be derived from the experimental data by applying a kinetic model developed earlier.[4,63] The transfer coefficient α for MV^{2+} reduction is much larger for particles prepared from $TiCl_4$ than those obtained from the hydrolysis of titanium isopropoxide, indicating participation of surface states (OH groups) in the electron-transfer event. (2) Drastic pH effects on the rate of MV^{2+} reduction by conduction-band electrons observed earlier[3] are confirmed for other acceptors and arise from the cathodic shift of the Fermi level of the particles with increasing pH. (3) A particularly favorable configuration for rapid electron transfer is achieved with acceptors which through suitable functionalities adhere to the semiconductor surface. Thus in the case of the amphiphilic viologen $C_{14}MV^{2+}$ the conduction-band process occurs on a subnanosecond time scale at high pH. Preirradiated samples give rise to hydrated electron generation via photoionization of $C_{14}MV^{+}$. (4) Simultaneous two-electron transfer from the conduction band of colloidal TiO_2 to cofacial dimeric viologen has been unambiguously demonstrated. By contrast, $Rh(bpy)_3^{3+}$, a potential two-electron acceptor, undergoes monoelectronic reduction by e^-_{CB}. These results should be of importance for the application of ultrafine semiconductor particles in artificial photosynthesis.

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Registry No. TiO_2, 13463-67-7; $TiCl_4$, 7550-45-0; MV^{2+}, 4685-14-7; $C_{14}MV^{2+}$, 79039-57-9; DV^{4+}, 87174-68-3; $Rh(bpy)_3^{3+}$, 47780-17-6.

Chain-Length Dependence of Electronic and Electrochemical Properties of Conjugated Systems: Polyacetylene, Polyphenylene, Polythiophene, and Polypyrrole

J. L. Brédas,[⊥,†] R. Silbey,*[†] D. S. Boudreaux,[‡] and R. R. Chance*[‡]

Contribution from the Department of Chemistry and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and Corporate Research Center, Allied Corporation, Morristown, New Jersey 07960.
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Abstract: The valence effective Hamiltonian (VEH) technique is used to compute ionization potentials, optical transition energies, and electron affinities of oligomers and polymers in four conjugated systems: polyacetylene, poly(*p*-phenylene), polythiophene, and polypyrrole. The theoretical results compare very favorably with experimental data on gas-phase ionization potentials, optical absorption, and electrochemical redox potentials. The latter case is especially important, and the calculated oxidation and reduction potentials are in remarkably good agreement with experiment. For polyacetylene the predicted oxidation potential is 0.4 V vs. SCE, and the predicted reduction potential is −1.1 V, both of which are in good agreement with experimentally observed oxidation and reduction onsets. In these systems, the electronic and electrochemical properties predicted by VEH theory for the oligomers extrapolate to those of the polymer with an inverse chain-length dependence.

Introduction

A number of organic polymers become electrically conducting on addition of electron donors or acceptors.[1-5] Thus far, the highest conductivities ($\sim$1000 Ω^{-1} cm^{-1}) have been obtained for acceptor doped poly(*p*-phenylene)[2] and acceptor doped polyacetylene.[3] Despite the enormous interest in these conducting polymer systems, many theoretical aspects of the problem remain poorly understood, especially the electronic properties of the "doped" (partially ionized) polymers. Progress is being made, however, in understanding the undoped polymer precursors. In a series of recent papers, we have demonstrated the utility of the valence effective Hamiltonian (VEH) method in understanding the ground-state properties of conjugated polymers, in particular, those which become highly conducting upon doping.[6-8] The VEH method employs atomic potentials derived from double-zeta (ζ) quality ab initio computations on small molecules[9] in calculations on large molecules. With this method, X-ray photoelectron spectra (X-ray PES), ionization potentials, and optical band gaps have been computed for polyacetylene, poly(*p*-phenylene), poly(*p*-phenylene sulfide), and poly(dibenzothiophene).[10] The theoretical X-ray PES spectra and ionization potentials are all in good agreement with experiment, as are the theoretical band gaps for the planar systems.[6-8,10]

A fundamental question in this area is the extent to which polymer properties can be predicted based on extrapolation from oligomer data.[11-13] This is fundamental, for example, in the

[⊥] Charge de Recherches du Fonds National Belge de la Recherche Scientifique (FNRS). Permanent address: Laboratoire de Chimie Theorique Appliquée, Facultes Universitaires de Namur, 5000 Namur, Belgium.
[†] Massachusetts Institute of Technology.
[‡] Allied Corp.

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understanding of the new optical transitions induced on doping polyacetylene. The currently favored explanation for these transitions suggests that they are due to the formation of solitons, e.g., kinks in the conjugated structure.[14] However, the extrapolation of the optical spectra of well-characterized radical anions of polyacetylene oligomers (shorter chain polyenes) explains in a rather straightforward manner the spectrum obtained for donor-doped polyacetylene.[13] This calls into question the uniqueness of the soliton explanation[14] and suggests an alternative based on a radical–anion (or polaron).[13]

In this paper we present VEH calculations on *oligomers* of polyacetylene (PA), poly(*p*-phenylene) (PPP), polythiophene (PTP), and polypyrrole (PPY) and compare them with VEH polymer calculations. For PTP and PPY, considerable uncertainty exists regarding the geometry of the polymers, particularly with regard to carbon–carbon bonds between monomer units. For this reason we have employed a semiempirical quantum mechanical technique designed for geometry prediction, MNDO (modified neglect of differential overlap).[15] The MNDO predicted geometry is used as input to the VEH program. Our calculations concentrate on optical "band gaps" and ionization potentials and are compared to optical and electrochemical data. The prediction of *electrochemical oxidation* and *reduction potentials* is of special interest considering recent activity in the application of conjugated polymers in rechargeable batteries.[16,17]

Theoretical and Computational Technique

The VEH method allows the calculation of ab initio Hartree–Fock quality one-electron energy levels from a set of parameterized one-electron atomic potentials.[9,18-20] No information pertaining to the excited states is included in the atomic potentials used to parameterize the VEH method. As a result, little weight should in principle be given to the energies of the unoccupied levels. However, for the planar systems considered previously, surprisingly good agreement is obtained between experimentally measured optical transition energies and the calculated LUMO–HOMO difference. This is surprising for two reasons: (1) as pointed out above, no excited states are included in the VEH parameterization; and (2) the band gaps for these molecules are determined in part by correlation effects[21] which are absent at the Hartree–Fock level of calculation used to parameterize VEH. Thus, the theoretical basis for obtaining optical transitions in the VEH model is weak, and there are undoubtedly other theoretical procedures which have a sounder basis—especially semiempirical procedures such as CNDO which are parameterized to reproduce optical transition energies.[12] Nevertheless, we have found that the VEH model performs quite adequately in calculating the lowest energy optical transitions, and we shall exploit this unexplained, but useful agreement with experiment to obtain trends in the band gaps and electron affinities of these molecules as a function of number of monomer units.

It is important to emphasize that the VDH technique is completely theoretical. No experimental information has been used to derive the VEH atomic potentials. Nevertheless, the technique gives ab initio double-ζ quality results with negligible computer time, since only one-electron integrals need to be evaluated and SCF iterative cycles are completely avoided. The VEH atomic potentials have not been parameterized for geometry optimization purposes and should be used with geometric parameters close to equilibrium. For systems whose geometries are experimentally unknown (as is the case of the majority of the large oligomers and polymers studied in this paper), we have used other techniques to obtain reasonable input geometries. Since ab initio techniques, even with small basis sets, rapidly become too expensive when large compounds are considered, we have chosen to optimize the geometries of all the studied oligomers and polymers with the MNDO (modified neglect of differential overlap) semiempirical procedure.[15] This method has been thoroughly tested on organic compounds containing carbon, hydrogen, nitrogen, oxygen, and sulfur and reproduces the experimental geometries fairly well.[22] We find that the VEH results are qualitatively unaffected by small differences in input geometries. This is illustrated for polypyrrole in Table I where we present the VEH ionization potentials and band gaps for four different geometries: the MNDO optimized geometry, the STO-3G optimized geometry,[23] and the experimental geometry of pyrrole[24] with inter-ring bond lengths of 1.45 and 1.49 Å. The ionization potential values fall between 5.68 and 5.98 eV and band gaps between 3.0 and 4.0 eV.

Table I. Evaluation of the VEH Ionization Potential (IP) and Band Gap (E_g) for Polypyrrole with Various Choices for the Geometry: MNDO Optimized Geometry (This Work), STO-3G Optimized Geometry,[23] and Experimental Ring Geometry (for Pyrrole Monomer)[24] with Inter-ring Bond Lengths of 1.45 and 1.49 Å

geometry	MNDO	STO-3G	experiment (monomer)	
$R_{C\text{-}N}$ (Å)	1.399	1.385	1.38	1.38
$R_{C=C}$ (Å)	1.410	1.363	1.37	1.37
$R_{C\text{-}C}$ (Å)	1.426	1.420	1.43	1.43
C-N-C (deg)	110.8	109.2	109.0	109.0
C-C-N (deg)	106.5	107.4	108.0	108.0
$R_{\text{inter-ring}}$ (Å)	1.453	1.474	1.45	1.49
	VEH Results			
IP (eV)	5.68	5.96	5.82	5.98
E_g (eV)	3.0	3.9	3.6	4.0

Results and Discussion

Our results are summarized in Table II. Included in the table are MNDO and VEH computed ionization potentials (IP), VEH computed and experimental band gaps (E_g), and experimental gas-phase ionization potentials when available. (For convenience we use the term "band gap" even when referring to the oligomers.) We have shown previously that the IP values for the polymers calculated from VEH theory are in good agreement with experiment[7,10] after including a solid-state polarization correction of $\sim$1.9 eV. From Table II the IP values for oligomers are also seen to be in reasonable agreement with gas-phase values, with VEH results being somewhat better than MNDO. For the polymer, VEH and MNDO IP values are significantly different. We think the VEH values are better, based on earlier comparisons with experiment and the fact that the VEH technique takes into account more properly the long-range interactions necessary in understanding the electronic structure of large bandwidth polymers.[9] All experimental data in Table II, including those for the polymers, are taken from optical absorption peaks; thus the E_g value for PA is given as 1.8 eV rather than the onset value (1.4 eV) which is usually quoted for E_g. No MNDO band gaps are given, since it is well known that they are much too large.

In Figure 1, we have plotted the experimental[26] and theoretical data for the band gap of the polyenes vs. reciprocal chain length

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Table II. Gas-Phase Ionization Potentials (IP) and Band Gaps (E_g)[a]

system	chain length	MNDO[b] IP	VEH IP	VEH E_g	experiment[c] IP (ref)	experiment[c] E_g (ref)
polyacetylene, PA	1	10.18	10.16	7.85	10.51 (25)	
	2	9.14	8.78	5.29	9.06 (25)	5.7 (26)
	3	8.64	8.12	4.09		4.6 (26)
	4	8.37	7.75	3.42		4.1 (26)
	6	8.09	7.35	2.70		3.4 (26)
	10	7.89	7.03	2.11		2.8 (26)
	∞	7.58	6.67	1.45		1.8 (14)
poly(*p*-phenylene), PPP	1	9.39	9.30	6.69	9.24 (27)	5.90 (11)
	2	8.70	8.34	4.88	8.32 (27)	4.92 (11)
	3	8.43	7.97	4.18	8.20 (27)	4.43 (11)
	∞	8.00	7.45	3.23		3.6 (2)
polythiophene, PT	1	9.51	9.29	5.51	8.95 (25)	5.37 (11)
	2	8.74	8.14	3.65		4.12 (11)
	3	8.46	7.71	2.93		3.52 (11)
	∞	7.92	7.01	1.71		
polypyrrole, PPY	1	8.57	8.13	7.01	8.23 (28)	5.96 (11)
	2	7.86	6.89	5.24	8.23 (28)	4.35 (11)
	3	7.59	6.43	4.35		3.59 (11)
	∞	7.10	5.68	2.99		3.0 (1)

[a] All energies are given in eV. [b] MNDO values for the polymers are extrapolated from oligomer data assuming a linear variation with reciprocal chain length. [c] Experimental IP values are taken from the first ionization peak observed in a gas-phase photoemission experiment; E_g values are taken from absorption peaks in solution spectra. Gas-phase E_g values for polyenes are about 0.2 eV higher in energy than those from solution experiments; the gas-phase value for ethylene ($n = 1$) is 7.65 eV.[26]

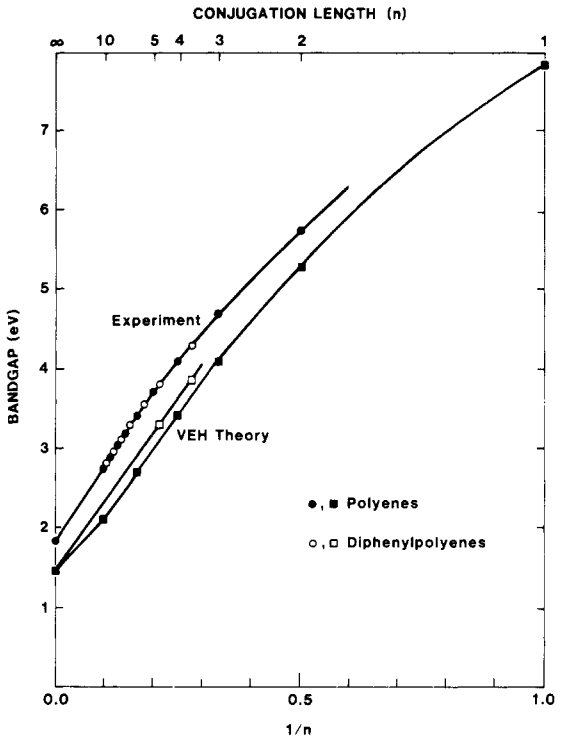

Figure 1. Band gap for polyenes,[26] $H(C{=}C)_nH$ and diphenylpolyenes (DPP),[29,30] $C_6H_5(HC{=}CH)_xC_6H_5$, plotted against reciprocal conjugation length. The highest band gap DPP result is for $x = 1$ (stilbene); the lowest DPP result is for $x = 7$. For DPP, n is the effective conjugation length computed as $x + 2.7$. All experimental data refer to absorption peaks in nonpolar organic solvents.

(n^{-1}), which is expected to give a linear relationship for large n. Also included in Figure 1 are data for the diphenylpolyenes (DPP) $C_6H_5(HC{=}CH)_xC_6H_5$.[29,30] These molecules are more stable than H-terminated polyenes, $H(HC{=}CH)_nH$; thus there are more experimental studies of DPP molecules.[29-31] When considering DPP as a model for the polyacetylene system, the effect of the phenyl end groups on the electronic properties must be considered. To do this we define an effective conjugation length, $n_{eff} = x + A$, so that A describes the extension of the conjugation length by the phenyl rings beyond the x-unit polyene sequence. The value of A is established by adjustment until the experimental band gap of a DPP with x double bonds is equal to that of a polyene with $x + A$ double bonds.[13] The results shown in Figure 1 use $A = 2.7$ and provide an excellent correspondence between the polyene and DPP experimental data.[32] This approach has been used previously[13] to show that the three optical transition energies characteristic of radical anions in DPP extrapolate to yield a good description of the near-infrared ("midgap") absorption[14] found on donor doping of polyacetylene, thus illustrating the nonuniqueness of the soliton description of the doped-PA data and suggesting a radical–ion (or polaron) explanation.[13]

We have carried out VEH calculations on two DPP molecules ($x = 1, 2$). The computed band gaps for these two molecules are plotted in Figure 1 with the same value of A used to define the effective conjugation lengths; the agreement with the calculations on polyenes is good. The VEH calculated ionization potentials for these DPP molecules are given Table III; these agree nearly perfectly with the VEH calculations on polyenes if the effective

Table III. Gas-Phase Ionization Potentials (eV) for Diphenylpolyenes, $C_6H_5(HC{=}CH)_xC_6H_5$

chain length(x)	VEH theory[a]	expt[b]
1	7.86 (7.84)	7.94
2	7.56 (7.57)	7.56
3	(7.39)	7.33
4	(7.27)	7.19
5	(7.17)	7.05
6	(7.10)	7.07
8	(7.00)	7.2 ± 0.2
∞	6.67 (6.67)	

[a] Values in parentheses are interpolated from polyene results in Table II. We use a linear $1/n_{eff}$ relationship and take $n_{eff} = x + 2.7$, consistent with experimental results in Figure 1. [b] Reference 34; IP values are taken from the first ionization peak observed in a gas-phase photoemission experiment.

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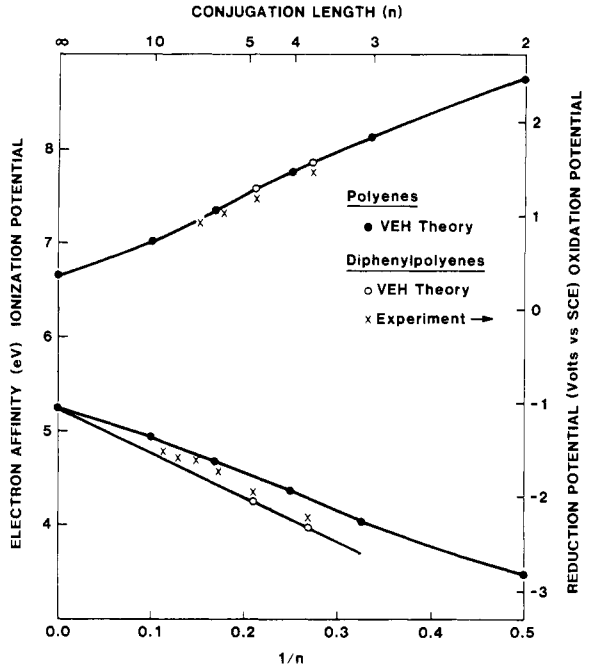

Figure 2. Electron affinity (lower curve) and ionization potential (upper curve) from VEH theory vs. $1/n$ for polyacetylene system; experimental reduction potentials[31] (lower ×'s) and oxidation potentials[36] (upper ×'s) vs. $1/n$. The experimental values are for diphenylpolyenes and are plotted vs. $1/n$ with n defined as in Figure 1.

conjugation lengths are again defined in the same way. In addition, the theoretical values of IP for these DPP molecules (as well as those inferred from the VEH calculations on polyenes again, with $A = 2.7$) are in excellent agreement with the experimental gas-phase IP data of Hudson et al.[34] This agreement is as good as that obtained by the CNDO/S2 semiempirical procedure,[35] but without the constant energy correction required for the CNDO/S2 calculated values, and, more significantly, without any input of experimental information other than molecular geometries. In fact, the excellent agreement between theory and experiment shown in Figure 1 and Tables II and III is obtained solely from atom connectivity and MNDO-determined geometries.

Another reason for considering the DPP molecules in such detail is that a fairly complete set of experimental oxidation[36] and reduction potentials[31] is available. Our interest in these theoretical predictions and their implications, particularly regarding the electrochemical properties of polyacetylene, is fueled by the current work on battery applications of polyacetylene[16] and other conjugated polymers.[17]

In Figure 2, we have plotted the theoretical values of the ionization potentials for the polyenes and DPP vs. n^{-1}; on the same plot are experimental oxidation potentials, E_{ox}, for DPP (i.e., for DPP $\rightleftarrows$ DPP$^{+\cdot}$ + e$^-$). An approximately linear correlation between IP and E_{ox} is expected[37-39] and found. Furthermore, we have plotted the theoretical values of the electron affinity (χ, where $\chi \equiv$ IP $- E_g$) vs. n^{-1} for these compounds and compared these to their reduction potentials, E_{red} (DPP + e$^-$ $\rightleftarrows$ DPP$^{-\cdot}$). E_{ox} and E_{red} values are given with respect to the saturated calomel electrode (SCE). In order to make quantitative comparisons to gas-phase IP and χ values, we have taken the zero of the SCE scale to be 6.3 V with respect to zero on the gas-phase scale. This same scale

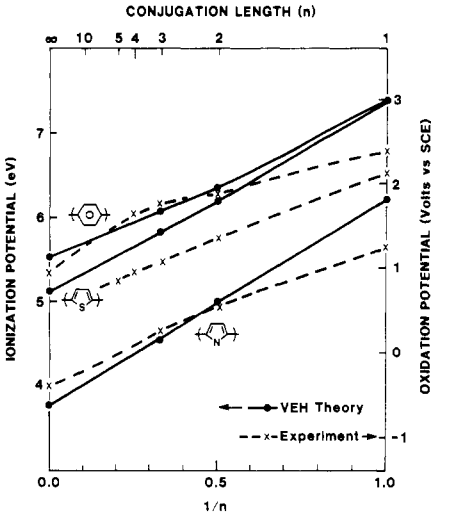

Figure 3. Ionization potential from VEH theory (solid lines) and experimental oxidation potentials[11,42,43,47] (dashed lines) vs. $1/n$ for poly(*p*-phenylene), polythiophene, and polypyrrole systems.

factor has been found previously[37-39] and also gives the best agreement between theory and experiment in our case. For reference to the solid state, this 6.3-eV scale factor can be viewed as being composed of two components: a polarization energy correction to adjust gas-phase IP values to solid-state values (typically 1.5–2.0 eV[6-8,40]) and a scale factor relating SCE to vacuum (typically 4.7 eV[41]).

The agreement between experiment and theory shown in Figure 2 is remarkably good, especially since our use of a constant 6.3-eV scale factor inherently involves an assumption of a chain-length-independent polarization energy correction to the theoretical values of IP. Other work showing a nearly linear relation between IP and E_{ox} also suggests a relatively constant polarization energy for a wide a variety of organic molecules.[37-39] The extrapolation in going from polyenes to polymer gives an oxidation potential of 0.4 V vs. SCE and a reduction potential of −1.1 V vs. SCE for PA. (The difference is precisely the theoretical E_g by construction.) Note that these values are for the polymer and correspond to the *first* oxidation or reduction potential of the polymer (removal or addition of one electron). Therefore, the E_{ox} and E_{red} values would correspond to *onset* values in terms of the observed oxidation or reduction of polyacetylene. Careful measurements by Shacklette[42] in a battery cell configuration (lightly doped PA vs. lithium) yield onset values of $E_{ox} = 0.2$ V and $E_{red} = -1.3$ V vs. SCE with uncertainties of about ±0.2 V. Rough estimates of the onset values from cyclic voltammetry[43] are consistent with these values.

We believe the agreement between theory and experiment for the redox properties of polyacetylene is quite satisfactory, since we have not explictly considered effects such as chemical and structural disorder,[12] dopant (counterion) intercalation, and dopant diffusion,[42] all of which can be of more importance in the energetics of polymer ionization than for the electrochemistry of oligomers in solution. It is also possible that a solvent shift would provide a differential between actual and oligomer extrapolated redox energies, though none is indicated in the comparison to experiment. The role of disorder is especially important for polyacetylene and is quite apparent in the optical absorption spectrum,[14] in Raman experiments,[33] and in ultraviolet photoemission spectra(UPS).[12] All of these experiments are sensitive to the quality of the trans

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Table IV. Oxidation and Reduction Potentials (Volts vs. SCE) of Conjugated Polymers

	oxidation potential		reduction potential	
polymer	VEH theory	expt (ref)	VEH theory	expt (ref)
polyacetylene, PA	0.4	0.2 (42, 43)	−1.1	−1.3 (42, 43)
poly(*p*-phenylene), PPP	1.2	0.9 (42)	−2.1	−2.1 (42)
polythiophene, PTP	0.7	0.6[a]	−1.0	
polypyrrole, PPY	−0.6	−0.4 (47)	−3.6	*b*

[a] Extrapolated from oligomer data in ref 11. [b] The reduction potential is more negative than −2.9 V since sodium naphthalide solution fails to dope polypyrrole.[48]

polyacetylene samples, and particularly to the cis to trans isomerization conditions employed. The same is true of the electrochemical experiments. In the reported UPS spectra, the π-electron contribution is seen only as a low energy tail in the spectra due to disorder.[12] (X-ray photoemission spectra, XPS, are somewhat better resolved and in fairly good agreement with VEH theory.[6]) Substantial improvements have now been made in the quality of trans polyacetylene films by careful control of isomerization conditions. This has resulted in dramatically better resolved optical absorption spectra,[44] with well-defined vibrational structure compared with the broad structureless spectra obtained in previous work.[14] This improvement is reflected in the electrochemical data reported here[42] and also in Raman experiments which show[45] less conjugation length dispersion than was evident in previous work.[33] We can anticipate that UPS and XPS spectra on better quality polyacetylene will show a more highly resolved π-electron contribution.

Figure 3 shows experimental[11] and theoretical values for the polyphenylene, polythiophene, and polypyrrole systems. Only oxidation potentials and IP values are considered, since sufficient E_{red} values for a meaningful comparison are not available. Generally, the agreement between theory and experiment is not as good as for polyacetylene. In particular, agreement for the monomers is poor, though experimental *gas-phase* IP values agree well with theory, as we noted previously in reference to Table II. We attribute this poor agreement to the nonreversibility of the oxidation of these monomers which leads to an underestimation of E_{ox}.[46] The E_{ox} value for poly(*p*-phenylene) is taken from Shacklette;[42] that of polypyrrole[47] is derived from the oxidation onsets in a cyclic voltammetry experiment.[47] Fairly good agreement between theory and experiment is found for these polymers. No electrochemical data are available for polythiophene. It should be pointed out that the bonding patterns in polypyrrole and polythiophene mimic that in cis polyacetylene. In fact, the highest valence band of PPY (or PTP) contains no contribution from the nitrogen (or sulfur) atoms. Although it is surprising that the IP value for PPY is so low (0.9 V lower than that of cis PA), this result is supported by available experimental data. The successful prediction of E_{ox} for PPY is an important demonstration of the predictive capabilities of the VEH technique. In fact, the agreement is even better if we use the IP values in Table I from alternate estimates for the PPY geometry: E_{ox} = 0.3 V for STO-3G geometry and 0.3–0.4 V for the "experimental" geometry. Note that the theoretical results for the monomers are a good indication of the limiting values for the polymers.

Table IV provides a summary of electrochemical data, both experimental and theoretical, for the four polymers considered here. Agreement with theory is quite good wherever experimental data are available. We also give predicted E_{red} values for all four polymers. Experimental data are available only for PPP and PA; agreement is good in both cases. E_{red} of PTP should be easily measurable since the predicted value is comparable to that of polyacetylene. For PPY, E_{red} is predicted to be −3.6 V (0.3 V more negative than lithium); such a negative potential would be difficult to observe because of electrolyte instability. No experimental observation of PPY reduction has been reported, even by alkali metal donors.[48]

Conclusions

The results of our calculations demonstrate that we may now predict with confidence the onset redox potentials of for conjugated polymers. This capability is particularly important given the current interest in polymer batteries; however, more needs to be done. For example, the open circuit voltage of acceptor-doped polyacetylene–lithium battery cell varies from 3.3 V at low charge (<1% doping) to about 3.8 V at high charge (~6% doping).[42] The present theory predicts the voltage at low doping levels extremely well. In order to predict the variation in voltage with charge, theory must include multiple ionization steps, i.e., knowledge of the complete band structure including all relaxation effects. Though such a theory is currently unavailable, we believe that the results of the present theory and some knowledge of the π-electron bandwidth will provide the first important steps toward understanding the electrochemical properties of these polymeric systems.

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