Geometrical and Electronic Structures of New π-Conjugated Pyrrole– and Furan–Nonheterocycle Copolymers

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The geometrical and electronic structures of new hypothetical pyrrole– and furan–nonheterocycle copolymers were theoretically investigated. Nonheterocycles include cyclopentadiene, silole, oxocyclopentadiene, and thiocyclopentadiene, whose homopolymers are of the quinoid forms in their ground states. AM1 band calculations show that in the ground states the aromatic forms of the copolymers containing cyclopentadiene or silole rings are more stable than the quinoid types, whereas the aromatic forms of the oxocyclopentadiene- or thiocyclopentadiene-containing copolymers are less stable. Modified extended Hückel band calculations predict that bandgaps of the copolymers in the ground states are smaller than those of the corresponding homopolymers. The absorption peaks of $\pi-\pi^*$ band transitions are estimated to appear at 1.68 eV for poly(pyrrolylenesilolylene) and 1.67 eV for poly(furylenesilolylene). Small bandgaps of the copolymers come from the fact that the copolymers consist of different types of cyclic units. Decomposition of the bandgaps reveals that the electronic effect of the heteroatoms (NH and O) in the copolymers is less than half of the effect found in polypyrrole and polyfuran. The small electronic effect decreases bandgaps of the aromatic forms and increases bandgaps of the quinoid types, in comparison to the average of the gaps of the corresponding homopolymers.

Introduction

During the past decade, π-conjugated polymers based on heterocyclic polymers have been extensively studied in search of very small bandgap polymers exhibiting intrinsic conductivities and excellent nonlinear optical properties.[1–21] In particular, many theoretical and experimental attempts have been made to modify the chemical structures toward quinoid forms for achieving such a goal since quinoid forms of heterocyclic polymers were reported to possess smaller bandgaps than the aromatic ones.[22] Poly(isothianaphthene) (PITN)[1] and poly(5,5′-bithiophenemethine) (PBTM)[2–3] are well-known examples of quinoid-type polymers which possess relatively small bandgaps, though the sizes of their bandgaps in the ground states are controversial.[23–25] PBTM possesses the aromatic and quinoid sequences due to a methine group inserted between two thiophene rings. Theoretical calculations[26,27] and experimental ^{13}C CP/MAS NMR investigations[28,29] have illustrated that the geometrical structure of PITN is quinoid in the ground state. Raman spectroscopic study has emerged as a powerful tool to identify the quinoid structures of PITN,[30] poly(2,3-R,R-thieno[3,4-*b*]pyrazine),[31] doped polythiophene,[32,33] and doped poly(*p*-phenylene).[34]

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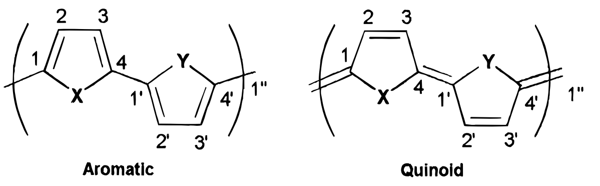
Recently, we have reported various simple nonheterocyclic polymers with quinoid structures in the ground states.[18−20] Though these nonheterocyclic polymers were predicted to possess small bandgaps compared to those of heterocyclic polymers, it was found that the quinoid forms possess larger bandgaps than the corresponding aromatic types. The same trend has been found in other theoretical work for various quinoid-type polymers such as PITN,[24,26,27] poly(isonaphthothiophene),[24,26,27] and polythieno[3,4-*c*]thiophene.[15] Therefore, it may be a general rule that the more stable the isomer, the larger the bandgap. In this regard, it is interesting to study ground-state structures and electronic properties of copolymers consisting of two different types of cyclic units: the homopolymer of one being aromatic in the ground state and the other being quinoid. Several kinds of such copolymers have been theoretically and experimentally investigated. Poly(thiopheneisothianaphthene) and poly(thiopheneisonaphthothiophene) were theoretically explored, and the bandgaps were calculated to be 1.0 and 0.5 eV, respectively.[14,16] The small bandgaps of their aromatic forms were attributed to reduced bond-length alternation. Poly(isothianaphthenebithiophene) was chemically and electrochemically synthesized and was reported to exhibit an absorption edge near 1.58 eV with a peak at 2.12 eV.[6] The conductivity of an electrochemically prepared sample reaches up to 5×10^{-3} S/cm. A theoretical bandgap of this polymer was reported to be 1.29 eV.[16] We have also investigated the electronic structures of some thiophene−nonheterocycle copolymers: poly(thienylenecyclopentadienylene) (PThPD), poly(thienylenesilolylene) (PThS), poly(thienyleneoxocyclopentadienylene) (PThOPD), and poly(thienylenethiocyclopentadienylene) (PThTPD).[21] Homopolymers of these nonheterocycles were predicted to be of the quinoid forms in the ground states.[18−20] Bandgaps of the copolymers were calculated to be smaller than those of the parent homopolymers including polythiophene (PT) in the ground states. Thiophene−silole copolymers have been chemically prepared with various ratios of silole contents.[35] These copolymers were reported to be air-stable and soluble in common organic solvents, depending on the content of silole and the nature of the substituents on silicon. Higher silole ratios cause bathochromic shifts, and the conductivity with iodine doping is 10^{-3}−10^{-1} S/cm. Two absorption peaks for $\pi-\pi^*$ transitions of poly(bithiophenesilole) were observed at 614 nm (2.05 eV) and 594 nm (2.13 eV). Our previous theoretical study of PThS predicted the $\pi-\pi^*$ transition to occur at 1.55 eV. More recently, a variety of copolymers containing aromatic donor and quinoid acceptor units has been electrochemically synthesized.[36] Their bandgaps estimated from the optical absorption edges were reported to range from 0.5 to 1.4 eV.



X = NH, Y = CH_2 : PPyPD
X = NH, Y = SiH_2 : PPyS
X = NH, Y = C=O : PPyOPD
X = NH, Y = C=S : PPyTPD
X = O, Y = CH_2 : PFuPD
X = O, Y = SiH_2 : PFuS
X = O, Y = C=O : PFuOPD
X = O, Y = C=S : PFuTPD

Figure 1. Aromatic and quinoid forms of the pyrrole and furan copolymers: poly(pyrrolylenecyclopentadienylene) (PPyPD), poly(pyrrolylenesilolylene) (PPyS), poly(pyrrolyleneoxocyclopentadienylene) (PPyOPD), poly(pyrrolylenethiocyclopentadienylene) (PPyTPD), poly(furylenecyclopentadienylene) (PFuPD), poly(furylenesilolylene) (PFuS), poly(furyleneoxocyclopentadienylene) (PFuOPD), and poly(furylenethiocyclopentadienylene) (PFuTPD).

In this study, we performed theoretical work to investigate the geometrical and electronic structures of new pyrrole− and furan−nonheterocycle copolymers shown in Figure 1. Geometrical structures of the copolymers were optimized through AM1 band calculations,[37] and their electronic properties were obtained from modified extended Hückel (MEH) band calculations.[24] Also, the bandgaps of the polymers were analyzed in terms of bond-length alternation along the conjugated carbon backbone, C1−C4 interactions near the Fermi level, and the electronic effect of the bridging groups which connect the C1−C4 atoms of the backbones.

Methodology

Several quantum-chemical methods (ab initio and semiempirical techniques such as modified neglect of diatomic overlap [MNDO] and complete neglect of differential overlap [CNDO] types) have been used to obtain the ground-state geometries of polymers. Because of computational time, the ab initio method may not be suitable for an infinite chain. To our knowledge, only *trans*-polyacetylene (PA) was studied through ab initio crystal orbital calculations.[38−40] It was also reported that ab initio calculations with small basis sets are subject to overestimating the bond-length alternation, and thus quite large basis sets are required to produce reasonable results. Therefore, an oligomeric approach has been widely employed to extract a polymeric structure from the optimized central unit of the corresponding oligomer such as a trimer, a tetramer, and so on. However, one should be careful when adopting this approach for determining the ground-state geometries of conjugated polymers and for estimating the relative stabilities of the aromatic and quinoid structures since these properties strongly depend on the types of terminal groups of an oligomer.[15,19,27]

It is well-known that Hartree−Fock (HF) level calculations greatly overestimate the bandgaps (E_g) of conjugated polymers and the calculated E_g at the HF level must be scaled down to compare with experimental values.[39,41,42] One may think of a simple scaling scheme to estimate the actual E_g of a conjugated polymer from a calculated one at the HF level. But, transferability of a scaling factor from one polymeric system to another is limited since the bandgap of a conjugated polymer

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usually arises from various factors. In fact, the CNDO/2 calculations have shown that a scaling factor obtained from a *trans*-PA system cannot be used for the polyfuran system.[43] Therefore, lower level approaches such as the valence effective Hamiltonian (VEH),[44] Hückel, and extended Hückel[45] methods have been widely used for predicting the E_g of one-dimensional conjugated polymers. Though non-HF-based models do not explicitly include electron correlation, the success of these models comes from parametrizations that yield reasonable bandgaps in comparison to experimental values.

We employed the solid-state version of the MNDO method (MOSOL) with an AM1 Hamiltonian to obtain the geometrical structures of the copolymers in Figure 1. The ground-state geometries of the polymers were obtained through full optimization of the geometrical parameters with the assumption of the anticoplanarity. Since conjugated cyclic polymers are nondegenerate in their ground states, total energy calculations were carried out at various inter-ring distances to examine the energetics of aromatic and quinoid forms of the polymers. The inter-ring distance was varied stepwise from the optimized one by 0.02 Å. The other geometrical parameters were optimized at each inter-ring distance.

The MEH method was adopted to calculate the electronic properties of the polymers using the geometrical parameters optimized through AM1 band calculations. The MEH approach adopts distance-dependable off-diagonal elements of the form

$$H_{ij}^{\alpha\beta} = K_1(H_{ii}^{\alpha\alpha} + H_{jj}^{\beta\beta})\exp(-K_2R^{\alpha\beta})S_{ij}^{\alpha\beta} \tag{1}$$

where K_1 and K_2 are adjustable parameters and were determined to be 1.41 and 0.13 Å^{-1}, respectively. $H_{ii}^{\alpha\alpha}$ is the energy integral which is assumed to be equal to the energy of an electron in the ith atomic orbital (AO) of the isolated atom, α in the appropriate state. $S_{ij}^{\alpha\beta}$ is the overlap between the ith AO of a center α and the jth AO of a center β, and $R^{\alpha\beta}$ is the distance between two centers α and β. This method was parametrized to reproduce *bandgaps defined as* λ_{max} *for the* $\pi-\pi^*$ *transition* of conjugated polymers and not the band edge as is often used to define the gap experimentally. Typically, the band edge is about 0.5 eV lower than the peak value. This approach has been shown to yield remarkably reliable band structures for a wide variety of conjugated polymers, including those with heteroatoms.[24,46] MEH parameters used in the calculations are listed in Table 1.

Recently, we have successfully decomposed the bandgaps of conjugated five-membered ring polymers using the following equation:[18,20,21,47]

$$E_g = \Delta E^{\delta r} + \Delta E^{1-4} + \Delta E^{el} \tag{2}$$

Table 1. Valence-Shell Atomic Parameters Used in the Modified Extended Hückel Band Calculations[a]

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	1.975	2	1	14.80	1.975
Si	3	0	17.30	1.750	3	1	8.15	1.750
S	3	0	20.00	2.117	3	1	13.30	2.117

[a] Ionization potentials (IP in eV), Slater orbital exponents (ζ in au).

Here $\Delta E^{\delta r}$ refers to a gap arising from bond-length alternation (δr) along the conjugated carbon backbone. Since E_g of *trans*-PA arises only from the bond-length alternation, the relationship between $\Delta E^{\delta r}$ and δr was derived from the calculated E_g and δr values for *trans*-PA as in eq 3.[47] ΔE^{1-4} corresponds to a contribution

$$\Delta E^{\delta r} = 16.1\delta r \tag{3}$$

from the interactions between C1 and C4 atoms of a *cis*-PA-type conjugated carbon backbone. The interactions between C1 and C4 atoms in the frontier orbitals are different from each other: one is bonding and the other antibonding. These interactions increase the bandgap of *cis-transoid* PA and decrease the gap of *trans−cisoid* PA.[47,48] The contribution (ΔE^{1-4}) to E_g can be evaluated by subtracting $\Delta E^{\delta r}$ from the bandgap (E_g') arising only from the carbon backbone of a conjugated polymer, E_g' being calculated by removing the atomic orbitals of the bridging groups from the Hamiltonian and overlap matrixes. The contribution from ΔE^{1-4} is small in *cis*-PA (0.2 eV) but becomes significant as the C1−C4 distance becomes shorter. In a five-membered ring system this effect amounts to 0.2−0.7 eV, depending on the size of the bridging atom.[18,20] This effect together with ΔE^{el} is in some cases crucial in determining the relative stability of aromatic vs quinoid forms of conjugated cyclic polymers. ΔE^{el} is due to the electronic interaction between a conjugated carbon backbone and moieties such as a bridging atom or group, pendent groups, and fused rings. Finally, ΔE^{el} is calculated by deducting E_g' from the estimated E_g of the copolymers. This electronic effect corresponds to the second-order energy correction which is proportional to the square of the overlap between the frontier crystal orbitals (CO) of the carbon backbone and moiety orbitals and which is inversely proportional to the energy difference between the levels corresponding to these orbitals. The ΔE^{el} of heteroatoms in heterocyclic polymers is so large that it dominates the bandgaps of the polymers and induces the aromatic forms into being more stable.[18,24,47] Since the copolymers in Figure 1 have two different bridging groups: X and Y, the total electronic effect of the bridging groups is separated to estimate the contribution from each bridging group: $\Delta E^{el} = \Delta E^{el}(X) + \Delta E^{el}(Y)$.[21] ΔE^{el}(X) can be estimated two different ways as follows:

$$\Delta E^{el}(X) = E_g(X) - E_g' \tag{4}$$

or

$$\Delta E^{el}(X) = E_g - E_g(Y) \tag{5}$$

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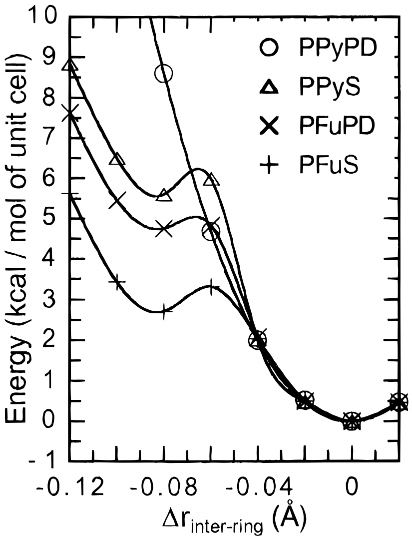

Figure 2. Energetics of poly(pyrrolylenecyclopentadienylene) (PPyPD), poly(pyrrolylenesilolylene) (PPyS), poly(furylenecyclopentadienylene) (PFuPD), and poly(furylenesilolylene) (PFuS) with the inter-ring distance. $\Delta r_{\text{inter-ring}}$ represents deviation from the inter-ring distance of the aromatic forms.

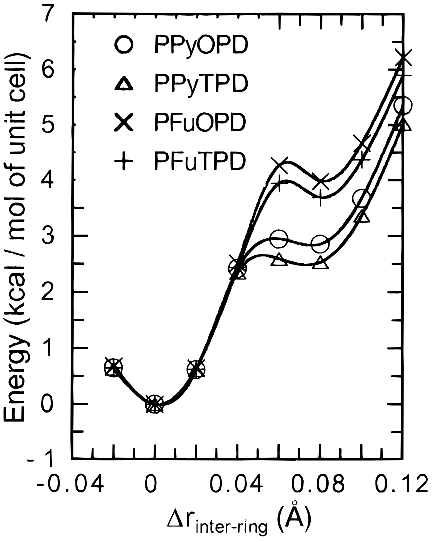

Figure 3. Energetics of poly(pyrrolyleneoxocyclopentadienylene) (PPyOPD), poly(pyrrolylenethiocyclopentadienylene) (PPyTPD), poly(furyleneoxocyclopentadienylene) (PFuOPD), and poly(furylenethiocyclopentadienylene) (PFuTPD) with the inter-ring distance. $\Delta r_{\text{inter-ring}}$ represents deviation from the inter-ring distance of the quinoid forms.

Here $E_g(X)$ corresponds to the bandgap of the polymeric backbone which possesses only X groups in every other ring and no Y groups in the other ring, and vice versa for $E_g(Y)$. $\Delta E^{el}(Y)$ can be calculated using the same equations where X and Y are transposed. Equations 4 and 5 are, however, not equivalent but complement each other since the electronic effects of X and Y are not independent but strongly correlate to each other. $\Delta E^{el}(X)$ in eq 4 refers to the electronic effect of X on the bandgap of the backbone which possesses only X groups in every other ring as a bridging atom, while $\Delta E^{el}(X)$ in eq 5 corresponds to the effect of X on the bandgap of the backbone which is already perturbed electronically due to the presence of the Y group. Therefore, if we assume that X groups go into the polymeric backbone to form five-membered rings ahead of the Y groups, we have to calculate the electronic effect of X using eq 4 and the effect of the Y group using eq 5 where X and Y are transposed. In the reverse case, we have to use eq 5 to estimate the electronic effect of X and eq 4, where X is replaced with Y, to compute the effect of the Y group. However, the same value of the total electronic effect, ΔE^{el} is produced regardless of the way we choose to calculate the individual electronic effect of the bridging groups. Therefore, we take the average of the values calculated, using both eqs 4 and 5, to determine the separate electronic effect of the bridging groups.

Ground-State Geometrical Structures

In the ground states, the aromatic forms of poly(pyrrolylenecyclopentadienylene) (PPyPD), poly(pyrrolylenesilolylene) (PPyS), poly(furylenecyclopentadienylene) (PFuPD), and poly(furylenesilolylene) (PFuS) are predicted to be more stable than the quinoid forms, whereas the aromatic forms of poly(pyrrolyleneoxocyclopentadienylene) (PPyOPD), poly(pyrrolylenethiocyclopentadienylene) (PPyTPD), poly(furylenethiocyclopentadienylene) (PFuTPD), and poly(furyleneoxocyclopentadienylene) (PFuOPD) are estimated to be less stable than their quinoid counterparts. Figure 2 shows the variations of the potential energies of copolymers containing cyclopentadiene or silole rings with inter-ring distance. Local minima which represent the quinoid forms are found at the inter-ring distance ca. 0.08 Å shorter ($\Delta r_{\text{inter-ring}} \approx -0.08$ Å) than the distances of the aromatic forms. The aromatic form of PFuS is only 2.7 kcal/mol of a unit cell more stable than its counterpart. Those of PFuPD and PPyS are more stable by 4.8 and 5.6 kcal/mol of a unit cell, respectively. However, the potential energy curve for PPyPD does not show a local minimum. Even at $\Delta r_{\text{inter-ring}} = -0.08$ Å, the intraring structure of PPyPD is estimated to be of an aromatic type. In Figure 3, the aromatic forms of the copolymers containing oxocyclopentadiene or thiocyclopentadiene rings are found to possess an inter-ring distance ca. 0.08 Å longer than the quinoid forms. Aromatic forms of PPyTPD and PPyOPD are less stable than the counterparts by only 2.4 and 2.8 kcal/mol of a unit cell, respectively. By comparison, those of PFuTPD and PFuOPD are less stable than their quinoid forms by 3.7 and 4.0 kcal/mol of a unit cell. It has been estimated that PPy and PF strongly favor the aromatic forms in their ground states.[47] We have also reported that poly(cyclopentadienylene) and polysilole slightly favor the quinoid forms, whereas poly(oxocyclopentadienylene) and poly(thiocyclopentadienylene) strongly favor the quinoid forms over their counterparts.[18,20] Therefore, it is deduced that the relative stabilities of the aromatic vs the quinoid forms of the copolymers are strongly related to those of their corresponding homopolymers.

Tables 2 and 3 represent the optimized geometrical parameters for the aromatic and quinoid forms of the copolymers. In general, the intraring structures of the copolymers are similar to those of the corresponding homopolymers. However, upon copolymerization, the short bonds of aromatic heterocycles become longer and the long bonds shorter, whereas the short bonds of aromatic nonheterocycles become shorter and the long bonds longer. In the quinoid forms, the trend is op-

Table 2. Optimized Geometrical Parameters (Bond Lengths in angstroms and Bond Angles in degrees) for Poly(pyrrolylenecyclopentadienylene) (PPyPD), Poly(pyrrolylenesilolylene) (PPyS), Poly(furylenecyclopentadienylene) (PFuPD), and Poly(furylenesilolylene) (PFuS) from AM1 Band Calculations: Aromatic (A) and Quinoid (Q) Forms

	PPyPD	PPyS		PFuPD		PFuS			PPyPD	PPyS		PFuPD		PFuS	
	A[a]	**A**	Q	**A**	Q	**A**	Q		**A**[a]	**A**	Q	**A**	Q	**A**	Q
1−2	1.417	1.422	1.497	1.392	1.470	1.394	1.479	3−4−1′	127.8	123.9	122.4	129.8	128.3	125.9	124.3
2−3	1.421	1.413	1.353	1.432	1.357	1.425	1.351	4−1′−2′	129.6	131.5	130.5	132.1	130.6	137.2	132.8
4−1′	1.429	1.424	1.347	1.422	1.342	1.416	1.337	1′−2′−3′	109.3	115.4	116.6	110.5	109.3	115.2	116.6
1′−2′	1.370	1.355	1.447	1.368	1.461	1.354	1.448	Y−1′−2′	109.4	108.0	105.4	109.5	107.6	108.4	105.6
2′−3′	1.460	1.467	1.363	1.465	1.363	1.472	1.364	δr[b]	0.041	0.043	0.119	0.055	0.115	0.057	0.116
1−X	1.397	1.397	1.409	1.403	1.417	1.402	1.415	1−4	2.273	2.275	2.308	2.242	2.270	2.242	2.272
1′−Y	1.513	1.811	1.790	1.514	1.512	1.810	1.795	1′−4′	2.364	2.630	2.659	2.365	2.382	2.623	2.660
1−2−3	107.5	107.6	108.6	106.9	108.1	107.2	108.2	l[c]	7.318	7.639	7.585	7.225	7.170	7.546	7.497
X−1−2	107.7	107.8	106.4	110.1	108.7	110.2	108.4								

[a] Bold-typed is the more stable isomer. [b] Average value of the bond-length alternation, defined as $\delta r = |R(1{-}2) - R(2{-}3) + R(3{-}4) - R(4{-}1') + R(1'{-}2') - R(2'{-}3') + R(3'{-}4') - R(4'{-}1'')|/4$. [c] Repeating unit length.

Table 3. Optimized Geometrical Parameters (Bond Lengths in angstroms and Bond Angles in degrees) for Poly(pyrrolyleneoxocyclopentadienylene) (PPyOPD), Poly(pyrrolylenethiocyclopentadienylene) (PPyTPD), Poly(furyleneoxocyclopentadienylene) (PFuOPD), Poly(furylenethiocyclopentadienylene) (PFuTPD) from AM1 Band Calculations: Aromatic (A) and Quinoid (Q) Forms

	PPyOPD		PPyTPD		PFuOPD		PFuTPD	
	A	**Q**[a]	A	**Q**	A	**Q**	A	**Q**
1−2	1.419	1.493	1.417	1.490	1.393	1.474	1.392	1.471
2−3	1.418	1.358	1.415	1.356	1.431	1.356	1.425	1.353
4−1′	1.426	1.354	1.433	1.365	1.420	1.344	1.426	1.351
1′−2′	1.366	1.463	1.372	1.466	1.364	1.464	1.370	1.467
2′−3′	1.472	1.363	1.467	1.363	1.479	1.363	1.474	1.363
1−X	1.398	1.409	1.401	1.410	1.405	1.415	1.409	1.418
1′−Y	1.516	1.492	1.501	1.476	1.515	1.497	1.501	1.484
1−2−3	107.6	108.4	107.8	108.7	106.9	108.1	107.2	108.2
X−1−2	108.1	106.7	107.8	106.4	110.4	108.7	109.8	108.3
3−4−1′	127.8	126.5	127.4	126.5	132.3	122.6	129.1	128.0
4−1′−2′	129.9	128.3	128.9	127.1	132.5	136.8	131.1	129.9
1′−2′−3′	109.8	110.3	109.5	109.9	109.7	110.5	109.3	110.1
Y−1′−2′	108.0	106.9	108.2	107.1	108.0	106.7	108.3	106.9
δr[b]	0.043	0.121	0.042	0.118	0.059	0.117	0.057	0.114
1−4	2.274	2.303	2.282	2.308	2.240	2.273	2.250	2.275
1′−4′	2.396	2.379	2.377	2.362	2.397	2.394	2.379	2.371
l[c]	7.346	7.257	7.358	7.267	7.256	7.174	7.278	7.191

[a] Bold-typed is the more stable isomer. [b] Average value of the bond-length alternation, defined as $\delta r = |R(1{-}2) - R(2{-}3) + R(3{-}4) - R(4{-}1') + R(1'{-}2') - R(2'{-}3') + R(3'{-}4') - R(4'{-}1'')|/4$. [c] Repeating unit length.

Table 4. Electronic Properties of Poly(pyrrolylenecyclopentadienylene) (PPyPD), Poly(pyrrolylenesilolylene) (PPyS), Poly(furylenecyclopentadienylene) (PFuPD), and poly(furylenesilolylene) (PFuS) Obtained from Modified Extended Hückel Band Calculations: Aromatic (A) and Quinoid (Q) Forms (All Units in eV)[a]

	PPyPD	PPyS		PFuPD		PFuS	
	A[b]	**A**	Q	**A**	Q	**A**	Q
E_g	1.94 (2.18)[c]	1.68 (2.15)	0.76 (0.32)	1.94 (2.14)	0.66 (0.47)	1.67 (2.11)	0.99 (0.58)
E_g'	0.09	0.20	2.29	0.30	2.37	0.42	2.29
$\Delta E^{\delta r}$	0.66 (0.72)	0.69 (0.83)	1.92 (1.78)	0.89 (0.89)	1.85 (1.83)	0.92 (1.01)	1.87 (1.79)
ΔE^{1-4}	−0.57 (−0.56)	−0.49 (−0.44)	0.37 (0.36)	−0.59 (−0.57)	0.52 (0.52)	−0.50 (−0.45)	0.42 (0.39)
ΔE^{el}	1.85 (2.03)	1.48 (1.76)	−1.53 (−1.82)	1.64 (1.82)	−1.71 (−1.88)	1.25 (1.55)	−1.30 (−1.61)
ΔE^{el} (X)	1.49	1.46	−1.49	1.28	−1.31	1.23	−1.25
ΔE^{el} (Y)	0.36	0.02	−0.05	0.37	−0.41	0.02	−0.05
IP	10.54	10.63	10.08	10.64	9.91	10.72	10.30
EA	8.61	8.95	9.31	8.71	9.24	9.05	9.31
highest valence bandwidth	2.36	2.28	2.62	2.35	2.86	2.25	2.69
lowest conduction bandwidth	1.95	2.08	2.45	2.00	2.57	2.13	2.45

[a] E_g is a *bandgap corresponding to the* $\pi - \pi^*$ *absorption peak* of a spectrum. $\Delta E^{\delta r}$, ΔE^{1-4}, and ΔE^{el} are the components of E_g, which arise from the bond-length alternation, C1−C4 interactions and electronic effect of the bridging groups, respectively. E_g' is a bandgap calculated only for the corresponding conjugated carbon backbone. [b] Bold-typed is the more stable isomer. [c] Numbers in parentheses are the average values of the corresponding properties of the homopolymers.

posite. Therefore, the δr value of each copolymer approximately corresponds to the average of those of the corresponding homopolymers. In the case of copolymers containing pyrrole rings, the change in C−C bond lengths of pyrrole rings is more obvious, and the intraring structures of the aromatic forms of PPyS, PPyOPD, and PPyTPD exhibit quinoid character in that they possess long C1−C2 and short C2−C3 bond lengths.

Electronic Structures of the Copolymers

Electronic properties of the aromatic and quinoid forms of the copolymers were estimated through the MEH band calculations and are summarized in Tables 4 and 5. From these calculations, the fact can be

Table 5. Electronic Properties of Poly(pyrrolyleneoxocyclopentadienylene) (PPyOPD), and Poly(pyrrolylenethiocyclopentadienylene) (PPyTPD), Poly(furyleneoxocyclopentadienylene) (PFuOPD), and Poly(furylenethiocyclopentadienylene) (PFuTPD) Obtained from Modified Extended Hückel Band Calculations: Aromatic (A) and Quinoid (Q) Forms (All Units in eV)[a]

	PPyOPD		PPyTPD		PFuOPD		PFuTPD	
	A	**Q**[b]	A	**Q**	A	**Q**	A	**Q**
E_g	0.53 (1.64)	1.79 (0.74)	0.05 (1.45)	2.04[c] (0.76)	0.59 (1.60)	1.91 (0.99)	0.13 (1.41)	2.13 (1.01)
E_g'	0.13	2.42	0.11	2.38	0.38	2.40	0.35	2.36
$\Delta E^{\delta r}$	0.69 (0.82)	1.95 (1.82)	0.68 (0.75)	1.90 (1.80)	0.95 (0.99)	1.88 (1.83)	0.92 (0.93)	1.84 (1.81)
ΔE^{1-4}	−0.56 (−0.55)	0.47 (0.48)	−0.57 (−0.56)	0.48 (0.49)	−0.57 (−0.56)	0.52 (0.51)	−0.57 (−0.57)	0.52 (0.52)
ΔE^{el}	0.40 (1.37)	−0.63 (−1.57)	−0.06 (1.26)	−0.34 (−1.54)	0.21 (1.16)	−0.49 (−1.35)	−0.22 (−1.05)	−0.23 (−1.32)
ΔE^{el} (X)	1.07	−1.15	0.91	−1.03	0.89	−0.97	0.76	−0.86
ΔE^{el} (Y)	−0.67	0.52	−0.97	0.69	−0.68	0.48	−0.98	0.63
IP	10.57	11.02	10.56	11.29	10.69	11.15	10.67	11.38
EA	10.05	9.23	10.51	9.25	10.10	9.23	10.54	9.25
highest valence bandwidth	2.35	1.45	2.35	1.16	2.30	1.61	2.31	1.36
lowest conduction bandwidth	1.13	0.20	0.79	0.56	1.15	0.25	0.80	0.52

[a] E_g is a *bandgap corresponding to the π−π^* absorption peak* of a spectrum. $\Delta E^{\delta r}$, ΔE^{1-4}, and ΔE^{el} are the components of E_g, which arise from the bond-length alternation, C1−C4 interactions and electronic effect of the bridging groups, respectively. E_g' is a bandgap calculated only for the corresponding conjugated carbon backbone. [b] Bold-typed is the more stable isomer. [c] Indirect transition is estimated to occur at a lower energy, 1.48 eV. [d] The numbers in parentheses are the average values of the corresponding properties of the homopolymers.

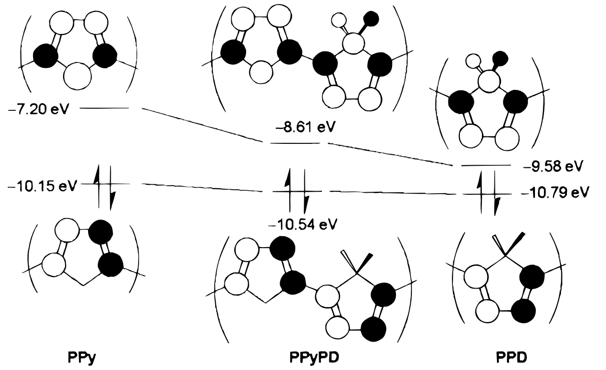

Figure 4. Energy correlation diagram for the aromatic forms of polypyrrole (PPy), poly(pyrrolylenecyclopentadienylene) (PPyPD), and poly(cyclopentadienylene) (PPD) near the Fermi level.

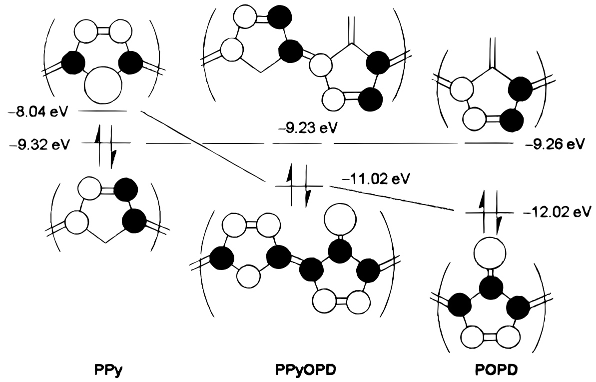

Figure 5. Energy correlation diagram for the quinoid forms of polypyrrole (PPy), poly(pyrrolyleneoxocyclopentadienylene) (PPyOPD), and poly(oxocyclopentadienylene) (POPD) near the Fermi level.

ascertained that the more stable isomer possesses a larger bandgap than its counterpart. The ground-state bandgaps of the copolymers, except those of the copolymers containing cyclopentadiene rings, are smaller than those of the homopolymers including PPy and PF. This result is consistent with the very recent experimental observation of bathochromic shifts of the absorption maxima of silole−pyrrole cooligomers compared to those of corresponding pyrrole oligomers.[49] Our theoretical work[21] of thiophene−nonheterocycle copolymers and other experimental work[35] of thiophene−silole copolymers have also showed that the π−π^* absorption peaks of the thiophene−copolymers shift toward longer wavelengths with increasing content of silole rings. PPyS and PFuS exhibit the smallest bandgaps among the pyrrole− and furan−copolymers. The π−π^* transitions are predicted to occur at 1.68 eV for PPyS and 1.67 eV for PFuS. In PPyTPD, an indirect transition is estimated to occur at 1.48 eV. The ionization potentials of the copolymers increase compared to those of PPy and PF. This phenomenon is more obvious in the quinoid-type copolymers PPyOPD, PPyTPD, PFuOPD, and PFuTPD. Therefore, it is expected that the copolymers are rather stable against the oxidation. The electron affinities also increase compared to those of PPy and PF. In fact, poly(thiophene−silole) copolymers were reported to be air-stable, and the small change in reduction and oxidation potentials of thiophene−silole oligomers compared to thiophene oligomers have been experimentally observed through cyclic voltametry determinations.[35] Bandwidths of the copolymers are narrow near the Fermi level relative to those of the homopolymers as observed in other copolymers.

The small bandgaps of the copolymers are obviously due to the result of the mixing of the two different types of cyclic units. As illustrated in Figure 4, the small bandgaps of the aromatic forms come from the incorporation of the nonheterocyclic rings whose homopolymers in the aromatic forms possess smaller bandgaps but are less stable. That is, the aromatic forms of cyclopentadiene and silole rings are responsible for the small bandgaps of PPyPD, PPyS, PFuPD, and PFuS in the ground state. In the case of quinoid forms, heterocyclic rings are responsible for the small bandgaps found in the ground-state PPyOPD, PPyTPD, PFuOPD, and PFuTPD. Figure 5 shows the energy correlation diagram for the quinoid-type PPyOPD near the Fermi level. Bandgap analysis reveals that the contributions from the bond-length alternations and C1−C4 interactions are almost equal to the average of those for the corre-

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sponding homopolymers. However, the electronic effect of the bridging groups decreases significantly since the effect of heteroatoms in the copolymers becomes smaller than a half of 3.5 eV for ΔE^{el}(NH) in PPy and a half of 3.1 eV for ΔE^{el}(O) in PF.[47] The ΔE^{el}(X) values in the copolymers containing cyclopentadiene or silole rings correspond to about 40% of the values of PPy and PF. In the copolymers containing oxocyclopentadiene or thiocyclopentadiene rings these values amount to only about 30%. As a result, the bandgap of each copolymer decreases in the aromatic form and increases in the quinoid one in comparison to the average value of the gaps of the corresponding homopolymers.

Conclusions

We investigated through theoretical work the geometrical and electronic structures of the copolymers possessing two different types of cyclic units whose homopolymers show different isomeric stabilities and electronic structures each other. It was found in the ground state that the isomeric stability of each copolymer is strongly related to those of the corresponding homopolymers. The ground-state bandgaps of the copolymers are estimated to be smaller than those of the corresponding homopolymers due to the result of the mixing of the two different types of cyclic units. Bandgap analysis reveals that the contributions from the bond-length alternations and C1−C4 interactions are, respectively, almost equal to the average values of those for the corresponding homopolymers. However, the electronic effect of heteroatoms in the copolymers becomes less than half of ΔE^{el}(X) found in PPy and PF. As a result, the bandgap of each copolymer decreases in the aromatic form and increases in the quinoid form in comparison to the average value of the gaps of the corresponding homopolymers.

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