Abstract

The kinetics of base-stacking in single-stranded DNA and RNA homopolymers has already been investigated back in 1979 via time-resolved UV-spectroscopy. In this study time-resolved IR-spectroscopy is used to obtain results with greater detail, which have improved the previous results. The used polymers were single-stranded poly(A) and poly(dA). The temperature dependence of these polymers was measured via FTIR spectroscopy, which showed a clear shift in absorption at a frequency of 1630 cm\(^{-1}\). Time-resolved infrared temperature jump experiments were used to study the stacking kinetics of the polymers at this frequency. These experiments were done at three different temperatures to calculate the transition energies between the stacked and un-stacked state. The results show improved relaxation times for both poly(A) and poly(dA) with smaller error bars. Furthermore a second relaxation time has been discovered for poly(A) which is not mentioned in experimental literature before. This relaxation was most noticeable at low temperatures. These results imply that there is another state between the stacked and un-stacked state. A second relaxation has not been discovered for poly(dA) due to a lower absorption of this polymer. The relaxation times for poly(dA) were also faster than for poly(A) at every temperature. This indicates that the backbone plays an important role in the stacking of bases. The stacking and un-stacking rates were successfully calculated from the relaxations combined with literature. The un-stacking rate increased when the temperature went up, as was expected. Successful calculations were made for the thermodynamics of the transition state. Un-stacking caused a positive transition entropy for both polymers while stacking was responsible for a negative transition entropy, which was in line with an increasing and decreasing degree of rotational freedom.