N-Methylated Poly(nonylbithiazole): A New n-Dopable, Conjugated Poly(ionomer)

M. David Curtis,* Haitao Cheng,
Jo Anna Johnson, and John I. Nanos

Department of Chemistry and
Macromolecular Science and Engineering Center
The University of Michigan
Ann Arbor, Michigan 48109-1055

Ramesh Kasim and Ronald L. Elsenbaumer

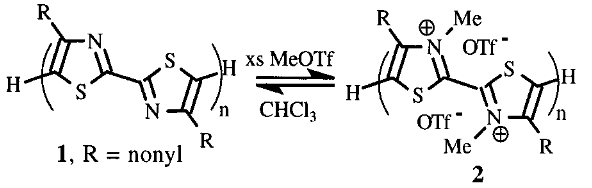
Department of Chemistry and
Department of Materials Science and Engineering
University of Texas, Arlington, Texas 76019

Lebzylisbeth Gonzalez Ronda and David C. Martin

Department of Materials Science and
Engineering and Macromolecular Science
and Engineering Center
The University of Michigan
Ann Arbor, Michigan 48109-2136

Received August 5, 1997
Revised Manuscript Received November 17, 1997

Recently, a new class of regioregular conjugated polymer, the poly(alkylbithiazoles) (PABTs),[1] was reported.[2,3] These new polymers are capable of reversible n-doping and have been employed in the construction of LEDs and lithium batteries.[3,4] The nonyl derivative (**1**, R = *n*-nonyl, $n \sim 52$, denoted as PNBT) especially shows unusual optical properties (J-aggregate formation) as a result of its crystallinity and $\pi-\pi$ stacking behavior.[3,5] In this communication, we report that the electrical, optical, and mechanical properties of PNBT may be tuned by methylation of the ring N-atom to give new, conjugated poly(ionomers), **2**. The altered properties of **2** vis-à-vis **1** provide a basis for the use of PABTs as sensor elements.



(1)

PNBT reacts with methyl triflate (MeOTf) in dry chloroform.[6] The extent of methylation, determined by elemental analysis for fluorine in the product, was controlled by the amount of MeOTf added and the reaction time and could be varied between 5 and 10% up to 100% (i.e., every N-atom methylated). The progress of the reaction was monitored by TLC with long-wavelength UV ("black light") detectors: the fluorescence of the starting PNBT is green/yellow, whereas the *N*-methylated polymer fluoresces orange. The IR spectra of the methylated materials show peaks at 1260, 1187, and 1032 cm^{-1}, characteristic of the triflate anion, $CF_3SO_3^-$.[7] The highly methylated polymers are insoluble in nonpolar solvents, e.g., toluene, but are readily soluble in more polar solvents, e.g., $CHCl_3$. Basic or nucleophilic solvents can demethylate the ring (see below).

The ^{1}H NMR spectra of the methylated polymers are complicated by the existence of the equilibrium shown in eq 1. Thus, in $CDCl_3$, fully methylated PNBT shows three peaks in the *N*-methyl region at δ 4.22, 4.21, and 3.96 ppm. The first peak is due to MeOTf formed by the attack of OTf$^-$ on the *N*-methyl group, and the other two peaks are attributed to HT and HH triads as formed in poly(3-alkylthiophenes).[8]

The lability of the *N*-methyl groups is also shown by thermal analysis. On the first heating cycle, DSC curves[9] of the fully methylated polymer show an endotherm (76 kJ/mol) starting at 128 °C and peaking at 172 °C that we attribute to the thermal elimination of MeOTf. There is no corresponding exotherm on the cooling cycle, and the second heating/cooling cycle produces a DSC curve identical with that of PNBT (Figure 1S). The TGA curve shows a 44% loss of weight (corresponding to loss of 2 mol of MeOTf/NBT group) starting at 100 °C and continuing to 450 °C, at which point the slope abruptly changes as the polymer backbone structure begins to degrade (Figure 2S).

The *N*-methyl group may be removed also under mild conditions by treatment with amines, e.g., $MeNH_2$(aq) or NH_3(g). This reaction proceeds in solid films of MPNBT, thus providing the ability to prepare multilayer films, as shown in Scheme 1, with only one spin-coating operation. Alternatively, methylation of a thin film of PNBT renders it insoluble in toluene. Then, a toluene-soluble polymer, e.g., poly(hexylthiophene), may

---

[1] **PABT**: poly(4,4′-dialkyl-2,2′-bithiazol-5,5′-diyl).

[2] Nanos, J. I.; Kampf, J. W.; Curtis, M. D.; Gonzalez, L.; Martin, D. C. *Chem. Mater.* **1995**, *7*, 2232.

[3] (a) Yamamoto, T.; Suganuma, H.; Maruyama, T.; Kubota, K. *J. Chem. Soc., Chem Commun.* **1995**, 1613. (b) Yamamoto, T.; Suganuma, H.; Maruyama, T.; Inoue, T.; Muramatsu, Y.; Arai, M.; Komarudin, D.; Ooba, N.; Tomaru, S.; Sasaki, S.; Kubota, K. *Chem. Mater.* **1997**, *9*, 1217.

[4] Curtis, M. D.; Cheng, H.; Nanos, J. I.; Nazri, G.-A. *Macromolecules*, in press.

[5] Gonzalez-Ronda, L.; Martin, D. C. *Macromolecules* **1997**, *30*, 1524.

[6] Typical procedure: PNBT (0.1 g) was dissolved in 100 mL of dry $CHCl_3$ with heating. To this solution was added 0.2 mL of $MeSO_3CF_3$ (MeOTf) at room temperature. The light yellow solution becomes orange and the greenish-yellow fluorescence of PNBT is replaced by an orange-reddish color under long-wavelength UV light. Further aliquots of MeOTf were added in 10 h intervals until 25 equiv of MeOTf was added. After 60 h, solvent and excess MeOTf were removed under vacuum. The product was analyzed for F (10.5%), corresponding to 55% methylation. With 4 equiv of MeOTf and a 10 h reaction time, the F analysis was 1.50%, corresponding to 6% methylation, whereas heating the PNBT solution with a large excess of MeOTf for 3 days gave 100% methylation (16% F).

[7] Zhang, N. W.; Li, Q.; Pakbaz, K.; Yoon, C. O.; Wudl, F. *Chem. Mater.* **1993**, *5*, 1598.

[8] (a) Review: Inganäs, O. *Trends Polym. Sci.* **1994**, *2*, 189−196. (b) Henderson, P. T.; Collard, D. M. *Chem. Mater.* **1995**, *7*, 1879. (c) McCullough, R. D.; Tristram-Nagle, S.; Williams, S. P.; Lowe, R. D.; Jayaraman, M. *J. Am. Chem. Soc.* **1993**, *115*, 4910. (d) McCullough, R. D.; Williams, S. P. *J. Am. Chem. Soc.* **1993**, *115*, 11608. (e) Chen, T.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233−244. (f) Chen, T.; Rieke, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 10087.

[9] Thermal analyses were performed on a Perkin-Elmer Series 7 Thermal Analysis System. The TGA runs were under nitrogen with a heating rate of 40 °C/min, and the DSC results were obtained on samples in a crimped aluminum boat under nitrogen at 20 °C/min.

S0897-4756(97)00549-8 CCC: $15.00

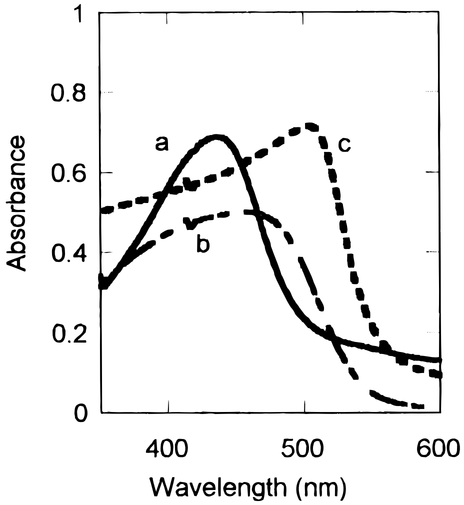


Figure 1. UV–vis spectra of thin films of MPNBT that is (a) 100% methylated, (b) 11% methylated, and (c) 55% methylated.

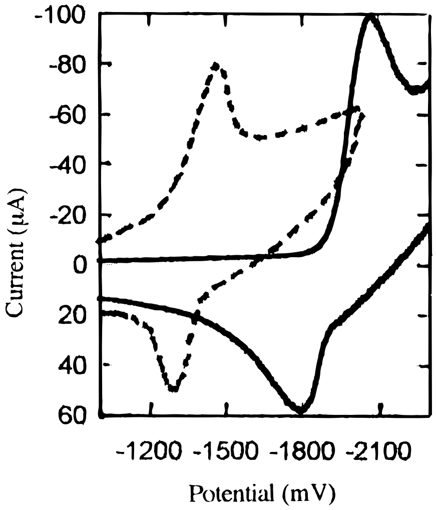


Figure 2. Cyclic voltammograms of MPNBT (100% methylated, dashed line) and PNBT (solid line) as thin films coated on the electrode.

then be spin-coated over the MPNBT, and the MPNBT then converted back to PNBT by heating under vacuum or by treatment with $NH_3(aq)$.

The physical properties of PNBT are enhanced by partial methylation. A polymer with 2.77% F, corresponding to 11% methylation, showed significant loss of crystallinity as revealed by XRD (Figure 3S) and a corresponding increase in tensile strength (Table 1S). The tensile strength at the break point was 10 ± 1 MPa for the methylated polymer vs 5 ± 2 MPa for the most crystalline polymorph[2] of PNBT (the "green" form). The modulus of elasticity also increased from 0.2 ± 0.05 GPa to 0.7 ± 0.3 GPa in going from the green PNBT to the methylated polymer. The loss of crystallinity and increased elasticity of MPNBT allow for the formation of superior films (less cracking, fewer pinholes, etc.). Pure PNBT is essentially an insulator ($\sigma < 10^{-13}$ S/cm). Methylation causes an increase in conductivity of approximately 5 orders of magnitude to approximately 10^{-9} S/cm. Although the optical bandgap of MPNBT is less than that of PNBT, the conductivity (a bulk property) is not directly related to the HOMO–LUMO gap (a molecular property).[10] The cause of the increase in conductivity may be related to a better film quality (fewer boundaries) or to the "ionic atmosphere" that facilitates charge transport.[10b–d]

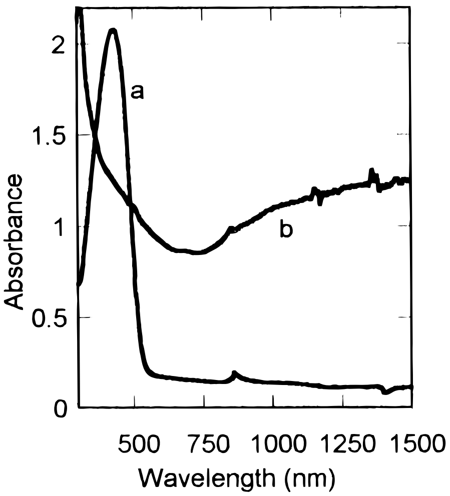


Figure 3. UV–vis–NIR spectra of MPNBT (100% methylated) film on ITO electrode at 0.00 V (solid line) and at −2.0 V vs $Ag/AgNO_3$ reference electrode in acetonitrile with Bu_4NBF_4 supporting electrolyte (see text).

Scheme 1

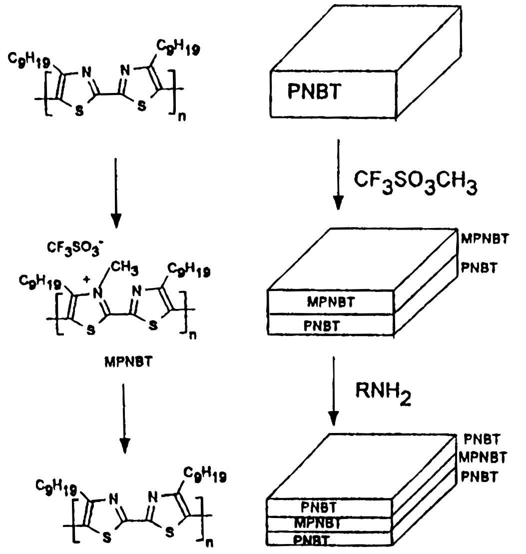


Table 1. Light Onset Electric Fields (V/cm) for the Various LEDs Described in the Text

LED configuration	light onset field
ITO‖MPNBT‖Al	1×10^7
ITO‖PPV‖Al	2.7×10^6
ITO‖PPV|MPNBT‖Al	4.3×10^6
ITO‖(PPV + MPNBT(9:1 blend)‖Al	1.1×10^6
ITO‖(PPV + MPNBT(3:1 blend)‖Al	2.1×10^6

Optical and electrochemical properties of PNBT are also altered by *N*-methylation. Figure 1 shows the UV–vis spectra of 11%, 55%, and 100% methylated MPNBT. The 11% methylated polymer shows a single, broad absorption with $\lambda_{max} = 458$ nm, while 55% methylated polymer shows a peak with $\lambda_{max} = 504$ nm, a relatively

---

(10) (a) Curtis, M. D.; McClain, M. D. *Chem. Mater.* **1996**, *8*, 936. (b) Scott, J. C. *Synth. Met.* **1993**, *54*, 9. (c) Dalton, E. F.; Surridge, N. A.; Jernigan, J. C.; Wilbourn, K. O.; Facci, J. S.; Murray, R. W. *Chem. Phys.* **1990**, *141*, 1413. (d) Savéant, J.-M. *J. Phys. Chem.* **1988**, *92*, 4526, and references therein.

sharp cutoff on the low-energy side, and a long tail to shorter wavelengths. The 100% methylated polymer has a sharper peak with $\lambda_{max} = 442$ nm. The corresponding optical bandgaps are 2.28, 2.19, and 2.41 eV for the 11%, 55%, and 100% methylated MPNBT, respectively. For comparison, the yellow, disordered form of PNBT has $\lambda_{max} = 438$ nm and an $E_{gap} = 2.52$ eV.[2] Thus, *N*-methylation causes a red-shift in the absorption spectra and a decrease in E_{gap} with the largest shifts occurring with the 55% methylated polymer. On the basis of electrostatic and steric repulsion, one would expect methylation to occur mostly on alternate rings in the 55% methylated material. This alternation would give rise to alternate electron-rich and electron-poor rings, and it has been observed that such copolymers have longer wavelength absorption than either homopolymer.[11]

Methylation also makes electrochemical reduction more facile. Figure 2 shows CV curves of films of PNBT and 100% MPNBT cast on ITO electrodes.[12] The parent PNBT shows a quasi-reversible redox couple with $E^{R}_{p/2} = -1.93$ V ($\Delta E_p = 260$ mV), but the methylated polymer is easier to reduce by 0.55 V: $E^{R}_{p/2} = -1.38$ V ($\Delta E_p = 190$ mV). Figure 3 shows the effect of reduction on the optical spectra of the films. The peak of MPNBT at 442 nm is replaced by a broad, featureless absorption that extends into the NIR due to free carriers. The color of the film changes from orange to blue-black during the reduction. The conductivity calculated from the NIR data using the Drude approximation,[13] $K = (2\sigma\omega\mu_0)^{1/2}$, where K = absorption coefficient (cm^{-1}), σ = conductivity, ω = frequency, and μ_0 = permeability of free space, is 5 S/cm. The n-doped polymer appears to be stable under inert atmosphere since several doping/dedoping cycles gave rise to identical spectra.

LEDs were constructed to test if MPNBT would act as an electron injection/transport layer.[14] The light onset electric fields (V/cm) are given in Table 1. The blend devices show lower onset fields than pure PPV, but the onset field increases with increasing concentration of MPNBT. The largest onset field is obtained with pure MPNBT. The bilayer device has a turn-on field intermediate between PPV and MPNBT. As deduced from their respective redox potentials and bandgaps, both the HOMO and LUMO of MPNBT should lie ca. 0.3 eV below those of PPV.[15] Hence, PPV should facilitate hole injection while MPNBT should do likewise for electron injection. Although the turn-on fields for the blend devices are lower than for PPV, the fact that the turn-on field for the two-layer device is higher than that for PPV alone suggests factors other than the frontier orbital energetics are important. One such factor may be the poor contact that MPNBT makes with the metal electrode.[16]

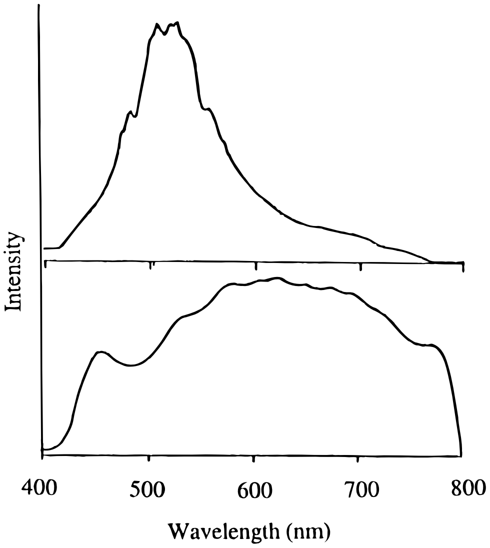


Figure 4. Electroluminescence spectra of an ITO||PPV: MPNBT (80:20 blend)||Al LED (top) and of an ITO||PPV|MPNBT||Al two-layer LED (bottom).

Figure 4 shows the EL spectrum of an ITO/PPV: MPNBT (80:20)/Al device made with an 80:20 blend of PPV and MPNBT compared to the EL spectrum of a two-layer device, ITO/PPV/MPNBT/Al. In the LED made from the polymer blend, the light emission occurs from the PPV, but the light emission is from the MPNBT in the two-layer device, as shown by comparing the spectrum to that of a single-layer MPNBT LED. The EL spectrum of MPNBT is much broader than its room-temperature photoluminescence (PL) spectrum, which shows a $\lambda_{max} = 558$ nm with $\Delta\lambda = 60$ nm at half-height. Since the bandgap of MPNBT and PPV are comparable,[15] exciton migration to one substance or the other is not particularly favored, so the light emission is most likely indicative of the recombination zone. At this time, we have insufficient data to comment further on these observations.

These results show that the physical, electrical, and optical properties of thiazole-containing polymers are easily modified by *N*-methylation. The methylation reaction places a formal positive charge on the ring N

---

(11) Yamamoto, T.; Zhou, Z.; Kanbara, T.; Shimura, M.; Kizu, K.; Maruyama, T.; Nakamura, Y.; Fukuda, T.; Lee, B.; Ooba, N.; Tomaru, S.; Kurihara, T.; Kaino, T.; Kubota, K.; Sasaki, S. *J. Am. Chem. Soc.* **1996**, *118*, 10389.

(12) Cyclic voltammograms were obtained with Princeton Applied Research potentiostat, Model 173, interfaced to a PC computer with a program written by Dr. S. Paras, Department of Chemistry, The University of Michigan. The program provides the voltage ramp and handles data collection and manipulation. Solvent was dry acetonitrile and the supporting electrolyte was tetrabutylammonium tetrafluoroborate (TBAF, 0.1 M). The concentration of the analyte was ca. 4 mM in bithiazole rings. The potentials are referenced vs Ag/AgNO$_3$ (1.3 mM) in 0.1 M Bu$_4$NPF$_6$ acetonitrile solution.

(13) Eliott, R. J.; Gibson, A. F. An Introduction to Solid State Physics and Its Application; The Macmillan Press: UK, 1974; pp 264–268.

(14) Typical LED construction: The polymers were dissolved in chloroform and the solution was filtered immediately prior to spin casting with an 0.2 μm syringe filter. ITO-coated glass plates (Photran Corp.) were thoroughly cleaned in an ultrasonic bath using trichloroethylene, acetone, 2-propanol, and deionized water in sequence. Photolithography was performed by casting a positive photoresist, exposure to UV, and development in NMe$_4$OH solution. The developed slides were etched in hot HCl to give a substrate with a 4 mm wide ITO strip. Polymer films were coated on the ITO by spin casting in an argon-filled glovebox. Thermal elimination of xanthate PPV precursor polymer was carried out by heating for 2 h at 180 °C under vacuum. Aluminum metal electrodes were deposited by thermal evaporation under 5×10^{-7} Torr pressure. The deposition rate was monitored with a 5 MHz crystal and was ca. 150 Å/s. Film thicknesses were measured with a profilometer. The active area was 4×4 cm^2. $I-V$ characteristics were measured with a Kiethley 236 Electrometer. EL spectra were recorded on a Tracor-Northern 1710A diode array spectrometer.

(15) Eckhardt, H.; Jen, K. Y.; Shacklette, L. W.; Lefrant, S. In *Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics, and Molecular Electronics*; Brédas, J.-L., Chance, R. R., Eds.; Kluwer Academic Publishers: The Netherlands, 1990; pp 305–320. (b) Helbig, M.; Hörhold, H.-H. *Makromol. Chem.* **1993**, *194*, 1607.

(16) He, Y.; Politis, J. K.; Cheng, H.; Curtis, M. D.; Kanicki, J. *IEEE Trans. Electron. Dev.* **1997**, *44*, 1282.

atom and increases the ionization potential and electron affinities as shown by cyclic voltammetry and UV−vis spectroscopy. The *N*-methylation is reversible. Preliminary results show that triflic acid protonates the ring N atom and causes the same type of changes in the fluorescence, etc., as *N*-methylation, thus opening the possibility that conjugated thiazole polymers may find application as sensing elements.

Acknowledgment. The authors thank the NSF for support of this research (Grant DMR-9510274). J.I.N. thanks the Plastics Institute of America for a supplemental fellowship.

Supporting Information Available: DSC and TGA curves for MPNBT, XRD patterns for PNBT and MPNBT, and a table of tensile data (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of this journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

CM9705496