

CONTROLLED POLYMER PHOTOSYNTHESIS

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Polymer science is shifting towards the study of systems which can exhibit some of the emergent properties of naturally occurring macromolecules. These properties (such as responsiveness, molecular recognition, self-assembly/compartmentalisation, and self-replication) can be realised through a deeper understanding and application of polymer synthesis methodology. This is particularly relevant when examining the impact of radical chemistry in polymer synthesis, culminating in the discovery of controlled radical polymerisation reactions such as reversible addition-fragmentation chain transfer (RAFT) and atom transfer radical polymerisation (ATRP). With the implementation of these reactions, a large scope of macromolecules varying in chain length distribution, end group functionality, architecture and backbone composition can be readily synthesised in a controlled manner. Recent advances in photochemistry, in particular heterogeneous photocatalysis, have offered new opportunities in expanding the scope of accessible properties at the molecular level.

In the first instance, we showed that bismuth oxide photocatalysis can facilitate RAFT polymerisation. Indeed, the versatility of RAFT polymerisation could be afforded by using a catalyst system which was readily available, non-toxic, easily removable and recyclable. After this, much of our work in controlled polymer photosynthesis was dedicated to investigating other polymerisation mechanisms facilitated by this catalysis paradigm.

In our attempts to perform ATRP under bismuth oxide photocatalysis, we found that ATRP initiation with RAFT propagation could be combined in one pot to obtain a controlled polymerisation. This, in effect, involves segmenting the RAFT agent (which forms both end groups) into its usual precursors, namely a dithiocarbonyl disulphide (which forms the ω -end group and termed the “Z-group” in a RAFT context) and an alkyl bromide (which forms the α -end group and termed the “R-group” in a RAFT context). An end group modularity is thus introduced into RAFT polymerisation. At the α -end, easy conjugation with functional initiators are demonstrated. At the ω -end (the propagating species), we not only demonstrate a degree of monomer versatility inherent to RAFT polymerisation, we also demonstrate a facile means to tune the molecular weight distribution.

Taking this work further, when the alkyl bromide initiating component is neglected, we encountered a more “skeletal” variant of RAFT whereby there is no true “R-group” present. Yet, a controlled polymerisation was observed, mediated by solely dithiocarbonyl disulphide photochemistry under bismuth oxide catalysis. Given the inherent symmetry of this species, we anticipate that a degree of architecture control can be facilitated with this system.