Macromolecules **2001,** *34,* 2495−2501

Synthesis, Characterization, and Electrooptical Properties of a New Alternating *N*-Dodecylpyrrole−Benzothiadiazole Copolymer

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Received October 4, 2000; Revised Manuscript Received January 31, 2001

ABSTRACT: The synthesis of a new processable alternating conjugated copolymer consisting of *N*-dodecylpyrrole and 2,1,3-benzothiadiazole repeat units (PDPB) is accomplished via condensation copolymerization of 2,5-bis(trimethylstannyl)-*N*-dodecylpyrrole and 4,7-dibromo-2,1,3-benzothiadiazole under the Stille coupling conditions using $Pd(PPh_3)_2Cl_2$ as a catalyst in dry THF. MALDI-TOF mass spectrometry revealed a perfect alternation of monomer units in PDPB and enabled the identification of hydrogen, bromine, and methyl end groups. As a consequence of its semiamphiphilic nature, PDPB can form stable and transferable monomolecular Langmuir films at the air−water interface. The interaction between the electron-releasing *N*-dodecylpyrrole and electron-withdrawing 2,1,3-benzothiadiazole units in PDPB results in an optical band gap of 2.03 eV and a red emission. Photoinduced absorption (PIA) and photoluminescence (PL) spectroscopy revealed that in a composite film of PDPB with a methanofullerene (PCBM) as acceptor the fluorescence and the intersystem crossing of the pristine polymer are strongly quenched. Bulk heterojunction photovoltaic cells of PDPB and PCBM (1:3 by weight) have been prepared and demonstrate that in such devices this quenching involves generation of charge carriers.

Introduction

The exciting applications envisaged for semiconducting polymers, such as light-emitting diodes (LEDs), field-effect transistors (FETs), and photovoltaic cells,[1] have stimulated the search for novel conjugated polymers with tailor-made properties.[2] In recent years considerable attention has been given to the preparation and properties of alternating conjugated copolymers in which the nature of the comonomers affords a novel means to design materials with improved functional properties that cannot be attained by the corresponding homopolymers.[3,4] As an example, copolymers consisting of alternating electron-rich and electron-deficient rings may exhibit a significantly red-shifted absorption and result in extremely low band gap materials.[5]

Although polypyrrole has received considerable attention as a conducting material in its oxidized form,[6] its semiconducting properties and the incorporation of polypyrrole in LEDs or FETs have not been considered in great detail, mainly because polypyrrole has a low-oxidation potential (−0.2 V vs SCE)[7] and is difficult to obtain and maintain in the undoped form. With a proper choice of a second monomer unit, however, the electron-rich character of pyrrole and its alkyl-substituted derivatives can be utilized to generate alternating copolymers with novel and fine-tunable semiconducting electronic and optical properties.[8−10] Nevertheless, such polymers have received only limited attention and have not been exploited as semiconductors in electrooptical devices.

Well-defined alternating heterocyclic copolymers are in general prepared using organometallic cross-coupling reactions such as the Stille[11,12] or Suzuki[8,13,14] reaction. Transition-metal-catalyzed polymerizations toward oligo- and polypyrroles have been described in recent years,[15−17] but only a limited number of alternating pyrrole-containing copolymers have been prepared, either via the Suzuki[8] or Stille cross-coupling reaction[9,10] or via alternative routes such as the conversion of precursor polymers using the Stetter reaction.[18]

Here we report the synthesis and characterization of a new processable conjugated alternating copolymer consisting of *N*-dodecylpyrrole and 2,1,3-benzothiadiazole rings via the Stille cross-coupling reaction (PDPB, Scheme 1). MALDI-TOF mass spectrometry is used in combination with SEC to analyze the molecular weight distribution of PDPB and to determine the nature of the end groups. A transoid conformation of benzothiadiazole and pyrrole units in PDPB forces the alkyl groups, present on only every second unit in the chain, to point into the same direction and thereby creates semiamphiphilic character. In accordance, we find that PDPB can be spread as a stable and transferable Langmuir film at the air−water interface.[19]

Photoinduced absorption (PIA) spectroscopy and photoluminescence (PL) quenching reveal that the photophysics of pristine PDPB thin films changes completely when it is mixed with a methanofullerene derivative (1-(3-methoxy-carbonyl)-propyl-1-phenyl-[6,6]-C_{61}, PCBM[20]). The PDPB:PCBM composite films are subsequently investigated as active layers for the construction of organic bulk heterojunction photovoltaic devices.

With this study we demonstrate that pyrrole-containing conjugated alternating copolymers with well-defined alternation can be synthesized and may hold a promise for optimization of electrooptical devices. Since the Stille coupling reaction is compatible with a variety of dibromoaryl monomers, this opens the way to a range of copolymers incorporating *N*-alkylpyrroles with tunable electrical and optical properties.

Experimental Section

Materials. All solvents used in the synthesis were AR grade. 4,7-Dibromo-2,1,3-benzothiadiazole (**3**) was prepared

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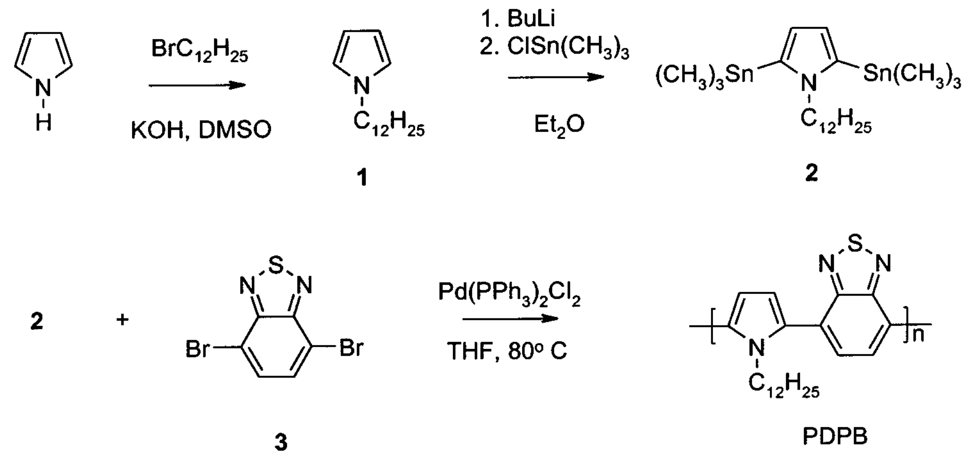
10.1021/ma001732e CCC: $20.00

Scheme 1. Synthesis of PDPB



according a to literature procedure by reacting 2,1,3-benzothiadiazole in 47% hydrobromic acid with bromine.[21] ^{1}H NMR, ^{13}C NMR, and GC-MS were used to characterize the product. Poly(ethylenedioxythiophene)−poly(styrenesulfonate) (PEDOT:PSS) was obtained from Bayer AG.

General Methods. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer at frequencies of 400.1 and 100.6 MHz with $CDCl_3$ as solvent and tetramethylsilane as an internal standard. Absorption spectra were obtained with a Perkin-Elmer Lambda 40P UV−vis or a Lambda 900 UV−vis−near-IR spectrometer. FT-IR and PL spectra were recorded using a Perkin-Elmer Spectrum-One UATR FT-IR spectrophotometer and with a Perkin-Elmer LS 50B spectrometer, respectively. Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer TGA 7 (heating the sample in a gentle stream of air), and a Perkin-Elmer Pyris 1 (calibrated with indium and cyclohexane) was used for differential scanning calorimetry (DSC).

A Shimadzu LC-10AT system combined with a Polymer Laboratories PL 500 Å column and UV detection (254 nm) was employed for size exclusion chromatography (SEC), using $CHCl_3$ as an eluent. Matrix-assisted laser desorption ionization−time-of-flight (MALDI-TOF) mass spectrometric measurements were made with a PerSeptive Biosystems Voyager DE-Pro MALDI-TOF mass spectrometer in a linear positive mode, with the employment of α-cyano-4-hydroxycinnamic acid or dithranol as a matrix.

Cyclic voltammetry was measured in a 0.1 M tetrabutylammonium hexafluorophosphate acetonitrile solution as supporting electrolyte using a Potentioscan Wenking POS73 potentiostat. The working electrode was a Pt disk (0.2 cm^2), the counter electrode was a Pt plate (0.5 cm^2), and a saturated calomel electrode was used as reference electrode calibrated against Fc/Fc$^+$.

Langmuir Films. Langmuir film experiments were performed with a homemade LB trough placed in a laminar-flow chamber at a subphase temperature of 20 °C. Ultra filter water from a deionizer setup was used as subphase. Spectroscopic grade chloroform was used as the spreading solvent (~0.1 mg/mL). The Langmuir film is compressed, and the change in surface pressure is monitored with a Wilhelmy plate.

Photoinduced Absorption. PIA measurements were performed between 0.25 and 3.0 eV by exciting thin films on quartz contained in a cryostat at 80 K with a mechanically modulated excitation beam (488 nm, 275 Hz, 25 mW, 2 mm diameter) of an argon ion laser (Spectra Physics 2025). The change in transmission of the probe light (ΔT) was monitored with a phase-sensitive lock-in amplifier using Si, InGaAs, and cooled InSb detectors. The photoinduced absorption, $-\Delta T/T$, is calculated from the change in transmission after correction for fluorescence, which is recorded in a separate experiment. The lifetime of the photoexcitations is determined by recording the intensity of the PIA bands as a function of the modulation frequency (ω) in the range 30−4000 Hz.

Photovoltaic Cells. The typical procedure for fabrication of the photovoltaic devices is as follows: A thin layer of PEDOT:PSS is spin-coated from aqueous solution after filtering through a Rezist 5.0 μm PTFE filter on a UV−ozone cleaned glass/ITO substrate, followed by spin-coating a filtered toluene solution of a mixture of PDPB:PCBM (1:3 wt %), in a laminar flow box. The thickness of the active layer is ~80 nm as determined with a Tencor P10 surface profiler. Finally, an aluminum back electrode on the top of the active layer was deposited in a vacuum (thickness ~ 100 nm). *I*/*V* characteristics were measured with a Keithley 2400 source meter under ~55 mW/cm^2 white-light illumination from a tungsten−halogen lamp filtered by a Schott KG3 filter. Both metal evaporation and *I*/*V* measurements are performed under inert atmosphere.

***N*-Dodecylpyrrole (1).** Freshly distilled pyrrole (20.5 g, 0.31 mol) in DMSO (50 mL) was added dropwise to a stirred slurry of powdered potassium hydroxide (40 g, 1 mol) in dimethyl sulfoxide (DMSO, 120 mL) under argon. The resulting green reaction mixture was stirred for another 30 min at room temperature, and 1-bromododecane (73 mL, 0.35 mol) was added dropwise. The resulting yellow reaction mixture was stirred overnight at room temperature under argon and then poured into water (2 L) and extracted with *n*-hexane, dichloromethane, and diethyl ether. The combined organic layers were washed thoroughly with water, dried over $MgSO_4$, and evaporated to get a yellow viscous liquid. This crude product was distilled under reduced pressure to afford colorless **1** (43 g, 60%); bp 107−108 °C (0.025 mbar). ^{1}H NMR (δ, $CDCl_3$): 6.62 (t, 2H, Py−$H_{2,5}$), 6.12 (t, 2H, Py−$H_{3,4}$), 3.83 (t, 2H, N−CH_2−), 1.73 (m, 2H, N−CH_2−CH_2−), 1.27 (m, 18H, −(CH_2)$_9$−), and 0.88 (t, 3H, −CH_3). ^{13}C NMR (δ, $CDCl_3$): 120.70 (Py−$C_{2,5}$), 108.06 (Py−$C_{3,4}$), 49.91 (N−CH_2−), 32.24, 31.90, 29.95, 29.88, 29.85, 29.82, 29.66, 29.53, 27.08, 22. 99 (−CH_2−), and 14.40 (−CH_3).

2,5-Bis(trimethylstannyl)-*N*-dodecylpyrrole (2). *n*-Butyllithium (1.6 M in hexane, 0.2 mol) was added dropwise over a period of 1 h to an ice-cooled stirred solution of *N*-dodecylpyrrole (23.3 g, 0.1 mol) in dry diethyl ether under argon. The reaction mixture was stirred at this temperature for 1 h prior to refluxing over an oil bath for 20 h, during which period the reaction mixture turned turbid. The mixture was cooled with an ice−salt mixture, and a solution of trimethyltin chloride (39.9 g, 0.2 mol) in dry diethyl ether was added with vigorous stirring. After the addition, the reaction mixture was brought to room temperature and stirred for another 2 h. Then the reaction mixture was diluted with diethyl ether, washed with water, dried over $MgSO_4$, and concentrated to afford a red viscous liquid. According to ^{1}H NMR, the crude product is a mixture of unreacted *N*-dodecylpyrrole (20%), 2-trimethylstannyl-*N*-dodecylpyrrole (10%), and 2,5-bis(trimethylstannyl)-*N*-dodecylpyrrole (70%). Fractionation by distillation under reduced pressure resulted in pure colorless 2,5-bis(trimethylstannyl)-*N*-dodecylpyrrole; bp 153−155 °C (0.02 mbar). ^{1}H

NMR (δ, $CDCl_3$): 6.47 (s, 2H, Py−$H_{3,4}$), 3.90 (t, 2H, N−C*H*$_2$−), 1.80 (m, 2H, N−CH_2−C*H*$_2$−), 1.35 (m, 18H, −(C*H*$_2$)$_9$−), 0.90 (t, 3H, −C*H*$_3$), and 0.39 (s, 18H, −Sn(C*H*$_3$)$_3$). ^{13}C NMR (δ, $CDCl_3$): 136.30 (Py−$C_{3,4}$), 119.45 (Py−$C_{2,5}$), 53.60 (N−*C*H$_2$−), 34.31, 32.22, 29.93, 29.84, 29.81, 29.77, 29. 72, 29.66, 27.35, 23.01 (−*C*H$_2$−), 14.45 (−*C*H$_3$), and −7.97 (−Sn(*C*H$_3$)$_3$).

Polymer Synthesis. Dichlorobis(triphenylphosphine)-palladium(II) (1 mol %) was added at once to a stirred solution of a mixture of 2,5-bis(trimethylstannyl)-*N*-dodecylpyrrole (0.56 g, 1 mmol) and 4,7-dibromo-2,1,3-benzothiadiazole (0.3 g, 1 mmol) in dry THF (20 mL) blanketed with argon, and the whole mixture was stirred at 90 °C for 20 h. During the course of the reaction, the color of the reaction mixture turned from pale yellow to orange to dark red. At the end of the reaction, the mixture was added dropwise to methanol with vigorous stirring. A red solid separated, was filtered, washed with methanol and *n*-hexane, and dried in a vacuum for 2 days. The isolated yield was about 60%. ^{1}H NMR (δ, $CDCl_3$): 7.8 (bs, 2H, Ar−H), 6.8 (bs, 2H, Py−H), 4.3 (bm, 2H, N−CH_2), 0.7−1.3 and (bm, 23H, −$(CH_2)_{10}$−CH_3). Apart from these major peaks, a set of sharp peaks at 7.75, 7.63, 6.94, 6.54, and 6.36 is present and assigned to the aromatic protons at the end of the polymer chain. FT-IR (film, cm^{-1}): 2921, 2852, 1698, 1583, 1544, 1478, 1465, 1394, 1344, 1267, 1214, 1121, 1073, 1030, 939, 872, 842, 759, and 719.

Results and Discussion

Polymer Synthesis and Characterization. PDPB was synthesized via a condensation polymerization between equimolar amounts of 2,5-bis(trimethylstannyl)-*N*-dodecylpyrrole (**2**) and 4,7-dibromo-2,1,3-benzothiadiazole (**3**) under Stille coupling conditions in the presence of a $Pd(PPh_3)_2Cl_2$ catalyst (Scheme 1). Initial experiments, carried out in dry dimethylformamide (DMF), resulted in short oligomers due to the poor solubility of the copolymer in DMF. However, by performing the reaction in dry THF, in which PDPB is readily soluble, a relatively high molecular weight copolymer could be obtained. As-synthesized PDPB is a dark red powdery solid material. The absence of any absorption in the near-IR and IR regions shows that as-synthesized PDPB is in the neutral (undoped) state. PDPB is readily soluble in a number of organic solvents, including chloroform, dichloromethane, toluene, *o*-xylene, and *o*-dichlorobenzene, is partially soluble in *n*-hexane and DMF, and is insoluble in acetonitrile and methanol. PDPB can be spin-cast from solution onto glass substrates to provide visually uniform red films.

The appearance of two prominent broad singlets centered at 7.8 and 6.8 ppm in the aromatic region of the ^{1}H NMR spectrum of PDPB, assigned to benzothiadiazole ring and pyrrole ring protons, respectively, reveals the existence of symmetry within the polymer chain and, hence, indicates a predominant alternation of the two units along the chain. In comparison to the corresponding monomers, the benzothiadiazole and pyrrole ring protons in PDPB are shifted downfield by 0.2 and 0.3 ppm, respectively. Small multiplet peaks at 7.75 and 7.63 ppm (benzothiadiazole) and 6.94, 6.76, 6.54, and 6.36 ppm (pyrrole) arise from end groups terminated with hydrogen. The absence of a characteristic singlet peak at 0.4 ppm in the ^{1}H NMR spectrum reveals that no trimethyltin end groups are present.

TGA (40−450 °C at 5 °C/min) revealed that PDPB is stable in air up to 125 °C with only 0.2% weight loss. Above 125 °C a monotonic decrease of weight indicates the possible decomposition of PDPB. DSC on PDPB (heating run from −100 to 150 °C, at 40 °C/min and subsequent cooling run) indicated the absence of any first-order phase transition such as melting and crystallization. However, a clear second-order glass transition (T_g) was observed at ∼27 °C, indicating that PDPB is a low-T_g copolymer.

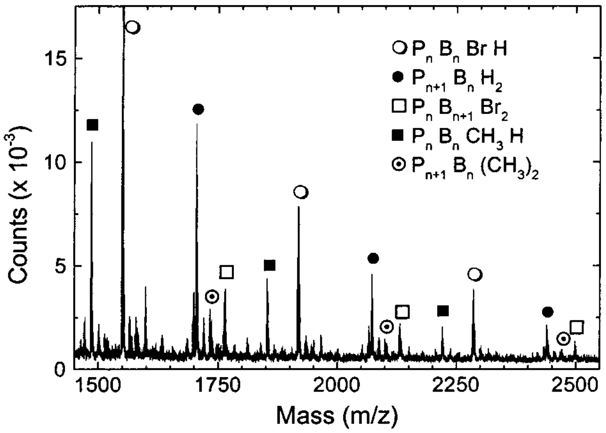


Figure 1. MALDI-TOF mass spectrum of a molecular weight fraction of PDPB recorded using a dithranol matrix. The inset shows the assignment of the various mass peaks to chains containing different end groups (P = *N*-dodecylpyrrole, B = 2,1,3-benzothiadiazole).

The number-average (M_n), weight-average (M_w), and most probable molecular weights of PDPB as inferred from SEC analysis using chloroform are about 7100, 14 600, and 10 040 g/mol, respectively, using polystyrene standards. The polydispersity index (M_w/M_n) is 2.06. Accordingly, PDPB contains polymer chains with a number-average degree of polymerization of $P_n = 20$ (i.e., 20 *N*-dodecylpyrrole and 20 2,1,3-benzothiadiazole units). Since PDPB is structurally quite different from the polystyrene standards, molecular weights from SEC analysis are unlikely to represent the true composition of PDPB. Therefore, PDPB was also analyzed in some detail with MALDI-TOF mass spectrometry, which revealed that PDPB chains with a mass up to $m/z \approx 6000$ g/mol are present. This suggests a maximum degree of polymerization of $P_{max} \approx 14$ (*N*-dodecylpyrrole-2,1,3,-benzothiadiazole units). This estimate for P_{max} is probably a lower limit to the actual P_{max} because there is often a discrimination against higher molecular weight species in MALDI-TOF mass spectrometry of polymers with a polydispersity of more than 1.5.[22] The lower molecular weight derived from MALDI-TOF as compared to that from SEC is, however, similar to a recent report on poly(3-alkylthiophene)s, in which monodisperse molecular weight fractions were analyzed and the actual molecular weight was found to be 1.6 times less than estimated from SEC.[23]

The MALDI-TOF mass spectrum of a sample of PDPB, recorded in reflector mode for increased resolution (Figure 1), shows a systematically repeating pattern of clusters. The repetition is in full agreement with the expected perfect alternation of *N*-dodecylpyrrole (P) and benzothiadiazole (B) units because of the absence of signals corresponding to chains in which one unit outnumbers the other one by more than one. From the mass peaks within each repeating cluster it seems that most polymer chains are terminated with hydrogen, methyl, or bromide end groups. In support of the proposed perfect alternation, we find that two bromine end groups are only present on chains in which the number of benzothiadiazole units is one higher than the number of *N*-dodecylpyrrole units and that two methyl

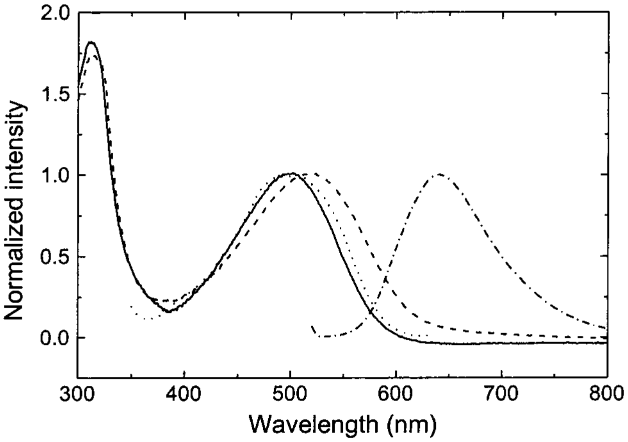


Figure 2. Normalized optical spectra of PDPB (a) absorption in chloroform (solid line), (b) absorption of spin-cast film on glass (dashed line), (c) photoluminescence in chloroform (dot–dashed line), and (d) photoluminescence excitation in chloroform (dotted line).

groups are only found in chains containing one extra *N*-dodecylpyrrole moiety in comparison with the benzothiadiazoles. The absence of any trimethyltin end group, as inferred through MALDI-TOF mass analysis, corroborates well with ^{1}H NMR spectral data discussed above.

Knowledge of end groups can, in general, be used to elucidate the various possible side reactions of the Stille coupling for obtaining AB type copolymers. In the practice of Stille polymerizations chain terminating side reactions such as destannylation, debromination, and methyl shift limit the molecular weight, while homocouplings may cause imperfections in the alternation of monomer units.[24] As a result, a mixture of oligomers with some degree of imperfection in the alternation of the two monomers is usually obtained. The presence of mainly hydrogen, methyl, and bromine end groups with perfect alternation of P and B units shows that in the present case the homocoupling is a minor side reaction and that debromination, destannylation, and methyl shift limit the polymer weight.

Optical Properties. The UV–vis spectra (Figure 2) of PDPB in chloroform solution and as spin-cast film on glass show a π–π^* absorption band at $\lambda_{max} = 502$ and 520 nm, respectively. The onset of the optical absorption in the film occurs at about 610 nm ($E_g = 2.03$ eV). The relatively long-wavelength (low-energy) absorption results from the alternation of electron-rich (*N*-dodecylpyrrole) and electron-deficient (2,1,3-benzothiadiazole) units, which is known to lower the optical band gap.[25] However, the band gap of 2.03 eV is larger than that for a closely related copolymer consisting of alternating unsubstituted pyrrole and benzothiadiazole units, which was found at 1.2 eV.[10] In the latter case there is evidence from NMR and X-ray crystallography for hydrogen bonding between the pyrrole N–H and the nitrogen of the benzothiadiazole, which enhances coplanarity and conjugation.[10] On the other hand, the λ_{max} of PDPB is at significantly higher wavelengths than the λ_{max} of related copolymers in which an *N*-hexylpyrrole-2,5-diyl unit is alternated with either 2,5-thienylene ($\lambda_{max} = 379$ nm) or 1,4-phenylene ($\lambda_{max} = 346$ nm) which lack the electron-withdrawing character of 2,1,3-benzothiadiazole-4,7-diyl.[26] The 18 nm red shift of λ_{max} of PDPB in the film in comparison to that observed for PDPB in a good solvent such as chloroform possibly indicates some interchain interaction or planarization in the solid state.

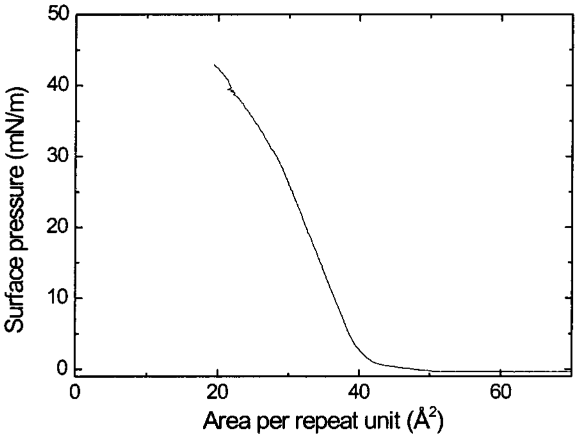


Figure 3. Surface pressure–area isotherm of PDPB at the air–water interface. Measurements were done at a subphase temperature of 20 °C and with a compression speed of 8 cm^2/min.

Dissolved in chloroform, PDPB exhibits a red photoluminescence with a maximum at $\lambda_{PL} = 640$ nm (Figure 2). The excitation spectrum, recorded by monitoring the PDPB emission at 640 nm, coincides with the absorption spectrum. A red shift of ~20 nm and a strong quenching of fluorescence were observed for a spin-cast thin film of PDPB. Comparison of the fluorescence of PDPB with those of the aforementioned copolymers poly(*N*-hexylpyrrole-2,5-diyl)-*co*-(2,5-thienylene) and poly(*N*-hexylpyrrole-2,5-diyl)-*co*-(1,4-phenylene), which emit yellow ($\lambda_{PL} = 526$ nm) and blue ($\lambda_{PL} = 443$ nm) light, respectively,[26] demonstrates the tunability of the emission characteristics in these alternating copolymers based on *N*-alkylpyrroles.

Langmuir Films. In comparison to the detailed investigation of the Langmuir films of poly(3-alkylthiophene)s and poly(*N*-alkylpyrrole)s, only a few heteroaromatic alternating copolymers have been considered for film formation at the air–water interface.[19,27] In general, these poly(3-alkylthiophene)s and poly(*N*-alkylpyrrole)s homopolymers do not form a stable and transferable Langmuir film, on their own, due to the lack of required hydrophilicity of the polymer backbone or an energetically unfavorable orientation of the polymer chain on the water surface.[28] We conjectured that the presence of a hydrophobic alkyl chain on only every second monomer unit in PDPB combined with the enhanced hydrophilicity of the conjugated chain by the incorporation of 2,1,3-benzothiadiazole rings might enhance the amphiphilic character of PDPB. The surface pressure–area (π–*A*) isotherm (Figure 3) shows that PDPB indeed forms a stable Langmuir film at the air–water interface with a limiting mean molecular area of ~40 Å^2. Since this area is based on the repeat unit of the copolymer, which contains a dodecyl chain, it is reasonable to assume that the limiting mean molecular area should be equal to, or higher than, 20 Å^2, which is the area of an alkyl chain (e.g., stearic acid) when spread at the water surface.[29] Molecular modeling indicated an expected molecular area of 33–38 Å^2 for the repeat unit of PDPB, indicating the monomolecular nature of the Langmuir film. The Langmuir film of PDPB could be transferred up to about 15 layers by the vertical dipping method with near unity transfer ratio values. The transfer was Y-type, i.e., transfer during

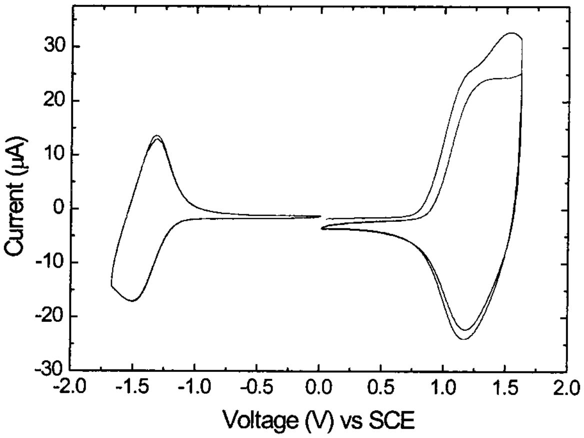


Figure 4. Cyclic voltammogram of a thin PDPB film on a Pt electrode in acetonitrile containing 0.1 M Bu_4NPF_6 as an electrolyte and recorded with a scan speed of 100 mV/s.

both up and down stroke and the transferred film looked visually uniform. Layer-by-layer transfer of the Langmuir film was also inferred through near linear increase of absorbance at 523 nm with the number of layers.

Electrochemical Properties. The electrochemical characteristics of a thin PDPB film on a Pt electrode were determined by cyclic voltammetry (Figure 4). The measurements were made in a 0.1 M Bu_4NPF_6 acetonitrile electrolyte with a scan rate of 100 mV/s. A broad oxidation wave was found at $E_{ox} \approx 1.1$ V vs SCE. The broad nature of the redox wave is similar to that found for alternating pyrrole–thiophene copolymers.[9,30] The oxidation potential at 1.1 V is about 0.5 V higher than those of alternating pyrrole–thiophene (AB) or thiophene–pyrrole–thiophene–benzothiadiazole (ABAC) copolymers[26] and reflects the electron-withdrawing effect of the 2,1,3-benzothiadiazole unit. At −1.4 V, a characteristic reduction wave of the 2,1,3-benzothiadiazole moiety is observed. The electrochemical band gap, calculated from the cyclic voltammetry data ($E_{ox} - E_{red}$), is about 2.5 V, somewhat higher than the optical band gap estimated from the absorption of a thin film (λ_{max} = 520 nm corresponds to 2.38 eV, and the onset is at 2.03 eV).

Photoinduced Absorption Spectroscopy and Photovoltaic Cells of Bulk Heterojunctions. Polymer-based organic solar cells consisting of a thin active layer of a mixture of a semiconducting polymer (e.g., poly(*p*-phenylenevinylene)s and poly(3-alkylthiophene)s) as a donor and an acceptor such as a soluble C_{60} derivative (e.g., 1-(3-methoxycarbonyl)-propyl-1-phenyl-[6,6]C_{61}, PCBM[20]) embedded between a transparent front electrode (indium–tin oxide) and a metal back electrode (aluminum) have received considerable attention in recent years.[31] Improvement of the efficiency of such bulk heterojunction devices can possibly be achieved through the modification of processing methods or by the employment of new functional semiconducting polymers.[32] The suitability of PDPB as an electron donor in combination with PCBM as an acceptor was studied using PIA spectroscopy. The PIA spectrum of a thin pristine PDPB film recorded at 80 K with excitation at 488 nm shows a single strong band at 1.14 eV (Figure 5) together with a weak absorption in the 0.5–0.85 eV region and a bleaching of the $\pi-\pi^*$ band at 2.12 eV (585 nm). The lifetime of the excitation associated with the 1.14 eV transition, as inferred from the modulation frequency dependence of $-\Delta T/T$, is 0.7 ms. These features are characteristic of a triplet state, and accordingly we assign the 1.14 eV PIA band to a $T_n \leftarrow T_1$ transition of PDPB in the photoexcited triplet state. At 80 K the luminescence of a PDPB film is found at 1.87 eV.

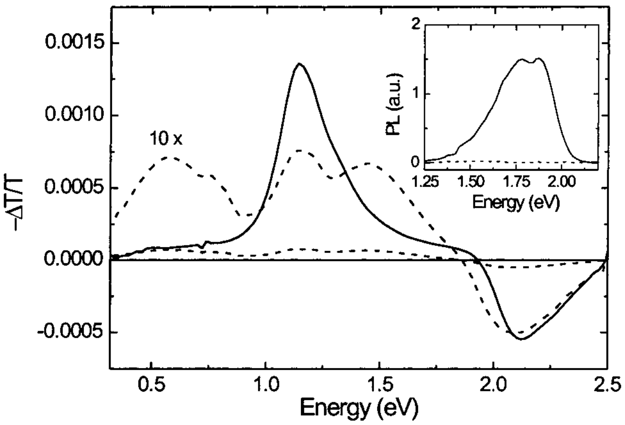


Figure 5. Photoinduced absorption spectra of PDPB (solid line) and PDPB:PCBM (1:1 wt %) (dashed line) thin films recorded at 80 K with 25 mW excitation at 488 nm. For clarity, the PIA spectrum of the mixed film is also shown on a 10-fold expanded vertical scale. The inset shows the corresponding photoluminescence spectra recorded under identical conditions.

The PIA spectrum of a composite film of PDPB and PCBM (1:1 wt %), recorded under identical conditions, is significantly different from that of the pristine PDPB film and exhibits a significant quenching of the $T_n \leftarrow T_1$ transition at 1.14 eV with a concomitant quenching of the photoluminescence. In the mixed film two weak PIA bands at 0.58 and 1.45 eV can be observed. Such a combination of low-energy and high-energy subgap transitions is highly characteristic of the formation of radical cations (polarons) in conjugated polymers. Hence, we assign these PIA bands to PDPB radical cations. Comparison of the PIA spectra of pristine PDPB and PDPB/PCBM reveals, however, that the formation of these radical cations is not necessarily enhanced by the presence of PCBM. On the other hand, PIA and PL spectra demonstrate that the presence of PCBM changes the photophysics of PDPB significantly. Especially the quenching of the PDPB fluorescence indicates that there is a new relaxation process for the singlet excited state, which is significantly faster than the typical nanosecond time scale fluorescence.[33] The two most likely mechanisms for this enhanced relaxation of the photoexcited singlet state of PDPB are energy and electron transfer to PCBM.[34−37] At present, the PIA and the PL spectra do not allow a conclusive discrimination between these two possibilities.

Although the photophysical experiments give no definite proof of a photoinduced charge transfer between PDPB and PCBM, working photovoltaic devices based on PDPB:PCBM blends have been made. Figure 6 shows the semilogarithmic *I*/*V* characteristics of a photovoltaic cell with a working area of 0.10 cm^2 in which the active layer consists of a 1:3 mixture by weight of PDPB and PCBM sandwiched between a PEDOT:PSS covered ITO front electrode and an aluminum back electrode. The cell exhibits a diode behavior in the dark with a rectification ratio of ~8300 at ±2 V, which shows that the device has little or no shunts. The diode showed no electroluminescence, confirming the PL experiment. Under white-light illumination (P_{in} = ~55 mW/cm^2) from a filtered tungsten–halogen lamp a clear photo-

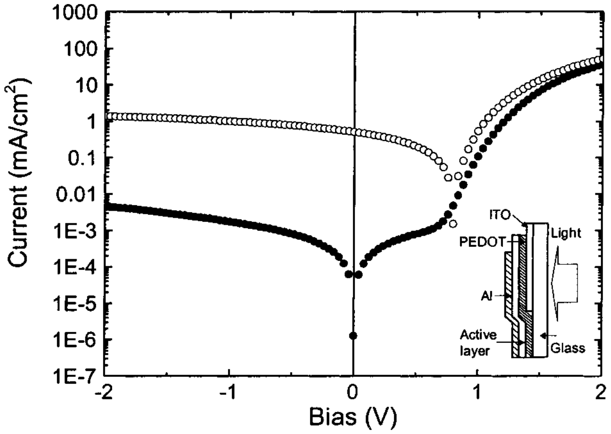


Figure 6. Semilogarithmic plot of the *I*/*V* characteristics of a photovoltaic device consisting of ITO/PEDOT:PSS/PDPB:PCBM(1:3 wt %)/Al under 55 mW/cm^2 white-light illumination (open circles) and in the dark (solid circles). The inset shows a schematic drawing of the configuration of the cell.

voltaic effect was observed, with a short-circuit current of $I_{sc} = 0.51$ mA/cm^2 and an open-circuit voltage of $V_{oc} = 0.80$ V. The fill factor (FF) calculated from FF = $(V_{max}I_{max})/(I_{sc}V_{oc})$, where V_{max} and I_{max} are the voltage and current for the maximum obtainable power, is 0.26. Devices made from pure PDPB or pure PCBM gave significantly lower short-circuit currents (0.9×10^{-4} and 0.02 mA/cm^2, respectively) under similar conditions (film thickness and light source) and demonstrate that the photovoltaic effect comes from the combination of the two materials. The calculated power conversion efficiency $\eta_{PCE} = (P_{out}/P_{in}) \times 100 = (FFV_{oc}I_{sc}/P_{in}) \times 100$ is ~0.2%, of the same order of magnitude as previously reported for π-conjugated polymer/fullerene bulk heterojunction solar cells[38] but less than the η_{PCE} of devices recently prepared under optimized processing conditions.[32]

The fact that a clear photovoltaic effect is observed demonstrates unambiguously that photoexcitation generates holes and electrons in the composite PDPB:PCBM films. The formation of these photogenerated charges may be assisted by the internal electric field in the cell, which enhances exciton dissociation at the PDPB:PCBM interface. Therefore, this result is not necessarily at variance with the possible absence of photoinduced charges in the PIA experiment.

Conclusions

The synthesis of a new processable alternating conjugated copolymer (PDPB), consisting of electron-rich *N*-dodecylpyrrole and electron-deficient 2,1,3-benzothiadiazole units, was accomplished via a palladium-catalyzed condensation polymerization. MALDI-TOF mass spectrometry revealed that PDPB chains contain up to about 30 aromatic units, possess a near-perfect alternation of the two monomers, and are mostly terminated with hydrogen, bromine, or methyl end groups. The strong variation of π electron density along the chain results in a reduction of the band gap of PDPB in comparison with related alternating copolymers based on *N*-hexylpyrrole and thienylene or phenylene units.[26] This demonstrates that the absorption, photoluminescence, and electrochemical characteristics of alternating conjugated copolymers can be varied considerably by adjusting the relative π electron density of the two units. Langmuir film forming experiments revealed that PDPB is one of the few conjugated polymers that spreads as a monomolecular film at the air–water interface and can be transferred layer-by-layer onto a substrate by vertical dipping. Photoexcitation of PDPB produces a metastable triplet state exhibiting a $T_n \leftarrow T_1$ transition at 1.14 eV. In composite films with a methanofullerene derivative, PDPB acts as an electron donor in the excited state, which enabled the construction of a polymer bulk heterojunction photovoltaic cell. With the synthesis of PDPB and the construction of a solar cell we have demonstrated that *N*-alkylpyrroles may hold a promise for application as a versatile comonomer in the preparation of new semiconducting polymers to be used in electrooptical devices.

Acknowledgment. We thank Professor J. C. Hummelen (University of Groningen) for a generous gift of PCBM, Dr. H. A. M. van Mullekom for providing 4,7-dibromo-2,1,3-benzothiadiazole, and Professor E. W. Meijer and Dr. J. A. J. M. Vekemans for stimulating discussions. This work is financially supported by the Dutch Ministry of Economic Affairs, the Ministry of Education, Culture and Science, and the Ministry of Housing, Spatial Planning and the Environment through the E.E.T. program (EETK97115) and by the Council for Chemical Sciences of the Netherlands Organization for Scientific Research (CW-NWO) and the Eindhoven University of Technology in the PIONIER program (98400).

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MA001732E