Macromolecules **1999,** *32,* 6933−6937

Synthesis of Substituted Poly(*p*-phenylenevinylene) Copolymers by the Heck Method for Luminescence Studies

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Received May 26, 1999; Revised Manuscript Received August 6, 1999

ABSTRACT: Heck carbon−carbon bond-forming polymerization was used to make segmented copolymers based on poly[1,8-octanedioxy-1,4-phenylene-1,2-ethenylene-1,4-phenylene-1,2-ethenylene-1,4-phenylene]. The Heck methodology yielded copolymers with molecular weights, polydispersities, and optical properties that are comparable to or better than those previously obtained for the same or very closely related polymers obtained by Wittig methodology. However, it proved important to have methoxy groups incorporated into the chromophore of the copolymers to get high yields of material with good degrees of polymerization. The obtained yields and purities for the Heck-derived polymers are better, in part due to the direct formation of desirable trans olefin linkages in the polyphenylenevinylene type chromophore units. Differential scanning calorimetric measurements show that placement of isopropyl groups on the central ring of the chromophoric fragment does not alter the polymer glass transition temperature relative to an unsubstituted copolymer but that placement of *n*-hexyl groups lowers the glass transition substantially. The decrease in T_g is attributable to copolymer self-plasticization by the *n*-hexyl groups.

Introduction

Since the discovery of electroluminescence in poly(*p*-phenylenevinylene) (PPV),[1] many researchers have explored variants of this structure, seeking higher and more efficient luminescence. Nominally fully conjugated PPV emits light in the green-yellow region of the visible spectrum,[2] but this color can be altered by incorporation of electron-donating and electron-withdrawing substituents on the polymer backbone or by limiting the conjugation length of the chromophore. Thus, by appropriate substitution, one can control the polymer's solubility and processability or control the color and efficiency of its electroluminescence (EL).[3]

A typical strategy for increasing PPV solubility has been the incorporation of long alkyl or alkyloxy side chains onto the fully conjugated backbone.[4] However, another method has been through the synthesis of block copolymers containing PPV-type chromophores separated by solubilizing polymethylene segments, with both types of units being of controlled length. Some of the first effective organic light-emitting diodes (LED) with blue light emission were fabricated using such copolymers containing *p*-distyrylbenzene type chromophores separated by nonconjugated segments (Figure 1).[5,6] This strategy offers control over the conjugation length of the chromophore in a way that is not possible using standard techniques of homopolymeric PPV synthesis and thus allows the synthesis of systems with short wavelength emission. Such copolymers not only offer the advantage of increased solubility and processability but also exhibit increased emission efficiency by improved confinement of excitons. For the purposes of this paper, we refer to these types of systems as segmented copolymers.

Segmented LED copolymers of the type shown in Figure 1 have typically been synthesized by variants of the Wittig olefination route.[6] However, conventional Wittig chemistry is limited in terms of compatibility with substituents that can accommodate the basic conditions of this reaction. In this report, we describe the use of the Heck reaction for carbon−carbon bond forming syntheses of LED segmented copolymers. The Heck reaction has previously been used for synthesis of fully conjugated PPVs,[7−10] but its use for synthesis of segmented copolymers of the type in Figure 1 has been limited.[11] In this article, the advantages of the Heck synthesis over previously employed Wittig routes for making the target copolymers are described. In addition, using the Heck methodology, we were able to explore some effects of alkyl side chain incorporation into the LED copolymer structure, in terms of emission wavelength and thermal transitions.

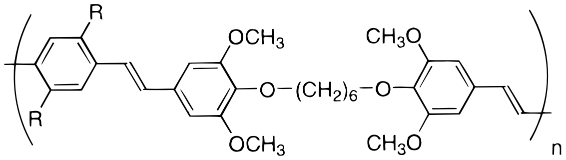

Figure 1. Blue-emitting segmented block copolymer.

Experimental Section

General. All commercially available materials were used as received unless noted otherwise. Tetrahydrofuran (THF) was distilled first from calcium hydride and then from sodium/benzophenone ketyl. 1,8-Bis(4-formyl-2,6-dimethyoxyphenoxy)-octane was synthesized as previously described.[6,12] 1,4-Di-*n*-hexylbenzene was synthesized as described in the literature.[13] Melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC-7 equipped with Pyris software, at a heating rate of 20 °C/min under nitrogen. Gel permeation chromatography (GPC) was performed on a Waters GPC system having a model 590 solvent delivery module equipped with a U6K injector and a model 410 differential refractometer. The data were collected using LabView software (National Instruments) and analyzed using the "GPC for Windows" software package (Mat Ballard; Melbourne, Australia). All GPC runs were conducted using

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10.1021/ma990825x CCC: $18.00

spectrophotometric grade THF at 30 °C. All molecular weights were calculated relative to monodisperse polystyrene standards. ^{1}H and ^{13}C NMR spectra were taken in $CDCl_3$ using a Bruker DPX-300 spectrometer at 300 and 75 MHz, respectively, and were referenced to residual $CHCl_3$ at δ 7.24 and 77.0 ppm. Solution photoluminescence spectra were taken on a Perkin-Elmer LS50B spectrometer. UV–vis absorbance spectra were taken on an IBM 9420 spectrometer. Elemental analyses were carried out by Dr. Gregory Dabkowski of the University of Massachusetts Microanalytical Laboratory.

LED Device Fabrication and Characterization. The LED devices were fabricated as follows according to standard procedures in our laboratory.[6] Solutions of the polymers (~20 mg/mL in $CHCl_3$) were spin-coated onto commercially available indium tin oxide (ITO)-coated glass plates (OFC Corp.) under inert conditions. The polymer films were typically ~90 nm thick. Before spin casting, copper wires were attached to the glass plates using a conductive epoxy. Calcium electrodes of ~90 nm thickness were evaporated onto the polymer films at about 10^{-6} Torr, followed by a protective coating of aluminum. The devices were characterized using a system constructed in our laboratory, which has been described elsewhere.[6,12] EL spectra were typically obtained at ~12 V driving voltage.

1,4-Dihexyl-2,5-diiodobenzene (1). This compound was synthesized according to a literature procedure[14] from 7.00 g (28.4 mmol) of di-*n*-hexylbenzene, 2.77 g (12.2 mmol) of periodic acid dihydrate, and 5.76 g (22.7 mmol) of iodine. The crude product was recrystallized twice from acetone to yield 6.14 g (43%) of **1** as colorless needles with mp 52–53 °C. (lit.[15] mp 53–54 °C). ^{1}H NMR: δ 7.55 (s, 2 H), 2.60 (t, 4 H), 1.55 (m, 6 H), 1.35 (m, 10H), 0.90 (m, 6H). ^{13}C NMR: δ 145.2, 139.7, 100.7, 40.2, 32.0, 30.6, 29.4, 23.0, 14.5.

1,4-Diisopropyl-2,5-diiodobenzene (2). This compound was synthesized analogously to compound **1** from 5.00 g (30.8 mmol) of *p*-diisopropylbenzene (Aldrich), 2.99 g (13.1 mmol) of periodic acid dihydrate, and 6.22 g (24.5 mmol) of iodine. The crude product was purified twice by recrystallization from acetone to yield 8.11 g (64%) of **2** as colorless needles with mp 93–94 °C. Elemental calcd for $C_{12}H_{16}I_2$: C, 34.81; H, 3.89; I, 61.30. Found: C, 34.79; H, 3.82; I, 61.10. ^{1}H NMR: δ 7.56 (s, 2 H), 3.05 (m, 2 H), 1.20 (d, 12 H). ^{13}C NMR: δ 150.3, 137.0, 101.9, 37.9, 23.4.

1,8-Bis(2,6-dimethoxy-4-formylphenoxy)octane (3). This compound was synthesized by the literature procedures.[6,12,16] All physical and spectral properties were in accord with previously published values.

1,8-Bis(4-formylphenoxy)octane (4). This compound was synthesized according to the literature procedure for **3**[6,12,16] from 20.0 g (0.16 mol) of 4-hydroxybenzaldehyde (recrystallized from water), 24.5 g (0.09 mol) of 1,8-dibromooctane, and 33.9 g (0.25 mol) of potassium carbonate. The crude product was recrystallized once from absolute ethanol to yield 53% of **4** as a white powder with mp 83–85 °C. Elemental calcd for $C_{22}H_{26}O_4$: C, 74.55; H, 7.39. Found: C, 74.35; H, 7.39. ^{1}H NMR: δ 9.85 (s, 2H), 7.80 (d, 4H), 7.00 (d, 4H), 4.05 (t, 4H), 1.85 (m, 4H), 1.45 (m, 8H). ^{13}C NMR: δ 191.2, 164.6, 132.4, 130.1, 115.1, 68.7, 29.6, 29.4, 26.3.

1,8-Bis(2,6-dimethoxy-4-vinylphenoxy)octane (5). To 16.0 g (44.9 mmol) of methyl triphenylphosphonium bromide suspended in 100 mL of THF at 0 °C under dry nitrogen was added dropwise 18 mL (44.9 mmol) of *n*-butyllithium (2.5 M in hexanes). The resulting orange solution was warmed to room temperature and stirred for an additional 10 min, and an attached addition funnel was charged with 5.0 g (10.5 mmol) of dialdehyde **3** in 50 mL of THF. The dialdehyde was added dropwise over 30 min, and the resulting yellow suspension was allowed to stir at room temperature overnight. The reaction mixture was filtered, and the filtrate was poured into 300 mL of water. The aqueous layer was back-extracted with either diethyl ether or dichloromethane. The combined organic layers were dried over anhydrous magnesium sulfate, filtered, and concentrated under vacuum. The crude product was purified by column chromatography on silica using diethyl ether as the eluent to yield 4.0 g (73%) of a white powder with mp 52–53 °C. Elemental calcd for $C_{28}H_{38}O_6$: C, 71.46; H, 8.14. Found: C, 71.70; H, 8.42. ^{1}H NMR: δ 6.61 (s, 4H), 6.60 (dd, 2H), 5.63 (d, 2H), 5.18 (d, 2H), 3.93 (t, 4H), 3.83 (s, 12H), 1.73 (m, 4H), 1.46–1.34 (m, 8H). ^{13}C NMR: δ 153.5, 137.3, 136.8, 133.0, 113.0, 103.4, 73.5, 56.1, 30.05, 29.4, 25.8.

1,8-Bis(4-vinylphenoxy)octane (6). This compound was synthesized by the same procedure as **5** using 3.0 g (8.5 mmol) of **4**, 12.9 g (36.1 mmol) of methyltriphenylphosphonium bromide, and 14.4 mL (36.1 mmol) of *n*-butyllithium (2.5 M in hexanes) to yield 1.2 g (40%) of **6** as shiny white plates with mp 113–114 °C. Elemental calcd for $C_{24}H_{30}O_2$: C, 82.24; H, 8.63. Found: C, 81.81; H, 8.43. ^{1}H NMR: δ 7.25 (d, 4H), 6.80 (d, 4H), 6.60 (dd, 2H), 5.53 (d, 2H), 5.10 (d, 2H), 3.90 (t, 4H), 1.75 (m, 4H), 1.30 (m, 8H). ^{13}C NMR: δ 159.3, 136.6, 130.6, 127.7, 114.8, 111.8, 68.3, 29.7, 29.6, 26.4.

Poly[1,8-octanedioxy-2,6-dimethoxy-1,4-phenylene-1,2-ethenylene-1,4-phenylene-1,2-ethenylene-3,5-dimethoxy-1,4-phenylene] (7). To a 100 mL round-bottomed flask fitted with a gas inlet and a condenser were added 0.50 g (1.06 mmol) of **5**, 0.35 g (1.06 mmol) of *p*-diiodobenzene, 8.0 mg of $Pd(OAc)_2$, and 55.0 mg of tri(*o*-tolyl)phosphine. The flask was flushed with argon, and 10 mL of DMF was added. The solution was heated to 85 °C, and 1 mL of triethylamine was added. The reaction was stirred at 85 °C for 2 days, cooled, and poured into a mixture of 200 mL of methanol and 20 mL of 2 N aqueous HCl. The resultant fibrous yellow polymer was vacuum-filtered and dissolved in $CHCl_3$. The chloroform solution was filtered through Celite to remove any insoluble catalyst residues, and the filtrate was precipitated into methanol. This precipitation procedure was repeated, and the product was dried under vacuum overnight to yield 0.28 g (48%) of yellow, fibrous polymer **7**. Elemental calcd for $(C_{34}H_{40}O_6)_n$: C, 74.97; H, 7.40. Found: C, 74.00; H, 7.27. ^{1}H NMR: δ 7.40 (s, 4 H), 6.90 (d, 4 H), 6.65 (s, 4 H), 3.90 (m, 4 H), 3.80 (s, 12 H), 1.80–1.20 (m, 12 H). ^{13}C NMR: δ 154.1, 137.8, 136.9, 133.2, 129.0, 128.0, 127.1, 104.1, 74.0, 56.6, 30.5, 29.8, 26.2.

Poly[1,8-octanedioxy-2,6-dimethoxy-1,4-phenylene-1,2-ethenylene-2,5-di-n-hexyl-1,4-phenylene-1,2-ethenylene-3,5-dimethoxy-1,4-phenylene] (8). This polymer was synthesized by the same procedure used for **7** from 0.50 g (1.1 mmol) of **5** and 0.53 g (1.1 mmol) of **1** to yield 0.44 g (57%) of yellow, fibrous **8**. Elemental calcd for $(C_{46}H_{64}O_6)_n$: C, 77.49; H, 9.05. Found: C, 77.53; H, 9.17. ^{1}H NMR: δ 7.40 (s, 2 H), 7.22 (d, 2 H), 6.94 (d, 2 H), 6.72 (s, 3 H), 6.48 (s, 1 H), 4.00 (m, 4 H), 3.90 (s, 12 H), 2.74 (m, 4 H), 0.90–1.80 (m, 30 H). ^{13}C NMR: δ 154.3, 138.9, 137.7, 135.5, 133.7, 129.8, 127.1, 125.8, 104.1, 74.1, 56.6, 33.7, 32.1, 31.8, 31.7, 30.5, 29.9, 29.8, 26.3, 23.1, 14.5.

Poly[1,8-octanedioxy-2,6-dimethoxy-1,4-phenylene-1,2-ethenylene-2,5-diisopropyl-1,4-phenylene-1,2-ethenylene-3,5-dimethoxy-1,4-phenylene] (9). This polymer was synthesized by the same procedure used for **7** from 0.50 g (1.1 mmol) of **5** and 0.44 g (1.1 mmol) of **2** to yield 0.39 g (59%) of yellow, fibrous **9**. Elemental calcd for $(C_{40}H_{52}O_6)_n$: C, 76.40; H, 8.33. Found: C, 76.19; H, 8.42. ^{1}H NMR: δ 7.44 (s, 2 H), 7.32 (d, 2 H), 6.88 (d, 2 H), 6.74 (s, 3 H), 6.50 (s, 1 H), 3.96 (m, 4 H), 3.90 (s, 12 H), 3.30 (m, 2 H), 1.76 (m, 6 H), 1.0–1.6 (m, 18 H). ^{13}C NMR: δ 154.1, 153.6, 144.0, 137.7, 135.4, 133.7, 130.6, 126.3, 123.2, 104.2, 74.0, 56.6, 30.5, 29.9, 29.4, 26.3, 24.6, 24.0.

Results and Discussion

Synthesis. Figure 2 shows the synthetic route to the monomers used in this study according to literature procedures. The basic monomers are 1,4-diiodo-substituted central core molecules with varying alkyl side chains and α,ω-divinyl flexible units containing the remainder of the chromophore and the eight-carbon segment for the flexible block of the copolymer. The central core components **1**–**2** were obtained by diiodination of 1,4-dialkylbenzene derivatives. This reaction proceeds readily without appreciable formation of monoreacted side products. The α,ω-divinyl flexible

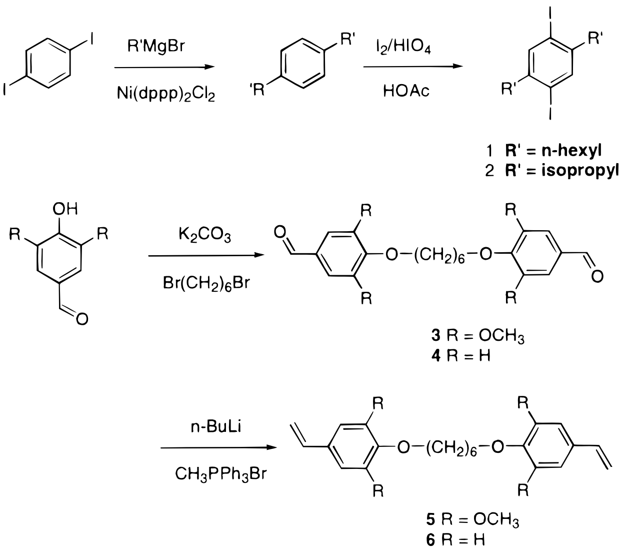

Figure 2. Synthesis of monomers.

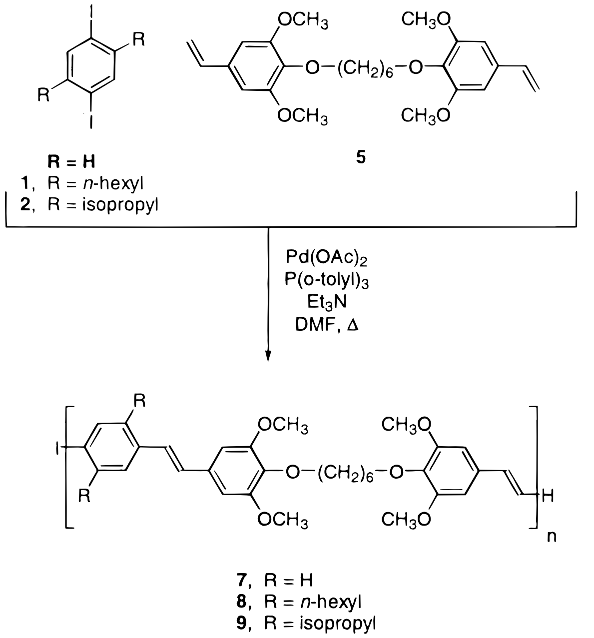

Figure 3. Heck synthesis of polymers.

units were synthesized by Wittig vinylation of 1,8-bis-(2,6-dimethoxy-4-formylphenoxy)octane (**3**) or its analogue without methoxy groups, **4**. Dialdehyde **3** is the standard flexible unit that has previously used in the Wittig synthesis of various PPV-based block copolymers. The vinylation of the dialdehydes to give **5**−**6** was a clean reaction whose only side product was triphenylphosphine oxide, which was easily removed by filtration through silica gel.

With some effort, we found the Heck polymerization (Figure 3) to be fastest and highest yielding when about 1.5 mol % of palladium catalyst with the hindered coadditive tris(*o*-tolyl)phosphine was used. In some of our earlier efforts, interruption of the catalytic cyclic caused precipitation of metallic palladium and vinylic end groups at ∼δ 5.40 could be observed, implying low molecular weights. The conditions reported in the Experimental Section gave the best results in our hands. Typically, the reaction had to be run for about 2 days to avoid major polymer contamination by unreacted starting material. The polymerizations using the methoxy-substituted monomer gave good elemental analysis results and GPC molecular weights of 40−70 000, with degrees of polymerization up to 100 and polydispersity indices less than 3.0 (Table 1).

Table 1. Characterization Data for Methoxy-Substituted Copolymers

polymer	R′	M_w	M_w/M_n	T_g/°C
7	H	43 800	2.8	80
8	*n*-hexyl	39 200	2.3	21
9	isopropyl	71 000	2.8	85

The success of the polymerization under these reaction conditions appears to be partly dependent on the solubility of the monomers. When we attempted the same synthesis with divinyl monomer **6** that did not contain methoxy groups, oligomeric material precipitated from the reaction mixture after only 2 h. Subsequent trials of the same reaction with a higher solvent/monomer ratio and higher mole percent of catalyst still produced only a low molecular weight (M_w = 5000) polymer, even though all components stayed in solution throughout the reaction. Black palladium metal precipitated out of the latter reactions, indicating that one of the steps in the catalytic cycle is not efficient under these conditions. We did not attempt a mechanistic investigation of this process. A similar synthesis attempted by Suzuki et al.[11] also gave product analysis data that suggest an inefficient catalytic cycle. Because of this, we concentrated our attention on the more amenable, methoxy-substituted copolymers.

The ^{1}H NMR spectra of the polymers synthesized by the Heck route show that they have ≥90% trans double bonds, judging by analysis of ^{1}H NMR peaks that have been assigned in previous work for polymers of the type in Figure 1. The high trans specificity of the product produced in this reaction is an important reason to choose it over less stereospecific routes. We saw no evidence of the formation of 1,1-vinylidene type units.

As further comparative evidence of the Heck methodology's efficacy, we synthesized the previously reported blue-emitting segmented copolymer **7** without additional substitution on the central benzene ring of the chromophore. This material was originally synthesized by a typical Wittig olefination route.[6] The isolated polymer yield was much better in the Heck method relative to that in the Wittig method, with an increase to ∼60% from ∼10%. The GPC weight-average molecular weight referenced to polystyrene was 43 800. This is a significant improvement over the Wittig synthesis result, in which the reported molecular weight was 34 000.

A major reason for this improvement over the Wittig methology is that the Heck method directly produces the desired polymer with trans double bonds, which are critical to maximize efficiency of luminescence and wavelength of output. The luminescent properties of the segmented LED copolymers are optimal when the double-bond configurations are <10% cis.[17] To achieve this tolerable percentage of cis bonds, Wittig methodology requires a post-polymerization isomerization step, accomplished by heating the crude polymer (having a mixture of cis and trans olefin bonds) with a trace of iodine in a solvent. The ensuing procedure of removing the undesired iodine and reprecipitating the isomerized polymer multiple times results in the mechanical loss of much of the desired all-trans product. Even worse, elemental analysis of isomerized products sometimes shows the presence of iodine, apparently due to ir-

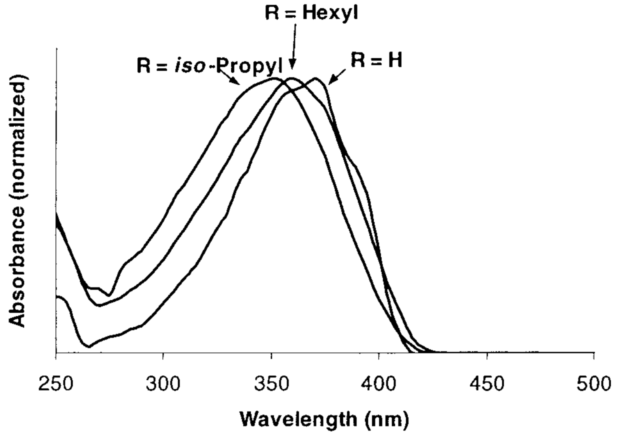

Figure 4. UV−vis absorbance of polymers **7**−**9**.

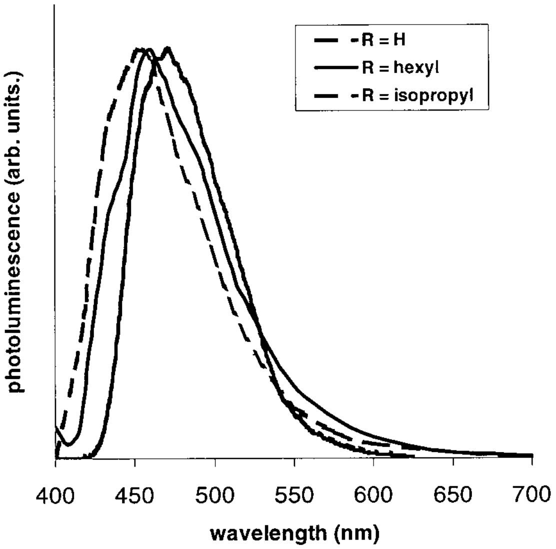

Figure 5. Photoluminescence of methoxy-substituted polymers **7**−**9**.

reversible reaction of the iodine with the electron-rich methoxy-substituted benzene rings on the chromophore segment. By comparison, the Heck reaction yields the same regular copolymer regiochemistry and double-bond configuration (or better) by methodology that is far less tedious, with a much higher yield and in better purity.

Optical Properties. The methoxy-substituted polymers **7**−**9** were characterized by UV−vis absorbance, photoluminescence, and electroluminescence spectroscopy. The UV−vis plots are shown in Figure 4. The spectra are similar in appearance, but there is a 20 nm red shift in changing the central ring substituents from R = isopropyl to R = *n*-hexyl to R = H. This shift is probably due to a decreased torsional angle about the central ring as R gets less bulky. Force field molecular modeling (Cerius^2, Molecular Simulations Inc.) of the isolated chromophore unit shows that the relative torsion of the central benzene ring is 40−50° when R = isopropyl, 25−30° when R = *n*-hexyl, and virtually zero when R = H. Hohloch et al.[18] have reported a related, torsion-induced blue shift in cyano-substituted model PPV oligomers. The twisting in the latter molecules was proven by X-ray crystallography.

All of the polymers **7**−**9** showed photoluminescence (PL, Figure 5) and electroluminescence (EL, Figure 6) in the blue region of the visible spectrum. The emission spectra for the alkyl-substituted copolymers are quite similar, despite the differences in their UV−vis spectra described above. In both the PL and EL spectra, the polymers with alkyl groups on the central benzene ring are blue-shifted by about 15 nm compared to the spectrum of parent polymer **7**. This is again presumably due to the torsion of the chromophores induced by the alkyl groups in **8** and **9**, which reduces the effective conjugation length of the chromophore.

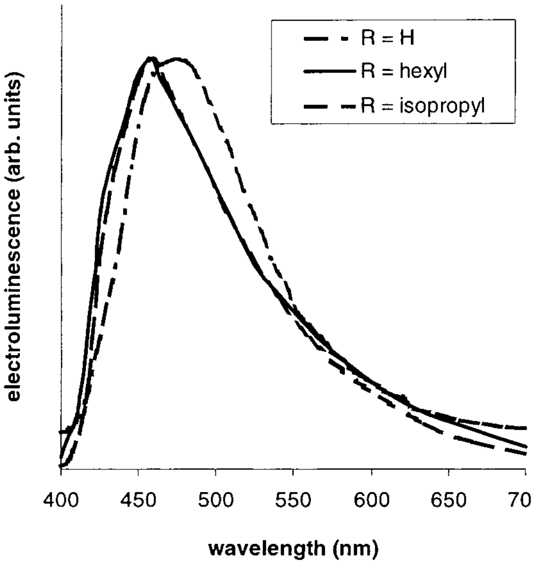

Figure 6. Electroluminescence of methoxy-substituted polymers **7**−**9**.

The presence of the bulky alkyl groups is also intended to increase the efficiency of the device by limiting exciton transfer between chromophores, since the chromophore units will be less likely to aggregate during the polymer film-casting process. If the average distance between chromophores is increased, the result should be a decrease in exciton transfer and related quenching events. This topic is currently under investigation in our laboratories. The λ_{max} of the solution PL is blue-shifted by 10−15 nm for the copolymers **8** and **9** and ~30 nm for copolymer **7** from that of the film photoluminescence, indicating that there are some solid-state effects even in the side-chain-substituted systems, although these shifts are small enough to be (at least in part) attributable to the difference in local environments between the solution and film spectra.

Thermal Analysis. The polymers were also investigated using differential scanning calorimetry (DSC). Parent polymer **7** showed only a glass transition (T_g) at ~80 °C, in good agreement with results for the previously described material obtained by the Wittig route. It has been shown[19] that, in this alternating block copolymer (i.e., **7**), this transition is associated with the phase-separated soft block of methylene units. Polymer **9**, substituted with isopropyl groups on the middle ring of the chromophore, showed a glass transition in the same region at 85 °C. However, the *n*-hexyl-substituted polymer **8** displayed a T_g of 21 °C. This difference in T_g is attributed to the fact that the hexyl group is sufficiently long and flexible to plasticize the oligomethylene soft block, whereas the isopropyl group is not effective as a plasticizer in these copolymers. The hexyl group has a similar shape to the soft methylene spacer block of the copolymer and therefore can act as a plasticizer. The hexyl groups are, in principle, efficient plasticizers since they are incorporated in the copolymer, albeit in the hard block. Thus, it is probable that a fraction of the hexyl groups can be incorporated into the phase separated soft block. The isopropyl groups, however, are shorter and are inefficient plasticizers; hence, they act only to increase solubility by breaking up chromophore packing rather than affecting the solid-state packing.

Acknowledgment. The authors gratefully acknowledge funding from the Air Force Office of Scientific Research and from Osram-Sylvania, Inc.

Supporting Information Available: DSC traces for polymers **7**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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