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Review

Metal-promoted C1 polymerizations

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ABSTRACT

C1 polymerizations provide a means to grow polymer chains one carbon atom at a time. Such methodology enables the synthesis of persubstituted polymers that are challenging to prepare using conventional C2 polymerizations, which typically utilize alkene-based monomers and thus grow polymer chains two carbons at a time. Persubstituted polymers feature higher densities of pendant functional groups and, as such, offer the potential to exhibit enhanced physical and/or chemical properties over their monosubstituted C2 polymer analogues. This review summarizes the various metals that have been used to promote C1 polymerizations in a catalytic or stoichiometric manner. Discussions are stratified according to the monomers used, which are formally carbenes or carbynes and typically employed as their respective ylides, isocyanides, diazo compounds, or geminal di- or trihalides. Emphasis is placed on the scope of the polymerization chemistry, underlying mechanisms, and outstanding opportunities in the field.

Contents

1. Introduction

Since the first half of the 20th century, synthetic polymers have become vital materials in contemporary society. Polyolefins in particular, such as poly(ethylene), poly(propylene), and poly(styrene) (see Fig. 1), have become ubiquitous and frequently find utility in consumer goods, building materials, and medicine, among other applications. As reflected in the nomenclature, polyolefins are comprised of multiple, unsaturated alkenes (olefins) that are interconnected through a process wherein the length of the growing polymer chain increases by two carbon atoms per monomer addition cycle. Such processes may be classified as “C2

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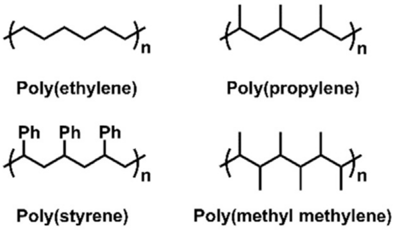

Fig. 1. Structures of various polymers.

polymerizations" and, depending on the monomer employed, can be conducted using free radical, anionic, cationic, or transition metal-catalyzed polymerization techniques [1].

While many polymers have been prepared using C2 polymerization methods, there are limitations that effectively prevent access to certain materials. For example, persubstituted polymers, which feature pendant (non-hydrogen) substituents on every atom of the backbone, are often incompatible with known C2 polymerization techniques for steric and/or electronic reasons. Regardless, polymers with such substitution patterns offer the potential to display relatively high densities of functional groups, adopt unusual architectures, or exhibit high crystallinities due to restricted bond rotation.

The prototypical example of a persubstituted polymer is poly(methyl methylene). While large quantities of poly(propylene) are synthesized every year, poly(methyl methylene) remains relatively unknown. Conventional polymerizations of 2-butene, a potential olefinic precursor to poly(methyl methylene), do not afford the persubstituted polymer as the major product; instead, a series of rearrangements results in the formation of one pendant methyl group for every three carbons atoms along the resulting polymer backbone (see Fig. 2) [2]. Similar isomerization phenomena are observed during the polymerizations of other internal olefins and, to the best of our knowledge, well-defined poly(alkyl methylene)s are not readily accessible through vinyl polymerization methodologies [3–5].

"C1 polymerizations" offer access to poly(alkyl methylene)s and other persubstituted polymers [6]. As the nomenclature implies, C1 polymerizations grow polymer chains in one carbon atom increments during the propagation step. The monomers for such polymerizations are formally divalent carbenes or trivalent carbynes (see Fig. 3a and b). Unfortunately, carbenes and carbynes are typically challenging to isolate and, as such, are generally introduced as their appropriate precursors or derivatives. Common examples include diazo compounds, ylides, geminal dihalides, trihalides, various transition metal complexes, and isocyanides (see Fig. 3c). In some cases, C1 polymerizations are accompanied by the condensation of small molecules (byproducts) which may serve to drive the reactions. Additionally, many C1 monomers require activation, predominately through the use of metals [6–8] or Lewis acids [6,8–10]. In the case of the former, polymerizations can be initiated through the addition of either stoichiometric or catalytic quantities of metal.

Herein we describe the use of various carbene and carbyne precursors in metal-promoted C1 polymerizations. The following two sections will focus on transition metal-catalyzed polymerizations of diazo compounds and isocyanides, which are among the most common monomers used in C1 polymerizations. The sections are further divided according to the metals used to facilitate such chemistry. Discussions will begin with copper, which was the first metal employed to catalyze the polymerization of diazo compounds, and later subsections will describe the use of other transition metal-based catalysts, including gold, palladium, rhodium, and nickel. The penultimate section will discuss C1 polymerizations that have been conducted using stoichiometric quantities of metals. Finally, concluding remarks as well as some perspectives for the field will be offered. Throughout the review emphasis will be placed on the scope of the polymerization chemistry, mechanistic insight, and potential opportunities for further development.

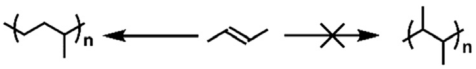

Fig. 2. The polymerization of 2-butene typically results in rearrangement.

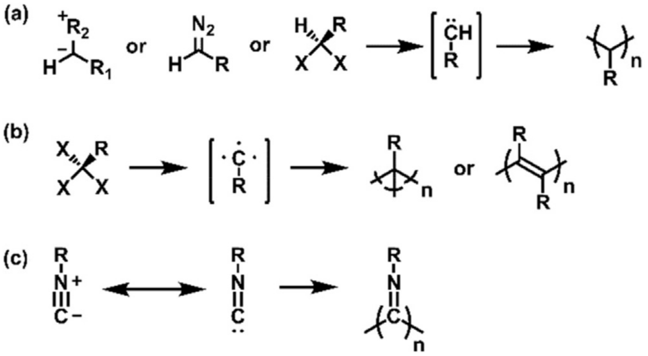

Fig. 3. Generalized examples of C1 polymerizations as conducted using (a) carbene, (b) carbyne, or (c) isocyanide precursors as monomers.

2. C1 polymerizations that utilize diazo-containing monomers

2.1. Copper-catalyzed polymerizations

In 1948, it was reported that treating an ethereal solution of diazomethane with copper powder resulted in the formation of poly(methylene), a C1 analogue of poly(ethylene), in about 10% yield after 24 h. The polymer, described by Ray and coworkers as a "brittle crystalline wax," was found to be insoluble in ether, but soluble in boiling benzene, toluene, or xylene [11]. Additional structural information was obtained using infrared (IR) spectroscopy where signals characteristic of poly(methylene) (e.g., 721, 732 and 1365 cm^{-1}), were recorded. The molecular weight of the polymer was determined to be 20 kDa using dilute solution viscometry. Various Cu(II) salts, including copper stearate, citrate, succinate, or benzoate, were also reported to afford poly(methylene) from diazomethane and, while the yields were similar to those obtained using copper powder, the polymers produced may be of relatively low molecular weight (cf., 2.2 kDa was reported for a polymer that was prepared using Cu(II) stearate) [12,13].

A similar reaction using diazoethane and copper powder in a 5:1 ratio afforded poly(methyl methylene) with a molecular weight of 5.8 kDa in over 80% yield [11]. Likewise, diazoethane polymerizations were promoted by the use of Cu(I) cyanide or Cu(II) sulfate, and provided similar quantities of polymers with molecular weights of 7.2 kDa and 2.5 kDa, respectively. The molecular weights of the polymeric products were increased to as high as 14 kDa by reducing the initial monomer concentration from 0.12 M to 0.06 M. Relatively high yields were reported with copper stearate which also enabled the use of monomer to catalyst ratios that were as high as 10,000 [13]. The IR spectra recorded for the polymers obtained from diazoethane were reported to differ from the data acquired for poly(methylene) as signals near 730 cm^{-1} were absent and a strong absorption near 1380 cm^{-1} was measured, consistent with the presence of methyl groups.