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Synthesis and Characterization of Poly(2,5-bis(*N*-methyl-*N*-hexylamino)phenylene vinylene), a Conjugated Polymer for Light-Emitting Diodes

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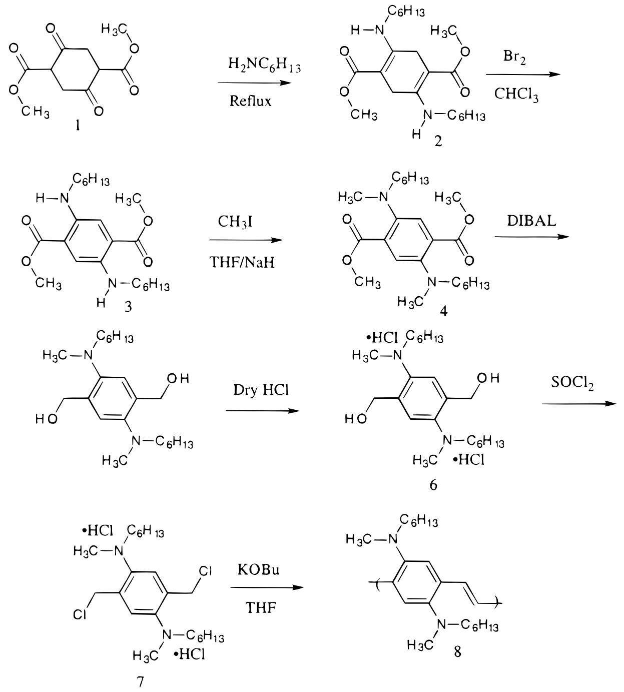
Introduction. Poly(phenylene vinylene)s (PPVs) and their derivatives are currently among the most studied of the conjugated polymer systems and have potential applications as active components for solid-state laser materials,[1] light-emitting diodes (LEDs),[2,3] photodiodes,[4] electroactive materials,[5] and organic transistors.[6] Generally, donor-substituted PPVs have higher efficiencies than unsubstituted PPV; hence, alkoxy-substituted PPVs such as poly(2,5-bis(2′-ethylhexoxy)-1,4-phenylene vinylene, BEHPPV, are often used as active layers in LEDs. Since amines are stronger donors than alkoxy groups, it would be of interest to synthesize amino-substituted PPV and determine the efficiency of LEDs made using amino PPVs as active layers. Furthermore, incorporating amino substituents allows for further tuning of the band gap and therefore the wavelength of emission. Until recently, amino-substituted bis(halomethyl)benzene compounds, a necessary precursor to amino-substituted PPVs, have not been synthesized due to the inherent difficulty of making these compounds. We recently reported the first successful synthesis of poly(2,5-bis(*N*-methyl-*N*-alkylamino)phenylene vinylenes.[7−10] Both poly[(2,5-bis(*N*-methyl-*N*-butylamino) and (2,5-bis(*N*-methyl-*N*-propylamino)] phenylene vinylenes (BAMPPVs) were polymerized from their respective monomer precursors using a strong base. ^{13}C NMR analysis of these derivatives was difficult because of the low solubility of these BAMPPV derivatives (solubilities were ~0.5 wt % in 100 °C xylene). It was also difficult to make LEDs from these polymers because of the poor solubility and film quality.

The use of longer alkyl chains on the amine functionalities should impart greater solubility. To this end, we decided to incorporate hexyl groups onto the amine functionalities to make poly(2,5-bis(*N*-methyl-*N*-hexylamino)) phenylene vinylene (BAMHPPV). The methyl group was kept mainly because previous attempts at making precursors for diethyl amino derivatives gave very poor conversion,[11] most likely because of the higher percentage of elimination reactions.

In this paper, we report on the properties of BAMHPPV, which is soluble enough for complete NMR analysis: ^{1}H NMR, ^{13}C NMR, gated acquisition spin−echo (GASPE) NMR, heteronuclear multiple quantum coherence (HMQC) NMR, and heteronuclear multiple bond coherence (HMBC) NMR; it gives approximately 35% yield in the polymerization reaction. The improved solubility made it possible to construct LEDs from this material.

Scheme 1



Experimental Section. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AMX-400 NMR spectrometer. Elemental analyses were performed by E&R Microanalytical Laboratories. IR spectra were obtained on a Nicolet 60SX spectrophotometer. Tetrahydrofuran, THF, was dried by distillation over a sodium−potassium amalgam. Unless otherwise stated, all reagents were used as received. All reactions were performed under nitrogen. Compound 1 was obtained from ACROS Organics. All melting points are uncorrected.

Monomer and Polymer Synthesis. Synthesis of the polymer is shown in Scheme 1.

(a) Methyl 2,5-Bis(hexylamino)-4-(methoxycarbonyl)cyclohexa-1,4-diene Carboxylate, Compound 2. Into a round-bottom flask were placed 30.0 g (132 mmol) of dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate (compound 1) and 300 mL of methanol. To this suspension, 35 mL (26.6 g, 263 mmol) of *n*-hexylamine was added dropwise via a dropping funnel. The mixture was refluxed overnight. An orange-yellow precipitate was observed. The contents were cooled to room temperature and filtered, and the residue was washed with ether. The product was then dried overnight under vacuum. The crude product was recrystallized from 900 mL of methanol/methylene chloride (8:1). Yield was 37.6 g (74%) of orange crystals: mp 120−122 °C. ^{1}H NMR ($CDCl_3$): 8.8, m, 4H; 3.65, s, 6H; 3.21, t, 4H; 1.5, m, 4H; 1.35, m(br) 12H; 0.9 t, 6H.

(b) Methyl 2,5-Bis(hexylamino)-4-(methoxycarbonyl)benzoate, Compound 3. Into a round-bottom flask were placed 34 g (86 mmol) of compound 2 and 200 mL of dichloromethane. To this solution, ~5 mL (ca. 13.8 g, 86 mmol) of bromine was added dropwise. The color changed from orange-red to yellow-orange. The contents were then refluxed for 2 h, cooled, and poured slowly into 1500 mL of a 10 wt % aqueous solution of sodium carbonate. A red slurry appeared

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and separated from the aqueous phase. The aqueous phase was extracted twice with 100 mL of dichloromethane. The combined organic phases were filtered and the filtrate was rotovapped and dried overnight under vacuum. The crude product was recrystallized from 1200 mL of methanol/methylene chloride (2:1). Yield: 25.2 g (74%). mp 104−105 °C. ^{1}H NMR (CD_2Cl_2): 7.28, s, 2H; 3.86, s, 6H; 3.14, t, 4H; 1.62, m, 4H; 1.36, m(br) 12H; 0.91 t, 6H.

(c) Methyl 2,5-Bis(hexylmethylamino)-4-(methoxycarbonyl)benzoate, Compound 4. Into a round-bottom flask were placed 24 g (61 mmol) of compound 3, approximately 8.4 g of sodium hydride (350 mmol), and 450 mL of dry THF. The mixture was stirred for 15 min, and then 14 mL (32 g, 228 mmol) of methyl iodide was added dropwise to the suspension. After all the methyl iodide was added, the red mixture was stirred for 2 h at room temperature. The red mixture was then heated to 80 °C overnight. The mixture turned from red to yellow overnight and was then cooled to room temperature. The completion of the reaction was verified by NMR. The mixture was filtered, the residue (mostly sodium iodide and unreacted sodium hydride) rinsed with dry THF, and the filtrate rotovapped to dryness. The semisolid was then redissolved in 500 mL of hexane, the solution stirred for 1 h after which approximately 5 g of silica gel were added, and the mixture stirred for another $^1/_2$ h. The mixture was filtered, the residue rinsed with 200 mL of hexane, and the combined filtrates rotovapped and dried overnight under vacuum. The yield was 17.5 g (68%) of a yellow-orange oil. ^{1}H NMR (CD_2Cl_2): 7.18, s, 2H; 3.58, s, 6H; 2.92, t, 4H; 2.70, s, 6H, 1.49, m, 4H; 1.26, m, 12H; 0.87, t, 6H.

(d) (2,5-Bis(hexylmethylamino)-4-(hydroxymethyl)phenyl)methan-1-ol, Compound 5. Into a round-bottom flask were placed 17.5 g (41 mmol) of compound 4 and 150 mL of dry toluene. The solution was cooled to 0 °C. To this cooled solution, 225 mL of 1.5 M DIBAL were added dropwise. After about 200 mL of DIBAL was added, the color changed from yellow to pale yellow. After all the DIBAL was added, the solution was warmed to room temperature and then heated to 40 °C for 15 min. The solution was cooled to room temperature and an additional 150 mL of toluene was added. The reaction was quenched carefully with 150 mL of methanol and diluted with an additional 100 mL of toluene and 100 mL of methanol (a very thick precipitate formed). The mixture was filtered, the residue washed with methanol and the filtrate rotovapped and dried overnight to yield a very pale yellow oil, the yield 12.1 g (81%), which was used immediately for the next step.

(e) (2,5-Bis(hexylmethylamino)-4-(hydroxymethyl)phenyl)methan-1-ol Dihydrochloride, Compound 6. The entire 12.1 g (33.2 mmol) of compound 5 were dissolved into 250 mL of methanol. Dry HCl was bubbled through the solution for approximately 15 min. The methanol was removed using the rotary evaporator, leaving a red-white solid. The red-white solid was stirred for 20 min in 100 mL of dry acetone and filtered, and the residue was rinsed three times with dry acetone. The residue was dried overnight under vacuum. The product was obtained as a white solid: mp 146 °C (dec), yield 11 g (76%). ^{1}H NMR (CD_3OD): 7.98, s, 2H; 5.07, s, 4H; 3.66, t, 4H; 3.34, s, 6H; 1.55, m(br), 4H; 1.30, m(br), 12H; 0.88, t, 6H. ^{13}C NMR (CD_3OD): 145.0, 139.7, 126.8, 66.3, 64.1, 49.7, 35.1, 29.8, 29.2, 26.3, 17.1.

Table 1. ^{1}H Assignments for Polymer 8

	^{1}H shift
H-1	7.88
H-3	7.69
H-5	2.81
H-6	3.05
H-7	1.69
H-8	1.39
H-9	1.28
H-10	1.28
H-11	0.87

(f) (2,5-Bis(chloromethyl)-4-(hexylmethylamino)phenyl)hexylmethylamine Dihydrochloride, Compound 7. To an ice bath-cooled flask containing 60 mL (845 mmol) of thionyl chloride, 11 g of compound 6 (25.2 mmol) were added slowly. The solution turned pale pink after about 10 min. The solution was then allowed to warm to room temperature. Excess thionyl chloride was removed by purging with nitrogen overnight. The residual red-white solid was dried under vacuum for 2 h. The solid was then stirred for 45 min in dry acetone and then filtered. The residue was rinsed four times more with dry acetone and dried overnight under vacuum. The product was obtained as an off-white solid with a yield of 10.58 g (89%). ^{1}H NMR (CD_3OD): 8.13, s, 2H; 5.07, s, 4H; 3.68, t, 4H; 3.33, s, 6H; 1.54, m(br), 4H; 1.29, m(br), 12H; 0.87, t, 6H. ^{13}C NMR (CD_3OD): 144.7, 138.3, 128.5, 75.0, 64.7, 51.5, 35.1, 29.7, 29.2, 26.3, 17.1; mp 156−161 °C (dec). Mass spectrometry *m*/*z* (HCl comes off under probe conditions): 400, 365, 329, 315, 295, 279, 259, 245, 209, 201, 187, 173, 159, 145, 130, 117, 103, 77. Infrared (cm^{-1}): 512, 522, 625, 678, 732, 832, 898, 930, 978, 1103, 1126, 1140, 1200, 1220, 1258, 1274, 1295, 1393, 1408, 1439, 1452, 1468, 1483, 1529, 2433, 2531, 2618, 2854, 2869, 2924, 2946, 2996, 3015, 3168.

(g) Polymer 8. Into a round-bottom flask was added 17.0 g (151 mmol) of potassium *tert*-butoxide and 800 mL of dry THF. To this solution, 8.48 g (19 mmol) of compound 7 was added. The suspension turned yellow almost immediately. After stirring for 3 h at room temperature, the suspension was precipitated into methanol and stirred overnight. The suspension was filtered and dried and the polymer residue was extracted twice for 24 h in a Soxhlet extractor. The yield was 2.16 g, 35%. Elemental analysis. Calcd for $C_{22}H_{36}N_2$: 80.43% C; 11.05% H, 8.53% N. Found: 80.17% C; 11.29% H; 8.43% N. Infrared (cm^{-1}): 484, 498, 511, 684, 724, 884, 952, 988, 1051, 1063, 1086, 1129, 1141, 1179, 1255, 1336, 1377, 1402, 1424, 1465, 1500, 2791, 2855, 2925, 2953, 3031,

NMR Analysis of Polymers. ^{1}H and ^{13}C NMR ($C_6D_5CD_3$, δ ppm, 57 °C) were run to confirm that the desired product was obtained. The ^{1}H NMR and ^{13}C NMR spectra were consistent with the proposed structure. The NMR assignments noted in Tables 1 and 2 were determined and confirmed using GASPE,[12] HMQC[13], and HMBC.[14]

Assignment of the alkyl groups attached to the nitrogen is fully consistent with literature assignment[15] of related amines and need not be discussed here. Assignments for the aromatic/alkene regions of the proton and carbon spectra was less obvious and required a long-range two-dimensional proton-carbon correlated spectrum for clarification. The crux of the problem is that the two protons in the aromatic region occur

Table 2. ^{13}C **Assignments for Polymer 8**[a]

	^{13}C shift
C-1	126.2
C-2	134.2q
C-3	118.5
C-4	148.4q
C-5	42.6
C-6	58.0
C-7	28.6
C-8	27.7
C-9	32.4
C-10	23.3
C-11	14.3

[a] From GASPE experiment, q = quaternary.

relatively close together at 7.88 and 7.69 ppm. As can be seen from Figure 1, both are relatively broad. From the short-range two-dimensional HMQC spectrum (Figure 1), the 7.88 and 7.69 ppm resonances correlate to the carbons at 126.2 and 118.5 ppm, respectively. Assignment as to ring (H-3) versus alkene (H-1) further required a two-dimensional long-range HMBC experiment. The supposition here was that, for the aromatic ring, the attached proton, H-3, should have strong 3-bond couplings to both C-4 and C-2 (i.e., both of the quaternary aromatic protons) and perhaps C-1. At the same time, the alkene proton, H-1, may or may not show strong 3-bond couplings into the ring, depending upon the orientation of the C-1 C−H bond. In the HMBC experiment the proton resonance at 7.69 ppm shows two strong correlations to carbons at 134.2 and 148.4 ppm and a slightly weaker correlation to the carbon at 126.2 ppm, while the proton at 7.88 ppm is only correlated to two carbons at 118.5 and 134.2 ppm. From this, the assignment of the latter proton at 7.88 to H-1, the carbon at 126.2 to C-1, and the respective assignment for C-3/H-3 can be made. Further, C-2 can now be assigned to 134.2 ppm. Assignment of the remaining quaternary carbon resonance at 148.4 ppm to C-4 is consistent with literature shifts for aromatic carbons attached to amine nitrogens. Further supporting the assignment of C-4, the HMQC long-range coupling spectrum shows strong correlation between C-4 and H-5 and H-6. To summarize the HMBC assignment, the ring proton, H-3, shows strong, 3-bond correlations to C-2 and C-4, and a weaker 3-bond coupling to C-1. The alkene proton, H-1, shows only one strong 3-bond correlation to C-2 and a relatively weaker 3-bond correlation to C-3.

Light-Emitting Diode Fabrication. To investigate the electroluminescent properties of BAMHPPV, we fabricated the following light-emitting device: indium tin oxide/BAMHPPV/aluminum quinolate/magnesium, ITO/BAMHPPV/Alq_3/Mg. All device fabrication and testing were performed in a nitrogen drybox. ITO-coated glass substrates were purchased from Donnelly Corp. and had a nominal sheet resistance of 20 Ω/square. Substrates were cleaned in ultrasonic baths of acetone, isopropyl alcohol, and methanol, dried in a stream of nitrogen, and then treated with a plasma etcher immediately prior to device fabrication. Single layers of BAMHPPV were spin-coated on ITO from xylene solutions. The film thickness of 100 nm was measured using a Tencor profiler. A 15-nm-thick layer of Alq_3 was deposited on top of the polymer film in a first bell jar. A 200-nm-thick cathode of Mg was deposited in a second bell jar at a base pressure of 10^{-6} Torr through a shadow mask to create (3 × 5)-mm^2 devices. For linear absorption characterization, single layers of BAMHPPV were spin-coated onto quartz substrates. Low-intensity photoluminescence and electroluminescence emission spectra were obtained with an optical multichannel analyzer (EG&G) mounted on a 27-cm flat field spectrometer. For electroluminescent devices, the current and light output versus the voltage were measured in forward bias. The

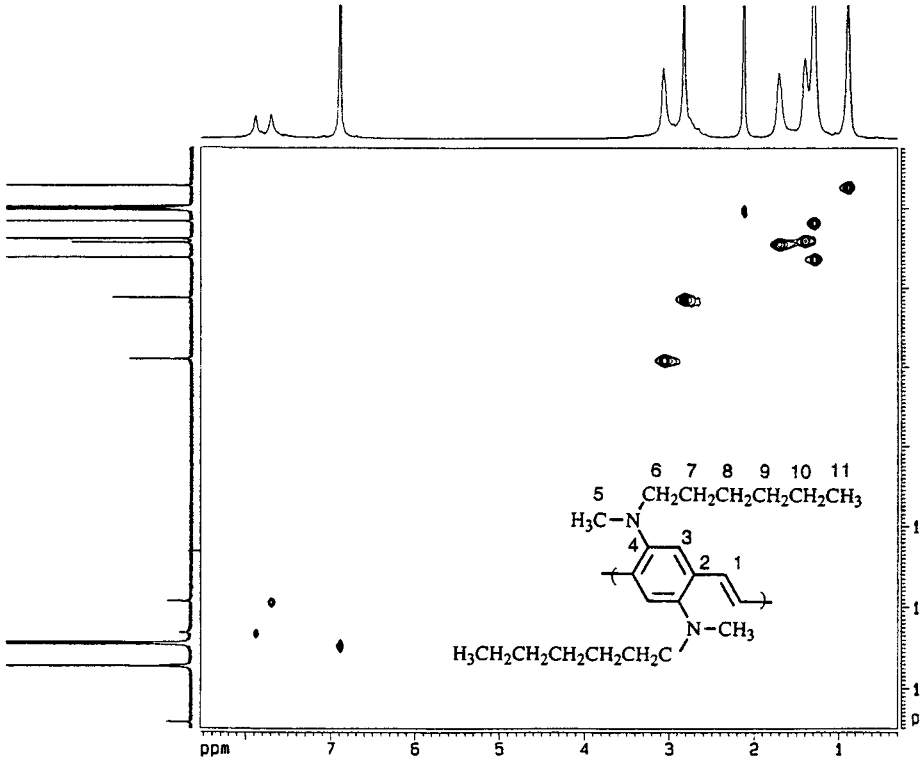

Figure 1. The two-dimensional proton−carbon short-range correlated spectrum (HMQC[13]) of polymer **8**, structure and numbering scheme.

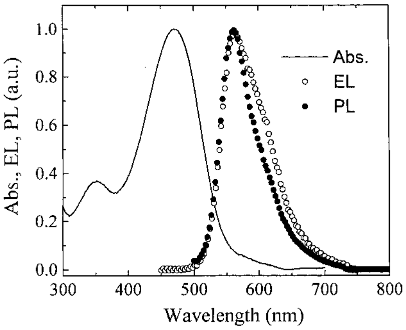

Figure 2. Linear absorption, electroluminescence (EL), and photoluminiscence (PL) emission spectra of BAMHPPV.

absolute value for the forward light output power (π steradian) was measured with a silicon photodiode calibrated using a National Institute of Standards and Technology traceable integrating sphere (Labsphere). Photometric units of cd/m^2 were calculated using the forward output power and the electroluminescence spectra of the device. External quantum efficiencies (%) were calculated in units of forward-emitted photons per injected charge in the device. The turn-on voltage of the device was defined as the voltage at which the light emission was 5 cd/m^2 and was limited by the sensitivity of our detector. Figure 2 shows the linear absorption spectrum together with the photoluminescence and electroluminescence spectra. The onset of the $\pi-\pi^*$ transition of BAMHPPV is around 550 nm and the maximum absorption is at 470 nm, which is 30−40 nm red-shifted with respect to that of PPV and about 40 nm blue-shifted to that of BEHPPV. This results are consistent with a nonplanar backbone,[16] most likely caused by steric interactions between the amine substituents and the vinylic proton. Both photoluminescence (PL) and electroluminescence (EL) spectra peaked at 564 nm. Figure 3 shows the current, luminance, and external quantum efficiency versus voltage. The device has a turn-on voltage of 10 V and exhibits a maximum external quantum efficiency of 0.3% at 12.5 V. This efficiency is comparable to that of ITO/(100 nm)BEH-PPV/Mg devices. A maximum luminance of 400 cd/m^2 is measured at 19.5 V. At a light output of 300 cd/m^2 the following efficiencies can be calculated: external quantum efficiency of 0.2% photons/injected carrier, efficiency of 0.45 cd/A, and a luminance efficiency of 0.08 lm/W.

Summary. A highly soluble version of bis(dialkylamino) PPV, namely, poly (2,5-bis(*N*-methyl-*N*-hexylamino)phenylene vinylene), (BAMHPPV), was synthesized in moderate yield. Good quality films were made from this polymer, enabling the construction of a light-emitting diode with an efficiency of 0.3% at 12.5 V and a maximum luminance of 400 cd/m^2 at 19.5 V.

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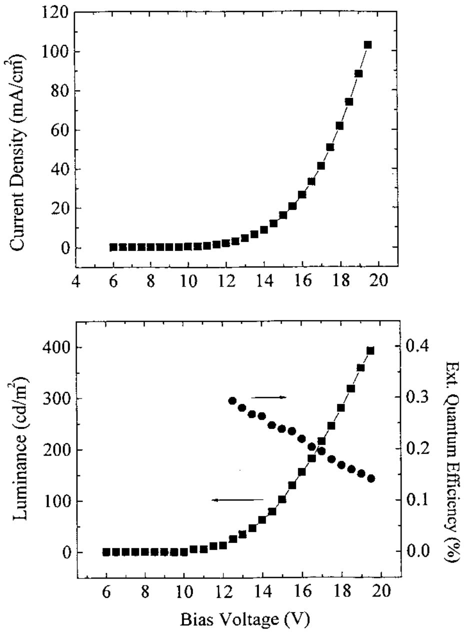

Figure 3. Current density, luminance, and external quantum efficiency versus bias voltage of an organic light-emitting ITO/BAMHPPV/Alq$_3$/Mg device.

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