0273-2289/01/9601-3/0215/$12.25

Soluble Substituted Poly-*p*-phenylenes— A New Material for Application in Light-Emitting Diodes

Synthesis and Characterization

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Abstract

Poly-*p*-phenylenes have attracted a great deal of attention with respect to their applications in displays, light-emitting devices, and batteries. However, the polymer poly-*p*-phenylene obtained by the Kovacic method is insoluble and intractable. The present study reports the preparation of soluble poly(*p*-phenylenes) by polymerization of derivatives of benzene in the presence of a specific aromatic nuclei. The resultant copolymer so obtained is soluble in common organic solvents such as chloroform and toluene. Preliminary studies have indicated that the polymer shows orange photoluminescence and electroluminescence when a potential of 7–10 V is applied to the device.

Index Entries: Poly-*p*-phenylene; toluene–naphthalene copolymer; light-emitting diode; photoluminescence; electroluminescence.

Introduction

Conjugated polymers have attracted a great deal of attention with respect to future applications in large area light-emitting devices and displays. Polymers that possess a delocalized π-electron system along the main chain, termed *conjugated polymers*, have been widely studied since the synthesis of polyacetylene was carried out in 1977. Conjugated polymers are a new class of electronic materials that combine the optical and electronic properties of semiconductors and find wide technologic uses in energy

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storage systems *(1,2)*, sensors *(3,4)*, optoelectronic devices *(5,6)*, drug delivery systems *(7)*, electromagnetic interference/electrostatic charge dissipation (EMI/ESD) shielding *(8,9)*, and light-emitting diodes *(10–12)*. Organic polymers have been expected to be applicable for practical electroluminescent devices because of their high fluorescence efficiency, semiconducting behavior, and possibility of wide selection of colors. Electroluminescent devices with green, yellow, blue, and red have been reported using multilayered film structures consisting of an emitter layer and a carrier transport layer.

There has been long-standing interest in the development of solid-state light-emitting devices. Efficient light generation is achieved in inorganic semiconductors with direct band gaps, such as GaAs, but these are not easily or practically used in large area displays. For this, systems based on polycrystalline ZnS have been developed, although low efficiencies and poor reliability have prevented large-scale production. Because of the high quantum yields of photoluminescence common in organic semiconductors, there has long been interest in the possibility of light emission by these semiconductors through charge injection under a high applied field. Light-emitting devices are fabricated by vacuum sublimation casting of the organic layers, and although the fluorescence emission is quite good, there are practical problems associated with the delocalized π-electron system along the polymer backbone, which confers rigidity to the chain. Many of the conjugated polymers are therefore rigid rod polymers with low solubility and intractibility. One way to improve the processibility is to copolymerize different monomers together and obtain a desired system with better solubility and good fluorescent property. Another way to solve the problem is to prepare a solution processible precursor that can be processed to obtain the desired polymer, e.g., poly(*p*-phenylene vinylene) (PPV). The light emission in the green-yellow part of the spectrum with reasonable high efficiency suggests that PPV can be used for the development of large area light-emitting displays *(13)*. Brouwer et al. *(14)* have made significant progress in developing an economic package for polymer light-emitting devices based on a poly(2-methoxy-5-2'-ethyl-hexyloxy)-1,4-phenylene vinylene (MEH-PPV) system by fabricating them on a substrate that exhibits a low-oxygen and water permeability. A Japanese group reports an extremely exciting development—writing with light on polyaniline films by incorporating TiO_2 particles. Their work relates to driving the photoinduced color change with visible light, which is carried out by incorporating visible light–sensitive semiconductor particles such as CdS and silicon.

In the present work, polymerization of toluene was carried out in the presence of naphthalene using anhydrous aluminum chloride and cupric chloride, and its application in the fabrication of light-emitting diodes was also investigated. The polymer so obtained was characterized by spectroscopic techniques such as Fourier transform infrared (FTIR) and ultraviolet-visible (UV-VIS) and by thermogravimetric analysis.

Materials and Methods

The synthesis of copolymer of toluene and naphthalene (Poly TN) was carried out by the conventional Kovacic method *(15)* using $AlC1_3$ and $CuC1_2$. A heterogeneous reaction mixture consisting of toluene and naphthalene was stirred for 4–6 h in the presence of anhydrous aluminum chloride and cupric chloride at 30°C. After the completion of the reaction, the reaction mixture was washed with hot HCl and consequently washed with distilled water in order to remove the excess aluminum chloride and cuprous chloride. The dark brown polymer obtained was dried under vacuum. The characterization of the resultant polymer was carried out by spectroscopic techniques and thermogravimetric analysis.

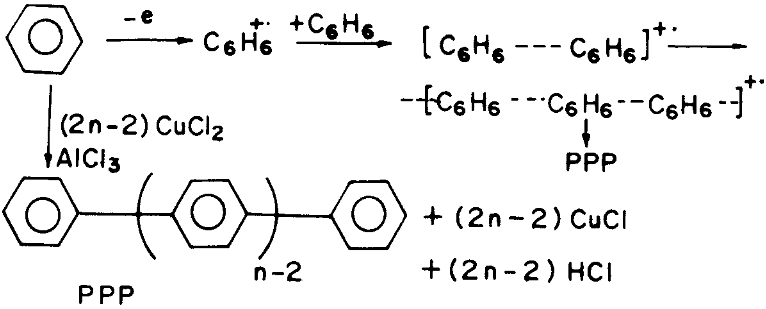
FTIR spectra of the polymer were recorded in KBr on a Perkin-Elmer GX 2000 Optica FTIR spectrophotometer. UV-visible spectra of the polymer in different solvents were recorded on a Shimadzu UV-1601 spectrophotometer. Thermogravimetric analysis of the polymer was recorded on a Mettler TA 3000 system under nitrogen atmosphere at a scan rate of 10°C/min.

Fabrication of Device

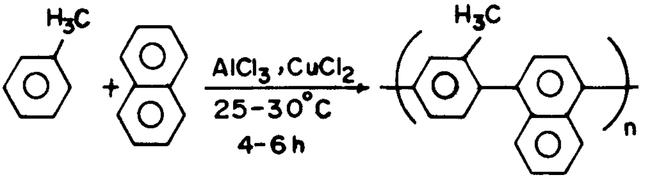
A pattern of indium-tin-oxide (ITO) coated on glass substrate (resistance of 20–40 Ω) was made using a suitable mask, which acts as a hole-injecting layer. A thin layer of the polymer film was vacuum deposited on an ITO electrode at a vacuum of 5×10^{-5} torr. Aluminum, which acts as the electron injecting layer, was also vacuum deposited using thermal evaporation. Voltage in the range of 7–10 V was applied between these two electrodes using Aplab power supply. I-V characteristics of the above device were measured using a Keithley Electrometer 610 D. The electroluminescence of the device was recorded using a Spex 1404 double-grating monochromator, with a resolution of 0.005 nm, attached with a photomultiplier detector and a data-processing system. The photoluminescence spectra were recorded on a Bentham 605 luminescence spectrometer.

Results and Discussion

Copolymer of toluene and naphthalene was prepared as a soluble polyphenylene derivative following the same methodology as that reported by Kovacic *(15)* for the synthesis of poly (*p*-phenylene). The general mechanism for the synthesis of poly (*p*-phenylene) is shown in Scheme 1. The propagation step of this oxidative coupling clearly is a dehydrogenation step via radical cations. The result is a light brown powder that is infusible and insoluble in any organic solvents. Scheme 2 illustrates the copolymerization of toluene and naphthalene in the presence of $AlCl_3$ and $CuCl_2$. The polymer obtained is reddish brown and is soluble in organic solvents such as chloroform, toluene, benzene, and *N*-methyl pyrrolidone.



Scheme 1. Synthesis of poly-*p*-phenylene.



Scheme 2. Synthesis of copolymer of toluene and naphthalene.

IR Studies

The FTIR spectrum of the copolymer in KBr is shown in Fig. 1. The spectrum shows characteristic peaks at 1645, 1447, 1384, 1020, 809, 669, and 466 cm^{-1}. The band at 809 cm^{-1} is indicative of the paralinkage in the polymer. The bands at 1645 and 1447 cm^{-1} are the characteristic bands attributed to the presence of C=C vibration and C-H deformation of the CH_3 group in the copolymer. The absorption band is at 1384 and 1020 cm^{-1} and indicative of the C-H in-plane deformation. The minor peaks at 1159 and 1104 cm^{-1} are characteristic bands of C-H in-plane deformation.

UV-VIS Spectrum

The absorption spectrum of the copolymer in *N*-methyl pyrrolidone and chloroform exhibits absorption bands at 488 and 304 nm and 468 and 249 nm, respectively (Fig. 2). The absorption bands at these wavelengths are associated with the different transitions of the conjugated aromatic system of the polymer. The shift in the absorption band values in the two solvents indicates stronger hydrogen bonding of the polymer with *N*-methyl pyrrolidone, thereby causing the absorption maximum to shift to higher value, implying that a lesser amount of energy is required to excite electrons from lower-energy to higher-energy states. The absorption spectrum of the vacuum-deposited polymer film on quartz plate shows absorption bands at 525, 491, and 306 nm (Fig. 3).

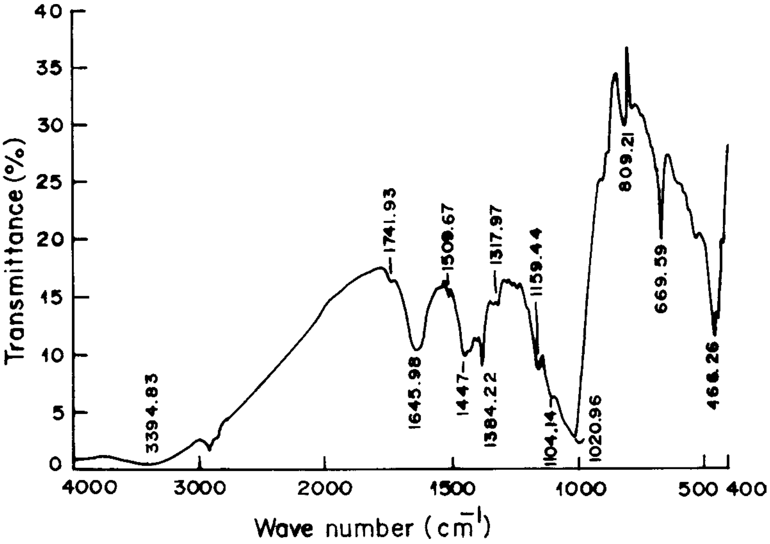


Fig. 1. FTIR spectrum of Poly (TN) in KBr.

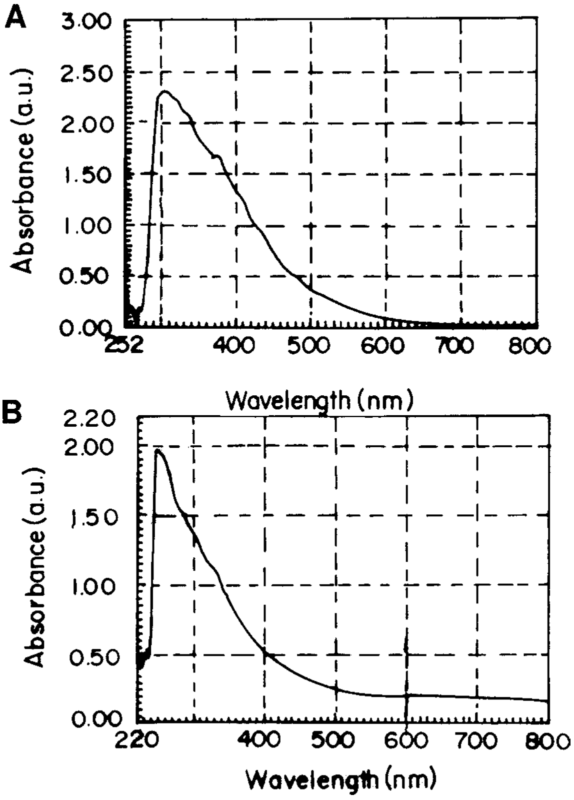


Fig. 2. UV-VIS absorption spectrum of poly (TN) in **(A)** *N*-methyl pyrrolidone and **(B)** chloroform. a.b., arbitrary units.

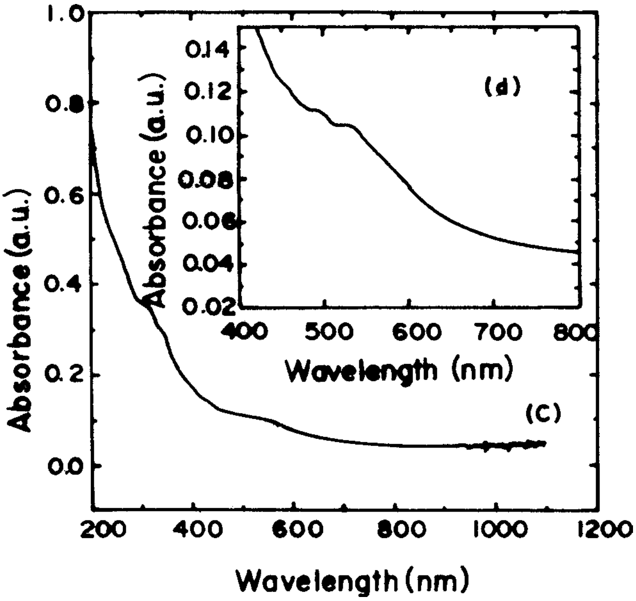


Fig. 3. UV-VIS absorption spectrum of vacuum-deposited Poly (TN) film on quartz plate. (c) 2nd absorption spectrum of Poly (TN) in the range 400–800 nm; (d) a.u., arbitrary units.

Thermogravimetric Analysis

Thermogravimetric analysis of the copolymer shows that the thermal stability of the copolymer in comparison to the parent polymer, poly-*p*-phenylene, was significantly lower. Poly-*p*-phenylene was thermally stable up to 450°C under ambient conditions, and the copolymer of toluene and naphthalene was found to be thermally stable up to 350°C (Fig. 4). A weight loss at 250°C might be attributed to some polymeric chain rearrangement in the polymer matrix. The sharp weight loss from 375 to 520°C might be attributed to the decomposition of the polymeric backbone.

I-V Characteristics of Device

To record the I-V characteristics of the copolymer film, a device was fabricated by vacuum depositing polymer film on an ITO electrode on the top of which a thin layer of aluminum was deposited. The schematic representation of the device is shown in Fig. 5. Devices of varying thickness were fabricated that emitted orange light when a voltage of about 10 V was applied across it. The I-V characteristics of the devices were also recorded. A typical I-V curve of the device is shown in Fig. 6. The I-V curve shows that the current rises steeply above 9 V, indicating the onset of light emission (threshold voltage). Threshold voltage of the device based on the copolymer was in the range of 7–10 V, depending on the thickness of the polymer layer.

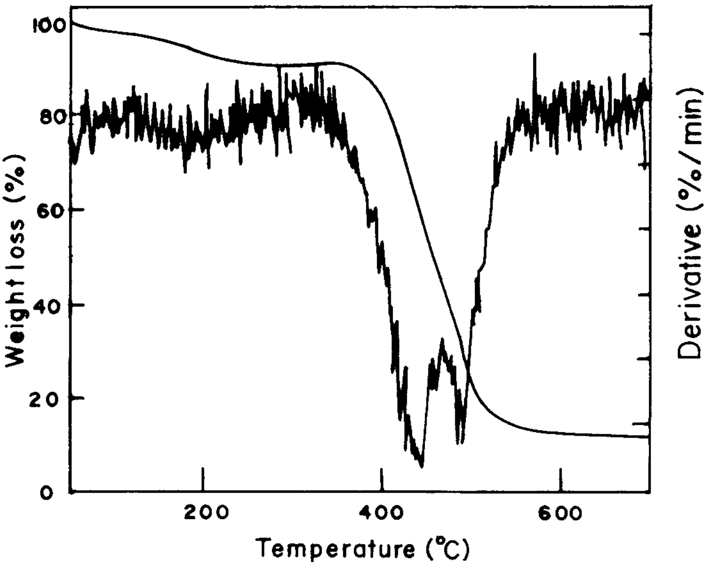


Fig. 4. Thermogravimetric analysis curve of Poly (TN) from 50 to 700°C under N_2 atmosphere at 10°C/min.

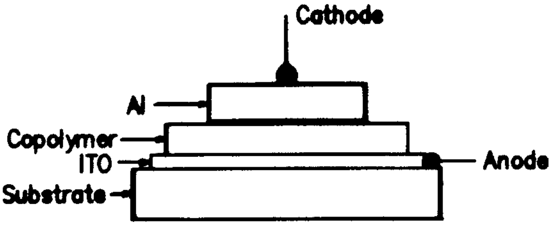


Fig. 5. Schematic diagram of polymer light-emitting device based on Poly (TN).

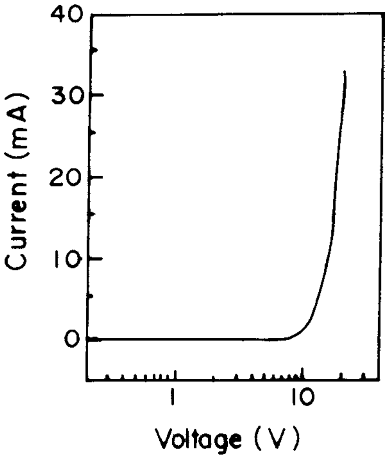


Fig. 6. I-V characteristics of ITO/Poly (TN)/Al (active area = 4 mm^2).

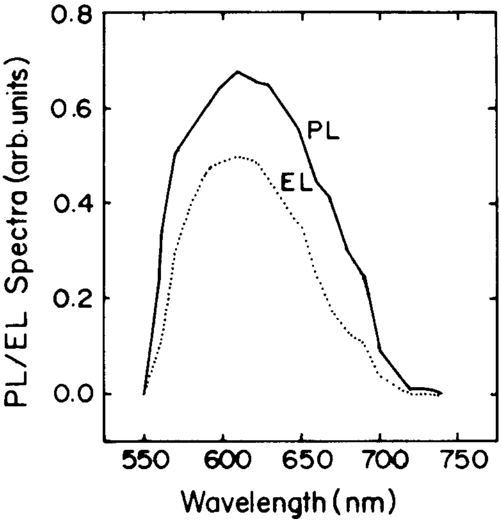


Fig. 7. Photoluminescence (PL) and electroluminescence (EL) spectra of poly (TN) device. a.u., arbitrary units.

Photoluminescence and Electroluminescence Spectra

The copolymer showed luminescence in the visible region (Fig. 7). The photoluminescence spectrum of the material was studied after vacuum depositing it on a fused silica substrate. The thickness of the film was about 1 μ. The photoluminescence spectrum showed a peak at 610 nm. The electroluminescence spectrum of the copolymer was studied on the device, and the peak position of the emission was observed at about 610 nm. In comparison with absorption spectrum, the emission spectrum shifted about 120 nm toward the red side. This results from the Frank-Condon shift owing to the difference in interatomic distance between the ground state (π electron) and the first excited state (π*). A similar shift has been observed for other polymeric systems and small molecular systems *(16,17)*.

Conclusion

We have synthesized a copolymer of toluene and naphthalene using the same methodology as for the synthesis of poly-*p*-phenylene and have shown its practical utility as a potential material for application in polymer light-emitting diodes.

Acknowledgments

We thank Prof. A. K. Raychaudhuri, Ex-Director, National Physical Laboratory, for his interest in this work. Thanks are also due to Dr. S. C. K. Mishra for recording the I-V plot of the device and to Dr. S. T. Lakshmi Kumar for recording the photoluminescence spectra of the copolymer.

References

1. Matsunaga, T., Daifuku, H., Nakajima, T., and Kawage, T. (1990), *Polym. Adv. Technol.* **1,** 33–40.
2. Trinidad, F., Montemayor, M. C., and Falas, E. (1991), *J. Electrochem. Soc.* **138,** 3186–3190.
3. Dhawan, S. K., Kumar, D., Ram, M. K., Chandra, S., and Trivedi, D. C. (1997), *Sensors Actuators B* **40,** 99–103.
4. Bartlett, P. N., Patricia, B. M. A., and Sin, K. L. C. (1989), *Sensors Actuators* **20,** 287–292.
5. Dhawan, S. K., Ram, M. K., Malhotra, B. D., and Chandra, S. (1995), *Synth. Met.* **75,** 119–122.
6. Kitani, A., Yano, J., and Sasaki, K. (1986), *J. Electroanal. Chem.* **209,** 227–234.
7. Okano, T., Bae, Y. H., and Kim, S. N. (1990), in *Pulsed and Self Regulated Drug Delivery*, Kost, J., ed., CRC, Boca Raton, FL, p. 17.
8. Dhawan, S. K., Koul, S., Chandra, S., and Venkatachalam, S. (1998), *J. Coated Fabrics* **28,** 29–36.
9. Shaclette, L. W., Colaneri, N. F., Kulkarni, V. G., and Wessling, B. (1992), *J. Vinyl Technol.* **14,** 118–122.
10. Ostergard, T., Kvarnstrom, C., Stubb, H., and lvaska, A. (1997), *Thin Solid Films* **311,** 58–61.
11. Leising, G., Tasch, S., Meghdadi, F., Athouel, L., Froyer, G., and Sherf, U. (1996), *Synth. Met.* **81,** 185–188.
12. Yang, Y. (June 1997), *Mater. Res. Soc. Bull.* 31–37.
13. Burroughes, J. H., Bradley, D. D. C., Brown, A. R., Marks, R. N., Mackay, K., Friend, R. H., Burns, P. L., and Holmes, A. B. (1990), *Nature* **347,** 539.
14. Brouwer, H. J., Krasnikov, V. V., Pham, T. A., Gill, R. E., and Hadziioannou, G. (1998), *Appl. Phys. Lett.* **73,** 708–711.
15. Kovacic, P. and Oziomek, J. (1964), *J. Org. Chem.* **29,** 100–112.
16. Burrows, P. E., Shen, Z., Bulovic, V., McCarty, D. M., Forrest, S. R., Cronin, J. A., and Thompson, M. E. (1996), *J. Appl. Phys.* **79,** 7991–8006.
17. Zenz, C., Graupner, W., Tasch, S., Leising, G., Mullen, K., and Scherf, U. (1997), *Appl. Phys. Lett.* **71,** 2566–2568.