

# Synthesis and Optical Properties of Acrylic Copolymers Containing AIQ<sub>3</sub> Pendant Group for Organic Light Emitting Diodes

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## 요 약

펜던트기가 tris(8-hydroxyquinoline) aluminum (AIQ<sub>3</sub>)으로 된 아크릴 단량체(HEMA-*p*-AIQ<sub>3</sub>) (HEMA = 2-hydroxyethyl methacrylate)를 각각 메틸메타크릴레이트(MMA), 아크릴로니트릴(AN), 순수 HEMA와 공중합하여 3가지 아크릴 공중합체 [MMA-*co*-HEMA-*p*-AIQ<sub>3</sub> (공중합체 1), AN-*co*-HEMA-*p*-AIQ<sub>3</sub> (공중합체 2), HEMA-*co*-HEMA-*p*-AIQ<sub>3</sub> (공중합체 3)]를 라디칼 공중합법으로 합성하였다. 25 wt%의 HEMA-*p*-AIQ<sub>3</sub>를 함유한 공중합체 1,2,3의 유리전이온도(T<sub>g</sub>)는 각각 158, 150, 126 °C로 나타났으며, 이는 유기발광다이오드(organic light emitting diodes, OLED)로써 지녀야 하는 우수한 열 안정성을 만족하였다. 그리고 이들 공중합체는 테트라하이드로퓨린, 디메틸포름아미드, 톨루엔 및 클로로포름 등과 같은 용매에 잘 용해되었으며, 자외선-가시광선의 흡수 및 발광 거동이 순수 AIQ<sub>3</sub>와 거의 동일함을 알 수 있었다. 또한 이들 공중합체를 스핀 코팅하여 녹색의 OLED 디바이스를 제조한 후 전류 밀도-전압 곡선을 비교하였다. 공중합체 3을 사용한 OLED 디바이스의 on-set 전압은 약 2 볼트로써 다른 두 공중합체 OLED 디바이스의 전압(공중합체 1: 약 3 볼트, 공중합체 2: 약 4 볼트) 보다 낮음을 알 수 있었다.

**주제어** : AIQ<sub>3</sub>, 유기발광다이오드, 아크릴레이트, 공중합체

**Abstract** : Three acrylic copolymers containing tris(8-hydroxyquinoline) aluminum (AIQ<sub>3</sub>) pendant group (25 wt%), acrylate-*co*-HEMA-AIQ<sub>3</sub> (25 wt%), were successfully synthesized by free radical polymerization from acrylates [methyl methacrylate (MMA), acrylonitrile (AN) or 2-hydroxyethyl methacrylate (HEMA)] with HEMA functionalized with AIQ<sub>3</sub> pendant groups (HEMA-*p*-AIQ<sub>3</sub>). The glass transition temperatures (T<sub>g</sub>) of MMA-*co*-HEMA-*p*-AIQ<sub>3</sub> (copolymer 1), AN-*co*-HEMA-*p*-AIQ<sub>3</sub> (copolymer 2) and HEMA-*co*-HEMA-*p*-AIQ<sub>3</sub> (copolymer 3) were found to be 158, 150 and 126 °C, respectively. They have good thermal stability: a very desirable feature for the stability of OLEDs. Their solubility, thermal properties, UV-visible absorption and photoluminescence behaviors were investigated. They were found to be soluble in various organic solvents such as tetrahydrofuran (THF), dimethylformamide (DMF), toluene and chloroform. It was also found that the UV-visible absorption and photoluminescence behaviors of these copolymers were similar to those of pristine AIQ<sub>3</sub>. Green organic light-emitting diodes (OLEDs) have also been fabricated using these copolymers as light emission/electron transport components obtained easily by spin coating, and their current density voltage (J-V) curves were compared. The OLED device of the copolymer 3 had the lowest turn-on voltage of about 2 V compared to other copolymer types devices.

**Keywords** : AIQ<sub>3</sub>, Organic light emitting diode, Acrylate, Copolymer

## 1. Introduction

The field of organic electronics has generated intense research efforts, spurred on by the promise of a viable alternative to the inorganic materials platform, especially for large-area, flexible electronics applications. Significant progress has been demonstrated towards the realization of efficient organic light emitting diodes (OLEDs) for flat-panel displays and lighting[1], thin-film

field-effect transistors (TFTs)[2], photodetectors for large-area detector arrays[3], and organic photovoltaic cells for low-cost solar energy generation[3,4]. In all of these organic device embodiments, optimization of charge injection/extraction and carrier transport is critically important towards their technological success. Efficient injection or extraction requires low energetic barriers while competent transport demands highly conductive transport layers.

Tris(8-hydroxyquinoline) aluminum (AIQ<sub>3</sub>), a complex first used in 1987 by Tang and Van Slyke for efficient organic light emitting diodes (OLEDs) that required low driving voltages[5],

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has since become one of the most powerful emitting materials for OLED devices. There has been abundant progress in its optical properties, such as color tuning[6-8], enhancement of electroluminescence (EL) and photoluminescence (PL) efficiency[9], and white light emission[10,11]. However, the majority of research in this area so far focused on field emission and electroluminescence of bulks of nanorods or nanowires for vacuum and OLED devices[12-15], and most of the AIQ<sub>3</sub> nanostructures used were synthesized by traditional vapor deposition based methods[12-14].

AIQ<sub>3</sub> is one of the most widely used electron-transporting, host emitting materials in OLEDs due to their thermal stability, easiness in synthesizing and purification, high fluorescence and good electron-transporting mobility. One disadvantage in the application of AIQ<sub>3</sub> is its limited processability, since it must be deposited via thermal evaporation, during which isomerization or oligomerization occur upon high-temperature sublimation[16]. Another disadvantage comes from the crystallization of AIQ<sub>3</sub>, which takes place under working conditions and may result in device failures. Therefore, materials with AIQ<sub>3</sub> are needed that combine the processing properties of polymers and the fluorescent properties of AIQ<sub>3</sub>. A convenient low cost manufacturing method is solution processing, such as spin coating and possibly inkjet printing in the OLED industry[17], with a mix of AIQ<sub>3</sub> and conducting polymer; however, phase separation occurred in their system and led to poor optical properties[18]. Also they found that the low solubility of AIQ<sub>3</sub> in most polymers makes it difficult to cast a homogeneous and transparent thin film. Several efficient methods to synthesize AIQ<sub>3</sub> containing polymers have been reported. Lu et al.[19] prepared a polymer fully functionalized with AIQ<sub>3</sub> in a post-polymerization step, and Meyers et al.[20] synthetic method was based on a fully functionalized monomer, which eliminated the cross-linking. However, the solubility of these polymers was not good. Also, Du et al.[21] synthesized a series of 8-hydroxyquinoline metal chelate containing polymers through the copolymerization of metaloquinolate-pendant monomers with methyl methacrylate (MMA) by the Meyers modified method.

In this regard, the following point was desirable and significant for our study: i) synthesis of the copolymers with 2-hydroxyethyl methacrylate (HEMA) functionalized with AIQ<sub>3</sub> pendant groups (AIQ<sub>3</sub>-HEMA) to increase solubility and, ii) development of a route for the facile fabrication of OLED using the resulting copolymers bearing AIQ<sub>3</sub>-HEMA (25 wt%). In this study, a series of polymers were synthesized using the radical copolymerization of various unsaturated monomers [MMA, acrylonitrile (AN), and HEMA] with AIQ<sub>3</sub>-HEMA. The structures of the monomers and copolymers were characterized by proton nuclear magnetic resonance spectroscopy (<sup>1</sup>H-NMR), Fourier

transform infrared spectroscopy (FT-IR) and thermal analysis was performed on differential scanning calorimeter (DSC), thermogravimetric analysis (TGA). The optical properties of copolymers were measured by UV-visible and PL spectrophotometer. Copolymer films were prepared by spin-coating of the copolymer solutions on quartz substrate.

## 2. Experimental

### 2.1. Materials

8-Hydroxyquinoline, HEMA, MMA and AN were purchased from Sigma Aldrich and were distilled before use. Hydroquinone and azobisisobutyronitrile (AIBN) were purified by recrystallization. Other solvents were purchased from Junsei Chemical and purified before use. Column chromatography was performed on silica gel (Merck silica gel 60, mesh size 0.2-0.5 μm).

### 2.2. Synthetic methods

#### 2.2.1. Synthesis of compound (1) and (2) in Scheme 1

5-Chloromethyl-8-quinolinol hydrochloride (1) was synthesized according to the literature procedure[22]. A 0.04 mol of 8-quinolinol was added into a solution of 50 mL of hydrochloric acid and 0.08 mol of 37% formaldehyde in a 250 mL three necked flask. The reaction mixture was treated with hydrogen chloride gas for 90 min and stirred for 10 h. The yellowish precipitates were obtained on a filtering and washed with acetone several times and dried under vacuum at 40 °C for 12 h.

5-(2-Methacryloxyethyl)oxymethyl-8-quinolinol (2) was synthesized according to the literature procedure[21]. The mixture of 0.0434 mol of sodium acetate, 0.04 g of hydroquinone and 40 g of HEMA was added to a 100 mL three necked flask with a magnetic stirrer and refluxed at 50 °C for 1.5 h. And then 0.0434 mol of compound (1) was added to the mixture and heated at 80 °C for 5 h. After cooling, the mixture was poured into a large amount of cooled water and neutralized with dilute ammonia. It washed with a large amount of water and collected by filtration and dried at room temperature in desiccator. The white solid product was obtained by four re-crystallizations from petroleum ether.

#### 2.2.2. Synthesis of AIQ<sub>3</sub> pendent monomer (3)

To a 150 mL three necked flask equipped with a nitrogen inlet and a magnetic stirrer, triethylaluminum (1 M solution in hexane; 10 mL, 0.01 mol) was added via syringe, and then subsequently adding 8-hydroxyquinoline (0.02 mol) in anhydrous THF. After 2 days of stirring, compound (2) (0.001 mol) in anhydrous THF was added. And then additional 8-hydroxyquinoline 0.019 mol in anhydrous THF was added; the mixture was stirred for 24 h. The mixture was filtered and removed

the insoluble AlQ<sub>3</sub> and purified by column chromatography (silica gel, 1 : 1 toluene/CHCl<sub>3</sub>); it was then concentrated under reduced pressure. The product was precipitated from petroleum ether and dried under vacuum at 40 °C.

### 2.2.3. Synthesis of copolymers (1, 2 and 3)

Copolymers 1, 2 and 3 were synthesized by radical polymerization from AlQ<sub>3</sub> pendant monomer (3), three monomers (MMA, HEMA and AN), initiator (AIBN, 0.1 wt%) and solvent (hexane/THF: 1/1) at 80 °C for 4 h. The reaction mixture was allowed to cool down to 60 °C for few h, and then to reflux at 100 °C for 1 h. The final reaction mixture was precipitated with methanol, washed several times and filtered the copolymer 1, 2 and 3 were obtained after drying in vacuum at 50 °C.

### 2.2.4. Fabrication of OLED device

Organic light-emitting diodes were fabricated by using successive spinning coating method of PEDOT/PSS (50 nm) and polymer containing AlQ<sub>3</sub> (100-200 nm), and then doping Al electrodes with LiF (0.5 nm) on top of ITO glass substrates. Prior to the deposition of organic layers, the ITO substrate was cleaned with UV ozone cleaner. The deposition of materials was performed under vacuum for 1 h. After doping Al electrode with LiF, the OLED materials was hardened for 10 min, and then annealed at 100 °C for 20 min. In this study, OLED device was composed of the hole injection & transfer layer, an emissive layer, the electron injection & transfer layer, and anode and cathode terminal: Anode (indium tin oxide, ITO)/poly(3,4-ethylenedioxythiophene-poly (styrenesulfonate), PEDOT-PSS/copolymer/lithium fluoride/cathode (Al).

## 2.3. Characterization

### 2.3.1. Structural analysis

<sup>1</sup>H NMR spectra were collected on a Varian Unity Plus 300 NMR spectrometer (USA) using chloroform-d (CDCl<sub>3</sub>) as a solvent. IR spectra were recorded on a Nicolet Impact 400D Fourier Transform Infrared Spectrometer by dispersing samples in KBr disc.

### 2.3.2. Thermal analysis

Thermal behaviors of each copolymer were determined with DSC (SSC/5200H MII, Seiko, Japan) at the heating rate of 10 °C/min (25~300 °C, 3 mg) under a nitrogen atmosphere. TGA was performed on a Perkin Elmer LTD (TGA7, USA) at a heating rate of 10 °C/min (30~600 °C, about 5 mg) under a nitrogen atmosphere.

### 2.3.3. Optical absorbance measurement

UV-visible and photoluminescence (PL) spectra were obtained

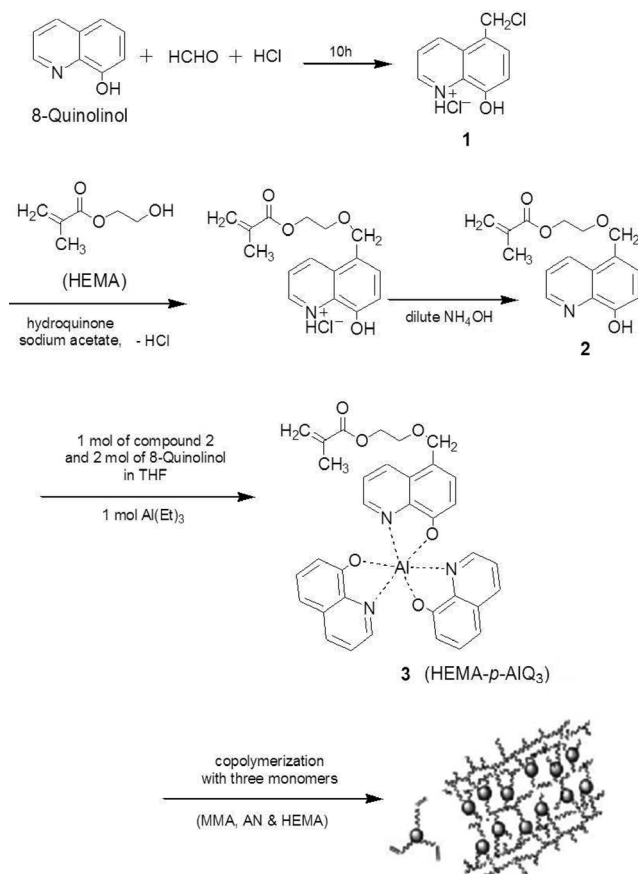
using a UV-visible spectrophotometer (S-3100, SCINCO, Korea) and fluorescence spectrophotometer (F-4500, Hitachi, Japan), respectively.

## 3. Results and Discussion

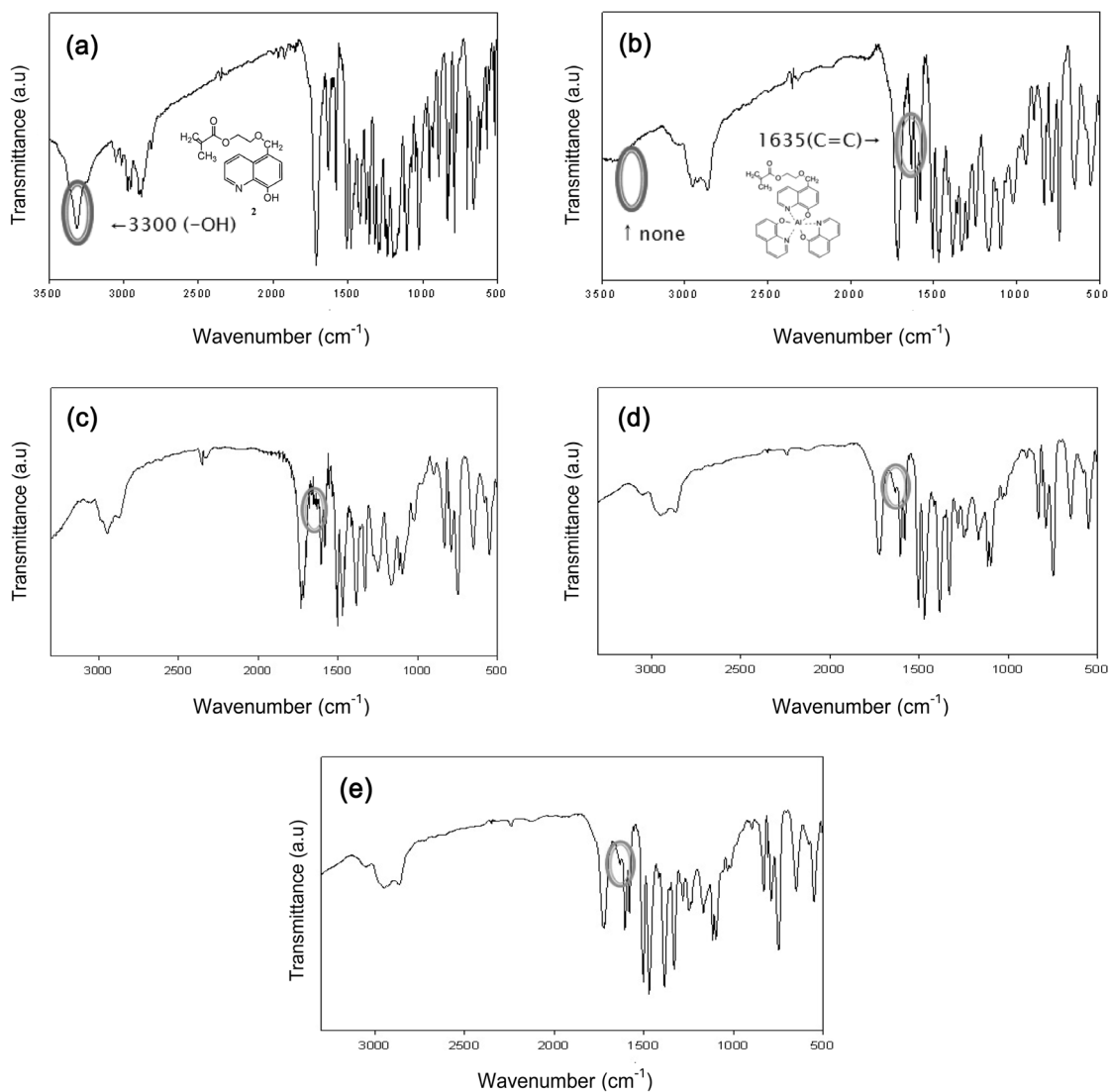
### 3.1. Identification of monomers and copolymers

The synthetic method of monomer and each copolymer is shown in Figure 1. In all copolymerizations the content of AlQ<sub>3</sub> was controlled to be 25 wt%. The chemical structures of compounds (2), (3) and copolymers 1, 2 and 3 were analyzed by FTIR (Figure 2). The FT-IR spectra of compounds (2) and (3) are shown in Figure 2(a) and (b). The characteristic absorption peak of OH at 3,300 cm<sup>-1</sup> in HEMA was completely disappeared upon reacting with Al(Et)<sub>3</sub>-compound (2) and (3). After copolymerizing with MMA (c), AN (d) and HEMA (e), the peak of C=C stretching at 1,635 cm<sup>-1</sup> was disappeared.

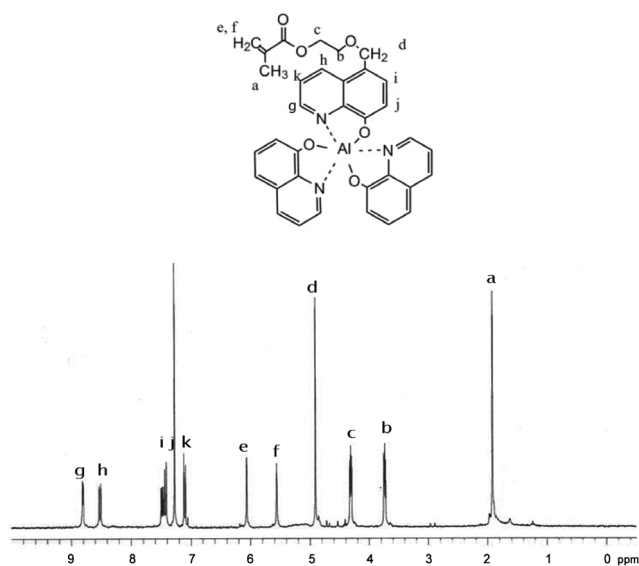
Figure 3 shows the <sup>1</sup>H NMR spectra of compound (3). There are three environment of hydrogen (H) atom in 8-hydroxy quinolinol molecule say namely g, h and i, j, k (I=j=k) as shown in insert of Figure 3. The corresponding peaks of sites g, h and i, j, and k of H atoms in <sup>1</sup>H NMR of 8-hydroxyquinolinol appear at about 8.8 (g site), 8.5 (h site), 7.4-7.6 (i site), 7.3 (j



**Figure 1.** Synthesis of the monomer and copolymers.



**Figure 2.** FT-IR spectra of compound 2(a), compound 3(b), copolymer 1(c), copolymer 2(d), and copolymer 3(e).



**Figure 3.** <sup>1</sup>H NMR spectra of the compound 3 in CDCl<sub>3</sub>.

site), 7.1 (k site) ppm, respectively. These results indicated that the targeted copolymers were successfully synthesized.

### 3.2. Thermal properties of copolymers

The thermal stability of the copolymers were determined by their thermo gravimetric analysis (TGA) in a Perkin Elmer LTD (TGA7, USA) at a scan rate of 10 °C/min under nitrogen atmosphere. Table 1 shows temperatures at 10%, 30%, 50% weight loss values of each copolymers and AlQ<sub>3</sub>. The copolymer 1 was more thermally stable (50% weight loss at 483 °C) than PMMA (50% weight loss temperature: 310 °C), AlQ<sub>3</sub> (50% weight loss temperature: 429 °C) and other copolymers (2 : 416 °C, 3 : 359 °C, respectively). The glass transition temperature (*T<sub>g</sub>*) of copolymers are shown in Table 1, but *T<sub>g</sub>* of AlQ<sub>3</sub> is not observed by Differential Scanning Calorimeter (DSC, SSC/5200H MII, Seiko, scanning range: 30-300 °C, scanning rate: 10 °C/min

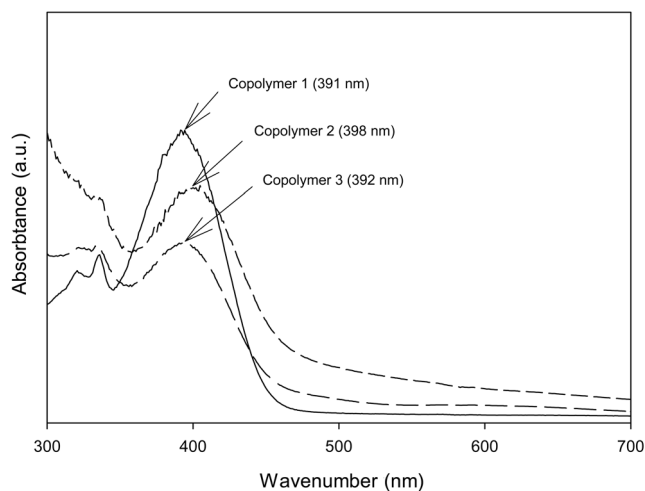
**Table 1.** Thermal properties of copolymers with AlQ<sub>3</sub>

Copolymers	Temperature (°C)			T <sub>g</sub> (°C)
	Weight loss 10%	Weight loss 30%	Weight loss 50%	
3(HEMA- <i>p</i> -AlQ <sub>3</sub> )	375	408	429	-
Copolymer 1(MMA- <i>co</i> -HEMA- <i>p</i> -AlQ <sub>3</sub> )	257	369	483	158
Copolymer 2 (AN- <i>co</i> -HEMA- <i>p</i> -AlQ <sub>3</sub> )	277	345	416	150
Copolymer 3 (HEMA- <i>co</i> -HEMA- <i>p</i> -AlQ <sub>3</sub> )	278	324	359	126

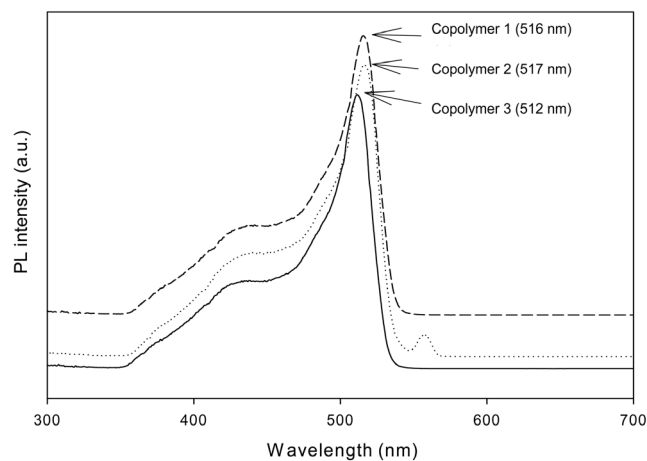
under nitrogen atmosphere). The glass transition temperatures (T<sub>g</sub>) of MMA-*co*-HEMA-*p*-AlQ<sub>3</sub> (copolymer 1), AN-*co*-HEMA-*p*-AlQ<sub>3</sub> (copolymer 2) and HEMA-*co*-HEMA-*p*-AlQ<sub>3</sub> (copolymer 3) were found to be 158, 150 and 126 °C, respectively. These results clearly show that the copolymers synthesized in this study have good thermal stability: a very desirable feature for the stability of OLEDs. Therefore, high operational lifetime can be expected for OLEDs using these compounds since it has been demonstrated that high T<sub>g</sub> materials lead to enhanced device stability and lifetime[23].

### 3.3. Optical properties of copolymers

Figure 4 shows that the UV-visible absorption spectra of the AlQ<sub>3</sub> containing copolymers in a dilute THF solution. All copolymers had green region absorption peaks in the range of 391-398 nm. The copolymers 1 and 3 (391-392 nm) showed almost the same peak positions with AlQ<sub>3</sub> (390 nm). But the copolymer 2 (398 nm) was a little red-shifted (about 8 nm) compared to AlQ<sub>3</sub>. This might be due to the influence of nitrile group (highest electron withdrawing group) in the chain of copolymer 2. A summary of photo-physical data of the three co-

**Figure 4.** UV-visible spectra of the copolymers 1, 2, and 3 in solution.**Table 2.** Optical properties of copolymers with AlQ<sub>3</sub>

Copolymers	λ <sub>max</sub> (nm) solution	
	UV-visible	PL
3(HEMA- <i>p</i> -AlQ <sub>3</sub> )	390	510
Copolymer 1 (MMA- <i>co</i> -HEMA- <i>p</i> -AlQ <sub>3</sub> )	391	516
Copolymer 2 (AN- <i>co</i> -HEMA- <i>p</i> -AlQ <sub>3</sub> )	398	517
Copolymer 3 (HEMA- <i>co</i> -HEMA- <i>p</i> -AlQ <sub>3</sub> )	392	512

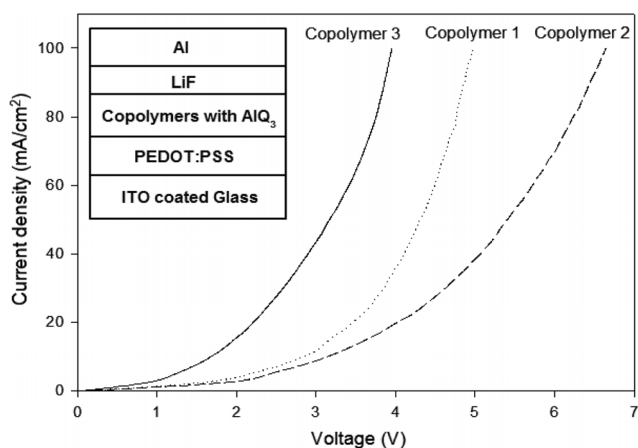
**Figure 5.** PL spectra of the copolymers 1, 2, and 3 in solution.

polymers is also given in Table 2.

Figure 5 shows that the photoluminescence spectra of the AlQ<sub>3</sub> containing copolymers in a dilute THF solution. Their peak fluorescence λ<sub>max</sub> are located at 516, 517, and 512 nm, respectively. Also all copolymers showed almost the same peak positions with AlQ<sub>3</sub> (510 nm). These results clearly indicated that the polymer backbone (PMMA, PAN and PHEMA) does not interfere with the photo-physical properties of the pendant AlQ<sub>3</sub> moiety. The solution absorption and emission of copolymers is a little higher-shifted values compared to that of AlQ<sub>3</sub>. These findings are consistent with previous reports that introduction of electron-withdrawing and/or -donating groups at the 5-position of 8-hydroxyquinoline can tune the emission wavelength[20].

### 3.4. Current-voltage characteristics of OLED devices

It was found that these copolymers could be dissolved in common solvents, such as THF/DMF/Toluene/CHCl<sub>3</sub> and enable convenient and scalable manufacturing methods (e.g., spin-coating and ink-jet printing methods). Therefore, the electron transport component of OLED device could be made simply by spin coating due to high solubility of copolymers with AlQ<sub>3</sub>.



**Figure 6.** J-V Characteristics of copolymers 1, 2, and 3 OLEDs.

pendant group. Current density-voltage analysis of OLED device was performed to investigate the effect of copolymer types. Figure 6 shows the current density-voltage (J-V) characteristics of layer device with different copolymer types. The structure of the fabricated OLED devices can be noted in the inset of Figure 6. Devices were based on PEDOT:PSS as a hole transport layer and acrylates copolymers having AlQ<sub>3</sub> as an electron transport layer. We noted that the use of copolymers with HEMA-*p*-AlQ<sub>3</sub> itself can enhance the OLED device performance by improving the main technological problems via a vapor deposition process faced by OLEDs. The current densities of all devices were found to be around 100 mA/cm<sup>2</sup> regardless of the type of copolymers. However, the operating voltage of device using three copolymers prepared in this study increased in the order of the copolymer 3 < copolymer 1 < copolymer 2. The device using copolymer 3 (HEMA-*co*-HEMA-*p*-AlQ<sub>3</sub>) had the lowest operating voltage. As a consequence, there is marked increase in emission intensity at the same operating voltage. On the other hands, the device using MMA-*co*-HEMA-*p*-AlQ<sub>3</sub> (copolymer 1) and AN-*co*-HEMA-*p*-AlQ<sub>3</sub> (copolymer 2) caused significant shift in the J-V characteristics to higher voltage. The lowest operating voltage of the device using copolymer 3 can be attributed to the different nature of the hole-impeding process. And this shift points to the role of the dopant molecules in forming hole traps, thus reducing their mobility in the hole transfer layer[10]. However, the exact mechanism of hole formation and the reason why the copolymers have different J-V characteristics is not clear at the present. More detailed studies should be made.

#### 4. Conclusions

A series of AlQ<sub>3</sub> containing copolymers were successfully synthesized by free radical polymerization with AlQ<sub>3</sub>-pendant monomer and three monomers (MMA, AN and HEMA). The

content of AlQ<sub>3</sub> in copolymers was fixed at 25 wt%. The FT-IR and <sup>1</sup>H NMR spectra confirmed the structure of MMA-*co*-HEMA-*p*-AlQ<sub>3</sub> (copolymer 1), AN-*co*-HEMA-*p*-AlQ<sub>3</sub> (copolymer 2) and HEMA-*co*-HEMA-*p*-AlQ<sub>3</sub> (copolymer 3). The T<sub>g</sub> of copolymers were between 120 °C and 160 °C, which testifies good thermal stability: a very desirable feature for the stability of OLEDs. These copolymers showed almost the same UV absorption peak positions as AlQ<sub>3</sub> (390 nm). All the copolymers containing AlQ<sub>3</sub> synthesized in this study showed similar photoluminescence as pure AlQ<sub>3</sub>. The PL emission peak positions of the copolymers ranged from 512 nm to 517 nm, similar to that of AlQ<sub>3</sub> (510 nm). The high solubility of copolymers with AlQ<sub>3</sub> pendant group made the electron transport component of OLED device possible simply by spin coating. The OLED device using copolymer 3 had the lowest turn-on voltage of about 2 V compared to other devices using copolymers 1 and 2.

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