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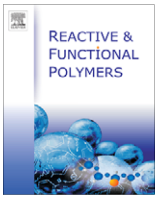

Effect of copolymer composition in poly(***N***-propargylamide) on helical structure and optical activity

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ABSTRACT

Homo- and co-polymerizations of a chiral ***N***-propargylamide (M**1** containing 2,2-dimethyl-5-oxo-1,3-dioxolane group) and an achiral ***N***-propargylamide (M**2** containing adamantane group) were carried out in the presence of (nbd)$Rh^+B^-(C_6H_5)_4$. All the (co)polymers synthesized were obtained in a yield $\geqslant$80%. Poly(**1**) assumed helices of a predominant handedness and exhibited an optical activity, while poly(**2**) formed helices of an equal amount of right- and left-handed screws and showed no optical activity. The maximum wavelength and CD signal intensity of the copolymers with varied M**1**/M**2** ratios demonstrated considerable composition dependence. This observation was explained by the synergic effects between the pendent groups during the formation of helical structures.

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1. Introduction

Chiral macromolecules occur extensively in nature and play big roles in organisms in the maintenance of their normal bioactivities. Some of these natural macromolecules are known to form stable helical structures. Stimulated by the elegant and beautiful helical structures in such biomacromolecules, and in particular their significant uses, chemists have made large efforts towards the design and synthesis of polymers able to form ordered helical structures [1–7]. These artificial helical polymers are well exemplified by polymers derived from methacrylates/acrylamides [8–12], silicones [6], isocyanides [7,13], substituted acetylenes [4,5,14,15], and isocyanates [16], among others. It is widely regarded that for the polymers to adopt helical conformations, non-covalent chemical bonds (e.g., hydrogen bonding and hydrophobic effects) and steric hindrance are the two underlying driving forces. The advances in organic chemistry and polymer chemistry afforded a great number of new helical polymers [17–20]. The Percec group [7] prepared helical polymers bearing fan-structured pendent groups. The crowded bulky side chains in these polymers forced the polymer backbones into adopting helical conformations. Yashima et al. [13] obtained helical polymers from substituted acetylenes with branched structures. The same group created the elegant double-helix polymers consisting of two complementary homopolymers of chiral amidines and achiral carboxylic acids with ***m***-terphenyl-based backbones [21]. Furthermore, interesting helical polymers were also reported by Novak and coworkers [22]. Helical polymers possess some potential applications in, for example, chiral catalysis, chiral recognition/resolution, and optical/electrical materials [23–26].

In our earlier studies, series of substituted polyacetylenes were synthesized [27–32], some of which could adopt helical structures [27–30], even at relatively high temperatures [33], demonstrating the high stability of the helical structures against heat. Besides the helical polymers of interest, polymeric emulsions consisting of helical polymers [34,35] and vinyl polymer hollow particles grafted with helical polymer chains [36] were also prepared. In addition, our investigations, together with the investigations of other groups, especially the Yashima [2,3], Masuda [4], and Tang [5] groups, have made large contributions to the progress of artificial helical polymers. Additionally, together we demonstrated that CD and UV–Vis spectroscopy are highly effective and simple for elucidating the helical structures formed in polymers.

Although helical structures could be formed in these polymers, the most intense CD signals and UV–Vis absorptions appeared at varied wavelength for different polymers; in most cases, λ_{max} = 350–410 nm. The different maximum wavelengths reflect the variation in helical pitches [30]. Nevertheless, a systematic

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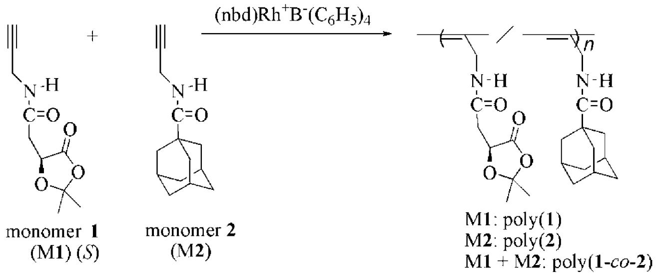

Fig. 1. Structures of monomers (M**1**, chiral; M**2**, achiral) and (co)polymers.

investigation into the occurrence of varied maximum wavelength in different helical polymers is still needed. This will be highly useful for the further design and synthesis of novel helical polymers.

To obtain more insights into the helical structures formed in substituted polyacetylenes, particularly the effects of substituent on the helical structures and optical activities, we conducted the present study. Herein, we designed and synthesized two substituted acetylene monomers, monomer **1** (M**1**) containing a chiral group and monomer **2** (M**2**) without a chiral group (Fig. 1). Both of the homopolymers were found to adopt helical conformations, but the maximum wavelengths were quite different. Poly(**1**) was found to take helices at a very low wavelength, namely 320 nm. Poly(**2**) showed a maximum wavelength at 410 nm and contains a pretty bulky substituent, and thus can provide the expected effects on the backbones of the copolymers derived from M**1** and M**2**. Therefore, M**1**/M**2** copolymers are ideal model polymers for the present research theme. Accordingly, we further carried out co-polymerizations of M**1** and M**2**, and the dependence of helical structures on the compositions was further investigated. The obtained results were of importance for further optimizing the structure of the helical polymers to have more desirable properties.

2. Experiments

2.1. Measurements

Melting point (mp) was measured by an X-4 micro-melting point apparatus. ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker AV600 spectrometer with $CDCl_3$ as solvent. FT-IR (Fourier Transform Infrared) spectra were recorded with a NICOLET NEXUS 670 infrared spectrometer (KBr tablet). Elemental analysis was carried out at The Beijing University of Chemical Technology Elemental Analysis Center. UV–Vis absorption and CD (circular dichroism) spectra were recorded in chloroform (c = 0.1 mM) on a Jasco 810 spectropolarimeter. Specific rotations were measured on a JASCO P-1020 digital polarimeter with a sodium lamp as the light source at room temperature. Molecular weights and molecular weight distributions of the polymers were determined by Gel Permeation Chromatography (GPC, Shodex KF-850 column) calibrated for polystyrenes with THF (tetrahydrofuran) as the eluent.

2.2. Materials

The solvents were purified by distilling under reduced pressure prior to use. The Rh-based catalyst, $(nbd)Rh^+B^-(C_6H_5)_4$, was prepared as reported [37]. Propargylamine (Aldrich), (*S*)-(+)-2,2-dimethyl-5-oxo-1,3-dioxolane-4-acetic acid (Aldrich), 1-adamantane carbonyl chloride (Aldrich), isobutyl chloroformate (Alfa Aesar), 4-methylmorpholine (Alfa Aesar), and pyridine (Aldrich) were used as received without further purification.

2.3. Synthesis of monomers

Monomer **1** (M**1**, as shown in Fig. 1) was synthesized according to the method introduced earlier [32,33]. The major synthetic procedure is described below. (*S*)-(+)-2,2-Dimethyl-5-oxo-1,3-dioxolane-4-acetic acid (5.0 g, 28.7 mmol), isobutyl chloroformate (3.7 ml, 28.7 mmol), and 4-methylmorpholine (3.6 ml, 28.7 mmol) were sequentially added to THF (200 ml). The solution was stirred at ambient temperature for about 10 min, and then propargylamine (2.0 ml, 28.7 mmol) was added to the solution. The solution was stirred for another 1 h, and then the white precipitate that formed in the course of the reaction was filtered off. The filtrate was washed with 2 M HCl aqueous solution three times and then with saturated $NaHCO_3$ aqueous solution for neutralization. After that, the solution was dried over anhydrous $MgSO_4$, filtered, and concentrated to give the target monomer. The crude monomer was purified by recrystallization from a THF/*n*-hexane solvent mixture. The analytical and spectroscopic data of M**1** were as follows:

M**1**: yield 55%, white solid, mp 88–92 °C.
M**1** IR (KBr, cm^{-1}): 3289 (H–N), 2347 (H–C≡), 1783 (C=O, ester), 1660 cm^{-1} (C=O, amide).
M**1** ^{1}H NMR ($CDCl_3$, 400 MHz, 20 °C, δ ppm): δ 1.55 ($O–C(CH_3)_2–O$, 6H), 2.23 (CH≡C, 1H), 2.50–2.80 ($C(=O)CH_2–$, 2H), 3.90–4.03 ($CH≡CCH_2$, C(=O)–CH–O), (3H), 5.98 ppm (NH, 1H).
M**1** ^{13}C NMR ($CDCl_3$, 400 MHz, 20 °C, δ ppm): δ 25.5, 30.5, 33.5, 71.0, 78.5, 81.1, 171.8, 173.4 ppm. Anal. Calcd. for $C_{10}H_{13}NO$: C, 56.86; H, 6.20; N, 6.63. Found: C, 56.90; H, 6.16; N, 6.64.

M**2** was prepared according to a reported synthetic route [33,38]. Pyridine (4.0 ml, 50.0 mmol), propargylamine (3.4 ml, 50.0 mmol), and 1-adamantanecarboxylic acid chloride (5.0 g ml, 25.0 mmol) were added to diethyl ether (150 ml) sequentially. The solution was stirred overnight at 0 °C. Then, the white precipitate that formed during the reaction was filtered off. The filtrate was collected and washed with 2 N hydrochloric acid three times and then with saturated aqueous $NaHCO_3$ solution to neutralize the solution. Then, the solution was dried over anhydrous $MgSO_4$, filtered, and concentrated to give the target monomer. The crude monomer was further purified by recrystallization from a THF/*n*-hexane solvent mixture. The analytical and spectroscopic data of M**2** are as follows: yield 41%, white crystal, mp 108–110 °C.

M**2** IR (KBr, cm^{-1}): 3309 (H–N), 2907 (C–H), 2373 (H–C≡), 1653 cm^{-1} (C=O)

M**2** ^{1}H NMR ($CDCl_3$, 400 MHz, 20 °C, δ ppm): δ 1.05–1.86 (m, 15H), 2.26 (CH≡C, 1H), 3.95 ($CH≡CCH_2$, 2H), 5.73 ppm (NH, 1H).
M**2** ^{13}C NMR ($CDCl_3$, 400 MHz, 20 °C, δ ppm): δ 20.9, 23.5, 30.2, 30.5, 30.7, 32.5, 24.7, 35.5, 3.6.4, 37.8, 71.1, 78.5, 175.5 ppm. Anal. Calcd. for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.10; H, 9.03; N, 6.42.

2.4. Polymerizations and co-polymerizations

As reported in an earlier report [39], polymerizations were carried out with $(nbd)Rh^+B^-(C_6H_5)_4$ as a catalyst in dry THF under nitrogen at 30 °C for 1 h with a monomer concentration of 0.5 M and a catalyst concentration of 5 mM. After polymerization, the solution containing the resulting polymer was poured into a large amount of hexane to precipitate the formed polymer. The precipitate was filtered, washed with acetone to exclude the residual monomer and catalyst, and then dried under reduced pressure. For the co-polymerizations, the total monomer concentration

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