2016 *Macromolecules* **2000,** *33,* 2016−2020

Bridging the Gap between Polyfluorene and Ladder-Poly-*p*-phenylene: Synthesis and Characterization of Poly-2,8-indenofluorene

S. Setayesh, D. Marsitzky, and K. Müllen*

Max-Planck-Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany

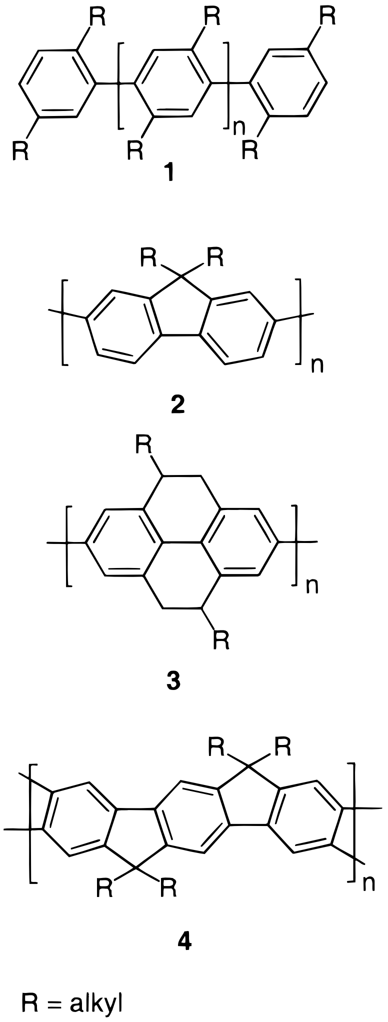
Received August 23, 1999; Revised Manuscript Received December 9, 1999

ABSTRACT: We present here a new derivative of poly-*p*-phenylene (PPP), the poly-2,8-indenofluorene (**8a,b**), to bridge the gap between 2,7-poly-9,9′-dialkylfluorene (PF) (**2**) and ladder-poly-*p*-phenylene (LPPP) (**4**). The monomer **7a,b** was synthesized starting from 6,12-dihydroindeno[1,2*b*]fluorene (**5**), which was four times alkylated, brominated with copper(II) bromide on an aluminum oxide matrix, and polymerized via a Ni(0)-mediated coupling reaction ($M_n \sim (3.3-3.9) \times 10^4$ (tuluene, polystyrene standards)). As expected, the wavelength data for absorption and emission are intermediate to those of PF and LPPP and prove the suitability of the polymer to be used as blue-light-emitting material in polymer light-emitting diodes. The polymer **8a,b** is stable up to 380 °C and shows thermotropic liquid crystalline behavior at high temperatures (250−300 °C). Oligomers of the 6,6′,12,12′-tetraoctylindenofluorene (**6a**) have been synthesized by Ni(0)-induced coupling of monobromo and dibromo (**7a**) compounds, to determine the effective conjugation length ($n_{\infty,\text{abs}} = 6-7$, $n_{\infty,\text{em}} = 5-6$).

The discovery of electroluminescence (EL) in conjugated polymers[1,2] gave an impetus to the development of light-emitting devices (LEDs) for display technology. Luminescent polymers offer considerable processing advantages over the well-established inorganic electroluminescent materials and organic dye molecules as they can be deposited via spin-coating over large areas. Another important benefit of conjugated polymers is that the color and emission efficiency can be fine-tuned by manipulation of the chemical structure.[3−6]

For multicolor display applications one needs light-emitting diodes with the three basic colors red, green, and blue. Although red and green emitters with long lifetime stability and good device performances are already available, there is still a great need for suitable blue emitters. Poly-*p*-phenylene (PPP) (**1**) (Scheme 1) and its derivatives have been studied as blue-light-emitting materials for some time and have been incorporated into LED devices.

Scheme 1. Poly-*p*-phenylene (1), Polyfluorene (2), Polytetrahydropyrene (3), and Ladder-Poly-*p*-phenylene (4)



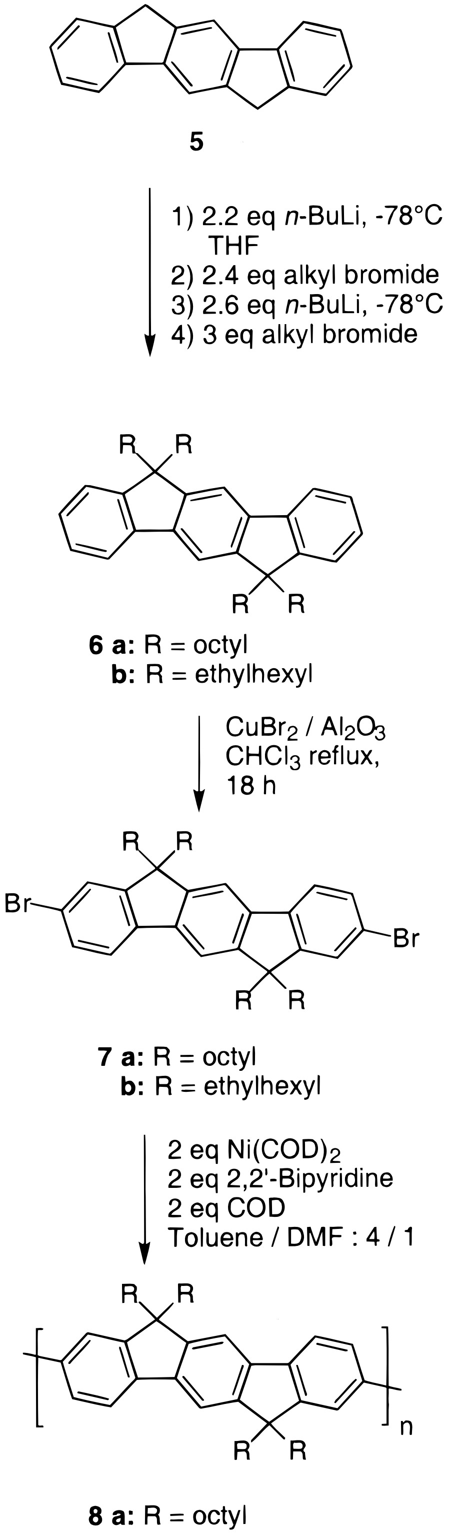
Although unsubstituted PPP[7] is an insoluble and intractable material, the introduction of sterically demanding solubilizing side chains leads to a considerable torsion about the phenylene−phenylene bonds, which seriously inhibits the conjugative interaction along the polymer chain. It is the remarkable feature of ladder-poly-*p*-phenylene (LPPP)[8] (**4**) that the bridging of neighboring phenylene groups causes a perfect flattening of the polymer π-system, at the same time allowing the attachment of solubilizing substituents without hampering the π-conjugation. The only disadvantage of the perfectly planarized LPPP (**4**) is the tendency to aggregate, which leads to excimer formation and undesired blue-green emission in LEDs. The "stepladder" polymers, polyfluorene (PF)[9] (**2**) and polytetrahydropyrene (PTHP)[10] (**3**), can be regarded as synthetically less demanding analogues of LPPP (**4**). Especially PF (**2**) gained much attention for the preparation of blue LEDs, due to its higher emission wavelength relative to PPP (**1**) and its high fluorescence quantum yield.[11,12] However, the emission maxima of PF (**2**) and PTHP (**3**) (~415 nm) are located at wavelengths where the human eye is not very sensitive. Therefore, to bridge the gap

---

* Corresponding author. e-mail: muellen@mpip-mainz.mpg.de.

10.1021/ma9914366 CCC: $19.00

Scheme 2. Synthesis of the 2,8-Poly-6,6′,12,12′-tetraalky-6,12-dihydroindeno[1,2*b*]fluorene (8)



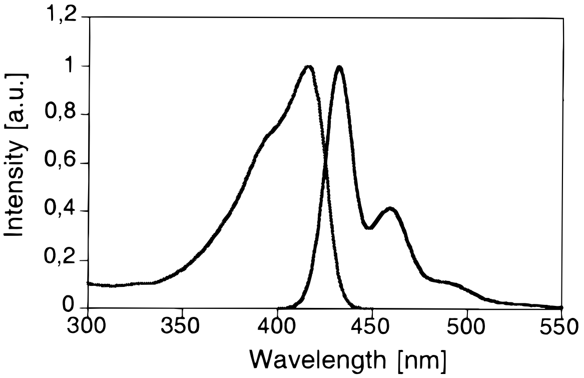


Figure 1. Absorption and emission spectra (excited at 390 nm) of the polymer **8a** in $CHCl_3$ solution.

between PF (**2**) and LPPP (**4**), we have synthesized the new 2,8-polyindenofluorene (2,8-PIF) (**8a,b**) containing three planarized phenylene rings.

In this paper we report on the preparation and the investigation of the optical and thermal properties of oligomers and polymers of 6,6′,12,12′-tetraalkyl-6,12-dihydroindeno[1,2-*b*]fluorenes (**6a,b**) as well as the determination of the effective conjugation length. We have denoted 6,12-dihydroindeno[1,2-*b*]fluorenes (**5**) as indenofluorene.

The synthesis of polyindenofluorene started from the well-known indenofluorene (**5**)[13,14] (Scheme 2), which was tetraalkylated using *n*-butyllithium and alkyl bromides. The resulting 6,6′,12,12′-tetraalkylindenofluorenes **(6a,b)** were selectively brominated in 2,8-positions with copper(II) bromide on an aluminum oxide matrix in carbon tetrachloride.[15,16] The reaction progress was monitored by FD mass spectroscopy and led to the desired 2,8-dibromo monomer **7a,b** in 99% yield. The polymerization of **7a,b** was affected under Yamamoto conditions with Ni(0) catalysis to yield the desired 2,8-PIF **(8a,b)**. To remove the bromine end groups, bromobenzene was added at the end of the polymerization, and the mixture was allowed to react for an additional 12 h. The ^1H NMR and ^{13}C NMR spectra of **8a** are consistent with the expected regioregular structure of the polymer. The signal between δ 7.90 and 7.78 ppm corresponds to the protons H-7 and H-1. The protons 3, 4, 5, 9, 10, and 11 of the indenofluorene repeating unit appear between δ 7.72 and 7.52 ppm. The signals between δ 2.3 and 0.5 can be ascribed to the aliphatic protons of the octyl chains. Only eight signals appear in the aromatic region of the ^{13}C NMR spectrum instead of the expected nine due to the overlap of two quaternary resonances at δ 140.29 ppm. The polymers exhibit good solubility in common organic solvents (e.g., THF, toluene, and chlorinated hydrocarbons); the solubility of the tetraethylhexyl derivative exceeds the solubility of the tetraoctyl-PIF.

Gel permeation chromatography (GPC) analysis (toluene, polystyrene standards) of 2,8-PIF (**8a**) shows a monomodal distribution with a number-average molecular weight (M_n) of approximately 3.3×10^4 g/mol and a weight-average molecular weight (M_w) of 1.7×10^5 g/mol (PD = 5.2). The number-average molecular weight (M_n) of the polymer **8b** is 3.9×10^4 g/mol ($M_w = 1.1 \times 10^5$ g/mol, PD = 2.75). However, it is well-known that the GPC analysis of rigid-rod polymers using polystyrene as calibration standard overestimates the molecular weight of rigid rod polymers by nearly 25%, due to the different behavior of the flexible coils in solution.[10] The higher value of polydispersity of **8a** in comparison to that of **8b** is likely a consequence of the lower solubility of the former polymer, which leads to partial precipitation of the growing polymer chain.

The absorption and fluorescence spectra of the 2,8-PIF **(8a)** in solution (chloroform, 0.033 g/L) are shown in Figure 1. The absorption maximum is located at 416 nm, while the emission spectrum (λ_{exc} = 390 nm) exhibits a vibronic fine structure with two sharp bands at 432 and 479 nm. The small Stokes shift of 16 nm is typical for ladder-type polymers. For the polymer **8b**, however, we observe a slight hypsochromic shift in comparison to **8a** (chloroform, 0.035 g/L, absorption band at 408 nm and two sharp emission bands at 428 and 453 nm, Stokes shift = 20 nm), which can be attributed to the enhanced torsion angle of the indenofluorene repeating units caused by the sterically demanding ethylhexyl chain. These values are between the absorption and emission data of poly-9,9′-dihexylfluorene (**2**) (absorption band at 383 nm, emission band at 415 nm)[12] and LPPP (**4**) (absorption band 438 nm, emission band 470 nm)[17] and point to the enhanced conjugation in 2,8-PIF compared to PF.

The thermogravimetric analysis (TGA) of 2,8-PIF **(8a,b)** reveals the excellent thermal stability of this novel stepladder polymer: a 5% weight loss can be recognized at 380 °C, while the main decomposition can be observed at 450 °C (41.24% weight loss). The differential scanning calorimetry (DSC) of a solution-cast sample shows no crystallization on heating for both polymers **8a,b**. For polymer **8a** we observe on heating two liquid crystalline phases transition at 250 and 290 °C. The wide-angle X-ray scattering (WAXS) shows a higher degree of order of the second thermotropic phase (290 °C) compared to the first one (250 °C). On cooling, the reverse transitions occur at 270 and 240 °C. Similar curves upon heating have been observed for the 2,7-poly-9,9′-dioctylfluorene at lower temperatures (heating, 159 °C; cooling, 81 °C). However, upon cooling only one phase transition temperature has been detected for the 2,7-poly-9,9′-dioctylfluorene.[11] In contrast, polymer **8b** with branched side chains exhibits a liquid crystalline phase transition at 290 °C with the reverse transition on cooling at 220 °C. Again, the 2,7-poly-9,9′-diethylhexylfluorene shows similar DSC traces with analogous transitions at lower temperatures (heating, 167 °C; cooling, 130 °C).[18] The exact nature of the liquid crystalline phases will be the subject of further publications.

For polymers, the effective conjugation length (ECL) is a highly important variable in determining the electronic properties such as band gaps, absorption coefficients, emission quantum yields, etc.[19] The ECL can be explained as the minimum number of repeating units necessary to produce saturation of a physical property, e.g., absorption or emission maxima. To determine the ECL, it was necessary to synthesize the oligomers of 2,8-PIF by the Ni(0)-mediated coupling reaction using a mixture of dibromo- and monobromoindenofluorene as chain limiters. The end-capping reagent 2-bromo-6,6′12,12′-tetraoctylindenofluorene was synthesized by interrupting the bromination reaction of **7a**. The resulting oligomers were separated by preparative HPLC (RP18 column) using a gradient elution with THF/methanol to afford indenofluorene oligomers up to $n = 5$, which were analyzed by FD and MALDI-TOF mass spectrometry and by UV and fluorescence spectroscopy (Table 1).

Table 1. Absorption and Emission (Excited at 390 nm) Maxima of the Oligomers

n	absorption [eV]	emission [eV]
1	3.54	3.31
2	3.33	3.05
3	3.23	3.93
4	3.10	3.90
5	3.08	3.89

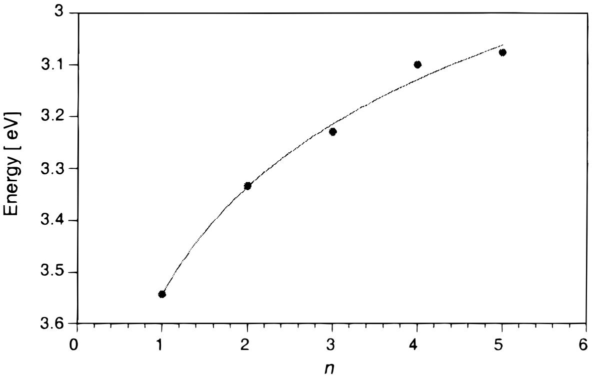


Figure 2. Determination of $n_{\infty,\mathrm{abs}}$ using the method of exponential fit (E versus n).[20,21]

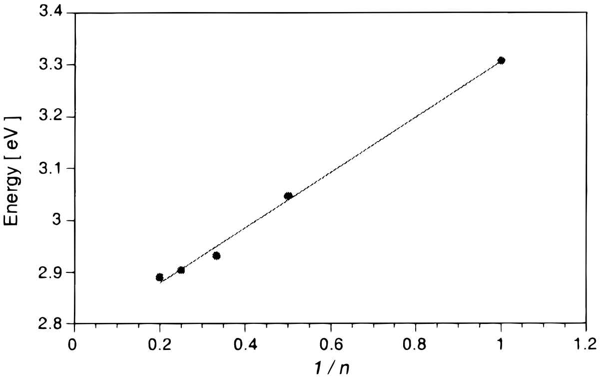


Figure 3. Determination of $n_{\infty,\mathrm{em}}$ using the method of linear fit (E versus n).[22]

To determine the effective conjugation length of poly-2,8-indenofluorene, we used the transition energy E_n derived from the longest wavelength absorption maxima and the shortest emission maxima of the oligomers in solution (chloroform,∼0.03−0.04 g/L). Two methods were applied: the plot of energy versus $1/n$ [20,21] and the method of the exponential fit,[22] where the energy is plotted versus n (n = number of indenofluorene units). The limiting wavelengths of 416 nm for absorption and 432 nm for emission are obtained from the high molecular weight polymer **8a**. The first method using the extrapolation of the energy versus $1/n$ gives an excellent correlation coefficient of 0.973. The calculated value for the energy E_{abs}, however, corresponds to 3.0 eV (414 nm), which is 2 nm away from the value for the high molecular weight polymer of 2.98 eV (416 nm). Using the method of exponential fit (Figure 2), we obtained a good correlation between the theoretical and experimental value of E_{abs}, giving a value of $n_{\mathrm{abs}} = 6-7$. For emission the effective conjugation length is determined to be $n_{\mathrm{em}} = 5-6$ (Figure 3) by both methods. These values are intermediate between those for PF (**2**)[12] and PTHP (**3**).[10]

In conclusion, we have presented the synthesis of the novel stepladder polymer 2,8-PIF via a Yamamoto-type polymerization. The polymers obtained exhibit high molecular weights, excellent thermal stability, and good solubility in common organic solvents. In addition, the 2,8-PIF shows LC phase forming behavior at high transition temperatures, making the polymer a good candidate for use as the active material in polarized LEDs.

The effective conjugation length determined for the oligomers of **8a** were $n_{\infty,\mathrm{abs}} = 6-7$ and $n_{\infty,\mathrm{em}} = 5-6$. Future work will focus on the preparation of 2,8-PIF and PF copolymers and on evaluating the electroluminescence properties of the polymers.

Experimental Section

Materials and General Procedures. The solvents used were of commercial p.a. quality; toluene was distilled from sodium, *N*,*N*-dimethylformamide (DMF) was distilled from calcium hydride, and tetrahydrofuran (THF) was dried over potassium. Indenofluorene was synthesized by the well-known procedure.[13,14]

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AMX 300 (300 and 75 MHz, respectively). UV−vis data were obtained on a Perkin-Elmer Lambda 9. Gel permeation chromatography (GPC) analysis was performed with PL-gel columns (10^3 and 10^4 Å pore widths) connected to a refractive index detector and toluene as solvent. The calibration was based on polystyrene standards with narrow weight distribution. TGA analysis was performed on a Mettler 500 thermogravimetric analyzer (heating rate 10 °C/min, N_2 atmosphere). DSC data were obtained on a Mettler TC 10 A (heating rate 10 °C/min, N_2 atmosphere).

6,6′,12,12′-Tetraalkyl-6,12-dihydroindeno[1,2*b*]fluorene (6a,b). To a solution of 6,12-dihydroindeno[1,2*b*]fluorene (**5**) (5 g; 19.69 mmol) in dry THF (300 mL) at −78 °C was added *n*-butyllithium (27 mL; 1.6 M solution in hexane). The mixture was allowed to warm to room temperature and was stirred for 1 h. After cooling to −78 °C, alkyl bromide (47.2 mmol) was added, and the solution was heated to room temperature and was stirred for 1 h. This procedure was repeated with *n*-butyllithium (32 mL; 1.6 M solution in hexane) and of alkyl bromide (60 mmol). The solution was poured into petroleum ether (PE), washed with water, and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (silica gel, PE). To remove excess of the alkyl bromide, the product was recrystallized from ethanol to give **6a** (11.56 g; 83.6%) and **6b** (10.95 g; 79.2%). **6a:** Anal. Calcd: C, 88.82; H, 11.18. Found: C, 88.84; H, 11.07. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.75 (dd, *J* = 4.6 Hz, 2 H), 7.63 (s, 2 H), 7.24−7.4 (m, 6 H), 2.01−2.06 (m, *J* = 3.6 Hz, 8 H), 1.06−1.19 (m, 40 H), 0.8 (t, *J* = 7 Hz, 12 H), 0.69 (m, 8 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 151.12, 149.98, 141.52, 140.57, 126.61, 122.84, 119.35, 113.85, 54.70, 40.66, 31.80, 30.03, 29.22, 29.18, 23.74, 22.25, 14.02. MS (FD) *m*/*z* (M+) = 702. **6b:** Anal. Calcd: C, 88.82; H, 11.18. Found: C, 88.77; H, 11.23. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.68 (dd, *J* = 4.6 Hz, 2 H), 7.63 (s, 2 H), 7.18−7.36 (m, 6 H), 1.94−2.08 (m, *J* = 3.6 Hz, 8 H), 0.35−1.02 (m, 60 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 150.91, 150.84, 149.73, 141.73, 140.38, 126.61, 123.99, 126.00, 119.13, 114.89, 54.47, 44.94, 44.50, 34.54, 33.91, 33.83, 33.71, 33.60, 28.32, 28.18, 28.00, 26.97, 26.85, 26.69, 22.75, 22.69, 14.08, 13.97, 10.38, 10.24, 10.04. MS (FD) *m*/*z* (M+) = 702.

2,8-Dibromo-6,6′,12,12′-tetraalkyl-6,12-dihydroindeno-[1,2*b*]fluorene (7a,b).[15,16] To a solution of 6,6′,12,12′-tetraalky-6,12-dihydroindeno[1,2*b*]fluorene **(6a,b)** (3.4 g; 4.84 mmol) in CCl_4 (100 mL) was added copper(II) bromide (20 g) on aluminum oxide. The mixture was refluxed for 18 h. The reaction was monitored by FD mass spectrometry. After bromination was completed the mixture was filtrated, and the organic filtrate was washed with water and dried over magnesium sulfate. The solvent was removed, and the product was recrystallized with ethanol to give the desired products **7a** (4.09 g; 98%) and **7b** (4.11 g; 99%). **7a:** Anal. Calcd: C, 72.54; H, 8.90. Found: C, 72.40; H, 8.91.^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.58 (d, *J* = 8.6 Hz, 2 H), 7.55 (s, 2 H), 7.53 (dd, *J* = 8.8 Hz, 2 H), 7.43 (d, *J* = 1.9 Hz, 2H), 1.95−2.00 (m, *J* = 3.6 Hz, 8 H), 1.40−1.17 (m, 40 H), 0.78 (t, *J* = 7 Hz, 12 H), 0.62 (m, 8 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 153.34, 149.91, 140.30, 139.91, 129.84, 126.14, 120.83, 120.77, 113.96, 55.10, 40.45, 31.75, 29.88, 29.15, 29.12, 23.65, 22.55, 14.00. MS (FD) *m*/*z* (M+) = 862. **7b:** Anal. Calcd: C, 72.54; H, 8.90. Found: C, 72.55; H, 8.89.^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.58 (d, *J* = 8.6 Hz, 2 H), 7.55 (s, 2 H), 7.53(dd, *J* = 8.8 Hz, 2 H), 7.43 (d, *J* = 1.9 Hz, 2 H), 1.95−2.00 (m, *J* = 3.6 Hz, 8 H), 1.40−1.17 (m, 40 H), 0.78 (t, *J* = 7 Hz, 12 H), 0.62 (m, 8 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 153.34, 149.91, 140.30, 139.91, 129.84, 126.14, 120.83, 120.77, 113.96, 55.10, 40.45, 31.75, 29.88, 29.15, 29.12, 23.65, 22.55, 14.00. MS (FD) *m*/*z* (M+) = 862.

2,8-Poly-6,6′,12,12′-tetraalkyl-6,12-dihydroindeno[1,2*b*]-fluorene (8a,b). A Schlenk tube containing DMF (15 mL), (1,5-cyclooctadiene)nickel(0) (193 mg; 0.7 mmol), 2,2′-bipyridyl (109 mg; 0.7 mmol), and 1,5-cyclooctadiene (76 mg; 0.7 mmol) was heated under argon at 80 °C for 30 min. The monomer **7** (300 mg; 0.35 mmol) was dissolved in dry toluene (60 mL) and added under argon to the DMF solution. The reaction mixture was maintained at 80 °C for 3−4 days in the dark. Bromobenzene (3 mg, 0.02 mmol) in 5 mL of toluene was added to the reaction. The mixture was allowed to react for an additional day. The reaction mixture was then poured into hydrochloric acid (concentrated)/methanol 1:1 (500 mL). The isolated polymer was dissolved in chloroform and reprecipitated in methanol. This procedure was repeated twice to give the polymer **8a** (208 mg; 85%) and (216 mg; 88%). **8a:** Anal. Calcd: C, 89.08; H, 10.92. Found: C, 88.80; H, 11.15. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.85 (m, 2 H), 7.65 (m, 6 H), 2.1 (m, 8 H), 1.2 (m, 48 H), 0.8 (t, *J* = 7 Hz, 12 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 151.93, 150.52, 140.71, 140.29, 125.96, 119.62, 119.52, 113.96, 54.91, 40.64, 31.82, 30.06, 29.21, 23.87, 22.59, 14.03. **8b:** Anal. Calcd: C, 89.08; H, 10.92. Found: C, 88.74; H, 11.29.^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.80 (m, 2 H), 7.63 (m, 6 H), 2.1 (m, 8 H), 0.9 (m, 50 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 151.41, 150.17, 140.21, 126.03, 122.91, 119.33, 115.04, 54.65, 44.81, 34.75, 34.02, 28.50, 28.13, 26.96, 28.50, 28.13, 26.96, 22.83, 14.14, 14.03, 10.42, 10.16.

Acknowledgment. Financial support from the European Commission (BRITE EURAM BE 97-4438, OSCA) and BMBF (OPTIMAS 03M1021B7) is gratefully acknowledged. The authors thank U. Scherf for fruitful discussions and M. Forster for performing the HPLC separation.

References and Notes

(1) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.

(2) Braun, D.; Heeger, A. J. *Appl. Phys. Lett.* **1991**, *58*, 1982.

(3) Salbeck, J. *Ber. Bunsen-Ges. Phys. Chem.* **1996**, *100*, 1667.

(4) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Brédas, J. L.; Löglund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121.

(5) Scherf, U. In *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R., Eds.; Marcel Dekker: New York, 1997; p 363.

(6) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed. Engl.* **1998**, *110*, 402.

(7) Gin, D. L.; Conticello, V. P. *Trends Polym. Sci.* **1996**, *4*, 217.

(8) Huber, J.; Müllen, K.; Salbeck, J.; Schenk, H.; Scherf, U.; Stehlin, T.; Stern, R. *Acta Polym.* **1994**, *45*, 244.

(9) Pei, Q.; Yang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7416.

(10) Kreyenschmidt, M.; Uckert, F.; Müllen, K. *Macromolecules* **1995**, *28*, 4577.

(11) Grell, M.; Bradley, D. D. C.; Inbasekaran, M. *Adv. Mater.* **1997**, *9*, 798.

(12) Kreyenschmidt, M.; Klaerner, G.; Fuhrer, T. Aschenhurst, J.; Karg, S.; Chen, W. D.; Lee, V. Y.; Scott, J. C.; Miller, R. D. *Macromolecules* **1998**, *31*, 1099.

(13) Ebel, F.; Deuschel, W. *Chem. Ber.* **1956**, *89*, 2794.

(14) Chardonnens, L.; Salamin, L. *Helv. Chim. Acta* **1968**, *51*, 1095.

(15) Kodomari, M.; Satoh, H.; Yoshitomi, S. *J. Org. Chem.* **1988**, *53*, 2093.

(16) Ranger, M.; Rondeau, D.; Leclerc, M. *Macromolecules* **1997**, *30*, 7686.
(17) Scherf, U.; Müllen, K. *Macromolecules* **1992**, *25*, 3546.
(18) Grell, M.; Knoll, W.; Lupo, D.; Meisel, A.; Miteva, T.; Neher, D.; Nothofer, H.-G.; Scherf, U.; Yasuda, A. *Adv. Mater.* **1999**, *11*, 671.
(19) Müllen, K.; Wegner, G. *Electronic Materials: The Oligomer Approach*; Wiley-VCH: New York, 1999.
(20) Schenk, R.; Ehrenfreund, M.; Huber, W.; Müllen, K. *J. Chem. Soc., Chem. Commun.* **1990**, 1673.
(21) Tolbert, L. M. *Acc. Chem. Res.* **1992**, *25*, 561.
(22) Meier, H.; Stalmach, U.; Kolshorn, H. *Acta Polym.* **1997**, *48*, 379.

MA9914366