

## CN-PPV의 합성과 전기 광학적 특성에 관한 연구

박지호, 권승호, 김진성, 유재수  
중앙대학교 화학공학과

### Synthesis of CN-PPV and Its electrical & optical properties

Ji Ho Park, Seung Ho Kwon, Jin Sung Kim, Jae Soo Yoo  
Dept. of Chemical Engineering, Chung-Ang University

#### Introduction

It was reported recently conducting polymers with the electrical and optical properties of semiconductors and metals. As the conducting materials[1]. Efficient injection properties of electrons have been required the use of metal electrodes with low work function, such as calcium(Ca), but these reactive metals present problems for device stability. Electrodes of cyano-substituted polymer made from stable metal, such as Aluminum(Al), Aluminum Lithium(Al-Li), can be used for electron injection. The higher electron affinitive polymer(CN-PPV), Poly(2,5-hexyloxy-1,4phenylene cyanovinylene) was reported by Greenham et al[2], and Dialkoxy substituted poly(p-phenylene vinylene) derivative with cyano-group on the vinylene units demonstrating very high internal efficiency in polymer light-emitting diodes were studied[3-4]. The polymer shows highly electron affinity owing to a strong electron withdrawing cyano group on the polymer backbone. Therefore, the high electron affinity to reduce the barrier to electron injection, air-stable metals with higher work function can be used as the cathode, and the stability of the polymer compared with PPV. The alkoxy groups enhance the solubility, and ensure processibility of the conjugated polymer. Electroluminescent device by polymer promises a new and exciting technology of emissive type. The advantage of organic emitting materials over classical semiconductors is in the possibility of designing new materials with different band gaps and electron affinities.

In this study, we synthesized poly(2,5-hexyloxy-1,4phenylene cyanovinylene), CN-PPV, as conjugated polymer and characterized its electrical and optical properties through fabricating a device

#### Experimental

##### A. Synthesis

##### A-1. Starting material

1,4-dihexyloxybenzene-2,5-dichloromethyl was prepared in a two step procedure from hydroquinone and sodium methoxide with bromohexane and subsequent recrystallization. As the result 1,4-dihexyloxy benzene was bischloromethylated by the reaction of formalin with hydrogen chloride to obtain the desired starting material.

##### A-2. Monomer1, 2

Monomer 1, 1,4-dihexyloxy-2,5-benzenedizcetonitrile, was obtained by cyano-substitution reaction from starting material. and monomer 2, 1,4-dihexyloxy-2,5-benzenedicarboxaldehyde, was prepared in a three step procedure from starting material. The first was acetylation, second was hydrolysis, and third was oxidation.

The polymer, CN-PPV, was synthesized by Knoevenagel condensation polymerization of equimolar quantities of monomer 1 and 2.

### A-3. Knoevenagel condensation polymerization

A mixture of monomer 1 and 2 in tert-butanol and anhydrous tetrahydrofuran was stirred at 35°C under nitrogen(N<sub>2</sub>) until dissolution was completely accomplished. Potassium tert-butoxide and a solution of tetrabutyl ammonium hydroxide(10%) were added quickly, the mixture was stirred vigorously at 35°C for a hour. Then the mixture was poured into methanol to precipitate the polymer. The dried polymer was redissolved in tetrahydrofuran and reprecipitate into methanol to give a dark red precipitate.

### B. Preparation of Polymer EL device

Electroluminescence device was fabrication on ITO(Indium-Tin Oxide)-glass. ITO-glass substrate with a surface resistance of 8Ω/sq was cleaned in ultra sonic baths of trichloroethylene(TCE), acetone, methanol, and distilled water and then dried in stream of nitrogen(N<sub>2</sub>)[5]. In fabricating the device having double layer, the poly(ethylene dioxy)thiophene mixed with poly(styrene sulphonic acid), PEDOT/PSS, was spin-coated on the patterned substrate by photolithography, and subsequently dried in vacuum oven at 95°C for 4hours. The polymer film was formed by spin-coating using solution of CN-PPV in chloroform solvent and its concentration of 10mg/ml, and after baking in vacuum oven at 70°C for 3hours. The cathode of device using Aluminum Lithium(AL-Li) was deposited method. The electrical and optical properties of fabricated devices were investigated by source measure unit (Keithley 236) and photometer (Minolta CS-100).

## Result and discussion

Synthetic route of CN-PPV was shown in Fig. 1. Number average molecular weight(M<sub>n</sub>) and polydispersity of synthesized CN-PPV were 6,168g/g-mol and 1.16, respectively.

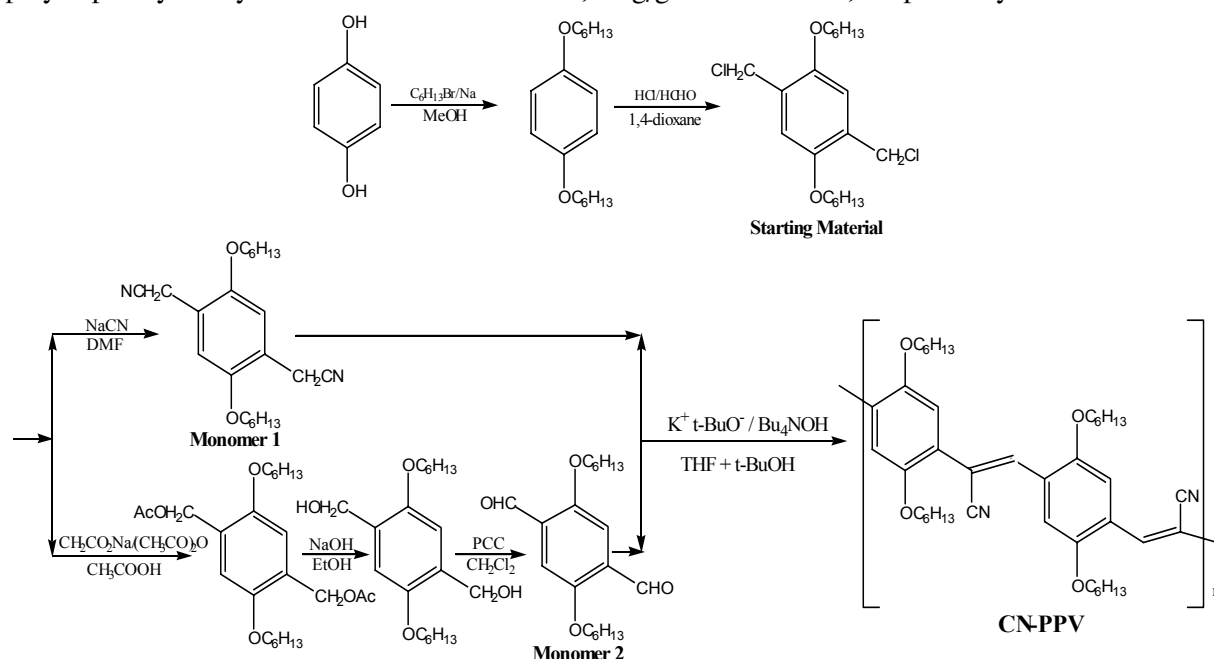


Fig. 1 Synthetic route of CN-PPV

Figure 2 represents the glass transition temperature( $T_g$ ) measured by Differential Scanning Calorimeter(DSC) analysis,  $T_g$  of CN-PPV was 151.69°C. These results demonstrate a good thermal stability of CN-PPV. and Figure 3 shows FT-IR spectrum of synthesized CN-PPV

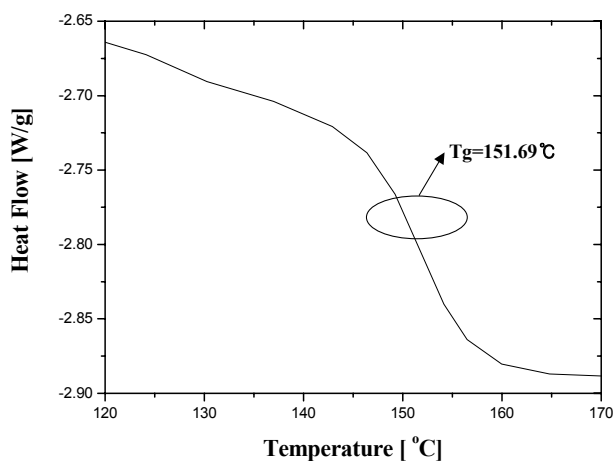


Fig. 2 Analysis of glass transition temperture( $T_g$ ) by DSC

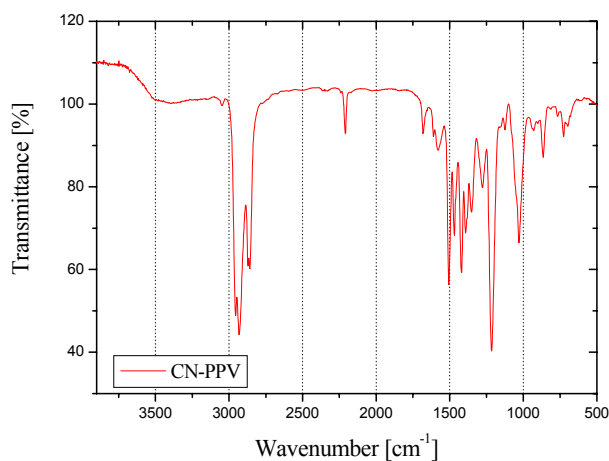


Fig. 3 FI-IR spectrum of synthesized CN-PPV

The device structure was a double layer sandwiched between electrodes. Figure 4 shows Light-emitting diodes.

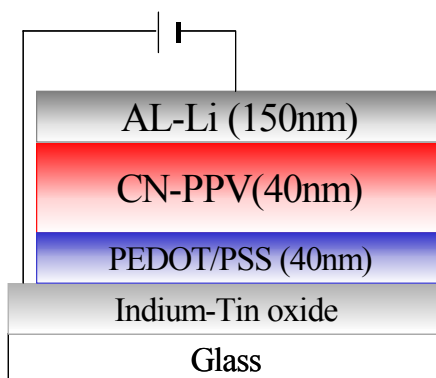


Fig. 4 Configuration of CN-PPV light-emtting diodes.

Through the analysis of the resulting Polymer was excellent solubility among common organic solvents, good thermal stability, and high electron affinity. The device of double layer using CN-PPV was fabricated in order to investigate the electrical and optical properties of polymer light-emitting diode. The PEDOT/PSS was introduced on ITO for improving the luminance and Power efficiency. The thickness of polymer thin film and Aluminum Lithium(Al-Li) as cathode was 40nm, 150nm, respectively. In investigating the fabricated device, turn-on voltage D.C 6V, and C.I.E of the device was X:0.659. Y:0.339. The luminance of about 100cd/m<sup>2</sup> was achieved at D.C 11V. as shown in Fig. 5.

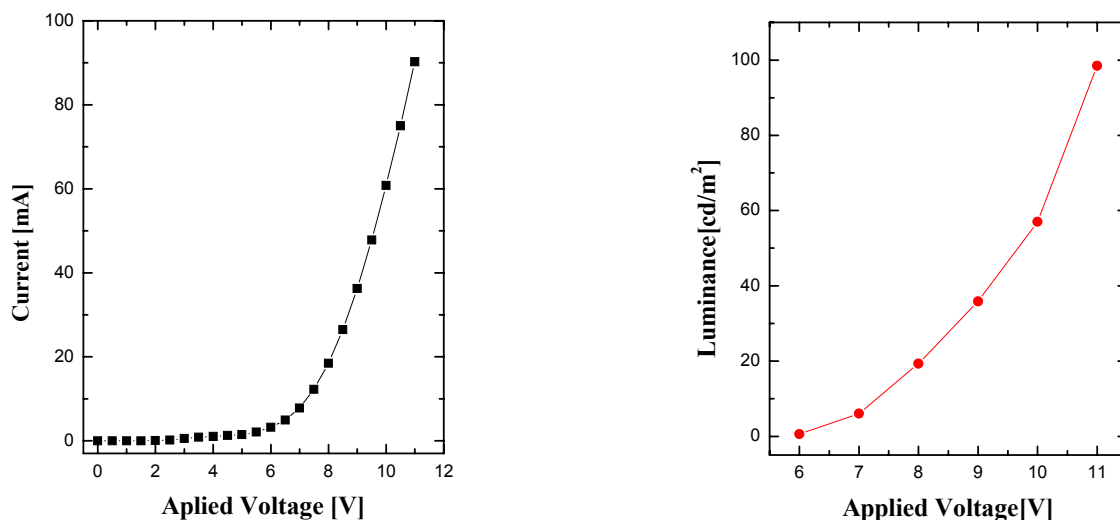


Fig. 5 Electro-Optical properties of fabricated device.

CN-PPV as conjugated polymer was synthesized and a double layer device using it was successfully fabricated in order to investigate the electrical and optical properties of polymer EL device. Synthesis of CN-PPV and the factors determining the electroluminescent properties of device such as luminance and power efficiency will be discussed in detail.

### Reference

- [1] US patent 5,514,878. May. 7. 1996.
- [2] N.C. Greenham, S.C. Moratti, D.D.C. Bradley, R.H. Friend, A.B. Holmes, Nature, 356,(1993), 628.
- [3] S.C. Moratti, R. Cervini, A.B. Holmes, D.R. Baigent, R.H. Friend, Synthetic Metals, 71, 2117-2120, 1995.
- [4] D.R. Baigent, P.J. Hamer, R.H. Friend, S.C. Moratti and A.B. Holmes, Synthetic Metals, 71, 2175-2176, 1995.
- [5] S. H. Kwon, S. H. Cho, J. S. Yoo, and J. D. Lee, J. Electrochem. Soc. **147**(8), 3120-4, 2000

### Acknowledgement

This work was supported by Intelligent Microsystem Center(IMC) in 21C Frontier R&D Program of Ministry of Science and Technology.