Energy Transfer Dynamics in Novel Macrocyclic Polymers
JERAINNE JOHNSON, RONG CHEN, THIEO HOGEN-ESCH, STEPHEN BRADFORTH, Department of Chemistry, University of Southern California, Los Angeles, CA 90089 — We have characterized the spectroscopy and dynamics of a novel molecular architecture that mimics natural light harvesting. Macrocyclic poly(9,9- dimethyl-2-vinylfluorene) PDMVF has chromophores attached to the polymer backbone that are arranged in a similar topology to the biological design in light harvesting antenna LH2. The polymer repeat can be tuned from 12 – 142 identical chromophore units. Ultrafast depolarization and exciton annihilation (EA) techniques have been used in analysis and provide complementary evidence of the occurrence of energy transfer (ET). Our results predict Forster type hopping on ~1 ps timescale. Direct evidence of ET is manifested in the depolarization, where the decay time constants are substantially faster than those obtained for reorientation of the free chromophore in solution. The time constants obtained are 700 - 900 fs and 7 - 8 ps. We speculate that the fast component results from ET dynamics with distinct bi-exponentiality due to conformational disorder. EA is a more direct way of measuring ET, since knowledge of the polymer conformation is not required. Isotropic transient absorption signals for PDMVF show strong dependence on excitation intensity. The population decay is due to $S_1-S_1$ EA lifetimes in the polymers, the amplitude of which depend on ring size, while an additional component at higher intensities corresponds to higher order annihilation dynamics.