Electronic Properties and Conformation Analysis of π-Conjugated Distyryl Benzene Derivaties

Cheol-Ju Kim

Department of Chemistry, Chonbuk National University, Chonju 561-756, Korea
Received September 28, 2001

A quantum-chemical investigation on the conformations and electronic properties of bis[2-{2-methoxy-4,6-di(*t*-butyl)phenyl}ethenyl]benzenes (**MBPBs**) as building block for π-conjugate polymer are performed in order to display the effects of *t*-butyl and methoxy group substitution and of kink(ortho and meta) linkage. The conjugation length of the polymers can be controlled by substituents and kink linkages of backbone. Structures for the molecules. *o*-, *m*-, and *p*-**MBPBs** as well as unsubstituted *o*-, *m*-, and *p*-**DSBs** were fully optimized by using semiempirical AM1. PM3 methods, and *ab initio* HF method with 3-21G(d) basis set. The potential energy curves with respect to the change of single torsion angle are obtained by using semiempirical methods and *ab initio* HF/3-21G(d) basis set. The curves are similar shape in the molecules with respect to the position of vinylene groups. It is shown that the conformations of the molecules are compromised between the steric repulsion interaction and the degree of the conjugation. Electronic properties of the molecules were obtained by applying the optimized structures and geometries to the ZINDO/S method. ZINDO/S analysis performed on the geometries obtained by AM1 method and HF/3-21G(d) level is reported. The absorption wavelength on the geometries obtained by AM1 method is much longer than that by HF/3-21G(d) level. The absorption wavelength of **MBPBs** are red shifted with comparison to that of corresponding **DSBs** in the same torsion angle because of electron donating substituents. The absorption wavelength of isomers with kink(orth and meta) linkage is shorter than that of para linkage.

Keywords : Conformation analysis, Potential energy curve, HOMO-LUMO gap, Conjugation length. Electronic properties.

Introduction

It has been well-known that poly(*p*-phenylene vinylene) (PPV) derivatives were utilized as the materials for conductive polymers. light emitting devices (LED). and electro-optic devices.[1-3] They have a good properties of π-conjugated electronic structure in polymer backbone. Conformation and physical properties. such as electronic. photophysical. and photonic properties of PPV and its derivatives have been extensively studied to explain the structure-properties relationship.[4-6] Although EL polymeric materials offer a number of advantages and various visible colors by the control of conjugation length theoretically. blue light-emitting materials show many problems. such as unstable mechanical properties. low processibility. and low quantum yield. The interest in the control of the conjugation length in polymers results from the purpose to control the color of the emission in LED devices. which would be related to absorption maximum in their absorption spectra.[3,4]

In conformational studies. the investigations for one torsion angle change were extremely performed not only on PPV derivatives. but also on various conjugated systems. such as biphenyl. 2,2'-bithiophene. 2,2'-bifuran. and 2,2'-bipyrrole. etc..[5,8,9] For PPV derivatives. the study on the

conformation showed that the twisted isomers are more stable than the coplanar ones due to the steric repulsion between the substituents with the vinylene. *Ab initio* calculations were used to explain the conformation of PPVs as well as various akyl-. alkoxy-. and other group-substuted derivatives. Conformational studies of dimethoxy- or dimethyl-substitued *trans*-stilbene at the *ab initio* HF 3-21G level that the former is of the coplanar structure due to the formation of hydrogen bonds between the methoxy group and the vinylene hydrogen. but in the latter the torsion angle is about 30° because of the repulsion between the methyl groups in ortho of the vinylene linkage and the hydrogen atom of vinylene. In recent. the investigation of potential energy curves in di. tri. or tetramethoxy-substituted PPVs at 6-31G(d) level were reported and the torsion angles depend on the substituted sites of methoxy groups. For the tetramethoxy-substituted PPVs. the vinylene group are twisted by about 23° with respect to the phenyl ring because the methoxy groups rotate around C(sp²)-O bond to avoid strong repulsions. It was focused that π-conjugation of polymer backbone are affected by steric repulsion of substituents and delocalization of electrons for PPV derivatives.[6,7]

Several approaches to achieve control of conjugation length of PPVs has been reported. One of the approaches is that the control of the ratio of conjugated PPV units to unconjugated polymer in copolymers.[10] Alternative attempt is the incorporation of the *p*-. *m*-. and *o*-phenylene unit in the polymer main chain and substitution of side groups with

*To whom correspondence should be addressed. Tel: +82-63-270-3419, Fax: +82-63-270-3408, E-mail: cjkim@moak.chonbuk.ac.kr

steric hinderance into the conjugated main chain.[3,11] To obtain blue light emission. one tried to incorporate *m-*. and *o*-phenylene units instead of *p*-phenylene unit in the polymer main chain. Ortho-linked polymer has the same electronic structure as the *para*-linked polymer. but it is expected that the conjugation length of *ortho*-linked polymer is shorter than *para*-linked polymer. because π-conjugation of polymer backbone was interrupted by *ortho-* and meta linkage. yielding a reduction of the π-conjugation length.[11] Son *et al.*[12] reported that cis linkage interrupt the conjugation, even though trans linkage have almost the same electronic structure. In recent. a distyrylbenzene derivative with two *t*-butyl groups and one benzyloxy group as bulky substituents each outer phenyl ring was systhesized by Lee *et al.*.[3(d)] The compound dispersed in the polycarbonate matrix showed a maximum absorption at about 358 nm and the emission at 432 nm. It can be expected that the compound is a candidate for blue light emitter.

In this paper, bis[2-{2-methoxy-4.6-di(*t*-butyl)phenyl}-ethenyl]benzenes (**MBPBs**) were chosen to investigate the effect of the conformations and electronic properties with respect to the control of the conjugation length by changing the position of vinylene group in PPV derivatives. It is shown that **MBPBs** are good candidates for blue light-emitting materials. To discuss the effect of the kink linkages for conjugation length we will obtain the potential energy curves and first transition wavelengths of *o-*. *m-*. and *p-***MBPBs**. It was observed that the potential energy curves of **MBPBs** calculated by AM1 method are qualitatively similar to those found out by the *ab initio* calculations. To obtain reliable information about conformation, we will report on a conformational analysis of **MBPBs** using HF/3-21G(d) *ab initio* calculations. We selected the HF/3-21G(d) *ab initio* method because of limitation of relatively large size of the molecules and the cost of calculations. In many cases, the potential energy curves with respect to the change of single torsion angle have obtained. However, there is only few study on the system with many torsion angle parameters. To estimate the absorption maxima of UV spectra with respect to conformational change, the ZINDO/S semiempirical method was employed. The first electronic transition energies were calculated from the ZINDO/S method using the optimized geometry obtained at each computational level.

Methods

MBPB is symmetric molecule which two identical substituents on benzene ring is 2-{2-methoxy-4.6-di(*t*-butyl)-phenyl}ethenyl moietie. This molecule have three (*o-*. *m-*. and *p-*) isomers according to the position of the substituents. *o-* and *m-* **MBPB** isomers are kink linkage of backbone in comparison with *p-* **MBPB**. It is well known that the kink linkages are mainly attributed to decrease of π-conjugation. As shown in Figure 1, the incorporation of methoxy-substituent in 2-position and *t*-butyl-substituents in 4- and 6-positions experiences a large steric hinderance, which induces a large torsion of the molecules. giving rise to an increase in
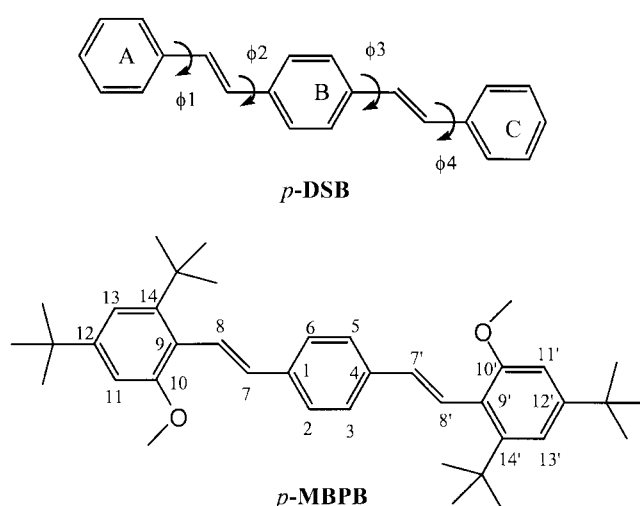
Figure 1. Structures of **DSBs** and **MBPBs**. Torsion angles (ψ_1 or ψ_4) of phenyl group (A or C) with respect to vinylene group (ψ_1: C_7-C_8-C_9-C_{10} ψ_4: C_7-C_8-C_9-C_{10}) and torsion angles (ψ_2 and ψ_3) of phenyl group (B) group with respect to vinylene group (ψ_2: C_8-C_7-C_1-C_2, ψ_3: C_8-C_7-C_4-C_5).

the rotation barrier against planarity. To obtain the optimized structures of **MBPBs**, semiempirical AM1, PM3 methods, and *ab initio* HF calculation with 3-21G(d) basis set are employed.[6,13] Structures of *o-*, *m-*. and *p-***MBSBs** were fully optimized by starting from initial structures of various torsion angles, respectively. One of the input structures were planar between phenylene units and vinylene group ($\psi_1=\psi_4=$ 0.0° and $\psi_2=\psi_3=0.0$°). Another structures were the conformations which phenyl groups were almost perpendicular to vinylene group ($\psi_1=\psi_4=90$° and $\psi_2=\psi_3=180$°). The other structure was the conformation which phenyl groups were almost perpendicular to vinylene group ($\psi_1=\psi_4=90$° and $\psi_2=\psi_3=90$°). The parameters of the optimized structures were summarized in Table 1. To investigate the effect of substituents, the optimized structures were compared with unsustituted PPV. *o*(*m*, *p*)-distyrylbenzenes (**DSBs**). To investigate the stable conformational structures for the building block of the polymers, *ab initio* HF calculations were carried out with the 3-21G(d) basis set in the Gaussian 98 package.[13] To display the potential energy curves for a variety of **MBPBs**, the torsional angles (ψ_1 and ψ_4) between the phenyl groups and the vinyl unit were fixed at optimized torsion angles. The torsion angles (ψ_1 and ψ_4) between the phenyl groups and the vinyl unit varies by 10 degree as shown in Figure 1 and the torsional angle was held fixed while the reminder of geometrical parameters of the molecule were fully optimized. During the geometrical optimizations, the phenyl units were restricted to the trans conformation with parallel geometry with respect to vinylene group.

Electronic properties of the molecules are obtained by applying the optimized structures and the selected geometries (maxima or minima) of potential curves to the ZINDO/S method.[13] The ZINDO/S method including configuration integral as employed in the *Gaussian* 98 package was used to calculate the singlet-singlet electronic transition energies

Table 1. Optimized geometric parameters. Bond lengths (Angstrom) and torsion angles (degree)

Molecules	Methods	C1-C7	C7-C8	C8-C9	ψ_1	ψ_2	ψ_3	ψ_4
p-DSB	HF/3-21G(d)	1.476	1.325	1.477	26.9	25.5	25.5	26.9
	AM1	1.452	1.344	1.453	22.9	22.1	22.1	22.9
m-DSB	HF/3-21G(d)	1.478	1.325	1.478	27.2	27.5	27.5	27.2
	AM1	1.454	1.343	1.453	23.0	23.6	23.6	23.0
o-DSB	HF/3-21G(d)	1.482	1.325	1.477	24.0	42.9	42.9	24.0
	AM1	1.456	1.343	1.453	21.9	35.1	32.1	22.0
p-MBPB	HF/3-21G(d)	1.477	1.323	1.487	92.6	156.4	156.4	92.6
	AM1	1.453	1.343	1.457	48.9	159.0	159.0	48.9
m-MBPB	HF/3-21G(d)	1.484	1.324	1.489	93.0	157.8	157.8	93.0
	AM1	1.454	1.343	1.457	48.7	158.7	158.7	48.7
o-MBPB	HF/3-21G(d)	1.484	1.324	1.489	45.7	36.8	58.5	104.3
	AM1	1.456	1.343	1.453	46.4	30.9	40.5	132.0

of the optimized conformers. To investigate the change of UV spectroscopic transitions with respect to the torsion angle, the optimized structures were selected. By using the results, the dependency of conjugation for the energy gaps is analyzed. The ZINDO/S method has been shown to yield reliable electronic structures for a wide variety of conjugated polymers, including those with PPV derivatives.[4,5,8]

Results and Discussion

Equilibrium Structures of DSBs and MBPBs For **DSBs** and **MBPBs**, optimized structures of the lowest energy conformer of each as obtained by AM1 method and HF/3-21G(d) method are displayed in Table 1. The atomic numbering is indicated in Figure 1. For unsubstituted PPV building block. o-, m-, and p-**DSBs**, the AM1 calculations predicted that the vinyl unit is twisted by 22.9°, 23.0°. and 21.9° with respect to the phenyl ring. respectively. The energy barrier over the planar conformation is very small as shown in Table 2. The *ab initio* calculations for unsubstituted PPV building block, **DSBs**, support the AM1 results. producing a quit flat potential energy curve up to the torsion angle of 30°. In the case of unsubstituted o-. m-. and p-**DSBs**, the torsion angles are considerably small. For para and meta isomers, the outer phenyl rings were rotated about vinylene linkages by 26.9° and 27.2° in *ab initio* calculation and 22.9° and 23.0° at AM1 calculation. Torsion angles for the inner phenyl ring (B) with respect to vinylene group are 25.5° (for p-**DSB**) and 27.5° (for m-**DSB**) from *ab initio* calculation. For ortho isomer, the torsion angles for the inner phenyl ring and the outer ring (A or C) with respect to vinylene group are 24.0° and 42.9°, respectively, in *ab initio* calculation. The outer torsion angles in o-**DSB** are smaller than that in p-**DSB** and m-**DSB**. but the inner torsion angles are larger than that in p-**DSB** and m-**DSB**. The twisted conformation in o-**DSB** is due to the steric repulsion between inner phenyl group and hydrogen of vinylene. Finally, the outer phenyl rings in p-**DSB** and m-**DSB** were distorted by about 50° with respect to the inner phenyl ring, but for o-**DSB** the outer rings are largely rotated by about 70°. For *trans*-stilbene. similar

results were already obtained at the 3-21G level by Lhost *et al.*[14] Another author reported that the phenyl rings were rotated about the vinyl groups by 7.9 ± 7.1° from the planar conformation by elastic neutron scattering diffraction measurements.[15] It imples that the potential energy curve is actually flat around the planar conformation.

Although torsion angles for **DSBs** in *ab initio* calculation are very close to that in AM1 calculation, the torsion angles for **MBPBs** are a little different manner each other. In the case of o-. m-, and p-**MBPBs**, the torsion angles are much larger than that of unsubstituted **DSBs**. For *para* and *meta* isomers, the outer phenyl rings were rotated about vinylene linkages by 90.0° in *ab initio* calculation. Torsion angles for the inner phenyl ring with respect to vinylene group are 151.6° (for p-**MBPB**) and 157.8° (for m-**MBPB**) in *ab initio* calculation. The outer ring with substituents are distorted with compare to the inner ring. For ortho isomer, the optimized structure is not symmetric conformation because of the large steric repulsion between vinylene hydrogens as well as substituents. When the torsion angles between the outer phenyl ring and inner one in o-**MBPB** are compared with p- or m-**MBPB**, the outer phenyl rings in the latter were distorted by about 20° with respect to the inner phenyl ring. but for the former the outer rings are largely rotated by about 80°. Finally, the torsion angles between the outer phenyl ring and inner one in o-**MBPB** is very large.

For unsubstituted and substituted molecules (**DSBs** and **MBPBs**). the single bond lengths in vinylene group for *ab initio* calculation are longer than that for AM1 calculation. However, the double bond length of the group in *ab initio* calculation is shorter than the length from AM1 result. Finally, in *ab initio* calculation the bond alternations are 0.151-0.160 Å and in the case of AM1 result the alternations are 0.108-0.113 Å. The differences for the bond alternation with respect to calculation methods affect in the obtained optical properties for unsubstituted and substituted molecules. The effect of the bond alternation in optical properties will be discussed later.

Conformational Analysis of DSBs and MBPBs. Recently, conformational analysis of organic molecules as

Table 2. Relative energies (in kcal/mol) and torsion angles (ψ) of DSBs and substituted **MBPBs** isomers are obtained by *ab initio* calculations perfomed at the HF/3-21G* level and AM1 methods

Molecules	planar I[a]	twist	perpendicular[b]	planar II[c]
p-DSB	0.66(0.23)[d]	0.0 (26.9°, 22.9°)[e]	4.86(3.38)	0.66(0.23)
m-DSB	0.58(0.27)	0.0 (27.2°, 23.0°)	4.80(3.38)	0.58(0.27)
o-DSB	0.43(0.24)	0.0 (24.0°, 21.9°)	5.12(3.49)	0.43(0.24)
p-MBPB	6.42(4.37)	0.74(0.07) (48.9°, 48.9°)	0.0	13.32(14.81)
m-MBPB	3.96(5.98)	0.76(0.08) (46.8°, 48.8°)	0.0	13.35(14.77)
o-MBPB	6.98(6.41)	0.0 (45.7°, 30.8°)	2.14(0.42)	18.98(16.14)

[a]Planar I conformation: $\psi_1 = \psi_4 = 0.0°$. [b]Perpendicular conformation: $\psi_1 = \psi_4 = 90.0°$. [c]Planar II conformation: $\psi_1 = \psi_4 = 180.0°$. [d]Values in parentheses are the relative energies for optimized structures by AM1 method. [e]First angle in parenthesis is the optimized angle by the HF/3-21G* level and second one is the optimized angle by AM1 method.

the model for PPV building block have been carried out from *ab initio* calculations using a various of basis sets. For the methoxy-substituted thiophene oligomers, Dicesare *et al.* reported that the HF/3-21G* and HF/6-31G** basis sets give identical potential energy surface with similar energy barriers and minima.[5] We have used the HF/3-21G(d) method as the more elaborated calculation in this paper to have resonable calculation times and because this basis set gives similar result in comparison with more elaborated basis sets. Potential energy curves of the unsubstituted **DSBs** and methoxy- and *t*-buthyl-substituted molecules. **MBPBs** isomers are obtained by *ab initio* 3-21G(d) as well as semiempirical (AM1 and PM3) calculation as shown in Figures 2-7. The energies and torsion angles of the minima and maxima of each molecule as obtained by the HF/3-21G(d) method are displayed in Table 2.

In optimized structures. the torsion angles between inner phenylene group (B) and vinylene group as well as between outer phenyl group (A and C) and vinylene group are displayed various values. but not planar. The *p*-orbitals of phenylene carbons are perpendicular to the *p*-orbitals of vinylene carbons. so that the resonance structure between phenylene and vinylene carbons may not expected. In the case of unsubstituted stilbene, it was reported that the potential energy curve is flat up to the torsion angle of 30° by using 3-21G basis set.[13] For dimethoxy PPVs, it was reported that the optimal torsion angles are in the range 20-30° and the energy difference between the planar and the twisted conformations varies from 0.2 to 1.0 kcal/mol by using 3-21G(d) basis set.[6] In our model. methoxy group and *t*-butyl adapted to the outer phenyl ring are attributed to increases torsion angle between phenylene and vinylene group because of the steric repulsion.[7,9]
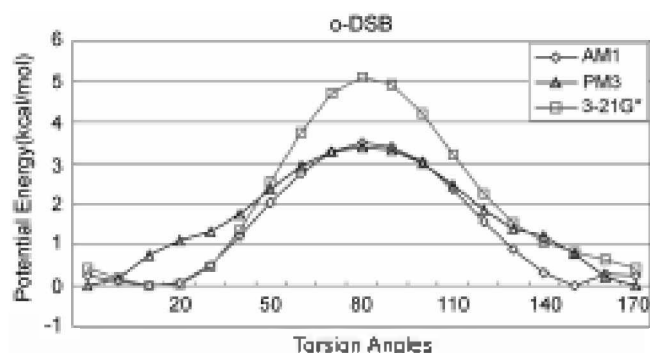
For the conformation analysis of **DSBs**. the twisted conformers are more stable than the coplanar structure
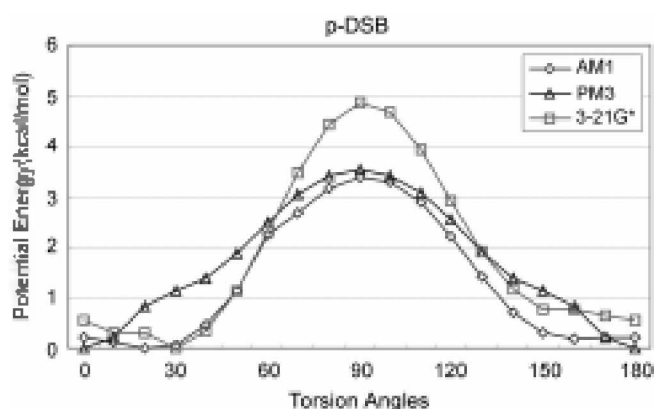
Figure 2. *Ab initio* 3-21G(d). PM3. and AM1 potential energy curve for *p*-**DSB**. Torsion angles of phenyl groups (A and C rings) with respect to vinylene group are varied with $\psi_1 = \psi_4$.
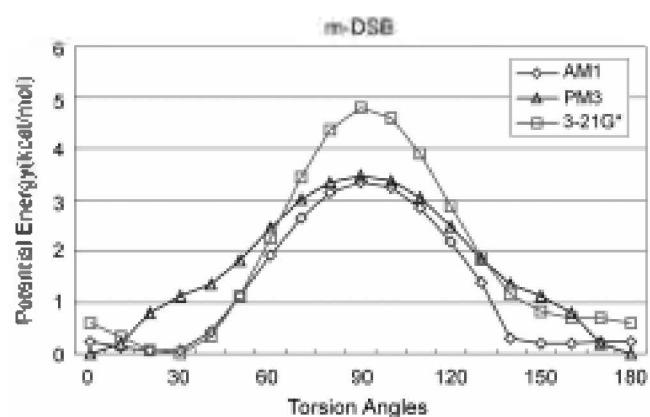
Figure 3. *Ab initio* 3-21G(d), PM3, and AM1 potential energy curve for *m*-**DSB**.

Figure 4. *Ab initio* 3-21G(d), PM3, and AM1 potential energy curve for *o*-**DSB**.

because of the steric repulsion. The potential energy curves of **DSBs** are displayed in Figures 2-4. It is clear that the HF/3-21G* and AM1 method gives similar potential energy surfaces except maximum energy barriers. However, the potential energy surfaces obtained from semiempirical PM3 method is not considerably realistic. The minimum structures were coplanar conformation where we expect some steric hinderance. even though the potential maximum is

similar to that of the AM1 method. The potential energy curves for *o*-, *m*-. and *p*-**DSB**s are very similar with respect to each calculation method.

Ab initio calculations performed at the HF/3-21G* level show that the most stable conformations of **DSB**s corresponds to twist structures with torsion angles around 25° as shown in Figures 2-4 and the twisted conformers of *o*-, *m*-. and *p*-**DSB**s are found to be more stable than the planar structure by 0.66, 0.58. and 0.43 kcal/mol, respectively, as shown in Table 2. Two factors are involved in the description of the molecular structure of the PPV derivatives. The steric hinderance between the hydrogen of phenyl group and that of vinyl group, which favors twisted conformations and the π-electron conjugation along the molecular frame, which favors the planarity of the molecule. The equilibrium structures of **DSB**s isomers can be considered as a compromise between these two factors. However the energy barrier between the twisted conformer and planar conformer is so small. It is expected that packing effects are enough to overcome these small energy barrier in solid state. The twisted conformers of *o*-, *m*-. and *p*-**DSB**s are found to be far more stable than the perpendicular structure by 4.86, 4.80. and 5.12 kcal/mol. respectively. The rotational energy barriers between the twisted and the perpendicular conformer are much higher than those between twisted and planar conformer. The perpendicular conformers are unfavorable energetically because π-electron conjugation in the molecular frame is interrupted. The barriers from AM1 caculation show considerably smaller than the results by *ab initio* calculations.

According to the conformation analysis of *o*-. *m*-. and *p*-**MBPB**s, the structures which the outer phenyl ring is perpendicular to the vinyl group are more stable than the coplanar or twist structure because of the steric repulsion of substituents. The potential energy curves of **MBPB**s are displayed in Figure 5-7. As shown in the conformational analysis of **DSB**s. the HF/3-21G(d) and AM1 method gives similar potential energy surfaces for **MBPB**s each other. The result from *ab initio* calculations performed at the HF/3-21G(d) level show that the most stable conformations of *p*-
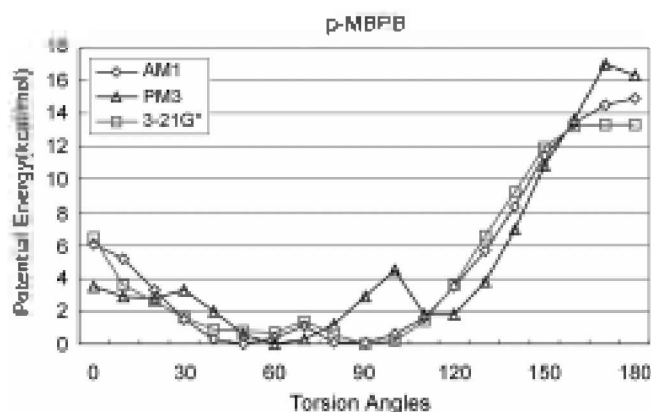

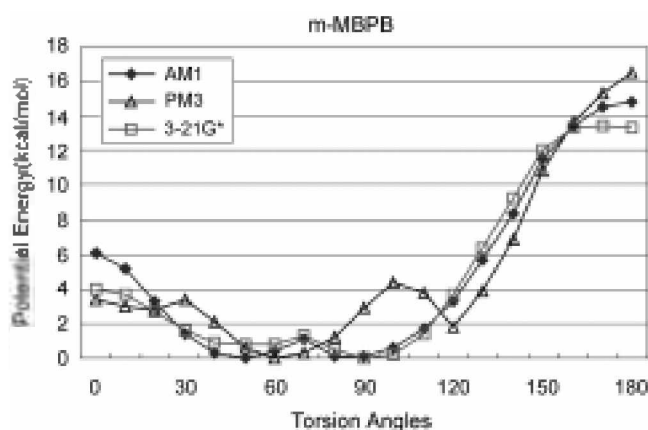**Figure 6.** *Ab initio* 3-21G(d), PM3, and AM1 potential energy curve for *m*-**MBPB**.
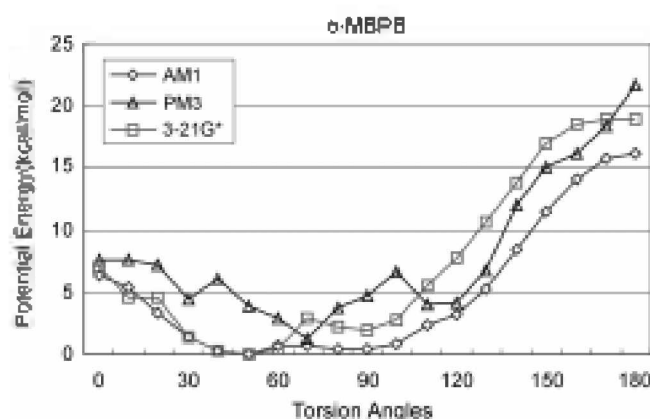

Figure 7. *Ab initio* 3-21G(d), PM3, and AM1 potential energy curve for *o*-**MBPB**.

and *m*-**MBPB**s corresponds to the perpendicular structure with torsion angles around 90° and the perpendicular structure of *p*- and *m*-**MBPB**s are found to be more stable than the twisted conformer by 0.74 and 0.76 kcal/mol, respectively, as shown in Table 2. The energy barriers between the perpendicular and the twisted conformers are obtained as 1.34 kcal/mol for *p*-**MBPB** and 1.32 kcal/mol for *m*-**MBPB**. For *p*-**MBPB** isomer, the potential energy of the planar structures are higher than those of the perpendicular structures. Z,Z and E,E conformers, by 6.42 and 13.32 kcal/mol. respectively. In the case of *m*-**MBPB** isomer. the energies are 3.96 and 13.35 kcal/mol. respectively. However, the most stable conformer of *o*-**MBPB** are found to the twisted structure with torsion angle 45.7°. The twisted conformer of *o*-**MBPB** is found to be more stable than the perpendicular conformer by 1.98 kcal/mol. The energy barrier between the perpendicular and the twisted conformers are obtained as 2.94 kcal/mol. The potential energies of two planar conformers of *o*-**MBPB** are higher than that of the twisted structure by 6.98 and 18.98 kcal/mol. respectively.

The origin of the potential energy curves of **MBPB**s results from steric repulsion between methoxy group and hydrogen atom in vinylene unit. The nearest OH distances at

Figure 5. *Ab initio* 3-21G(d), PM3, and AM1 potential energy curve for *p*-**MBPB**.

Table 3. ZINDO/S results for electronic transition wavelengths (nm) of **DSBs** and **MBPBs** for optimized structures by using *ab initio* HF/3-21G (d) and AM1 methods

Molecules	planar I	twist[a]	perpendicular	planar II
p-DSB	315(337)[b]	307(333)	287(296)	315(337)
m-DSB	295(307)	296(307)	288(298)	295(307)
o-DSB	293(321)	291(317)	281(295)	293(321)
p-MBPB	328(348)	303(321)	290(301)	327(349)
m-MBPB	304(318)	293(304)	290(302)	303(317)
o-MBPB	312(332)	290(310)	284(298)	303(323)

[a]The transition wavelengths at angles given in Table 2. [b]Values in parentheses are the transition wavelengths for optimized structures by AM1 method.

optimized structures of **MBPBs** are around 2.30 Å which is longer than the distances (about 2.0 Å) at the corresponding planar structures. This fact results from the compromise 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 vander Waals radii of the atoms (O: 1.4 Å and H: 1.2 Å).[16] The steric repulsion is predominant, although a π-conjugation favor the planar conformer due to the large overlap between the phenylene and the vinylene units.

Electronic Properties of DSBs and MBPBs. The first electronic transition energies were calculated from ZINDO/S semiempirical method using the optimized geometry obtained at each calculation levels. For *o*, *m*, and *p*-**MBPBs** and **DSBs** the transition wavelengths in optimized geometries are displayed in Figure 8. The transition energies are absolutely depend on the torsion angle between vinylene and phenyl rings and electron donor properties of methoxy group. The predicted λ_{max} values for optimized structures of *o*, *m*, and *p*-**MBPBs** are more red shifted than that for the corresponding **DSBs** at each torsion angle. The red shift calculated is attributed to the electron donor properties of the methoxy group and steric hinderance of *t*-butyl group.

The electronic transition energies from ZINDO/S calculation strongly depend on the optimized geometric parameters in the calculations for the same torsional angle. In fact, transition energies for optimized structures from semiempirical AM1 and PM3 methods are smaller than those for geometries optimized at *ab initio* calculation. Each geometrical parameter may influence the transition energies obtained by ZINDO/S calculation. For methoxy-substituted bithiophene system, DiCesare *et al.* reported that the structure calculated from *ab initio* method gives the methoxy groups as twisted relatively to the molecular frame. whereas in the structure from semiempirical methods methoxy groups placed in coplanar with the rest of the molecule.[5] However. the transition energies for unsubstituted **DSBs** are displayed the same tendency as methoxy-substituted **MBPBs** in our calculation. To find another geometrical factor for the transition energy. we have investigated the effect of the bond alternation of vinylene linker group for each calculation. It was mentioned in equilibrium geometries that the bond
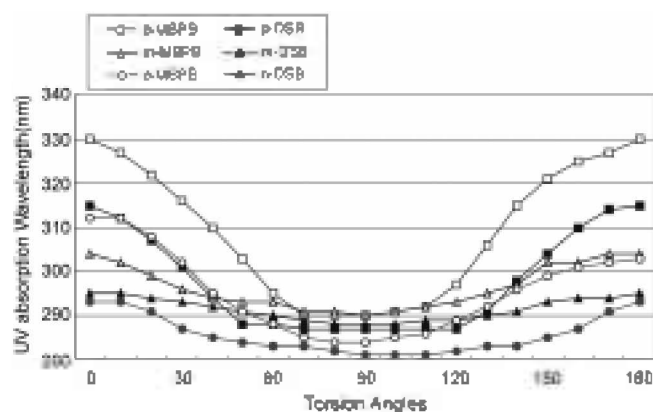
Figure 8. First singlet-singlet electronic transition wavelengths (nm) of **DSBs** and **MBPBs** predicted by ZINDO/S calculation from starting geometries at *ab initio* 3-21G(d) level and for various torsion angles.

alternation of the structure optimized at the HF/3-21G(d) method gives larger than that of the structure from semiempirical methods. It is indicated that the result of AM1 calculation give more conjugate geometry than *ab initio* calculation.

For each calculation method used to obtain optimized geometries. the absorption wavelength is considerably different. However. the wavelength decreases as the molecule becomes more twisted. This tendency is well known and is due to decrease in the overlap between p_z orbitals of carbon atoms in the phenyl ring and vinyl group as the torsional angle increase. This induces to a reduction in the electronic conjugation length and an increase in the electronic transition energy.

$$\lambda_{max}(\text{Predict}) = \lambda_0 - (\Delta\lambda/2)(\sin\varphi + \sin^2\varphi).$$

where λ_0 is the absorption wavelength of optimized geometry at torsion angle. $\varphi = 0°$, and $\Delta\lambda$ is the difference between the absorption wavelengths at 90° and 0°.

The electronic transition energies at the potential minima (or maxima) for *o*-. *m*-, and *p*-**MBPBs** and **DSBs** are shown in Table 3. For unsubstituted *o*. *m*, and *p*-**DSBs** the torsion angles, ψ_1 (and ψ_4) are 26.9°. 27.2°, and 24.0°, respectively, from result at the HF/3-21G* level. The torsion angles are not different each other. The absorption wavelengths of *o*, *m*, and *p*-**DSBs** are calculated at optimized geometry from HF/3-21G* level and AM1 method. The wavelength from the former are 307. 292. and 289 nm. respectively and the values from the latter are 333, 307, and 317 nm, respectively. However. it is shown that electronic properties of *o*-, *m*-, and *p*-**MBPBs** strongly depend on the planarity of phenyl groups and vinylene groups. For *p*-**MBPB** structure with ψ_1=90°, the energy gap increase by 0.52 eV compared with its planar structure. In the cases of *o*, and *m*-**MBPBs** with ψ_1=90°, the energy gap increase by 1.29 and 1.15 eV, respectively, compared with its planar structure.

The planarity between vinylene and phenyl group is affected to produce the changes in electronic properties.[4,6,7] HOMO-LUMO gaps are small by increasing the planarity.

At a torsion angle of 90°, the energy gaps of the conjugated systems increase to maximum due to the reduced π overlap between the phenyl ring and the vinylene unit. Since the interaction between the phenyl rings and the vinylene unit is antibonding in HOMO and bonding in the LUMO, the reduction of π overlap stabilizes the HOMO level, but destabilizes the LUMO level. The degree of the stabilization of the HOMO energy level is smaller in energy than the destabilization of the LUMO energy level.[6,7] For *o, m,* and *p-*MBPBs and DSBs the wavelength. λ_{max} values according to change of conformations are predicted as shown in as shown in Figure 8.

In summary, the potential energy curves are similar shapes each other in building block of PPV polymers. including the vinyl groups and phenyl groups. It is shown that the steric repulsion interactions between phenyl ring and vinyl group are subjected to similar type. Although we can synthesize the fully conjugate molecules, λ_{max} values according to change of conformations will changes because of the steric repulsion interaction and the difference of π-conjugation.

Conclusion

The potential energy surfaces predicted by AM1 and *ab initio* methods are quite shallow around the planar conformations (-40°~40°) for *o, m,* and *p-*DSBs, but around the perpendicular conformations (30°~120°) for *o, m,* and *p-*MBPBs. This fact results from the compromise between two factors, a repulsion interaction and a π-conjugation effect. The repulsion interation is mainly attributed to the short distances between hydrogen atoms on the phenylene and the vinylene unit for DSBs. However, in the case of MBPBs, there are repulsion not only between an oxygen atom in methoxy group and a H atom on the vinylene units. but also between hydrogen atoms on the inner phenylene and the vinylene units. The distances are too short compared to the sum of the vander Waals radii of H and O atoms, 1.4 Å for O and 1.2 Å for H. The π-conjugation effect results from the fact that the large overlap between the p orbitals of C atoms linking between the phenylene and the vinylene units gives stable conformation. For unsubstituted DSBs the π-conjugation effect is predominant, but for substituted MBPBs the repulsion interaction favors.

Another factor which is subject to π-conjugation is kinked structures of polymer backbone. *Ortho-* or *meta-*linkage of polymer backbone results in kinked structures which disrupt the conjugation in polymer. For *o, m,* and *p-*MBPBs the potential energy surfaces are similar each other, but the first transition wavelength of *o,* and *m-*MBPBs are considerably shorter wavelength than that of *p-*MBPB. Consequently, the π-conjugation length can be controlled by kink linkage. such as *ortho-* or *meta-*linkage of polymer backbone, although

stability and packing of polymers should be considered.

References

1. Bradley, D. D. D. *Synth. Metals* **1993**, *54*, 401.
2. Kraft. A.: Grimsdale. A. C.: Holmes. A. B. *Angew. Chem. Int. Ed.* **1998**, *37*, 402.
3. (a) Song. S. Y.: Shim. H. K. *Synth. Metals* **2000**, *111-112*, 437. (b) Ahn, T.: Song. S.-Y.: Shim. H.-K. *Macromolecules* **2000**, *33*, 6764. (c) Ahn, T.: Jang, M. S.: Shim, H.-K.; Hwang, D.-H.: Zyung. T. **1999**, *32*, 3279. (d) Pang. Y.; Li, J.: Hu. B.: Karasz, F. E. *Macromolecules* **1998**, *31*, 6730. (e) Ryu. H. K.: Kim. W. Y.: Nahm. K. S.: Han. Y. B.: Lee. C.: Lee. Y. S. *Bull. Korean Chem. Soc.* **2001**, in press.
4. (a) Meyers, F.: Heeger. A. J.: Bredas. J. L. *J. Chem. Phys.* **1992**, *97*, 2750. (b) Stalmach, U.: Detert. H.: Meier, H.: Gebhardt. V.; Haarer. D.: Bacher, A.: Schmidt. H.-W. *Optical Materials* **1998**, *9*, 77.
5. (a) Belletete. M.: Mazerolle. L.: Desrosiers. N.: Leclere. M.: Durocher. G. *Macromolecules* **1995**, *28*, 8587. (b) Dicesare. N.: Belletete. M.; Leclere. M.; Durocher, G. *J. Mol. Struct. (Theochem)* **1999**, *467*, 259. (c) Dicesare, N.: Belletete, M.: Raymond, F.: Leclere, M.; Durocher. G. *J. Phys. Chem.* **1997**, *A101*, 776. (d) Dicesare. N.: Belletete. M.: Leclere. M.: Durocher. G. *J. Phys. Chem.* **1998**, *A102*, 5142.
6. Hong, S. Y. *Bull. Korean Chem. Soc.* **1999**, *20*, 42.
7. Hong, S. Y.: Marynick. D. S. *Macromolecules* **1992**, *25*, 3591.
8. Peri. J. W.: Hwang, L.; Yu. W.; Heeger. A. J. *Macromolecules* **2000**, *33*, 2462.
9. Karpfen. A.: Choi. C. H.: Kertesz. M. *J. Phys. Chem. A* **1997**, *101*, 7426.
10. (a) Miller. R. D.: Klaerner. G. *Macromolecules* **1998**, *31*, 2007. (b) SoKolik. I.; Yang. Z.: Karasar. F. E.: Morton. D. C. *J. Appl. Phys.* **1993**, *74*, 3584.
11. Jacobs. S.: Eevers, W.: Verreyt. G.: Geise. H. J. *Synthetic Metals* **1993**, *61*, 189.
12. Son. S.: Dodabalapur. A.: Lovinger. A. J.: Galvin. M. E. *Science* **1995**, *269*, 375.
13. (a) Frisch. M. J. *et al. Gaussian 98*: Gaussian, Inc.: Pittsburgh. Pennsylvania, 1998. (b) Foresman, J. B.: Frisch, A. Geometry Optimization, in *Exploring Chemistry with Electronic Structure Methods*. Gaussian Inc.: 1996.
14. Lhost. O.: Bredas. J. L. *J. Chem. Phys.* **1992**, *96*, 5279.
15. Mao. G.: Fischer. J. E.: Karasz. F. E.: Winokur. M. J. *J. Chem. Phys.* **1993**, *98*, 712.
16. Weast, R. E. *Handbook of Chemistry and Physics*, 70th Ed.; CRC Press Inc.: Bocaraton, Florida. U.S.A., 1990; p D-190.
17. Han. J. H.: Lee. Y. S.: Nahm. K. S.: Cho. E. H.: Ko. S. B.: Kim. C.-J.: Jeon. I. C.: Lee. W. H.: Suh. E. K.: Lee. Y. H. *Bull. Korean Chem. Soc.* **1999**, *20*, 1093.
18. Ni. J. P.: Ueda. Y.; Ichino. Y.; Yase, K.; Wang, D. K. *Thin Solid Film* **2000**, *363*, 86.
19. Yang. Z.: Sokolik. I.: Karasz, F. E. *Macromolecules* **1993**, *26*, 1188.