Electrochemical Post-functionalization of Poly(3-(2-ethylhexyl)thiophene) Facilitated by Forming the Ordered Structure

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π-Conjugated polymer films are promising materials for organic electronic devices due to their unique optoelectronic properties.[1] To improve the performance of these devices, huge number of efforts have been devoted to investigating the effects of the structures of π-conjugated polymer films on their optoelectronic properties. Recently, electron transfer-driven post-functionalization methods (e.g., electrochemical post-functionalization (*e*PF)) have been regarded as powerful approaches to impart various functionalities to π-conjugated polymer films.[2] In such methods, their structures should also serve as a crucial role for the efficacy of the reaction; however, the relationship between their structures and the electron transfer-driven post-functionalization has never been discussed.

Here, we clarified the relationship between the structures of π-conjugated polymer films and the efficacy of the electron transfer-driven post-functionalization by performing the *e*PF of poly(3-(2-ethylhexyl)thiophene) (P3EHT) films (Figure 1). Changing solvents to prepare P3EHT films resulted in providing P3EHT films with different structures (i.e., amorphous and crystalline structures). The amorphous P3EHT films were not electrochemically chlorinated, whereas P3EHT films possessing crystalline features were successfully chlorinated. *In situ* conductance measurements of P3EHT films concluded that the reactivity difference between both P3EHT films was because of their electrical conductivity.

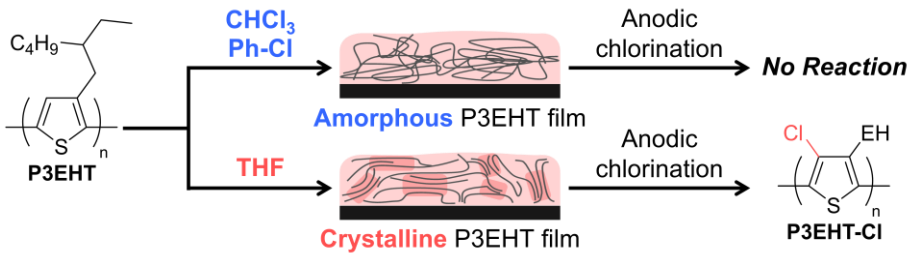

Figure 1. Relationship between the structures of P3EHT films and the reactivity on anodic chlorination.

References

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