Effect of Photo-initiator on Photosensitive Emission Polymer

Tang-Hao Liu¹, Wen-Tung Cheng¹* and Jiang-Jen Lin²

¹. Department of Chemical Engineering, National Chung Hsing University, Taichung 40227, Taiwan.
². Institute of Polymer Science and Engineering, National Taiwan University, Taipei 10617, Taiwan.

A photosensitive emission polymer containing trimethylolpropane triacrylate as reactive monomer, Norrish I and II photo-initiators, pentaerythritol tetrakis (2-mercaptoacetate) as photo-sensitizer, and bis (n-salicylidene-4, 4’-diaminophenyl) methane named H₂L¹ and Alq₃ as emitters were studied in this paper. The UV-visible absorption and photoluminescence spectra were particularly employed to examine the influence of the chemical structure of photo-initiator on the emission properties of photosensitive polymer. The results show that photo-initiators, such as I369 and I907, reduced the emission intensity due to the nitrogen in their chemical structure and the UV-visible absorption overlapping with the excitation of the emitters; whereas the photo-initiators of I184, I500, I651, and BP could provide extra energy to enhance the emission intensity of H₂L¹ and Alq₃ respectively. In addition, through the photolithography process, the resolution of photosensitive emission polymer is about 15 μm for demonstration.

Keyword: Photosensitive polymer; Light emitting material; Photo-initiator; UV-visible absorption; Photoluminescence spectra

1. Introduction

Organic materials for electro-luminous devices can be classified into two categories mainly as organic light emitting diodes (OLEDs) according to molecules weight. Modern organic light emitting diode consists of two or more different layers to enhance electro-optical properties and stability [1, 2]. Two methods are popular for fabrication. The more common one is manufactured by vacuum deposition for OLEDs [3]. The advantage of this technique is well to define multi-layer devices of high quality, but it is restricted to functional molecules of low molar mass with extraordinary thermal stability. In addition, huge instrumental expense is required, resulting in relatively high cost. An alternative method for the fabrication of PLEDs is via spin-coating [4, 5], screen printing [6, 7], contact print [8, 9] and ink jetting [10], etc. In where the materials can be useful and no longer limited by their molar mass, but their solution and forming film is difficulty. The advantage of the spin-coating technique is that the production costs are dramatically reduced because the large areas can be coated. However, the potential disadvantage of using spin coating to fabricate multi-layer devices is that the coated layers could be partially dissolved by the following steps. This was thought to cause the overshoot effect on the PLEDs [11]. In addition, the solution process like shadow masking and printing have poor multi-layer capability and low-resolution of pixels. In order to make the spin-coating method suitable to fabricate multi-layer of OLEDs, a useful method to avoid re-dissolution is developed to cross-link the coated layer before applying the next one. Hwand et al. present a blue light emitting copolymer with distyrylbenzene chromophore, electron transporting aromatic oxadiazole, and photocrosslinkable cinnamoyl groups [12]. The PL quantum efficiency of the chromophore was increased with increasing the degree of photo-polymerization and depending on the rigidity of the polymer backbone [13]. Spiliopoulos et al. synthesized two acrylic monomers bearing an emissive stilbene-based chromophore and the polymerization using AIBN as initiator to obtain two homopolymers and their
backbone consisted of poly(methacrylate) (PMMA), and pendant stilbenoid chromophores [14]. Domercq et al. synthesized a series of cross-linkable TPD-based copolymers containing cinnamate-based moieties to obtain photo-cross-linkable polymers and soluble arylamine-based hole transporting moiety with various ionization potentials [15]. According to the above way, OLEDs can be photo-lithographically patterned in the similar to photo-resist materials.

In photolithograph method, photo-initiator is an important factor, which affects the rate of photo-curing reaction and degrees of harden. When photo-initiator absorbs light and then forms reactive initiating species, such as radicals, $H^+$, or cationic radicals. The absorbed energy will fragment the photo-initiator and transit electron from ground state to excited state to produce reactive initiating species, which will transfer its energy to induce photo-polymerization of reactive monomer for highly cross-linked films. The photo luminescent mechanism of the OLEDs is similar to the fragment of photo-initiators. Therefore, the optical properties, such as UV-visible absorption and emission of the photo-initiator and the emitter will influence each other, that is, the properties of the photo-initiator depend on its chemical structure and it would affect the photoluminescence of the emitter.

There are two polymerization mechanisms using for curing photo-crosslinkable OLEDs system: free radical and cationic polymerization. Matthew et al. reported a number of light-emitting polymerizable liquid crystals (acylates and methacrylates as reactive mesogens) based on 2,7-disubstituted-9,9-dialkylfluorene, which does not use photo-initiator in photo-polymerization, so high exposure energy (500Jcm$^{-2}$) is need [16]. Contoret et al. synthesized a series of photocrosslinkable electroluminescent liquid crystals containing methacrylate and diene photopolymerizable end groups for multilayer of OLEDs. They also did not use photo-initiator to induce photopolymerization and need longer expose time [17].

The free radical polymerization does not use photo-initiator causing some problems such as the need of more powerful energy and long exposure time. Cationic polymerization usually use photo acid generator (PAG) as photo-initiator in photo-cross linkable OLEDs system. Some reports have been demonstrated based on several emission materials with cross-linkable oxetane [18-22] group and a photo acid as a cationic initiator [19]. There are some disadvantages of the PAG used in photo-cross-linkable OLEDs system, for example, PAG is a metal complex and may be producing Brønsted acid after exposed to introduce the degradation of OLEDs. Furthermore, in the transparent thin film, cationic is slower and may take a few seconds to reach completion and for commercial viewpoint, PAG is more expensive than free radical photo-initiator used in photolithograph method. Kim et al. encapsulated organic light-emitting devices (OLEDs) on glass substrate and exposing light energy at 1260 mJ/cm$^2$ to induce photo polymerizable blend consists of pentaerythritol and photoinitiator, which does not affect the EL characteristic to increase the lifetime of the device in air [20].

The photolithograph method using free radical photo-initiator has been well established to fabricate printed circuit board (PCB). Nevertheless, the exposure energy may be quenched by oxygen, solvent, impurities, additives or recombination reactions and de-active the photo-curing reaction [21]. To improve the above issues, photo-sensitizer is added to the photosensitive material. A photo-sensitizer is defined as a molecule that is able to absorb light and transfer the excitation to another molecule that is a photo-initiator. Polythiolene is an excellent photo-sensitizer and crossing agent.

To reduce the cost for small-molecular OLEDs by vacuum deposition as well as solve the problems of the low-resolution and the over shoot effect of PLEDs caused by spin-coating, this work intends to prepare photosensitive emission materials using the blend method. A photosensitive polymer containing trimethylolpropane triacrylate, TMPTA, as reactive monomer, photo-initiator, pentaerythritol tetrakis (2-mercaptopetate), polythiolene, as photo-sensitizer, and emission material is formulated in this study. In where, the light emitting material is azomethine type compounds, bis (N-salicylidene-4,4' -diaminophenyl)methane named H2L1. The synthesis rout of H2L1 has been published in the literatures [22, 23]. The aromatic azomethine compounds with metal complexes attracted attention since 1960 because they exhibit fluorescence in water and are well known in analytical chemistry [24, 25] for excellent properties like mechanical strength [26], thermal stability [27], nonlinear
optical [28], liquid crystal [29], environmental resistance [30], and fiber-forming properties [31]. The new application of azomethine compounds and their complexes is apply to EL device. Niu et al. synthesized two functional conjugated polyazomethines containing triphenylamine unite as hole transport material for organic electronic device [32]. Peng et al. used chemical vapor depositing polymerization as an effective method to fabrication conjugated polyazomethine films as constituents in organic-electroluminescence devices [33]. To demonstrate the suitable for common used in OLED, tris-8-hydroxy quinoline aluminium (Alq3) will be used in this study, which is a common electron transfer and emission material applied in OLED.

Furthermore, in this study the UV-visible absorption spectra and photoluminescence spectra are particularly employed to examine the effect of the chemical structure of photo-initiator on the emission properties of photosensitive polymer. The objective of this investigation is to experimentally analyze the relationship between the chemical structures of the commercially available Norrish type I and Norrish type II photo-initiators and the photoluminescence properties of the photosensitive polymer.

2. Experimental

2.1. Materials

Tris-8-hydroxy quinoline aluminium, Alq3, 4,4'-methylenedianiline and salicylaldehyde used to synthesis emitter, H2L1 were purchased from Aldrich Chemical Co.. Trimethylolpropane triacrylate (TMPTA, Ucb Chemicals) and pentaerythritol tetraakis (2-mercaptoacetate) (polythiolene, Aldrich Chemical Co.) were reactive monomer and photo-sensitizer, respectively. According to the photochemical routs of free radical, two kinds of photo-initiators were purchased from Ciba Specialty Chemicals Inc. and Janssen Chimica, (Figure 1). All reagents were used as received and without further purification.

Norrish I photo-initiators include: 1-hydroxycyclohexyl phenyl ketone (Irgacure184, I184), 2-benzyl-2-N, N-dimethylamino-1-(4-morpholinophenyl)-1-butanoine (Irgacure369, I369), 2, 2-dimethoxy-2-phenyl acetophenone (Irgacure651, I651), and 2-methyl-1-[4- (methylthiol)phenyl]-2-morpholino propan-1-one (Irgacure907, I907). Norrish II photo-initiators involve Irgacure500 or I500 (50% benzophenone + 50% hydroxycyclohexyl phenyl ketone) and benzophenone (BP). Methanol and chloroform were solvent.

2.2. Synthesis of emission material, bis (n-salicylidene-4,4'-diaminophenyl)methane, H2L1 (Scheme 1)

In 250 ml flask, salicylaldehyde was slowly poured into the methanolic solution of 4, 4'-methylenedianiline with 2:1 molar ratio at 60-70 °C. The products were obtained in 93% yield as a yellow powder. The precipitate was separated with filter and the solvent was removed by vacuum distillation followed by re-crystallization with toluene/methanol co-solvent placing in refrigerator for 48 hrs. The products were obtained in 82% yield.

1H-NMR (CDCl3) for H2L1: ’ (ppm) 4.042 (s, 2H), 6.918-6.963 (t, 2H), 7.009-7.036 (d, 2H), 7.221-7.258 (m, 8H), 7.351-7.400 (m, 4H), 8.625 (s, 2H), 13.229 (s, 2H); Anal. Calcd. for H2L1 (C27 H22 N2O2): C, 79.78; H, 5.46; N, 6.89; O, 7.87. Found: C, 80.05; H, 5.54; N, 6.94; O, 7.37.
Scheme 1. Synthesis of bis (n-salicylidene-4,4'-diaminophenyl)methane, namely, H$_2$L$_1$.

2.3. Preparation of photosensitive emission polymer

The solution samples were prepared by dissolving the different kinds and various amount of photo-initiators in the mixture solution of emitters (H$_2$L$_1$ and Alq$_3$, 0.5x10$^{-4}$ mole), TMPTA (5x10$^{-4}$ mole), and polythiolene (5x10$^{-4}$ mole) in chloroform. The film samples were prepared by casting the solution with above formula on the quartz glass substrate followed by soft curing at 70 °C for 30min. Then the film was irradiated (standard UV lamp, λ=360nm) for 20min and finally was baked at 100°C for 30min to remove residual solvent.

2.4. Measurement

Proton nuclear magnetic resonance (1H-NMR) was performed with Nuclear Magnetic Resonance Spectrometer (HNMR, Varian Unity Inova FT-NMR spectrometer 300MHz) using TMS as internal standard in deuterium chloroform solution (CDCl$_3$). Photoluminescence spectra (PL) were detected by Photoluminescence spectroscopy (Perkin Elmer LS 55 Luminescence spectroscopy) and spectrophotometer with a 20 kW xenon discharge lamp as excitation source; Ultraviolet-visible (UV-vis) spectra were obtained with Shimadzu, UV-1601. Determination of the composition and purity of the azomethine compounds was made by element analysis (EA, Heraeus CHN[O] Rapld F002 Elemental Analyzer) to determine the C, H, N and O contents.

3. Results and Discussion

In conventional photolithographic method, photo-initiator is an important factor, so we probe into the effects of commercial photo-initiators on emission property. In this work, the photofragmentation reaction and UV-vis absorption and emission property of photo-initiators are analyzed. Figure 1 shows the photogragmentation reaction of Norrish type I photo initiators (I184, I369, I651, and I907) and Norrish type II photo initiators (I500 and BP) used in this study. As shown in the figure, I184 and I500 fragment to form benzyol and α-hydroxycyclohexyl radical; I369 fragment to form 4-morpholinobenzoyl and n, n-dimethyl-1-phenylbutan-2-amine radical; I651 fragment to form benzyol, dimethoxybenzyl, and methyl radical; I907 fragment to form 4-(methylthio)benzoyl and 4-isopropylmorpholine radical; and BP was excited to form an intermediate excited electron transfer complex (exciplex) and then becomes ketyl radical, respectively, after absorbing light. In addition, based on the chemical structure containing nitrogen, the photo-initiators can be classified into two categories in this study. One group is I369 and I907; and other group is I184, I500, I651 and BP. Figure 2 compares UV-vis absorption spectra of H$_2$L$_1$ with I184, I369, I500, I651, I907, and BP, respectively. This figure shows the absorptions of H$_2$L$_1$ at 343, 268 and 244nm, I184 at 245nm, I369 at 330nm, I500 at 249nm, I651 at 253nm, I907 at 315nm, BP at 250nm. As shown in the figure, the maximum absorptions of I184, I500, I651 and BP are located around 250nm attribute to the π→π* transition; whereas I369 and I907 have the maximum absorption around 320nm, which is longer than that of I184, I500, I651 and BP because of the highly electron donating substitution of alkylthio and alkylamino at the para-position of the aromatic ring of benzyol. The resulting effect is a red shift of the photo-initiator maximum absorption wavelength [34]. H$_2$L$_1$ has long absorption wavelength (about 343nm) and short absorption regions (about 244nm), and then the photo-initiators could be classified into two categories according to absorption regions due to different chemical structure. According to this, I184, I500, I651 and BP belong to short absorption and I369 and I907 are long absorption because of the alkylthio and alkylamino substituted at the para-position of the aromatic ring of benzyol.

The emission spectra in chloroform solution of all materials used in this study were shown in Figure 3(a). This spectra shows that I369 and I907 has similar emission spectra to H$_2$L$_1$ at about 520nm but I184, I500, I651, BP, TMPTA and poly-thiolene are different emission spectra from

H$_2$L$^1$ at about 420-450nm. Also, the inset shows the excitation spectrum of H$_2$L$^1$ at the region of 250-500nm and then emits fluorescence at 520nm.

Figure 2. UV-vis absorption spectra of H$_2$L$^1$ and photo-initiators in chloroform solution: (a) (H$_2$L$^1$ and I184), (b) (H$_2$L$^1$ and BP); (c) (H$_2$L$^1$ and Irgacure500 as well as I500), (d) (H$_2$L$^1$ and I369), (e) (H$_2$L$^1$ and I651) and (f) (H$_2$L$^1$ and I907).

Compare the excitation spectrum (the inset of Figure 3(a)) of H$_2$L$^1$ with the absorption spectra of photo-initiators (Figure 2), they indicate that the absorptions of I184, BP, I500 and I651 do not overlap with the excitation of H$_2$L$^1$, so they may not reduce the exciting energy of H$_2$L$^1$, furthermore, their emission energy may reabsorb by H$_2$L$^1$ to enhance its emission intensity. But I369 and I907 exhibit the overlap between their absorption and the excitation of H$_2$L$^1$, so they may reduce the exciting energy of H$_2$L$^1$ and reduce its emission intensity.

To confirm the above result, Figure 3(b) shows the emission spectra of H$_2$L$^1$ (0.5x10$^{-4}$ mole) in the mixture of photo-initiators (I184, I369, I500, I651, I907, and BP, 10$^{-4}$ mole) and 5ml chloroform solution containing polythiolene (5x10$^{-4}$ mole) and TMPTA (5x10$^{-4}$ mole). As shown in the figure, the mixtures of H$_2$L$^1$ with I184, I500, I651, and BP exhibit higher emission intensity than that without photo-initiators and with I369 and I907, respectively. In the other words, I184, I500, I651, and BP could enhance the emission intensity of H$_2$L$^1$ in the system because it attribute to the excitation of H$_2$L$^1$ at ultra-violet light region which just right overlap the absorption of I369 and I907. In addition, nitrogen and amine is an effective quencher and reduce the emission intensity of polymeric light emitting material in the present of I369 and I907 due to electron transfer [35, 36].

According to the above results, therefore, the photo initiator of I651 was selected as photo-initiator for a further study. Figure 4(a) and (b) show the emission spectra of the mixture of TMPTA, polythiolene, H$_2$L$^1$ and amount of I651 in chloroform solution and the film, respectively. In Figure 4(a), the emission intensity of the solutions is increased with increasing the amount of I651. Additionally, Figure 4(b) shows the emission intensity of the films to exhibit similar trend to the solution, but the emission intensity is shapely lower than that in solution and red shift about 20nm. This phenomena may attribute to the amount of emitter in solution is more than that at film. Because the concentration at film is slight more than in solution, but the volume of film is great less than that of solution. The reason due to the amount emitter in solution is great more than that at film and cause the emission intensity of solution is great more than that of film. In additional, the inset shows the absorption spectrum of the substrate glass, it indicates that the substrate glass would absorb light from 200-330nm, it also decreased the energy of exciting light of emitter to fluorescent and reduced the emission intensity of the film. Furthermore, in the process of prepare film, the solvent must remove, it causes the volume is decreased and concentration of emitter in film is increased, so the distance between emitters is also decreased. It is the reason to cause the emission of film red shift.

Figure 5 shows the UV-vis absorption of Alq3 compares with photo-initiators, I184, BP, I500, I369, I651 and I907, respectively. The figure indicates that the absorptions of Alq3 at 260 and 390nm. Figure 6 shows the photoluminescence spectra and the effect of photo-initiators on emission intensity of Alq3. Figure 6(a) shows the excitation and emission spectrum of Alq3 (10$^{-7}$M). It indicates that Alq3 was excited in the region from 280 to 480nm and emits fluorescence at 520nm.
Figure 3. Emission spectra of H$_2$L$^1$ and photo-initiators (a) in chloroform solution and (b) different photo-initiators ($10^{-4}$ mole) in chloroform solution which contains H$_2$L$^1$ ($0.5 \times 10^{-4}$ mole), TMPTA ($5 \times 10^{-4}$ mole), and polythiolen (5$ \times 10^{-4}$ mole).

Figure 6 (b) shows the emission spectra of photo-initiators ($10^{-4}$ mole) in Alq3 solution ($10^{-5}$M, chloroform as solvent), which presents the same trend as H$_2$L$^1$ as emitter, I184, BP, I500 and I651 exhibit positive effect to enhance the emission intensity of Alq3 solution but I369 and I907 have negative effect. The results could be attributed to the same reason as H$_2$L$^1$ as emitter.

Figure 7 (a) shows the emission spectra of Alq3 solution ($10^{-3}$M) with different amount of I651 (0.2, 0.5, 1.0 and 5.0 mole). Figure 7 (b) shows the emission intensity of the films exhibit similar trend to the mixture in solution. The results indicate that the emission intensity increase with the increasing the amount of I651 both in solution and at film. The emission intensity of film is also sharply less than that of solution could be attributed to the same reasons of the amount of emitter which is irradiated and the absorption of substrate glass.

Additionally, the emission of film is red shift than that of solution about 50nm, it could attribute to the increase of concentration and the decrease of distance of emitter, as the same reasons of H$_2$L$^1$ as emitter.

Figure 8 shows the pattern of free radical photosensitive polymeric light emitting material composed from TMPTA ($5 \times 10^{-4}$ mole), polythiolen (5$ \times 10^{-4}$ mole), and H$_2$L$^1$ ($0.5 \times 10^{-4}$ mole) with I651 ($10^{-4}$ mole) after photolithographic process under optical microscope (50 x), which the resolution of line width is about 15 $\mu$ m.

4. Conclusion

In this study, the UV-visible absorption spectra and photoluminescence spectra were employed to examine the influence of the chemical structure of photo-initiator on the emission properties of photosensitive polymer with bis (N-salicylidene-4, 4'-diaminophenyl) methane.

Because the absorption and emission are not in the excited region but in the excited
region of emitters, the photo-initiators of I184, I500, and I651 do not share the energy that excites emitter, and thus their emission may be used to enhance the emission intensity of polymeric light-emitting material. In addition, for demonstration, a clear pattern, which resolution of line width is about 15 μm, was fabricated by photosensitive emission polymer through photolithographic process in this work.

Figure 5. UV-vis absorption spectra of Alq3 and photo-initiators in chloroform solution: (a) (Alq3 and I184), (b) (Alq3 and BP), (c) (Alq3 1500), (d) (Alq3 and I369), (e) (Alq3 and I651) and (f) (Alq3 and I907).

Figure 6. The photoluminescence spectrum of Alq3 (a) excitation and emission, in where the inset shows chemical structure of Alq3 and (b) different photo-initiators (10^-4 mole) in Alq3 solution (10^-5 M).

Figure 7. Emission spectra of (a) Alq3 solution (10^-3 M) with various amount of I651 as photo-initiator and (b) solid film blends with Alq3 (0.5x10^-4 mole), TMPTA (5x10^-5 mole), polythiolene (5x10^-5 mole), and different amount of I651 as photo-initiator.
Figure 8. Photographic pattern of photosensitive emission polymer composed from TMPTA (0.002mol), polythiolen (0.004mol), and H2L1 (0.002mol) with I651 (0.002mol) under optical microscope (50 x), which units of line width and line space are μm.

References