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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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98%), and BIS (*N*, *N*'-methylenebisacrylamide, 98%) were used as received. (nbd)$Rh^+B^-(C_6H_5)_4$ was prepared as reported by Schrock and Osborn (1970).

2.2. Measurements

Molecular weights and molecular weight distributions of the (co)polymers were determined by gel permeation chromatography (GPC) (Waters 515-2410 system) calibrated using polystyrene as standards and tetrahydrofuran (THF) as eluent. Circular dichroism (CD) and UV–vis absorption spectroscopy measurements were conducted on a Jasco 810 spectropolarimeter. Melting point (mp) was measured with an X-4 micromelting point apparatus. ^1H NMR (nuclear magnetic resonance) spectra were collected in $CDCl_3$ using a Brucker AV600 spectrometer and FTIR spectra (KBr pellet) were obtained using a Nicolet NEXUS 670 spectrophotometer. Specific rotations were measured using a Jasco P-1020 digital polarimeter.

2.3. Monomer synthesis

Monomer 1 (M1, *N*-propargyl abietamide, presented in Fig. 1) was synthesized and identified as reported by Deng et al. (2008). Abietic acid (3.53 g, 8.77 mmol) was dissolved in THF (150 ml), and isobutyl chloroformate (1.14 ml, 8.77 mmol) and *N*-methyl morpholine (0.96 ml, 8.77 mmol) were added to the solution. The solution was stirred at 30 °C for 0.5 h. Propargylamine (0.6 ml, 8.77 mmol) was dropwise added into the solution and the mixture solution was stirred at 30 °C for 3.5 h. The mixture was filtered through a filter paper and the white precipitate was discarded. The filtrate was washed thrice with 2 M HCl and once with saturated $NaHCO_3$ to neutralize the solution. The solution was dried over anhydrous $MgSO_4$, filtered through a filter paper, and concentrated by rotary evaporation to give the target monomer. The coarse monomer was purified further by recrystallization twice from THF/hexane.

The major reactions for forming M1 are described in Fig. S1 (Supporting Information). Briefly, isobutyl chloroformate and abietic acid reacted to form an intermediate, in which *N*-methyl morpholine acted as catalyst. The intermediate and propargylamine reacted to form monomer M1. Monomer 2 (M2, *N*-propargyl 2-ethylbutylamide) and monomer 3 (M3, *N*-propargyl acrylamide) are presented in Fig. 1, and were prepared as described by Deng et al. (2008). The raw materials for synthesizing M2 and M3 were 2-ethylbutyric acid and acrylic acid (Aldrich), respectively.

M1, obtained at a yield of 47%, had the following properties: yellow solid, mp 127–128 °C. FTIR (KBr): 3307 (N–H), 2124 (≡*CH*), 1693, 1524 (amide group), 2959, 1465, 1386 cm^{-1} (abietic acid group). ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): σ 5.7 (1H, $(CH_3)_2$ CHC=*CH* abietic acid group), 5.3 (1H, >C=*CH* abietic acid group), 3.7 (2H, $COOCH_2$), 2.3 (1H, –C≡*CH*), and 2.27–0.72 (28H, other protons).

2.4. Synthesis of (co)polymers

Polymerizations of M1 were carried out with (nbd)$Rh^+B^-(C_6H_5)_4$ as catalyst in a dry solvent ($CHCl_3$, CH_2Cl_2, or THF) at 30 °C for 4 h under nitrogen, with [M1] = 1.0 M. After polymerization, the solution was poured into a large amount of hexane to precipitate the formed polymer, and the polymer was collected by filtration through a filter paper and dried under reduced pressure.

Copolymerizations of M1 and M2 were carried out in a same manner with [M1] + [M2] = 1.0 M.

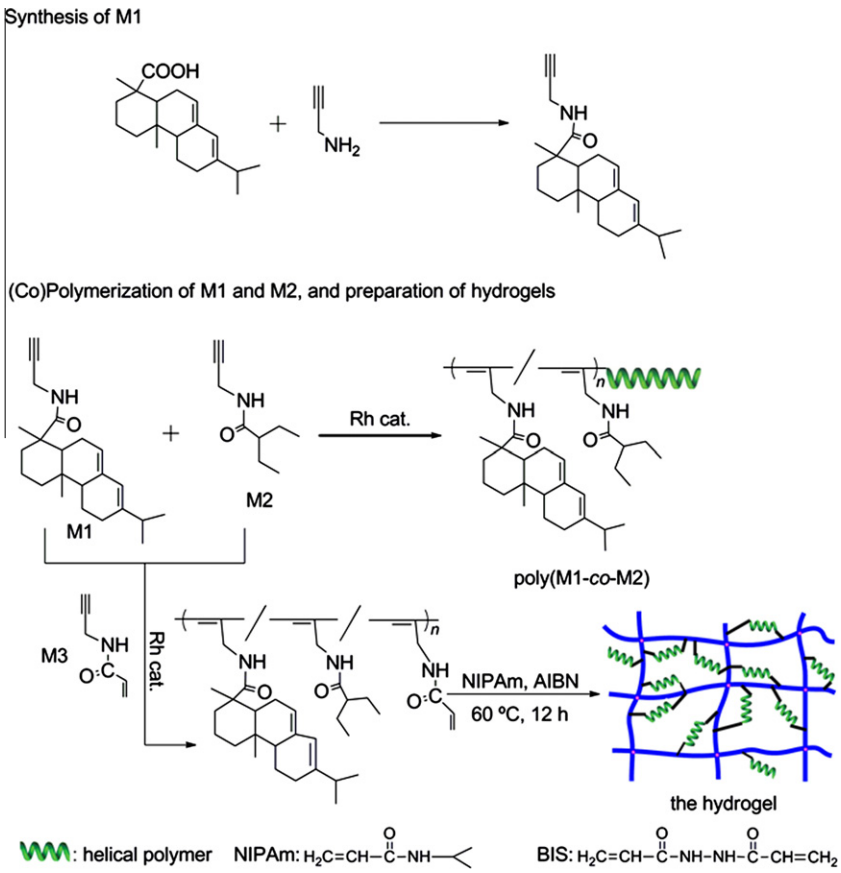

Fig. 1. Schematic illustration of synthesis of M1, (co)polymerization of M1/M2, and preparation of chiral hydrogels.