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Metallopolymers with transition metals in the side-chain by living and controlled polymerization techniques

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ABSTRACT

Work on side-chain transition metal-containing polymers prepared by controlled and living polymerizations is summarized, including living anionic polymerization (LAP), ring-opening metathesis polymerization (ROMP) and controlled radical polymerization (CRP) such as atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer polymerization (RAFT), and nitroxide-mediated polymerization (NMP). These polymers include metallocene-containing polymers, ferrocenylsilane polymers with additional metal at the side chain, metal carbonyl complex polymers, and ligated metal complex polymers.

Contents

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1. Introduction

Incorporation of metal centers into macromolecules has led to materials that combine the catalytic, magnetic, and electronic properties of metals with desirable mechanical and processing properties of polymeric frameworks. Research in this area has flourished over the past 30 years, as metallopolymers (or organometallic polymers) have been used as materials for a variety of applications such as sensing, catalysis and media storage [1–13]. Recent advances in polymerization techniques have provided ample opportunities to prepare polymers with tunable chemistry and compositions with predetermined molecular weight and low polydispersity index values (PDI). Furthermore, living and controlled polymerization techniques allow for the preparation of well-defined polymers with diverse topologies including gradient, grafted, and block copolymers [14,15].

Metallopolymers can be classified by the position where the metal center is incorporated into the macromolecule. The most extensively studied metallopolymers are those when the metal center is included in a linear polymer. Generally, there are two major classes of metal-containing linear polymers: main-chain metallopolymers (Class I) in which the metal center is incorporated as an integral part of polymer backbone, and side-chain metallopolymers (Class II) in which the metal center is a pendant group away from the polymer backbone (Fig. 1). Other types of metallopolymers include star-shaped (Class III) and dendritic (Class IV) macromolecules. Many review articles have summarized main-chain, star-shaped, and dendritic metal-containing polymers and can be found elsewhere [16–21]. This review will focus on Class II, specifically, on side-chain transition metal-containing polymers.

2. Background

Synthetic challenges plagued the metallopolymer field for decades, as it was exceptionally difficult to prepare high molecular weight organometallic polymers. The majority of metallopolymers prepared from the mid to late 20th century were primarily of low molecular weight, insoluble in common solvents, and incapable of being properly analyzed by nuclear magnetic resonance (NMR) and gel permeation chromatography (GPC). Most early studies in the 1960s and 1970s involved the preparation of side-chain ferrocene-containing polymers from vinyl-, acrylate-, and methacrylate-ferrocene containing monomers due to the facile preparation of ferrocene derivatives via electrophilic substitution. However, initial free radical, cationic, and anionic polymerization techniques mostly produced polymers with low molecular weight and broad molecular weight distributions [22–24]. Several studies emerged in the 1980s detailing the electrochemical and plasma polymerization of poly(vinylferrocene) [25–30]. Polymer films of controllable thicknesses were prepared from electrode surfaces and the electron propagation properties of the metallopolymer films were studied. These initial studies of metallopolymer-modified electrodes allowed for the understanding of charge transport in redox active polymer films.

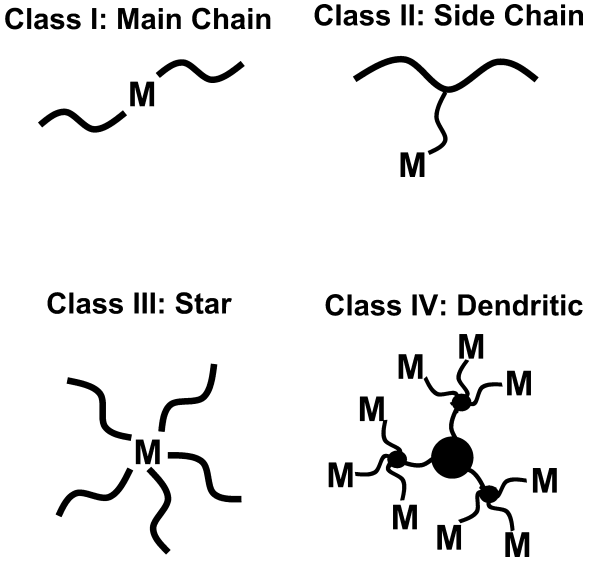

Fig. 1. Classes of metallopolymers.

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