Reversible addition-fragmentation chain-transfer (RAFT) of ethylene under mild conditions – Synthesis of polar-apolar copolymer

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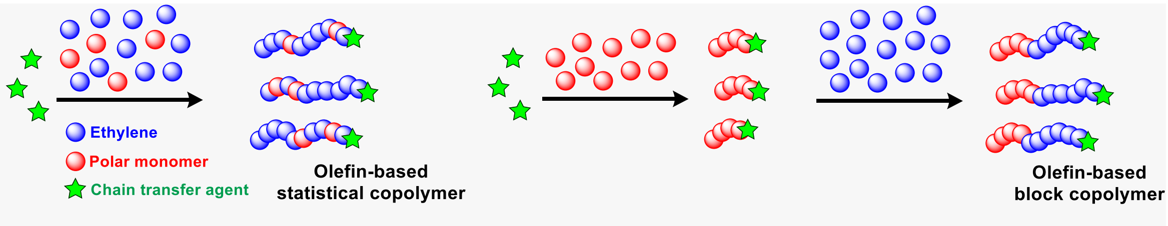
Polyethylene (PE) is the most widely used plastic in the world with ethylene being the most important feedstock for the chemical industry. Ethylene is usually polymerized under harsh conditions (>200 °C, >1000 bar) or using catalytic amounts of metal complexes. These conditions are generally unsuitable to copolymerize ethylene with polar monomers. On the other hand, reversible-deactivation radical polymerization (RDRP)[1] is an excellent candidate for this purpose. In this context, statistical or block copolymerizations of ethylene with polar vinyl monomers using RDRP are expected to lead to a new generation of sophisticated polyolefin-based materials.

Our group demonstrated that RDRP of ethylene is possible by using reversible addition–fragmentation chain-transfer (RAFT) with xanthates under mild conditions (<80 °C, <250 bar)[2]. Good control over molar-mass distributions was obtained with low dispersities and molar masses consistently increasing during polymerization. On the downside, the inherently low stability of the propagating polyethylenyl radical led to a significant side reaction generating dead PE from the RAFT intermediate radical species and thus decreasing the percentage of livingness and chain-end functionalization[3]. By tuning the electron-donating moiety of the xanthate, a more stable radical intermediate could be generated, thus avoiding, to some extent, the generation of dead PE chains.

The presented work follows these studies on RAFT homopolymerization of ethylene and copolymerization with polar monomers. Indeed, the synthesis of statistical copolymers of ethylene and vinyl acetate with low content (<10%) of vinyl acetate (EVA) are easily accessible by this technique. Besides, xanthate-functionalized PVAc of different molar masses can be chain extended in the presence of ethylene to achieve well-defined PVAc-*b*-PE block copolymers.



Scheme 1 – Synthesis of olefin-based polar-apolar copolymers

References

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