Theoretical Study of the Conformations and Electronic Structures of Phenylene–Pyrrole and Phenylene–Furan Copolymers

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Received December 20, 1991

ABSTRACT: A theoretical study of the conformations and electronic structures of phenylene–pyrrole and phenylene–furan copolymers with methyl and methoxy substituents on the phenylene ring was performed. Torsional potential surfaces for the corresponding monomers were calculated using the partial retention of diatomic differential overlap method. The preferred structures of the copolymers were predicted to be coplanar except for the alkyl-substituted pyrrole system, where strong steric repulsion between the alkyl and HN groups was found. Hydrogen bonding between the oxygen of the alkoxy group and the hydrogen bound to the pyrrole nitrogen was found to play a key role in keeping the dialkoxy-substituted pyrrole analog coplanar. The electronic structures of the copolymers were calculated with the modified extended Hückel band method. The calculated electronic properties of the copolymers, except for the bandwidths, are similar to those of the homopolymers and are in excellent agreement with experimental observations. The three highest dispersive valence bands of the copolymers are separated from each other by 0.6–0.7 eV. The highest valence bandwidths of the copolymers are about one-third of those of the corresponding homopolymers and are probably responsible, in part, for the much lower conductivities of these systems.

Introduction

Conjugated polymers based on *cis*-polyacetylene, such as poly-*p*-phenylene (PPP), polythiophene (PT), polypyrrole (PPy), and polyfuran (PF), have been extensively studied because of their electrical properties and relative environmental stability. Owing to their remarkable optical and electrochemical properties, various technical applications of conjugated polymers have been proposed, such as rechargeable and solar battery cells,[1] electrooptical switching devices,[2] microsensors,[3] permanent information storage devices,[4] rectifiers,[5] and electrochromic films.[6] These emerging potential applications have provided a driving force for improving the physicochemical and optical properties (solution and melt processability, environmental stability, mechanical integrity, controllable electrical and optical properties, etc.). Structural modification of conjugated polymers has been exploited to achieve such goals. For example, 3-alkyl derivatives of PT[7,8] and PPy[7] show both melt and solution processability, allowing fiber, blend, and composite formation.

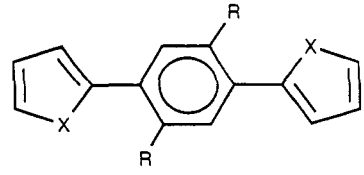
Because of the ease of functionalization of phenylene rings, copolymers of phenylene with heterocyclic systems have been synthesized and characterized by several different techniques.[9-12] Recent electron energy loss spectroscopy (EELS) investigations[10] have shown that the band gaps of these copolymers can be continuously varied upon changing the molar ratio of the components. Previous work on alternating regular copolymers which contain arylene and bithiophene[11] or bifuran[12] repeat units showed that the band gaps of the electrochemically prepared copolymer films are rather close to those of the pure heterocyclic polymers and that their conductivities, when doped with $NOPF_6$ or ClO_4^-, are of the order of 10^{-1}–10^0 S/cm^{-1}, or 2–3 orders of magnitude lower than those of the homopolymers.[13] Our theoretical work[11] on the conformation of the thiophene analogs showed that the twisted isomers are more stable than the coplanar ones due to the steric repulsion of the pendant groups with the sulfur atom.

There are many geometrical factors which can affect the conductivity of conjugated polymers, including morphology, planarity, and degree of polymerization. Electronic factors such as band gaps, ionization potentials, electron affinities, and bandwidths of the polymers are also obviously important. Among these factors, the conformational attributes of the polymer backbone and the electronic band structures are the most amenable to theoretical study and will be the focus of this study.

In this paper, we report conformational and electronic structural studies of poly(1,4-di(2-furanyl)-2,5-disubstituted phenylenes) and poly(1,4-di(2-pyrrolyl)-2,5-disubstituted phenylenes). We consider methyl and methoxy groups, symmetrically attached to the phenylene ring, as substituents. We are mainly concerned in this study with the effects of the pendant groups on electronic structures and planarity of the copolymers. The potential energy surfaces for the conformational degrees of freedom of the monomers are obtained by performing the partial retention of diatomic differential overlap (PRDDO) calculations.[14] The electronic structures of the copolymers are calculated using the modified extended Hückel (EH) method.[15]

Conformational Analyses

Since previous work[11] on the thiophene analogs showed that the aromatic forms are more stable than the quinoidal forms, conformational analyses of these systems were limited to the aromatic forms and focused on the torsional angle (θ) between the phenylene ring and heterocyclic ring. The torsional potential energy surfaces were constructed by varying θ in 15° increments for the unsubstituted monomers, **1a** and **2a**, from 0° to 90°, and



1 : X = NH
2 : = O

a : R = H
b : = CH_3
c : = OCH_3

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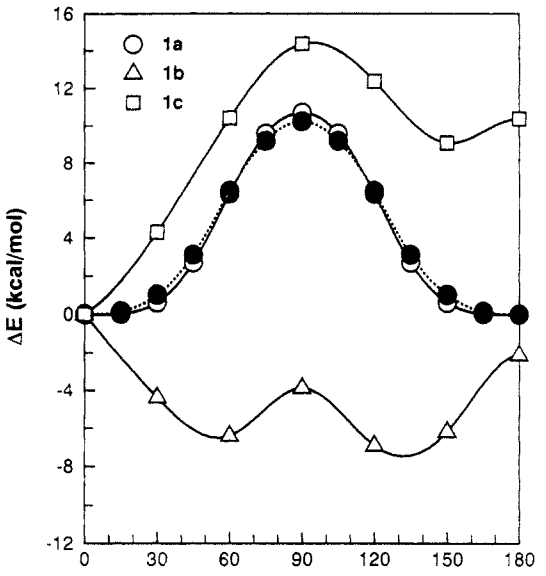


Figure 1. Torsional potential curves of 1,4-di(2-pyrrolyl)-2,5-disubstituted benzenes. The shaded circles represent the potential curve for **1a** with a complete PRDDO geometry optimization at each point (see text).

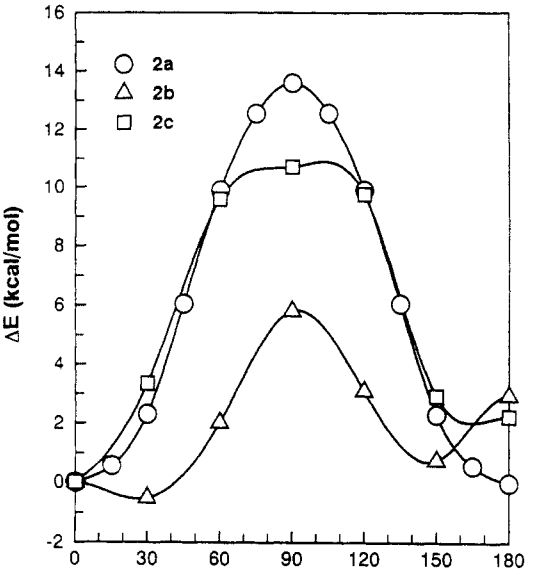


Figure 2. Torsional potential curves of 1,4-di(2-furanyl)-2,5-disubstituted benzenes.

in 30° increments for the disubstituted systems, **1b**, **1c**, **2b**, and **2c**, from 0° to 180°. For computational efficiency, the intra-ring parameters were optimized using the modified neglect of diatomic overlap (MNDO) method.[16] The PRDDO method was employed to optimize the inter-ring parameters (distances and angles) and dihedral angle of pendant groups at each θ value. For comparison, the potential surface of **1a** was calculated by performing full optimizations with the PRDDO method, and is shown in Figure 1. The agreement between these two approaches is excellent. The PRDDO method has been shown to be a useful tool for predicting the conformations as well as geometries of relatively large molecules,[17] while semiempirical methods[18] such as MNDO and CNDO (complete neglect of diatomic overlap) are often unrealistic in favoring perpendicular conformations for these extended systems with partial conjugation. For example, MNDO potential curves obtained from full optimizations showed minima at $\theta = 90°$ for the polymers in this study, except for **1c**, which had a minimum at $\theta = 60°$.

The torsional energy surfaces for the pyrrole-containing monomers **1a–c** are shown in Figure 1, while those for the furan-containing monomers **2a–c** are illustrated in Figure 2. With the exceptions of the methyl-substituted systems (**1b** and **2b**), the coplanar structures of these systems are the most stable, and significant rotational barriers (greater than 10 kcal/mol) are found. The energy surface around the planar conformation of the parent pyrrole system (**1a**) is very flat up to $\theta \approx 30°$, unlike the case of the analogous furan monomer (**2a**). The closest distance between phenyl hydrogen and the hydrogen attached to the pyrrole nitrogen is 2.16 Å for the planar conformation of **1a**. This is shorter than the sum of the van der Waals radii (2.4 Å).[19] At a twist angle of 30°, this distance increases to 2.4 Å. Therefore, the flatness of the potential energy of **1a** in the range $\theta = 0$–30° arises from a compromise between the effects of conjugation, which favors a coplanar structure, and the consequences of steric repulsion between the hydrogens, which favors a nonplanar structure. The corresponding furan system **2a** does not have such repulsions because of the absence of a hydrogen on the oxygen in the ring.

The methyl derivatives behave in a markedly different fashion. The coplanar structure of **1b** is the *maximum* on the potential energy surface and two minima are found, one at ~55° and the other at ~130°. This implies that the steric repulsion between the methyl substituent and hydrogens in the pyrrole ring is strong enough to overcome the stabilization due to the delocalization of the π electrons and to adversely affect the coplanarity. Since there is no hydrogen attached to the oxygen in the furan ring of **2b**, the steric repulsion is much weaker. The preferred structure of **2b** is predicted to have a 30° torsional angle, with a maximum rotational barrier of ~6 kcal/mol. The coplanar structure with $\theta = 0°$ is only 0.5 kcal/mol less stable than the structure with a 30° twist. Because of this flat potential energy surface near the planar conformation, it is expected that the coplanar conformation of **2b** is quite possible in the polymeric solid form, since the lattice energy may well favor a coplanar structure. A planar structure for **2b** is also supported by the observed optical spectrum and conductivity,[12] which is very similar to that of **2a**. Similar cases have been observed experimentally. For example, the *bi*thienyl in the gas phase[20] is found to be twisted by ca. 34°, while in the solid phase,[21] it is coplanar. An analogous situation occurs for biphenyl.[22,23]

The torsional potential curve for the methoxy derivative **1c** is shown in Figure 1. The coplanar structure with $\theta = 0°$ is ca. 10 kcal/mol more stable than the $\theta = 180°$ conformation. The distance between the oxygen of the methoxy group and the hydrogen on the nitrogen of the pyrrole ring of **1c** is 2.02 Å when $\theta = 0°$. This is much smaller than the sum of the van der Waals radii[19] of hydrogen and oxygen (2.6 Å). However, in this case the interaction is attractive and corresponds to hydrogen bonding of MeO to HN. Two of these interactions exist in the monomeric species and are clearly the reason for such a large stabilization of the $\theta = 0°$ form. In contrast, the coplanar structure of **2c** with $\theta = 0°$ is only slightly more stable than the $\theta = 180°$ structure. The stabilities of **1c** and **2c** with $\theta = 180°$ are comparable to those with $\theta = 150°$. This is likely due to a compromise between the stabilization due to the conjugation and the steric repulsion between the methoxy group and the hydrogen in a heterocyclic ring.

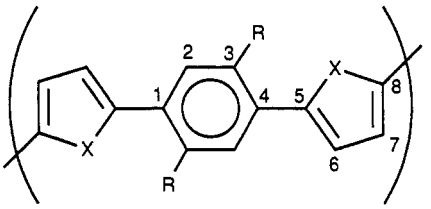
Table I
Geometrical Parameters[a] for the Title Polymers (Bond Lengths in Angstroms and Bond Angles in Degrees)

	3a	3b[b]	3c	4a	4b[c]	4c
1–2	1.380	1.370	1.375	1.375	1.376	1.383
2–3	1.361	1.374	1.366	1.361	1.377	1.373
3–4	1.374	1.386	1.398	1.386	1.395	1.397
4–5	1.462	1.466	1.460	1.454	1.467	1.462
5–6	1.349	1.343	1.352	1.340	1.342	1.344
6–7	1.394	1.404	1.404	1.408	1.408	1.408
7–8	1.344	1.352	1.354	1.342	1.341	1.341
5–X	1.380	1.382	1.371	1.365	1.368	1.365
8–8′	1.439	1.446	1.448	1.447	1.451	1.451
1–2–3	122.5	124.4	122.3	122.5	124.9	122.0
2–3–4	121.7	117.2	120.6	121.7	118.6	119.4
3–4–5	122.9	122.6	122.6	121.6	124.2	121.3
4–5–6	130.8	132.0	130.7	132.1	131.8	131.4
5–6–7	108.3	108.2	108.7	106.7	107.1	106.9
6–7–8	109.3	108.8	107.9	107.3	107.3	107.1
X–5–6	106.1	106.6	106.3	109.7	109.0	109.4
5–X–8	110.5	110.3	110.5	107.0	107.5	107.1
7–8–8′	131.9	130.2	130.9	132.1	131.9	131.7
3–C(H_3)		1.493			1.502	
3–O(CH_3)			1.383			1.379
O–C(H_3)			1.402			1.398

[a] See 2 for notations. [b] 130°-twisted structure. [c] Planar structure with the torsional angle of 0°.

Electronic Structures

Geometrical structures for the polymers (Table I) were obtained by performing full PRDDO optimizations, except for the torsional angles between the rings and C–H and N–H bond lengths, of the corresponding dimers. Except for **3b** (the methyl derivative of the pyrrole system), all



3 : X = NH a : R = H
4 : = O b : = CH_3
c : = OCH_3

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polymers were assumed to be coplanar. For **3b**, it was assumed that the twist angle was 130°, as predicted by the conformational analysis of the corresponding monomer **1b**. The C(sp^3)–H, C(sp^2)–H, and N–H bond lengths were fixed at 1.10, 1.08, and 0.99 Å, respectively. Band calculations were performed using the modified EH method.[15] This method employs modified off-diagonal elements of the form

$$H_{ij}^{\alpha\beta} = K_1(H_{ii}^{\alpha\alpha} + H_{jj}^{\beta\beta}) \exp(-K_2 R^{\alpha\beta}) S_{ij}^{\alpha\beta} \quad (1)$$

where K_1 and K_2 are adjustable parameters, previously[15] 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 is designed to reproduce band gaps defined as the $\pi - \pi^*$ λ_{max} of the optical spectra (as opposed to the band edge) of conjugated polymers. This approach has been shown[15] to yield remarkably accurate band gaps for a wide variety of conjugated polymers, including those with heteroatoms. It also produces bandwidths consistent with EELS observations. The valence orbital exponent (ζ) used for oxygen was 2.275, and the valence-state ionization potential (VSIP) of the oxygen 2p orbitals was 14.8 eV. The atomic parameters used for the nitrogen 2p orbitals are ζ = 2.150 and VSIP = 14.4 eV.

Table II
Electronic Properties of the Title Polymers

polymers[a]	E_g[b] (eV)	E_f (eV)	highest valence bandwidths (eV)
3a	3.23	−11.07	1.01
3b	4.17	−11.29	0.49
3c	3.12	−10.82	1.06
4a	3.04 (3.2)	−11.07	1.02
4b	3.12[c] (3.2)	−11.08	0.99
4c	2.93 (2.9)	−10.84	1.08
PPy[d]	3.18 (3.2)	−10.39	3.11
PF[d]	2.93 (3.0)	−10.84	3.43
PPP[d]	3.44 (3.4)	−12.17	3.46

[a] See 2 for notations. **3b** is in the 130°-twisted structure and **4b** in the planar structure with the torsional angle of 0°. [b] The value in parentheses is the experimental λ_{max} of the optical spectrum from ref 12. [c] E_g for the 30°-twisted structure is calculated to be 3.42 eV. [d] Data for PPy, PF, and PPP are obtained from ref 15 and references therein.

The predicted electronic properties of the copolymers are shown in Table II along with those of the homopolymers, PPy, PF, and PPP. Experimental values, when available, are presented in parentheses for comparison. The calculated band gaps of the furan systems are comparable to the corresponding experimental values.[12] Even though the pyrrole analogs have not been characterized yet, we believe that their band gaps are likely to be of about the same accuracy as those of the furan analogs. Contrary to the thiophene analogs,[11,15] whose band gaps are larger than that of PT, the band gaps of the unsubstituted copolymers **3a** and **4a** are similar in value to those of PPy and PF. This is probably due to the fact that **3a** and **4a** are coplanar, while the thiophene analog is twisted. No significant difference is found between the electronic properties of the pyrrole and furan analogs. The predicted band gaps of the pyrrole-containing polymers are ~0.2 eV larger than those for the furan analogs, as is the case for PPy and PF. The Fermi levels of the copolymers are predicted to be slightly lower than the corresponding values for PPy and PF. The highest valence bandwidths are about one-third of those for the homopolymers, PPy, PF, and PPP. A similar trend of bandwidths upon copolymerization was also predicted.[24] Since the copolymers have unit cells ~3 times as large as the homopolymers, the dispersion constants are similar in value to those of the homopolymers, consistent with EELS measurements[10] on phenylene–thiophene copolymers. Incorporation of substituents has no significant effect on the electronic properties unless the substituents affect the coplanarity of the polymers (however, methoxy groups have a weak tendency to lower the band gaps and to raise the Fermi levels[15]). The twisted structure of **3b** with θ = 130° allows for the mixing of σ and π orbitals and leads to a large band gap and a narrow highest valence bandwidth (half that of **3a**). Therefore, the electrical properties of **3b** are expected to be similar to that of the corresponding thiophene analog[11] whose conductivity is low (on the order of 10^{-6} S/cm) upon $NOPF_6$ doping.

The π-band structures of **3a** and **4a** are shown in Figure 3. They are quite similar to each other. Nine of the 16 π bands in Figure 3 are occupied. Similar π-band features are expected for the disubstituted copolymers. Valence bands 4, 8, and 9 are dispersive and separated from each

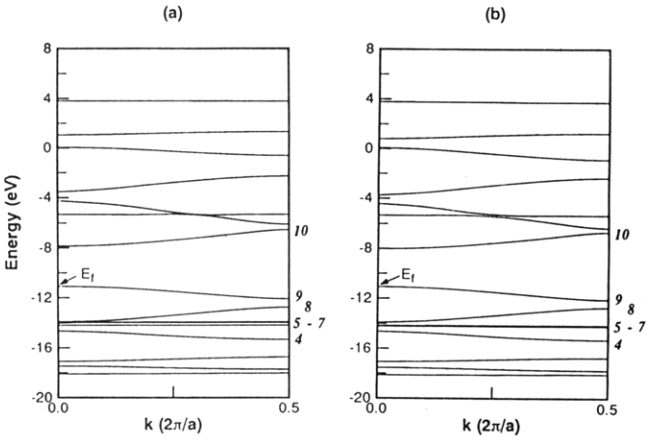

Figure 3. Modified extended Hückel π-band structures of (a) poly[1,4-di(2-pyrrolyl)phenylene] and (b) poly[1,4-di(2-furanyl)-phenylene].

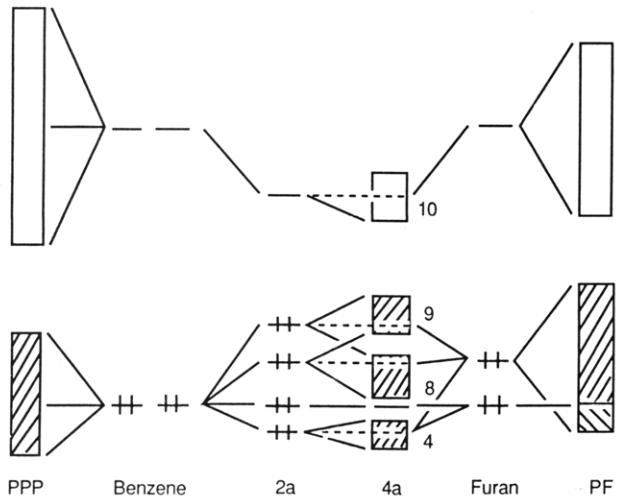

Figure 4. Schematic energy correlation diagram for poly[1,4-di(2-furanyl)phenylene] with related molecules and polymers.

other by 0.6–0.7 eV. Three bands, 5–7, are nondispersive and almost degenerate. To facilitate understanding of the correlation between the bands of the copolymer and those of the corresponding homopolymer, and between the energy levels of the molecules, it is convenient to examine the energy correlation diagram (Figure 4). The total bandwidths of bands 4, 8, and 9 are comparable to those of the homopolymers. These bands are quite symmetrical with respect to the corresponding molecular orbitals, and their dispersions are much smaller than those of the homopolymers because of the larger unit cell of the copolymer. The bottom of the lowest unoccupied conduction band (LUCB) 10 lies at a location similar to that found for PF, and the top of the highest occupied valence band (HOVB) 9 is near the PF Fermi level. The LUCB 10 and the HOVB 9 arise mainly from the corresponding dispersive bands of the homopolymers. The interactions near the Fermi level are presented in Figure 5 for the lowest unoccupied crystal orbital (LUCO) and the highest occupied crystal orbital (HOCO). These interactions within and between the rings are identical to those of the homopolymers, and similar to those found near the Fermi level in a valence effective Hamiltonian (VEH) study[24] of the copolymer poly(1,4-phenylene-2′,5′-thienylene). That is, the HOCO possesses an aromatic type of bonding and LUCO displays a quinoidal type of bonding. Therefore, the geometrical change of the copolymers upon doping is expected to occur toward a quinoidal structure, as in the case of the homopolymers. Band 8 mixes with band 9

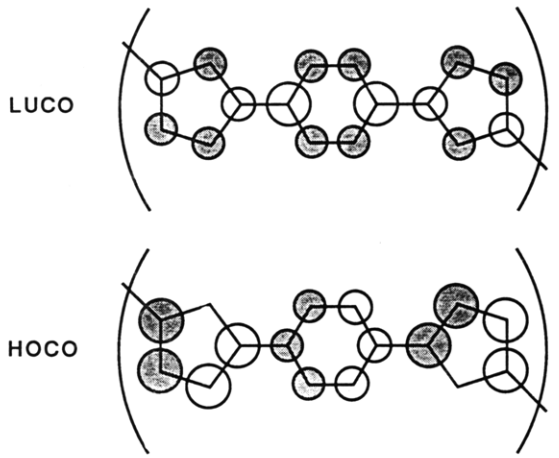

Figure 5. Interactions near the Fermi level for the polymers **3a** and **4a**. LUCO and HOCO represent the lowest unoccupied and the highest occupied crystal orbitals, respectively.

near the band edge of the Brillouine zone, resulting in a band separation of ca. 0.6 eV. Three flat bands 5–7 originate from the flat bands of the homopolymers. The bottom of band 4 lies near the bottom of the PPP valence band. This band is significantly less dispersive than bands 8 and 9, because it has larger contributions from the phenylene ring, one of three rings in the unit cell.

The bandwidths of these polymers are smaller (about one-third) than those of the corresponding homopolymers. Bandwidths near the Fermi level of conjugated polymers are known to be related to electrical-transport phenomena via mobilities of electrons and holes. The narrower the bandwidths, the smaller are the mobilities of electrons or holes. Therefore, the narrower bandwidths of the copolymers studied here are expected to be one of the important factors contributing to lower conductivities of the copolymer films.

Conclusions

The copolymer consisting of *bi*furan and a disubstituted phenylene ring is essentially coplanar in the ground state and the electronic properties, except for the bandwidths, are similar to those of the homopolymers. This is significantly different from that previously found for the thiophene analogs, where steric interactions force the polymers to be nonplanar. The pyrrole analogs, except for the alkyl derivative (which is nonplanar with a large rotational barrier), are quite similar to the furan analogs. The alkyl substituent significantly affects the coplanarity of the pyrrole analog because of steric repulsion between the alkyl group and the NH of a pyrrole ring. This changes the electronic properties drastically. It is expected from the conformational analysis of the methoxy-substituted monomer that the coplanar structure ($\theta = 0°$) of alkoxy-substituted pyrrole analogs is rather stable, due to the strong hydrogen bondings of RO···H–N.

The optical property of a conjugated polymer may be modulated through copolymerizations since the band gap varies by changing the molar ratio of the components. This study demonstrated that copolymers with a 2:1 (heterocyclic ring:benzene) ratio have band gaps which are close to those of pure heterocyclic polymers, while the highest valence bandwidths are about one-third of those of the homopolymers. The three highest dispersive valence bands are separated from each other by 0.6–0.7 eV. The narrower bandwidths of the copolymers seem to be one of the factors which cause the conductivities of the copolymer films to be lower by 2–3 orders of magnitude than those of the homopolymers.

Acknowledgment. This work was supported by the Defense Advanced Research Projects Agency, monitored by the Office of Naval Research, and the Robert A. Welch Foundation (Grant Y-743).

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