The RNA polymerases I; II; and III are essential enzymes which transcribe DNA into RNA. In 2006, Roger Kornberg won the Nobel Prize in Chemistry for his 2001 high resolution structure of Pol II which is composed of twelve subunits in unit stoichiometry. Despite this success, crystal structures of Pol I and III, with two and five additional subunits respectively, remain elusive. Using TAP-Tag purification technology, partial denaturation of the protein complexes and subcomplex assembly experiments in tandem with mass spectrometry we have been able to characterize the composition of subcomplexes and subspecies deriving from Pol I & III. This has enabled us to improve our understanding and knowledge of the subunit architecture of these critical enzymes. We have focused our attention particularly on the initiation heterotrimer in Pol III and termination heterodimer in Pol I and III. One particular challenge has been to determine the composition of a possible ‘half-enzyme’ species (which forms under specific disruptive solution conditions) due to the size of this sub-species and the large number of stoichiometric possibilities. Recently we have also begun to investigate with mass spectrometry the Pol III elongation complex in which a RNA-DNA transcription bubble is bound to the Pol III catalytic site.