Polymer 154 (2018) 253–257

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Short communication

Chiral teletransmission in the *cis-cisoidal* sequence of copoly(substituted acetylene)s by multiple stage solvent exchange of the copolymer solution through a membrane

Lijia Liu[a,*], Yuanyuan Gu[a], Yudan Wang[a], Toshiki Aoki[b,**], Guan Wang[a,c], Takeshi Kaneko[b], Masahiro Teraguchi[b]

[a] *Key Laboratory of Superlight Materials and Surface Technology, Ministry of Education, College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin, 150001, China*
[b] *Graduate School of Science and Technology, Niigata University, Nishi-ku, Niigata, 950-2181, Japan*
[c] *Institute of Petrochemistry, Heilongjiang Academy of Sciences, Harbin, 150040, China*

HIGHLIGHTS

- Chirality teletransmission in the *cis-cisoidal* polyacetylenes by solvent-exchange.
- Much efficient chiral transmission by solvent-exchange than that by copolymerization.
- CD signal changes in a stepwise manner by solvent-exchange.

ARTICLE INFO

Keywords:
Chirality
Helical polymer
Polyacetylene
Cis-cisoidal
Chiral polymer

ABSTRACT

Copoly(4-dodecyloxyl-3,5-dihydroxymethyl-phenylacetylene/*p*-pinanyldimethylsilylphenylacetylene) (copoly(**1**/**2**)) consist of both the *cis-cisoidal* sequence of achiral 4-dodecyloxyl-3,5-dihydroxymethyl-phenylacetylene (**1**) and *cis-transoidal* sequence of chiral *p*-pinanyldimethylsilylphenylacetylene (**2**). The reactivity ratios of **1** and **2** in the copolymerization were estimated as $r_1 = 1.49$ and $r_2 = 0.50$, respectively. By replacing THF (a good solvent) of copoly(**1**/**2**) solution with methanol (a poor solvent) gradually by concentration-driven permeation through a membrane for several times, stepwise increase in the CD intensity at 308 nm arisen from the *cis-cisoidal* main-chain was observed. The local chirality in chiral **2** units was successfully transmitted to the *cis-cisoidal* sequence of achiral **1**. Even when the molar ratio of **1**/**2** reaches 50, this method of the multiple-stage-solvent-exchange is still effective for transmitting the local chirality in **2** to the *cis-cisoidal* sequence **1** in the copolymer. Directly adding methanol to the copoly(**1**/**2**)'s solution and annealing of copoly(**1**/**2**) in THF/methanol could not realize this chiral teletransmission. Hence, this new method of the multiple stage solvent exchange in the copolymer solution through a membrane is suitable and efficient to realize the efficient chirality transmission and amplification in the *cis-cisoidal* polyacetylene.

1. Introduction

Biosystems have dynamic structures whose functions are based on the chirality relay [1]. A local chirality influences chiral conformation or configuration at a remote site, i.e., chiral information can be ‘transmitted’ or “amplified” in such systems [1]. Inspired by this fact, chirality transmissions and amplifications within many synthetic systems, such as polymers and supramolecular assemblies, have been widely explored [1–15]. Although chirality transmission following “surgent and soldiers” effect or “majority rules” has been realized in copolymers having a single conformation in the main chain [1,12,16], there have been only few reports regarding the chirality transmission in the copolymer having two or more kinds of main chain conformations [17,18].

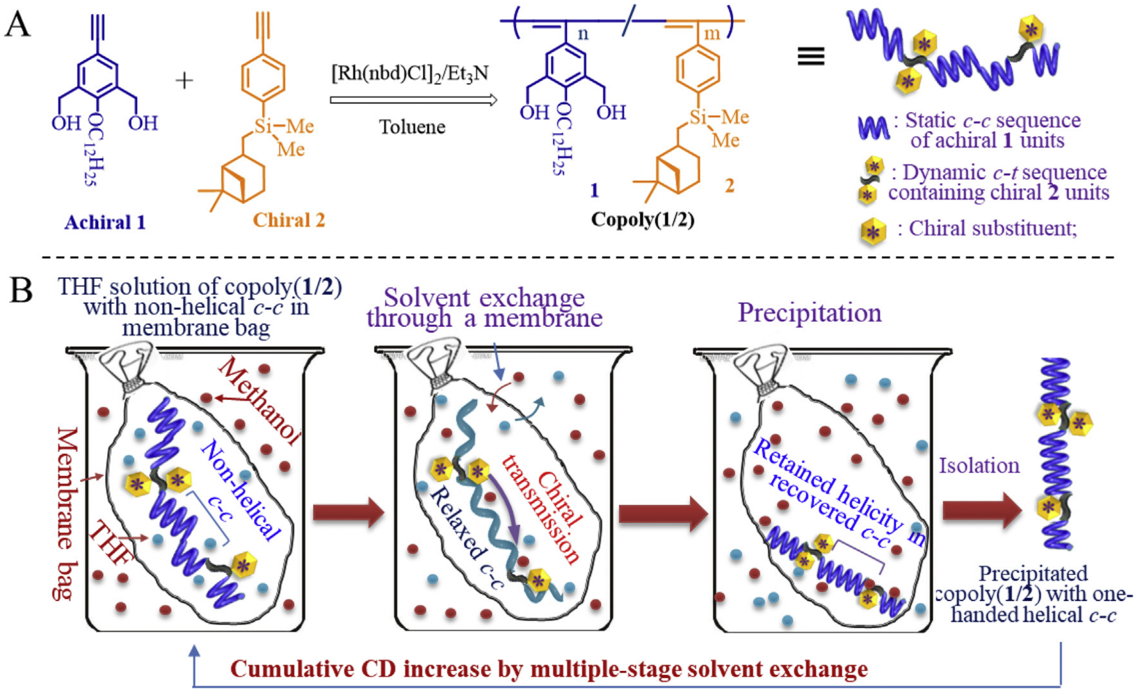
The control of the helix sense of poly(substituted acetylene)s has been an attractive field, it can be realized by 1) chiral induction on

---

[*] Corresponding author.
[**] Corresponding author.

E-mail addresses: liulijia@hrbeu.edu.cn (L. Liu), toshaoki@eng.niigata-u.ac.jp (T. Aoki).

https://doi.org/10.1016/j.polymer.2018.09.023
Received 25 May 2018; Received in revised form 6 September 2018; Accepted 9 September 2018



Scheme 1. Copolymerization of achiral **1** with chiral **2** by an achiral initiator system (A), and chirality teletransmission along the *cis-cisoidal* sequence of achiral **1** from chiral units **2** in copoly(**1**/**2**) by multiple stage gradual solvent exchange through a membrane (B).

dynamic helical polymers as the pioneering studies reported by Yashima [12,16]; 2) the asymmetric-induced polymerization (**AIP**) of chiral acetylenes [23–26], and 3) the helix-sense-selective polymerization (**HSSP**) of achiral acetylenes using a chiral initiator system reported by Aoki [27–31]. Most poly(substituted acetylene)s are helical *cis-transoidal* polymers, only a few of them take a *cis-cisoidal* helix [8,13,16,19–22]. Chiral induction and amplification in the *cis-transoidal* polyacetylenes has been intensively explored. In general, transmission of chiral information in a static polymer bearing high helix inversion barriers, such as polyisocyanide [32], polymethacrylates [33] and *cis-cisoidal* poly(substituted acetylene)s [23] is realized during copolymerization and requires a rather higher amount of chiral units [16]. There are no reports regarding the post-treatment triggered chirality transmission and amplification in *cis-cisoidal* main chain of a copoly (substituted acetylene). Here, we report to find new chirality teletransmission in the *cis-cisoidal* main chain triggered by the post-treatment. i.e., multiple stage solvent exchange of the copolymer solution through a membrane (Scheme 1).

2. Results and discussion

In previous study, the one-handed helical *cis-transoidal* polyphenylacetylene (poly(**2**), Scheme S1) bearing (−)-*β*-pinanyl pendent groups prepared by **AIP** [25,26] showed a strong negative and a strong positive circular dichroism (CD) signals at 370 nm and 328 nm, respectively (Fig. 1C); meanwhile, the one-handed helical *cis-cisoidal* poly (**1**) synthesized by **HSSP** of achiral **1** bearing two hydroxy groups showed a weak positive and a strong negative CD signals at 450 nm and 308 nm, respectively (Fig. 1C) [27,28]. In the UV–vis spectra, the *cis-cisoidal* poly(**1**) showed a much stronger absorption at 308 nm and a weaker absorption at 430 nm than the *cis-transoidal* poly(**2**) (Fig. 1C) [19,27,28].

Here, achiral phenylacetylene **1** bearing two hydroxy groups was copolymerized with chiral phenylacetylene **2** by using an achiral catalytic system in toluene to produce copoly(**1**/**2**)s (Scheme 1 and S1.3). It was found that the consumption of phenylacetylene **1** was faster than that of phenylacetylene **2** during the copolymerization. Then the reactivity ratios of the phenylacetylenes **1** and **2** in the copolymerization were estimated as $r_1 = 1.49$ and $r_2 = 0.50$, respectively. (see S2 in the Supporting Information) These indicate that phenylacetylene **1** having two hydroxy groups showed the higher reactivity than phenylacetylene **2** having no hydroxy group. And it tends to form long sequence of **1** units in the resulting copoly(**1**/**2**)s. Judging from their UV spectra (Fig. 1A) and reactivity ratios, it is suspected that copoly(**1**/**2**)s may tend to form block-like structures. Therefore, structure of copoly ($\mathbf{1}_{9.9}$/**2**) was analyzed based on the highly selective photocycloaromatization (**SCAT**) of the *cis-cisoidal* polyacetylene and Raman spectral analysis (see S3 in the Supporting Information). After the complete finish of the SCAT reaction of copoly($\mathbf{1}_{9.9}$/**2**), both the unreacted *cis-transoidal* residue and the formed cyclic trimer of **1** were found in the SCAT products (Fig. S2). In the Raman spectra, the *cis-transoidal* poly(**2**) (Fig. S3, b) showed the large peak of the *cis*-C=C bond at the lower wave-number than the *cis-cisoidal* poly(**1**) (Fig. S3, a), copoly($\mathbf{1}_{9.9}$/**2**) showed the wide peak of *cis*-C=C bond at both the positions of the *cis-cisoidal cis*-C=C bond and the *cis-transoidal cis*-C=C bond. The results indicate that copoly($\mathbf{1}_{9.9}$/**2**) contains both the *cis-cisoidal* sequence and the *cis-transoidal* sequence, i.e., it tends to take a *c-c/c-t* block like structure, in which the *cis-cisoidal* sequence consists of **1** units and the *cis-transoidal* sequence may consists of both **2** units and **1** units (Scheme S2 in the Supporting Information).

The appearance of typical *cis-cisoidal* pattern of CD signal at 308 nm of copoly(**1**/**2**) (Fig. 1A, d-f) indicates that the original chirality in **2** could be transmitted to the *cis-cisoidal* sequence of achiral **1**, that is, an one-handed helicity has been induced in the sequence of achiral **1** during the copolymerization by an achiral Rh catalyst system (see supporting information S1.4). However, the induced CD absorption bands of the copolymers assigned to the *cis-cisoidal* sequence were very weak indicating the efficiency of this chirality transmission from **2** units to the *cis-cisoidal* sequence **1** was very low during the copolymerization [34].

Since the hydrogen bonds between the hydroxy groups in the sequence of achiral **1** stabilize the *cis-cisoidal* conformation and make its helix inversion barrier higher [19,27], to realize efficient chirality transmission and amplification (= teletransmission) in sequence **1**, its