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Multiscale modeling of charge transfer in polymers with flexible backbones (ESI)

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1 Inverse participation per monomer (IPR) value of crystalline PE oligomers

As shown in Figure 1, the *IPR* values of the HOMOs (SOMOs) of neutral (positively charged) PE chains increase with increasing chain length. The *IPR* values of cation SOMOs are similar to those of neutral HOMOs.

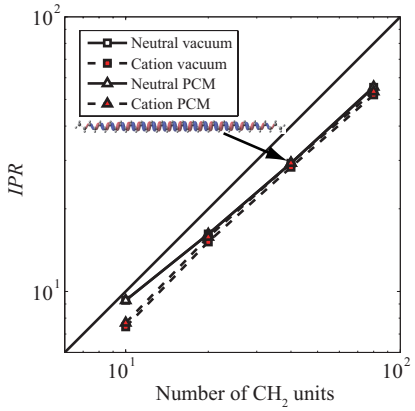

Fig. 1 The *IPR* values of the HOMOs (SOMOs) of neutral (positively charged) all-*trans* PE chain calculated in vacuum and with PCM solvent. The inset shows the HOMO of neutral $C_{40}H_{82}$.

2 Inverse participation per monomer (IPR) value of amorphous (liquid) $C_{12}H_{26}$

As shown in Figure 2, the frequency distribution of the *IPR* values of the HOMOs of $C_{12}H_{26}$ chains takes it maximum when the IPR value is around 9-10, which is 20-30% shorter than those of longer PE oligomers ($C_{40}H_{82}$, $C_{100}H_{202}$, and $C_{200}H_{402}$) in the amorphous phase.

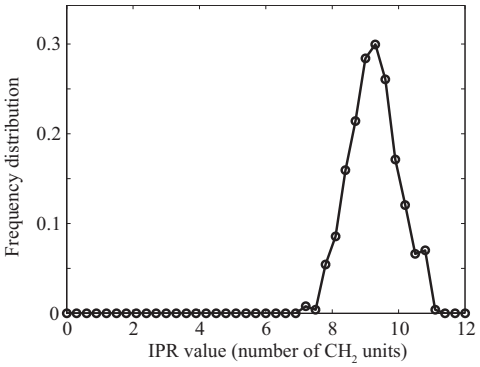

Fig. 2 The *IPR* values of the HOMOs of $C_{12}H_{26}$ molecules in the amorphous (liquid) phase.

3 Time evolution of the hole localized state

Figure 3 shows the time evolution of the IPR value of the HOMO of $C_{100}H_{202}$ chain in the amorphous phase. The hole localized region in the oligomer chain do not vary drastically by the thermal fluctuation of the chain in the time scale comparable to hole hopping (ns). In addition, it is likely that the change in the conformation and therefore the electronic structure of PE oligomer becomes smaller for longer PE chains. Figure 3 also indicates that the time scale of the fluctuation of IPR value is faster than that of hole hopping. A more detailed study will be conducted in the future.

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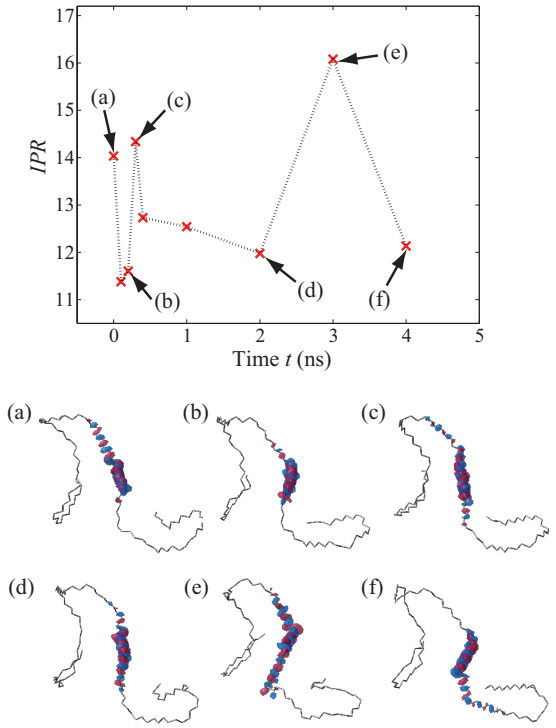

Fig. 3 Time evlolution of the *IPR* value of the HOMOs of $C_{100}H_{202}$ molecules in the amorphous phase.

4 Relation between electronic couplings and density of PE (oligomers)

Figure 4 shows the electronic coupling between $C_{12}H_{26}$ molecules in the face-to-face configuration with varying inter-molecular distance.

When the size of the hopping sites ($C_{12}H_{26}$ or -$C_{12}H_{24}$- segments) are comparable, as a first-order approximation, the distance between hopping sites d is proportional to $\rho^{-1/3}$, where ρ is the density of the hopping sites. Because the difference in ρ of amorphous PE and $C_{12}H_{26}$ is around 10%, the difference in the distances between hopping sites of the two materials is around 3%. Therefore, the change in the electronic couplings due to the density difference is few tens of percent (see Figure 4).

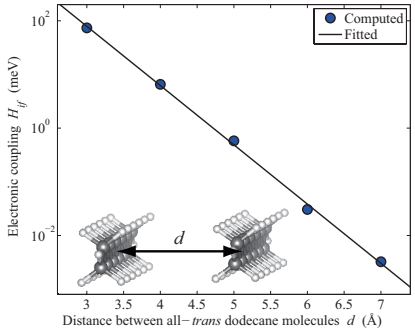

Fig. 4 Relation between electronic couplings and distance between all-*trans* $C_{12}H_{26}$ molecules. The configuration of molecules is shown in the inset. The solid line represents the linear regression.

5 Validity of the cutoff distance (r_c)

In order to reduce the computational complexity, we computed only the Marcus parameters for hole transfer between molecules for which the distance of closest approach between carbon atoms in each molecule is smaller than the cutoff radius $r_c = 7$ Å. Figure 5 shows the hole mobility computed at various cutoff radii. At $r_c = 7$ Å, the hole mobility is clearly converged with respect to the cutoff radius.

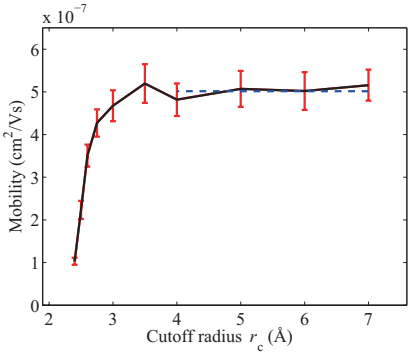

Fig. 5 Computed hole mobility as a function of the cutoff radius. The broken line shows the interval average from $r_c = 4$ to 7 Å. The reorganization energies evaluated for the molecules with fixed dihedral angles are used to compute the hopping rates. The temperature is set to 300 K.