First-principles Determination of Electronic Charge Transport Properties in Polymer Dielectrics Using a Crystalline-based Model System

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ABSTRACT

There are various models for describing the charge transport in polymers but it is unclear how to choose the appropriate one for a given system. In this study, we determine the relevant charge transfer model for several insulating polymers by evaluating the Marcus parameters for electron and hole transfer with the aid of first-principles calculations. As expected, except for electron transfer in polyethylene and isotactic polypropylene, non-adiabatic (polaron) hopping takes place in most polymers, owing to the small inter-chain electronic interactions (10–100 meV) and large polaron formation energy (100–1000 meV). Therefore, the first-principles based parameter-free, multi-scale modeling approach, which we developed for evaluating the hole transfer property in polyethylene, can be used to study the electronic carrier transport properties in wide variety of polymers. The computed Marcus parameters indicate that the electron and hole mobilities in syndiotactic polystyrene and polytetrafluoroethylene are larger than the hole mobility in polyethylene and isotactic polypropylene, which agrees with experimental data. The strong chain-length dependence of the computed Marcus parameters indicates that slight change in the polymer structure can result in significant variations in the charge mobility.

Index Terms—first-principles calculation, charge transfer, mobility, polymers, space charge, hopping, polyethylene, polypropylene, polytetrafluoroethylene, polystyrene, polyethylene terephthalate

1 INTRODUCTION

Theoretical characterization of charge transport in organic polymers is required for tailoring the electrical properties of insulating polymers. This is because electrical breakdown and degradation of the material is strongly correlated with the motion of charges in the material. In recent years, first-principles density functional theory studies have been conducted to investigate the charge transport characteristics in polyethylene (PE) [1–3]. These studies offered insight regarding the electronic structure, however, the kinetics of charge transport remained unclear. To understand this, atomistic interactions (electronic interactions between carrier hopping states, interaction between carriers and the distortion of polymer chains, etc.) that cannot be considered from the electronic structure of the system alone, have to be considered. The problem becomes difficult in the case of charge transport in polymeric semiconductors and dielectrics because the strengths of these interactions are comparable [4]. Consequently, one has to select and refine the appropriate charge transport model for the system under consideration.

With the aid of first-principles calculations, we have recently evaluated the microscopic interactions that contribute to hole transport in PE and demonstrated that hole transfer in PE takes place in the non-adiabatic (polaron) hopping regime [5,6]. Furthermore, based on our findings, we have developed a parameter-free, multi-scale computational approach consisting of first-principles calculation, molecular dynamics simulation, and kinetic Monte Carlo simulation to evaluate the carrier mobility in PE. In [5–8] we have predicted the hole mobility in amorphous as well as crystalline PE with reasonable accuracy. Indeed, multi-scale computational approaches are frequently used to study charge transport in organic semiconductors, however, as discussed in more detail

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in [6], we have proposed a computational approach that can handle polymers with flexible backbones, which is a typical feature of most insulating polymers.

In the case of polymer dielectrics, up to the present, most studies have dealt with PE [1–3,5–8], and therefore, it is interesting to see if our parameter-free modeling approach could be applied to carrier conduction in various insulating polymers. In this study, we investigate charge transport properties in a set of polymers having more complex chemical structures than that of PE with the aid of first-principles calculations.

In this study, carrier conduction in isotactic polypropylene (i-PP), polytetrafluoroethylene (PTFE), syndiotactic polystyrene (s-PS), and polyethylene terephthalate (PET) are studied because PP and fluorinated polymers are used for power cables and electrets. PET is one of the most common types of material for thin-film electrical insulators, and is widely used for flexible electronics, battery and motor insulations, and all these materials are used for dielectric capacitors.

2 COMPUTATIONAL METHODS

Figure 1 shows the structural formulae and molecular structures of the polymers under consideration. In this study, we (1) evaluate the electronic structure of each polymer and (2) compute the Marcus parameters. The geometric structure of the polymers must be determined at atomic resolution, to obtain a sensible electronic structure. Here, we make use of the experimentally determined crystal structures. The crystal structure of PE, i-PP, PTFE, s-PS, and PET are taken from refs. [9–11] and references therein. We have utilized room temperature and ambient pressure crystal structures. The number of chains in the unit cells of crystalline PE, i-PP, PTFE, s-PS, and PET are 2, 4, 1, 2, and 1, respectively, and the number of monomers in the chains are 1, 4, 7.5, 4, and 1, respectively, and

\[ \text{Eq. (1)} \]

\[ N_i(E) = \sum_{p \in A} N_{ip}(E), \]

where

\[ N_{ip}(E) = \sum_q Q_{pq}^i G(E - \varepsilon_i) \]

\[ Q_{pq}^i = T_{pq} C_{ip} S_{pq} \]

Here, \( p \) and \( q \) are the indices of the basis functions, \( \varepsilon_i \) and \( C_i \) are the energy and the molecular orbital coefficients of MO \( i \), respectively, \( G \) is the Gaussian (full width at half maximum: 0.2 eV), and \( S \) is the overlap matrix. By summing \( Q_{pq}^i \) over \( i \), we have the Mulliken charge.

We have computed the PDOS for a single polymer chain and for a bundle of several polymer chains (here, the cluster model, Figure 2). Unlike the core-shell model [13] where the geometrical structure of the bundle of polymer chains are relaxed, in the case of the cluster model, the coordinates of the atoms are fixed at their crystalline positions. We do not relax the coordinates because in general, correct inter-chain distance cannot be obtained even with the functional with van der Waals correction (See Ref [14] for details).

2.2 MARCUS PARAMETERS AND CHARGE CONDUCTION CHARACTERISTICS

The non-adiabatic (polaron) charge hopping rates can be described by the non-empirical Fermi golden rule [15]. In the high-temperature limit, the form becomes [15]:

\[ \text{Eq. (2)} \]

\[ T_{ij} = \sum_{pq} T_{pq} \delta_{ip} \delta_{jq} S_{pq} \]

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The high-temperature approximation can be the source of error when computing the carrier hopping rates between insulating polymer chains [8]. However, we adopt the Marcus rate because we do not aim for precise determination of the charge mobility in this work. We compute the hopping rates for reference purposes only.

Having computed the Marcus parameters, the charge transport regime can be classified according to the Marcus parameters, for example, quasi-free conduction ($H \gg \lambda, \Delta G$) and polaron hopping ($H \ll \lambda$) [18].

## 3 RESULTS AND DISCUSSION

### 3.1 ELECTRONIC STRUCTURE OF POLYMERS

Figure 3 shows the PDOS and MOs of various polymers. The HOMOs of the PE chain and the PE cluster mainly originate from the carbon atoms and are well localized to the PE backbone, whereas the LUMOs of the PE chain and the PE cluster mainly originate from the hydrogen atoms and are less localized to the polymer backbone. The PE cluster LUMOs show a strong inter-chain nature. These results are in line with the findings obtained using periodic boundary conditions [19]. Although we could not thoroughly examine the basis set convergence in the case of the cluster model, our results also indicate that the LUMO of the cluster tends to localize to the inter-chain state rather than oozing out to the outer surface of the cluster.

The PDOS and MOs of i-PP are similar to those of PE, which is not that surprising given that both PE and i-PP are saturated hydrocarbons. On the other hand, the PDOS and MOs of PTFE are quite different compared to those of PE; (1) the HOMOs have almost equal contribution from carbon and fluorine atoms, (2) the LUMOs mainly originate from carbon atoms, and (3) are well localized to the polymer backbone.

With regard to the s-PS chain, the frontier orbitals (HOMO and LUMO) resemble those of benzene molecules (data not shown), and are π molecular orbitals. The orbitals above and below those mainly originating from the benzene frontier orbitals resemble those of PE and i-PP chains, and their orbital energies are similar as well. This indicates that the interaction between the frontier orbitals of benzene and those of the alkane chains (the backbone of s-PS) is weak. One may find this surprising, given that the benzene rings are linked to the alkane chains by covalent bonds. The interaction is weak probably due to the large energy difference between the benzene and alkane frontier orbitals.

The HOMO of PET resembles the benzene HOMO and is strongly localized around the benzene ring, whereas the LUMO of PET is distributed not only over the benzene ring but over the C=O bond as well. The molecular orbital that resembles the benzene LUMO is roughly 1 eV above the LUMO of the PE chain. The difference in the energies of these orbitals is probably the consequence of the difference in the π conjugation length.

With the exception of the PE and i-PP LUMOs and the PET HOMO, the energies of the frontier orbitals of the clusters are...
Figure 3. MOs and PDOS of (a) PE, (b) i-PP, (c) PTFE, (d) s-PS, and (e) PET oligomers. The left half of each subfigure shows the electronic state of a single polymer chain, and the right half shows that of the cluster model. The blue and black bars represent energy levels of the unoccupied and occupied orbitals, respectively.
relatively unchanged from those of the single chains. For PE and i-PP, the change in the energy of the LUMO is most likely due to the large interactions between the LUMO of each polymer chain. This is sensible because the LUMO of PE is weakly localized to the chain, and therefore the overlap between the LUMOs of the neighboring chains is large. As for the PET cluster, the change in the energy of the HOMO is probably caused by the electrostatic interactions between the nearby PET chains that are essentially polar. Except for the PE and i-PP cluster LUMOs, both the frontier orbitals of the single chains and those of the cluster models are strongly localized to each polymer chain. The orbitals of some of the cluster models are (seemingly) delocalized over several polymer chains. This is because (1) all the polymer chains in the cluster model are identical, (2) interaction between the chains is small, and/or (3) the cluster model is highly symmetrical (see ref. [20] for details). However, this delocalization is achieved only when $H \gg \lambda, kT$. Again, the extent of carrier delocalization should be evaluated by calculating the Marcus parameters, and it is difficult to discuss the carrier transfer characteristics from the PDOS or the MOS alone.

The HOMO and LUMO of PE clusters are a few eV higher than those of PTFE cluster in energy. Regarding the HOMO-LUMO gaps, those of the s-PS and PET clusters are smaller than those of the PE and PTFE clusters. Computed HOMO-LUMO (band) gaps show not only qualitative but also quantitative agreement with the experimental data (see, for example, ref. [21]). Although the energies of the HOMO and LUMO are closely related to the carrier injection properties, we will not discuss it in further detail because it is beyond the scope of this study.

Computed Marcus parameters of PE, i-PP, PTFE, s-PS, and PET oligomers are shown in Figure 4. The reorganization energies tend to decrease with increasing oligomer chain length. The non-monotonic chain length dependences of the reorganization energies in i-PP are presumably due to the terminal effect; the impact of the polymer terminal is larger for shorter chain lengths. As expected from the discussion above, the electronic couplings for electron hopping between the PE chains and those between the i-PP chains are extraordinarily large. It should be noted that the computed electronic couplings are subject to significant error for this particular case because the interactions are no longer weak. The electronic couplings and reorganization energies depend strongly on the polymer chain length. This implies that the charge transport properties in these polymers can be modified by changing the tacticity or the side chain structure, which influences the stiffness (and therefore the charge localization length) of the polymers.

As we have shown in ref. [6], the characteristic length of the hole localized states in amorphous PE roughly matched the PE Kuhn length. Here the Kuhn length is the characteristic length scale in terms of the geometric structure of polymer chains in the amorphous phase. Although we did not confirm that this relation holds for other polymers, in this study, it is assumed that the characteristic length of the electronic structure is comparable to that of the geometric structure. Further verification of this point will be conducted in the future. Figure 5 shows the electronic couplings, $H$, and reorganization energies, $\lambda$, of the oligomers of each polymer. The lengths of the oligomers are chosen so as to match the Kuhn length of the respective polymers.

According to the classification criteria given in Sec. 2.2, electron and hole transfer in PTFE, hole transfer in PE and i-PP, and electron transfer in PET all occur in the polaron hopping regime. Therefore, carrier mobilities in various polymers can be predicted with the aid of the multi-scale modeling method, which we have proposed in refs. [6,8]. Electrons and holes in s-PS and holes in PET would probably show intermediate charge transfer properties between polaron hopping transport and band-like or quasi-free conduction. Note that carrier transport may occur in the disorder-based hopping regime if $\Delta G \gg H, \lambda$.

Currently and to the best of our knowledge, the carrier mobilities in the crystalline phase of i-PP, PTFE, s-PS, and PET have not been reported. Thus, as shown in Table 1, we evaluated the carrier hopping rates between PE, i-PP, PTFE, PS, and PET oligomers whose lengths coincide with their respective Kuhn lengths. The computed hopping rates cannot be directly compared with the experimental carrier mobilities.
because we compute the Marcus parameters only for the oligomers in the crystalline orientation; moreover, the free energy differences, $\Delta G$, are set to zero. Nevertheless, the computed carrier hopping rates are in line with experimental findings in that the carrier mobilities in s-PS and PET are larger than those in PE and i-PP [24]. The experimental charge mobilities in Teflon fluorinated ethylene propylene (FEP) are smaller than those in PE [25], which may seem contradictory to our results. However, this is presumably due to the difference in the geometric structure of FEP and PTFE; it is likely that the charge localization length in FEP is shorter than that in PTFE as a result of the asymmetric polymer chain structure; the reorganization energies for charge transfer in FEP is probably larger than those of PTFE.

A more detailed analysis is necessary to thoroughly understand and potentially predict the carrier transfer properties in polymeric dielectrics. Applying the multi-scale modeling approach to various polymers will be a topic for future work. In addition, we encourage benchmark studies of DFT functionals for insulating polymers to be conducted in the future.

6 CONCLUSION

We have investigated the carrier transport characteristics in various polymer dielectrics, namely PE, i-PP, PTFE, s-PS, and PET, by computing the Marcus parameters for electron and hole transfer with the aid of first-principles calculations. We show that, with the exception of electron transfer in PE and i-PP, electron and hole transfer occurs in the polaron hopping regime due to the large effect of molecular reorganization upon carrier transfer and the small electronic interactions between charge localized states. In line with experimental findings, our rough estimation of the charge hopping rates implies that the carrier mobilities in s-PS and PET are larger than the hole mobility in PE and i-PP. Our results indicate that the slight modification of the polymer structure can drastically change the charge transport characteristics in polymer dielectrics. Future studies will include quantitative computation (prediction) of the carrier mobilities in various polymers by applying our first-principles based modeling technique.

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REFERENCES


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