



Synthesis of novel helical poly(*N*-propargylamides) containing azobenzene pendant groups and effects of substitution groups on azobenzene on the stability of helix

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ABSTRACT

A series of novel *N*-propargylamides bearing substituted azobenzene pendant groups ($R-C_6H_4-N=N-C_6H_4-CONHCH(CH_3)CONHCH_2C\equiv CH$, $R = CH_3CH_2N(CH_2)_2OOC(CH_2)_3CH_3$ (**V₁**), $R = CH_3CH_2N(CH_2)_2OOCCH_2NHCOCH_3$ (**V₂**), $R = H$ (**V₃**)) were synthesized and polymerized with $[Rh(nbd)Cl]_2$ as a catalyst to obtain the corresponding polymers (**Poly(V₁₋₃)**). The azobenzene chromophores in the side chains of **Poly(V_{1,2})** contained bulky electron-donating substituents, while the azobenzene in **Poly(V₃)** did not bear this kind of substituent. The introduction of substituted azobenzene chromophores into the side chains of poly(*N*-propargylamides) was found to increase the hydrogen bond strength, steric repulsion and electrostatic interactions between the neighboring side chains. These factors worked together to improve the helical stability of poly(*N*-propargylamides). The solubility of these poly(*N*-propargylamides) was increased by introducing substituents into the azobenzene chromophores. CD and UV-vis spectra showed that all the poly(*N*-propargylamides) took the helical structures with predominantly one-handed screw sense, which were tight helices. Furthermore, the unsubstituted azobenzene groups in the side chains of **Poly(V₃)** also arranged to form the helical conformation. The helical structures of **Poly(V₁₋₃)** remained stable at various temperatures (5–60 °C). **Poly(V_{1,2})** exhibited good helicity in polar solvent, which indicated that the bulky substituents, electrostatic and steric repulsion between the adjacent side chains lessened the effect of polar solvent on the hydrogen bonding. The main chains of **Poly(V_{1,3})** still kept helical sense after the isomerization of *trans*-azobenzene to the *cis* form upon UV irradiation. The helical array of azobenzene side chains in **Poly(V₃)** experienced reversible arrangement–disarrangement upon photoirradiation.

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1. Introduction

Synthesis and precise control of optically active helical polymers have received considerable attention in the past decades due to their unique structures, chiroptical properties and many important applications in chiral discrimina-

tion, chiral separation, enantioselective catalysis, chemical sensor, and optical liquid crystalline materials [1–8]. In nature, the helical conformation of biomacromolecules plays very critical role in organism (e.g., DNA or protein). Recently much effort has been devoted to the design and synthesis of helical polymers. Significant progress has been achieved in this field. Several types of helical polymers, such as polyisocyanides [9,10], poly(tritylmethacrylates) [11], polypeptides [12,13], and polyacetylenes [14,15], have been prepared. Masuda and coworkers reported that

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the helical poly(*N*-propargylamides) could be polymerized by some monosubstituted *N*-propargylamides with Rh catalysts [16,17]. The appropriate pendant groups in their side chains can induce the main chains to twist to form the helical structures. This type of helical poly(*N*-propargylamides) can be classified as dynamic helical polymers.

Previous studies revealed that the helical structures of polyacetylenes could be stabilized by the intramolecular hydrogen bonding or steric repulsion between the side chains [18,19]. However, most polyacetylenes only maintained the stable helical structures in nonpolar solvents at room temperature. The helical conformation would be destroyed and transformed into random coil structure under certain conditions, specifically at high temperature, in polar solvents or upon UV light irradiation [20–24].

Azobenzene moieties are one kind of typical photosensitive chromophores. Their *cis* and *trans* forms can be reversibly isomerized upon photoirradiation. Many polymers bearing azobenzene chromophores have been explored extensively because of the unique optical properties [25–29]. Recently, some helical poly(*N*-propargylamides) containing azobenzene moieties have been synthesized, and the reversible transformation of higher order structures triggered by azobenzene isomerization were studied [6,30–32]. Sanda and coworkers synthesized the helical poly(*N*-propargylamides) bearing designed azobenzene moieties. The reversible transformation of helical side chains upon photoirradiation was observed, while their main chains still kept the helical structures upon the UV irradiation [30]. Zhou and coworkers investigated the effect of the photoisomerization of azobenzene groups on the chiroptical properties of polymers [32]. However, the helical conformations of most poly(*N*-propargylamides) containing azobenzene moieties were still affected by the external stimulus, such as polar solvents and temperature. The unstable helical structure of poly(*N*-propargylamide) limited its application in many fields, especially as chiral separation materials. Therefore, design and synthesis of stable helical poly(*N*-propargylamides) would be highly desirable.

In this paper, we report our recent efforts in the synthesis of novel stable helical poly(*N*-propargylamides), in which *L*-alanine and bulky substituted azobenzene groups were introduced into the side chains. The intramolecular hydrogen bond strength of these polymers was enhanced by increasing the number of amide groups in the side chains. The bulky substituents were introduced into azobenzene moieties to increase the steric repulsion between the neighboring azobenzene chromophores. In addition, these new designed azobenzene moieties contained electron-withdrawing and electron-donating substituents at both ends, which could be considered as dipolar electro-optic chromophores [33,34]. It was reported that there was electrostatic interaction between adjacent dipoles [35,36]. As a result, this interaction between the azobenzene dipoles in the side chains of poly(*N*-propargylamides) would increase the twist degree of the main chain to maintain the helical structure. Although many poly(*N*-propargylamides) were synthesized and studied, the stable helical poly(*N*-propargylamides), especially stable under external stimulus, was hardly reported.

Our study aimed at a combination of all these factors mentioned above to increase the helical stability of poly(*N*-propargylamides). In addition, we also studied the effects of different substitution groups on azobenzene on the stability of helix under different conditions, such as heat, solvent and photoirradiation.

2. Experiment

2.1. Material

N-Ethyl-*N*-hydroxyethylaniline (from Wujiang Sanyou Dye Company), dicyclohexylcarbodiimide (DCC), *N*-hydroxysuccinimide (NHS), dimethylaminopyridine (DMAP), *N,N*-dimethyl-formamide (DMF), 4-aminobenzoic acid, *N*-acetylglycine, valeric acid and *L*-alanine (from Medicine Group of China), propargylamide (from Shanghai Darui Fine Chemical Company), nitrosobenzene (From TCI), [Rh(nbd)Cl]₂ (from Alfa Aesar) and other chemicals are of analytical grade except as noted.

2.2. Measurements

FT-IR spectra were recorded on a NEXUS 670 FTIR spectrometer. The samples were prepared as KBr pellets. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker DRX 400 MHz spectrometer using perdeuterodimethyl sulfoxide (DMSO-*d*₆) or perdeuteriochloroform (CDCl₃) as solvent. UV-vis absorption spectra were measured on a UV-1900 PC spectrometer. Ionization impact mass spectra (MS) were obtained with an Agilent 5793N instrument at 70 eV. Elemental analysis was conducted on a Carlo Erba 1106 apparatus. Molecular weights were determined by gel permeation chromatography (GPC) on a PerkinElmer Series 200 apparatus and a refractive index detector. The elution phase was DMF (0.01 mol/L LiBr) at a flow rate of 1.0 mL/min at 40 °C through a Waters Styragel column. Linear Polystyrene was used as the calibration standard. Polymer solutions were filtered through a Whatman 0.45-μm polytetrafluoroethylene (PTFE) filter before being injected into the systems. Circular dichroism (CD) spectra were recorded in a quartz cell (thickness: 1 cm) at room temperature using a Jasco J810 spectropolarimeter. Specific rotations ([α]_D) were measured on a Perkin-Elmer 343 polarimeter with a sodium lamp as a light source at 20 °C.

2.3. Monomer synthesis

2.3.1. Synthesis of *N*-ethyl-*N*-(2-valeryloxyethyl)aniline (**II**₁)

A three-necked flask was charged with a mixture of *N*-ethyl-*N*-hydroxyethylaniline 3.300 g (20 mmol), valeric acid 2.75 mL (25 mmol) and 30 mL DMF. The mixture was stirred and cooled in an ice bath under nitrogen. Then, DCC 6.190 g (30 mmol) and DMAP 0.368 g (3 mmol) were added. The mixture was stirred overnight and then the solvent was removed under reduced pressure. The residue was washed with water for several times. The crude product was dissolved in methylene chloride and filtered to remove the insoluble solid. The solvent was removed under reduced pressure. The crude product was purified by silica gel chromatography with methanol and

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