Development of separation materials using controlled/living radical polymerization

Huaisong Wang, Xiangchao Dong, Meixian Yang

The development of new separation materials to meet growing demands has always been a major concern of separation science and technology. Controlled/living radical polymerization (CRP) is a technique with many advantages for polymer synthesis. Polymers with low polydispersities and desirable architectures can be prepared using this technique. The application of CRP in the development of polymer-related separation materials has dramatically increased in recent years. In this article, we introduce the mechanism and the advantages of CRP for polymer synthesis and material modification. We also review the development of separation materials in different formats via CRP and their applications.

Keywords: Capillary electrophoresis; Controlled/living radical polymerization (CRP); Microsphere; Molecularly-imprinted polymer; Monolithic column; Multifunctional material; Polymer modification; Polymer synthesis; Separation material; Surface modification

Huaisong Wang, Xiangchao Dong*, Meixian Yang
College of Chemistry, Nankai University, Tianjin 300071, PR China

*Corresponding author.
Tel.: +86 22 2350 4694;
E-mail: xcdong@nankai.edu.cn

1. Introduction

The development of novel stationary phases to satisfy the demands of various applications has always been a major concern in chromatographic and electrophoretic analyses. New materials with various formats, functions or better properties have continually been invented [1–4]. Meanwhile, many advanced synthetic methods and strategies have been employed in the preparation process. Among these methods, controlled/living radical polymerization (CRP) has shown special advantages and potential for applications related to polymer synthesis and modification [5]. The merits of CRP include controlled processes for synthesizing polymers with the desired molecular weight, more homogenous structures or low polydispersity and the possibility of making multi-functional materials. An increasing number of materials [e.g., inorganic-organic composites, polymeric microspheres, molecularly imprinted polymers (MIPs) and monolithic materials] have been prepared via CRP for different separation processes. In this article, we present recent developments of material prepared by the CRP technique. We summarize the advantages of using CRP and demonstrate them with citations.

2. Properties and advantages of CRP

Polymer and polymer-modified materials are important stationary phases that have been widely used in chromatographic and electrophoretic analyses. These materials have special advantages (e.g., higher stability in extreme pH environments, flexibility for introducing different functionalities and sufficient retention of organic compounds). However, polymer-related stationary phases generally have lower column efficiency than traditional C_{18}-bonded silica due to their heterogeneous structures and higher mass-transfer resistance. Since more homogenous structures and evenly distributed thin polymeric layers can be created by CRP, the weaknesses of polymer-related materials can be minimized using CRP, although the drawbacks may not be completely eliminated, because some relate to intrinsic properties of the polymers.

In the preparation of total polymer and polymer-modified materials, radical polymerization is the most frequently used technique due to its good properties (e.g., easy reaction procedure and compatibility with various monomers). However, the weakness of conventional radical polymerization is obvious. Polymers obtained

 0165-9936/$ - see front matter © 2011 Elsevier Ltd. All rights reserved. doi:10.1016/j.trac.2011.07.012

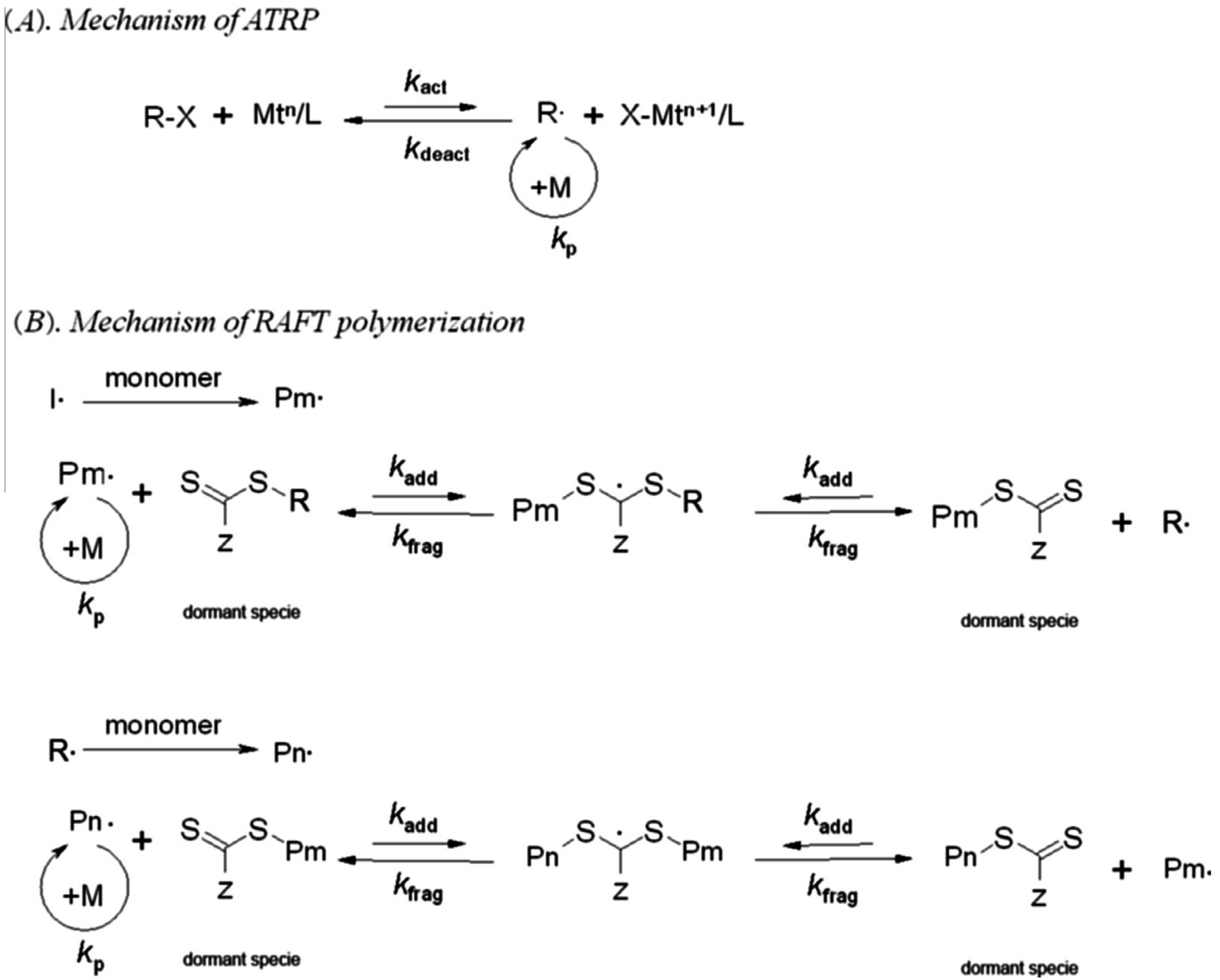

Figure 1. Mechanism of ATRP (A) and RAFT (B) processes. In (A), Mt^n represents the metal ion in oxidation state n and L represents a ligand. In (B), $I^{\bullet}$ is the radical from the conventional initiator; R is the homolytic leaving group of the RAFT chain transfer agent; and, Z is an activating group.