

Synthesis of Benzothiadiazole-Based Liquid Crystalline Polyacrylates for Polarized Light Emitting Diodes

Yung-Hsin Yao, Liang-Rern Kung and Chain-Shu Hsu*

Department of Applied Chemistry, National Chiao Tung University, 1001 Ta Hsueh Road, Hsinchu 300, Taiwan, Republic of China

*(*Author for correspondence; Tel.: +886-3-5131523; Fax: +886-3-5131523; E-mail: cshsu@mail.nctu.edu.tw)*

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Abstract

Two benzothiadiazole-based liquid crystalline polyacrylates were synthesized. These polymers revealed a nematic liquid crystal phase and exhibited photoluminescence as well as polarized electroluminescence when incorporated into light-emitting diode applications. The polymers showed dichroic ratios of about 8.3–8.8 in UV-vis absorption and photoluminescence emission. The polymer with vinylene linkages (**P2**) showed better electroluminescence device performance than that with acetylene linkages (**P1**). The **P2** device emitted red light at 604 nm with a turn-on voltage at 6 V, and a maximum polarized luminance of 235 cd/m² at 12 V, with an efficiency of 0.09 cd/A and a polarization ratio of 6.5.

Introduction

During the last few decades, liquid crystalline polymers have been extensively investigated, not least because of their unusual mechanical, optical and rheological properties [1–3], and the considerable possibility to utilize them as polarized emitters in organic light emitting diode structures [4, 5]. Such a polarized light source became of interest for a backlight in a liquid crystalline display, since it could replace a combination of a normal backlight and a polarizer. The expected benefit is that power efficiency can be enhanced because absorption by the polarizer can be avoided. With their unique self-organizing nature and fluidity, polymeric liquid crystalline materials generally have good processability, allowing simple fabrication by solution processes, and an intrinsically high durability [6, 7].

The synthesis of several liquid crystalline polymers containing mesogenic conducting groups, either hole (benzothiadiazole) or electron (oxadiazole) transport moieties, has been reported [8–11]. These materials showed charge transport and electroluminescence (EL) properties which resulted from high electron and/or hole drift mobilities owing to the aligned and stacked structures in the mesophase [12]. Moreover, it was reported recently that electroluminescent devices using the aforementioned materials exhibited polarized emissions [13–15]. Among various molecular alignment techniques, cooperative alignment of a pendant chromophore within a liquid crystalline material has been extensively studied [16]. The conventional meth-

od to achieve monodomain alignment of liquid crystals is to use an alignment layer. The alignment layer should permit hole injection and transport from the anode to the aligned emission layer. Common alignment materials include polyimide doped with hole-transporting materials [17], for example, poly(*p*-phenylene vinylene) [18–20] and poly(3,4-ethylene-dioxythiophene) (PEDOT)-poly(styrene-sulfonic acid), which show good conducting, transparency and film-forming properties [21].

Recently, we reported polarized EL of a liquid crystalline polyacrylate based on bistolane mesogen with PEDOT as an alignment layer [22]. This device emitted in the blue region with a dichroic ratio of 6.1 and a brightness of 3 cd/m² at 14 V. In this work, the syntheses and comparative investigation of two benzothiadiazole-based liquid crystalline polymers are described. The electronic properties as well as the polarized EL properties of these polymers have been evaluated.

Experimental

Materials and instrumentation

All manipulations involving air-sensitive reagents were performed under an atmosphere of dry argon. All reagents, unless otherwise specified, were obtained from Aldrich, Acros, and TCI Chemical Co. and were used without further purification. All solvents were carefully dried and purified under a nitrogen flow. ¹H- and ¹³C-NMR spectra

were recorded using a Varian 300 spectrometer and were referenced to tetramethylsilane. Gel permeation chromatography was performed with a VE-2001 gel permeation chromatograph in tetrahydrofuran (THF) using a calibration curve of polystyrene standards. Polarized UV-vis spectra were measured with a Shimadzu UV-1601 spectrophotometer with a polarizer placed between the sample and the detector. Spectra were measured with the polarizer aligned parallel and perpendicular to the rubbing direction. Polarization ratios were defined as the parallel to the perpendicular intensity. Polarized photoluminescence (PL) measurements were measured with a Shimadzu RF-5301 PC spectrofluorophotometer with a polarizer.

Polarized device fabrication and characterization

Polarized polymer light-emitting diodes were fabricated on indium tin oxide (ITO) coated glass substrates cleaned sequentially in ultrasonic baths of detergent, deionized water, 2-propanol, deionized water, and acetone. UV-ozone treatment was carried out for 3 min as the final step of cleaning to improve the contact angle just before film formation. Onto the ITO-coated glass a layer of PEDOT film was spin-coated from an aqueous dispersion. After baking, the PEDOT was rubbed by a rubbing machine and was used as the alignment layer. Solutions of the liquid crystalline polymers in toluene were prepared and spin-coated on top of the rubbed-PEDOT surface. After annealing for 1 h, calcium (35 nm) and aluminum (100 nm) cathodes were deposited onto the aligned emitting films by thermal evaporation through a shadow mask. The polarized device properties were determined with a Photo Research PR-650 Spectra Scan instrument. Spectra were measured with the polarizer aligned parallel or perpendicular to the rubbing direction.

Synthesis

6-{4-[2-(7-Bromo-2,1,3-benzothiadiazol-4-yl)-1-ethynyl]phenoxy}-1-hexanol (1)

Compound **1** was synthesized according to a similar method reported in the literature [23]. 6-[4-(1-Ethynyl)phenoxy]-1-hexanol (0.92 g, 4.25 mmol), bis(triphenylphosphine) palladium(II) chloride (0.02 g, 0.03 mmol), copper(I) iodide (0.03 g, 0.14 mmol), triphenylphosphine (0.07 g, 0.26 mmol), and 4,7-dibromo-2,1,3-benzothiadiazole (0.5 g, 1.7 mmol) were dissolved in 50 mL of triethylamine under an atmosphere of nitrogen. The mixture was heated at 80 °C for 24 h. The solvent was removed by a rotatory evaporator and ethyl acetate was added to the crude product. The ethyl acetate solution was extracted with ammonium chloride and then washed with water, saturated NaCl solution, and dried over anhydrous MgSO₄. After the ethyl acetate solution had been removed, the crude product was purified by column chromatography (silica gel, ethyl acetate-to-hexane ratio 1:1), with a yield

of 0.6 g (86%) of a yellow compound with a melting point of 102–103 °C.

¹H-NMR (CDCl₃, δ, ppm): 1.40–1.60 (m, 6H), 1.80–1.84 (m, 2H), 3.64–3.69 (t, *J*=6.6 Hz, 2H), 3.97–4.01 (t, *J*=6.6 Hz, 2H), 6.88–6.91 (d, *J*=8.4 Hz, 2H), 7.61–7.64 (d, *J*=7.5 Hz, 2H), 7.81–7.84 (d, *J*=7.5 Hz, 2H).

¹³C-NMR (CDCl₃, δ, ppm): 25.3, 26.2, 28.7, 32.1, 62.3, 67.8, 92.6, 92.9, 110.4, 114.1, 117.9, 122.0, 124.2, 136.0, 136.2, 151.0, 157.2, 159.6.

6-[4-(2-{7-[2-(4-Pentylphenyl)-1-ethynyl]2,1,3-benzothiadiazol-4-yl}-1-ethynyl)phenoxy]-1-hexanol (2)

6-[4-[2-(7-Bromo-2,1,3-benzothiadiazol-4-yl)-1-ethynyl]phenoxy]-1-hexanol (1.0 g, 2.25 mmol), bis(triphenylphosphine) palladium(II) chloride (0.02 g, 0.02 mmol), copper(I) iodide (0.02 g, 0.1 mmol), triphenylphosphine (0.05 g, 0.18 mmol), and 1-ethynyl-5-pentylbenzene (0.6 g, 3.48 mmol) were dissolved in 50 mL of triethylamine under an atmosphere of nitrogen. The mixture was heated at 80 °C for 24 h. The solvent was removed by a rotatory evaporator and ethyl acetate was added to the crude product. The ethyl acetate solution was extracted with ammonium chloride and then washed with water, saturated NaCl solution, and dried over anhydrous MgSO₄. After the ethyl acetate solution had been removed, the crude product was purified by column chromatography (silica gel, ethyl acetate-to-hexane ratio 1:1), with a yield of 0.97 g (83%) of a yellow compound with a melting point of 87–88 °C.

¹H-NMR (CDCl₃, δ, ppm): 0.87–0.92 (t, *J*=7.2 Hz, 3H), 1.25–1.62 (m, 12H), 1.80–1.82 (m, 2H), 2.60–2.66 (t, *J*=7.5 Hz, 2H), 3.66–3.68 (t, *J*=5.4 Hz, 2H), 3.98–4.02 (t, *J*=6.3 Hz, 2H), 6.89–6.91 (d, *J*=9.0 Hz, 2H), 7.20–7.22 (d, *J*=8.1 Hz, 2H), 7.56–7.60 (m, 4H), 7.74 (s, 2H).

¹³C-NMR (CDCl₃, δ, ppm): 14.0, 22.5, 25.6, 26.3, 28.9, 31.0, 31.5, 32.1, 35.6, 62.3, 67.8, 92.5, 92.9, 114.1, 114.4, 117.9, 119.8, 133.4, 134.2, 136.0, 143.4, 157.4, 159.6.

6-[4-(2-{7-[2-(4-Pentylphenyl)-1-ethynyl]2,1,3-benzothiadiazol-4-yl}-1-ethynyl)phenoxy]-1-hexyl acrylate (M1)

6-[4-(2-{7-[2-(4-Pentylphenyl)-1-ethynyl]2,1,3-benzothiadiazol-4-yl}-1-ethynyl)phenoxy]-1-hexanol (0.8 g, 1.53 mmol) was dissolved in a mixture of dried THF and triethylamine (1.1 mL, 7.65 mmol) under an atmosphere of nitrogen. After the solution had been cooled in an ice-water bath to 0 °C, acryloyl chloride (0.4 mL, 4.6 mmol) was added dropwise. The reaction mixture was allowed to warm slowly to room temperature and was stirred overnight. The solid formed was taken into ethyl acetate and washed with water. The organic layer was dried over anhydrous MgSO₄. After filtration, the solvent was removed by rotary evaporation and purified by column chromatography (silica gel, ethyl acetate-to-hexane ratio 1:4), with a yield of 0.5 g (86%) of a yellow compound with a melting point of 64–65 °C.

¹H-NMR (CDCl₃, δ, ppm): 0.87–0.92 (t, *J*=6.0 Hz, 3H), 1.25–1.82 (m, 14H), 2.60–2.66 (t, *J*=7.5 Hz, 2H), 3.98–4.02 (t, *J*=6.3 Hz, 2H), 4.16–4.20 (t, *J*=6.6 Hz, 2H), 5.80–5.84 (dd, *J*=10.5, 1.5 Hz, 1H), 6.08–6.17 (dd, *J*=10.5, 17.4 Hz, 1H), 6.38–6.44 (dd, *J*=17.1, 1.5 Hz, 1H), 6.89–6.91 (d, *J*=8.7 Hz, 2H), 7.20–7.22 (d, *J*=8.1 Hz, 2H), 7.56–7.60 (m, 4H), 7.74 (s, 2H).

¹³C-NMR (CDCl₃, δ, ppm): 14.1, 22.5, 26.0, 26.2, 28.6, 28.9, 31.1, 31.5, 35.6, 62.7, 67.8, 92.6, 92.9, 114.1, 114.3, 118.0, 119.7, 128.7, 129.6, 133.4, 134.2, 136.0, 136.9, 143.5, 157.4, 159.6, 166.6.

6-{4-[(E)-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolane-2-yl)-1-ethenyl]phenoxy}-1-hexanol (3)

6-[4-(1-Ethenyl)phenoxy]-1-hexanol (3.0 g, 13.66 mmol) and pinacol borane (2.64 mL, 20.66 mmol) were dissolved in 10 mL of toluene under an atmosphere of nitrogen. The mixture was heated at 90 °C for 12 h. The product was isolated by pouring the solution into water and the solution was filtered. The crude product was purified by column chromatography (silica gel, ethyl acetate-to-hexane ratio 1:4), with a yield of 4.5 g (90%) of a yellow liquid.

¹H-NMR (CDCl₃, δ, ppm): 1.20 (s, 12H), 1.40–1.60 (m, 6H), 1.78–1.82 (m, 2H), 3.64–3.69 (t, *J*=7.2 Hz, 2H), 3.97–4.01 (t, *J*=6.3 Hz, 2H), 6.80–6.92 (d, *J*=34.5 Hz, 2H), 6.94–6.96 (d, *J*=6.0 Hz, 2H), 7.56–7.60 (d, *J*=11.4 Hz, 2H).

¹³C-NMR (CDCl₃, δ, ppm) : 24.1, 25.6, 26.2, 28.9, 32.1, 62.2, 67.8, 83.6, 114.1, 122.5, 128.3, 128.4, 150.5, 158.2.

6-{4-[(E)-2-(7-Bromo-2,1,3-benzothiadiazol-4-yl)-1-ethynyl]phenoxy}-1-hexanol (4)

Compound **4** was synthesized according to a similar method reported in the literature [24]. 6-{4-[(E)-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolane-2-yl)-1-ethenyl]phenoxy}-1-hexanol (0.77 g, 2.22 mmol), 4,7-dibromo-2,1,3-benzothiadiazole (1.0 g, 3.4 mmol), K₂CO₃ (2.4 g, 16.8 mmol), Aliquat 336 (0.4 g, 1.0 mmol), and Pd(PPh₃)₄ (0.02 g, 0.02 mmol) were dissolved in a mixture of 10 mL of toluene and 2 mL of degassed water. The solution was refluxed with vigorous stirring for 48 h under an argon atmosphere. At the end of the reaction, the solid formed was taken into ethyl acetate and washed with water. The organic layer was dried over anhydrous MgSO₄. After filtration, the solvent was removed by rotary evaporation and purified by column chromatography (silica gel, ethyl acetate-to-hexane ratio 1:1), with a yield of 1.2 g (83%) of an orange compound with a melting point of 104–105 °C.

¹H-NMR (CDCl₃, δ, ppm): 1.43–1.62 (m, 6H), 1.78–1.82 (m, 2H), 3.63–3.67 (t, *J*=7.5 Hz, 2H), 3.96–4.00 (t, *J*=6.3 Hz, 2H), 6.89–6.92 (d, *J*=8.7 Hz, 2H), 7.39–7.56 (m, 4H), 7.78–7.91 (m, 2H).

¹³C-NMR (CDCl₃, δ, ppm): 25.6, 26.2, 28.9, 32.1, 62.3, 67.8, 110.3, 113.8, 115.5, 119.1, 129.6, 131.6, 134.2, 141.5, 142.0, 157.9, 158.3.

4,4,5,5-Tetramethyl-2-[(E)-2-(4-pentylphenyl)-1-ethynyl]-1,3,2-dioxaborolane (5)

1-Ethynyl-5-pentylbenzene (4.8 g, 31.66 mmol) and pinacol borane (6.4 mL, 47.46 mmol) were dissolved in 10 mL of toluene under an atmosphere of nitrogen. The mixture was heated at 90 °C for 12 h. The product was isolated by pouring the solution into water and the solution was filtered. The crude product was purified by column chromatography (silica gel, ethyl acetate-to-hexane ratio 1:4), with a yield of 8.4 g (91%) of a yellow liquid.

¹H-NMR (CDCl₃, δ, ppm): 0.92–0.97 (t, *J*=7.2 Hz, 3H), 1.20 (s, 12H), 1.40–1.60 (m, 6H), 2.61–2.67 (t, *J*=6.3 Hz, 2H), 6.80–6.92 (d, *J*=32.7 Hz, 2H), 6.93–6.96 (d, *J*=8.7 Hz, 2H), 7.55–7.60 (d, *J*=7.2 Hz, 2H).

¹³C-NMR (CDCl₃, δ, ppm) : 14.0, 22.5, 24.0, 31.5, 35.5, 83.6, 122.5, 124.9, 127.7, 133.3, 144.1, 150.4.

6-[4-((E)-2-{7-[(E)-2-(4-Pentylphenyl)-1-ethenyl]-2,1,3-benzothiadiazol-4-yl}-1-ethynyl)phenoxy]-1-hexanol (6)

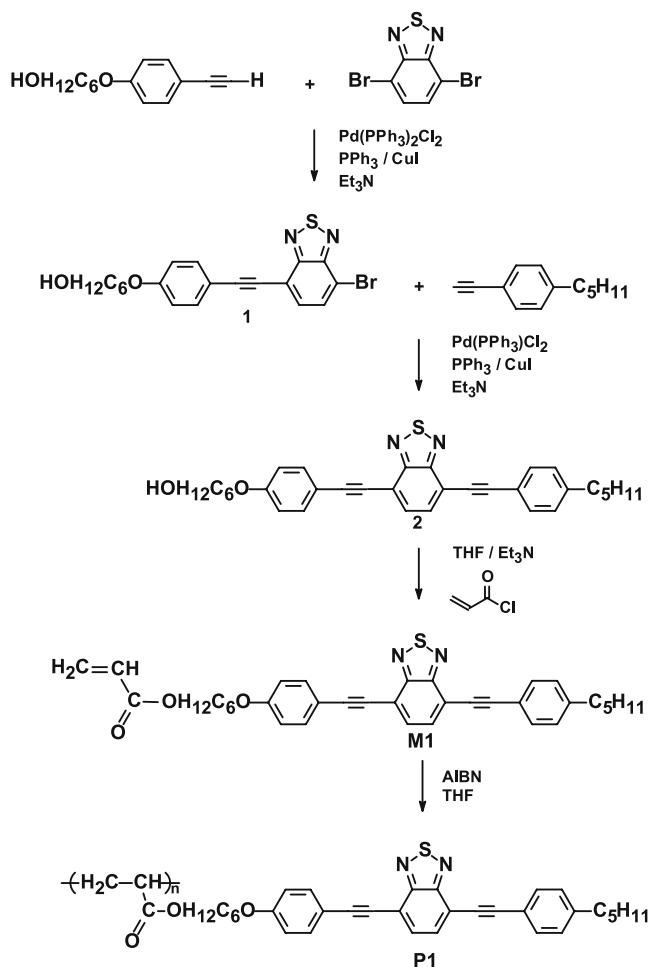
6-{4-[(E)-2-(7-Bromo-2,1,3-benzothiadiazol-4-yl)-1-ethynyl]phenoxy}-1-hexanol (0.6 g, 1.38 mmol), 4,4,5,5-tetramethyl-2-[(E)-2-(4-pentylphenyl)-1-ethynyl]-1,3,2-dioxaborolane (0.59 g, 2.07 mmol), K₂CO₃ (1.22 g, 10.9 mmol), Aliquat 336 (0.2 g, 0.5 mmol), and Pd(PPh₃)₄ (0.01 g, 0.01 mmol) were dissolved in a mixture of 10 mL of toluene and 2 mL of degassed water. The solution was refluxed with vigorous stirring for 48 h under an argon atmosphere. At the end of the reaction, the solid formed was taken into ethyl acetate and washed with water. The organic layer was dried over anhydrous MgSO₄. After filtration, the solvent was removed by rotary evaporation and purified by column chromatography (silica gel, ethyl acetate-to-hexane ratio 1:1), with a yield of 0.52 g (83%) of an orange compound with a melting point of 82–83 °C.

¹H-NMR (CDCl₃, δ, ppm): 0.92–0.97 (t, *J*=7.5 Hz, 3H), 1.25–1.65 (m, 12H), 1.80–1.85 (m, 2H), 2.61–2.66 (t, *J*=7.8 Hz, 2H), 3.65–3.70 (t, *J*=6.6 Hz, 2H), 3.99–4.02 (t, *J*=6.6 Hz, 2H), 6.91–6.94 (d, *J*=8.7 Hz, 2H), 7.20–7.23 (d, *J*=8.1 Hz, 2H), 7.55–7.66 (m, 8H), 7.90–7.98 (m, 2H).

¹³C-NMR (CDCl₃, δ, ppm): 14.0, 22.5, 25.6, 26.2, 28.8, 31.0, 31.5, 32.1, 35.6, 62.2, 67.8, 114.3, 115.4, 126.3, 129.0, 129.4, 130.8, 132.3, 133.7, 135.5, 144.0, 149.1, 158.2.

6-[4-((E)-2-{7-[(E)-2-(4-Pentylphenyl)-1-ethenyl]-2,1,3-benzothiadiazol-4-yl}-1-ethynyl)phenoxy]hexyl acrylate (M2)

6-[4-((E)-2-{7-[(E)-2-(4-Pentylphenyl)-1-ethenyl]-2,1,3-benzothiadiazol-4-yl}-1-ethynyl)phenoxy]-1-hexanol (0.4 g, 0.78 mmol) was dissolved in a mixture of dried THF and triethylamine (0.56 mL, 3.9 mmol) under an atmosphere of nitrogen. After the solution had been cooled in an ice-water bath to 0 °C, acryloyl chloride (0.18 mL, 1.95 mmol) was added dropwise. The reaction



Scheme 1. Synthesis of 6-[4-(2-{7-[2-(4-Pentylphenyl)-1-ethynyl]2,1,3-benzothiadiazol-4-yl}-1-ethynyl)phenoxy]-1-hexyl acrylate (**M1**) and poly{6-[4-(2-{7-[2-(4-Pentylphenyl)-1-ethynyl]2,1,3-benzothiadiazol-4-yl}-1-ethynyl)phenoxy]-1-hexyl acrylate} (**P1**).

mixture was allowed to warm slowly to room temperature and was stirred overnight. The solid formed was taken into ethyl acetate and washed with water. The organic layer was dried over anhydrous MgSO_4 . After filtration, the solvent was removed by rotary evaporation and purified by column chromatography (silica gel, ethyl acetate-to-hexane ratio 1:4), with a yield of 0.4 g (90%) of an orange compound with a melting point of 71–72 °C.

$^1\text{H-NMR}$ (CDCl_3 , δ , ppm): 0.92–0.97 (t, $J=7.2$ Hz, 3H), 1.25–1.82 (m, 14H), 2.61–2.64 (t, $J=7.5$ Hz, 2H), 3.98–4.03 (t, $J=6.3$ Hz, 2H), 4.16–4.20 (t, $J=6.6$ Hz, 2H), 5.80–5.84 (dd, $J=10.5$, 1.5 Hz, 1H), 6.08–6.17 (dd, $J=10.2$, 17.4 Hz, 1H), 6.38–6.44 (dd, $J=17.1$, 1.5 Hz, 1H), 6.89–6.94 (d, $J=8.7$ Hz, 2H), 7.20–7.22 (d, $J=8.4$ Hz, 2H), 7.55–7.63 (m, 8H), 7.90–7.92 (m, 2H).

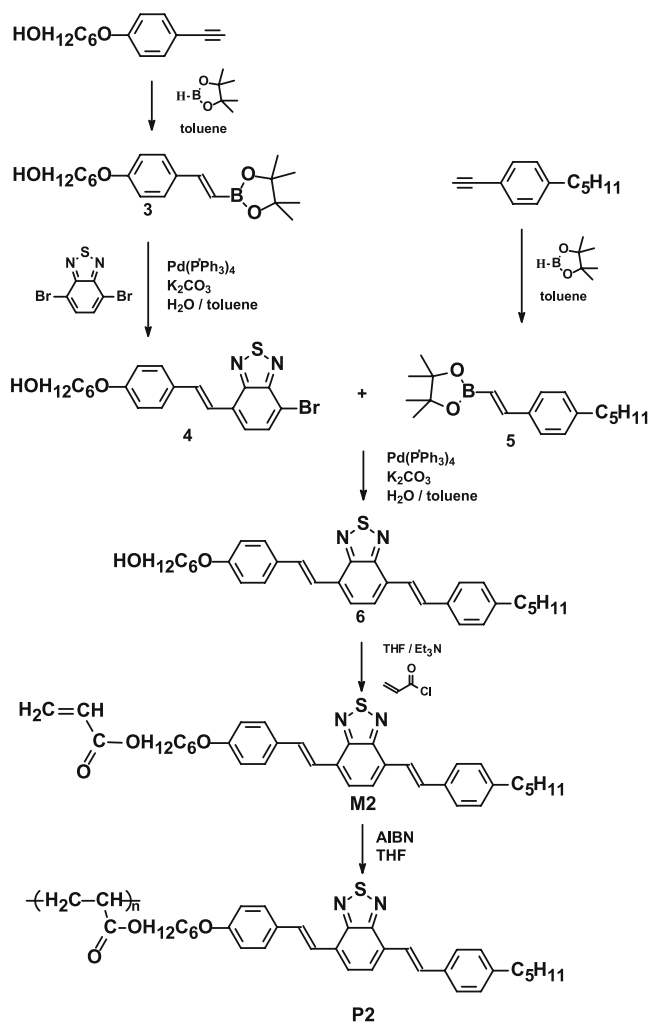
$^{13}\text{C-NMR}$ (CDCl_3 , δ , ppm): 13.9, 22.5, 26.1, 26.3, 28.6, 28.9, 31.1, 31.5, 35.6, 62.7, 67.8, 114.3, 115.4, 115.6, 126.3, 129.0, 129.4, 130.8, 132.1, 133.8, 135.5, 144.0, 149.2, 158.2, 166.5.

Poly{6-[4-(2-{7-[2-(4-pentylphenyl)-1-ethynyl]2,1,3-benzothiadiazol-4-yl}-1-ethynyl)phenoxy]-1-hexyl acrylate} (**P1**)

Monomer **M1** (0.5 g) and initiator 2,2'-azobisisobutyronitrile (AIBN) (1 wt%) were dissolved in THF (1.0 g/mL). The mixture was stirred at 60 °C for 24 h under a nitrogen atmosphere. The product was isolated by pouring the reaction mixture into methanol and was purified by reprecipitation in methanol three times, giving a yield of 0.38 g (76%) of a yellow compound.

Poly{6-[4-(*E*)-2-{7-[(*E*)-2-(4-pentylphenyl)-1-ethenyl]-2,1,3-benzothiadiazol-4-yl}-1-ethynyl]phenoxy]hexyl acrylate} (**P2**)

Monomer **M2** (0.5 g) and initiator AIBN (1 wt%) were dissolved in THF (1.0 g/mL). The mixture was stirred at 60 °C for 24 h under a nitrogen atmosphere. The product was isolated by pouring the reaction mixture into methanol and was purified by reprecipitation in methanol



Scheme 2. Synthesis of 6-[4-(*E*)-2-{7-[(*E*)-2-(4-Pentylphenyl)-1-ethenyl]-2,1,3-benzothiadiazol-4-yl}-1-ethynyl)phenoxy]hexyl acrylate (**M2**) and poly{6-[4-(*E*)-2-{7-[(*E*)-2-(4-pentylphenyl)-1-ethenyl]-2,1,3-benzothiadiazol-4-yl}-1-ethynyl]phenoxy]hexyl acrylate} (**P2**).

Table 1. Polymerization results and phase-transition temperatures of polymers poly{6-[4-(2-{7[2-(4-pentylphenyl)-1-ethynyl]2,1,3-benzothiadiazol-4-yl}-1-ethynyl)phenoxy]-1-hexyl acrylate} (**P1**) and poly{6-[4-((E)-2-{7-[(E)-2-(4-pentylphenyl)-1-ethynyl]-2,1,3-benzothiadiazol-4-yl}-1-ethynyl)phenoxy]hexyl acrylate} (**P2**).

Polymer	Yield (%)	M_n	M_w	M_w/M_n	Phase-transition temperatures
P1	76.3	8,600	15,600	1.81	G 92 °C N 170 °C I I 156 °C N 65 °C G
P2	80.4	9,600	18,400	1.92	G 79 °C N 126 °C I I 124 °C N 59 °C G

G glassy state, N nematic phase, I isotropic.

three times, giving a yield of 0.4 g (80%) of an orange compound.

Results and discussion

Synthesis and characterization

The benzothiadiazole-based liquid crystalline polyacrylates were prepared according to the synthetic routes depicted in Schemes 1 and 2. The acrylate monomer **M1** was obtained by coupling of dibromobenzothiadiazole with 6-[4-(1-ethynyl)-phenoxy]-1-hexanol and 1-ethynyl-5-pentyl benzene followed by esterification with acryloyl chloride, whereas **M2** was obtained from coupling of dibromobenzothiadiazole with ethenyldioxaborolane, **3** and **5**, then esterification with acryloyl chloride. The polymerizations of **M1** and **M2** were performed as shown in Scheme 1 using AIBN as the initiator in THF.

Table 1 lists the molecular weights and phase-transition temperatures of **P1** and **P2**.

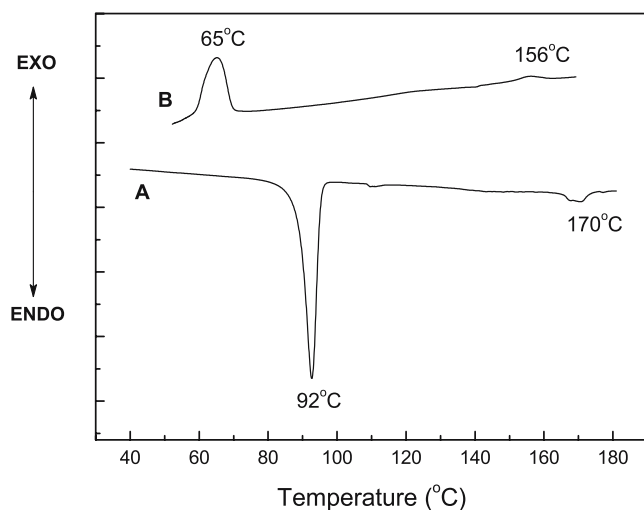


Figure 1. Differential scanning calorimetry thermogram of poly{6-[4-(2-{7[2-(4-pentylphenyl)-1-ethynyl]2,1,3-benzothiadiazol-4-yl}-1-ethynyl)phenoxy]-1-hexyl acrylate} (**P1**): A second heating scan, B first cooling scan.

Liquid crystalline phase behavior

Liquid crystalline behavior and phase transitions of **P1** and **P2** were examined with a polarizing optical microscope equipped with a hot stage. The results are summarized in Table 1. Figure 1 depicts the representative differential scanning calorimetry (DSC) thermograms of **P1**. The heating scan shows a crystalline-to-nematic phase transition at 92.4 °C and a nematic-to-isotropic phase transition at 169.7 °C. On the cooling scan, the isotropic-to-nematic and crystallization endotherms at 155.5 and 65.0 °C are observed. Figure 2 exhibits the typical nematic texture for polymer **P1**. As can be seen from Table 1, polymer **P2** also reveals the nematic liquid crystalline behavior. No glass transition was observed for both polymers in the DSC curves.

Optical properties

Aligned samples for further experiments were prepared by annealing the polymers on PEDOT-coated glass plates. The PEDOT surface was mechanically rubbed prior to spin-coating of the polymers.

The optical properties of aligned **P1** and **P2** were characterized by UV-vis absorption along with PL emission, as shown in Table 2. To estimate the degree of alignment achieved, the polarized spectra were recorded



Figure 2. Polarizing optical micrograph of **P1**: nematic droplet texture obtained at 150 °C.

Table 2. The UV-vis absorption, photoluminescence (PL) emission, and polarization ratios of polymers **P1** and **P2**.

Polymer	UV-vis absorption (nm)	PL emission (nm)	Polarization ratio	
			UV-vis ($UV_{\parallel}/UV_{\perp}$)	PL ($PL_{\parallel}/PL_{\perp}$)
P1	492	583	8.5	8.3
P2	517	603	8.8	8.6

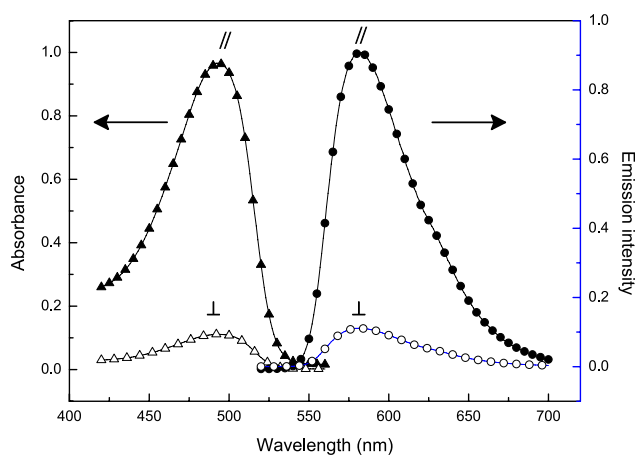


Figure 3. Polarized UV-vis absorption and polarized photoluminescence emission spectra of **P1**. (// polarizer parallel to rubbing direction, \perp polarizer perpendicular to rubbing direction).

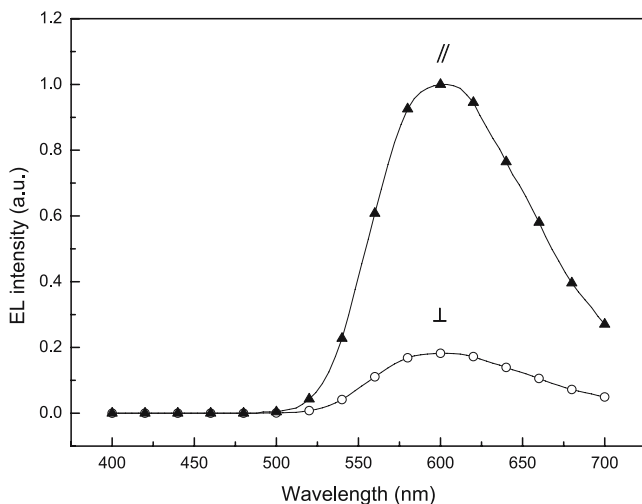


Figure 4. Polarized electroluminescence (EL) spectra of poly{6-[4-((E)-2-{7-[(E)-2-(4-pentylphenyl)-1-ethenyl]-2,1,3-benzothiadiazol-4-yl]-1-ethynyl)phenoxy]hexyl acrylate} (**P2**) in the indium tin oxide (ITO)/aligned poly(3,4-ethylene-dioxythiophene)-poly(styrenesulfonic acid) (PEDOT)/**P2**/Ca/Al device.

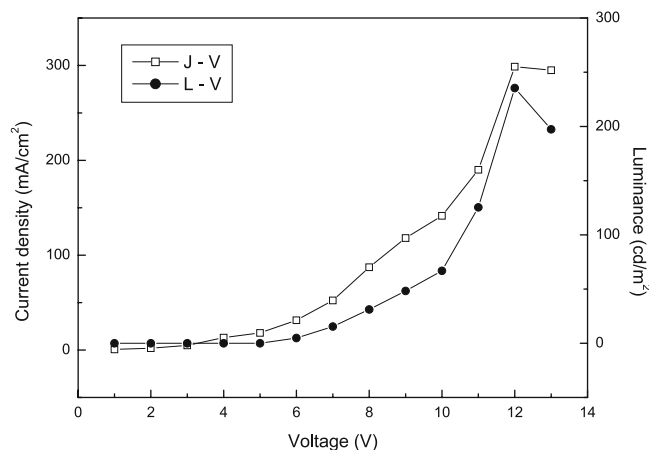


Figure 5. J - V and L - V curves of **P2** in the ITO/aligned PEDOT/**P2**/Ca/Al device.

with the polarizer placed parallel and perpendicular to the rubbing direction. Figure 3 shows polarized UV and PL spectra of **P1**. The results indicate that absorbance parallel to the rubbing direction was much higher than that perpendicular to the rubbing direction. This means that the mesogens of polyacrylate are aligned parallel to the rubbing direction. The dichroic ratios calculated from the polarized UV and PL spectra are in the range from 8.3 to 8.8 (Table 2).

Polymer light-emitting diodes

To examine the potential application of these polymers, light-emitting devices were constructed with **P1** or **P2** as the active layer between the ITO anode and the Ca/Al cathode. Luminance-voltage and current density-voltage characteristics for the EL devices are illustrated in Figures 4 and 5. **P1** and **P2** devices yielded maximum emissions at 580 and 604 nm with turn-on voltages of 4 and 6 V, respectively. The intensity of the emitted light recorded parallel to the rubbing direction was approximately 1 order of magnitude greater than that from the perpendicular direction at the same applied voltage. This indicates that the chromophores were aligned predominantly along the rubbing direction. Table 3 summarizes all the EL data for two devices. Compared with other EL polymers with mesogen pendants [25], the single-layer EL devices consisting of **P1** or **P2** showed lower turn-on voltages. The luminance intensity increases as the applied voltage increases and achieves a maximum luminance of 85 and 235 cd/m^2 for **P1** and **P2**, respectively. These luminances are significantly better than those in our previous

Table 3. Polarized device properties of polymers **P1** and **P2**.

Polymer	EL _{max} (nm) at $V_{\text{turn on}}$	$V_{\text{turn on}}$ (V)	Luminance (max) (cd/m^2)	Efficiency (max) (cd/A)	Polarization ratio ($EL_{\parallel}/EL_{\perp}$)
P1	580	5	85	0.03	4.0
P2	604	6	235	0.09	6.5

report for a similar pendant liquid crystalline polymer [22]. Compared with our previous report, the middle phenyl ring of the chromophore was replaced with a benzothiadiazole group. According to the literature [8, 9], the mesogen with a benzothiadiazole group has better hole-transport properties, which not only increases the current density but also increases the efficiency of the recombination of electrons and holes. This is the reason why **P1** and **P2** show much higher EL efficiencies than previous polymers.

Conclusion

The results presented here illustrate that, in principle, benzothiadiazole-based bistolane or bisstilbene incorporated onto polyacrylate exhibits liquid crystalline behavior and gives polarized EL. The observation of polarized EL from aligned **P1** and **P2** illustrates the potential use of mesogenic materials for polarized emitter applications. Further systematic studies are now necessary to improve the dichroic ratio and to increase the efficiency of these systems.

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