FEMTOSECOND TRANSIENT ABSORPTION STUDIES ON THE PROTON INDUCED STRUCTURAL TRANSITIONS OF POLYCYTIDYLIC POLYMERS

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Transient absorption (TA) and fluorescence spectroscopies were used to study and characterize the structural transitions in polycytidylic acid (poly (rC)) as a function of pH. At pH 7 poly (rC) is single stranded and its TA signal is biexponential with a contribution from a monomer-like unstacked base population with about 1ps lifetime and from a stacked base population in the single stranded helix with about 10 ps lifetime. Poly(rC) adopts a double stranded helical structure in the pH region from 5.6 to 4. We find a range of lifetimes in the transients of poly (rC) at pH 4.5. Poly (dC) was found to be double stranded at pH 7 with TA signal similar to the signal of the double stranded poly (rC) at pH 4.5. The different behavior with pH is explained with the different backbone conformation these two homopolymers have. A lifetime of 4 ps is found in the transients of the hemiprotonated poly (rC). Using tunable pump-probe transient absorption we were able to isolate and characterize this component. Its appearance as well as the increased fluorescence quantum yield at these conditions and the rise of the charge transfer band in the ground state absorption, is due to a new type of charge delocalization in the polymer. The long lifetimes are attributed to different types of base stacking in the hemiprotonated double helix and are consistent with the fluorescence decay.