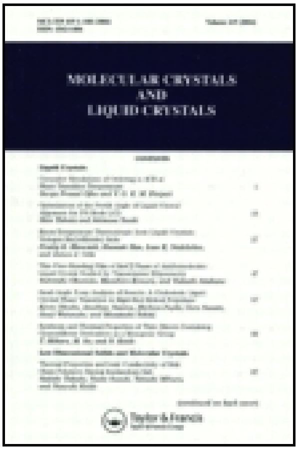

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Electroluminescence from Polyphenylene-Based Materials

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Version of record first published: 04 Oct 2006

To cite this article: Hwan Kyu Kim, Ki-Dong Kim & Taehyoung Zyung (1997): Electroluminescence from Polyphenylene-Based Materials, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 295:1, 27-30

To link to this article: http://dx.doi.org/10.1080/10587259708042788

Mol. Cryst. Liq. Cryst., 1997, Vol. 295, pp. 27–30
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ELECTROLUMINESCENCE FROM POLYPHENYLENE-BASED MATERIALS

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Abstract Poly(phenylene) and its copolymers are a new family of electroluminescent materials with high thermal stability. Their photoluminescent and physical properties were modified in a controlled fashion by copolymerization of the cyclohexadiene-1,2-diacetate monomer (DAC) with both vinylbiphenyl (VBP) and vinyl-N-carbazole (VCZ). Polyphenylene thin films exhibited green photoluminescence centered around 520 nm. The incorporation of unaromatized comonomers into polyphenylene films blue-shifted wavelengths of maximum photoluminescence centered around 500 nm for the DAC/VBP copolymer (8:2). Similarly, polyphenylene thin films exhibited green electroluminescence centered around 505 nm for a device configuration of Al(-)/polyphenylene/ITO(+). The incorporation of unaromatized comonomers into polyphenylene films blue-shifted wavelengths of maximum electroluminescence centered around 495 nm for a device configuration of Al(-)/DAC-VBP copolymer (8:2)/ITO(+).

INTRODUCTION

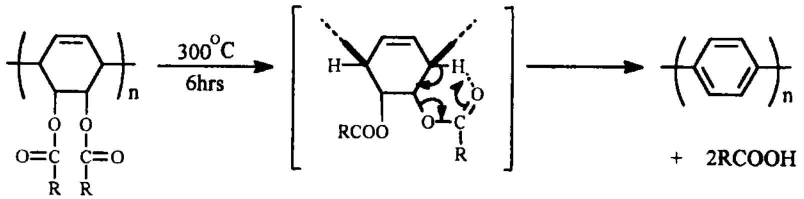
Electroluminescent (EL) devices based on organic thin layers have attracted much attention due to their academic interest and potential applications as large-area flat--panel displays. A variety of conjugated polymers have been reported to exhibit electroluminescence[1-4]. Electroluminescenc in conjugated polymers is well- known to be generated by recombination of electrons injected into the conduction band and holes into valence band to form singlet excitons.

Previously it was reported that new spin-coatable, photoimageable polymers based on polyphenylene with the aim of using them as optical waveguides or low dielectric materials were developed[5-7]. The synthesis of polyphenylene precursors was achieved by radical polymerization of cyclohexadiene-1,2-diacetate. Copolymers with vinyl monomers as comonomers were also synthesized by radical copolymerization, in order to further tune chemical, physical and optical properties[8]. A polyphenylene precursor thin film was made by spin-coating on various substrates such as quartz, NaCl disc, or ITO glass etc. The precursor film was converted into polyphenylene films by curing at 300 °C under inert atmosphere. In a similar way, use of a soluble derivative of polyphenylene allows fabrication of the light emitting diodes by casting the polymer film from solution with heat treatment required. We observed that polyphenylene thin films exhibited green photoluminescence, contrast to a previous report[9]. The incorporation of unaromatized comonomers into polyphenylene films blue-shifted wavelengths of photoluminescence for polyphenylene-based materials and tuned visible light emission from diodes made from polyphenylene-based materials with various consecutive phenyl units separarted by unaromatized comonomers such as vinylbiphenyl or vinyl-N-carbazole. In this paper, we have demonstrated and evaluated the application of poly(phenylene)-based materials for light-emitted diode.

RESULTS AND DISCUSSION

1,3-Cyclohexadiene-5,6-diacetate polymerized very easily to produce homopolymer precursors. The yield of homopolymers was gravimetrically calculated and was in the range of 55 to 60 %. Molecular weights (M_n) based on poly(styrene) standards were 20,000 to 40,000 g/mol with polydispersities (M_w/M_n) of less than 2. The radical copolymerization of vinylbiphenyl or vinyl-N-carbazole with 3,5-cyclohexadiene-1,2-diacetate using AIBN at 60 °C was performed to produce a thermally stable poly(phenylene)-based copolymer with a polymer yield of 40 - 75 %, respectively[7,8]. GPC traces showed that the number-average molecular weight of the copolymers was in the range of 30 x 10^3 to 40 x 10^3 g/mol and the relatively narrow molecular weight distribution of the copolymers ($M_w/M_n \approx$ 1.80) was retained. The copolymer composition was analyzed by ^{1}H NMR.

The poly(phenylene) precursors could be aromatized to poly(phenylene) by heating in thin films. The thermal processes were monitored by thermogravimetric analysis (TGA), IR spectroscopy, and UV spectroscopy. TGA analysis of the diacetate precursor was roughly consistent with the value expected for the loss of two acetic acid molecules followed by aromatization, as shown in SCHEME 1.



SCHEME 1. Thermal conversion of a PPP precursor into a poly(phenylene).

The aromatized polymer was stable for several hours at elevated temperatures.

The reaction probably proceeds via a cyclic transition state, since the carboxylic acid is a good leaving group. Similar TGA results were obtained for other copolymer precursors such as the DAC/VBP copolymer or the DAC/VCZ copolymer.

IR data of poly(phenylene) prepared from the diacetate precursor was observed at 812 cm^{-1} for the C-H out-of-plane bending band of the phenyl groups. The spectra of the poly(phenylene) oligomers had an absorption between 840 and 800 cm^{-1} for the C-H out-of-plane bending band for the phenylene groups. As the number of consecutive phenylene units increased, this peak shifted to lower wavenumbers and attained a limiting value of 802 cm^{-1} for a highly conjugated polymer[8,10]. From IR data, the poly(phenylene) consists of approximately six consecutive phenylene units, separated by unaromatized sections, probably due to the 1,2-repeat unit structure. The precise structure of the unaromatized unit is unknown. Similar IR data obtained from the pyrolysis of the DAC/VBP copolymer (8:2) was observed at 814 cm^{-1} for the C-H out-of-plane bending band of the phenyl groups.

Typical UV spectra of the poly(phenylene) prepared from diacetate precursors showed a maximum absorption around 320 nm tailing into the visible region. Aromatization at higher temperatures (> 300 °C) results in a red shift. The UV absorption of the polymer increases with increasing number of consecutive phenylene rings and shifts toward 380-390 nm for a highly conjugated polymer. When compared with UV spectra of poly(phenylene) oligomers, this poly(phenylene) had an average six consecutive phenylene units, which is consistent with the value obtained from IR data. Thermal conversion of the DAC/VBP copolymer was also studied by thermogravimetric analysis, IR spectroscopy, and UV spectroscopy. Similar results were obtained from heat-treatment of the copolymer.

Electroluminescent properties of poly(phenylene)-based materials was studied as follows: A polyphenylene precursor thin film was made by spin-coating on various substrates such as quartz or ITO glass etc. The precursor film was converted into polyphenylene films by curing at 300 ^{o}C under inert atmosphere. We observed that polyphenylene thin films on quartz exhibited green photoluminescence centered around 520 nm, contrast to a previous report[9], as shown in FIGURE 1. The incorporation of unaromatized comonomers into polyphenylene films blue-shifted wavelengths of maximum photoluminescence centered around 500 nm for the DAC/VBP copolymer and tuned visible light emission from diodes made from polyphenylene-based materials with various consecutive phenyl units separarted by unaromatized comonomers. We, however, observed that a polyphenylene copolymer thin film for the DAC/VCz copolymer (19/1) exhibited yellow photoluminescence centered around 580 nm. Also, we expected that the incorporation of unaromatized comonomers into polyphenylene films blue-shifted wavelengths of maximum photoluminescence from polyphenylene-based materials with consecutive phenyl units separarted by unaromatized comonomers.

This can be explained by the increasing number of consecutive phenylene rings from the highly effective aromatization of polyphenylene copolymer precursor by the base-catalyzed nitrogen atom of carbazole units. Similarly, we observed that polyphenylene thin films exhibited green electroluminescence centered around 505 nm for a device configuration of Al(-)/polyphenylene/ITO(+). The incorporation of unaromatized comonomers into polyphenylene films blue-shifted wavelengths of maximum electroluminescence centered around 500 nm for the Al(-)/DAC-VBP copolymer (8:2)/ITO(+).

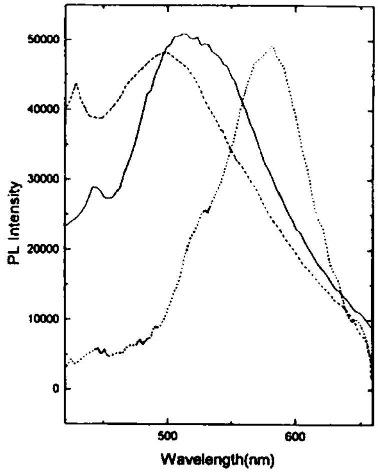


FIGURE 1. Photoluminescence spectra of the present polyphenylenethin film (-); the DAC/VBP copolymer (8:2) thin film (--), and the DAC/VCZ copolymer(19:1) thin film (.....) on quartz ($\lambda_{excitation}$=351 nm).

ACKNOWLEDGEMENT

The research work was supported by the Korean Ministry of Education Research Fund for Advanced Materials at Hannam University in 1995.

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