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Preparation and application of abietic acid-derived optically active helical polymers and their chiral hydrogels

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HIGHLIGHTS

- Chiral helical (co)polymers were synthesized from abietic acid.
- Chiral hydrogels were prepared from the chiral helical copolymer.
- The hydrogels demonstrated enantioselective recognition towards L-alanine.
- This study opens new uses of abietic acid.

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ABSTRACT

A novel chiral monomer *N*-propargyl abietamide, M1, was synthesized from abietic acid and catalytically polymerized with (nbd)$Rh^{+}B^{-}(C_6H_5)_4$ (nbd = norbornadiene), providing polymer [poly(1)] with a molecular weight of 13,000–36,000 at a yield of 59–84%. Poly(1) did not form stable helices in tetrahydrofuran at room temperature whereas copolymerization of M1 and the achiral *N*-propargylamide monomer, M2, led to the formation of helical optically active copolymers as indicated by circular dichroism studies, UV–vis spectroscopy, and specific optical rotation measurements. Hydrogels were prepared based on an optically active helical copolymer, poly($M1_{0.32}$-*co*-$M2_{0.68}$) that exhibited enantioselective recognition toward L-alanine. The novel chiral polymers derived from abietic acid are expected to find applications in such areas as chiral recognition, chiral resolution, and chiral catalysis.

1. Introduction

Abietic acid has an aromatic diterpene structure with three rings, three chiral carbon atoms, two conjugated C=C bonds, and a reactive carboxyl group. Due to this structure, abietic acid and its derivatives show biological activity and intriguing chirality (Matsushita et al., 2005). These compounds have found applications in such areas as the manufacturing paper, printing inks, adhesives, and synthetic rubber (Stonecipher and Turner, 1970). Wang et al. (2008) and Liu et al. (2010) prepared curing agents as alternatives to petrochemical-based agents, and Wang et al. (2012) prepared antimicrobial compounds and polymers. Other functional polymers such as photosensitive polymers, photo-crosslinkable polymers, and pressure-sensitive adhesives can also be made from abietic acid (Kwak et al., 2007; Kim et al., 2003; Paiva et al., 2000).

The present study investigated the feasibility of using abietic acid-derived compounds to generate chiral polymers. Chiral macromolecules occur widely in nature and some of them are known to form stable helical conformations. These artificial helical polymers not only show unique electronic, magnetic, and optical properties, but also possess molecular-recognition (Miyabe et al., 2011), asymmetric synthesis (Megens and Roelfes, 2011), and optical resolution abilities (Tamura et al., 2011; Liu et al., 2009; Yashima et al., 2009; Rudick and Percec, 2008; Fujiki, 2008). In the current study, helical poly(*N*-propargyl amide)s with pendant abietic acid groups were synthesized and the recognition ability of chiral hydrogels consisting of abietic acid-derived polymers was demonstrated.

2. Methods

2.1. Materials

Solvents were distilled by standard methods. All the chemicals, unless otherwise noted, were obtained from Aldrich. Abietic acid was isolated from crude abietic acid (75%) by using diphenylamine (Palkin and Harris, 1934). Isobutryric acid (99%), propargylamine (98%), isobutyl chloroformate (98%), *N*-methyl morpholine (98%), AIBN (azodiisobutyronitrile, 98%), NIPAm (*N*-isopropyl acrylamide,

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