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Old meets new: Combination of PLA and RDRP to obtain sophisticated macromolecular architectures

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Abstract

This review article highlights the research focused on the synthesis of polylactide (PLA) based copolymers by combination of reversible-deactivation radical polymerization (RDRP) techniques with ring-opening polymerization (ROP) processes. In particular atom-transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer (RAFT) polymerization, and nitroxide-mediated polymerization (NMP) will be addressed as polymerization (RDRP) techniques mechanistically different from ROP in the design of various sophisticated macromolecular structures. The combination of ROP with RDRP techniques has been extensively applied to prepare PLA copolymers. We discuss the synthetic methods applicable to prepare linear and star-shaped block copolymers by use of heterofunctional initiators as well as other end functionalization methods. This is complemented with the adaption of the synthetic pathways generally used for the preparation of comb and graft copolymers, *i.e.*, macromonomer, grafting-from and grafting-onto approaches, to the requirements of PLA-based building blocks.

List of abbreviations

AGET	Activator generated by electron transfer
AlpGP	1,2:3,4-Di- <i>O</i> -isopropylidene-6- <i>O</i> -acryloyl-α-D-galactopyranose
ATRP	Atom-transfer radical polymerization
BEMP	2-tert-Butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine
BGMA	cis-1,3-Benzylidene glycerol methacrylate
BIEMA	2-Bromoisobutyryl methacrylate
BMBIBPC	2,2-Bis(methylene-2-bromoisobutyrate) propionyl chloride
BnA	Benzyl acrylate

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