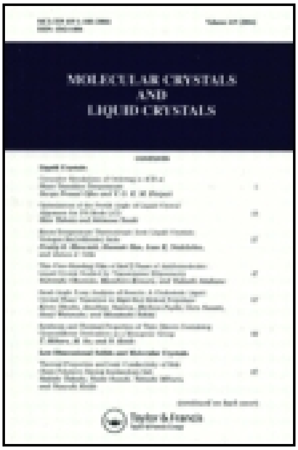

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Synthesis and Properties of Highly Phenyl-Substituted Fluorene Copolymers Containing Hole and Electron Transporting Moieties Via Diels-Alder Polymerization

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SYNTHESIS AND PROPERTIES OF HIGHLY PHENYL-SUBSTITUTED FLUORENE COPOLYMERS CONTAINING HOLE AND ELECTRON TRANSPORTING MOIETIES VIA DIELS-ALDER POLYMERIZATION

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Highly phenyl-substituted fluorene copolymers with hole and electron transporting moieties in the main chain were synthesized by using Diels-Alder polymerization. These polymers show good solubility in common organic solvents, high thermal stability, and strong blue photoluminescence in solid films. Cyclic voltammetry studies revealed that these polymers possess low-lying HOMO energy levels ranging from -5.99 to -6.00 eV.

Keywords: Diels-Alder reaction; highly phenyl-substituted fluorene copolymer; photoluminescence

INTRODUCTION

Fluorene-based polymers have emerged as blue emitting materials suitable for use in polymer light-emitting diodes (PLEDs) because of their highly efficient photoluminescence (PL) and electroluminescence (EL), and also as host material for internal color conversion techniques [1]. Various

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polyfluorene copolymers were synthesized with emission colors covering the entire visible regions [2,3]. One area of ongoing research is the quest for a stable blue-emitting material. Polyphenylene-based materials have been the main focus of interest, with polyfluorenes being a subject of particular attention in recent years. Although poly(9,9-dialkylfluorene)s can be prepared in good yield with molar mass [4] and have been used to make efficient blue-emitting devices [5], they still have a few of problems as potential candidates for blue LEDs.

Firstly, they tend to form yellow- or green-emitting aggregates or excimers on heating during device formation or operation. Secondly, there is an imbalance in charge carriers due to large injection barriers, and differential charge carrier mobilities.

Until now, however, most of fluorene-based polymers have been synthesized by using transition metal catalyzed polymerization [6,7]. High purities for all materials should be essential for good LED performance since some impurities including metal catalysts act mostly as quenching sites for excitons. Therefore, in this article, we describe the synthesis and characterization of highly phenyl-substituted fluorene copolymers via Diels-Alder polymerization without transition metal catalyst to get polymers with intrinsically high purity. In addition, high molecular weights are expected to be achieved because the retro Diels-Alder reaction should be prevented by the loss of carbon monoxide during the thermal polycondensation.

EXPERIMENTAL SECTION

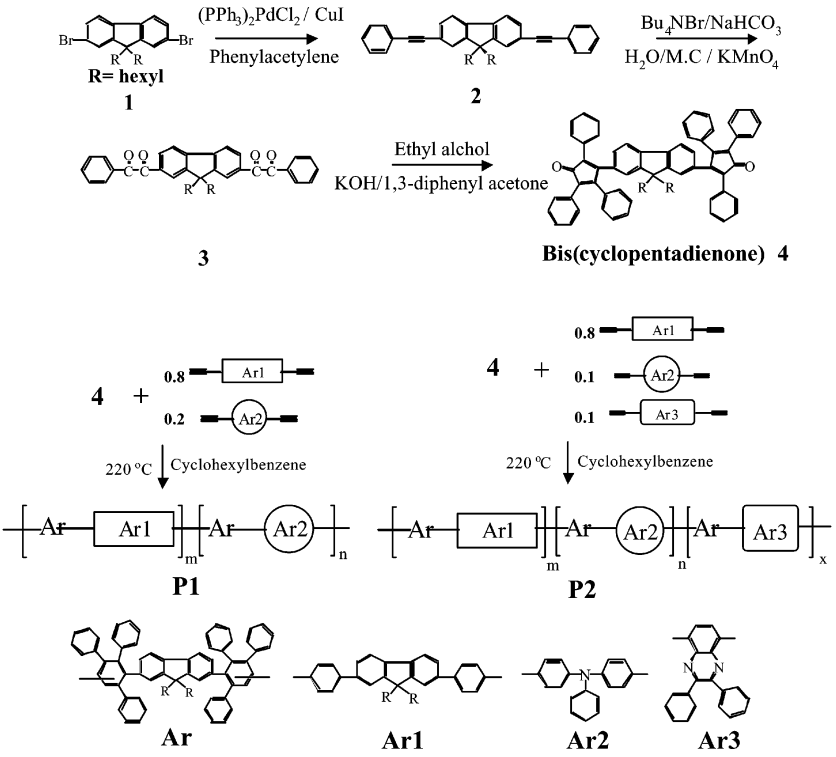
Materials

2,7-Bis(4-ethynylphenyl)-9,9-di-n-hexylfluorene,bis(4-ethynylphenyl) phenylamine and 5,8-diethynyl-2,3-diphenylquinoxaline were prepared as described in the literature [8–10]. Synthesis of 2,7-bis(phenyloxoacetyl)-9,9-di-n-hexylfluorene **3** was described in our previous publication [11].

Synthesis

2,7-Bis(3-oxo-2,4,5-triphenylcyclopenta-1,4-dienyl)-9,9-di-n-hexylfluoene (4)

A solution of **3** (4.6 g, 7.6 mmol) and 1,3-diphenylaceton (3.4 g, 16.1 mmol) in 150 mL of absolute ethanol was brought to near boiling. A solution of potassium hydroxide (0.31 g) in 6.2 mL of water was then added and the resulting black solution was refluxed for 3 h. The reaction mixture was cooled, and the black precipitate was filtered, washed with ethanol, and recrystallized from ethanol containing 5% methylene chloride to give 4.5 g (62%) of compound **4**. m.p: 235 $\sim$ 237°C. ^{1}H NMR ($CDCl_3$, δ): 7.44–7.46 (d,



SCHEME 1 Synthesis of the bis(cyclopentadienone) monomer **4** and the corresponding polymers.

2H), 7.13–7.26 (m, 26H), 6.96–6.98 (d, 4H), 6.88–6.90 (d, 2H), 6.82 (s. 2H), 1.42–1.50 (t(br), 4H), 1.15–1.20 (m, 4H), 0.95–1.05 (m, 4H), 0.82–0.90 (m, 10H), 0.25 (br, 4H)

Synthesis of P1

A 50 mL ample was charged with a suspension of compound 4(0.4 g, 0.42 mmol) and cyclohexylbenzene (2.1 mL). To this mixture was added 2,7-bis(4-ethynylphenyl)-9,9-di-n-hexylfluorene (0.18 g, 0.34 mmol) and bis(4-ethynylphenyl)phenylamine (24.7 mg, 0,08 mmol), giving an initial concentration of reactants in the solvent of 0.4 mol/L followed by degassing by a freeze-pump-thaw technique. The ample was then purged with argon, sealed, and placed in oil bath at 220°C for 48 h. After cooling to room temperature, 20 mg of *p*-tolylacetylene for end-capping was added and then the ample was resealed followed by stirring at 200°C for further 5 h. The clear viscous yellow liquid was cooled, and diluted with toluene, and precipitated into methanol. The obtained polymer was dissolved with chloroform. The solution was filtered through a micro filter to remove residual particles and reprecipitated in methanol. The obtained polymer was dried in a vacuum oven at 40°C for 2 days. Yield: 0.44 g (76%).

Synthesis of P2

P2 was synthesized as similar as described in **P1**, using 0.4 g (0.42 mmole) of compound **4**, 0.18 g (0.34 mmol) of 2,7-bis(4-ethynyl phenyl)-9,9-di-n-hexylfluorene, 12.3 mg (0,04 mmol) bis(4-ethynylphenyl)-phenylamine and 13.9 mg (0.04 mmole) of 5,8-diethynyl-2,3-diphenyl-quinoxaline to give 0.5 g (86%) of **P2**.

RESULTS AND DISCUSSION

As shown in Scheme 1, Diels-Alder polycondensation of the bis(cyclopentadienone) (**4**) and the corresponding diacetylene monomer was performed in a Schlenk tube so that we could visually monitor the reaction. The reaction mixture was prepared in cyclohexylbenzene in a sealed tube. The tube was degassed by a series of freeze-pump-thaw cycles, sealed, and immersed in a thermo-regulated bath held at 220°C. After polymerization, the resulting polymers were recovered by dilution of the viscous reaction mixture with toluene, followed by precipitation into methanol. The polymer with light yellow fibrous materials was readily soluble in common organic solvents. In FT-IR spectroscopy, intense streching band at 1710 cm^{-1}, which is attributed to the carbonyl groups in the bis(cyclopentadienone) monomer disappeared after polycondensation. The molecular weights of these polymers were determined by GPC using THF as an eluent and polystyrene as a standard. The number-average molecular weights (M_n) and weight-average molecular weights (M_w) of the polymers ranged from 19,000 to 40,100 and 91,500 to 192,700, respectively, with a polydispersity index ranging from 4.7,4.8. The polymer loses less than 5% of their weight on heating to 400°C, demonstrating their good thermal stability.

The absorption and emission spectra of the polymers obtained for diluted chloroform solution and thin film are illustrated Figure 1. P1 shows absorption maximum at 342 nm in chloroform solution, whereas its absorption maximum of the film is hypsochromically shifted by 6 nm (336 nm). These results indicate the difference of the polymer chain conformation between in a solution phase and in a solid phase. Polyfluorenes have been reported to have the twisted conformational structure caused by the phenyl-phenyl torsion [12]. The absorption maxima of P2 in solution and solid state are very similar to the P1.

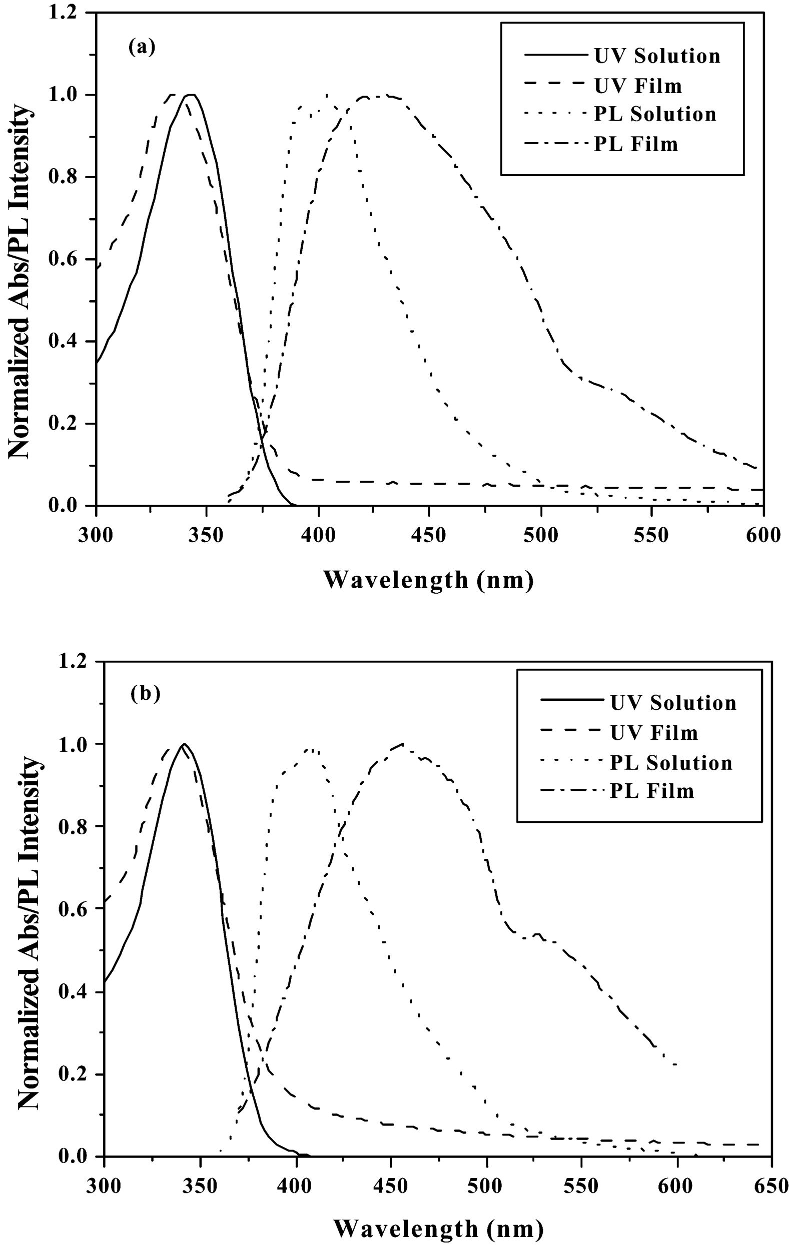


FIGURE 1 UV-vis absorption and PL spectra of P1 (a) and P2 (b) in chloroform solution and films.

In the case of PL spectra, both polymers show deep blue luminescence in solution. The PL maximum of P1 in solution appear at 404 nm, whereas P2 shows PL maximum in a lower energy region (410 nm) than P1. In comparision with the solution PL spectra, P1 and P2 as solid state exhibit bathochromically shifted by 26 nm and 46 nm, respectively. A significantly larger bathochromic shift in emission than in absorption from the solution to film states suggested that a stronger chromophore interaction took place in the excited state, rather than in the ground state. In additon, the greatly broadened PL spectra in solid state compared with their solution PL may be caused by the highly phenyl-substituted units, that enhance the interchain interaction, in the film due probably to the efficient chain stacking by a phenyl side chain. The interchain interactions play a factor for the red-shiftness of PL spectra of the polymers compared with those in solution. In the case of the interchain interactions related to polyfluorenes, it has been reported that excimer formation is favored over chain aggregation. The featureless emission around 530 nm in the PL spectra of P1 and P2 films is caused by excimer formation.

Figure 2 shows the cyclic voltammograms of the polymers in 0.1 M tetrabutylammonium tetrafluoroborate ($TBABF_4$) in acetonitrile, which were performed in a three-electrode cell system with a Ag/AgCl reference at the scan rate of 20 mV/s. In the absence of a direct measurement of the

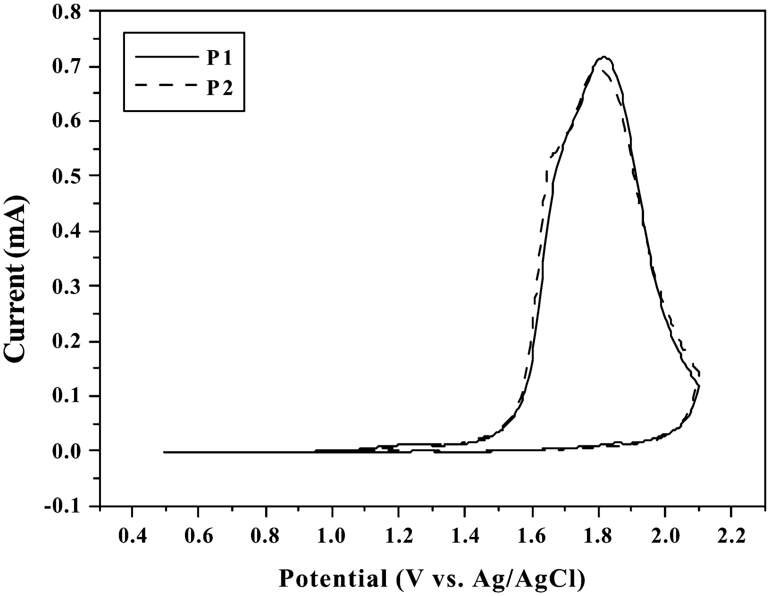


FIGURE 2 Cyclic voltammograms of the polymers P1 and P2.

reduction potential, the lowest unoccupied molecular orbital (LUMO) energy levels were obtained by the substraction of the optical band gap, calculated from the absorption edge of a polymer solution. The HOMO/LUMO energy values of the polymers are $-5.99/-2.72$ for P1 and $-6.00/-2.73$ for P2. Intensive studies on the EL properties of these polymers in LED are in progress.

CONCLUSIONS

In this paper, we have shown that it is possible to synthesize highly phenyl-substituted fluorene copolymers with intrinsically high purity by using Diels-Alder polymerization. The polymers were shown to have good solubility in common organic solvents and thermal stabilities. The polymers showed strong blue PL emission at 430 nm and 456 nm in solid state, respectively. The chemical tuning of other derivatives of highly phenyl-substituted fluorene copolymers and further studies on their properties with EL devices are in progress.

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