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Research highlights in 2007

In our research we use single-molecule spectroscopy to study nanoscale structure and optical properties of organic and polymeric materials.

(1) Relationship between structure and optical properties of π-conjugated polymers

Conjugated polymers are subject of intense research as active materials for future optical and electronic devices. In many such devices, photophysical processes of absorption, migration of the absorbed energy and its subsequent emission play crucial roles in the device function. The photophysical processes are determined by the unique conformation of individual polymer chains. The complexity of the study of conjugated polymer photophysics requires measurements on individual isolated polymers chains by the use of single molecule spectroscopy. We used a novel fluorescence polarization microscope in combination with molecular dynamics calculations to determine the conformation of isolated chains of the conjugated polymer MEH-PPV on a true single-molecule level. We have found a narrow distribution of defect cylinder conformations in a poor-solvent matrix, and two defect coil conformations in a good-solvent matrix. The conformations were further related to the photophysical properties of MEH-PPV by measuring fluorescence intermittency and fluorescence spectra on the same chains. We have obtained direct evidence that the photophysics is determined by the chain conformations, and that even subtle changes in the polymer microscopic structure can qualitatively affect the photophysical properties.

Further, we have studied the effect of chemical structure of a conjugated polymer on its conformation in solid state and on the related polymer photophysical properties. We used a graft copolymer consisting of a polythiophene backbone and polystyrene branches. The presence of the branches prevents the molecule from forming a collapsed globule-like conformation. We have observed exponential decrease of fluorescence intensity and low degree of emission polarization from single chains of the grafted polymer, indicating emission from multiple segments and lack of energy transfer due to the extended chain conformation.

In summary, we found a strong correlation between the microscopic structure and chemical composition on one hand, and the photophysical properties, and the mechanism of exciton localization especially, on the other. There results are expected to have broad implications for applications of the conjugated polymer materials.
(2) **Study of nanoscale physical properties of thin polymer films**

Amorphous polymer films are complex systems with large structural heterogeneities on microscopic level. With the potential of applications of polymer solids for nanoscale devices there appears a need for characterization of polymer physical properties and their dynamics on sub-micrometer scales. One of the most important physical parameters is local polarity of the polymer. We used the sensitivity of fluorescence lifetime on solvent polarity of a benzanthrone derivative to study the heterogeneity of local environment in polymer films on the scales of a few hundreds of nm by ensemble confocal microscopy, and on the molecular level by single molecule detection. We found that in all studied polymers there are two kinds of incorporation sites of the dye that differ by local polarity. In two of the polymers studied, PMMA and PVAc, we observed a large heterogeneity in the physical properties of the polymers on meso-scales, i.e. on the order of a few hundreds of nm. The single-molecule study showed further increase in the heterogeneity of the environment at molecular-level scale, providing a complete picture on the hierarchy of the thin-film physical properties.

**List of papers (original articles)**


**Review paper**