Reactive and Functional Polymers 109 (2016) 131–136

Contents lists available at ScienceDirect

Reactive and Functional Polymers

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

Synthesis and chiroptical properties of novel helical polyacetylenes containing fluorene pendant groups in the side chains

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ARTICLE INFO

Article history:
Received 11 May 2016
Received in revised form 20 October 2016
Accepted 31 October 2016
Available online 2 November 2016

Keywords:
Polyacetylene
Helical structure
Fluorene
Stability
Photoluminescence

ABSTRACT

A series of novel substituted acetylene monomers bearing fluorene pendant groups ($C_{13}H_9COCH_2CH_2CO$-R-$CH_2C{\equiv}CH$, R = NH (**IV$_1$**), R = O (**IV$_2$**), R = NHCH(CH_3)CONH (**IV$_3$**), R = NHCH(CH_3)COO (**IV$_4$**)) have been synthesized and subsequently polymerized with $[Rh(nbd)Cl]_2$ as a catalyst to obtain the corresponding polyacetylenes (**Poly**(**IV$_{1-4}$**)). The ^{1}H NMR spectra demonstrated that all the obtained polyacetylenes had high *cis*-stereoregular structures. The results of CD (circular dichroism) and UV–vis spectra showed that **Poly**(**IV$_{3,4}$**) took a tight helical structure, while **Poly**(**IV$_{1,2}$**) did not. The chiral amino acid units in the side chains of **Poly**(**IV$_{3,4}$**) induced the main chain to form the helical conformation. In addition, owing to the large steric repulsion and π-π interaction between the bulky fluorene groups, **Poly**(**IV$_{3,4}$**) showed good helical stability at various temperatures (−10–60 °C) and in strong polar solvents. Especially, the CD intensity of **Poly**(**IV$_3$**) was enhanced with increasing the solvent polarity. Moreover, **Poly**(**IV$_{1-4}$**) also showed good photoluminescent (PL) properties. The nonconjugated aliphatic spacer and the twisting of the polymer main chain were favorable to improve the PL efficiency.

1. Introduction

Optically active helical polymers have attracted much interest in recent years due to the unique structure, chiroptical property and many important applications in chiral separation, enantioselective catalysis, chiral discrimination, chemical sensor, molecular wires and optical liquid crystalline materials [1–9]. In the past decades, many types of helical polymers such as polyisocyanides [10,11], poly(tritylmethacrylates) [12], polypeptides [13,14], and polyacetylenes [15,16] have been successfully synthesized.

Substituted polyacetylenes were widely studied in recent years [15–19]. Some substituted acetylenes monomers bearing appropriate pendant groups could be polymerized with certain catalysts to obtain helical polymers. For example, several polyacetylenes carrying chiral amino acid units in their pendant groups, such as poly(*N*-propargylamides), exhibited well defined helical structures [20]. Their helical conformation could be stabilized by the intramolecular hydrogen bonding interactions. However, many polyacetylenes only maintained the stable helical structure in nonpolar or low-polar solvents at room temperature. Their helical conformation would be transformed into random coil structure when the hydrogen bonding was destroyed, especially at high temperature or in strong polar solvents [21,22]. Steric repulsion between the side chains was considered as another important driving force for polyacetylenes to stabilize the helical conformation [23]. However, too bulky pendant groups in the side chains were unfavorable to the helical stability. [24]. Recently, we have reported the synthesis of several poly(*N*-propargylamides) carrying bulky azobenzene pendant groups [25], which took a stable helical structure at high temperature and in polar solvents due to the electrostatic and steric repulsion between the adjacent side chains.

The unstable helical structure of polyacetylenes upon external stimuli limited their applications in many fields such as chiral separation, enantioselective catalysis and chemical sensor, and so on. In order to tackle these challenges, in this paper, a series of novel polyacetylenes containing bulky fluorene pendant groups were successfully synthesized. The effect of this kind of bulky fluorene groups on the stability of helical structure at various temperatures and in polar solvents was investigated. Different from many other bulky aliphatic pendant groups [22,23], the aromatic fluorene pendant groups had a large rigid planar structure. The bulky 2-substituted fluorene pendant group could increase the steric repulsion which was favorable for polymers to stabilize the helical structure under certain conditions. In addition, the parallel-displaced π-π stacking interactions are well-known to stabilize the double helical structures of DNA [26]. Therefore, the π-π interaction between the rigid fluorene units might be another driving force to stabilize the helical structure of polyacetylenes.

The fluorene based small molecules, oligomers, and polymers have received considerable attention in the past decades due to their high photoluminescence efficiency [27]. The polymers carrying fluorene moieties as pendant groups are potentially good candidates for the applications in chemistry and biology [28]. Recently, it was reported that

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http://dx.doi.org/10.1016/j.reactfunctpolym.2016.10.015
1381-5148/

the fluorescence properties of the pyrene-carrying copolymers greatly depended on their secondary structure [29]. Therefore, the photoluminescent properties of the as-synthesized fluorene based polyacetylenes were also studied.

2. Experiment

2.1. Material

Fluorene (from Shanghai Haiqu Chemical Industry Co., Ltd), *N,N′*-dicyclohexylcarbodiimide (DCC), *N*-hydroxysuccinimide (NHS), 4-dimethylaminopyridine (DMAP), *N,N*-dimethylformamide (DMF), succinic anhydride, L-alanine and propargyl alcohol (from Medicine Group of China), propargyl amide (from Shanghai Darui Fine Chemical Company), $[Rh(nbd)Cl]_2$ (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. ^{1}H NMR spectra were recorded on a Bruker DRX 500 MHz spectrometer using perdeuterodimethyl sulfoxide (DMSO-d_6) or perdeuterochloroform ($CDCl_3$) as solvent. UV–vis absorption spectra were measured on a UV-1900 PC spectrometer. High-resolution mass spectra (HRMS) were obtained with a Bruker microTOF-QII mass spectrometer. 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) using a Jasco J810 spectropolarimeter. Specific rotations ($[\alpha]_D$) were measured on a Perkin-Elmer 343 polarimeter with a sodium lamp as a light source at 20 °C. Fluorescence measurements were carried out at room temperature using Shimadzu RF5301 fluorescence spectrophotometer.

2.3. Monomer synthesis

2.3.1. Synthesis of 4-(9H-fluoren-2-yl)-4-oxobutanoic acid (**II**)

A three-necked flask was charged with a mixture of fluorene 9.97 g (60 mmol), succinic anhydride 6.910 g (60 mmol), dry nitrobenzene 80 mL. The mixture was stirred and cooled in ice bath under nitrogen. $AlCl_3$ 20.00 g (150 mmol) was added in portions at 0 °C. The mixture was stirred in ice bath for 72 h and then the solution was dumped into large amounts of dilute hydrochloric acid at 0 °C. The crude product was filtered and washed with water and petroleum ether to give 4-(9H-fluoren-2-yl)-4-oxobutanoic acid (**II**) 15.96 g, yield 96%. ^{1}H NMR (DMSO-d_6, 500 MHz) δ (ppm): 2.60 (2H, t, –C***H***$_2$COOH), 3.28–3.32 (2H, m, –C***H***$_2$CH$_2$COOH), 4.01 (2H, s, 9***H***-fluorene), 7.38–8.19 (7H, m, Ar-***H***), 12.13 (1H, brs, ***H***OOC–). HRMS (ESI) ($C_{17}H_{14}O_3Na^+$): calcd, 289.0841; found, 289.0825.

2.3.2. Synthesis of (S)-2-(4-(9H-fluoren-2-yl)-4-oxobutanamido)propanoic acid (**III**)

A three-necked flask was charged with a mixture of **II** 2.66 g (10 mmol), NHS 1.15 g (10 mmol), DMAP 0.18 g (1.50 mmol) and 60 mL DMF. The mixture was stirred and cooled in an ice bath under nitrogen, and then the solution of DCC 3.10 g (15 mmol) in 15 mL DMF was added at 0 °C. It was stirred at room temperature for 48 h. The solution was filtered to remove the white powder. The active ester solution was concentrated to ~20 mL under reduced pressure and then this solution was transferred to another three-necked flask, which was charged with L-alanine 0.89 g (10 mmol), 5 mL aqueous solution of sodium bicarbonate. The mixture was stirred under nitrogen at room temperature for 72 h. Then, the pH of the reaction mixture was adjusted to 3–4 by using dilute hydrochloric acid solution, and then the resulting mixture was extracted three times with ethyl acetate. The ethyl acetate extracts were combined and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. The crude product was purified by silica gel chromatography with methylene chloride as the eluent to give (*S*)-2-(4-(9H-fluoren-2-yl)-4-oxobutanamido)propanoic acid (**III**) 1.12 g, yield 30%. ^{1}H NMR (DMSO-d_6, 500 MHz) δ (ppm): 1.24–1.29 (3H, d, –CHC***H***$_3$), 2.52–2.61 (2H, t, –C***H***$_2$CONH–), 3.28–3.34 (2H, t, –C***H***$_2$CH$_2$CONH–), 4.01 (2H, s, 9***H***fluorene), 4.21–4.26 (1H, m, –NHC***H***(CH$_3$)CO–), 7.39–8.18 (7H, m, Ar-***H***), 8.10 (1H, brs, –N***H***CO–), 12.31 (1H, brs, ***H***OOC–). IR (KBr, cm^{-1}): 1540 (–CONH–), 1670 (–CONH–), 3330 (–NH–). HRMS ($C_{20}H_{19}NO_4Na^+$): calcd, 360.1212; found 360.1243.

2.3.3. Synthesis of N-ethynyl-4-(9H-fluoren-2-yl)-4-oxobutanamide (**IV$_1$**)

A three-necked flask was charged with a mixture of **II** 2.66 g (10 mmol) and 60 mL DMF. The solution was stirred and cooled in an ice bath under nitrogen for 30 mins, and then propargylamine 0.85 mL (12 mmol), DCC 3.09 g (15 mmol) and DMAP 0.18 g (1.50 mmol) was added at 0 °C. The solution was stirred at room temperature for 5 days, and then the solution was filtered to remove the undissolved solid. The filtrate was poured into 300 mL water. The precipitate was collected by filtration and washed twice with petroleum ether. The crude product was purified by silica gel chromatography with methylene dichloride as the eluent to give white solid *N*-ethynyl-4-(9H-fluoren-2-yl)-4-oxobutanamide (**IV$_1$**) 1.33 g, yield 44%. ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 2.23 (1H, t, –C≡C***H***), 2.68 (2H, t, –C***H***$_2$CONH–), 3.43 (2H, t, –C***H***$_2$CH$_2$CONH–), 3.94 (2H, s, 9***H***-fluorene), 4.06–4.08 (2H, d, –C***H***$_2$C≡CH), 6.14 (1H, brs, –N***H***CO–), 7.36–8.16 (7H, m, Ar-***H***). IR (KBr, cm^{-1}): 650 (–C≡CH–), 1540 (–CONH–), 1670 (–CONH–), 2130 (–C≡C–), 3250 (–C≡CH), 3330 (–NH–). HRMS (ESI) ($C_{20}H_{17}NO_2Na^+$): calcd, 326.1157; found 326.1138.

2.3.4. Synthesis of ethynyl 4-(9H-fluoren-2-yl)-4-oxobutanoate (**IV$_2$**)

ethynyl 4-(9H-fluoren-2-yl)-4-oxobutanoate (**IV$_2$**) was synthesized from **II** and propargylalcohol by the analogous procedure. Yield 50%. ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 2.50 (1H, t, –C≡C***H***), 2.86 (2H, t, –C***H***$_2$COO–),3.41 (2H, t, –C***H***$_2$CH$_2$COO–), 3.97 (2H, s, 9***H***-fluorene), 4.74–4.75 (2H, d, –C***H***$_2$C≡CH), 7.38–8.17 (7H, m, Ar-***H***). IR (KBr,cm^{-1}): 680 (–C≡CH), 1650–1750 (C═O), 2130 (–C≡C–), 3250 (–C≡CH). HRMS (ESI) ($C_{20}H_{16}O_3Na^+$): calcd, 327.0997; found, 327.0963.

2.3.5. Synthesis of (S)-4-(9H-fluoren-2-yl)-4-oxo-N-(1-oxo-1-(prop-2-yn-1-ylamino)propan-2-yl)butanamide (**IV$_3$**)

(*S*)-4-(9H-fluoren-2-yl)-4-oxo-*N*-(1-oxo-1-(prop-2-yn-1-ylamino)propan-2-yl)butanamide (**IV$_3$**) was synthesized from **III** and propargylamine by the analogous procedure. Yield 51%. $[\alpha]_D = -32^\circ$ (c = 0.1 g/dL, in THF). ^{1}H NMR (DMSO-d_6, 500 MHz) δ (ppm): 1.20–1.21 (3H, d, –CHC***H***$_3$), 2.55 (2H, t, –C***H***$_2$CONH–), 3.10 (1H, s, –C≡C***H***), 3.24–3.33 (2H, t, –C***H***$_2$CH$_2$CONH–), 3.85–3.87 (2H, d, –C***H***$_2$C≡CH), 4.01 (2H, s, 9***H***-fluorene), 4.24–4.27 (1H, m, –NHC***H***(CH$_3$)CO–), 7.39–8.19 (7H, m, Ar-***H***), 8.15 (1H, d, –CON***H***CH(CH$_3$)–), 8.25 (1H, t, –CON***H***CH$_2$–). IR (KBr, cm^{-1}): 650 (–C≡CH–), 1540 (–CONH–), 1670 (–CONH–), 2130 (–C≡C–), 3250 (–C≡CH), 3330 (–NH–). HRMS (ESI) ($C_{23}H_{22}N_2O_3Na^+$): calcd, 397.1528; found, 397.1503.

2.3.6. Synthesis of (S)-prop-2-yn-1-yl 2-(4-(9H-fluoren-2-yl)-4-oxobutanamido)propanoate (**IV$_4$**)

(*S*)-prop-2-yn-1-yl2-(4-(9H-fluoren-2-yl)-4-oxobutanamido)propanoate (**IV$_4$**) was synthesized from **III** and propargylalcohol by the analogous procedure. Yield 50%. $[\alpha]_D = -21^\circ$ (c = 0.1 g/dL, in THF). ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 1.43–1.45 (3H, d, –CHC***H***$_3$), 2.46 (1H, s, –C≡C***H***), 2.69 (2H, t, –C***H***$_2$CH$_2$CONH–), 3.34–3.48 (2H, m, –C***H***$_2$CH$_2$CONH–), 3.93 (2H, s, 9***H***-fluorene), 4.60–4.66 (1H,