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Ruthenium in Living Radical Polymerisation

Living radical polymerisation has become an important technique in precision polymer synthesis for the construction of new polymers with tailor-made structural complexities. In order to assemble structurally well-defined polymers, in terms of molecular weights and molecular weight distributions, their polymerisation must be controlled. However, the control of the reactivity of the propagating chain ends was difficult, until the recent discovery of living (controlled) radical polymerisation. Due to its unique tolerance to water, radical polymerisation can be performed as suspension, dispersion and emulsion processes.

Most of these living radical polymerisations are based on transition metal catalysis (via reversible activation of a carbon-halogen terminal) or nitroxide-mediated processes.

Recently, workers at Kyoto University, Japan, have examined the living radical suspension polymerisation of methyl methacrylate (MMA) in water and alcohols using $RuCl_2(PPh_3)_3$ catalyst/activator and an organic halide initiator, such as $PhCOCHCl_2$ or CCl_3Br, in the presence and absence of aluminium(III) isopropoxide, $Al(O\textit{i}\text{-}Pr)_3$, at 80°C (T. Nishikawa, M. Kamigaito and M. Sawamoto, *Macromolecules*, 1999, **32**, (7), 2204–2209).

With ruthenium(II)-initiation, living radical suspension polymerisation of MMA proceeded to give poly(MMA) with controlled high molecular weights ($\bar{M}_n$) and narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n$ = 1.1 to 1.3). In water, the $PhCOCHCl_2/RuCl_2(PPh_3)_3$ initiating system gave poly(MMA) of $\bar{M}_n \sim 10^5$ and $\bar{M}_w/\bar{M}_n \sim 1.1$, even in the absence of $Al(O\textit{i}\text{-}Pr)_3$.

Polymerisations were faster in water than in organic solvents, such as toluene. The radical mechanism of the polymerisation was confirmed and the high stabilities of the dormant carbon-halogen terminal and of the ruthenium catalyst in water and alcohols were demonstrated. Ruthenium complexes are known to be weakly oxophilic and sometimes water tolerant.

This living radical suspension polymerisation may also be used with other metal complexes or monomers and be applicable to the precision synthesis of block and random copolymers.