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Use of the Pariser–Parr–Pople Approximation To Obtain Practically Useful Predictions for Electronic Spectral Properties of Conducting Polymers

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ABSTRACT: Use of a Pariser–Parr–Pople model for estimating band gaps (E_g) for several potentially conducting conjugated polymers of recent interest gives good correlation with experimental values by extrapolation of computed E_g values as a function of reciprocal chain length of model oligomers. Hydrocarbon polymers of 1,3-phenylene, 1,4-phenylene, 1,4-phenylenevinylene, perinaphthalene, and related monomers seem well modeled by this method, as well as polymers of heterosubstituted conjugated monomers such as 2,5-pyrrole, 2,5-thiophene, 2,5-thiophendiylvinylene, and related species. The method should be useful as an inexpensive best first approximation to the band gaps of putative conjugated polymers and hence of interest to synthetic polymer chemists interested in such molecules.

Predictive computational chemistry can play an important role in the rapidly growing field of conducting doped polymers,[1-7] if it can help systematically to identify polymers that are most likely to have desirable electronic properties. We find that use of a variation of the well-known Pariser–Parr–Pople (PPP) semiempirical model for predicting electronic excited-state transition energies leads to predictions for long-wavelength excitation energies—i.e., band gaps, E_g—that are generally in good agreement with experimental results to date. Since the PPP method is highly approximate, it cannot hope to substitute for the hypothetical rigor of higher level, more expensive computational prediction, but we feel that the results obtained at negligible expense show the usefulness of the model as a practical method for finding electronic transition energies for conjugated molecules, where more precise methods are unavailable or economically impractical.

Various methods have been used to study the electronic nature of conducting polymers, ranging from Hückel-type models[8] to CNDO-S2[9] and MNDO[10-11] semiempirical methods. Use of ab initio methods in such cases is prohibitively expensive for any but the simplest model system. Recently, Brêdas[12-16] adapted the valence-effective Hamiltonian (VEH) method of Nicolas and Durand[17] for application to electronic properties of polymer and achieved a good practical degree of success in modeling polymer electronic properties, using geometries obtained by other methods. The VEH method was designed for prediction of valence band properties and has proved successful in this role. Although the theoretical basis for the success of the VEH model in application to optical spectroscopy is less clear,[12] VEH is one of the more successful—though not yet widely available—methods of obtaining useful predictive information concerning electronic properties of polymers.

The Pariser–Parr–Pople (PPP) model[19,20] is well adapted for obtaining π-symmetry electronic transitions for conjugated systems, and though it has a number of notable limitations[19-21] it has the advantages of wide availability, computational parasimony, and a good record of success in predicting π-type transition energies and intensities.[21-25] We used the Hinze–Beveridge PPP model with configuration interaction (PPP–CI) model to obtain spectral transition energies and intensities for oligomers of increasing chain length in a number of conjugated model systems and then applied the experimentally well-known[9,26-28] reciprocal rule for polymers, which states that many properties of homopolymers tend to vary linearly as functions of reciprocal chain length. For all computations, the parameters and algorithms are those given by the original workers[21] and will not be further described herein. Geometries for the oligomers used were obtained by extrapolation from known or similar cases or by comparison to monomer geometric parameters. In general, geometric changes of $\sim$0.04 Å in bond lengths or 5° in bond angles gave only small changes in the spectra predicted, as expected[14] for cases where small geometric changes do not actually change the basic repeat unit symmetry of the oligomer.

Table I shows PPP–CI long-wavelength transition energies and intensities for a variety of oligomeric species, with comparative experimental data. The agreement is good (as in PPP studies of other types of molecules[21-25]) considering that the PPP prediction corresponds to the energy of a putative gas phase 0–0 vertical transition without accounting for any macroscopic effects (e.g., solvent effects). Even in good solution phase studies, UV–vis bands tend to be broad and featureless, whereas polymer spectra must often be obtained on solid films or by reflectance, with attendant broadening and signal–noise problems. In most of the case studies, a long-wavelength transition with large oscillator strength (>0.7) was obtained, implying a strong transition. In a few cases a longer wavelength band of weak intensity was predicted, so the more intense transition was taken as representing the band gap, while the lower intensity band was taken as being part of the long-tailing absorption to low energy that is observed in many such cases. Table I thus enumerates the most intense long-wavelength bands (as well as predicted and experimental ionization potential data[29]) for various oligomeric species. Good agreement is found between predicted and observed E_g values for oligomeric conjugated species, thus encouraging extrapolation by the reciprocal

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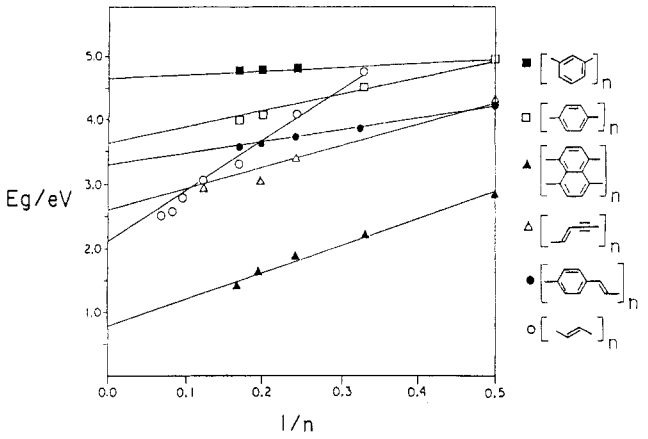


Figure 1. PPP–SCF–CI band gaps E_g as a function of reciprocal chain length n in oligomers of some conjugated hydrocarbons.

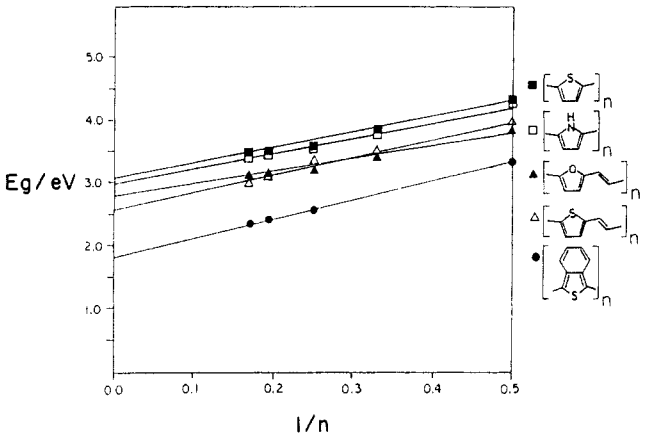


Figure 2. PPP–SCF–CI band gaps E_g as a function of reciprocal chain length n in oligomers of some conjugated heterocycles.

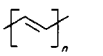
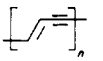
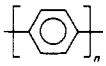
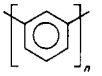
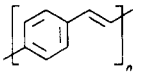
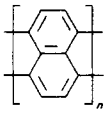
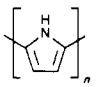
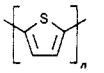
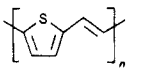
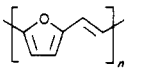
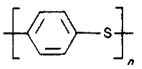
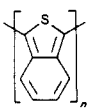
chain rule to find E_g for polymeric cases of hypothetical infinite chain length.

Figures 1 and 2 show plots of PPP–CI band gaps as functions of reciprocal chain length for the oligomer studies, with assumed linear extrapolation to infinite chain length. All plotted data show excellent linearity based upon reduced χ^2 analysis by unweighted least squares. Table II shows the correlation of extrapolated PPP–CI polymer band gaps with experimental or VEH data—the agreement of predicted and observed data confirms the efficacy of this model for reasonably good predictions of E_g. In general, the model tends to overestimate slightly E_g relative to the observed values. Important experimental trends are well reproduced. The predicted decrease in E_g on going from poly(2,5-thiophene) to poly(*iso*-thianaphthene) has been recently confirmed.[31] Also, poly(1,4-phenylene) and poly(1,4-phenylenevinylene) are found to have similar band gaps substantially smaller than that for poly(1,3-phenylene), implying that the former two are of a similar conducting nature, and more effective than the latter—this is as noted in higher levels of computation.[14]

Poly(perinaphthalene) is found to have an extremely small band gap, in accordance with VEH work and with experimental observation of good conductivity in the doped state.[32] Overall, the agreement between predicted and experimental trends is quite good, especially considering the modest investment in computational effort involved.

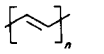
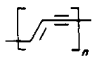
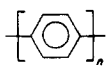
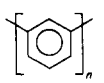
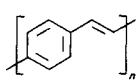
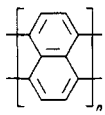
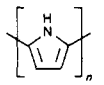
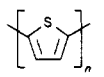
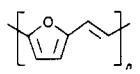
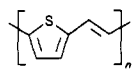
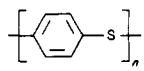
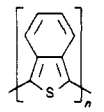
The recent work of Soos[33-36] has already demonstrated that detailed application of the PPP model to modeling the electronic properties of oligomer chains yields good agreement with the observed properties. Electronic transitions of finite polyenes and heteroatom-containing

Table I
PPP–SCF IP's and E_g's for Conjugated Planar Oligomers

monomer unit	no. units (n)	corr IP/eV[a]	E_g/eV[c]
	2[b]	8.84 (9.06)[d]	5.97 (5.7)[d]
	3	7.83	4.59 (4.3)[d]
	4	7.41	4.04 (4.1)[d]
	6	6.88	3.28 (3.4)[d]
	8	6.71	3.02
	10	6.57	2.79 (2.8)[d]
	12	6.39	2.52
	15	6.36	2.51
	1[b]	8.79	5.71
	2	7.72	4.29
	4	7.08	3.35
	5	6.95	2.94
	8	6.78	2.89
	2	8.29 (8.32)[d]	4.98 (4.92)[d]
	3	7.91 (8.20)[d]	4.52 (4.43)[d]
	5	7.56	4.05
	6	7.49	3.96
	2	8.27 (8.32)[d]	4.93 (4.92)[d]
	4	8.07	4.82
	5	8.04	4.79
	6	8.02	4.75
	1[b]	8.52 (8.46)[e]	5.23
	2	7.79	4.20
	3	7.46	3.89
	4	7.34	3.75
	5	7.28	3.68
	6	7.25	3.62
	1[b]	7.70	
	2	6.58	2.84
	3	6.04	2.23
	4	5.72	1.85
	5	5.52	1.61
	6	5.35	1.41
	1[b]	8.31 (8.23)[d]	5.04 (5.96)[d]
	2	7.66	4.25 (4.34)[d]
	3	7.29	3.77 (3.59)[d]
	4	7.10	3.53
	5	6.99	3.39
	6	6.92	3.29
	1[b]	8.72 (8.95)[d]	5.41 (5.37)[d]
	2	7.73	4.31 (4.12)[d]
	3	7.34	3.83 (3.52)[d]
	4	7.14	3.58
	5	7.10	3.50
	6	7.01	3.40
	1[b]	8.12	4.70
	2	7.38	3.80
	3	7.12	3.46
	4	6.94	3.30
	5	6.71	3.07
	6	6.43	2.88
	1[b]	8.14	4.48
	2	7.41	3.64
	3	7.16	3.32
	4	7.04	3.16
	5	6.98	3.08
	6	6.97	3.04
	3	7.92	5.88
	4	7.79	5.79
	6	7.72	5.74
	2	6.83	3.16
	4	6.33	2.51
	5	6.22	2.37
	6	6.15	2.29

[a] PPP–SCF energy of highest doubly occupied MO in eV minus 1.6 eV empirical correction. [b] This compound not used in plots of electronic properties vs. reciprocal chain length. [c] All computations were carried out at geometries simulated as closely as possible from data on monomers or similar species. Experimental values of IP and E_g are in parentheses. [d] Reference 38. [e] Reference 39.

Table II
PPP-SCF-CI and Experimental E_g's for Conducting Polymers[a]

polymer	PPP-SCF E_g/eV	VEH[a] E_g/eV	exptl EG/eV
	2.15	1.4	1.8[a]
	2.58	2.1	2.1[a]
	3.61	3.5	3.4[a]
	4.61	4.5	4.9[a]
	3.33	2.5	3.0[a]
	0.73	0.44[b]	
	2.99	2.99	3.0[a]
	3.08	1.6	2.7[a]
	2.79		2.4[c]
	2.53	1.6	2.2[c]
	5.63	3.5[d]	3.4[d]
	1.85	0.5[e]	~1.5[f]

[a] PPP-SCF E_g's are obtained by extrapolating data in Table I to $1/n = 0.00$, where E_g is most intense low-energy transition. References 12, 15, 16, and 18. [b] Reference 32. [c] Reference 39. [d] Reference 40. [e] Reference 41. [f] Reference 31.

cyanine dyes are well modeled by extrapolation of PPP predictions vs. inverse chain length, as in our results. Soos' computations also slightly overestimate the absorption peaks in polyacetylene, in a fasion analogous to our typical results. Overall, Soos' work effectively shows the ability to analyze polymer electronic properties such as band gap by using the approximate PPP model. Our results show that the use of PPP–CI electronic properties are similarly effective in modeling the experimentally observed properties of more complex oligomers and polymers.

Although the PPP–CI method has limitations, it is readily available[37] and reproduces experimental conjugated molecule electronic spectra well. This work shows the applicability of the PPP method to obtain good estimates of polymer band gaps quickly and easily. Thus, the PPP method should prove useful for quick predictions by the experimental chemist who is not a theoretician to decide which conjugated polymers are not worth concentrating effort upon and which are worth more concentrated effort based upon prediction of favorable band gaps.

Acknowledgment. We acknowledge the support of a University of Massachusetts Joseph P. Healey Endowment Grant and Air Force Grant AFOSR 86-0100 in this research.

Registry No. (Ethene)$_2$, 106-99-0; (ethene)$_3$, 2235-12-3; (ethene)$_4$, 1482-91-3; (ethene)$_6$, 2423-92-9; (ethene)$_8$, 2588-89-8; (ethene)$_{10}$, 2423-94-1; polyethylene, 9002-88-4; 1-buten-3-yne, 689-97-4; (1-buten-3-yne)$_2$, 108663-96-3; (1-buten-3-yne)$_4$, 108663-97-4; (1-buten-3-yne)$_5$, 108663-98-5; (1-buten-3-yne)$_8$, 108663-99-6; (1,4-phenylene)$_2$, 92-52-4; (1,4-phenylene)$_3$, 92-94-4; (1,4-phenylene)$_5$, 3073-05-0; (1,4-phenylene)$_6$, 4499-83-6; (1,3-phenylene)$_4$, 92-06-8; (1,3-phenylene)$_5$, 16716-13-5; (1,3-phenylene)$_6$, 4740-51-6; 1,4-phenylenevinylene, 100-42-5; (1,4-phenylenevinylene)$_2$, 6928-98-9; (1,4-phenylenevinylene)$_3$, 108664-00-2; (1,4-phenylenevinylene)$_4$, 108664-01-3; (1,4-phenylenevinylene)$_5$, 108664-02-4; (1,4-phenylenevinylene)$_6$, 108664-03-5; 1,4,5,8-naphthalene, 91-20-3; (1,4,5,8-naphthalene)$_2$, 198-55-0; (1,4,5,8-naphthalene)$_3$, 188-72-7; (1,4,5,8-naphthalene)$_4$, 188-73-8; (1,4,5,8-naphthalene)$_5$, 85600-63-1; (1,4,5,8-naphthalene)$_6$, 108772-56-1; 2,5-pyrrole, 109-97-7; (2,5-pyrrole)$_2$, 10087-64-6; (2,5-pyrrole)$_3$, 3260-45-5; (2,5-pyrrole)$_4$, 86450-98-8; (2,5-pyrrole)$_5$, 108664-04-6; (2,5-pyrrole)$_6$, 108664-05-7; 2,5-thiophene, 110-02-1; (2,5-thiophene)$_2$, 492-97-7; (2,5-thiophene)$_3$, 1081-34-1; (2,5-thiophene)$_4$, 5632-29-1; (2,5-thiophene)$_5$, 5660-45-7; (2,5-thiophene)$_6$, 88493-55-4; 2,5-thiophenevinylene, 1918-82-7; (2,5-thiophenevinylene)$_2$, 108664-06-8; (2,5-thiophenevinylene)$_3$, 108664-07-9; (2,5-thiophenevinylene)$_4$, 108664-08-0; (2,5-thiophenevinylene)$_5$, 108664-09-1; (2,5-thiophenevinylene)$_6$, 108664-10-4; 2,5-furanvinylene, 1487-18-9; (2,5-furanvinylene)$_2$, 108664-11-5; (2,5-furanvinylene)$_3$, 108664-12-6; (2,5-furanvinylene)$_4$, 108664-13-7; (2,5-furanvinylene)$_5$, 108664-14-8; (2,5-furanvinylene)$_6$, 108664-15-9; (1,4-phenylthio)$_3$, 108664-16-0; (1,4-phenylthio)$_4$, 108664-17-1; (1,4-phenylthio)$_6$, 108664-18-2; (2,5-thiophendiylvinylene)$_2$, 108664-19-3; (2,5-thiophendiylvinylene)$_4$, 108664-20-6; (2,5-thiophendiylvinylene)$_5$, 108664-21-7; (2,5-thiophendiylvinylene)$_6$, 108664-22-8.

References and Notes

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Notes

Preparation of Soluble Poly(carbonyldioxyglyceryl methacrylate)

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Polymers containing a high density of polar substituents are of interest for a number of applications. Fluorinated and cyano polymers[1] have been investigated as piezoelectric materials, while heavily oxygenated polymers[2] and polyions[3] have been considered as components of solid electrolyte solutions.

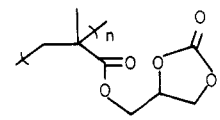
A third potential application of polar polymers is as hosts for dyes in nonlinear optical films.[4] The incorporation of strongly polar functionalities in the host media will likely increase the solubility of the dyes used as the nonlinear optically active components. Furthermore, when a suitable polymer–dye mixture is electric field poled, the dipoles in the polymers should align with the field resulting in an acentric environment in which the dye guests might tend to be nonrandomly oriented as well. A bulk noncentrosymmetric transition moment is a major requirement for the active component of second-order nonlinear optical materials.[5]

The cyclic carbonate functionality combines a relatively high dipole moment[6] and strong coordinating power with chemical stability (especially compared to the dicyanomethyl group[2]). For incorporation into hosts for nonlinear optics, it would be desirable to graft such a functional group onto an amorphous polymer of potentially high T_g that would be soluble in a volatile solvent. Therefore, polymethacrylate **1** is an attractive synthetic target.

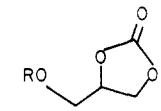
Monomer **4**, the precursor to **1**, has been previously employed in two polymerizations[7] as well as several copolymerizations.[8] However, it does not appear that soluble **1** has ever been prepared before. Indeed, one claim[7a] in the patent literature describes **1** as brittle and insoluble. In this paper we describe our synthesis of *soluble* **1** as well as its precursors from readily available starting materials.

Results

Synthesis of 3. Because of the ready availability of **2** (obtained in >97.5% purity by the base-catalyzed reaction of commercially available 3-(allyloxy)-1,2-propanediol with diethyl carbonate), we examined the Pd-mediated de-



1



2, R = CH_2=CH−CH_2

3, R = H

4, R = CH_2=C(CH_3)−C(=O)

alkylation of **2** to give **3**. Glycerol formation was minimized when the deallylation was carried out at ambient rather than elevated temperatures. The time needed for >90% conversion was markedly dependent on the activity of the Pd catalyst and the quantity of toluenesulfonic acid added. The yield of **3** was typically 70%, with contamination by <5% glycerol and ≤5% of **2**.

Synthesis of 4. The esterification of **3** with methacryloyl chloride was first attempted in Et_2O. Problems arose because of the immiscibility of **3** with Et_2O, and a polar phase remained separated from the ethereal solution throughout the reaction. Some of the newly synthesized **4** was lost to polymerization or decomposition in this phase. Phase-separation problems were avoided when THF was used as the solvent since **3** is miscible with THF. While the crude yield of **4** was 40–50% from ether, a 77% yield was achieved with THF as the solvent.

Synthesis of 1. Monomer **4** was polymerized in toluene with AIBN as initiator. When **4** was used without chromatographic purification, the polymer was completely intractable. When THF-derived **4** was first purified by flash chromatography on neutral Al_2O_3 with Et_2O elution, the resulting polymer was soluble in Me_2SO and DMF if isolated at <50% conversion but only ≤25% soluble at 60% conversion. Compound **4** synthesized in Et_2O and purified by flash chromatography or HPLC gave a polymer that was completely soluble in Me_2SO and DMF after >50% conversion. Unfortunately, a significant amount of **4** is lost to the Al_2O_3 columns. Also, chromatography did not remove an impurity that was originally present in the methacryloyl chloride (^{1}H NMR δ 1.9, 1.7). This last impurity did not appear to affect the polymerization.

Discussion

There have been other reported syntheses of **3**, although

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