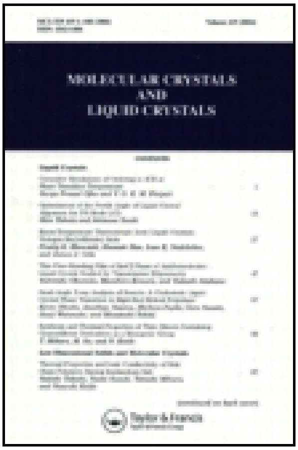

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Synthesis and Luminescent Properties of Hyperbranched Poly(P-Phenylene)s by Molecular Architecture Engineering

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Hyperbranched poly(p-phenylene)s, as a new family of electroluminescent materials, were synthesized by both Suzuki reaction and a nickel-catalyzed Grignard coupling reaction. P_48 and P_410 showed the UV absorption band at the longer wavelength than P_38 and P_310, even though they have the same number of consecutive phenyl groups. Photoluminescent (PL) spectra of P_48 and P_410 showed a blue emission at 490–496 nm, while P_38 and P_310 thin films showed a maximum PL peak around 420–440 nm in the deep blue region.

Keywords: hyperbranched poly(p-phenylene)s; electroluminescent materials; blue emission

INTRODUCTION

Electroluminescence (EL) devices based on polymeric thin layers have attracted much attention because of their academic interests and potential utility of this technology in a wide variety of applications such as large area flat-panel displays and light-emitting diodes.[1-2] EL polymeric materials offer advantages such as low operating voltages, three primary R/G/B colors, fast response time, high quality of display and ease of device processability with semiconductor technologies, compared to inorganic EL materials. Since the first report of the polymer light-emitting diodes based on poly(*p*-phenylenevinylene)[3], a

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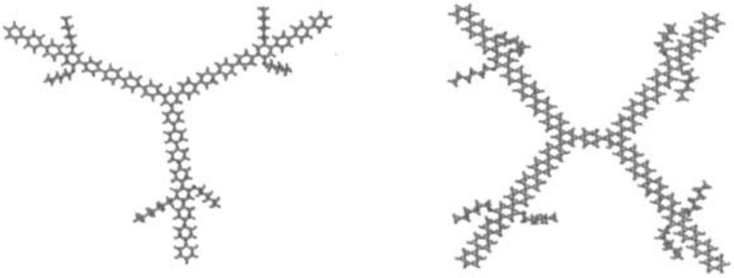
number of different polymers have been synthesized and extended efforts have been made to obtain high performance devices from polymeric materials. Recently, our main materials efforts have been focussed on developing blue light-emitting diodes capable of operating at ambient temperature, low voltages and easy processability with low price.[4-5]

Very recently, we prepared processable alkoxy-substituted PPP-based copolymers as a new type of the blue EL materials using the well-known Suzuki reaction of alkoxy-substituted aromatic boronic esters with various aryl halides. The functionalized side chains allow the PPP-based materials to remain soluble during polymerization as well as processing, thereby offering new opportunities for potential application as electroluminescent materials.[5-6] Also, these present polymers are easy tune of chemical and optical properties through various structural design.[7] In this paper, hyperbranched poly(p-phenylene), the geometry of which is depicted in Scheme 1, has been studied as a candidate for active materials in blue-light -emitting diodes.



P_38 P_48

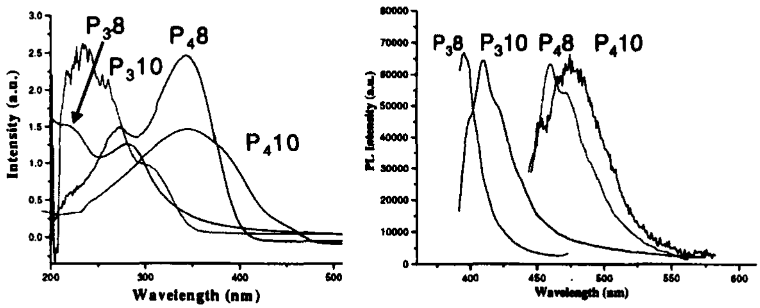
SCHEME 1 Chemical structures of hyperbranched oligo(p-phenylene)s (8 of consecutive phenyl units in 3 arms and 4 arms: P_38 and P_48).

RESULTS AND DISCUSSION

Hyperbranched oligo(p-phenylene)s were synthesized as follows:[7] The Pd-catalyzed coupling reaction of phenylboronic acid with bromobenzene derivatives was applied to build-up the desired oligo(p-phenylene)s as a side arm of the hyperbranched oligo(p-phenylene)s.

The chemical structures were identified by ^{1}H- and ^{13}C-NMR, and FT-IR spectroscopies. The number-average molecular weight (Mn) of the hyperbranched oligo(p-phenylene)s was determined by GPC in the range of 6.8 x 10^3 to 8.7 x 10^3 with the polydispersity index (Mw/Mn) range of 1.5-2.5. They are readily soluble in common organic solvents such as methylene chloride, dichloroethane, tetrahydrofuran, toluene, and so forth. Their thermal properties were examined by TGA and differential scanning calorimetry (DSC). They have the melting temperature range of 207 to 228 °C. They exhibit thermal resistance up to 450 °C and alkoxy side chain decomposes at the beginning step around 450 °C in nitrogen, while poly(p-phenylene) derivatives are quite thermally stable up to 550 °C in nitrogen.[2] An oligo(p-phenylene) of [$P_3$8] showed a starting weight loss at 400 °C. Other oligo(p-phenylene)s have a similar thermal behavior.

Their IR spectra were observed at the 806 cm^{-1} for the C-H out-of-plane bending band of the phenyl group. As the number of consecutive phenylene units increased, this peak shifted to lower wavenumber and attained a limiting value of 802 cm^{-1} for a highly conjugated polymer.[8] Typical UV spectra of hyperbranched oligo(p-phenylene)s showed a maximum absorption around 300-360 nm tailing into the visible region (see Figure 1(a)). Their UV absorption increases with the number of the consecutive phenylene groups.



(a) (b)

FIGURE 1 UV absorbance (a) and PL spectra (b) of hyperbranched poly(p-phenylene)s.

Surprisingly, $P_4$8 and $P_4$10 showed the UV absorption band at the longer wavelength than P_38 and P_310, even though they have the same number of the consecutive side phenyl groups. The aromatic ring in hyperbranched poly(p-phenylene)s are already twisted out of conjugation by about 22°.[1] Any further increase in this torsion angle might lead to a blue shift in the UV absorption due to the decrease of π-conjugation length. In the case of P_48 and P_410, the additional phenyl group in the main chain, compared to P_38 and P_310, could already twist in backbone enough to release or lessen the torsion angle in the side consecutive phenyl arms in hyperbranched poly(p-phenylene)s, producing longer π–conjugation length. It also gives a red-shift. The photoluminescent spectra of P_38 and P_310 showed a maximum peak of 400-420 nm in the dilute solution and 420-440 nm in the hyperbranched poly(p-phenylene) thin films. The photoluminescent spectra of P_48 and P_410 showed a maximum peak of 490-496 nm, since they have a lesser torsion angle than P_38 and P_310 (see Figure 1(b)).

ACKNOWLEDGEMENT

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