Quantum-chemical Study of Effects of Alkoxy Substitution on the Conformations and Electronic Properties of Poly(*p*-phenylenevinylenes)

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We have performed a quantum-chemical investigation on the conformations and electronic properties of a variety of methoxy-substituted poly(*p*-phenylenevinylenes) (PPVs) to elucidate the effects of alkoxy substitution. Geometrical parameters for the polymers were fully optimized through Austin Model 1 (AM1) semi-empirical Hartree-Fock (HF) band calculations. Electronic properties of the polymers were obtained by applying the AM1 optimized structures to the modified extended Hückel method. To confirm validity of the AM1 conformational results, we also carried out *ab initio* HF calculations with the 6-31G (d) basis set for a variety of methoxy-substituted divinylbenzenes. It is found that the potential energy surfaces of alkoxy-substituted PPVs are quite shallow around the planar conformations, suggesting that the prepared films possess a variety of conformations with different torsion angle in the solid state, depending on the synthetic conditions. When two alkoxy groups are concurrently substituted at the adjacent sites in the phenylene ring, these groups are subject to rotating around the C(sp^2)–O bonds by 70-80° to avoid the strong steric repulsion between them. Consequently, the overlap between the π-type p orbital of oxygen and the π molecular orbitals of the polymer decreases. This leads to a wide gap and a high oxidation potential for tetramethoxy-substituted PPV, compared to those of dialkoxy-substituted PPV.

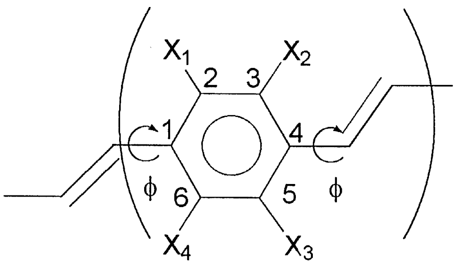
Introduction

Poly(*p*-phenylenevinylene) [PPV] and its alkoxy-substituted derivatives have been extensively investigated due to their electrical conductivities upon oxidative doping, nonlinear optical activities and luminescent properties.[1] PPV films exhibited a conductivity of 100 S/cm when doped with H_2SO_4.[2] These films, however, could not be effectively doped with weak oxidants such as iodine enough to produce appreciable increase in the electrical conductivity. Recently, Ahlslog *et al.* reported a much higher conductivity[3] of 10^4 S/cm for the stretched films (stretching ratio=10) doped with H_2SO_4. Alkoxy-substituted PPVs have been known to possess small band gaps and low oxidation potentials compared to those of PPV. Bathochromic shift[4,5] from the UV-Vis absorption peak of PPV was observed in the absorption spectra of poly(2-methoxy-1,4-phenylenevinylene) [P2MxPV]. It was reported that P2MxPV films were able to be doped with iodine to yield a conductivity of about 1.0 S/cm.[5] These films doped with AsF_5 exhibited a conductivity of *ca.* 100 S/cm. Dialkoxy-substituted PPVs[6~8] dislayed much smaller band gaps and lower oxidation potentials than unsubstituted PPV. These phenomena were explained by destabilization of the highest occupied molecular orbital (HOMO) of the polymer chain through the antibonding interaction with the π-type p orbital of oxygen in the alkoxy group.[9] Stretched poly(2,5-dimethoxy-1,4-phenylenevinylene) [P25MxPV] fibers at a draw ratio of 8 demonstrated a conductivity of 1200 S/cm when doped with iodine.[10]

In this regard, Jin *et al.* synthesized tetramethoxy-substituted PPV[11] in order to develop a highly conductive material. However, they found that poly(2,3,5,6-tetramethoxy-1,4-phenylenevinylene) [PTMxPV] could not be doped with iodine and gave a poor conductivity of 1.1×10^{-2} S/cm when doped with $FeCl_3$. The absorption peak of PTMxPV was also observed to shift to a shorter wavelength relative to that of PPV. Blue shift of the absorption peak and the poor conductivity of PTMxPV were presumably attributed to decrease in the effective π-conjugation between the phenylene and vinylene units due to the steric effect exerted by the four methoxy groups.

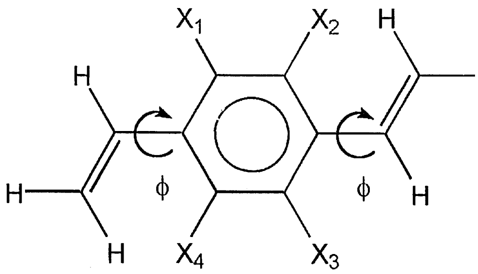
A conformational study[12] of dimethoxy-substituted *trans*-stilbene demonstrated at the *ab initio* Hartree-Fock (HF) 3-21G level that the molecule is of the coplanar structure due to the formation of weak hydrogen bonds between the methoxy side group and the vinylene linkage, implying that the phenylene ring may be in the same plane as the vinylene linkage in P25MxPV. Therefore, PTMxPV, which has four methoxy groups, may be of the planar conformation, too. If so, why did PTMxPV exhibit a poor electrical conductivity, a high oxidation potential and a large band gap compared to those of P25MxPV? This question attracted our attention and stimulated us to investigate the effects of alkoxy substitutions on the conformations and the electronic properties of PPV derivatives.

In this study, a variety of methoxy-substituted PPVs were chosen to investigate the effect of substitution site and the number of alkoxy substituents on the conformations and electronic properties of PPVs. Geometrical parameters and electronic properties of the polymers were obtained through quantum-chemical calculations. A detailed description for the computational methods will be given in the next section.



X_1, X_2, X_3, X_4 : H or OCH_3

Figure 1. Unit cell of poly(1,4-phenylnenevinylenes) and torsion angle (ϕ) of vinylene units with respect to the phenylene rings PPV=poly(1,4-phenylenevinylene), P2MxPV=poly(2-methoxy-1,4-phenylenevinylene), P3MxPV=poly(3-methoxy-1,4-phenylenevinylene), P23MxPV=poly(2,3-dimethoxy-1,4-phenylenevinylene), P25MxPV=poly(2,5-dimethoxy-1,4-phenylenevinylene), P26MxPV=poly(2,6-dimethoxy-1,4-phenylenevinylene), P36MxPV=poly(3,6-dimethoxy-1,4-phenylenevinylene), P235MxPV=poly(2,3,5-trimethoxy-1,4-phenylenevinylene), P236MxPV=poly(2,3,6-trimethoxy-1,4-phenylenevinylene), PTMxPV=poly(2,3,5,6-tetramethoxy-1,4-phenylenevinylene).



X_1, X_2, X_3, X_4 : H or OCH_3

Figure 2. 1,4-Divinylbenzenes with a variety of methoxy substitutions and torsion angle (ϕ) of vinyl groups with respect to the benzene ring: DVB=1,4-divinylbenzene, DV2MxB=1,4-divinyl-2-methoxybenzene (X_1=OCH_3), DV3MxB=1,4-divinyl-3-methoxybenzene (X_2=OCH_3), DV23MxB=1,4-divinyl-2,3-dimethoxybenzene (X_1=X_2=OCH3), DV25MxB=1,4-divinyl-2,5-dimethoxybenzene (X_1=X_3=OCH_3), DV26MxB=1,4-divinyl-2,6-dimethoxybenzene (X_1=X_4=OCH_3), DV36MxB=1,4-divinyl-3,6-dimethoxybenzene (X_2=X_4=OCH_3), DV235MxB=1,4-divinyl-2,3,5-trimethoxybenzene (X_1=X_2=X_3=OCH_3), DV236MxB=1,4-divinyl-2,3,6-trimethoxybenzene (X_1=X_2=X_4=OCH_3), DV2356MxB=1,4-divinyl-2,3,5,6-tetramethoxybenzene (all Xs=OCH_3).

Methodology

Since there are two different types of substitution sites on the phenylene ring (substitution site 2 is equivalent to the site 5 and different from the sites 3 and 6), there could be several isomers for each substituted PPV (see Figure 1). Therefore, we also compared the heats of formation and electronic properties of the isomers. For ground-state structures of methoxy-substituted PPVs, we employed the solid state version of the modified neglect of diatomic overlap HF method (MOSOL)[13] with Austin Model 1 (AM1) hamiltonians. This version adopts the Born-von Kármán periodic boundary condition and Bloch functions for crystal calculations. Six representative wave vectors (k) were chosen from 0 to π/a (a is the unit cell length) with regular intervals. The neighboring unit cells as far as the third nearest ones were involved in the lattice sum. The geometrical parameters (bond length, bond angles, and dihedral angles) in the unit cell depicted in Figure 1 were optimized. The AM1 method greatly reduces computational time compared to *ab initio* HF techniques, and is known to produce reliable ground-state structures and quite satisfactory conformational behaviors (torsion angles) for a variety of conjugated molecules in comparison with *ab initio* and experimental data though the method yields low rotational barriers.[14] We also optimized the planar structures of the polymers to compare the energies of both conformations. To confirm validity of the AM1 conformational results for the polymers, *ab initio* HF calculations for small molecules, analogous 1,4-divinylbenzenes (DVBs) in Figure 2 were carried out with the 6-31G(d) basis set in the Gaussian 94 package.[15] It has been reported that the 6-31G(d) calculations for a variety of conjugated molecules show torsion potentials superior to the density functional technique.[16] To construct the potential energy curves for a variety of methoxy-substituted DVBs, the torsion angle (ϕ) between the benzene ring and the vinyl units varies by 10° as shown in Figure 2 and at each torsion angle the geometrical parameters were fully optimized. Throughout the geometrical optimizations, we considered the vinylene units to be in the *trans*-form with respect to the phenylene rings.

Table 1. Valence shell atomic parameters used in the modified extended Hückel band calculations. Ionization potentials (IP in eV), Slater orbital exponents (ζ in a.u.)

Atom	n	l	IP	ζ	n	l	IP	ζ
H	1	0	13.60	1.300				
C	2	0	21.40	1.625	2	1	11.40	1.625
O	2	0	32.30	2.275	2	1	14.80	2.275

Electronic properties of the polymers were obtained by applying the AM1 optimized structures to the modified extended Hückel (MEH) method.[17(a)] The MEH method adopts for the off-diagonal elements a new form, which has an additional distance-dependent empirical factor. This approach was parameterized to reproduce band gaps defined as the λ_{max} for the π–π* transition of conjugated polymers, and not the band edges as are often used to define the gaps experimentally. Typically, the band edge is about 0.5 eV lower than the peak value. The MEH method has been shown to yield remarkably reliable band structures for a wide variety of conjugated polymers, including those with heteroatoms.[17] MEH parameters used in the calculations are listed in Table 1.

Conformational Study of Methoxy-substituted PPVs

In unsubstituted PPV, the AM1 band calculations predict that the vinylene unit is twisted by 18.4° with respect to the

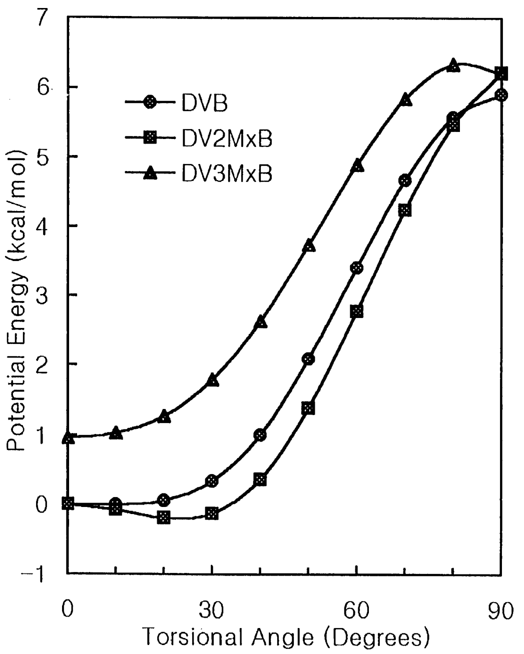


Figure 3. Ab initio 6-31G(d) potential energy surfaces (PES) for DVB, DV2MxB, and DV3MxB with the torsion angle of vinylene units (see Figure 2 for the acronyms). The PES for DV2MxB is referenced for the construction of that for DV3MxB.

phenylene ring and that the energy barrier over the planar conformation is less than 0.1 kcal/mol of unit cell. As shown in Figure 3, the *ab initio* calculations for 1,4-divinylbenzene support the AM1 result, producing a quite flat potential energy curve up to the torsion angle of 30°. Similar results were also obtained for *trans*-stilbene at the 3-21G level.[12] Also, elastic neutron-scattering diffraction measurements[18] on oriented PPV demonstrated that the phenylene rings were rotated about the vinylene linkages by 7.9±7.1° from the planarity. The relatively large root-mean-square angular deviation of 7.1° implies that the potential curve is actually flat around the planar conformation and that the rotational barrier may be quite small.

Upon incorporating a methoxy substituent, the torsion angle and the rotational barrier slightly increase. According to the AM1 band calculations, the twisted form of P2MxPV with a torsion angle of 19.7° is slightly more stable by 0.1 kcal/mol of unit cell than the planar form. In poly(3-methoxy-1,4-phenylenevinylene) [P3MxPV], the optimal torsion angle and the rotational barrier are estimated to be somewhat larger, 28.2° and 0.8 kcal/mol of unit cell, respectively. The *ab initio* molecular calculations show the conformational behavior similar to that found for P2MxPV but different from that for P3MxPV. In Figure 3, the potential energy curve for 1,4-divinyl-2-methoxybenzene (DV2MxB) exhibits a quite shallow surface within ±40° around the planar conformation. The minimum appears at about 23° and is lower in energy by 0.2 kcal/mol than the potential surface at the torsion angle of 0°. However, the potential energy curve for 1,4-divinyl-3-methoxybenzene (DV3MxB) shows a minimum at the torsion angle of 0°.

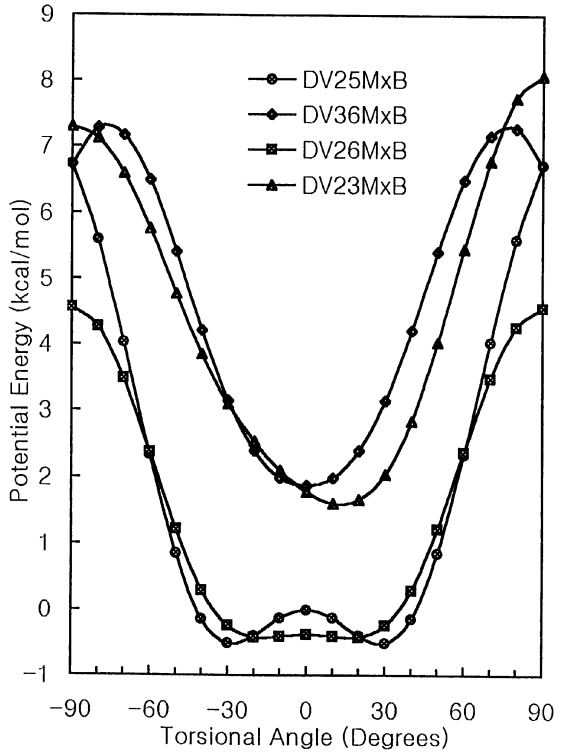


Figure 4. Ab initio 6-31G(d) potential energy surfaces (PES) for DV25MxB, DV36MxB, DV26MxB, and DV23MxB with the torsion angle of vinylene units (see Figure 2 for the acronyms). The PES for DV25MxB is referenced for the construction of PES for others.

For dimethoxy PPVs, the optimal torsion angles are in the range of 20-30° and the energy difference between the planar and the twisted conformations varies from 0.2 to 1 kcal/mol of unit cell, depending on the substituted sites. The optimal torsion angle for P25MxPV is estimated to be 22° and the rotational barrier is calculated to be only 0.2 kcal/mol of unit cell. At the 6-31G(d) level, a similar conformational behavior is observed with a torsion angle of about 30° and a rotational barrier of 0.5 kcal/mol for 1,4-divinyl-2,5-dimethoxybenzene as shown in Figure 4. On the contrary, the 3-21G calculations[12] for 1,1-(*trans*-1,2-ethenediyl) bis-2,5-dimethoxybenzene showed a minimum at the torsion angle of 0°. The planarity of the molecule was attributed to

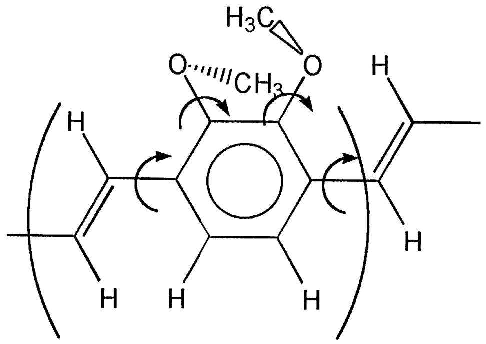


Figure 5. Directions of rotating methoxy groups and twisting vinylene units in poly(2,3-dimethoxy-1,4-phenylenevinylene).

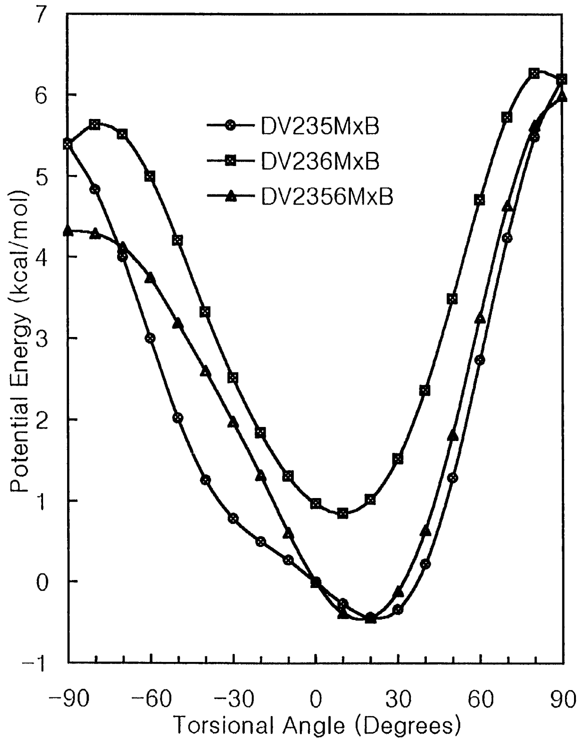


Figure 6. Ab initio 6-31G(d) potential energy surfaces (PES) for DV235MxB, DV236MxB and DV2356MxB with the torsion angle of vinylene units (see Figure 2 for the acronyms). The PES for DV235MxB is referenced for the construction of that for DV236MxB.

weak hydrogen bonding between oxygen in the methoxy group and hydrogen in the vinylene unit. The AM1 band calculations predict relatively large torsion angles and large energy differences between the planar and the twisted conformations for poly(2,6-dimethoxy-1,4-phenylenevinyl-ene) [P26MxPV] and poly(3,6-dimethoxy-1,4-phenylenevinylene) [P36MxPV] whereas the *ab initio* 6-31G(d) calculations predict the planar conformation for 1,4-divinyl-3,6-dimethoxybenzene (DV36MxB) and a very flat potential surface up to ±30° for 1,4-divinyl-2,6-dimethoxybenzene (see Figure 4). When two methoxy groups are attached at substitution sites 2 and 3, both AM1 and *ab initio* methods predict that the methoxy groups rotate around the C(sp^2)–O bond by 70-80° in the direction away from each other in order to avoid a strong repulsion between them (see Figure 5). This phenomenon is also found in poly(2,3,5-trimethoxy-1,4-phenylenevinylene) [P235MxPV], poly(2,3,6-dimethoxy-1,4-phenylenevinylene) [P236MxPV] and PTMxPV. In these polymers, the potential energy curves are unsymmetrical and the vinylene units are twisted in the direction away from the rotated 3-methoxy group. The optimized torsion angles are 23-25° with respect to the phenylene unit and the energy differences between the planar and the twisted conformations are 0.7-1 kcal/mol of unit cell. Compared to the AM1 results, the 6-31G(d) calculations estimate the relatively small torsion angles and the small energy differences, but exhibit similar conformational behaviors as in Figure 6. Table 2 presents AM1 results for heats of formation and geometrical features for the planar and the twisted conformations of PPV and the methoxy-substituted PPVs.

Table 2. AM1 results for heats of formation and geometrical features for the planar and the twisted conformations of PPV and the methoxy-substituted PPVs (see Figure 1 for the acronyms)

	Torsion angle[a]	ΔH_f (kcal/mol)	H···H distance (Å)[b]	O···H distance (Å)[c]	C=C-O-C dihedral angles[d]
PPV	0°	38.7	2.04	-	-
	18.4°	38.6	2.11	-	-
P2MxPV	0°	2.7	2.04	2.26	0°
	19.7°	2.6	2.13	2.33	0.8°
P3MxPV	0°	4.9	2.15	2.03	0.3°
	28.2°	4.1	2.28	2.17	15.7°
P25MxPV	0°	-32.4	2.00	2.26	0.2°
	22.0°	-32.6	2.11	2.35	2.0°
P26MxPV	0°	-30.9	2.09	2.03	0.2°, 0.8°
	27.5°	-31.7	2.24	2.16	1.1°, 15.2°
P36MxPV	0°	-29.0	2.18	2.07	0.4°
	28.9°	-30.0	2.38	2.22	20.1°
P23MxPV	0°	-28.0	2.13	2.08	76.3°, 74.8°
	23.9°	-28.5	2.24	2.17	73.3°, 73.1°
P235MxPV	0°	-63.3	2.08	2.08	78.7°, 74.1°, 0.7°
	24.6°	-64.0	2.20	2.17	75.5°, 72.2°, 1.1°
P236MxPV	0°	-61.1	2.24	2.11	77.7°, 74.3°, 67.2°
	23.0°	-62.1	2.31	2.23	75.8°, 68.8°, 34.6°
PTMxPV	0°	-94.5	-	2.12	77.3°, 75.1°
	24.0°	-95.2	-	2.21	74.2°, 73.9°

[a] Torsion angle between the phenylene and the vinylene units (see Figure 1). [b] The nearest distance between two hydrogen atoms; one in the phenylene ring and the other in the vinylene unit. [c] The nearest distance between oxygen in the methoxy group and hydrogen in the vinylene unit. [d] Dihedral angle between the methoxy group and the phenylene ring.

It seems at the 6-31G(d) level that methoxy substitutions at substitution sites 3 and/or 6 make the polymer chain planar. The planarity is observed in DV3MxB and DV36MxB. Also, relatively small torsion angles are found for 1,4-divinyl-2,3-dimethoxybenzene, 1,4-divinyl-2,3,6-trimethoxybenzene, and 1,4-divinyl-2,3,5,6-tetramethoxybenzene. This fact cannot be explained by the formation of hydrogen-type bonding which Lhost and Bredas argued since the nearest O··H distance (2.32 Å) in planar DV2MxB is close to that (2.28 Å) in planar DV3MxB. Note that the potential energy curve for DV2MxB shows a minimum at a torsion angle of about 23°, not at a torsion angle of 0°.

In summary, both AM1 and *ab initio* methods predict quite shallow potential surfaces around the planar conformations for PPV and the methoxy-substituted PPVs. This fact results from the compromise between two opposite forces: a repulsion and a π–conjugation. A repulsion arises from the fact that the closest distances between H atoms in the phenylene and the vinylene units, and between an O atom in the methoxy group and a H atom in the vinylene unit are too short compared to the sum of the van der Waals radii of the respective atoms (O:1.4 Å and H:1.2 Å).[19] A π–conjugation favors the planar form due to the large overlap between the

Table 3. MEH results for electronic properties of PPV and the methoxy-substituted PPVs (see Figure 1 for the acronyms)

	Torsion angle[a]	λ_{max} (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)
PPV[b]	0°	2.70	-11.78	-9.08
	7.9°[c]	2.77	-11.80	-9.03
	18.4°	3.02	-11.87	-8.85
P2MxPV[d]	0°	2.53	-11.53	-9.00
	19.7°	2.89	-11.62	-8.73
P3MxPV	0°	2.63	-11.57	-8.94
	28.2°	3.30	-11.75	-8.44
P25MxPV[e]	0°	2.18	-11.12	-8.94
	22.0°	2.61	-11.23	-8.62
P26MxPV	0°	2.56	-11.39	-8.83
	27.5°	3.20	-11.57	-8.37
P36MxPV	0°	2.32	-11.18	-8.86
	28.9°	3.02	-11.37	-8.35
P23MxPV	0°	2.76	-11.59	-8.83
	23.9°	3.26	-11.73	-8.47
P235MxPV	0°	2.52	-11.27	-8.75
	24.6°	3.03	-11.42	-8.38
P236MxPV	0°	2.69	-11.42	-8.73
	23.0°	3.04	-11.43	-8.39
PTMxPV	0°	2.71	-11.35	-8.64
	24.0°	3.20	-11.50	-8.29

[a] Torsion angle between the phenylene and the vinylene units (see Figure 1). [b] Experimental λ_{max} values are in the range of 2.6-2.9 eV [ref. 8, 20-22]. [c] A twisted angle between the phenylene ring and the vinylene was measured to be 7.9±7.1° by an elastic neutron-scattering experiment [ref. 18]. [d] Two experimental λ_{max} values are reported: 2.6 [ref. 5] and 2.9 eV [ref. 23]. [e] Experimental λ_{max} values are in the range of 2.2-2.8 eV [ref. 6-8, 24].

π–type p orbitals of C atoms linking the phenylene and the vinylene units. Methoxy substitutions slightly increase the torsion angles and the rotational barrier, mainly depending on the substituted sites. The methoxy groups rotate around the C(sp^2)–O bond to avoid strong repulsions when they are concurrently attached to substitution sites 2 and 3 or 5 and 6. The rotated methoxy groups would hamper the effective packing of the polymer chains in the solid state. Therefore, vinylene units in PTMxPV films are expected to be more twisted than those in PPV, P2MxPV and P25MxPV films.

Electronic Properties of Methoxy-substituted PPVs

The calculated electronic properties of PPV are given in Table 3. A small deviation from the planarity is found not to produce appreciable changes in the electronic properties. At a relatively large torsion angle of 18.4°, the band gap of PPV increases by 0.3 eV due to the reduced π overlap between the phenylene ring and the vinylene unit. Since the interaction between the phenylene ring and the vinylene unit is antibonding in the HOMO and bonding in the lowest unoccupied molecular orbital (LUMO), the reduced π overlap between them stabilizes the HOMO and destabilizes the LUMO. It is found that the destabilization of the LUMO energy level is greater in energy than the stabilization of the HOMO energy level. The MEH λ_{max} values are in excellent agreement with the experimental values[8,20-22] of 2.6-2.9 eV. Halliday *et al.* showed the variation of the λ_{max} values of PPV films prepared from different conditions.[21] From the comparison of the MEH and experimentally observed λ_{max} values, it is suggested that prepared PPV films possess a diversity of conformations with relatively small torsion angles, depending on the synthesis conditions. The small energy difference between the planar and the twisted conformations and the flat potential curve of DVB within ±30° also support this suggestion.

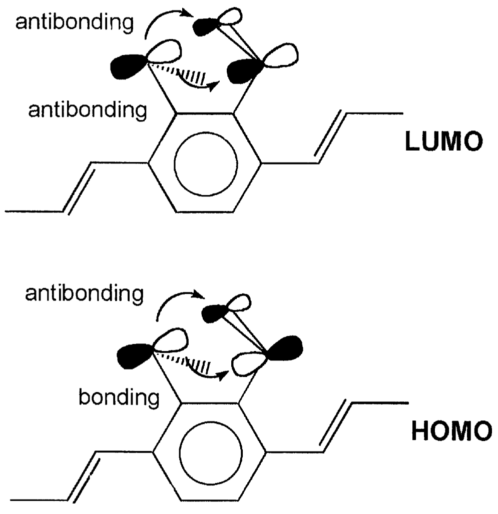


Figure 7. Schematic illustration of interactions between neighboring methoxy groups at the HOMO and LUMO levels of poly(2,3,5,6-tetramethoxy-1,4-phenylenevinylene).

Upon incorporating a methoxy substituent, the λ_{max} values decrease by 0.1-0.2 eV compared to that of unsubstituted PPV. The HOMO energy level of PPV is pushed up by 0.25 eV due to an antibonding interaction with the π–type p orbital of oxygen. These could be supported by the experimental observations of bathochromic shift of the absorption peak[4,23] and iodine doping[5] of P2MxPV. When the vinylene linkage is twisted with respect to the phenylene ring, the λ_{max} value of P2MxPV increases from 2.53 to 2.89 eV. Two reported values (2.6 and 2.9 eV)[5,23] for the UV-Vis absorption peak of P2MxPV films surprisingly agree with our estimations for the planar and the twisted forms, implying that P2MxPV in one film is mainly of the planar conformation and in the other film primarily consists of the twisted structure. In the twisted form of P3MxPV, the methoxy group is out of the phenylene plane and this further increases the λ_{max} value to 3.30 eV.

It is found that the electronic properties of dimethoxy-substituted PPVs strongly depend on the substituted sites. The λ_{max} value increases from 2.18 to 2.76 eV and the HOMO energy level becomes lower in the order: P25MxPV<P36-MxPV<P26MxPV<P23MxPV. That is, the symmetrically substituted PPVs have smaller band gaps and higher HOMO levels than the unsymmetrically substituted ones. In P23MxPV, the large torsion angle of methoxy groups with respect to the phenylene ring results in the much less overlap

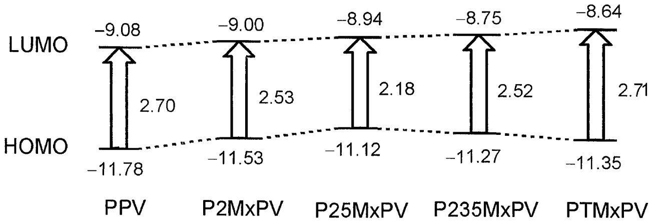


Figure 8. Variations of the HOMO and LUMO levels (in eV) and the band gaps for the planar conformations of PPV and some methoxy-substituted PPVs (see Figure 1 for the acronyms).

between the π–type p orbitals of C(sp^2) and O atoms and, accordingly, produces the largest λ_{max} value. In the twisted conformations of P25MxPV and P23MxPV, the band gaps increase by 0.4-0.5 eV compared to their planar forms. In P36MxPV and P26MxPV, on twisting of the vinylene unit, further increase in the band gaps appears due to the rotation of methoxy groups at substitution site 3 or 6. Among the dimethoxy-substituted PPVs, to our knowledge, only P25MxPV has been experimentally prepared and characterized. Again, our estimated λ_{max} values (2.18 and 2.61 eV) for the planar and twisted conformations of P25MxPV are in excellent agreement with the experimental measurements[6~8,24] ranging from 2.2 to 2.8 eV. Therefore, in combination with the information on the conformational behavior of P25MxPV, it is inferred that prepared P25MxPV films possess a variety of conformations with different torsion angles depending on the synthetic conditions. Compared to those of PPV, the λ_{max} values of P25MxPV decrease by 0.4-0.5 eV and the HOMO energy levels are higher in energy by 0.65 eV in accord with the experimental observations.[6~8]

In *tri-* and *tetra*-methoxy substituted PPVs, some or all of the methoxy groups are out of the phenylene plane and, consequently, do not effectively interact with the π–system of the PPV chain. Therefore, it is expected that the reduced antibonding interaction between the methoxy groups and the phenylene ring greatly stabilize the HOMOs and the LUMOs of these polymers. However, the HOMO levels are slightly pushed down and the LUMO levels are, on the contrary, pushed up. To elucidate these unexpected results, we examined the HOMO and the LUMO of PTMxPV. As illustrated in Figure 7, there are σ–type interactions between neighboring methoxy groups. The interaction between C in a methoxy group and O in the neighboring methoxy group is antibonding in both LUMO and HOMO and, consequently, destabilizes both levels. And the interaction between O atoms in the neighboring groups is bonding in the HOMO and antibonding in the LUMO. Therefore, it turns out that the interaction between the neighboring methoxy groups accounts for the unexpected predictions on the shift of the HOMO and LUMO levels of tri- and tetramethoxy substituted PPVs. In Figure 8 is shown the effect of increasing methoxy substituents on the band gaps and the Fermi levels for planar conformations of various PPVs. The oxidation potential of PTMxPV is predicted to be similar even in the twisted conformation to that of P2MxPV. This prediction is inconsistent with the experimental observations that PTMxPV could not be doped with iodine while P2MxPV could be. The incapability of iodine-doping of PTMxPV may be ascribed to difficulty in iodine-diffusion into the films due to the rotated methoxy groups and the somewhat twisted backbone. Unfortunately, to the best of our knowledge, there has been no direct measurement on oxidation potentials of these polymers for comparison.

Conclusions

From the AM1 and ab initio 6-31G(d) calculations, the potential energy curves for PPV, P2MxPV and P25MxPV are expected to be quite flat and symmetrical around the planar conformations. Our calculated λ_{max} values for the planar and the twisted conformations surprisingly agree well with a wide range of the experimental values. Therefore, it could be concluded that the prepared films may possess a variety of conformations with different torsion angles between the phenylene and vinylene units, depending on the synthetic conditions. On going from PPV to P25MxPV, the band gap and the oxidation potential decrease since the antibonding interaction between the methoxy group and the phenylene ring becomes strong as the number of methoxy groups increases.

In PTMxPV, in comparison with PPV, P2MxPV and P25MxPV, the energy difference between two conformations becomes relatively large and, moreover, the methoxy groups are twisted by about 75° with respect to the phenylene ring. As a result, the vinylene units of PTMxPV films are more plausible to be twisted since the rotated methoxy groups may hinder the effective packing of the polymeric chains in the solid state. The band gap and the oxidation potential of PTMxPV are estimated to increase compare to those of PT25MxPV in agreement with the experimental observations. The increases in them are found to mainly come from the rotation of the methoxy groups which induces a great decrease in the antibonding interaction with the phenylene ring.

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