometer.

2.3 Evaluation of photosensitivity in DFR

The photosensitivity of HABI photoinitiator comprised of BCIM, LCV and methoxy DSPs as photosensitizer was evaluated in the dry film. Photopolymer solutions containing a poly (styrene-*co*-methylmethacrylate-*co*-methacrylic acid) as a base polymer (50wt parts), an EO-modified bisphenol-A dimethacrylate oligomer as a crosslinker (50wt parts), photoinitiators, and solvents were prepared. The solutions were coated on 16 μm thick-polyethylene terephthalate film

using bar coater. By drying in an oven at 110°C for 15min, 30μm thick-photopolymerizable films were prepared. The photoinitiator system containing BCIM, LCV and C1 as photosensitizer was used as reference (Scheme 3). Light source is high-pressure Hg Lamp.

Scheme 3 Photoinitiator system as reference

2.4 Fluorescence decay analyses

GaN laser diode pumped single-photon counting fluorescence decay analyses were conducted using equipment which was described before [10-12].

3. Results and Discussion

3.1 Synthesis and UV absorption spectra of methoxy DSPs

To study the effect of methoxy substituent on photosensitivity of DSP, eleven methoxy DSPs were synthesized according to Scheme 3. These methoxy DSPs can be divided into three groups: momo-methoxy, di-methoxy and tri-methoxy DSP. Their UV-vis absorption spectra in chloroform are shown in Figure 1. From the Figure 1, the position and number of methoxy substituent have obvious influence on UV-absorption of DSP. The UV absorption maxima of most methoxy DSPs are about 380-400 nm with ϵ of above 2×10^4 . Except for 245TMOP-DSP, the cut-off of UV-absorption spectra for all DSPs is below 450 nm, which is expected for practical stability under the yellow light. These UV absorption character make most methoxy DSPs promising as photosensitizer for HABI.

3.2 Photosensitivity of methoxy DSPs

BCIM was chosen as for evaluation. To evaluate the photosensitivity of methoxy DSPs and C1 was chosen as a reference photosensitizer. Using a model formulation we prepared test dryfilm samples. Photosensitivity results of methoxy DSPs are shown in Figure 2. Figure 2 is showing 24DMOP-DSP was the most efficient photosensitizer among all methoxy DSPs. Also comparing with photosensitivity of 35 mJ.cm⁻² of C1 reference, the photosensitivity of 24DMOP-DSP was 14 mJ.cm⁻², and was increased by 1.5 times. Figure 3 is showing SEM of

micro-pattern obtained test film resist which used 24DMOP-DSP as a photosensitizer, indicating excellent pattern shape with high resolution of 10 μm with 25 μm resist thickness.

Figure 1 UV-Vis absorption spectra of all methoxyl DSPs in chloroform solution. the concentration is 2×10^{-4} molL⁻¹

Figure 2 Photosensitivity for all methoxy DSP as photosensitizer.

BCIM as HABI, LCV as hydrogen donor, C1 as reference, high pressure Hg lamp as light source.

Figure 3 SEM of micro-pattern fabricated thick photoresist containing 24DMOP-DSP as photosensitizer.

High pressure Hg lamp as light source

3.3 Mechanism study

It was described that methoxy DSPs, especially for 24DMOP-DSP, can be used as an efficient photosensitizer for HABI photoinitiator systems. We tried to know why 24DMOP-DSP is efficient. Figure 4 is showing photobleaching of 24DMOP-DSP. For instance, the absorption around 400 nm decreased very fast with the irradiation of 365 nm light. Photobleaching speed of all methoxy DSPs is shown in the Figure 5, indicating that methoxy substituent influenced on photobleaching speed of methoxy DSPs. The conversion can be calculated according to the following equation, and photobleaching speed is defined as irradiation time to 20% conversion.

$$C = \frac{100(OD_0 - OD_t)}{OD_0} \%$$

Figure 4 UV-vis absorption spectra of 24DMOP-DSP changes with the time of 365 nm light irradiation in chloroform. Concentration is 2×10^{-4} molL⁻¹

¹H NMR spectra of 3MOP-DSP in deuterated chloroform before and after irradiation are shown in Figure 6. It was clearly seen that the new signals (1', 2' and 3') appeared after irradiation, indicating configuration change of DSP. There are two C=C groups in DSP's structure. DSP can undergo configuration change from EE to EZ to ZZ (Figure 6), resulting in change of UV absorption after irradiation.

The layer near to the bottom of DFR is difficult to be photo-cured due to "filter-effect" of photoinitiator systems. In the HABI photoinitiator system, the main function of photosensitizer is to absorb UV-light and to transfer its energy to HABI. Compared with conventional photosensitizer C1, therefore, more UV light will reach the deep layer due to photobleaching of 24DMOP-DSP as photosensitizer (shown in Figure 7), resulting in higher photosensitivity. There remain further discussion and study. This isomerization reaction may also be considered as an energy wasting side-reaction for photosensitization of BCIM by excited DSP.

Figure 5 Photobleaching of methoxy DSPs: Conversion vs time of irradiation.

Figure 6 H NMR spectra of 3MOP-DSP in CDCl₃ before and after irradiation of 365 nm light

Figure 7 Proposed mechanism for effect of photobleaching property of photosensitizer for HABI systems

Two DSPs; 24DOM-DSP and 4MOP-DSP were subjected to fluorescence decay analyses in order to confirm excited singlet state energy or electron transfer path for photosensitization of DSP to HABI. This time also we asked this experiment to Tsukuba University. Equipments and procedures were shown in previous report [10]. We defined the dynamic fluorescence quenching efficiency, D , as showing in Figure 8, then obtained them from fluorescence lifetime data with and without BCIM using a single photon counting method. Results were summarized in Table 1. 24DOMP-DSP and 4MOP-DSP have medium fluorescence lifetime (3.33 and 3.46 ns, respectively) among studied photosensitizers. The dynamic fluorescence quenching efficiency, D , for both were somewhat different (0.40 and 0.11, respectively), consisting with faster photospeed of 24DMOP-DSP than 4MOP-DSP. Also among all photosensitizers studied, 24DMOP-DSP reached to maximum quenching ability and this consists with DSP's high photospeed.

Table 1 Fluorescence decay and quenching results

Photosensitizer Observed Wavelength	ave. τ /ns	D	Excitation /nm	Emission observed /nm	Photospeed/ mJ.cm ⁻²
DMOP-DSP	3.33	0.4	410	460	197
MOP-DSP	3.46	0.11	410	460	278
DBA	11.44	0.28	410	460	175
C1	4.01	0.21	410	460	150
Pyraz	2.53	0.08	410	450	240
NKX-1342	0.6	0	410	480	572
N-Me-90AD	11.66	0.51	410	460	207
NJ2	2.34	0.18	410	460	191
NJ1	1.79	0.09	410	460	179
ACR-2	10.97	0.26	410	460	174

Figure 8 Fluorescence quenching efficiency and photosensitivity

Fluorescence quenching efficiency (D):

Fluorescence quenching efficiency efficiency was derived from fluorescent lifetime measurement using eq. (1)

$$D = 1 - \tau_0 / \tau \quad (1)$$

τ_0 : fluorescence lifetime without quencher [ns]

τ : fluorescence lifetime with quencher [ns]

Quencher: BCIM, 1.5 wt parts

4 . Conclusion

Eleven methoxy DSPs were newly synthesized and evaluated as a photosensitizer for

HABI photoinitiator system in DFR. Among all methoxy DSPs, 24DMOP-DSP was the most photosensitive. Compared with 35 mJ.cm⁻² of C1 as reference, the photosensitivity for 24DMOP-DSP as photosensitizer is about 14 mJ.cm⁻², and is increased about 150 %. The photobleaching property of 24DMOP-DSP, derived from configuration change of *E* to *Z*, is one of key factors to high performance of 24DMOP-DSP such as high photosensitivity and excellent pattern. DSP undergoes a photoisomerization around its double bond and its excited singlet state is easily quenched by BCIM.

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