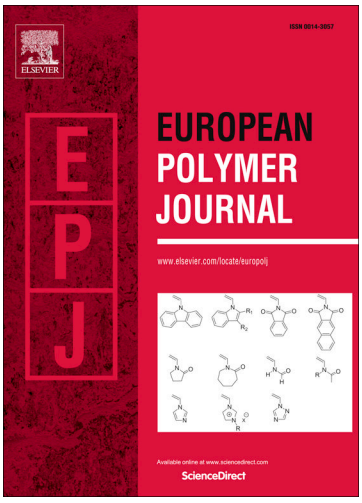

Synthesis of sequence-controlled polymers via sequential thiol-ene and amino-yne click reactions in one pot

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Synthesis of sequence-controlled polymers via sequential thiol-ene and amino-yne click reactions in one pot

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ABSTRACT: Sequence-controlled polymers are prepared by the combination of thiol-ene click reaction and amino-yne click reaction. Due to the high selectivity of the amine unit and thiol unit toward thiolactone, methacrylate, propiolate, etc., the sequence of the resulting polymers can be easily controlled by monomer-addition sequence. Moreover, thiol-ene click reaction and amino-yne click reaction can be carried out under mild conditions without need of any catalyst. Different kinds of sequence-controlled copolymers have been prepared by the combination of thiol-ene click reaction and amino-yne click reaction in one pot. NMR spectra and GPC traces confirmed the formation of polymers with high molecular weight and controlled sequence structure. Therefore, we provide a new method for the preparation of functional polymers with well-controlled sequences.

Introduction

Due to the promising potential in data storage[1], biological[2] and material applications[3], sequence-ordered polymers, in which the chemically distinct units are arranged in order[4], have become a hot research area recently. In nature, biomacromolecules, such as proteins and DNA, are formed in well-aligned sequences, endowing organisms with complicated and diverse functions. While there is still a lot of room for growth in this area, the field is progressing rapidly and there are quite a few techniques now to provide various levels of sequence-control in synthetic polymers. Inspired by nature, the polymerizations utilizing DNA or RNA as templates to tune the sequences of the resulting polymers, have been developed. For examples, Liu *et al.* prepared sequence-defined polymers using DNA-templated polymerization[5]; Benner[6] and Kool's[7] group reported the use of non-natural base pairs via the polymerase chain reaction *in vitro* sequence-regulated polymerization. Though biological polymerization approaches are excellent in sequence control, they are limited in the aspect of structural diversity. In comparison, chemistry methods give access to a much broader range of chemical structures of sequence-defined polymers. Moad and co-workers have studied single-monomer addition in the RAFT process[8]. Kamigaito and coworkers used metal-catalyzed radical addition reactions and a step-growth process for the preparation of sequenced copolymers[9-11]. Sequence-defined functional polymers were synthesized by copolymerization of donor and acceptor comonomers by Lutz[12-14]. Li *et al.* prepared a series of sequence-defined polymers via short sequence-defined oligomers[15-17]. Boyer *et al.* prepared sequence-defined oligomers by sequential PET-RAFT single-unit monomer insertion[18]. However, in most cases, these approaches require time-consuming reactions, as well as multi-pot processes or the use of templates.

In order to overcome these problems, click chemistry came into our sight. Since its introduction by Sharpless in 2001[19], "click" chemistry has led to tremendous development in various research areas[20-26]. Its high efficiency and orthogonal reactivity simplify the experimental setup and reduce the efforts of reaction workup and product isolation in a multistep processes, which makes click chemistry a powerful candidate for preparing sequence-ordered polymers[27, 28]. Guan *et al.* used copper-catalyzed alkyne-azide cyclization to prepare bioinspired modular elastin-mimic sequence-defined polymers[29]. Gao *et al.* prepared a series of sequence-ordered polymers by the combination of thiol-ene and thiol-yne chemistry[30]. Sequence-defined