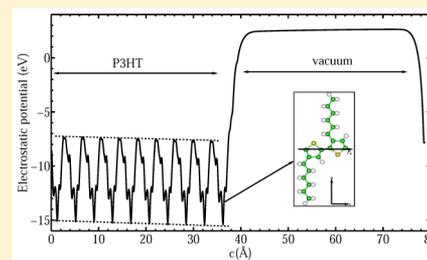


# Spontaneous Polarization Induced by Side Chains in Ordered Poly(3-hexylthiophene)

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**ABSTRACT:** We have found that ordered poly(3-hexylthiophene) (P3HT) exhibits spontaneous polarization along the backbone direction. This effect is caused by the lack of inversion symmetry due to head-to-tail side-chain arrangement. We have also shown that spontaneous polarization in ordered P3HT keeps significant values even at room temperature when the effects of thermal disorder are important. Consequently, it has a strong effect on electronic properties of the material. For example, at the interface between the crystalline and amorphous domain in P3HT, the electric field caused by spontaneous polarization confines the delocalized HOMO state to one side of the crystalline domain.



## INTRODUCTION

Organic semiconductors have gained a lot of interest in past decades due to their potentially large utilization in optoelectronic devices.<sup>1–5</sup> However, there are still many open questions regarding their electronic and transport properties. Many issues arise from the complexity of the structure of realistic organic semiconductors. Organic solar cells are mostly composed of two different materials. Conjugated polymers used as materials for organic solar cells have complex structure composed of mixed amorphous and crystalline domains.<sup>6,7</sup> Therefore, it is important to take into account all significant effects that take place at the interfaces between different materials or between different domains of the same material. At the interfaces, the effects of spontaneous polarization in materials can play an important role.

Spontaneous polarization is an intrinsic property of a material that it exhibits in the absence of external electric field. It occurs in crystals that do not have a center of inversion symmetry.<sup>8</sup> Such materials are referred to as pyroelectrics. The subgroup of pyroelectrics is ferroelectrics where external electric field alters the orientation of electric dipoles that cause the spontaneous polarization. There are many materials that are known to have high values of spontaneous polarization, such as some oxides, nitrides, etc.<sup>8–11</sup> Within the class of conjugated polymers, polyvinylidene fluoride (PVDF) is reported to have the highest spontaneous polarization of 0.04–0.2 C/m.<sup>2,12,13</sup>

Despite the fact that P3HT serves as a model conjugated polymer and that it has been widely investigated, the effects of spontaneous polarization in this material have not been discussed before. In this paper, the importance of spontaneous polarization in ordered regioregular poly(3-hexylthiophene) (P3HT) is pointed out for the first time. We show that this effect arises from head-to-tail side-chain arrangement which breaks the symmetry along the backbone chain. First, we have calculated spontaneous polarization of ideally crystalline P3HT

using density functional theory (DFT)<sup>14</sup> and modern theory of polarization. Next, we demonstrate that the effects of thermal disorder reduce this polarization but still keep it at a significantly large value. Finally, we discuss the effects of spontaneous polarization in crystalline P3HT on electronic properties of the interface between crystalline and amorphous P3HT where the interface is perpendicular to the backbone direction of the P3HT chain.

## METHODOLOGY

Under the modern theory of polarization,<sup>15–18</sup> total polarization given as a sum of ionic and electronic polarization can be expressed as

$$\mathbf{P} = \mathbf{P}^{\text{ion}} + \mathbf{P}^{\text{elec}} = \frac{1}{V} \sum_k q_k \mathbf{r}_k + \frac{2ie}{(2\pi)^3} \sum_n \int_{\text{BZ}} d\mathbf{k} \langle u_{n\mathbf{k}} | \nabla_{\mathbf{k}} | u_{n\mathbf{k}} \rangle \quad (1)$$

where  $V$  is the unit cell volume;  $q_k$  and  $\mathbf{r}_k$  are charges and positions of ions;  $u_{n\mathbf{k}}$  are the Bloch functions; and  $n$  runs over all occupied bands. The electronic part is calculated using the Berry phase approach. Polarization along axis  $i$  is defined as a multivalued quantity, modulo  $e\mathbf{a}_i/V$ , where  $\mathbf{a}_i$  is the lattice vector along the  $i$ -direction. To obtain a single value for spontaneous polarization, it should be calculated in reference to spontaneous polarization in the centrosymmetric structure.

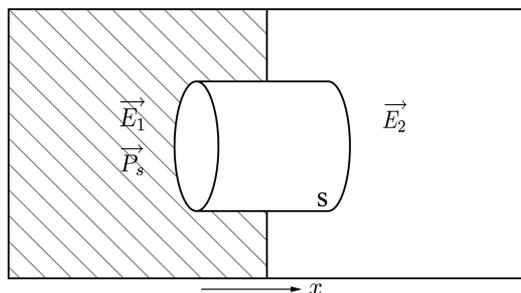
Spontaneous polarization of an ideal crystal can be calculated using this theory as implemented in several DFT-based computer codes. To calculate the effective polarization in a thermally disordered structure, calculations of systems involving a large number of atoms are required. Standard DFT-based codes are limited to several hundreds of atoms and cannot be used for such systems. An alternative way to extract the

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polarization of the material is from the calculation of electric fields in the system consisting of alternating layers of the material and vacuum. Let us consider such a system consisting of a material with spontaneous polarization  $P_s$  along the  $x$ -



**Figure 1.** Sketch of the interface between a material with spontaneous polarization and vacuum.

direction and vacuum, as shown in Figure 1. Polarization in the dielectric medium is given by the formula

$$\mathbf{P} = \mathbf{P}_s + \epsilon_0 \chi \mathbf{E} \quad (2)$$

where  $\epsilon_0$  is the electric permittivity of vacuum;  $\chi$  is the electric susceptibility of material; and  $\mathbf{E}$  is the electric field in material. From the definition of the electric displacement vector, it follows that

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P} \quad (3)$$

while the Maxwell equation for  $\mathbf{D}$  reads

$$\oint_S \mathbf{D} \cdot d\mathbf{S} = \rho \quad (4)$$

If we assume that there is no free charge at the interface between material and vacuum ( $\rho = 0$ ), we obtain the equation  $D_1 = D_2$  for the  $x$ -projections of the electric displacement vector in material and vacuum, respectively. Using eqs 2 and 3, we then obtain

$$P_s = \epsilon_0 E_2 - \epsilon_0 \epsilon_r E_1 \quad (5)$$

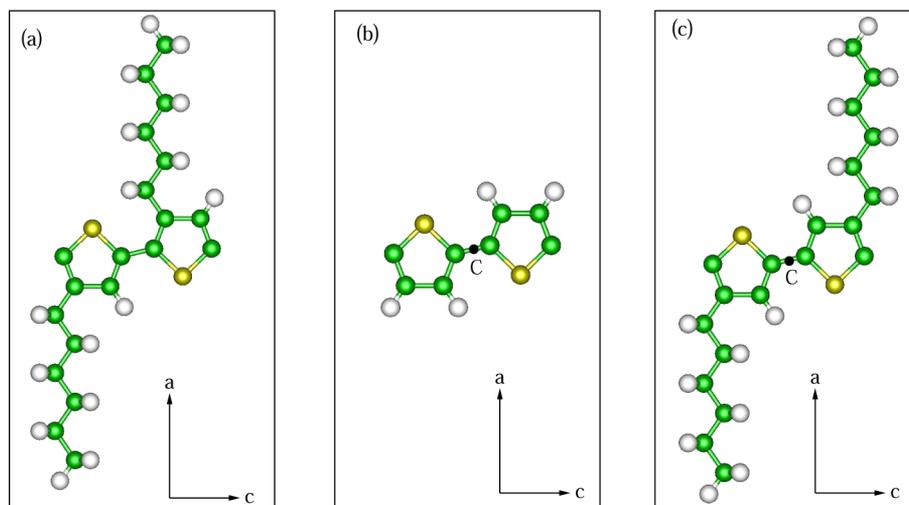
where  $\epsilon_r$  is the relative permittivity of material. Hence, spontaneous polarization can be easily obtained with known electric fields in material and vacuum, which can be calculated as electrostatic potential derivatives.

## RESULTS

### Spontaneous Polarization of Ideally Crystalline P3HT.

Spontaneous polarization of ideally crystalline P3HT was calculated using DFT as implemented in ABINIT<sup>15,17–19</sup> and Quantum ESPRESSO packages.<sup>17,20</sup> We used norm-converging pseudopotentials with LDA expression for the exchange–correlation term. There are several crystalline structures of P3HT reported in the literature.<sup>21–31</sup> We have considered the aligned structure (Figure 2a), where chains are mutually aligned in the  $\pi$ – $\pi$  stacking direction ( $b$ -direction, not shown in Figure 2). Unit cell parameters for this structure at 0 K, obtained from energy minimization calculated using classical potentials,<sup>32</sup> are  $a = 15.55 \text{ \AA}$ ,  $b = 4.1 \text{ \AA}$ , and  $c = 7.77 \text{ \AA}$ , and all angles are  $90^\circ$ . The obtained value for the spontaneous polarization in the backbone direction from both calculations is  $6.0 \times 10^{-3} \text{ C/m}^2$ . In the other two directions spontaneous polarization is 0. We have additionally checked that the value of spontaneous polarization in the backbone direction remains almost the same upon the structure relaxation. For comparison, spontaneous polarization in nitrides (GaN, InN, AlN) takes values from 2.9 to  $8.1 \times 10^{-2} \text{ C/m}^2$ ,<sup>9</sup> while BaTiO<sub>3</sub> has one of the highest reported spontaneous polarizations of around  $0.9 \text{ C/m}^2$ .<sup>11</sup>

To understand the origin of the spontaneous polarization in the backbone direction, we have calculated the polarization in that direction for the structure without side chains, which is actually polythiophene (PT), shown in Figure 2b. This structure does not have spontaneous polarization in the backbone direction. Additionally, we considered the P3HT unit cell with tail-to-tail side-chain arrangement (Figure 2c). This structure does not show pyroelectric properties as well. Therefore, we have concluded that spontaneous polarization in the first unit cell arises from head-to-tail arrangement of side chains. Atoms in side chains do not have their inversion symmetry pairs, which breaks the symmetry. On the other hand, structures shown in Figure 2b and Figure 2c exhibit

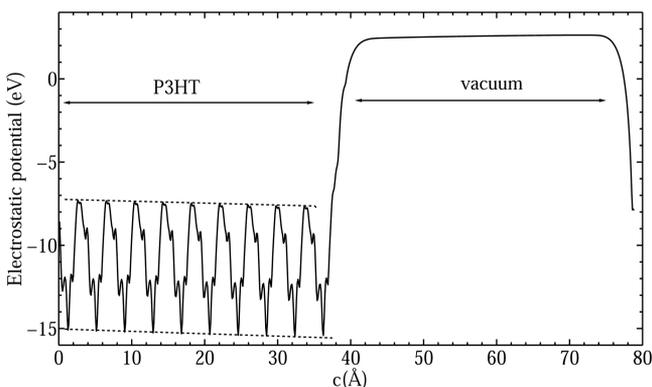


**Figure 2.** (a) P3HT unit cell with head-to-tail side-chain arrangement, (b) PT unit cell, and (c) P3HT unit cell with tail-to-tail side-chain arrangement.

inversion symmetry where each atom has its corresponding pair.

Structures with head-to-head and tail-to-tail side-chain arrangement are not regioregular, and they are not able to form well-ordered crystalline structure. Therefore, crystalline structure with head-to-tail arrangement of side chains is more representative. Regarding different types of P3HT unit cells, we expect that each unit cell with the lack of the inversion symmetry would have nonzero spontaneous polarization. To check this, we have calculated spontaneous polarization in the shifted structure of P3HT that we considered in our previous works.<sup>33–35</sup> In this structure, two subsequent P3HT chains in the  $\pi$ – $\pi$  stacking direction are mutually shifted by the half of the unit cell in the backbone direction. The unit cell parameters for shifted structure at 0 K are  $a = 15.55$  Å,  $b = 8.1$  Å, and  $c = 7.77$  Å, and all angles are  $90^\circ$ .<sup>35</sup> The calculated spontaneous polarization in the backbone direction is  $6.2 \times 10^{-3}$  C/m<sup>2</sup>, which is nearly the same as that for aligned structure. Therefore, we conclude that spontaneous polarization is robust upon the structure change if the asymmetric arrangement of side chains is preserved. Recently, P3HT unit cell with  $P2_1/c$  symmetry group was proposed.<sup>31</sup> This symmetry group is centrosymmetric, and spontaneous polarization in this structure is not expected to occur.

To check the reliability of the alternative method for spontaneous polarization calculation described in the previous section, we have calculated the electrostatic potential along the backbone direction in the supercell that consists of a 10 thiophene ring long rigid P3HT chain and a vacuum region of the same length as the P3HT chain. This potential is shown in Figure 3. Within the material, potential is periodic with an

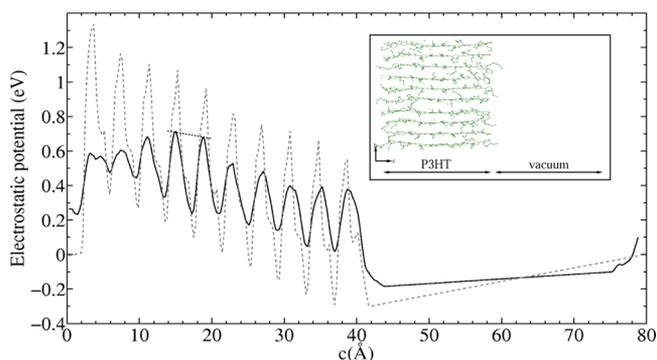


**Figure 3.** Electrostatic potential along the rigid P3HT chain and vacuum. This potential is one-dimensional, obtained from three-dimensional potential by averaging in two other dimensions.

additional linear trend arising from the electric field caused by spontaneous polarization. The peaks of this potential correspond to atom positions. The electric field in P3HT was calculated as a negative derivative of the envelope that connects the peaks. In vacuum, the potential is linear, and electric field is calculated as its negative derivative. The relative permittivity of P3HT is taken to be 4.0.<sup>36</sup> Using eq 5 calculated polarization is  $5.6 \times 10^{-3}$  C/m<sup>2</sup>, which is very close to the value obtained using DFT-based codes and modern theory of polarization.

**Spontaneous Polarization of Thermally Disordered P3HT.** Next, we consider the effects of temperature on polarization of P3HT. At nonzero temperature the atoms are displaced from their equilibrium positions, and periodicity of

the structure is broken. This effect is known as thermal or dynamic disorder and is significant in conjugated polymers.<sup>6,33,34,37,38</sup> Side chains of P3HT are more disordered than backbone chains. It is expected that spontaneous polarization induced by side chains is lower at finite temperature than in a perfectly ordered chain. We used the structures that we produced to investigate the effects of thermal disorder in P3HT.<sup>33,34</sup> Each of the structures contains 2520 atoms arranged in 10 chains. Due to the high number of atoms, electrostatic potential cannot be extracted from DFT-based codes. We instead applied the DFTB+ code,<sup>39</sup> which is based on the density functional tight-binding method.<sup>40</sup> This method is an approximation of classical DFT where Kohn–Sham orbitals are represented by a linear combination of atomic orbitals and two center approximation is made in the Kohn–Sham Hamiltonian matrix. To check if DFTB+ gives the same results as ABINIT or Quantum ESPRESSO, we have calculated electrostatic potential for the structure we used to test the method for the spontaneous polarization calculation. This potential (shown in Figure 4 with a dashed line) was calculated



**Figure 4.** Averaged electrostatic potential along the interface of the disordered P3HT chain and vacuum at 300 K (solid line) and at 0 K (dashed line). The inset shows the structure used to calculate the potential along the interface of thermally disordered P3HT and vacuum.

as Coulomb potential from the point charges at atom positions, where the charge of an atom is a sum of its ion and electron charges. Obtained potential differs from the potential obtained by DFT-based codes in two ways: (1) it does not contain the exchange–correlation term and (2) atoms are modeled as point charges which is not the case in DFT-based codes. These two differences result in the potential shift and its amplitude oscillation reduction in the P3HT domain. However, potential shape and electric fields in P3HT and vacuum remained almost the same, which resulted in the spontaneous polarization of  $6.3 \times 10^{-3}$  C/m<sup>2</sup>. Therefore, DFT-based codes can be replaced by the DFTB+ code to calculate the spontaneous polarization for large systems.

Averaged electrostatic potential along the backbone direction of P3HT at 300 K for one structure is shown in Figure 4. The potential envelope within the P3HT domain is not unique as for rigid chains. Consequently, the choice of the envelope would affect the obtained value for electric field and spontaneous polarization. To avoid this issue, we took several different structures and calculated averaged electric field. The electric field is calculated in the middle of chains in order to exclude the effects of higher disorder present at the chain edges. The calculated value of polarization is  $3.6 \times 10^{-3}$  C/m<sup>2</sup>, which

is lower than for the rigid chain. However, this value is significant and shows the important feature that spontaneous polarization in ordered P3HT exists even at room temperature. It is possible that a finite chain used in our simulation exhibits a higher degree of disorder than long realistic chains and that the true value of polarization at room temperature might be even higher. Spontaneous polarization is expected to vanish only for completely disordered chains, as in amorphous domains.

Electrostatic potential in vacuum is linear, and there is no uncertainty of the value for the corresponding electric field. It would be interesting to compare the values for the electric field for structures with rigid and thermally disordered chains since the spontaneous polarization is linearly dependent on the electric field in vacuum (eq 5). The value for the electric field in vacuum for the structure with the rigid chain is  $8.0 \times 10^7$  V/m, while the corresponding value for thermally disordered chains (averaged over different structures) is  $3.4 \times 10^7$  V/m. The ratio between these electric fields is close to the ratio between spontaneous polarizations for corresponding structures. Therefore, the electric field in vacuum can be used as a good measure for the estimation of the effect of thermal disorder on the spontaneous polarization in conjugated polymers.

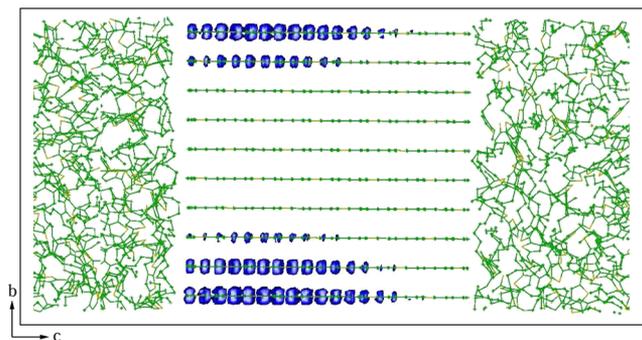
Next, we estimate the possible effect of spontaneous polarization in P3HT on characteristics of P3HT/fullerene blends relevant for solar cell applications. In P3HT/fullerene-based heterojunctions the characteristic length of each domain is on the order of 10 nm. If we assume that layers of P3HT and C60 are arranged in an ideal superlattice where each domain is 10 nm long and that P3HT polarization is perpendicular to the domain interface, we obtain a potential drop in the C60 domain of around 0.9 V at low temperature and around 0.5 V at room temperature (relative permittivity of C60 is taken to be  $3.6^{41}$ ). These are significant values of potential drop that should strongly affect the performance of bulk heterojunction-based devices. The spontaneous polarization of P3HT can be obtained by experimental electric measurements.<sup>13</sup> Having in mind that the structure of P3HT samples is complex, the experimentally obtained value can differ from that obtained by a theoretical approach. While the superlattice model is certainly a simplification of real bulk heterojunction, it demonstrates the importance of the effect of spontaneous polarization, and one should expect a potential drop of the same order of magnitude in real bulk heterojunctions.

### EFFECTS OF SPONTANEOUS POLARIZATION ON ELECTRONIC STATES AT THE INTERFACE BETWEEN CRYSTALLINE AND AMORPHOUS P3HT

Realistic conjugated polymers contain both crystalline and amorphous domains. Average spontaneous polarization in an amorphous domain is 0 due to random orientation of dipoles. If spontaneous polarization exists in a crystalline domain, there is a discontinuity of the polarization at the interface between the crystalline and amorphous domain, analogously to the interface between material with spontaneous polarization and vacuum shown in Figure 1. Hence, there is a surface charge density at the end of the crystalline domain induced by spontaneous polarization, which affects the energy levels in both domains.

In our previous work,<sup>35</sup> we have investigated the electronic states at the interface between crystalline and amorphous domains in P3HT where we found that the highest states in the valence band were delocalized and belonged to the crystalline domain. We have investigated two interface types: (1) a sharp interface between crystalline and amorphous domains where

the interface surface is perpendicular to the  $\pi$ - $\pi$  stacking direction (type A interface) and (2) a more realistic interface composed of chains extended from the crystalline into the amorphous domain in the backbone direction (type B interface). In the case of the type A interface, spontaneous polarization in P3HT does not have any influence on electronic states as there is no spontaneous polarization along the  $\pi$ - $\pi$  stacking direction. On the other hand, in the case of a type B interface, spontaneous polarization effects exist, but they are relatively weak due to the soft transition from ordered to disordered chains. Such transition corresponds to slow spontaneous polarization decline from  $P_s$  to 0. Now, we investigate the effects of spontaneous polarization in the backbone direction on the electronic states at the interface between crystalline and amorphous domains where the interface surface is perpendicular to the backbone direction (type C interface). Following the same procedure as in our previous work,<sup>35</sup> the amorphous structure was generated by Monte Carlo simulation by compressing the large box until the density of the amorphous domain reached an experimental value of  $1.1 \text{ g/cm}^3$ . The temperature during the simulation was 1000 K. Finally, the amorphous domain was cooled to 0 K. The crystalline domain was kept rigid all the time during the simulation. To calculate the electronic structure for obtained atomic structure, the DFTB+ code was used. As expected, the wave function of the highest state in the valence band (Figure 5) is delocalized and belongs to the crystalline domain.



**Figure 5.** Wave function moduli squared of the highest electronic state in the valence band of the type C interface. Isosurfaces correspond to the probability of finding a hole inside the surface of 75%.

However, due to spontaneous polarization in the backbone direction, the state is confined at one side of the crystalline domain. As one may notice, this interface type is sharp and hence not very realistic. To build a more realistic interface model, effects of thermal disorder and disorder at the crystalline domain edges should be included. We have shown above that spontaneous polarization does not vanish with thermal disorder. Additionally, we have shown in our previous paper<sup>35</sup> that the introduction of an intermediate region between ideal crystalline and amorphous regions (referred to interface type A') does not qualitatively change the results. Based on these two conclusions, we expect that localization of the wave function at one side of the crystalline domain would be present even in the realistic model. This effect will be completely absent only in the case of centrosymmetric P3HT structure, as that proposed in ref 31. Therefore, spontaneous polarization can significantly affect the electronic properties of conjugated polymers.

## CONCLUSIONS

In conclusion, we have shown the existence of spontaneous polarization along the backbone chain in ordered P3HT. This effect is caused by inversion symmetry breaking arising from head-to-tail arrangement of side chains. We proposed the method to calculate spontaneous polarization in large and realistic systems. Then, we applied the method to calculate spontaneous polarization for disordered crystalline P3HT at 300 K and showed that spontaneous polarization is still significant at room temperature. Effects of spontaneous polarization are important at the interfaces between materials with different spontaneous polarization. We have demonstrated that spontaneous polarization confines the hole states at one side of the crystalline domain of P3HT in the presence of the interface between the crystalline and amorphous domain. In organic solar cells electric fields caused by spontaneous polarization can assist or hinder charge separation at the interfaces between different materials, depending on the relative orientation of polarization vectors.

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### Notes

The authors declare no competing financial interest.

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