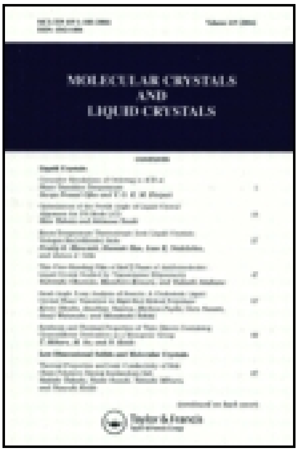

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Rotational Effect on the One-Dimensional π-Conjugated Polymer

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We have investigated the modulation of the physical and electronic properties including their band structure of poly(1,4-phenylene diethynylene-co-9,10-anthracenylene) by the co-axial rotation of π-conjugated polymer chain in the periodic boundary condition framework. The estimated rotational barrier was calculated to 2.38 kcal/mol per cell, suggesting that the aromatic rings of phenylene and anthracenylene were freely rotating each other at the room temperature. On the other hand, bandgap dramatically changes 2.0–3.0 eV by the rotation of aromatic rings. This result suggests that the electronic properties of this polymer should be influenced by rotational effect at the ambient condition.

Keywords Density of states; electronic band structure; electronic material; organic polymer; rotational effect

1. Introduction

Π-conjugated polymers are one of the most important materials for post silicon electronic devices, because of their broad utility as well as processability suitable for fabricating devices through the print process. Recently, organic materials based electronic devices such as light emitting diode [1,2], field effect transistor, and photo voltaic cell become available commercially, therefore, it will be important to understand the electronic property of these polymers [3–10]. There are many theoretical researches of electronic property of them, however these researches are restricted only in the static structure. However, the electronic properties of polymer should be different from static structure because the polymer chain has many kinds of disorder mode such as bending, rotating, and stretching mode at the room temperature. Hence in this study, we have examined poly(1,4-phenylene diethynylene-co-9,10-anthracenylene) (P-ph-an) [1,2] that could be modified relationship of phenyl and anthracenynl groups by the free co-axial rotation of these rings, as a model of

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Address correspondence to Shigekazu Ohmori, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan; Fax: +81 29 861 4413; E-mail: ohmori-sh@aist.go.jp the structural and electronic properties modulation of π-conjugated polymer chain in the periodic boundary condition framework.

2. Computational Method

Figure 1 shows (a) the unit cell of P-ph-an and (b) its monomer (Ph-an) calculated in this work, where Tv is translation vector of this polymer and ϕ is angle between the planes of phenyl and anthracenyl groups. All geometrical optimisations of P-ph-An (with estimating parameter Tv) and Ph-an with fixed angle ϕ were taken at the B3LYP level density functional theory (DFT) calculation with a standard 3-21 G basis set. All DFT calculations were carried out using Gaussian03 program package [11]. It should be noted that these levels of theory give reasonable features for several molecular device systems [3–10]. Total and partial density of states (DOS) were calculated from the electronic band structures and population analysis of wave functions of calculation results.

3. Results and Discussions

Figure 2 shows the heat of formation (ΔH_f) profiles of P-ph-an and Ph-an with changing ϕ, which were standardized with minimum point. The most stable conformations of polymer and monomer were found at $\phi = 0$ degree. Changing rotation angle ϕ, ΔH_f of P-ph-an was increased to $2.38\,\mathrm{kcal \cdot mol^{-1} \cdot cell^{-1}}$ at the $\phi = 90$ degree conformation, that value was much larger than that of Ph-an. This result indicates that the rotation mode of aromatic rings in the P-ph-an had higher barrier than that of monomer, whereas these values were enough small for activation at room temperature. Figure 3a shows change in the bond lengths around acethyl group of P-ph-an and Ph-an. The length of the triple bonds (C-C) in the P-ph-an and Ph-an were decreased with $\phi = 0$ to 90 degree, contrary of inter-connect bonds between acetyl-phenyl (Bz-C) and acethyl-anthracenyl (An-C) groups. In the $\phi = 90$ degree conformation, these bond lengths of P-ph-an have almost same values as monomer's

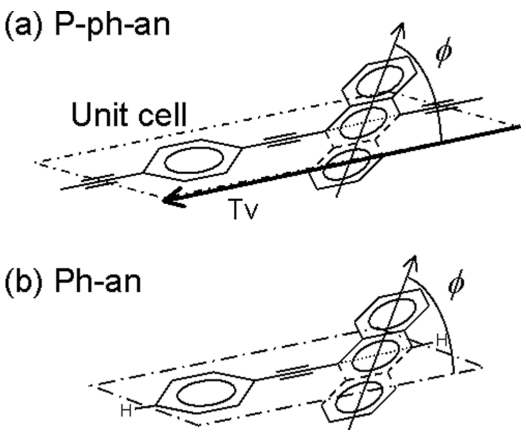

Figure 1. Schematic illustrations of P-ph-an and Ph-an. Unit cell of this polymer contains a phenyl and antracenyl units linked with two acethyl groups. Tv is translation vector of this polymer and ϕ is angle between the planes of phenyl and anthracenyl groups.

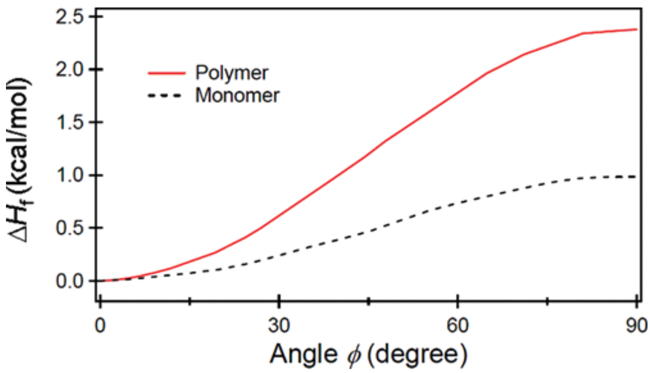

Figure 2. Free energy profiles of P-ph-an and Ph-an with changing rotation angle ϕ.

geometry, suggests that the long-range interaction through the polymer chain was disappeared at this conformation. In addition, the bond length between acethyl-anthracenyl groups were always shorter than that of acetyl-phenyl groups indicates that the interaction of former was stronger than that of later. On the other hand, parameter Tv, that is length of unitcell, stretches within 0.02 Å by the rotation; this value was about 0.14% of Tv length as shown in Figure 3b. Minimum bandgap of P-ph-an were increased with ϕ, contrary to maximum bandgap.

Figure 4 shows the electronic band structure and DOS profile of P-ph-an at the most stable conformation ($\phi = 0$ degree). The electron occupied and virtual states were drawn with solid and dashed lines, respectively. The highest occupied crystal orbital (HOCO) and the lowest unoccupied crystal orbital (LUCO) were found at

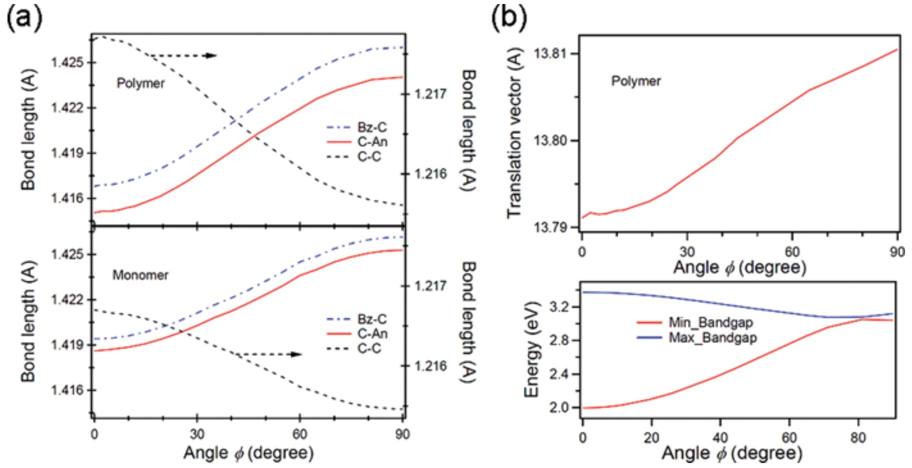

Figure 3. Schematic diagrams of (a) bond length modulation around acethyl group (C-C: triple bond at acethyl group, Bz-C: single bond between acetyl-phenyl groups, and An-C: bond between acethyl-anthracenyl groups) in the Ph-an and P-ph-an, and (b) unit cell length Tv and bandgap variation in the P-ph-an with changing rotation angle ϕ.

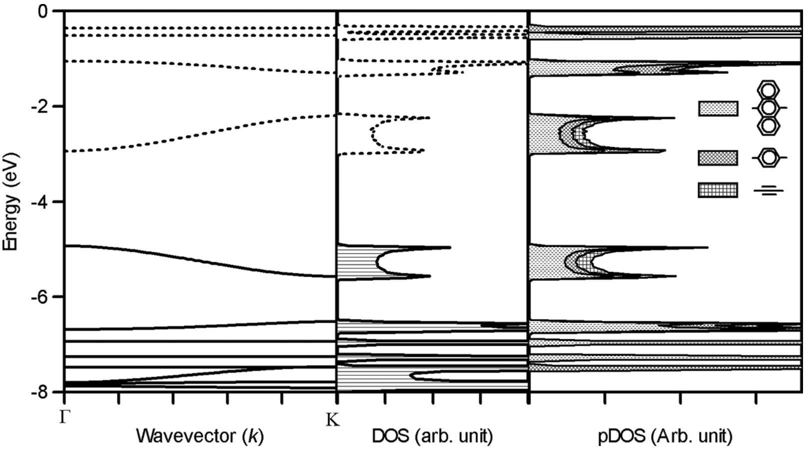

Figure 4. Electronic band structure and DOS of P-ph-an. The occupied and unoccupied states were drawn with solid and dashed lines, respectively. The partial DOS of anthracenyl, phenyl, and acethyl groups were drawn together.

−4.932 and −2.937 eV, both of which were placed in the Γ point. The bandgap of this conformation was estimated 1.995 eV, which well agrees with experimental result of derivative of this polymer [1,2]. The individual bands could be specified with dispersed and non-dispersed ones with varying wavevector k. The dispersed bands, including frontier bands, should have conjugated π-orbital through the polymer chain, contrary of non-dispersed ones. The DOS of this polymer has spikes at the HOCO and LUCO that were originated Van Hope singularity of one-dimensional electronic property. The contribution of each segment (anthracenyl, phenyl, and acethyl groups) in the DOS could be illustrated as partial DOS (pDOS). According to pDOS analysis, it was demonstrated that every segments were contributed to the DOS around HOCO and LUCO, suggesting that the polymer was conjugated through the chain. When the rotation angle ϕ was increased, band structures were changed as shown in Figure 5. All dispersed bands become flatten by the diminishing in the π-conjugation of aromatic rings, while non-dispersed bands were not changed. Then the bandgap of this polymer was increased from 2.0 to 3.0 eV with changing to the $\phi = 90$ degree. All bands become flat because of disappearing π-conjugation through the polymer chain. This effect should have an effect on the electronic

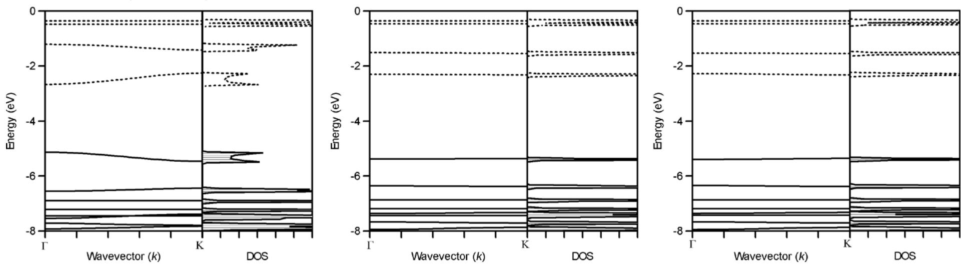

Figure 5. Change in electronic band structure and DOS profiles of P-ph-an with changing rotation angle ϕ.

properties of P-ph-an. It would be one reason for blue shift with varying driving voltage in the electroluminescence measurements [2].

4. Conclusion

In conclusion, we have investigated electronic properties of P-ph-an in terms of the rotation effect of aromatic rings in the π-conjugated one-dimensional polymer. It was found that this polymer has enough low energy barrier for rotating aromatic rings at the room temperature. On the other hand, the electronic band structures and DOS were dramatically changed with varying ϕ. In particular, gandgap of this polymer changes from 2.0 to 3.0 eV by the varying conformation of phenyl and anthracenyl groups. This result indicated that the rotational effect of aromatic rings should not be negligible in this polymer.

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