

## **Organometallic free radical reactivity in functional group tolerant polymerization**

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In terms of their functional group tolerance neutral nickel(II) catalysts possess a unique profile. They allow for polymerizations in aqueous systems, yielding e.g. highly ordered nanocrystals of linear polyethylene. On the other hand, they are not compatible with polar vinyl monomer monomers like acrylates as also understood from identification of decomposition pathways. An inconclusive and partially contradictory picture existed for the particular case of methyl methacrylate (MMA). From a detailed mechanistic analysis of organometallic intermediates and their reactivity under NMR as well as pressure reactor conditions, and of polymer microstructures, we have evolved a comprehensive picture. A simultaneous free-radical chain growth (of MMA) and an insertion polymerization (of ethylene) are compatible with each other, and the growth cycles and active species do not interfere. PMMA and linear PE homopolymer mixtures are formed. Deactivation pathways result in the formation of Ni(I) species. These can be reactivated for chain growth by reaction with deliberately generated organic radicals. These findings inspire polymerization schemes combining free-radical and insertion reactivity.