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Electronic properties of polymers based on thienothiadiazole and thiophene

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Ab initio crystal orbital (CO) studies on the geometric and the electronic structures of poly(thienothiadiazole) (Poly-1a) and periodic copolymers of thienothiadiazole and thiophene with the ratio of 1:1 (Poly-2b) and 1:2 (Poly-3b) are presented. In Poly-1a and Poly-2b, considerable change in the geometries is found to occur as one moves from their oligomers to the polymers. Although thienothiadiazole oligomers have a very small highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) separation, the corresponding polymer (Poly-1a) has a considerably large band gap. On the contrary, the geometric and electronic structures of Poly-3b are almost identical to those of the oligomer, and Poly-3b possesses a direct band gap of 1.3 eV estimated by simple scaling. The reasons for these differences are discussed in terms of orbital interactions and nonbonding molecular orbitals in the oligomers, and the reduced π-conjugation and enhanced intercell interaction in the polymers. © *1996 American Institute of Physics.* [S0021-9606(96)50814-X]

I. INTRODUCTION

Electrically conducting polymers have been the focus of enormous theoretical and experimental interest during the last more than a decade. These new materials, also called synthetic metals, combine the electrical properties of metals with the advantages of polymers such as lighter weight, greater workability, resistance to corrosion, and lower cost. Currently major efforts in the field of conducting polymers are on the molecular designing of novel conjugated polymers with low band gaps (E_g).[1–5] Polymers with low band gaps are expected to show not only good intrinsic conductivity but also good nonlinear optical properties.[6] For successful molecular designing of conducting polymers, one needs to have a complete understanding of the relationship between the chemical structure of a polymer and its electronic and conduction properties. Once such an insight has been achieved, desired electronic properties could be obtained by specific synthesis after molecular design.

Various routes are presently followed for designing novel conducting polymers. One exciting possibility in this direction is provided by the quasi-one-dimensional copolymers which can have tailor-made conduction properties depending on the choice of two semiconducting components, their relative amounts, and their arrangement in the polymer chain. It is already well known that copolymerization[7–10] can considerably influence the electronic properties of its constituent homopolymers. Recent theoretical and experimental investigations have shown that the low band gap polymers can also be obtained from the copolymerization of alternating aromatic-quinoid units or donor–acceptor units.[11–13] Using this strategy, various novel polymers have been proposed.

In this paper we investigate the electronic and geometric structures of the polymers based on thienothiadiazole and thiophene units (diagram 1). The thienothiadiazole monomer (molecule 1a in diagram 2) is known to have a very small separation between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), being lower than that of isothianaphthene[14,15] whose polymer is one of the lowest band gap conjugated polymers ($E_g \approx 1.0$ eV).[16] If the low HOMO-LUMO separation of thienothiadiazole can be carried over to its polymer, one should expect a very low band gap polymer. We report in this paper the results of our investigations of the electronic structures of poly(thienothiadiazole) (Poly-1a) and periodic copolymers of thiophene and thienothiadiazole (Poly-2b and Poly-3b) shown in diagram 1. Though poly(thienothiadiazole) has not yet been synthesized, there is a report on the synthesis of the copolymer (Poly-3b) by Tanaka and Yamashita,[15] who have reported the band gap of 0.9 eV for this copolymer.

II. METHOD OF CALCULATION

All the calculations of these polymers were performed on the basis of the *ab initio* one-dimensional self-consistent-field crystal orbital (SCF-CO) method. The minimal basis set
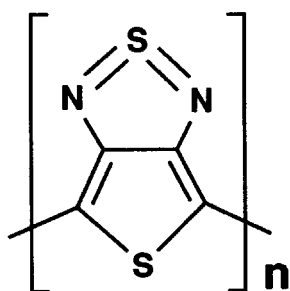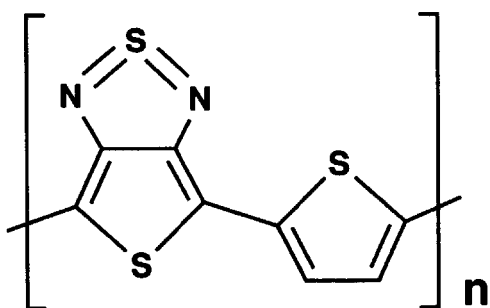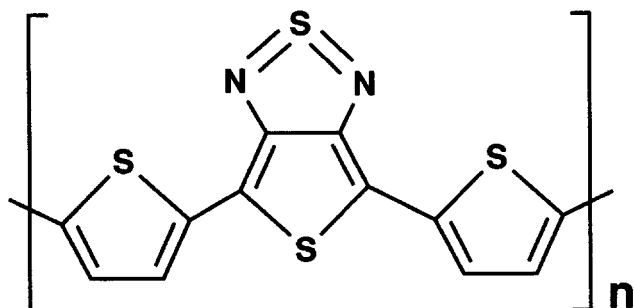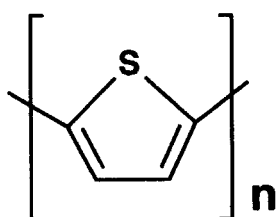
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[a]Corresponding author.

Poly-1a

Poly-2b

Poly-3b

PT (polythiophene)

Diagram 1.

(STO-3G) was used because of the size of the systems considered. The program employed for the present calculation is able to handle the screw axis symmetry as well as the translational symmetry. The energy gradient method was employed for optimizing the geometries of the polymers, assuming them to be planar. The geometry of Poly-3b was estimated by calculating ten structures, due to its size. The number of the representative wave vectors was chosen as 21 with regular intervals in the Brillouin zone. The overlap and electron-repulsion integrals were calculated as far as the fourth, third, and second nearest neighboring cell for Poly-1a, Poly-2b, and Poly-3b, respectively (~20 Å from the central cell on an average).

To understand better the relationship between the nature of the polymers and their geometries, we also carried out *ab initio* molecular orbital (MO) calculations using the same basis set (STO-3G). In order to compare the results obtained from the ultraviolet (UV) spectra, the excitation energies were calculated for the oligomers with various chain-lengths using the single excitation configuration interaction (SECI) method. The MO calculations were carried out using the GAUSSIAN 92 program.[17]

III. RESULTS AND DISCUSSION

A. Electronic properties of polymers

Let us first examine the electronic properties of Poly-1a, Poly-2b, and Poly-3b. It may be noted that Poly-2b and Poly-3b are periodic copolymers of thiophene and 1a units in the ratio of 1:1 and 2:1, respectively. For the sake of comparison, polythiophene (PT) was also studied. For the calculations of these polymers, their geometries optimized by the energy gradient method were employed. From the band structures of all the four polymers shown in Fig. 1, it is found that the band gap decreases with an increase in the ratio of thiophene ring and that Poly-3b shows a considerably small direct gap of 5.97 eV (Table I). Simple scaling with the experimental band gap of PT (2.0 eV) (Ref. 18) gives a band gap of 1.3 eV for Poly-3b, though it is not so small as the experimental one (0.9 eV).[15] Note that the interchain π-conjugation through S–N contact, as supposed by Tanaka and Yamashita,[15] for the explanation of the small gap of Poly-3b is not taken into account here, but such an effect seems not to be important as mentioned later. We also see that the HO and especially LU bandwidths of Poly-1a, Poly-2b, and Poly-3b are smaller compared to those of PT, except for the HO bandwidth of Poly-1a which is somewhat larger than that of PT. The HO bandwidth decreases as the ratio of the thiophene ring increases (Table I). It is also interesting to note that the change of the band gap values in these polymers are the result of a decrease in the ionization-potential (IP) values and an increase in the electron-affinity (EA) values [i.e., highest occupied crystal orbital (HOCO) and lowest unoccupied CO (LUCO) levels move closer each other]. It therefore means that these polymers can be more easily doped than PT (through *p*- and *n*-type doping). However, on the basis of our calculations, copolymers as well as Poly-1a
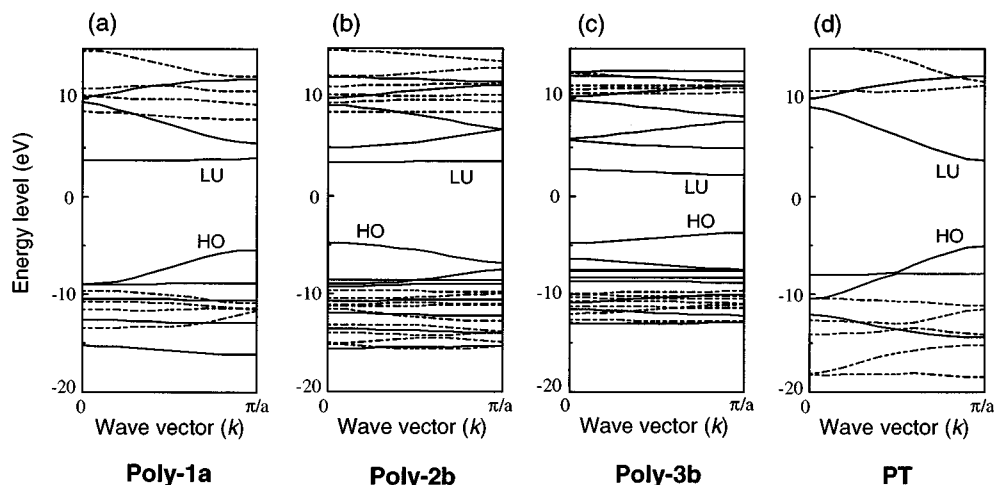
FIG. 1. Band structures of (a) Poly-1a, (b) Poly-2b, (c) Poly-3b, and (d) PT. Solid and dashed lines indicate those from π- and σ-orbitals, respectively. HO and LU designate the highest occupied and the lowest unoccupied bands, respectively.
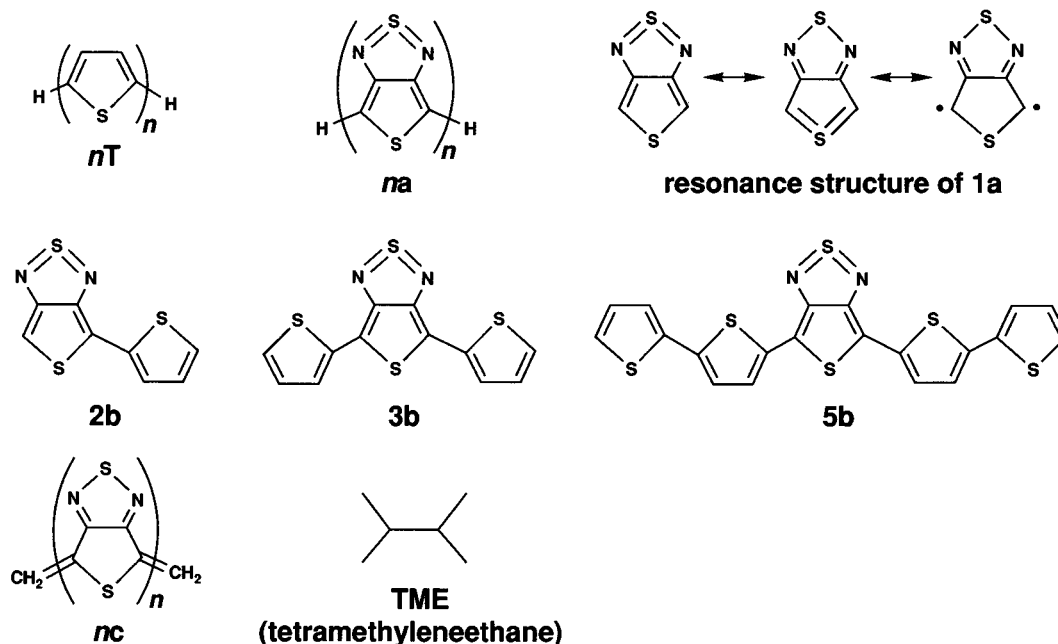

Diagram 2.

cannot become a good conducting materials, due to their small bandwidths and the large band gap for Poly-1a.

The optimized geometries of Poly-1a, Poly-2b, Poly-3b, and PT are depicted in Fig. 2. Note that the optimized bond lengths of PT are in agreement with those by the 6-31G basis set within the error of ± 0.02 Å.[19] Poly-1a is found to have a geometry quite different from PT. In Poly-1a, intercell bond C_1-C_1' (1.33 Å) and C_2-N bond (1.30 Å) are a double bond and C_1-C_2 bond (1.48 Å) a single bond. The S_1-C_1 and S_2-N bond lengths in Poly-1a are close to the S_1-C_1 bond length in PT, implying hereby that the resonance effects (diagram 2) are not important in Poly-1a. It should be noted that the geometry of Poly-1a is neither aromatic (as in PT) nor quinoid because the π-conjugation along the polymer backbone is disrupted at the C_2-C_2' bond. The localization of the π-electrons in Poly-1a therefore leads to the flat bands. In case of Poly-2b, the 1a unit geometry is almost identical to that of Poly-1a and the thiophene unit is found to take a

TABLE I. Calculated electronic properties of polymers (in eV).

Polymer	E_g^a	Bandwidth		IP	EA
		HO	LU		
Poly-1a	^{ind}9.13	3.54	0.24	5.48	−3.64
Poly-2b	^{dir}8.14	2.03	0.25	4.83	−3.31
Poly-3b	^{dir}5.97	1.03	0.50	3.82	−2.15
PT	^{dir}8.85	2.92	5.35	5.16	−3.70

^{a}The signs, ind and dir, show an indirect and direct band gap, respectively.

quinoid structure as a result of strong influence of 1a. Interestingly, clear difference is observed in the geometry of Poly-3b from those of Poly-1a and Poly-2b. In Poly-3b, aromatic nature of the thiophene units is maintained by the C_1–C_3 and C_6–C_6' single bonds, and the geometry of 1a unit is supposed to have a resonance structure without distinct bond alternation. These characteristics are derived from the stabilization through the successive two thiophene rings in a Poly-3b chain.

From π-AO bond population given in Table II, one can see that the bonding features of Poly-1a and Poly-2b differ from those of PT and Poly-3b. The intercell bonds in Poly-1a and Poly-2b have a very large population of 0.17 as compared to PT (0.03), as indicated in the optimized geometries. From the population analysis of Poly-3b we see that the thiophene unit has almost the same π-character with that of PT and that π-conjugation of 1a spreads homogeneously within the unit even in the S–C, S–N bonds. Atomic charges and π-electron densities are also summarized in Table II. The atoms S_1, S_2, and S_3 are positively charged and atoms N are

negatively charged. Charge transfer between 1a and thiophene units in the two copolymers Poly-2b and Poly-3b is very small; 1a unit is charged by −0.10 in Poly-2b and −0.03 in Poly-3b, suggesting that no significant charge-transfer occurs between these two units in the ground state.

The frontier orbitals (HOCO and LUCO) of each polymer are shown in Fig. 3. These patterns of all the polymers correspond to those at the Brillouin zone boundary ($k = \pi/a$) except for Poly-2b, for which the data at the zone center ($k=0$) is used because the direct band gap shows minimum value at these k points. One can see a clear difference between the patterns of Poly-1a and PT. The signs of the orbital coefficients of the HOCO (LUCO) in Poly-1a resemble those of the LUCO (HOCO) in PT. It is worth noting that the atoms C_2 and C_2' make a relatively smaller contribution to the HOCO and LUCO of Poly-1a, in contrast to their contributions to the frontier orbitals of PT. The degree of π-conjugation, therefore, along the main chain of Poly-1a is expected to be smaller than that in PT. The orbital patterns of Poly-2b as well as those of thiophene unit are similar to those of Poly-1a, suggesting hereby that 1a units exert a great influence on their electronic structures. Note that the characters of the intercell bonds of Poly-1a, Poly-2b are bonding and antibonding in the HOCO and the LUCO, respectively, while those of PT show the opposite natures. Being different from Poly-1a and Poly-2b, the orbital patterns of both 1a and thiophene units of Poly-3b are similar to the patterns of the corresponding orbitals of PT with antibonding and bonding natures in the intercell bonds of the HOCO and the LUCO, respectively. The contributions of the atoms C_2 and C_2' to the frontier orbitals are also quite small in Poly-3b,
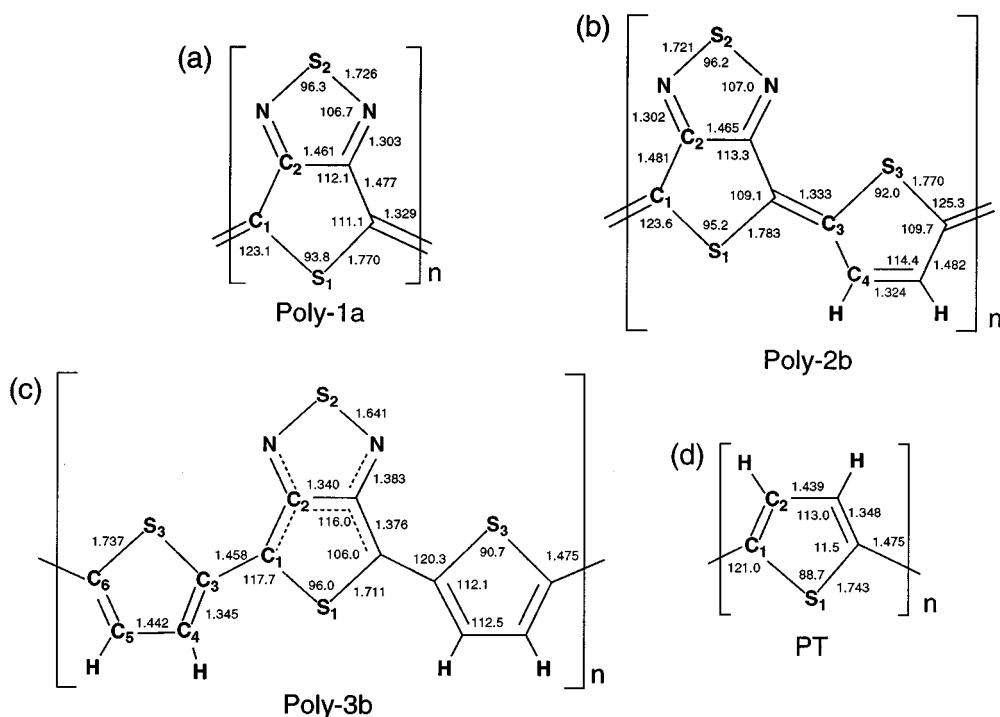

FIG. 2. Optimized geometries of each polymer shown in diagram 1. Bond lengths and angles are in Å and deg, respectively.

TABLE II. Calculated net charge, π-AO population, and π-AO bond population of each polymer.[a]

	Poly-1a	Poly-2b	Poly-3b	PT
Net charge (π-AO population)[b]				
S_1	0.28 (1.87)	0.21 (1.89)	0.34 (1.61)	0.26 (1.78)
C_1	−0.10 (1.05)	−0.11 (1.08)	−0.13 (1.14)	−0.11 (1.06)
C_2	0.06 (1.02)	0.06 (1.02)	0.01 (1.08)	−0.11 (1.05)
N	−0.30 (1.10)	−0.31 (1.10)	−0.34 (1.23)	
S_2	0.43 (1.80)	0.42 (1.81)	0.54 (1.52)	
S_3		0.27 (1.87)	0.28 (1.77)	
C_3		−0.09 (1.02)	−0.10 (1.06)	
C_4		−0.07 (1.00)	−0.09 (1.07)	
C_5			−0.09 (1.06)	
C_6			−0.11 (1.06)	
π-AO bond population				
S_1–C_1	0.015	0.012	0.053	0.035
C_1–C_2	0.027	0.028	0.098	0.153
C_2–C_2'	0.045	0.045	0.073	0.061
C_2–N	0.151	0.151	0.081	
N–S_2	0.027	0.026	0.058	
C_1–C_1' (inter cell)	0.170			0.029
C_1–C_3		0.167	0.040	
S_3–C_3		0.018	0.035	
S_3–C_6			0.035	
C_3–C_4		0.031	0.149	
C_6–C_5			0.153	
C_4–C_5			0.062	
C_1–C_3' (inter cell)		0.167		
C_6–C_6' (inter cell)			0.030	

[a]See Fig. 2 for the atomic notations.
[b]π-AO population is shown in the parentheses.

provided less π-conjugation along the polymer backbone resulting in narrow bandwidths. Because the π-conjugation along a polymer backbone is very weak in Poly-3b, the delocalization through the interchain S–N contact, suggested in Ref. 15, probably does not play an important role in such a small band gap of Poly-3b. Despite the above common features in the orbital patterns of the polymers, it still remains unclear (i) why the increase in the portion of thiophene units reduce the band gap, giving such a small band gap in Poly-3b and (ii) why the orbital patterns of the HOCO and the LUCO of PT get reversed in Poly-1a and Poly-2b.

In order to check the influence of geometry on the electronic properties, we have also calculated the electronic properties of Poly-1a with the geometries taken from the x-ray result,[15] as shown in Table III. Three types of bond lengths were employed for the C_1–C_1' bond. In all the cases, the band gap of Poly-1a gets reduced strongly as C_1–C_1'
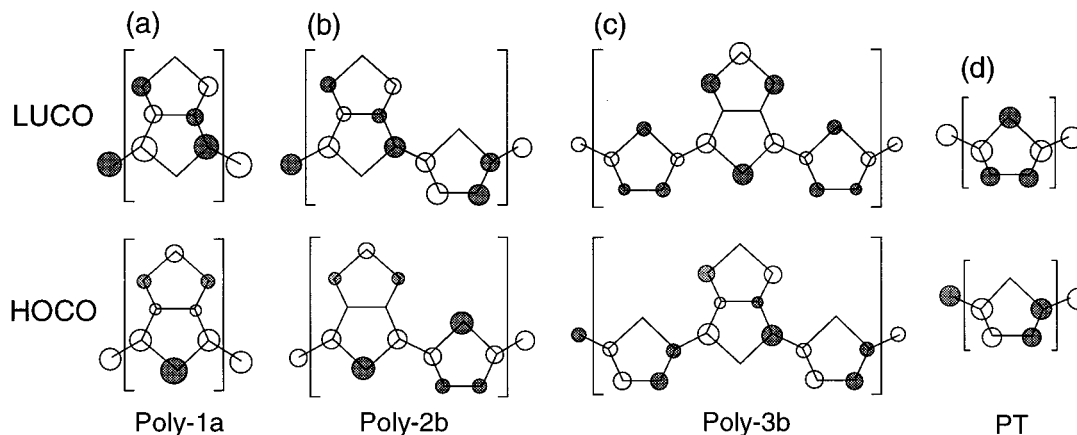

FIG. 3. Orbital patterns of (a) Poly-1a, (b) Poly-2b, (c) Poly-3b, and (d) PT. All these patterns correspond to those at the Brillouin zone boundary ($k = \pi/a$) except for those of Poly-2b which correspond to zone center ($k = 0$).

TABLE III. Calculated electronic properties of Poly-1a using different geometries.

Polymer	Geometry	C_1–C_1' bond length[a] (Å)	Relative energy[b] (eV)	E_g^c (eV)	Bandwidth (eV) HO	Bandwidth (eV) LU	IP (eV)	EA (eV)
Poly-1a	Optimized[d]	1.33	0.0	^{ind}9.13	3.54	0.24	5.48	−3.64
	X-ray result (1)[e]	1.33	+1.26	^{dir}7.28	3.88	1.07	4.44	−2.84
	X-ray result (2)[e]	1.40	+1.35	^{dir}6.38	4.07	1.48	4.02	−2.36
	X-ray result (3)[e]	1.45	+1.59	^{dir}5.71	4.20	1.78	3.71	−2.00
PT	Optimized[d]	1.48		^{dir}8.85	2.92	5.35	5.16	−3.70

[a]See Fig. 2 for the position of C_1 atom.
[b]Positive values indicate instability as compared with the optimized Poly-1a.
[c]ind and dir mean indirect and direct gap, respectively.
[d]The geometry obtained by the energy gradient method was used.
[e]The geometry of the unit cell is derived from the x-ray result in Ref. 15 (S_1–C_1=1.71 Å, C_1–C_2=1.39 Å, C_2–N=1.35 Å, N–S_2=1.61 Å, and C_2–C_2=1.44 Å; as for the atomic notations shown in Fig. 2).

bond-distance becomes longer. The stability of Poly-1a is also found to decrease with an increase in the C_1–C_1' bond length. Furthermore, the bandwidths of HOCO and LUCO increase with an increase in the C_1–C_1' bond length. In all the geometries, no significant change in the orbital pattern is observed [Fig. 3(a)]. The reasons for such observed behavior of Poly-1a with the change in the C_1–C_1' bond length shall be discussed later.

B. Electronic properties of molecules

Ab initio MO calculations were further performed for deeper understanding of the electronic structure of poly-(thienothiadiazole) and the copolymers with the minimal (STO-3G) basis set. One-particle picture (SCF approximation) deteriorates for estimating an energy gap, so that excitation energies were calculated on the basis of the single excitation configuration interaction (SECI) method for the molecules displayed in diagram 2. The geometry optimization was performed prior to the SECI calculations for the molecules shown in Fig. 4.

Comparison of the geometries of 1a and 2a with that of the unit cells of Poly-1a and Poly-2b (Fig. 2) shows that S_1–C_1 and S_2–N bonds in the molecules are shorter than the corresponding bonds in the polymers. However, the lengths of the bonds in these molecules are not so short as to regard them as double bonds. In the case of 2a and 3a, the geometry of 1a unit is essentially preserved and the C_1–C_1' bond is quite long ($\sim$1.43 Å). One can thus notice a significant change in the geometries as one moves from oligomers (molecules) with several rings to infinite polymers in Poly-1a and Poly-2b. The geometry of 1c resembles that of Poly-1a because the C_1–C_3 and C_2–N bonds of 1c can be regarded as double bonds and the S_1–C_1 and S_2–N bonds are quite long. On the other hand, the geometry of Poly-3b is found to preserve that of 3b in which thiophene and 1a units have the same geometries as the original molecules. It may be noted that the optimized geometry of 3b is similar to the experimental results.[15]

The excitation energies for the various molecules along with their experimental results are given in Table IV. The trend of the theoretical results is in agreement with the ex-

perimental results. In both the nT and na oligomers indicated in diagram 2, the excitation energies decrease with an increase in the length of the oligomer, due to the orbital interactions between the HOMO-HOMO and the LUMO-LUMO. The excitation energies of na show much smaller value than those of the corresponding thiophene oligomers, nT (n=1–3). The excitation energy of 3a becomes extremely small with a value of 1.97 eV. Molecule 3b has a larger transition energy than 3a, whereas Poly-3b has a smaller band gap than Poly-1a (Table I). The SECI was also performed for the molecules nc (n=1–3), which have similar geometries as the unit cell of Poly-1a. Molecules nc are calculated to have larger excitation energies than the corresponding molecules na, though these values are still smaller than those of corresponding nT. From the aforementioned discussion, the following three facts are obtained: (i) The excitation energies of 1a, 2a, 3a, and even of 3b are very small, showing a good agreement with experiment. The extension of 1a unit to 2a and then to 3a lowers both the excitation energy as well as the HOMO-LUMO separation. (ii) The geometry of 1a is different from that of the unit cell of Poly-1a, and the geometry of 2b also different from the structure of Poly-2b. (iii) The unit cell of Poly-3b has a geometry similar to 3b molecule, due to the separation of two thiophene rings.

Let us now look at the reason why 1a shows such a small excitation energy compared to thiophene. This may be explained by discussing the case of tetramethyleneethane (TME) (diagram 2). TME has been studied from the viewpoint of a possible high-spin molecule[22–24] because TME has non-Kekulé geometry and has two degenerate nonbonding molecular orbitals (NBMOs) at the Hückel level. As shown in Fig. 5, TME is in a triplet state at the Hückel level but the electron correlation brings a more stable singlet state with a very small HOMO-LUMO separation due to through-space interaction. The introduction of the p_π orbital of the sulfur atom causes an interaction between the HOMO of TME and p_π of S atom. No orbital interaction occurs between the LUMO and S p_π, due to the symmetry restriction. Because the HOMO-LUMO separation is considerably small in TME, that of 1a shows a small value, too. Note that substitution by
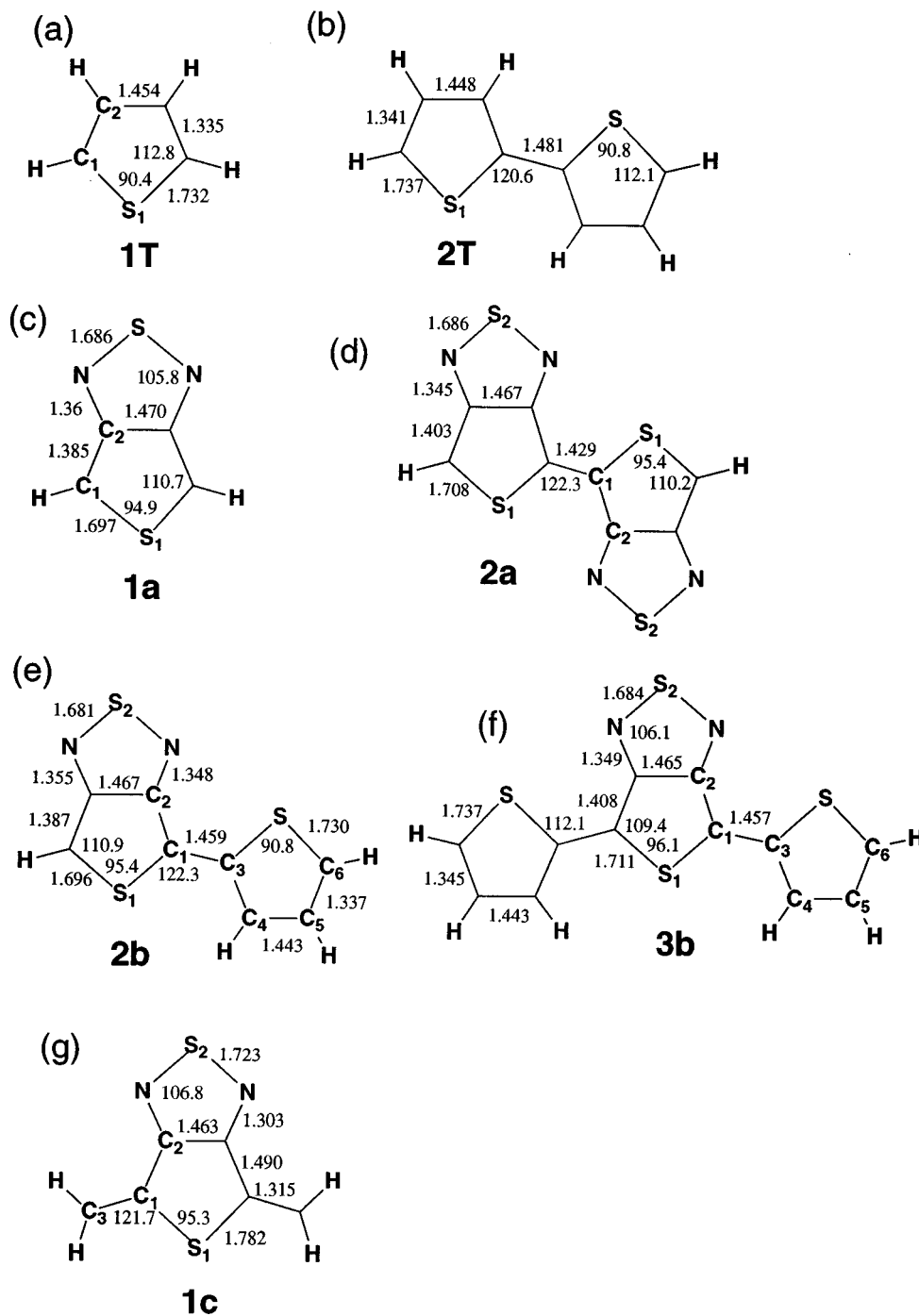
FIG. 4. Optimized geometries of (a) 1T, (b) 2T, (c) 1a, (d) 2a, (e) 2b, (f) 3b, and (g) 1c. Bond lengths and angles are shown in Å and deg, respectively.

nitrogen does not significantly affect the separation as the substitution just lowers the energies of the MOs.

C. Extension from molecule to polymer

The reasons for the different behaviors between oligomers *na* and Poly-1a are still not completely clear. It needs to be noted that substantial changes in electronic states may occur as a result of the transition from molecules (oligomers, *na*) to Poly-1a. To examine such an interesting transition of electronic and geometric structures, effect of the chain length was investigated for longer oligomers with up to 10 units, as shown in Fig. 6. Owing to the dimensional restriction, the HOMO-LUMO separation is used instead of the excitation energy since it is confirmed from Table IV that the HOMO-LUMO separation has good correlation with the excitation energy. For longer oligomers ($n \geq 4$ for nT, na, nb and $n \geq 3$ for nc), fixed geometries built up from the optimized geometries of the dimer and trimer were utilized for the calculation. The HOMO-LUMO separation decreases with increasing n in every oligomer because of the interaction between

TABLE IV. Calculated excitation energies (in eV) of the various molecules (diagram 2).[a]

Molecule	Excitation energy	HOMO-LUMO separation	Expt.[b]	IP	EA
1T	8.33	14.75	5.77[c]	7.22	−7.53
2T	6.59	11.90	4.11[d]	6.00	−5.90
3T	5.81	10.70	3.49[d]	5.56	−5.24
1a	3.79	8.03	2.99[e]	4.94	−3.09
2a	2.64	5.52	···	3.46	−2.06
3a	1.97	4.09	···	2.65	−1.44
2b	3.37	7.17	···	4.36	−2.81
3b	2.94	6.46	2.01[f]	3.92	−2.54
1c	6.93	11.47	···	6.31	−5.06
2c	5.79	10.07	···	5.56	−4.51
3c	5.50	9.71	···	5.24	−4.47
TME	2.69	4.60	···	2.67	−1.93

[a]The geometries were optimized before calculating their excitation energies, except 3c whose geometry is built from 2c.
[b]The experimental excitation energy is determined from λ_{max} of the UV spectrum.
[c]From Ref. 20.
[d]From Ref. 21.
[e]From Refs. 14, 15.
[f]From Ref. 15.

the HOMO-HOMO and the LUMO-LUMO. There is a marked decrease in the separation of *na* at $n \geq 4$ and very low separation is observed at $n = 10$ (0.43 eV). The crossing of *nT* and *nc* lines is observed at about 10 units.
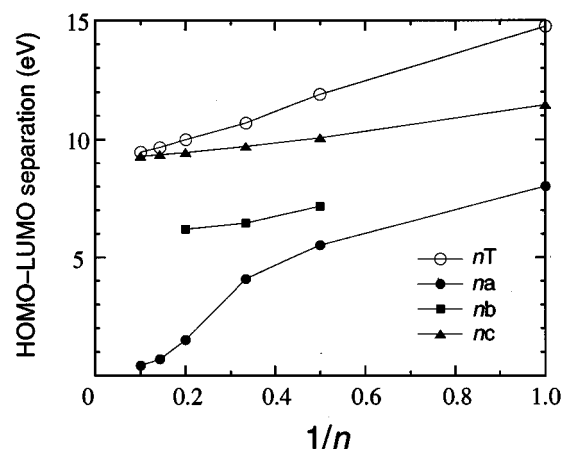

FIG. 6. Plot of the HOMO-LUMO separation as a function of oligomer length. Open circles, closed circles, squares, and triangles indicate *nT*, *na*, *nb*, and *nc*, respectively. Lines are the guides for the eye.

From the results mentioned above, we show the changes in the energy levels of the frontier orbitals with an increase in the number of 1a units in Fig. 7. The corresponding changes in the energy levels of the frontier orbitals of PT with an increase in the number of thiophene units are, for the sake of comparison, illustrated in Fig. 8. It is interesting to note that the patterns of the frontier orbitals in both the oligomers of thiophene (*nT*) and PT ($k = \pi/a$ for both the HOCO and the LUCO) are same (Fig. 8), whereas the patterns of the frontier orbitals of the *na* get reversed in Poly-1a
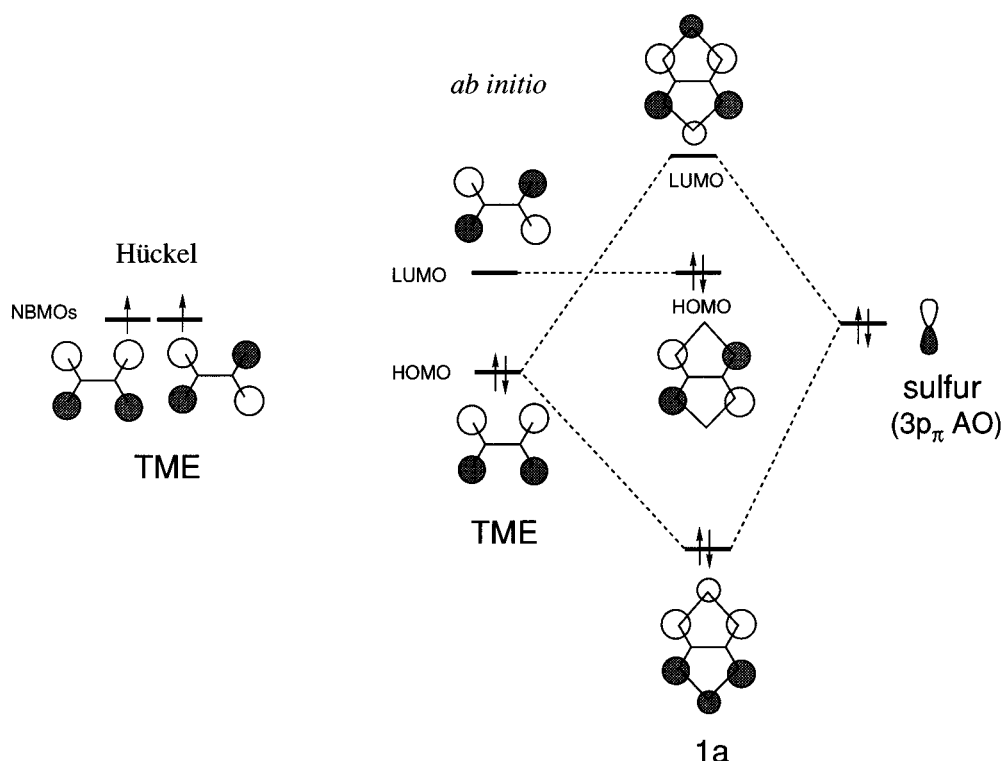

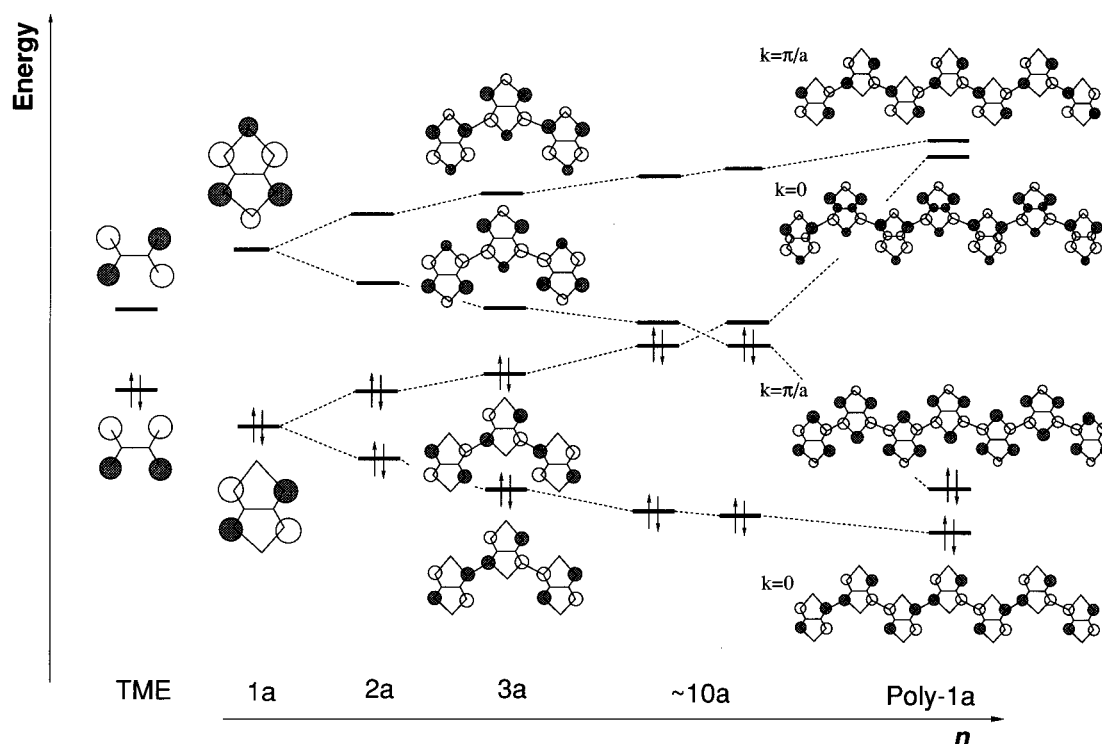FIG. 5. Models of orbital interaction between TME and $3p_\pi$ orbital of the S atom.

FIG. 7. Illustration of the evolution of the electronic properties of Poly-1a from its oligomers. In the case of oligomers, only the orbitals in which all the C_1-C_1' bonds are either bonding or antibonding have been shown. Orbital patterns of the oligomers have been simplified in order to stress the importance of the orbital interactions (HOMO-HOMO and LUMO-LUMO).

($k=\pi/a$ for the HOCO and $k=0$ for the LUCO) (Fig. 7). Because the low-gap state seen in 7a–10a is unstable, rearrangement of the geometry as well as the electronic states are expected to occur, being similar in the charge-density-wave (CDW) state of polyacetylene (PA).[25] This drastic change of na at $n\sim10$ in the geometry and the electronic state will lead to the characteristics of nc. Therefore the larger band gap of Poly-1a than that of PT can be understood from the extrapolation of the nc and nT lines in Fig. 6. Although the orbital patterns of the HOMO and LUMO of 10a is actually not similar to those of 1a nor to Poly-1a, due to the orbital mixing between the two MOs closely situated. Further extension of a na chain will give the patterns of nc or Poly-1a.

As far as the π-conjugation is concerned, it is weaker in both the na oligomers and Poly-1a than in the corresponding thiophene systems. But in the case of Poly-1a, the bonding and antibonding nature of the intercell bond (C_1-C_1') becomes significant, due to the relatively small intracell interaction (orbital coefficients of atoms C_2 and C_2' in both the frontier orbitals are quite small). From the frontier orbital patterns, Poly-1a can be regarded as a derivative of the linearly aligned isolated ethylene molecules. Therefore in Poly-1a, although the contribution of the intracell interactions to its both HOCO and LUCO is quite small, the intercell interaction through C_1-C_1' bond is quite large, leading to a large band gap and small bandwidths. In other words, the orbital patterns of intercell C_1-C_1' bonds can determine the energy levels or orbitals in the case of polymers. On the basis of this, one can explain the observed dependence of the band

gap and the stability of Poly-1a on the C_1-C_1' bond length (Table III). Longer intercell bond weakens the intercell interaction, resulting in the smaller band gap and less stability. In the case of Poly-2b the transition is supposed to occur too, judging from the geometry and orbital patterns, accompanying with the change to the quinoid structure of thiophene unit. The reason for the lower band gap of Poly-2b than Poly-1a is the weakening of the localization upon the intercell C_1-C_1' bond, as can be seen in the bond distance (see Fig. 2).

The CO patterns of Poly-3b are directly correlated with orbital interactions in the oligomers without transition like PT. Stability of aromatic structure of the thiophene unit compared to quinoid structure may overcome the instability of the 1a geometry, signifying the retention of the nature of the oligomer. Extremely narrow gap of Poly-3b can be also expected from the extrapolation of nb in Fig. 6. This low gap mainly arises from the low gap nature of 1a unit and the orbital interactions of the frontier MOs.

It is also probable that both Poly-1a and Poly-2b, if succeeded in synthesis, may show a very small transition energy because the synthesized polymer is usually an oligomer with a finite length. One may, however, say that Poly-1a and the copolymers Poly-2b and Poly-3b are not expected to be better candidates than PT for intrinsic conductivity in view of their smaller bandwidths. Note that the conductivity of a system somewhat similar to Poly-3b has been reported to be rather low in the I_2-doped state (6×10^{-3} S/cm).[26]
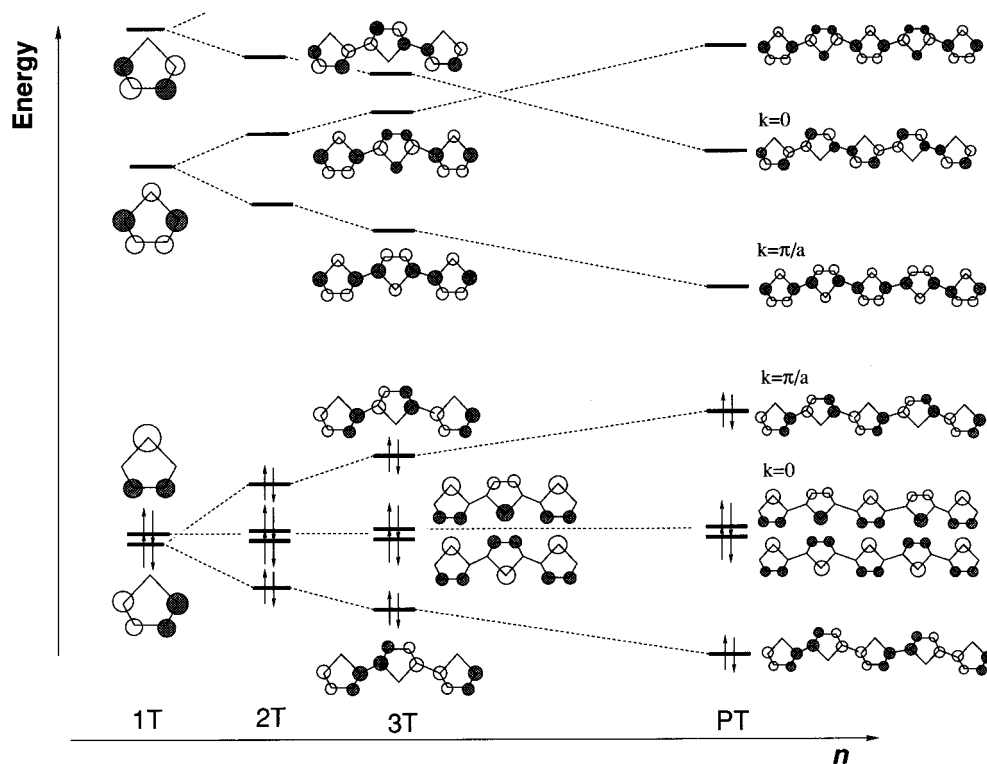
FIG. 8. Illustration of the evolution of the electronic properties of polythiophene (PT) from its oligomers. In the case of oligomers, only the orbitals in which all the C_1–C_1' bonds are either bonding or antibonding have been shown. Orbital patterns of the oligomers have been simplified in order to stress the importance of the orbital interactions (HOMO-HOMO and LUMO-LUMO).

IV. CONCLUDING REMARKS

The geometric and the electronic properties of poly-(thienothiadiazole) (Poly-1a) and the periodic copolymers of thienothiadiazole and thiophene units with the ratio of 1:1 (Poly-2b) and 1:2 (poly-3b) have been investigated with the aid of the *ab initio* crystal orbital method.

The optimization of Poly-1a showed a quite different geometry from that of the corresponding molecule with a short intercell and a long C_1–C_2 bonds. Probably due to a strong localization in the intercell bond and a weak delocalization within a thienothiadiazole unit, Poly-1a showed a gap larger than that of polythiophene (PT) and the bandwidths not so large. From the study of its oligomer, it becomes clear that the electronic and geometric structures obviously change in the oligomer with about 10 units and that a small gap is realized in this range.

Poly-2b showed a geometry similar to that of Poly-1a in which even a thiophene ring changed to a quinoid structure, due to the thienothiadiazole unit. The band gap of Poly-2b is reduced because of the weakening of the intercell interaction.

The geometry of Poly-3b is extremely different from that of Poly-1a and Poly-2b. By the two successive thiophene rings, the properties of Poly-3b are almost same as those of its oligomer and the orbital of Poly-3b can be explained in terms of the extension of the HOMO-HOMO and the LUMO-LUMO interactions like PT. The small HOMO-LUMO separation seen in thienothiadiazole molecule was discussed by means of the nonbonding molecular orbitals

(NBMOs) of tetramethyleneethane and the narrow gap of Poly-3b (1.3 eV by a simple scaling) is supposed to be originated in this. Though Poly-3b is expected to possess low band gap nature, it is not expected to be a better candidate than PT for the conducting polymer, due to the relatively small π-conjugation along polymer backbone.

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