



# Helix-sense-selective polymerization of achiral substituted acetylene in chiral micelles for preparing optically active polymer nanoparticles: Effects of chiral emulsifiers



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## ABSTRACT

This paper reports helix-sense-selective polymerizations (HSSPs) of achiral acetylene monomer performed in chiral micelles, by which optically active helical polymer emulsions were directly obtained. The chiral micelles were constructed by chiral emulsifiers, in which achiral acetylene underwent HSSPs in the presence of catalyst [(nbd)RhCl]<sub>2</sub>. The chiral emulsifiers possessed different alkyl chain lengths and different amino acid groups, and their effects on HSSPs were investigated in detail. The obtained polymer emulsions were characterized by TEM, circular dichroism and UV–vis absorption spectroscopy techniques. It is demonstrated that the polymer chains constructing the emulsions adopted helical structures of predominantly one-handed screw sense, from which the emulsions exhibited remarkable optical activity.

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## 1. Introduction

Optically active helical polymers have become of great interest and importance because of their unique helical structures and intriguing optical activity [1]. Particularly, the intriguing helical structures and optical activity afford helical polymers with significant applications in optical resolution [2], chiral catalysts [3], chiral sensors [4], etc. So far a great number of artificial optically active helical polymers have been prepared [5,6]. However, a majority of the synthetic helical polymers were prepared by starting from enantiomeric monomers. As a consequence, the types and numbers of synthetic helical polymers are highly restricted by the limited chiral monomers and especially their high cost. To solve this problem, asymmetric polymerizations were created by which achiral monomers can be used in stead of chiral monomers to prepare optically active helical polymers [7].

According to polymerization mechanism and conformations of the polymers, asymmetric polymerizations fall into three major categories: (1) asymmetric synthesis polymerization; (2) helix-sense-selective polymerization (denoted as HSSP hereafter); and

(3) enantiomer-selective polymerization [7]. A series of optically active polymers were constructed by asymmetric polymerization [7–14]. Among the three polymerization approaches, HSSP may be the most attractive and important one because it directly provides optically active helical polymers by using achiral monomers [7,9]. Up to date HSSPs have been successfully utilized in preparing helical polymers derived from methacrylates/methacrylamides (and vinyl derivatives) [10], isocyanides [11], phenylacetylene and substituted acetylenes [6b,12], and carbodiimides [13]. Chiral initiators, chiral catalysts, chiral structure-directing agents, and external asymmetric field [10–14] can be utilized to achieve HSSPs. Chiral micelles, which can provide a unique asymmetric environment, have found important applications in chiral recognition, chiral separation and enantioselective synthesis [15]. In the earlier work, we successfully performed HSSPs of achiral substituted acetylene in chiral micelles and directly obtained optically active helical substituted polyacetylene nanoparticles [16]. As an important extension of the methodology, in the present study we performed more HSSPs in chiral micelles to acquire deeper insights into this novel technique. The effects of chiral emulsifiers on HSSPs of achiral substituted acetylene in chiral micelles were investigated. Compared to other analogous techniques, HSSPs in chiral micelles are advantageous in directly providing optically active helical polymer nanoparticles, which have constructed a novel research field of high importance in both science research and practical applications [17].

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## 2. Experimental

### 2.1. Materials

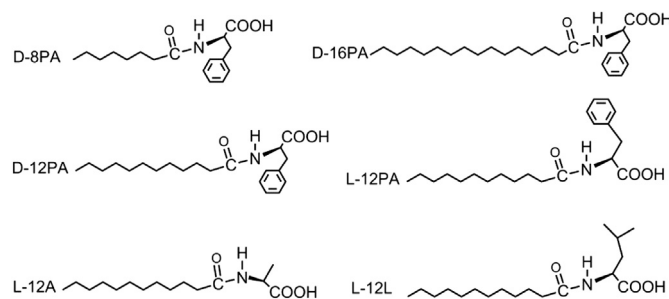
Isobutyl chloroformate (Alfa), 4-methylmorpholine (Alfa), 2-phenylisobutyric acid (TCI), and propargylamine (Aldrich) were used as received. Dodecanoyl chloride, palmitoyl chloride, octanoyl chloride, *L*-phenylalanine, *D*-phenylalanine, *L*-alanine, *L*-leucine, [(nbd)RhCl]<sub>2</sub>, sodium hydroxide (NaOH), sodium dodecyl sulfate (SDS), tetrahydrofuran (THF), chloroform (CHCl<sub>3</sub>), triethylamine and *N,N*-dimethylformamide (DMF) were purchased from Aladdin Reagent Co., (Shanghai, China) and directly used without further purification. Achiral acetylene monomer (M1), structurally presented in Scheme 1, was synthesized according to the method reported previously [18]. Deionized water was used for all the polymerizations.

### 2.2. Measurements

Fourier transform infrared (FTIR) spectra were recorded with a Nicolet NEXUS 670 spectrophotometer (KBr tablet). Molecular weights (Mn) and molecular weight distributions (Mw/Mn) of the polymers were determined by GPC (Waters 515-2410 system), using polystyrenes as standards and THF as eluent. Circular dichroism (CD) and UV–vis absorption spectra were conducted on a JASCO J-810 spectropolarimeter. Transmission electron microscopy (TEM) images were performed on an H-800 (Hitachi) transmission electron microscope at an accelerating voltage of 200 kV. Emulsions were cast onto a carbon-coated copper grid. Polymer particle size was determined from TEM images. Raman spectra were recorded on a Renishaw in Via-Reflex confocal Raman microscope with an excitation wavelength of 514 nm.

### 2.3. Synthesis of chiral emulsifiers

The chiral emulsifiers are structurally presented in Scheme 2. They were synthesized by the reaction of amino acid with acyl chloride. Dodecylphenylalanine (*L*-12PA or *D*-12PA) chiral emulsifiers were synthesized according to the method reported earlier [16]. Chiral emulsifiers derived from hexadecylphenylalanine (16PA), octylphenylalanine (8PA), dodecylalanine (12A) and dodecyleucine (12L) were synthesized as new compounds according to the same method by using the corresponding acyl chloride and amino acids. Taking *L*-12A chiral emulsifier as example, the major synthetic procedure is described below. 100 ml NaOH (1 M) aqueous solution and 1.34 g (0.015 mol) *L*-alanine were added into a one-neck flask. After the system was cooled to 0 °C, 3.31 ml (0.014 mol) dodecanoyl chloride was dropwise added and maintained for 5 h at 0 °C. Then 16 ml hydrochloric acid (12 M) was



Scheme 2. Structure of chiral emulsifiers.

added to the mixture. Subsequently the white precipitate was filtered, washed three times with deionized water, and dried at 45 °C for 24 h. The other chiral emulsifiers were synthesized in the same way. The FTIR data of the chiral emulsifiers are as follows:

*D*-8PA: Yield 65%. FTIR (KBr): 3308 (H–N), 2927, 2856 (–CH<sub>2</sub>–), 1709 (C=O), 3052, 1615, 1557, 1456, 744, 697 cm<sup>-1</sup> (benzene ring).

*D*-16PA: Yield 86%. FTIR (KBr): 3309 (H–N), 2918, 2850 (–CH<sub>2</sub>–), 1703 (C=O), 3065, 1608, 1540, 1470, 721, 698 cm<sup>-1</sup> (benzene ring).

*L*-12A: Yield 78%. FTIR (KBr): 3326 (H–N), 2919, 2851 (–CH<sub>2</sub>–), 1704 (C=O), 1470 cm<sup>-1</sup> (CH<sub>3</sub>).

*L*-12L: Yield 81%. IR (KBr): 3329 (H–N), 2922, 2852 (–CH<sub>2</sub>–), 1700 (C=O), 1471 cm<sup>-1</sup> (CH<sub>3</sub>).

### 2.4. Polymerization and preparation of polymer emulsions

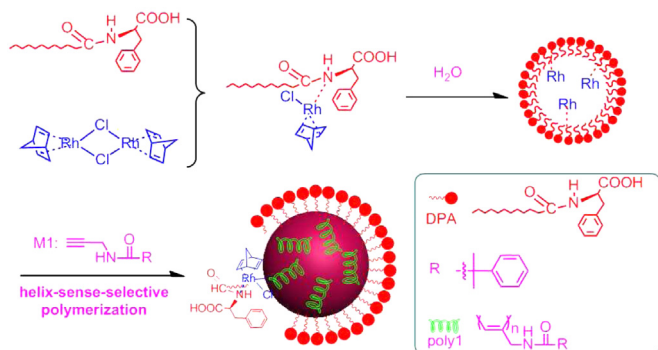
The polymerizations were carried out in a 50 ml three-neck flask equipped with a stirrer, a N<sub>2</sub> inlet, and a reflux condenser. Taking the HSSP of M1 in 12PA-Rh chiral micelles as example, the polymerization procedure is as follows: 0.87 g (2.5 mmol) of 12PA, 1.3 mg (0.003 mmol) of [(nbd)RhCl]<sub>2</sub> and 2 ml of triethylamine were added to the flask, after which the mixture was stirred at 400 rpm for 20 min at 30 °C to guarantee the coordination of 12PA with [(nbd)RhCl]<sub>2</sub>. Then 15 ml of deionized water was dropwise added, forming chiral micelles. The solution was deoxygenated by purging with N<sub>2</sub> for 30 min to make sure an inert environment, after which 0.05 g (0.25 mmol) of M1 (dissolved in 2 ml DMF) was dropwise added. The solution kept at 30 °C for 3 h and then yielded polymer emulsion.

In order to obtain pure polymer particles, the obtained emulsions were first washed with 10 wt.% NaOH aqueous solution and then the aqueous phase was excluded by centrifugation with a rotational speed of 20,000 rpm. This process was repeated for three times.

## 3. Results and discussion

### 3.1. Strategy for HSSPs

The major procedure of HSSPs in chiral micelles is illustrated in Scheme 1. The HSSP includes three main steps. Firstly, the chiral emulsifier and Rh catalyst were dissolved in DMF and then coordinated under ultrasound condition, forming the chiral complex composed of chiral emulsifier and Rh catalyst. Secondly, deionized water was dropwise added in the chiral complex solution, resulting in chiral micelles. Thirdly, a substituted acetylene monomer (M1 in Scheme 1) was dropwise added into the chiral micelle system and HSSP of the monomer was performed at 30 °C for 3 h. The



Scheme 1. Schematic representation of HSSP of achiral acetylene in chiral micelles.

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