

# Origin of the Broken Conjugation in *m*-Phenylene Linked Conjugated Polymers

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**ABSTRACT:** A quantum-chemical study of conformations and electronic structures of poly(*m*-phenylene) [PMP] and the related polyphenylenes was performed to elucidate the origin of the broken conjugation found in *m*-phenylene linked conjugated polymers. Potential energy curves of the polymers as a function of both torsion and helical angles were constructed through semiempirical Hartree–Fock band calculations at the Austin model 1 (AM1) level. It is found that two helical conformations of PMP are possible: one with a helical angle ( $\alpha$ ) of 72° and the other with  $\alpha = 144^\circ$ . The former is identical with the conformation of an oligomer in the solid state, *m*-deciphenyl structure. Our calculations predict that both helices are more stable by 2.5 kcal/mol per phenyl ring than the anti-coplanar conformation and that they exhibit absorption peaks at 5.8 eV. The electronic structure of PMP is, however, not affected significantly by increasing the planarity of a PMP chain but affected by copolymerization with other conjugated units. This implies that localization occurs in the *m*-phenylene ring itself. We examined the electronic structures of PMP and the related copolymers and found that the weak conjugation along the *m*-phenylene linked conjugated backbone is related to the inherent nodal nature of the frontier molecular orbitals of the unit even in the planar conformation.

## Introduction

Since Burroughes et al. first reported a light-emitting diode (LED) based on poly(*p*-phenylenevinylene) in 1990,<sup>1</sup> photo- and electroluminescent properties of a variety of conjugated polymers have been intensively investigated in search of new highly efficient LED materials for three primary colors: red, green, and blue. Polyphenylenes, among conjugated polymers, are attractive candidates for blue light-emitting materials because of their large band gaps.<sup>2–5</sup> The first blue LED was fabricated with poly(9,9-dihexylfluorene), emitting light with a peak at 470 nm (corresponding to photon energy of 2.6 eV).<sup>2</sup> Poly(*p*-phenylene) [PPP] was immediately introduced as another blue LED, suggesting that light emission might be a general feature of conjugated polymers.<sup>3</sup> Blue light emitters have also been obtained through controlling in several ways conjugation length along conjugated backbones. Attaching bulky side groups is one way to tune color, by inducing steric distortion of a conjugated chain.<sup>6</sup> Another way is to incorporate nonconjugated segments such as silylene and ether groups into a conjugated backbone.<sup>7</sup> Broken conjugation has been also successfully achieved using *m*-phenylenes as an interrupting block.<sup>8–12</sup>

Though insertion of *m*-phenylene units has experimentally demonstrated excellent linearity of optical properties with the inverse of conjugation length<sup>8–10</sup> and greatly enhanced photoluminescence efficiency of the polymers,<sup>11,12</sup> the way in which the units break conjugation

is unclear.<sup>10</sup> One possible source of the optical effect is through a twisting of neighboring units out of local planarity. We will refer to this simply as “twisting”. Another source might be in the phase relationships at the linked sites and the sizes of the orbital coefficients at those sites. We will call this an orbital effect. X-ray analyses of *m*-oligophenylys have shown that phenyl rings are randomly twisted along the chain<sup>13</sup> or form a helical structure,<sup>14</sup> supporting the idea that chain twisting might be responsible for the broken conjugation. However, *m*-oligophenylys show UV absorption peaks at wavelengths (near 250 nm in chloroform) much shorter than *p*-oligophenylys. Moreover, there is no appreciable variation of the peak position with the size of the oligomer (ranging from biphenyl to 16 phenyl rings<sup>15</sup>), indicating that the conjugation does not extend beyond biphenyl. This may be construed as an indication that the *m*-phenylene unit breaks conjugation due to the orbital effects of the frontier molecular orbitals (MOs), because conjugation cannot be completely lost unless the torsion angle between adjacent phenylene rings is sufficiently large. To explore the conformation and electronic structure of poly(*m*-phenylene) [PMP], it is desirable to understand the origin of the broken conjugation found in conjugated polymers having *m*-phenylene segments.

In this work, the conformational behaviors and electronic properties of PMP and its vinylene copolymers were investigated through quantum-chemical band calculations so as to elucidate how the *m*-phenylene unit induces broken conjugation. To our knowledge, there has been no satisfactory explanation of this effect yet.

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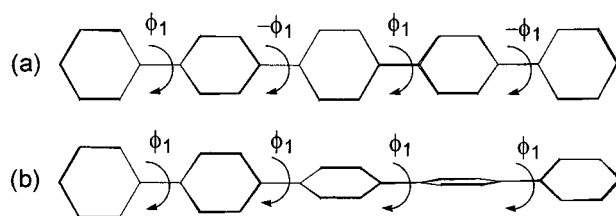
For comparison, we also included the analogues of PMP: PPP and polyfluorene (PFI) in this study because crystal structures of PPP<sup>16</sup> and its oligomers<sup>17–22</sup> as well as their optical properties<sup>2,4,5,23,24</sup> are abundant.

### Methodology

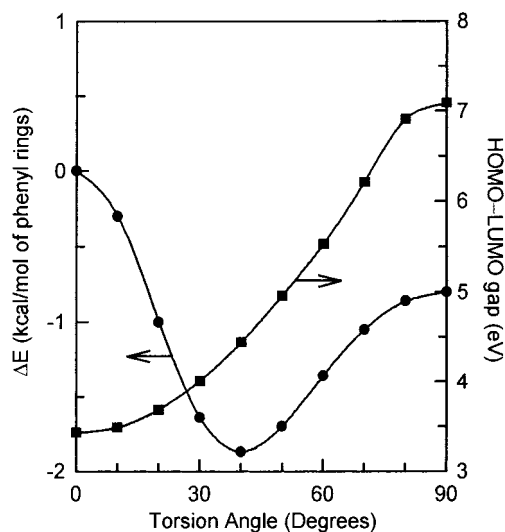
The recent rapid growth of computer technologies and development of quantum-chemical program packages make it possible to calculate precisely molecular properties at a very high level. However, such a high-level calculation (including electron correlation with a large basis set) for a polymeric system is still restricted to a small unit system in practice.<sup>25</sup> For relatively large systems,<sup>26–30</sup> polymeric structures have been obtained from the calculations on oligomeric structures or from the experimental measurements. Moreover, it is well-known that Hartree–Fock level calculations greatly overestimate the HOMO–LUMO gap of a conjugated polymer. On the other hand, inclusion of electron correlation leads to a significant underestimation of the gap.<sup>26</sup> Therefore, one should perform numerical experiments to estimate how much electron correlation should be included to reproduce the experimentally observed HOMO–LUMO gap.<sup>27</sup> In this regard, well-defined semiempirical methods are still attractive for a large or an unknown polymeric system.

We employed the solid-state version of the MNDO method (MOSOL)<sup>31</sup> with the AM1 Hamiltonian to optimize geometrical parameters and to investigate the conformational behavior of PMP and the related polymers. This version adopts the Born–von Kármán periodic boundary condition and Bloch functions for crystal calculations. The AM1 method has been successfully used to investigate geometrical structures and conformations of large molecules in particular, although the method yields low rotational barriers.<sup>32</sup> For the geometrical optimizations, we chose six wave vectors with a regular interval from 0 to  $\pi/a$  (where  $a$  is a translation vector) and imposed  $D_{2h}$  constraints on *p*-phenylene and  $C_{2v}$  on fluorene and *m*-phenylene monomer units. The cutoff value used for interactions between atoms was set to 40 Å for all the polymers except PFI systems, the value being somewhat larger than the length of the largest unit ( $C_{54}H_{36}$ ). For the PFI system, this value was set to 45 Å because of the large size of the fluorene unit. All the calculations were performed for isolated single polymer chains without consideration of any intermolecular effects.

To examine the conformational behavior of the polymers, we studied two different ways of rotation. One way is to rotate the rings about the rotational axis alternately (Figure 1a). That is, a torsion angle ( $\phi$ ) between two adjacent rings is given by  $\phi_i = (-1)^{i+1}\phi_1$ . Total energies were calculated by varying the torsion angle by 10°, from 0° to 180° (90° for PPP due to its symmetry plane including the rotational axis), to construct potential energy curves. In the other rotation mode we studied, the rings were rotated consecutively in the same direction:  $\phi_i = \phi_1$ , producing a helical structure (Figure 1b). Because a helical symmetry operator is not included in our MOSOL version, we determined a helical angle ( $\alpha$ ) of the chains by the number ( $n$ ) of the rings in the repeat unit, with the relationship of  $\alpha = (m \times 360^\circ)/n$  where  $m$  is any integer, representing the number of turns which the unit cell makes. At each helical angle, the torsion angle between the adjacent rings is optimized along with other geometrical parameters.



**Figure 1.** Two different ways of rotating phenyl rings out-of-plane: (a) an alternately twisted structure and (b) a helical structure.



**Figure 2.** Potential energy and HOMO–LUMO gap for alternately twisted structures of poly(*p*-phenylene) as a function of the torsion angle between the adjacent phenyl rings.

**Table 1. Valence Shell Atomic Parameters Used in the Modified Extended Hückel Band Calculations**

atom	<i>n</i>	<i>l</i>	<i>H<sub>ii</sub></i> (eV)	$\zeta$ (au)	<i>n</i>	<i>l</i>	<i>H<sub>ii</sub></i> (eV)	$\zeta$ (au)
H	1	0	−13.60	1.300				
C	2	0	−21.40	1.625	2	1	−11.40	1.625

Electronic properties were calculated by using the AM1 optimized structures in the modified extended Hückel (MEH) method.<sup>33</sup> This method expresses the off-diagonal elements of the EH method in a modified form, which has an additional distance-dependent empirical factor. This was parametrized to reproduce experimental  $\lambda_{\max}$  values for the  $\pi$ – $\pi^*$  transitions of some conjugated polymers such as *trans*-polyacetylene and PPP, not onset values that have been usually related to band gaps.<sup>33</sup> This approach has predicted  $\lambda_{\max}$  values of a variety of conjugated polymers with fairly good accuracy compared to experimental values.<sup>33–36</sup> Atomic parameters used in the MEH calculations are presented in Table 1.

### Poly(*p*-phenylene)

Shown in Figure 2 are the calculated potential energies and HOMO–LUMO gaps of poly(*p*-phenylene), when the phenylene rings are twisted alternately by torsion angle  $\phi$ . A minimum of the potential energy curve is found at  $\phi = 40^\circ$ , being 1.9 kcal/mol per phenyl ring lower in energy than the planar conformation. Helical structures of the PPP chain are estimated to produce essentially the same conformational behavior as the alternately twisted structures, because the rotational axes are collinear in these polymers. The torsion angle at the minimum is close in value to the

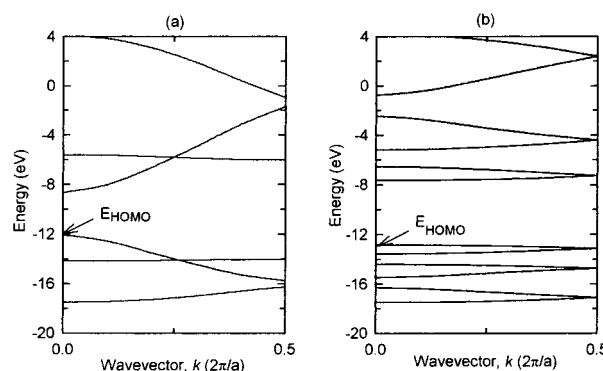
one observed from an electron diffraction study of gaseous biphenyl<sup>21</sup> and the ones predicted from other theoretical investigations<sup>37–41</sup> for biphenyl and a single polymer chain. Twisting of the phenyl rings has been ascribed to steric hindrance exerted by the ortho hydrogens. The atomic distance between these hydrogens is calculated to be 1.90 Å in the planar conformation and 2.33 Å at  $\phi = 40^\circ$ . Our predicted HOMO–LUMO gap at  $\phi = 40^\circ$  is 4.44 eV, quite large compared to the experimental UV–vis absorption  $\lambda_{\text{max}}$  values (3.2–3.4 eV)<sup>23</sup> of PPP films.

There is, however, much evidence for a nearly planar conformation of PPP in the solid state, though the exact torsion angle is not yet known. X-ray analyses of the crystal structures of biphenyl,<sup>17</sup> *p*-quaterphenyl,<sup>18</sup> and the higher oligomers<sup>22</sup> at room temperature have demonstrated that the chains are planar, presumably due to intermolecular forces. Also, a neutron diffraction study of a deuterated biphenyl crystal has revealed that the phenyl rings are nearly planar, with a torsion angle of about  $10^\circ$ .<sup>20</sup> X-ray analysis of PPP powder indicated a somewhat large torsion angle of about  $20^\circ$ , with the phenyl rings alternately twisted along the chain axis.<sup>16</sup> Both full-potential linearized augmented-plane-wave and pseudopotential calculations have yielded the torsion angle of  $17^\circ$  for 3-dimensional crystalline PPP.<sup>39</sup> Cuff and Kertesz compared theoretical and experimental Raman spectra of PPP and concluded that the polymer chain would be nearly planar with a torsion angle less than  $20^\circ$ .<sup>42</sup> Our predicted HOMO–LUMO gap at  $\phi = 20^\circ$  is 3.69 eV, larger by ca. 0.4 eV than the experimental values. At this torsion angle, the distance between the ortho-hydrogen atoms is predicted to be 2.01 Å. Palmer and Ladik have estimated the quasiparticle band gap of PPP to be 2.3 eV at  $\phi = 22.7^\circ$ .<sup>29</sup> The local-density functional approach has predicted the band gap of PPP to be 1.99 eV at the planar structure and 2.54 eV at the equilibrium conformation with  $\phi = 34.8^\circ$ .<sup>41</sup>

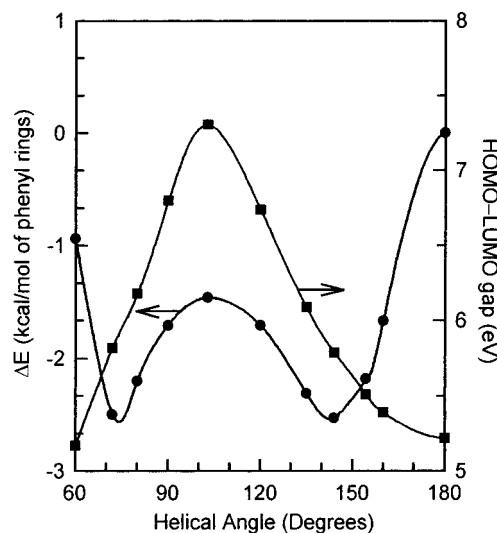
The electronic structure of PPP is predicted to vary significantly with the torsion angle between neighboring phenyl rings. As the torsion angle changes from 0 to  $90^\circ$ , the HOMO–LUMO gap increases from 3.43 to 7.09 eV. Widths of the HOMO and LUMO bands decrease from 3.67 to 0.22 eV and from 6.95 to 0.34 eV, respectively. These large variations indicate strong orbital interactions between neighboring phenyl rings near the Fermi level, and effective propagation of the interactions along the chain in the planar conformation. The HOMO–LUMO gap, HOMO bandwidth, and energy gap (8.0 eV) between two flat bands in the planar conformation (see Figure 3) are quite close to the experimental values: the bandwidth estimated as 3.5 eV by UPS measurements<sup>43</sup> and the energy gap between two flat bands being ca. 7 eV by an EELS investigation.<sup>44</sup> Ab initio band-structure calculations with the 3-21G basis set have produced HOMO bandwidths of 4.91 and 4.45 eV at torsion angles of 0 and  $22.7^\circ$ , respectively.<sup>30</sup>

### Poly(*m*-phenylene)

Unlike the case of a PPP chain, the neighboring local rotational axes of PMP are not collinear. This leads PMP to adopt a helical conformation, rather than an alternately twisted structure. In fact, the AM1 calculations show that any helical structures of PMP with  $\alpha$  close to or larger than  $60^\circ$  are more stable than the anti-coplanar conformation ( $\alpha = 180^\circ$ ), while the alternately



**Figure 3.** Comparison of MEH-calculated  $\pi$ -band structures for the planar conformations of (a) poly(*p*-phenylene) and (b) poly(*m*-phenylene).



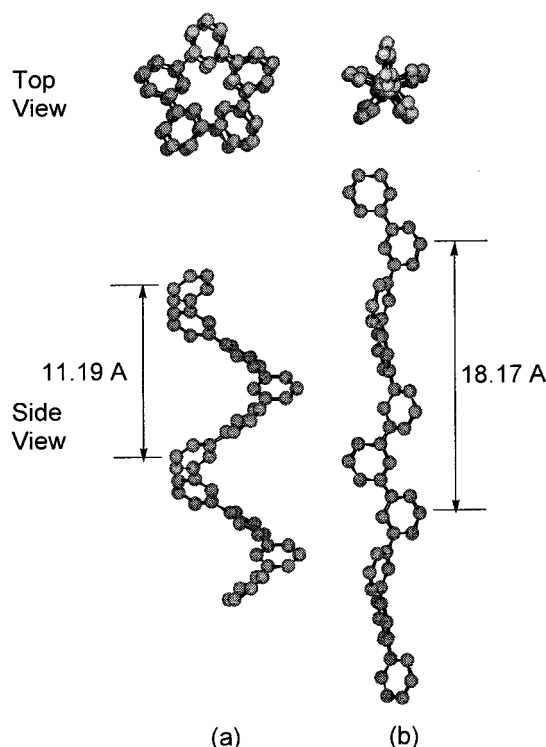
**Figure 4.** Variation of the potential energy and HOMO–LUMO gap for helical structures of poly(*m*-phenylene) with the helical angle.

twisted structures are less stable. The helices with  $0^\circ < \alpha < 60^\circ$  are so unstable that we could not obtain optimized structures with our treatment for them. The instability of the helices comes from strong repulsion between hydrogen atoms located in different phenylene rings.

As shown in Figure 4, the potential energy curve of PMP with a helical angle shows two minima at  $\alpha = 72^\circ$  and  $144^\circ$ , where PMP chains form 5/1 and 5/2 helices, respectively, consisting of five phenyl rings in a unit cell (see Figure 5). These helices are roughly isoenergetic with each other, being lower in energy by 2.5 kcal/mol per phenyl ring than the anti-coplanar conformation. The AM1 calculation predicts that PMP chains with  $\alpha = 72^\circ$  will have phenyl rings twisted by  $41.7^\circ$ , with a unit cell length of 11.19 Å. In the helical structure with  $\alpha = 144^\circ$ , the phenyl rings are twisted with an angle of  $138.2^\circ$ , and the length of the unit cell is estimated to be 18.17 Å. The energy barrier between two helices amounts to 1.0 kcal/mol per phenyl ring in the 7/2 helical conformation, whose helical and torsion angles are  $102.9^\circ$  and  $87.8^\circ$ , respectively.

In both helices, the closest distance between hydrogen atoms in different phenyl rings is calculated to be 2.36 Å, which is nearly double the van der Waals radius for hydrogen. It appears that stabilization of these helices is achieved by relieving van der Waals repulsion be-





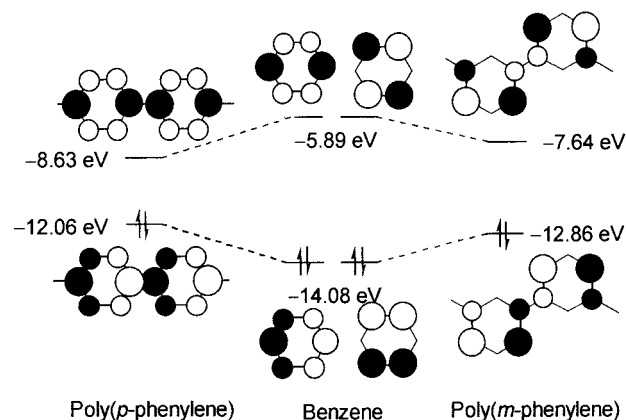
**Figure 5.** Two possible helical conformations of poly(*m*-phenylene) chain with a helical angle of (a) 72° and (b) 144°. Hydrogen atoms are not shown for clarity. In the top view the color gets darker when a ring goes down along the chain.

tween the hydrogen atoms. The H...H distance in the anti-coplanar structure is estimated to be 1.86 Å.

The first helical structure mentioned above surprisingly accords well with a *m*-deciphenyl structure determined from a single-crystal X-ray diffraction study undertaken by Williams et al.<sup>14</sup> They found that crystalline *m*-deciphenyl adopts a helical conformation with a helix pitch of 11.22 Å and that the five phenyl rings are rotated by sequential torsion angles of 53°, 34°, 44°, 44°, 34°, etc. (average value = 41.8°), along the chain. On the other hand, to our knowledge, there has been no experimental observation in oligomers of the helical conformation of PMP with  $\alpha = 144^\circ$ .

The helices with  $\alpha = 72^\circ$  and  $144^\circ$  are calculated to show essentially the same HOMO–LUMO gaps: 5.82 and 5.79 eV, respectively. These values are certainly larger than the experimental observations (5.0 eV) in the absorption spectra for *m*-oligophenylys in chloroform.<sup>15</sup> On the other hand, the HOMO–LUMO gaps (5.22 eV) calculated for the anti-coplanar conformation is close to the experimental values. PMP cast films<sup>8</sup> have shown a  $\pi$ – $\pi^*$  transition energy of 4.74 eV, lower than the oligomers in solution have, indicating that a PMP chain in the film has a greater degree of planarity than the one in solution. The predicted HOMO–LUMO gap at  $\alpha = 160^\circ$  is 5.39 eV, where the closest distance (2.02 Å) between the hydrogen atoms is similar to that found in twisted PPP with a torsion angle of 20°.

In comparison with PPP, the HOMO–LUMO gap of PMP is predicted to be quite large and the widths of the HOMO and LUMO bands are quite narrow, even at the anti-coplanar conformation ( $\alpha = 180^\circ$ , see Table 2 and Figure 3). Also, variation of the electronic structures of PMP with helical angle is relatively small. As the conformation of the chain varies from anti-coplanar (2/1) to 7/2 helices, the HOMO–LUMO gap



**Figure 6.** Frontier molecular orbital energy correlation diagram for planar conformations of poly(*p*-phenylene), poly(*m*-phenylene), and benzene.

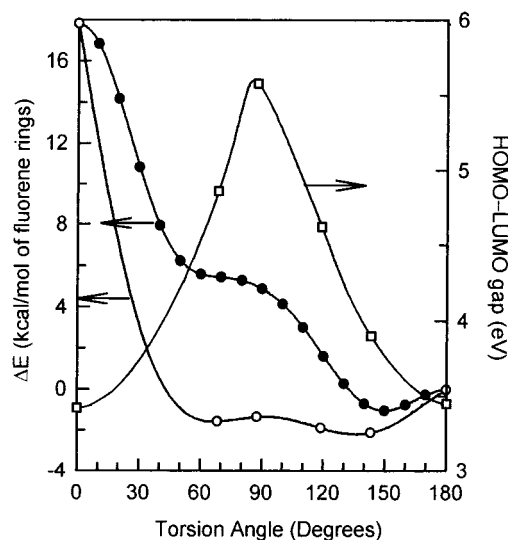
**Table 2.** MEH-Calculated Electronic Properties (in eV) of PPP, PMP, and PFI in the Planar Structures

	PPP	PMP	PFI
$E_g^a$	3.43	5.22	3.45
$E_{\text{HOMO}}$	−12.06	−12.86	−11.94
$E_{\text{LUMO}}$	−8.63	−7.64	−8.49
HVBW <sup>b</sup>	3.67	0.71	1.83
LCBW <sup>c</sup>	6.95	1.09	2.54

<sup>a</sup> HOMO–LUMO gap. <sup>b</sup> Highest valence bandwidth. <sup>c</sup> Lowest conduction bandwidth.

increases by 2.1 eV, and the widths of HOMO and LUMO bands decrease from 0.71 to 0.04 eV and from 1.10 to 0.02 eV, respectively. These findings indicate that PMP possesses weaker  $\pi$ -conjugation along the chain than PPP, even in the planar conformation.

We have compared the frontier MOs of benzene, PPP, and PMP to elucidate the reason for the weak  $\pi$ -conjugation of PMP along the chain (see Figure 6). Note that the MEH calculation produces a larger HOMO–LUMO gap (8.19 eV) for benzene than does the density functional theory (DFT) calculation, which estimates the gap of 6.61 eV using a hybrid functional B3LYP method with a 6-311+G(d) basis set, which is implemented in the Gaussian 98 package.<sup>45</sup> This is because MEH parametrization was carried out for conjugated polymer, not for monomer. We hope the trends are right. There are two sets ( $e_{1g}$  and  $e_{2u}$ ) of doubly degenerate  $\pi$ -MO levels for benzene. In each set, there are two different types of MO's. One type has large MO coefficients on para C atoms and small coefficients on the other C atoms, while the other type of MO has a nodal plane through the para C atoms and large coefficients on the others. In PPP, where benzene rings are linked successively at para positions, interactions between the former type MOs are much stronger than those between the latter type MOs, resulting in very dispersive valence and conduction bands at the Fermi level and a small gap between the bands. On the other hand, in PMP, where benzene rings are bonded consecutively at meta positions, the latter type MOs (the ones with a nodal plane passing through the para carbons) interact more strongly with each other than do the former type MOs, developing into the highest valence and the lowest conduction bands. These bands are, however, not very dispersive, leading to localization of electrons and a large gap between the bands. A similar trend was observed for a class of planarized polyphenylenes.<sup>46</sup>



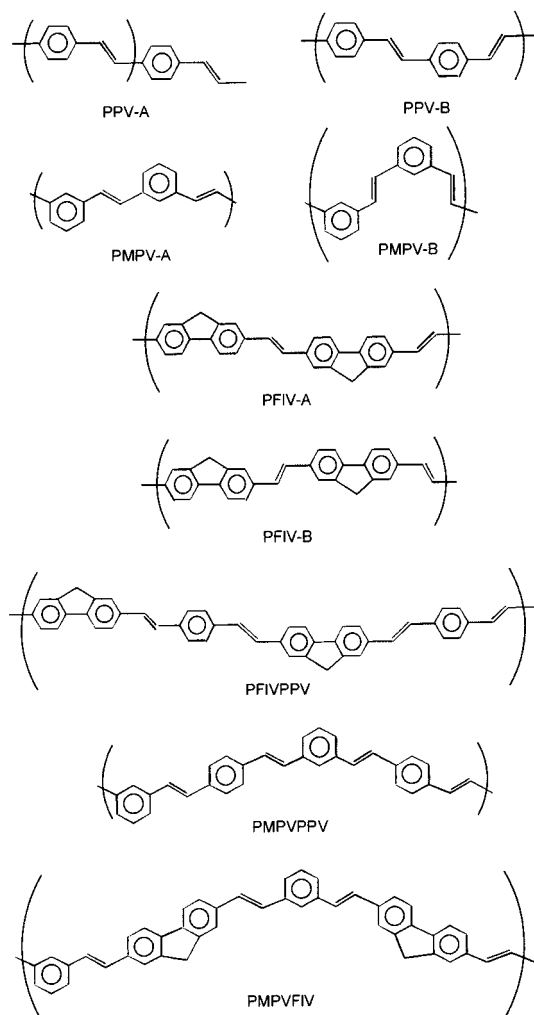
**Figure 7.** Potential energy curves of (a) alternately twisted (●) and (b) helical (○) structures and variation of the HOMO-LUMO gap (□) of helical polyfluorene with respect to the torsion angle between the neighboring fluorene units.

### Polyfluorene

Figure 7 presents potential energy curves for both alternately twisted and helical structures of PFI as a function of the torsion angle between the adjacent fluorene units. The potential curve for the helical structures was constructed with few helical angles in the range  $72^\circ$ – $180^\circ$ , because of the large size of the fluorene unit. The angle between the adjacent rotational axes is calculated to be  $156.3^\circ$  in the anti-coplanar structure; the axes of PFI are not collinear. Therefore, as found in PMP, the helical structures turn out to be more stable than the alternately twisted structures at any given torsion angle,  $\phi$ . The potential curve for the helices is quite flat in the range of  $50^\circ \leq \phi \leq 160^\circ$ , though it apparently shows two minima at  $\phi \approx 68^\circ$  ( $\alpha = 72^\circ$ ) and  $143^\circ$  ( $\alpha = 144^\circ$ ). The syn-coplanar conformation of a PFI chain is predicted to be quite higher in energy than the anti-coplanar one, by ca. 18 kcal/mol per fluorene unit.

PFI chains at  $\alpha = 72^\circ$  and  $144^\circ$  form 5/1 and 5/2 helices, respectively, in the same way as found in PMP. It is estimated that the 5/2 helix is more stable than the 5/1 helix only by 0.54 kcal/mol per fluorene unit and more stable than the anti-coplanar structure by 2.11 kcal/mol. The energy barrier between these two helices is estimated to be ca. 0.8 kcal/mol per fluorene unit. Interestingly, these helices possess quite similar helical pitches, but different HOMO-LUMO gaps, in contrast to PMP: 39.96 Å and 4.86 eV for the 5/1 helix and 41.69 Å and 3.90 eV for the 5/2 helix. The closest distances between the hydrogen atoms in the different phenyl rings are calculated to be 3.00 and 2.24 Å at the 5/1 and 5/2 helices, respectively. The distance in the anti-coplanar structure is 1.88 Å.

To our knowledge, there has been no structural investigation of polyfluorenes until very recent work by Grell et al.<sup>47</sup> They observed development of an absorption peak at 437 nm (2.84 eV) in addition to a main peak at 384 nm (3.23 eV), depending on the solvent and thermal treatments of the poly(9,9-dioctylfluorene) films. The spectrum evolution was ascribed with the help of X-ray scattering experiments to the intrachain conformational change from a helix to an anti-coplanar



**Figure 8.** A variety of phenylenevinylene copolymers with trans configurations investigated in this study.

structure. The energy difference between two peaks is quite similar to the one (0.45 eV) between our calculated HOMO-LUMO gaps of the 5/2 helix and anti-coplanar conformation. Later, Lieser et al.<sup>48</sup> performed electron and X-ray diffraction measurements on highly oriented poly(9,9-bis(2-ethylhexyl)-fluorene-2,7-diyl) [PF2/6] films on a polyimide substrate and found that the PF2/6 chains favor a 5/2 helix in a trigonal crystal system with  $a = b = 16.7$  Å and  $c = 40.4$  Å. They concluded that the polymer chains favor a 5/2 helix ( $\alpha = 144^\circ$ ) from structural data and torsion angle dependence of the electronic transition energy ( $S_0 \rightarrow S_1$ ) of bifluorene (BF) through HF/6-31G calculations. A conformational study at the HF/6-31G(d) level has revealed that two minima in the potential curve of BF are located at torsion angles of  $45^\circ$  and  $135^\circ$ , with energy barriers of 3.4 kcal/mol over syn- and anti-coplanar conformations.<sup>49</sup>

The HOMO-LUMO gap for the anti-coplanar structure of PFI is estimated to be the same as that of PPP in the planar structure, indicating that the methylene group linking the two phenyl rings does not affect the  $\pi$ -electronic structures near the Fermi level. The highest valence and lowest conduction bandwidths of PFI are, however, much narrower than those of PPP, because the lower symmetry of PFI does not allow bands to cross each other. The calculated HOMO-LUMO gap is comparable with the experimental observations (3.2–3.5 eV) of poly(9-alkylfluorene) and poly(9,9-dialkylfluorene)

**Table 3. Comparison of Heats of Formation between Isomers and Electronic Properties (in eV) of a Variety of Phenylenevinylene Copolymers**

	PPV-A	PPV-B	PFIV-A	PFIV-B	PMPV-A	PMPV-B	PFIVPPV	PMPVPPV	PMPVFIV
$\Delta H^a$	0	-0.01	0	0.07	0	0.08			
$E_g^b$	2.70	2.70	2.97	2.96	4.04	4.21	2.86	3.46	3.45
$E_{\text{HOMO}}$	-11.78	-11.78	-11.79	-11.79	-12.44	-12.46	-11.79	-12.16	-12.07
HVBW <sup>c</sup>	2.33	2.32	1.43	1.43	0.58	0.53	0.74	0.26	0.06
H...H <sup>d</sup>	2.04	2.04	2.03	2.03	2.04	2.01	2.03	2.04	1.87

<sup>a</sup> Relative heats of formation (kcal/mol) between two different types of the isomers. <sup>b</sup> HOMO–LUMO gap. <sup>c</sup> Highest valence bandwidth. <sup>d</sup> The closest H...H distance in Å; one hydrogen atom in the phenylene ring and the other in the vinylene unit.

films.<sup>4,5,24</sup> Alkyl groups are known not to significantly change the optical properties of conjugated polymers, unless they cause steric hindrance and greatly modify conformations of the polymer chains.

Variation of electronic structures of PFI with the torsion angle is not so large, compared to that found in PPP. The HOMO–LUMO gap varies from 3.45 to 5.58 eV on going from the anti-coplanar structure to the helix with  $\alpha = 90^\circ$  ( $\phi = 87.5^\circ$ ). This is due to the fact that the fluorene unit is already “planarized”.

### Phenylenevinylene Copolymers

Incorporation of a vinylene linkage is known to reduce steric hindrance between the hydrogen atoms in PPP, resulting in increased planarity of polymeric chains. Elastic neutron-scattering diffraction measurements on oriented poly(1,4-phenylenevinylene) (PPV) have demonstrated that the phenylene rings are rotated about the vinylene linkages by  $7.9 \pm 7.1^\circ$ .<sup>50</sup> The relatively large root-mean-square angular deviation of  $7.1^\circ$  implies that the potential curve of PPV with respect to the torsion angle may be flat around the planar conformation, with a quite small rotational barrier. In fact, *ab initio* calculations on *trans*-stilbene<sup>51</sup> at the HF/3-21G level and on divinylbenzene<sup>52</sup> at the HF/6-31G(d) level have shown that these molecules are planar in the ground state, with quite flat potential energy curves up to  $30^\circ$ . AM1 band calculations on PPV have indicated that a twisted conformation with the torsion angle of  $18.4^\circ$  is slightly preferred to the planar conformation by less than 0.1 kcal/mol.<sup>52</sup>

Even if the vinylene units are not in the same plane as the phenylene rings, the deviation from planarity is expected to be relatively small, producing only minor change in electronic properties of the vinylene copolymers. Generally, *trans* configurations with respect to the vinylene linkage have been observed through IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectroscopic measurements,<sup>53</sup> though in poly[(*m*-phenylenevinylene)-*alt*-(*p*-phenylenevinylene)]<sup>54</sup> an appreciable amount of *syn* configuration has been found. To appreciate the effect of the *m*-phenylene unit in the planar conformation, we optimized planar structures for a variety of phenylenevinylene copolymers with *trans* configurations as shown in Figure 8 and obtained the corresponding electronic structures of the copolymers.

For poly(*p*-phenylenevinylene) (PPV), poly(*m*-phenylenevinylene) (PMPV), and poly(fluorenediylvinylene) (PFIV), two different types of isomers are predicted to essentially possess the same stability and electronic properties. On the basis of these results, we examined the electronic structures of only one type of isomer for poly(fluorenediyl vinylene-*co-p*-phenylenevinylene) (PFIVPPV), poly(*m*-phenylenevinylene-*co-p*-phenylenevinylene) (PMPVPPV), and poly(*m*-phenylenevinylene-*co*-fluorenediylvinylene) (PMPVFIV). The

results are summarized in Table 3. The closest H...H distances in the planar structures for these vinylene-phenylene copolymers, except that for PMPVFIV, are similar to that found in the twisted PPP with a torsion angle of  $20^\circ$ , supporting that these copolymers may have a planar structure in the solid state. The H...H distance in PMPVFIV is calculated to be 1.87 Å, suggesting that the polymer chain may be twisted even in the solid state.

The calculated HOMO–LUMO gaps (2.70 eV) for both types of PPV isomers are comparable with the experimental observations<sup>55</sup> of 2.6–3.1 eV. Woodruff<sup>56</sup> found evolution of an additional absorption peak around 500 nm (2.5 eV) of PPV films prepared from freshly synthesized and undialyzed poly(sulfonium chloride) salt. This peak was also observed in the reflectance spectra of oriented PPV and assigned to the  $\pi$ – $\pi^*$  transition associated with the 0–0 vibronic transition.<sup>57</sup>

When *p*-phenylene units are replaced with fluorene units, the HOMO–LUMO gap is predicted to increase by 0.3 eV. This is due to the fact that in fluorene there are two phenylene units, which produce a larger HOMO–LUMO gap. The replacement does not change the HOMO energy level but lifts the LUMO energy level. The same trend is found in PFIVPPV. The HOMO–LUMO gap of PFIVPPV is between the gaps of PPV and PFIV, in parallel with the ratio of phenylene to vinylene unit. The calculated HOMO–LUMO gap of PFIVPPV is comparable with absorption  $\lambda_{\text{max}}$  values of poly(9,9'-di-*n*-hexylfluorenediyl vinylene-*alt-p*-phenylenevinylene) films<sup>11</sup> and poly[9,9-*n*-dihexyl-2,7-fluorenediylvinylene-*alt*-2-methoxy-5-(2-ethylhexyloxy)-*p*-phenylenevinylene] films:<sup>58</sup> 410 nm (3.02 eV) and 430 nm (2.88 eV), respectively.

As expected from our comparative study on PPP and PMP, when *p*-phenylene units are substituted with *m*-phenylene units, a large change in the electronic structures appears in the copolymers. In comparison with those of *p*-phenylenevinylene copolymers, the HOMO and LUMO levels of *m*-phenylenevinylene copolymers are lowered and elevated, respectively, resulting in large HOMO–LUMO gaps for the copolymers. This comes from the nodal nature of the HOMO and LUMO of the *m*-phenylene units, as described in the previous section. It is remarkable that the HOMO–LUMO gap of a *m*-phenylene-containing polymer drastically decreases as the conjugation length increases from PMP to PMPVPPV and PMPVFIV via PMPV. This indicates that the effect of the nodal nature is weakened with conjugation length.

The HOMO–LUMO gap of PMPVFIV is predicted to be similar to that of PMPVPPV while the gap of PPV is estimated to be narrower than that of PFIV. This fact also comes from the reduced effect of the nodal nature in PMPVFIV because the conjugation length increases due to two phenyl rings in the fluorene unit. The



calculated HOMO–LUMO gap of PMPVFIV is comparable with the experimental observations (3.25 eV)<sup>11</sup> from the UV–vis absorption peaks of poly(9,9'-di-*n*-hexylfluorenediylvinylene-*alt*-*m*-phenylenevinylene) films. The absorption peak of alkoxy-substituted PMPVPV films,<sup>54,59</sup> however, has been observed at a lower photon energy of 3.0 eV, presumably due to the electron-donating nature of alkoxy groups.

## Conclusions

AM1 band calculations for a single chain of the polyphenylenes predict that a PMP chain is twisted in the ground state as much as PPP and PFI chains are. Moreover, the energy difference between the twisted and planar conformations of PMP is also similar to those found in PPP and PFI. Therefore, the broken conjugation of PMP chains is apparently not due to twisting of the conjugated chains.

On the other hand, there is much evidence that broken conjugation of the *m*-phenylene unit arises from the inherent nature of the frontier MOs. That is, in comparison with PPP, PMP shows little variation of the HOMO–LUMO gap with the torsion angle, relatively flat bands near the Fermi level, and a large band gap. These facts demonstrate that  $\pi$ -conjugation along a PMP chain is quite weak even at the planar structure. Examination of the MOs of PMP reveals that the weak conjugation comes from the nodal nature of the frontier MOs. This fact is further supported by comparison of electronic structures of phenylenevinylene copolymers.

In conclusion, we suggest that the broken conjugation of PMP chains is not solely due to twisting of the conjugated chains but due to the phase and coefficient relationships in the orbitals of PMP.

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