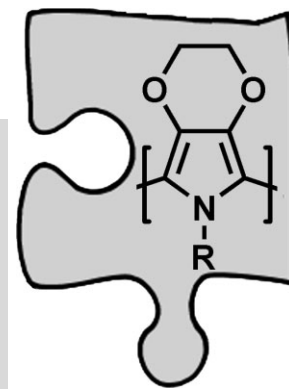


DOI: 10.1002/adma.200502312

Poly(3,4-alkylenedioxyppyroles): The PXDOPs as Versatile Yet Underutilized Electroactive and Conducting Polymers**

By Ryan M. Walczak and John R. Reynolds*



The poly(3,4-dioxypyrrrole) (PXDOP) family of conducting and electroactive polymers has now been developed to the point that multiple synthetic routes allow many functionalized polymers with controllable optoelectronic and redox properties. These properties, which include high conductivity, multicolor cathodic and anodic electrochromism, and rapid redox switching, allow these materials to be used in a variety of applications that potentially include conducting coatings, electrochromic windows and displays, chemical sensors, bioactive materials, and mechanical actuators. Surprisingly, the scientific literature published on the PXDOP derivatives has been isolated and sparse compared to that of other conducting polymers. This report will highlight the synthesis and materials properties of PXDOPs and show how these powerful materials fit into the frontier of conducting polymers research.

1. Completing the Puzzle

Perhaps the most attractive aspect of conjugated and conducting polymers is the ability to fine-tune their optoelectronic properties with straightforward synthetic modifications. Because of this synthetic flexibility, seemingly related properties, such as redox potential and electronic bandgap, can be decoupled and orthogonally modified without drastic adjustment of the fundamental materials synthesis process. Thus, a new material with a desired set of properties can be realized by utilizing the current body of knowledge and logically

searching for the correct “puzzle piece”. To date, a large library of polyheterocycles with extremely diverse materials properties has been published.^[1–4] Some of the many interesting properties of polyheterocycles include electrochromism,^[5–7] electroluminescence,^[8,9] and optically transparent conductivity,^[10] resulting in their use as photovoltaics,^[11] charge dissipators,^[10] chemical and biochemical sensors,^[2,5,12–16] and drug-delivery systems.^[17] Fine-tuning and optimization of the conducting polymer properties for these systems is achieved by modification of the polymer backbone or its pendent groups. One significant discovery was that polythiophene (PTh) could be made soluble while maintaining its high conductivity by the substitution of an alkyl chain onto the polymer repeat unit.^[2,18–23] In addition to solubility, it has been shown that the variation of the chemical functionality of pendent groups on the PTh backbone has a tremendous effect on the polymer properties and can induce water solubility, hydrogen bonding, and polymer-chain aggregation as just a few examples.^[15]

When an ethylenedioxy bridge is fused onto the 3- and 4-positions of the thiophene ring in 3,4-ethylenedioxythiophene (EDOT), the resulting polymer PEDOT^[24] (also called PEDT) possesses a lower bandgap (1.6 versus 2.2 eV), lower

[*] Prof. J. R. Reynolds, R. M. Walczak
The George and Josephine Butler Polymer Research Laboratory
Department of Chemistry
Center for Macromolecular Sciences and Engineering
University of Florida
Gainesville, FL 32611 (USA)
E-mail: Reynolds@chem.ufl.edu

[**] We gratefully acknowledge National Science Foundation (INT-0339735) and the Air Force Office of Scientific Research (F49620-03-1-0091) for funding the initial XDOP chemistries developed in our laboratory.

monomer and polymer oxidation potentials (in fact, EDOT can be easily electropolymerized, whereas thiophene, due to its higher oxidation potential, is more difficult), and different color states, including a highly conducting and transparent doped state when compared with PTh.^[10,25] These property differences are due to the propensity of the oxygen atoms to donate electron density into the π -system, which raises the highest occupied molecular orbital (HOMO). It was also found that the electronic and optical properties of PEDOT can be tuned by varying the size and composition of the alkylene bridge.^[26] This family of poly(3,4-alkylenedioxythiophene) derivatives, commonly referred to as the PXDOTs, has been shown to have a variety of properties compared with those of PEDOT because of the slightly different electron-donating character of the substituent bridges and by different polymer secondary and tertiary interactions. The PXDOT family shares a oxidation potential similar to that of the polypyrrole (PPy) family of polymers, approximately 0.0 V versus saturated calomel electrode (SCE). However, PPy has a higher bandgap of approximately 2.7 eV.^[27,28] In contrast, the poly(*p*-phenylene) (PPP) and poly(*p*-phenylenevinylene) (PPV) derivatives exhibit high bandgaps, but are not easily oxidized,^[29] and the poly(isothianapthene) (PITN) family of polymers exhibit low bandgaps and are also not easily oxidized.^[30]

The poly(3,4-dioxypyrrrole) (PXDOP) derivatives, which are the subject of this report, combine the 3,4-dioxysubstitu-

tion structural fragment, as in PEDOT, with the already electron-rich pyrrole ring to yield a family of polymers with unique properties, including middle to high bandgaps and very low oxidation potentials.^[31] Figure 1 (not intended to be comprehensive) simplistically organizes this dichotomy of bandgap and oxidation potential of the polymer families described above. The combination of a low oxidation potential with a high bandgap is unique to the PXDOP family of polymers as they can be derivatized on the nitrogen, disrupting the degree of conjugation.

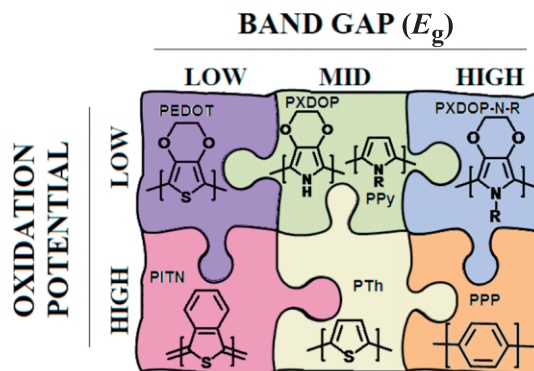


Figure 1. Completing the puzzle. Shown in blue, the *N*-substituted PXDOP family of polymers exhibit high bandgaps coupled with low oxidation potentials.



Dr. John R. Reynolds is a Professor of Chemistry at the University of Florida with expertise in polymer chemistry and serves as an Associate Director for the Center for Macromolecular Science and Engineering. His research interests have involved electrically conducting and electroactive conjugated polymers for over 25 years with work focused on the development of new polymers by manipulating their fundamental organic structure in order to control their optoelectronic and redox properties. His group has been heavily involved in the areas of developing new polyheterocycles and visible and infrared light electrochromic materials, as well as research into light emission from polymer and composite light-emitting diodes (both visible and near-IR) and light-emitting electrochemical cells (LECs). Further work is directed to using organic polymers and oligomers in photovoltaic cells. He obtained his M.S. (1982) and Ph.D. (1984) degrees from the University of Massachusetts in Polymer Science and Engineering published over 200 peer-reviewed scientific papers, and served as co-editor of the "Handbook of Conducting Polymers", was published in 1998. More details of his research can be found at <http://www.chem.ufl.edu/~reynolds/>.



Ryan M. Walczak is a Ph.D. candidate in the Department of Chemistry at the University of Florida advised by Prof. Reynolds. Currently, his research is devoted to developing new methodologies for the synthesis of heterocycles, their conversion into conjugated polymers, and the optimization of their physical, redox, and optical properties. A native of Buffalo, NY, Walczak graduated with his B.S. in Chemistry from the State University of New York at Buffalo in 2001.

Although a significant body of literature on many of these polymers and their derivatives exists, the PXDOPs have been cursorily researched by only a few groups. This report will explore how their flexible and adaptable repeat unit structure, high bandgap, high conductivities, biocompatibility, and low half-wave potential, $E_{1/2}$, makes them strong candidates for a wide variety of applications.

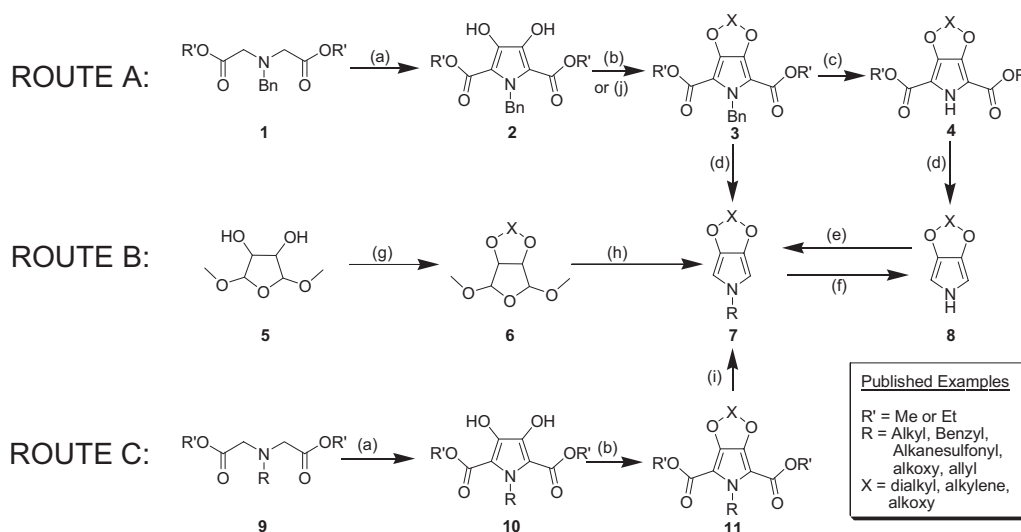
2. Synthesis of XDOP Monomers

Monomer synthesis has probably been the most limiting factor in the progress of XDOP and PXDOP research. Whereas the synthesis of thiophene derivatives is fairly straightforward due to the ring's stability and tolerance towards sometimes harsh synthetic conditions, the XDOP derivatives are much less forgiving. In fact, the very properties that make the XDOP family highly desirable from a materials properties perspective elevate the difficulty of monomer synthesis. For example, in the original synthetic route,^[32] which parallels a similar synthetic route developed for the thiophene derivatives, the flexible nitrogen atom must be protected during the synthesis and later deprotected and refunctionalized; this adds extra synthetic steps and makes the synthesis less atom efficient when compared with the thiophene syntheses. Additionally, due to their low oxidation potential, care must be taken when handling these compounds so that they do not decompose during workup, purification, and storage.

Scheme 1 illustrates the three most common routes towards XDOP derivatives. The original route, labeled as Route A, was pioneered by the groundbreaking work of Merz et al.^[32,33] and later expanded upon in our group.^[34–37] This route closely

resembles that of an old, well-exploited route towards 3,4-dioxythiophene derivatives.^[38] Route A begins with diester **1**, which is ring-closed to the 3,4-dihydroxypyrrrole derivative **2** via a Hinsberg condensation with diethyl oxalate. The alkylene bridge or the alkyl group is then substituted under Williamson conditions with the corresponding alkyl halide or sulfonate to yield **3**. Alternatively, compound **2** could be subjected to Mitsunobu conditions with the appropriate diol to yield **3**.^[39] This compound can then be catalytically debenzylated followed by saponification/decarboxylation to yield the *N*-hydro derivative **8**, or the benzyl group can be left intact to yield **7**. The *N*-hydro derivative **8** can be easily alkylated with a variety of substituents to yield the respective XDOP-*N*-R.^[34] Route A has been the most widely published route and has yielded the simple XDOP systems, the more complicated crown ether derivatives, and the *N*-alkylated derivatives.^[34,40]

As stated earlier, this route is somewhat undesirable due to the poor atom efficiency of the decarboxylation and debenzylation steps. To overcome some of these problems, two alternative routes have been developed to boost yields and efficiencies. As shown in Route B,^[41] compound **5**, synthesized in one step from the commercially available 2,5-dimethoxy-3,4-dihydrofuran by oxidation with potassium permanganate, was alkylated with an alkyl halide to produce compound **6**. This precursor was easily converted into its 3,4-dialkoxyppyrrrole derivative **7** by the deprotection of **6** into its dialdehyde followed by subsequent condensation with a primary ammonium salt. If product **7** was substituted with an *N*-benzyl group, it could be easily converted into its *N*-hydro derivative by deprotection in sodium/liquid ammonia, followed by aqueous workup. This route was found to be shorter and easier than Route A and able to produce a wide variety of monomeric



Scheme 1. Synthetic routes to XDOPs. a) Diethyl oxalate/NaOEt/EtOH; b) alkyl halide or sulfonyl ester/NaH/dimethylformamide (DMF); c) Pd(C)/H₂/AcOH, Δ , several days, or trifluoroacetic acid (TFA)/H₂SO₄; d) 1. NaOH/H₂O, Δ , 2. H⁺, 3. triethanolamine, Δ ; e) alkyl halide or sulfonyl ester/NaH/DMF; f) R = Bn: 1. Na/NH₃, 2. NH₄Cl/H₂O; g) alkyl halide or alkyl sulfate/NaOH, or sulfonyl ester/NaH/dioxane; h) 1. 2 N HCl or H₂SO₄ for 30 min, or *p*-toluenesulfonic acid (*p*-TSA)/tetrahydrofuran (THF)/H₂O, 70 °C for 2 h, 2. buffer to pH 6 with NaOAc, i) 3. RNH₂Cl, 25 °C, 10–15 h; j) diol/diethyl azodicarboxylate (DEAD)/PPh₃/THF.

substituents, but has the distinct disadvantage (to date!) of being only able to produce 3,4-dialkoxypyrrroles as opposed to the closed-ring analogues.

Another alternative, Route C, has been reported by Kim et al.^[42] in which the functionality of the pyrrole nitrogen was built in before the condensation reaction. The synthetic pathway is very similar to that of Route A, but precludes the need for deprotection and *N*-functionalization steps. Although this route is limited in its flexibility towards substitution of the nitrogen atom, it allows for a wide range of substitution of the 3,4-dioxy moiety, and is particularly attractive for the scale-up of a lead compound.

3. PXDOP Synthesis

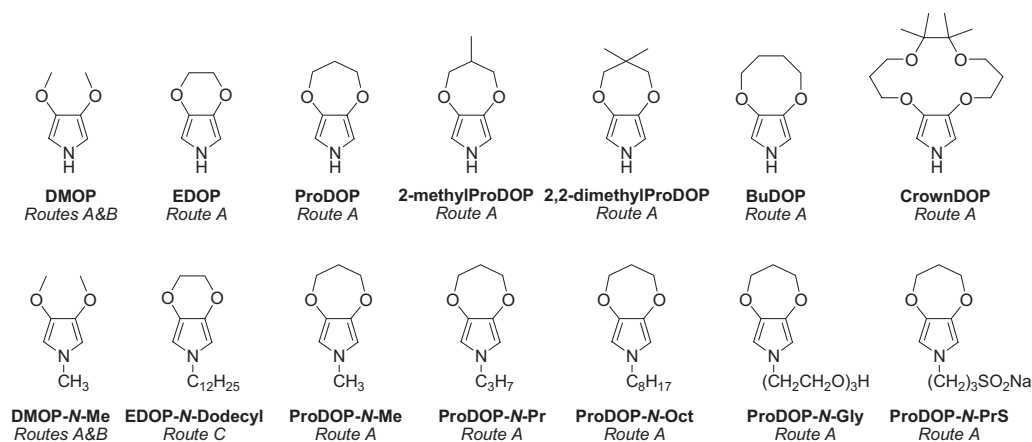
Most commonly, the XDOP derivatives have been polymerized oxidatively, either electrochemically or chemically. Scheme 2 lists the XDOP derivatives that were oxidatively polymerized and the synthetic route in which they were made from Scheme 1. It can be seen that a significant family of various dialkyl, alkylene, *N*-hydro, and *N*-alkyl derivatives have been studied.

These various monomers, although deceptively similar in structure, produce polymers with a large variety of properties. Table 1 illustrates the various structure–property relationships of the monomers from Scheme 2 and their respective polymers. It can be seen that the monomer oxidation potential ($E_{p,m}$) of most of the *N*-hydro monomers^[35,37] is found between 0.95–1.20 V versus SCE (one notable exception is DMOP, with an $E_{p,m}$ of 0.84 V^[32,43]), whereas the *N*-alkylated derivatives^[32,44] possess a monomer oxidation potential that is almost 200 mV lower. This phenomenon can be attributed to the *N*-alkyl group donating electron density into the π -system, raising the HOMO with respect to its *N*-hydro derivative. All monomers except for DMOP-*N*-Me and EDOP-*N*-Dodecyl were electropolymerized onto platinum-button electrodes.

As illustrated by the repeated scanning electrodeposition results in Figure 2, electroactive films are easily prepared

from a 1–10 mM solution of monomer in an organic solvent/electrolyte system which is potentiodynamically swept from a potential more negative than that of the polymer reduction to a potential slightly more positive than that of the monomer peak oxidation potential. One striking difference between the *N*-hydro and the *N*-alkylated derivatives is the number of potential sweeps that are required for the formation of an adequate film on the electrode surface. The *N*-hydro derivatives polymerize readily and require only about 20 sweeps for scan rates between 50 and 200 mV s⁻¹ to produce a film with a high degree of electroactivity and spectroscopic activity. This efficient electropolymerization behavior is also typical of PXDOT derivatives, of which many have been studied.^[5] However, the *N*-alkylated derivatives (except for the methyl-substituted derivative) require as many as 150 scans to form a good film. This effect is most likely due to an increased solubility of oligomers in solution, which prevents nucleation onto the electrode surface. Mixed solvents are often used to overcome this issue.^[45] In the case of the electropolymerized XDOPs, the alkyl chain may also prevent the heteroatom from coordinating to the electrode surface, decreasing the adsorption characteristics of the polymer as it forms. Interestingly, deposition of ProDOP-*N*-Gly, which contains an alcohol, and of ProDOP-*N*-PrS, which contains a sulfonate, require less scans, probably due to the functional group interacting with the electrode surface.

Another interesting observed phenomenon is that the $E_{1/2}$ of the *N*-alkylated polymers are 200 mV greater than that of the *N*-hydro polymers, in contrast with the monomer oxidation potentials, which exhibit the opposite effect. This higher redox potential in the *N*-alkylated derivatives can be explained by the distortion of the polymer backbone that the *N*-alkyl substituent causes. The sterically demanding substituent prevents the polymer from adopting its preferred 180° pyrrole torsion angle (full π -overlap), and decreases the effective conjugation length, effectively lowering the HOMO. This backbone distortion gives rise to elevated bandgaps relative to the *N*-hydro derivatives, providing unique optical properties of full visible-light transmissivity with a low oxidation potential.



Scheme 2. XDOP monomers used in oxidative polymerization reactions and their synthetic routes.

Table 1. Structure–property relationships of the polymers produced from the monomers in Scheme 2. $E_{p,m}$: monomer oxidation potential; E_g : bandgap (eV) as the onset of the π – π^* transition of the neutral polymer film; ΔT : change in transmissivity; λ_{max} : wavelength of maximum absorption.

Monomer	Monomer $E_{p,m}$ [V vs. SCE]	Polymer $E_{1/2}$ [V vs. SCE]	E_g [eV]	Maximum reported conductivity [S cm ⁻¹]	Polymer film electrochromism [a]	ΔT [%]	λ_{max} [nm]
DMOP	0.84	–0.17	2.1	200	orange (n)	13	520
EDOP	1.07	–0.24	2.0	83	red (n)	59	537
ProDOP	1.09	–0.24	2.2	95	sky blue (d) orange (n) brown (i)	70	522
2-MethylProDOP	1.12	–0.15	2.2	–	gray-blue (d) orange (n) red-brown (i)	51	530
2,2-DimethylProDOP	1.17	–0.03	2.2	–	light blue (d) orange (n) red-brown (i)	76	534
BuDOP	1.07	–0.21	2.2	–	light blue-gray (d) orange (n) blue-gray (d)	61	533
CrownDOP	0.94	–0.31/0.49 [b]	2.4	–	yellow (n) transparent gray (d)	43	490
DMOP- <i>N</i> -Me	0.87	inactive	3.0	0.001	dark brown (d)	–	–
EDOP- <i>N</i> -Dodecyl	chemically polymerized	–	3.3	0.028	–	–	–
ProDOP- <i>N</i> -Me	0.84	0.10	3.0	–	deep purple (n) dark green (i) blue (d)	25 [c]	476
ProDOP- <i>N</i> -Pr	0.85	0.18	3.4	–	–	14 [c]	476
ProDOP- <i>N</i> -Oct	0.86	0.20	–	–	–	–	–
ProDOP- <i>N</i> -Gly	0.88	0.21	3.4	–	colorless (n) pink (i) tan (i)	50 [c]	460
ProDOP- <i>N</i> -PrS	0.59	0.24	2.9	0.001	gray-blue (d) colorless (n) pink (i) gray (i) blue-gray (d)	18 [c]	460

[a] (d) fully doped/oxidized polymer, (i) intermediate/partially oxidized polymer, (n) neutral/unoxidized polymer. [b] Two distinct polymer redox processes were observed. [c] Polymer λ_{max} was taken as the maximum absorbance value in the visible region of the spectrum.

4. XDOP as a Unit within Complex Repeat Unit Structures

It has been demonstrated that the XDOP derivatives are not limited to homopolymers. As shown in Scheme 3, a series of XDOP-cyanovinylene polymers also bearing a thiophene or an EDOT repeat unit were synthesized.^[34,46] Synthesis is achieved by protecting the EDOP nitrogen followed by conversion to the aldehyde via the Vilsmeier–Haack reaction to yield compounds **13** or **16**. The resulting aldehyde was then reacted in a Knoevenagel condensation with the appropriate thienylacetonitrile, followed by deprotection to yield compounds **14** and **17**. The resulting electrodeposited polymers, whose properties are summarized in Table 2, exhibit a bandgap-compression effect, where the HOMO of the donor repeat unit and the lowest unoccupied molecular orbital (LUMO) of the acceptor unit are coupled. Thus, low bandgaps of 1.1 eV are reported for both derivatives. The similar

bandgaps exist despite the fact that one polymer contains a thiophene repeat unit and the other an EDOT unit. This phenomenon can probably be explained by the fact that the HOMO exists predominantly on the EDOP portion of the molecule regardless of the structure of the other aryl group. These polymers have another unique property in that their low-lying LUMO allows them to be n-doped, which is the only such example reported in the literature for a PXDOP derivative.

Scheme 3 also illustrates the synthesis of PXDOP-vinylene derivatives.^[42,47] This clever route consisted of the synthesis of compound **11** via Route C in Scheme 1. The diester was reduced to the diol **19** with LAH and converted to the corresponding thioether **20** or sulfoxide **22**. These monomers were subjected to a polymerization in which the PXDOP-vinylene derivatives **21** were synthesized in moderate to high molecular weights of about 5000–25 000 g mol⁻¹. The polymer properties are listed in Table 2 and demonstrate that they all exhibit

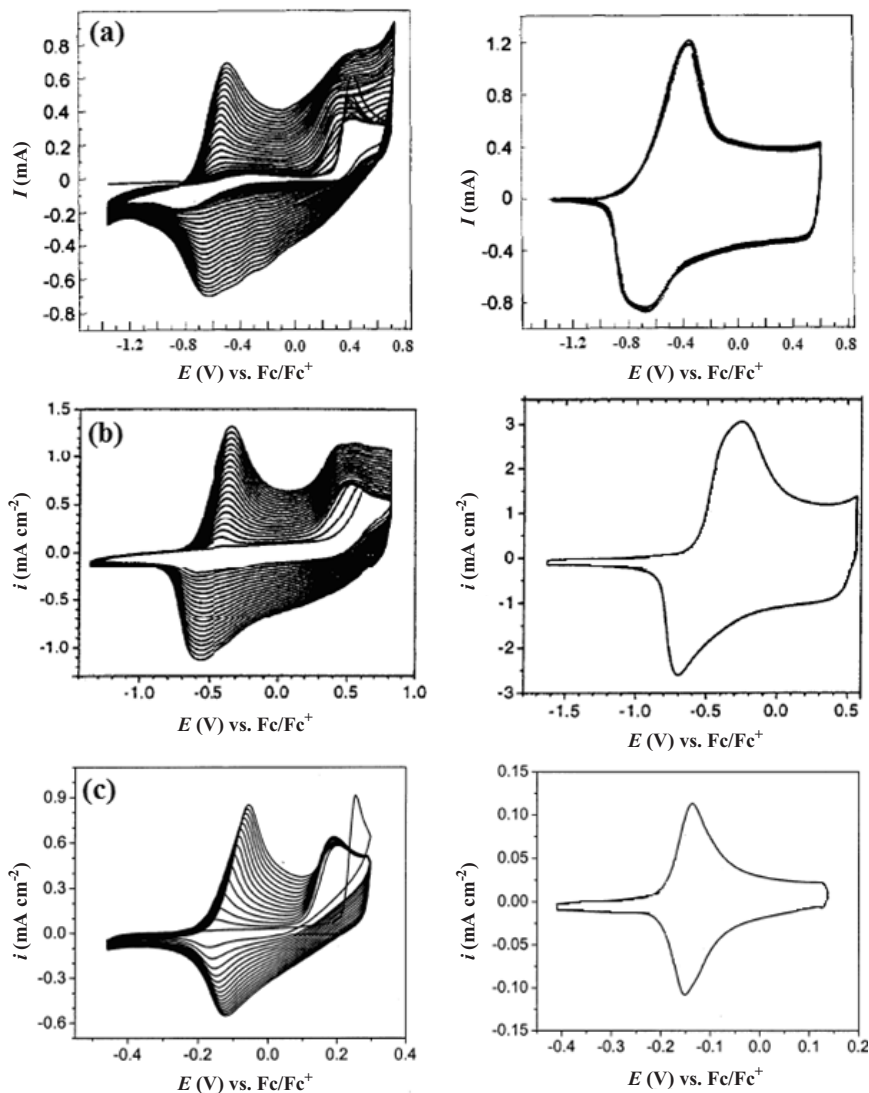


Figure 2. Potentiodynamic electropolymerization (left column) and polymer cyclic voltammograms (right column) of a) PDMOP (the x-axis was converted from potential versus Ag/AgCl to potential versus ferrocene (Fc/Fc^+), b) PProDOP, and c) PProDOP-N-PrS. Reproduced and adapted with permission from [37] (Copyright 2000 American Chemical Society), [43] (Copyright 1996 Elsevier), and [44] (Copyright 2003 American Chemical Society).

low bandgaps, on the order of 1.1–1.7 eV, and moderate conductivities. In fact, polymer **22a** exhibits the highest conductivity to date for an *N*-alkylated PXDOP derivative, which is not surprising because the vinylene linkage minimizes the steric distortion that the *N*-alkyl functionality imparts on the polymer backbone.

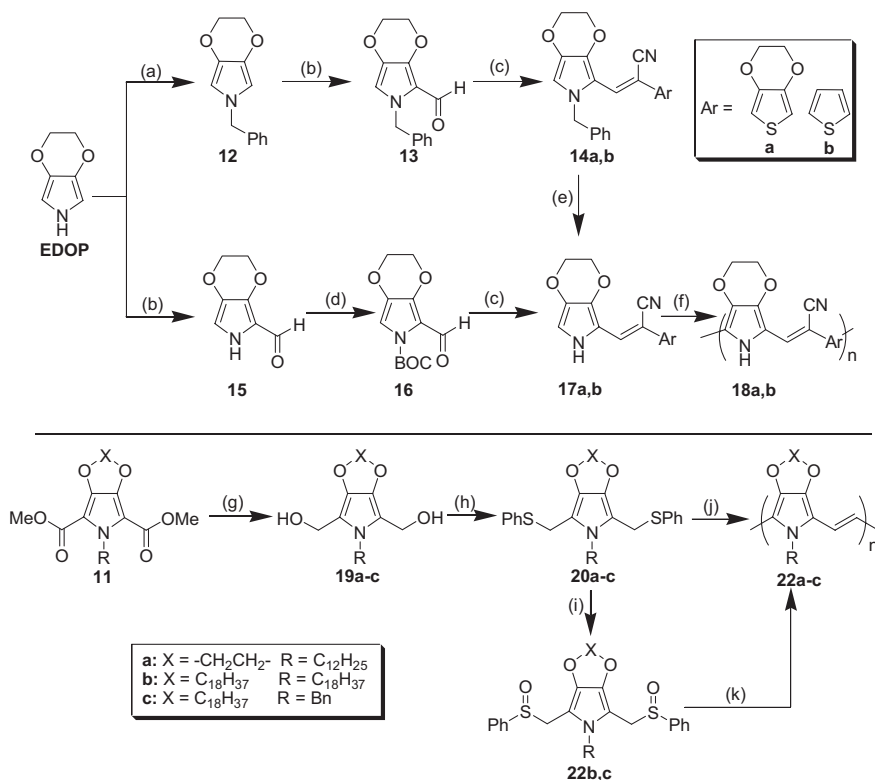
5. Some Interesting and Unique PXDOP Properties

XDOP derivatives conveniently electropolymerize into films that have a variety of interesting properties. One such property, electrochromism, is defined as a change in the optical spectrum of a material as a function of applied potential. The PXDOP family of polymers is especially attractive because their bandgaps lie in the region of 1.1–3.3 eV and thus can fully span the near IR, through the entire visible and into the UV range of the electromagnetic spectrum. The human eye is sensitive to slight changes in the optical spectra in the visible region, and consequently, a large variation of color states exist for the different PXDOP derivatives. Figure 3a illustrates the spectroelectrochemistry (a technique of measuring the optical spectrum of a polymer film as an electrochemical potential is applied) of PProDOP-*N*-PrS as a function of applied potential.^[44] It can be seen that the polymer, whose π, π^* absorption in the UV region is strong, exhibits a very low absorbance

Table 2. Properties of electrodeposited XDOP-cyanovinylene polymers. M_n : number-average molecular weight; M_w : weight-average molecular weight.

Polymer	M_n [g mol ⁻¹]	M_w/M_n	Polymer $E_{1/2}$ [V vs. SCE]	E_g [eV]	Conductivity [a] [S cm ⁻¹]	Polymer film electrochromism [a]	λ_{max} [nm]	ΔT [b] [%]
18a	–	–	–1.4 [c], 0.4	1.1	–	–	394	2%
18b	–	–	0.7	1.1	–	–	401	7%
22a	13 000	1.53	–	1.57	0.45	blue-black clear yellow (n) (d)	659	–
22b	4800	–	–	1.68	0.00011	deep blue transparent (n) (d)	580	89%
22c	25 000	2.78	–	1.62	0.003	deep blue transparent (n) (d)	618	61%

[a] (d) fully doped/oxidized polymer, (n) neutral/unoxidized polymer. [b] Transmittance change upon doping at the reported λ_{max} . [c] The negative value is reported as an *n*-doping process, whereas the positive value is reported as a *p*-doping process.



Scheme 3. Synthesis and polymerization of XDOP-vinylene derivatives. a) NaH/THF/PhCH₂Br; b) POCl₃/DMF/CH₂Cl₂; c) ArCH₂CN/*t*-BuOK/*t*-BuOH; d) (BOC)₂O/Et₃N/4-dimethylaminopyridine/CH₂Cl₂ (BOC: *t*-butyl carbamate); e) Na/NH₃; f) anodic polymerization; g) LiAlH₄/THF; h) PhSH/ZnI₂/CH₂Cl₂; i) *m*-chloroperbenzoic acid/CHCl₃; j) *t*-BuOK/THF; k) 1. *t*-BuOK/THF, 2. vacuum, 80 °C.

throughout the visible region, rendering it transparent to the human eye. As the polymer is gradually oxidized, absorption processes attributed to polarons and bipolarons emerge into the visible, giving the polymer color.

Illustrated in Figure 3b are color swatches obtained from the colorimetric measurements of various PXDOP derivatives.^[44,48] It can be seen that a striking number of color states can be achieved by making only minimal changes to the monomer structure. For example, PEDOP is a red neutral polymer, whereas PProDOP is orange. Furthermore, the electrochromic effect generates a wide variety of other colors, illustrated in Figure 3b, and listed in more detail in Table 1, including pink, brown, and blue. It is evident that a full palette of colors is accessible within this one family of polymers.

The color-switching pathway is unique to each individual polymer. For example, Figure 4 illustrates the relative luminance values (in essence, the transmissivity of the film as sensed by the human eye) of PEDOP and PProDOP at various potentials. It can be seen that PEDOP switches from a highly absorbing neutral state (red) to a transmissive oxidized state. In stark contrast, PProDOP is more transmissive in its neutral state (orange), goes through an absorbing state when partially oxidized, and finally becomes highly transmissive in

its fully oxidized state. This mid-switch absorbing state is a deep brown color, as shown in Figure 3. The full switching characteristics of PEDOP may be considered as desirable for an electrochromic window because of the high luminance change. PProDOP on the other hand gives a more complex electrochromic switch where light could be attenuated at an intermediate potential but transmitted in the extreme doped and undoped states. It is impossible to surmise a priori that the seemingly insignificant substitution of a single methylene carbon onto the pendent area of the polymer repeat unit would cause such a drastic change in the polymer properties and, as such, the synthesis of each new monomer/polymer system provides a new color set to be added to the palette.

As stated in the introduction, much of the allure of PXDOP derivatives comes from their low oxidation potentials coupled with elevated bandgaps. Since most of the previously reported redox electroactive polymers have bandgaps below 3.0 eV, they are at least partially absorbing in their neutral state. Polymers with a narrow gap are highly absorbing in the visible region in the neutral state and, when doped, become

transparent due to the polaronic and bipolaronic species absorbing in the near IR. These materials are said to be *cathodically coloring*. A bandgap above 3.0 eV in its neutral state (elevated by the aforementioned steric distortion of the backbone) will generally be optically transparent in the visible region of the spectrum. The polaronic and bipolaronic species are hypsochromically shifted into the visible region. The resulting polymer is colored in its oxidized state, and is said to be *anodically coloring*. A dual electrochromic device,^[49] whose primary application is for variable-contrast electrochromic windows and displays, is constructed with one electrode composed of an anodically coloring polymer, the other electrode composed of a cathodically coloring polymer, and separated by an electrolyte. Such a device utilizes the simultaneous transparency of both polymers in one state and, upon reverse bias, the simultaneous absorption of the two polymers. Figure 5 shows the construction and optical properties of such a device. If two polymers absorbing an additively broad range of wavelengths in the optical spectrum were to be coupled, then a very high contrast dual electrochromic device could be fabricated.

A limited number of conductivity studies have been performed on various PXDOP derivatives. Most noteworthy is

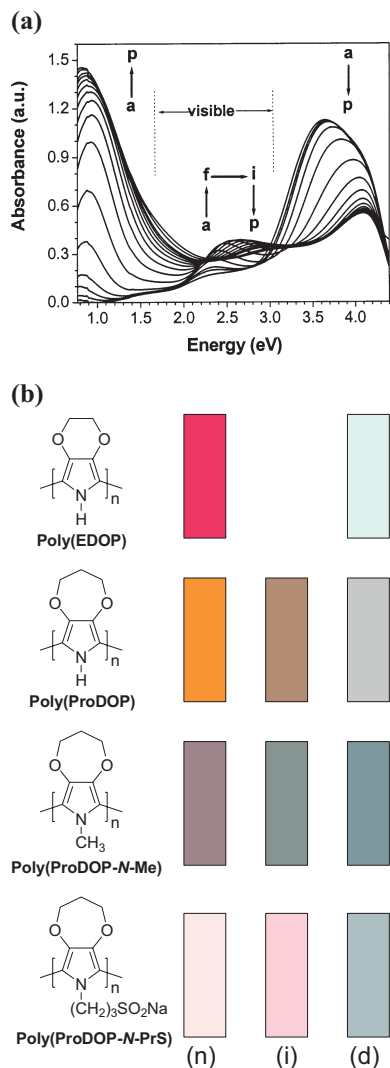


Figure 3. a) Spectroelectrochemistry of PProDOP-N-PrS at applied potentials of a) -0.40 , b) -0.30 , c) -0.25 , d) -0.20 , e) -0.15 , f) -0.10 , g) -0.05 , h) 0.00 , i) $+0.05$, j) $+0.10$, k) $+0.15$, l) $+0.20$, m) $+0.25$, n) $+0.30$, o) $+0.40$, and p) $+0.50$ V. Reproduced and adapted with permission from [44]. Copyright 2003 American Chemical Society. b) $L^*a^*b^*$ color swatches (coordinate values obtained from [44] and [48]) of various PXDOP derivatives in their (n) neutral/unoxidized, (i) intermediate/partially oxidized, and (d) fully doped/oxidized states.

the study by Merz and Graf^[43] where freestanding films of doped PDMOP exhibited conductivities in excess of 200 Scm^{-1} . When thick, freestanding polymer films of PDMOP were stretched, they exhibited a 40 % increase in conductivity with 25 % strain, indicating that the stress-induced orientation of the polymer fibers could be a valuable way to improve the materials properties of PXDOP derivatives. Electrochemically prepared films of PEDOP and PProDOP exhibited conductivities of 83 and 95 Scm^{-1} , respectively. These values reported are the highest to date in the literature for their respective systems, and there is a var-

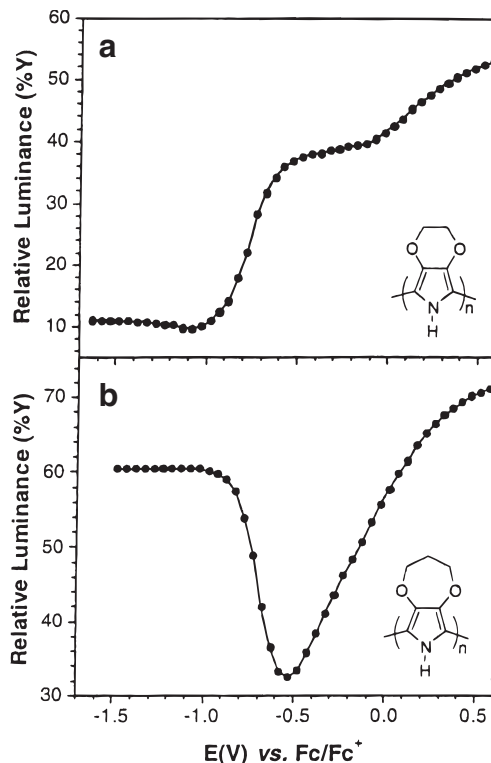


Figure 4. Relative luminance values for $1 \mu\text{m}$ thick films of a) PEDOP and b) PProDOP as a function of applied potential. Reproduced with permission from [37]. Copyright 2000 American Chemical Society.

iability of about one order of magnitude depending on the polymerization conditions, dopant ion, and film thickness. The conductivities of these *N*-hydro derivatives are promising, and optimization of the polymerization conditions should yield even higher conductivities. An example of one such optimization process is illustrated by an interesting study of the percolation threshold of various PXDOP derivatives, performed by Zotti et al.^[50] As seen in Figure 6, the maximum conductivity for a sample of PDMOP was achieved upon approximately 50 % doping, which consequently corresponded to the peak oxidation potential of the polymer. It is presumed that Merz and Graf may have been able to achieve conductivities even greater than their reported 202 Scm^{-1} by simply setting the dopant level to 50 %.

The introduction of an alkyl substituent onto the heteroatom was found to lower the conductivity by several orders of magnitude. This lower conductivity was not surprising because the twisting of the polymer backbone prevents efficient π -stacking, thus disrupting the mechanism of charge percolation. Alas, a high bandgap and anodic coloration comes at the sacrifice of conductivity, but through further optimization of polymer structure and other conditions, a happy medium between anodic coloration and conductivity may eventually be found.

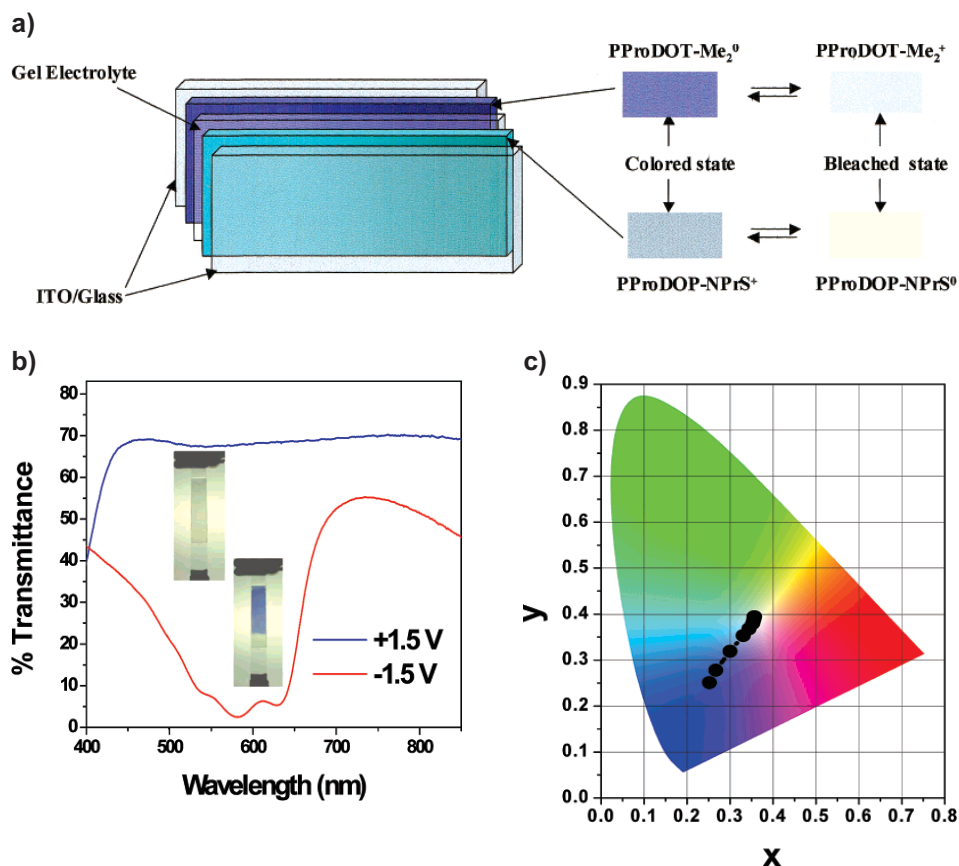


Figure 5. a) The general construction of a dual polymer electrochromic device. ITO: indium tin oxide. b) The transmission percent (%T) of the device as a function of applied potential and digital photographs of the device in its two electrochromic states. c) Plot of the hue and saturation values of the device at various potential on a Commission Internationale de L'Eclairage (CIE) 1931 colorimetry plot. Reproduced with permission from [49]. Copyright 2002 American Chemical Society.

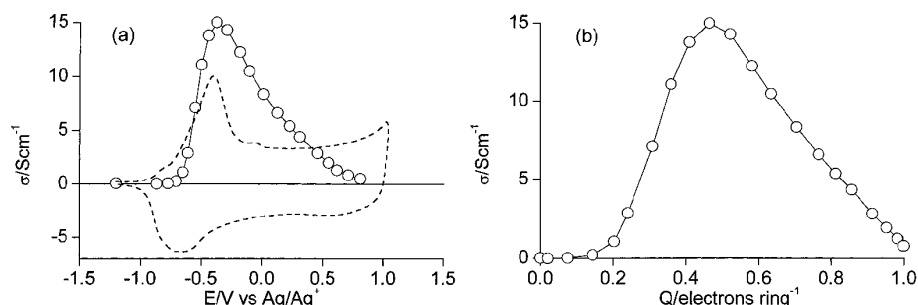


Figure 6. In situ conductivity (σ) measurements of PDMOP in 0.1 M Bu_4NClO_4 /acetonitrile a) as a function of potential (E) and b) as a function of charge (Q , doping level). The dashed line in (a) represents the cyclic voltammogram of PDMOP. Reproduced with permission from [50]. Copyright 2000 American Chemical Society.

6. Why Have PXDOP Derivatives Been Underutilized?

It is clear that the PXDOP family of polymers presents to the conducting polymer community a unique set of properties that could be employed for a variety of applications, both

commercially and academically. It is in fact surprising that they have not received more attention. However, there are some significant obstacles to be overcome before they can make a larger impact. Many of them have been addressed recently:

a) Laborious and inefficient synthesis: As illustrated in previous sections, Route A in Scheme 1 has, up until very recently, been the sole synthetic route to XDOP derivatives. However, the emergence of Routes B and C have demonstrated that conditions can be optimized. If more attention was focused on the

optimization of reaction conditions in parallel with the optimization of polymer properties, a good handful of lead compounds could be produced on a large scale.

b) Not commercially available: For several years now, commercial sources of pyrrole, thiophene, EDOT, and their respective derivatives have been commercially available from

large chemical suppliers. However, recent new commercial availability greatly facilitates the researchers who would like to avoid monomer synthesis.

c) Disorganized and sparse published scientific literature: Since the original synthesis of DMOP in 1992, there has not been a focused review article published on the dioxypyrrrole derivatives. Therefore, their significance may not be apparent compared with the widespread and organized attention given to the other polyheterocycle families. Perhaps this short report could serve as a starting point for more focused research into the PXDOP derivatives.

7. Recent Advances Demonstrating PXDOP Versatility

There have been several publications in recent years that utilize PXDOP derivatives in applications that have great potential for widespread use. Perhaps the most visible application would be for the electrochromic windows market. Some recent research dedicated to the dual electrochromic devices described above have led our group to a patent on the technology, which has the potential to be used as electrochromic windows.^[51] A patent issued to the Japan Carlit Company utilizes PXDOP derivatives in electrolytic capacitors.^[52] Kodak has patented the use of PEDOP doped with poly(styrene sulfonate) (PSS) to compete with Bayer AG's highly successful Baytron product line.^[53] They have also received a number of patents utilizing this PEDOP-PSS blend in photographic anti-static coatings. PEDOP has demonstrated potential as a polymeric actuator with an electrochemical microstrain gauge due to its propensity to change its volume upon doping/dedoping.^[54] These results demonstrate the potential of PXDOPs in artificial-muscle research. PDMOP films demonstrate a change in electrochemical property upon exposure to different vapors. This observed "solvoconductive" behavior could be explored further for chemical-sensor applications.^[50,55] Perhaps some of the most exciting potential applications of PXDOP derivatives are their use in biological systems. Our group demonstrated how the oxidized forms of PXDOP derivatives are stable to a variety of biological reductants.^[36] This stability is in contrast to other conducting polymers, whose $E_{1/2}$ values are higher and thus more susceptible to biological reduction. Since the oxidized form of the conducting polymer has unusually stable conductivity, the PXDOPs seem to be the best candidate to be used under biological (in vivo) conditions (e.g., in tissue engineering applications). This same stability of the conducting form to chemical composition may also prove important in the development of DNA sensors and related applications which would be activated by torsionally induced steric interactions.

One should consider in what other applications these polymers might find utility as conducting polymers may be important elements in a number of active organic devices. While this type of discussion is a bit speculative, one can consider the fundamental redox and optical properties of these poly-

mers and suggest applications for which they may or may not be viable. As the PXDOP family has especially low oxidation potentials, applications as neutral organic electronic materials (i.e., semiconductors in field-effect transistors, light-absorbing and charge-transporting materials in photovoltaic cells, and emissive materials in polymer light-emitting diodes) are unlikely but certainly not out of the question. The ability to form doped and conductive complexes, such as PEDOP/PSS,^[53] suggests the PXDOP family may be used as new hole-transport or injecting layers. Since soluble compositions of these polymers can be formed, the polymers can be considered for use in printed and other patterned devices. The high stability of the redox switching, along with the high doping levels accessible, suggests the PXDOPs may be useful charge-storage materials in flexible batteries and supercapacitors. Finally, compared with thiophene polymers, the pyrrole N-H bond provides a separate chemical functionality that increases aqueous compatibility. This moiety can also be considered for incorporation into hydrogen-bonding, self-assembling molecules and polymers that may ultimately yield highly ordered electroactive materials.

8. Concluding Remarks

It is evident that the PXDOP family of conducting polymers exhibits a wide variety of useful and unique properties. Due to synthetic challenges and the rarity of examples in the scientific literature, very little progress has been made in the field compared with other conducting polymers. However, because of some recent advances in the synthesis, availability, and properties of these polymers, especially in the fields of electrochromic windows and biological sensors, it seems clear that this family is ready for more extensive research.

Received: October 28, 2005

Final version: December 15, 2005

- [1] J. L. Reddinger, J. R. Reynolds, *Adv. Polym. Sci.* **1999**, *145*, 57.
- [2] R. D. McCullough, *Adv. Mater.* **1998**, *10*, 93.
- [3] A. Moliton, R. C. Hiorns, *Polym. Int.* **2004**, *53*, 1397.
- [4] J. W. Schultze, H. Karabulut, *Electrochim. Acta* **2005**, *50*, 1739.
- [5] L. Groenendaal, G. Zotti, P.-H. Aubert, S. Waybright, J. R. Reynolds, *Adv. Mater.* **2003**, *15*, 855.
- [6] A. Cirpan, A. A. Argun, C. R. G. Grenier, B. D. Reeves, J. R. Reynolds, *J. Mater. Chem.* **2003**, *13*, 2422.
- [7] A. A. Argun, P.-H. Aubert, B. C. Thompson, I. Schwendeman, C. L. Gaupp, J. Hwang, N. J. Pinto, D. B. Tanner, A. G. MacDiarmid, J. R. Reynolds, *Chem. Mater.* **2004**, *16*, 4401.
- [8] G. Gigli, O. Ingnas, M. Anni, M. De Vittorio, R. Cingolani, G. Barbarella, L. Favaretto, *Appl. Phys. Lett.* **2001**, *78*, 1493.
- [9] I. Perepichka, D. Perepichka, H. Meng, F. Wudl, *Adv. Mater.* **2005**, *17*, 2281.
- [10] L. B. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, J. R. Reynolds, *Adv. Mater.* **2000**, *12*, 481.
- [11] C. J. Brabec, N. S. Sariciftci, J. C. Hummelen, *Adv. Funct. Mater.* **2001**, *11*, 15.
- [12] D. T. McQuade, A. E. Pullen, T. M. Swager, *Chem. Rev.* **2000**, *100*, 2537.
- [13] J. L. Reddinger, J. R. Reynolds, *Chem. Mater.* **1998**, *10*, 3.

- [14] J. L. Reddinger, J. R. Reynolds, *Macromolecules* **1997**, *30*, 673.
- [15] J. Roncali, *J. Mater. Chem.* **1999**, *9*, 1875.
- [16] E. Smela, *Adv. Mater.* **2003**, *15*, 481.
- [17] J.-M. Pernaut, J. R. Reynolds, *J. Phys. Chem. B* **2000**, *104*, 4080.
- [18] T.-A. Chen, R. D. Rieke, *J. Am. Chem. Soc.* **1992**, *114*, 10 087.
- [19] R. D. McCullough, R. D. Lowe, *J. Chem. Soc., Chem. Commun.* **1992**, 70.
- [20] R. D. McCullough, R. D. Lowe, M. Jayaraman, D. L. Anderson, *J. Org. Chem.* **1993**, *58*, 904.
- [21] R. D. McCullough, S. Tristram-Nagle, S. P. Williams, R. D. Lowe, M. Jayaraman, *J. Am. Chem. Soc.* **1993**, *115*, 4910.
- [22] R. S. Loewe, S. M. Khersonsky, R. D. McCullough, *Adv. Mater.* **1999**, *11*, 250.
- [23] R. S. Loewe, P. C. Ewbank, J. S. Liu, L. Zhai, R. D. McCullough, *Macromolecules* **2001**, *34*, 4324.
- [24] Note that any abbreviation in this document beginning with the letter "P" refers to the polymeric form of the molecule. For example, "PEDOT" is the abbreviated form of "poly(EDOT)".
- [25] G. Heywang, F. Jonas, *Adv. Mater.* **1992**, *4*, 116.
- [26] A. Kumar, D. M. Welsh, M. C. Morvant, F. Piroux, K. A. Abboud, J. R. Reynolds, *Chem. Mater.* **1998**, *10*, 896.
- [27] K. Doblhofer, K. Rajeshwar, in *Handbook of Conducting Polymers*, 2nd ed. (Eds: T. A. Skotheim, R. L. Elsenbaumer, J. R. Reynolds), Marcel Dekker, New York **1998**, p. 531.
- [28] J. H. Kaufman, N. Colaneri, J. C. Scott, G. B. Street, *Phys. Rev. Lett.* **1984**, *53*, 1005.
- [29] G. Leising, S. Tasch, W. Graupner, in *Handbook of Conducting Polymers*, 2nd ed. (Eds: T. A. Skotheim, R. L. Elsenbaumer, J. R. Reynolds), Marcel Dekker, New York **1998**, p. 847.
- [30] M. Pomerantz, in *Handbook of Conducting Polymers*, 2nd ed. (Eds: T. A. Skotheim, R. L. Elsenbaumer, J. R. Reynolds), Marcel Dekker, New York **1998**, p. 277.
- [31] Note that concepts of "low," "mid," and "high" are relative, but low bandgap is roughly defined as <2.0 eV, high bandgap as >3.0 eV, low oxidation potential as <0.5 V versus SCE, and high oxidation potential as >0.5 V versus SCE.
- [32] A. Merz, R. Schwarz, R. Schropp, *Adv. Mater.* **1992**, *4*, 409.
- [33] A. Merz, R. Schropp, E. Dotterl, *Synthesis* **1995**, 795.
- [34] K. Zong, J. R. Reynolds, *J. Org. Chem.* **2001**, *66*, 6873.
- [35] C. L. Gaupp, K. Zong, P. Schottland, B. C. Thompson, C. A. Thomas, J. R. Reynolds, *Macromolecules* **2000**, *33*, 1132.
- [36] C. A. Thomas, K. Zong, P. Schottland, J. R. Reynolds, *Adv. Mater.* **2000**, *12*, 222.
- [37] P. Schottland, K. Zong, C. L. Gaupp, B. C. Thompson, C. A. Thomas, I. Giurgiu, R. Hickman, K. A. Abboud, J. R. Reynolds, *Macromolecules* **2000**, *33*, 7051.
- [38] E. W. Fager, *J. Am. Chem. Soc.* **1945**, *67*, 2217.
- [39] K. Zong, L. B. Groenendaal, J. R. Reynolds, unpublished.
- [40] T. Murashima, Y. Uchihara, N. Wakamori, H. Uno, T. Ogawa, N. Ono, *Tetrahedron Lett.* **1996**, *37*, 3133.
- [41] A. Merz, T. Meyer, *Synthesis* **1999**, 94.
- [42] I. T. Kim, J. Y. Lee, S. W. Lee, *Chem. Lett.* **2004**, *33*, 46.
- [43] A. Merz, S. Graf, *J. Electroanal. Chem.* **1996**, *412*, 11.
- [44] G. Soenmez, I. Schwendeman, P. Schottland, K. Zong, J. R. Reynolds, *Macromolecules* **2003**, *36*, 639.
- [45] F. Larmat, J. R. Reynolds, B. A. Reinhardt, L. L. Brott, S. I. Clarson, *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 3627.
- [46] C. A. Thomas, K. Zong, K. A. Abboud, P. J. Steel, J. R. Reynolds, *J. Am. Chem. Soc.* **2004**, *126*, 16 440.
- [47] T. Murashima, K. Hirai, Y. Une, Y. Uchihara, H. Uno, N. Ono, *Tetrahedron Lett.* **1998**, *39*, 5397.
- [48] B. C. Thompson, P. Schottland, K. Zong, J. R. Reynolds, *Chem. Mater.* **2000**, *12*, 1563.
- [49] I. Schwendeman, R. Hickman, G. Soenmez, P. Schottland, K. Zong, D. M. Welsh, J. R. Reynolds, *Chem. Mater.* **2002**, *14*, 3118.
- [50] G. Zotti, S. Zecchin, G. Schiavon, L. Groenendaal, *Chem. Mater.* **2000**, *12*, 2996.
- [51] J. R. Reynolds, K. Zong, I. Schwendeman, G. Sonmez, P. Schottland, A. A. Argun, P.-H. Aubert, *US Patent 6 791 738*, **2004**.
- [52] H. Yamamoto, M. Oshima, M. Koga, *JP Patent 2002-134363*, **2002**.
- [53] D. J. Savage, B. A. Schell, B. K. Brady, *US Patent 5 665 498*, **1997**.
- [54] C. Bohn, S. Sadki, A. B. Brennan, J. R. Reynolds, *J. Electrochem. Soc.* **2002**, *149*, E281.
- [55] B. Vercelli, S. Zecchin, N. Comisso, G. Zotti, A. Berlin, E. Dalcanale, L. B. Groenendaal, *Chem. Mater.* **2002**, *14*, 4768.