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Conformation and effective conjugation length in single short and long chain luminescent conjugated polymers

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Spectral and polarization changes during the fluorescent time trace of symmetric (DOO-) and asymmetric (MEH-) PPV derivative polymers, after spin-casting in a polystyrene matrix are observed by single molecule spectroscopy and interpreted within the framework of a molecular exciton based model. While overall, absorption dipoles exhibit anisotropic alignment, the polymer can be divided into two regions: one characterized by a relatively isotropic arrangement of absorption dipoles and emission from a single conjugated segment, and another with a greater alignment of absorption dipoles and multiple site emission. Under the assumption of rapid energy transfer to a single emitting segment in the first region and energy thermalization in the other, results are in good agreement with model predictions of a shortening of the average conjugation length of emitting segments of ~1.5 monomers during photo-bleaching. In contrast, both model and experiment indicate there is no shortening in short chain polymers in which absorption dipoles are aligned.

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