



Digest paper

Recent advances in acetylene-based helical oligomers and polymers: Synthesis, structures, and properties

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ABSTRACT

In this review, we describe the recent advances in the chemistry of helical polymers and oligomers containing acetylene units in the main chain. Owing to their great benefits such as high availability and handleability, good reactivity, rigidity, linearity, and low bulkiness, acetylene units have been utilized and incorporated in helical folding oligomers and polymers such as oligo- and poly(*m*-phenylene ethynylene)s. General synthetic methods as well as the structures, functions, and properties of acetylene-based helical oligomers and polymers are discussed by focusing on recent examples from 2009 to 2017.

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Introduction

Helical polymers have unique and interesting structures that preferentially adopt entropically unfavorable compact conformations.^{1–11} Natural helical polymers are often found in biological macromolecules such as DNA, proteins, and polysaccharides, and such helical structures play diverse and important roles in biological phenomena and structural stability. Since the first discovery of helical polypropylene in the 1950s¹, various artificial helical polymers have been discovered and synthesized and intensively studied over half a century. As reviewed in detail by Yashima,² Nakano,³ Li,⁴ Jeong,⁵ and others,⁶ artificial helical polymers and oligomers have been synthesized not only for mimicking biological helical structures and their functions, but also for developing new artificial helical structures and unique functions such as molecular recognition, chiral recognition, reaction fields, and asymmetric catalytic fields.⁷

In particular, acetylene-based foldamers such as poly(arylene ethynylene)s (poly-AEs) are recognized as one of the most attractive and reliable helical motifs. These have been widely synthesized and investigated due to their ease of preparation, the host ability inside pores, and structural diversity. In 1997, helical folding oligo(*m*-phenylene ethynylene)s (oligo-PEs) were synthesized and studied in detail for the first time by Moore and Nelson.⁸ Later, the related oligo(arylene ethynylene)s (oligo-AEs) and poly-AEs were studied by Moore,^{8,15,16} Hecht,⁹ Abe and Inouye,^{17,18,27,28,30} Yamaguchi,¹⁰ and Yashima.^{42–47} The helical conformation can be easily achieved and controlled by intramolecular π - π interactions, solvophobic interactions and hydrogen bondings, and intermolecular host-guest interactions between the host polymers and guest molecules.² Furthermore, it is possible to induce a one-handed helical structure by introducing chiral auxiliaries into the main or side chains of the polymer, or the addition of a chiral guest molecule. In addition, acetylene-based chiral helical polymers have received considerable attentions from the viewpoints of chiroptical properties, chiral host-guest chemistry, supramolecular chemistry, chiral molecular dynamics, and asymmetric catalysis.

In the studies on acetylene-based polymers, acetylene units have been frequently used as spacers for connecting arene units. In general, simple *o*- and *m*-phenylene oligomers and polymers are well known to form a helical structure in the solid state and a random coil structure in solution.¹¹ This is mainly due to entropic reasons and the steric hindrance between neighboring phenylene units. The steric hindrance can be reduced by introducing an acetylene spacer between the phenylene groups, thus resulting in the more favorable helical folding in the solid and solution states. In addition, the introduction of acetylene units does not cause significant structural changes because of their small size. Furthermore, the C–C triple bond is linear yet flexible, so that macromolecules containing acetylene units can often adopt distorted structures. Therefore, helical forming acetylene-based polymers such as poly-PEs with structural diversity have been reported so far. The hollow structures derived by the introduction of acetylene moieties and the attachment of functionalities to the arylene bridges can induce molecular recognition ability inside the helix. Therefore, the synthesis methods, structures, properties as well as molecular dynamics have received much interest in polymer chemistry, host-guest chemistry, materials science, and supramolecular chemistry.

In 2001, Nakano and Okamoto,^{3,12} and Rowan, Nolte, Sommerdijk and coworkers¹³ reported exhaustive reviews on the synthesis of helical polymers, while Moore *et al.* reviewed foldamers.¹⁴ In 2009, Yashima comprehensively summarized the synthesis, properties, structures, and functions of all helical polymers synthesized between 2001 and 2009.^{2b} In 2016, he updated a review on

helical polymers, oligomers, small molecules, and supramolecules in terms of the supramolecular helical assembly.^{2a} However, there are no reviews on acetylene-based helical polymers. In this review, we focus on recent advances in acetylene-based helical polymers and oligomers since 2009. In particular, we describe the synthesis, structures, properties, functions and molecular dynamics of a series of poly-AEs, including some representative examples reported in important pioneering studies before 2009. In this review, we use the term “polymer” in a broad sense, including relatively shorter oligomers, and accordingly use “oligomer” if the compounds have chain lengths shorter than 10 mer or molecular weights lower than 5000 (Fig. 1).

General synthetic method for acetylene-based helical polymers

Three methods are mainly used for synthesizing acetylene-containing polymers (Fig. 2A). The most representative strategy is polymerization by Sonogashira coupling, which involves the reaction of halogenated arylacetylenes using Pd and Cu catalysts to afford poly-AEs. The use of dihaloarenes with diethynylarenes also enables the synthesis of diverse alternating copolymers. Another advantage that it is possible to intentionally incorporate various aromatic units by changing the reactant in each step. The second method is polymerization by the Cu-catalyzed Glaser-Hay coupling of diethynylarenes, which is often used for the synthesis of poly(arylene diethynylene)s. The third method is the formation of diethynylplatinum by the reaction of platinum(II) salts and terminal arylacetylenes. This method furnishes stable platinum-tethered diethynylene polymers in good yields.

The thus-obtained arylene-ethynylene polymers often show helical folding behavior due to various intra- and intermolecular interactions caused by the inner and outer side chains as well as the polymer main chain (Fig. 2B). For example, solvophobic interactions, intramolecular hydrogen bonding between the polymer

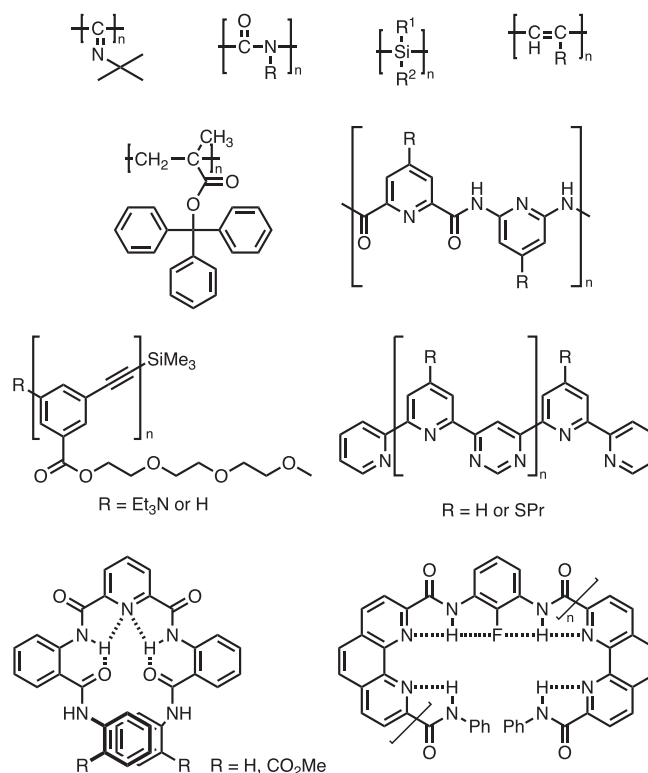


Fig. 1. Representative structural motifs of helical foldamers.

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