**Video S1  HTPB311 - Four Temperatures Video Description**

The following information describes the parameters for the molecular dynamics video associated with this publication ‘Understanding and controlling the glass transition of HTPB oligomers’. The video displays 4 independent simulations taken from the same cooling sequence of 70 HTPB10_311 molecules. We show simulations from four different temperatures situated above and below the calculated glass transition temperature of 182K. Each simulation has been visualised and captured with the VMD (Visual Molecular Dynamics) software. In total, each simulation has 500 000 timesteps with every 200th timestep being captured, resulting in 2500 frames per video. All simulations have been performed in the constant-$NPT$ ensemble, with the same molecule and visualisation state being identified for each temperature. The simulation cell contains a total of 7280 atoms (70 molecules) however the remaining 69 molecules have been omitted for clarity of the molecular motion of the individual, selected molecule.

In the 100K simulation (Top left), the structure of the HTPB oligomer is conformationally locked in place between its neighbours. This behaviour is characteristic to glassy nature of the HTPB system at this temperature where very few molecular degrees of freedom are available. As the simulated system is warmed to 200K (Top right) initial indications are apparent of the modes of molecular motion that first become available nearer the glass transition temperature. The terminal $\text{CH}_3\text{OH}$ groups obtain some degree of rotational freedom and, within the main chain, there is some crankshaft motion at time-marks 00:28, 00:38 and 01:10 during the video. At 250K (Bottom Left) and crankshaft motion of the trans groups becomes more prolific and at 300K (Bottom Right) it can be observed throughout the simulation.