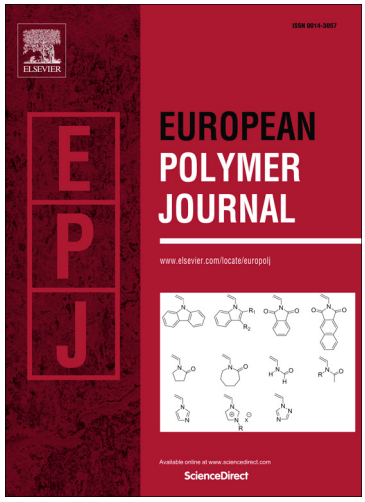

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Continuous flow copper-mediated reversible deactivation radical polymerizations

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ABSTRACT

Copper-mediated reversible deactivation radical polymerization (RDRP) has been one of the most powerful synthetic strategies to obtain well-defined macromolecules. The current scientific and engineering challenges still remained, including but not limited to batch-batch variety, time-consuming process, induction time and hot spot effect. The utility of microflow technique has been proved to be an alternative methodology to improve the polymerization process. This feature article highlighted recent new progress in continuous flow RDRP in the last five years. Cu(I), Cu(0) and Cu(II) were respectively reviewed as catalyst in consecutive order. The outlook of copper-mediated RDRP in microreactor was also discussed.

Contents

1. Introduction

Since the pioneering work about living anionic polymerization was reported by Szwarc and co-workers, living polymerizations have been the central topic in polymer chemistry.[1] In the past two decades, reversible deactivation radical polymerization (RDRP) has achieved noteworthy progress in synthesis of well-defined polymers, including but not limited to transition-metal-mediated RDRP,[2-4] reversible addition fragmentation transfer (RAFT)[5] polymerization and nitroxide-mediated polymerization (NMP).[6] The principle of RDRP was reversible deactivation between the propagating radicals and dormant species, which enabled low radical concentration and reducing bimolecular termination and other side reactions.

Transition-metal-mediated RDRP (copper,[7,8] iron,[9] cobalt[10] and iridium,[11] *etc*) has attracted much interest from both academia and industry for production of value-added polymeric materials. Copper (Cu(0), Cu(I) and Cu(II)) was most deeply investigated and widely used in virtue of high activity, easy to handle, commercial available and low cost. Atom transfer radical polymerization (ATRP), Cu(I)-mediated RDRP, was originally presented in 1995.[2-4] The well-known classical mechanism of ATRP was that Cu(I) activated an alkyl halide *via* an inner sphere electron transfer (ISET) process to form a radical and Cu(II). The radical propagated with monomer before deactivation with Cu(II) to return to the alkyl halide (persistence radical effect (PRE)).[12] The stoichiometric Cu(I) to alkyl halide resulted unendurable metal

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