Ultrafast Photogeneration of Charged Carriers on Conjugated Polymer Chains in Dilute Solution

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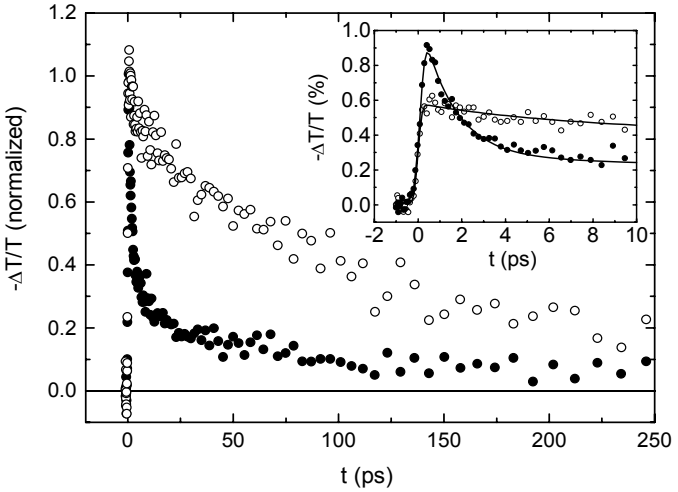
Conjugated polymers combine the electronic and optical properties of metals or semiconductors with the processability and mechanical properties of polymers. These electronic polymers offer promise for use in applications particularly in the area of optoelectronics where semiconducting luminescent polymers can be used to fabricate large area, flexible devices such as light-emitting diodes, displays, integrated circuits, solar cells and lasers. Here we present results on the dynamics of the photoexcited charge carriers in the 100 femtosecond time regime in conjugated polymer MEH-PPV film (a derivative of poly (phenylene vinylene)) as well as in dilute polymer solution in which the behavior approaches that of single polymer chains. The results obtained by means of an unique all-optical technique carried out in zero applied electric field are fundamental for our understanding of the nature of photoexcitations in this novel system. **Physical Review B, In press.**



Dynamics of the photoinduced carriers for an MEH-PPV film (filled circles) and a 0.1 % w/v MEH-PPV solution in carbon tetrachloride (open circles). The inset shows the same data without normalization.

Despite many recent advances in understanding the electronic properties of conjugated polymers, the charge carrier photogeneration mechanism has remained an open question. We have thoroughly investigated polaron photogeneration in thin films of semiconducting polymers using ultrafast spectroscopy. Our results demonstrated photogeneration of polarons in less than 100 fs with appreciable quantum yield (~ 10%) that is independent of the excitation wavelength. These data allowed us to rule out several photogeneration mechanisms proposed in the literature. However, another question remained open: Can polaron pairs be directly photogenerated on isolated polymer chains or must such charge carriers result from interchain charge transfer? In the latter case, the photogeneration of charge pairs would require interchain interactions between neighboring chains in the solid state.

We have used ultrafast photoinduced absorption by infrared-active vibrational (IRAV) modes, an unique all-optical technique carried out in zero applied electric field with subpicosecond time resolution, to investigate the photogeneration of polarons in films and solutions of the prototypical luminescent polymer, MEH-PPV, (poly[2-methoxy-5-(2'-ethyl)hexyloxy-1,4-phenylene vinylene]). The IRAV absorption provides an unambiguous optical signature for carriers on the polymer chains as confirmed by the spectroscopy of chemically doped conjugated polymers. We report here studies of the ultrafast photoinduced IRAV absorption of MEH-PPV films and solutions; the data clarify the role played by the interchain interaction in the charge photogeneration and recombination mechanisms. In dilute polymer solutions, polaron pairs are photogenerated within less than 250 fs with quantum efficiencies $\phi ch \sim 3$ % (about one-third of that for polymer films) and have significantly slower recombination dynamics.

A paper based on this work has been accepted for publication in Physical Review B (in press); this work was presented recently in a talk at the International Conference for Synthetic Metals (ICSM'2004) held in Australia.

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Education:

In the last four years, one undergraduate student (Cesare Soci), and three post-Doctoral fellows (Paulo Miranda, Qinghua Xu, and Arthur Dogariu) have been involved in the project reported here as well as other related projects aimed at exploring the carrier photoexcitation in conjugated polymers. Paulo Miranda is presently an assistant professor at Instituto de Física de São Carlos, while Arthur Dogariu is a Senior Scientist at the NEC Research Institute in Princeton, NJ. Qinghua Xu and Cesare Soci are continuing their studies on related issues.

Societal Impact:

The ability to detect charge carriers photoexcitations at ultrashort time scales is a very powerful technique that has contributed significantly to our fundamental understanding of the nature of photoexcitations in these novel polymer semiconductor systems. This understanding should enhance our ability to develop novel device applications as well as improve the design of the existing ones which include light-emitting diodes, displays, integrated circuits, solar cells, and lasers.