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Click polymerization for preparation of monolithic columns for liquid chromatography

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ABSTRACT

In recent years, polymerizations based on click reactions (thiol-ene, thiol-yne, thiol-Michael, thiol-epoxy and amine-epoxy) have been utilized to prepare monolithic columns. These polymerization systems are easily carried out under mild conditions. Either hybrid or organic monolithic columns fabricated by click polymerization demonstrated homogeneous network structures. For separation of small molecules, the column efficiencies, such as plate height with less than 10 μm, have been greatly improved comparing with organic monolithic columns prepared with free radical polymerization. In this review, we will summarize recent progress on the preparation of monolithic columns and their chromatographic performances.

Contents

1. Introduction

In the past two decades, monolithic columns have been rapidly developed in the aspect of preparation techniques and characterization methods, and widely applied in high performance liquid chromatography (HPLC), capillary electrochromatography (CEC) and capillary liquid chromatography (CLC) [1–28]. As for preparation techniques, the conventional free radical polymerization (Fig. 1a) is one of the most common methods comparing with sol-gel chemistry due to its facile implementation and lots of commercially available functional monomers. However, it is still a matter of great concern to improve the separation efficiency of small molecules on polymer-based monolithic columns. Researchers have attempted to control the polymerization process by living radical polymerization, as well as to prepare hypercrosslinked monoliths with large surface area [25,29–35]. These improvements gave us some hints that homogeneous network structure and adequate surface area could facilitate the improvement the chromatographic performance for polymer-based monolithic columns.

Click reaction, which features simplicity, selectivity, efficiency and high conversion under mild conditions, has become a versatile toolbox in the applications of organic synthesis, bioconjugation, surface modification, polymer science, etc. (Fig. 1b and 2a-e) [36–42]. Particularly, the click reaction has been employed for direct construction of advanced polymers, such as linear polymers using double-functional monomers (A_2-monomer) as schemed in Fig. 2f.

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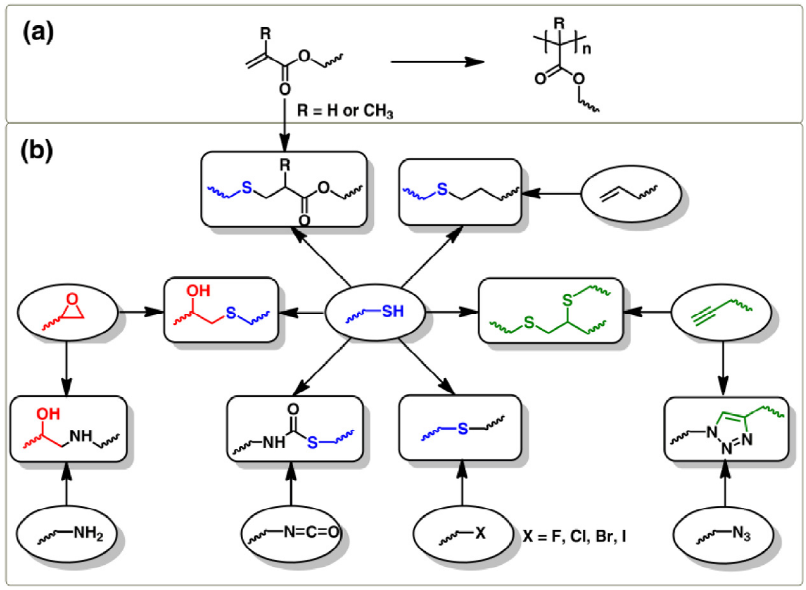

Fig. 1. Linkages formation by (a) free radical polymerization and (b) click polymerization.

Tang and co-workers have summarized the developments of polymerizations based on alkyne-azide and thiol-yne click reactions using the terminology with "click polymerization" in their reviews [43–45]. If one A_2-monomer is replaced with a trifunctional monomer (B_3-monomer), the click polymerization would generate hyperbranched polymers or three dimensional gels (Fig. 2g). It is not difficult to understand that the polymerization of multifunctional monomers like A_4-type also produce hypercrosslinked polymers, which are insoluble and in various forms, such as gels, films and bulk materials [46–49]. As photoinitiated thiol-based reactions are rapid and high efficient, Prasath and co-workers have utilized thiol-ene polymerization to prepare monodisperse macroporous or nonporous functional beads by a home-made microfluidic device equipped with UV light [50]. Compared with traditional synthesis methods, click polymerization as a novel technique demonstrates great potential for preparation of novel materials with high crosslink density.

Recently, click polymerization was adopted to fabricate monolithic columns according to the experience-based prescription that the prepolymerization mixture was composed of monomers, porogenic solvents and an initiator if necessary. These polymerization systems are controllable and easily carried out under mild

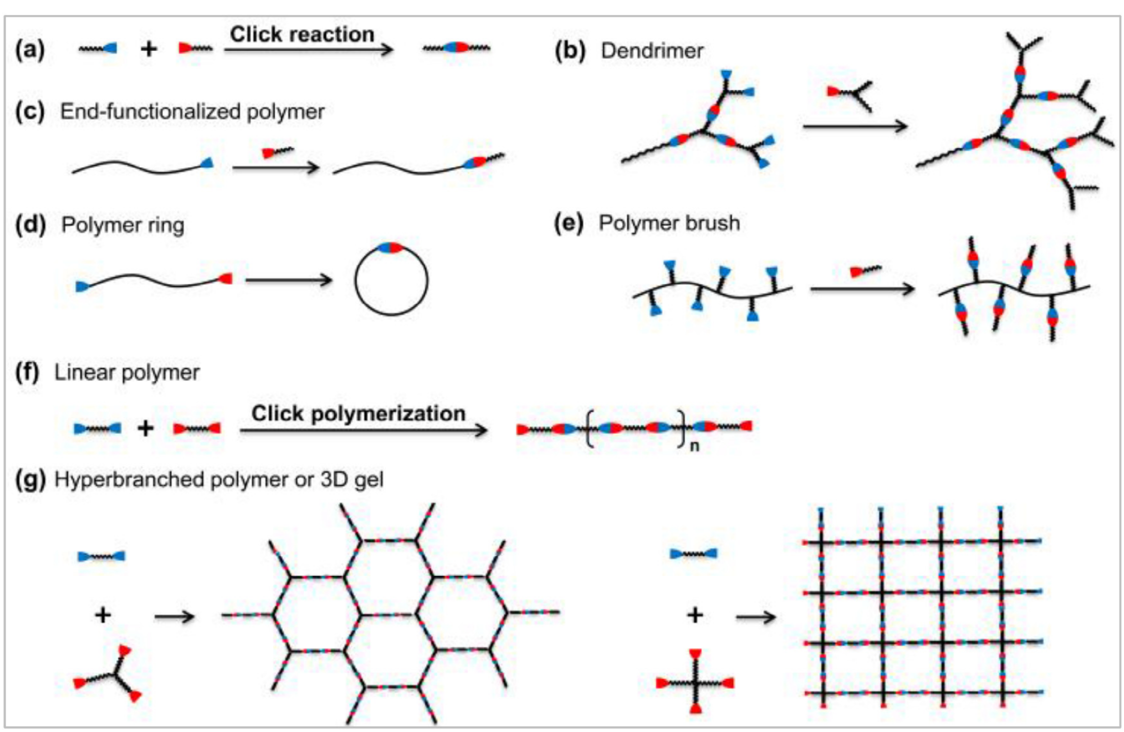

Fig. 2. Examples of macromolecular structures synthesized by click (polymerization) reactions.