

Synthesis, Chiroptical Properties of a Helical Polyacetylene Derivative Carrying Urea Moieties^{*}

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Abstract A novel phenylacetylene derivative containing urea groups was synthesized and polymerized with a Rh catalyst to give the corresponding polymer, poly(**1**) with moderate number-average molecular weights. The poly(**1**) was soluble in toluene, CHCl₃, CH₂Cl₂, THF, DMF, and DMSO, but insoluble in hexane, diethyl ether and MeOH. The specific rotation and circular dichroism (CD) spectroscopic studies revealed that poly(**1**) took predominantly one-handed helical structures. The presence of intramolecular hydrogen bonding was confirmed by liquid-state IR spectroscopy. The helicity of poly(**1**) could be tuned by temperature and anion. The helical conformation of the polymer was stable against Br[−] but susceptible to F[−].

Keywords: Anion; Helix; Hydrogen bonding; Polyacetylene; Urea group.

INTRODUCTION

Synthetic helical polymers have been attracted much interest. Study on nonbiological helical polymers may lead to a better understanding of mechanism for helix formation in biopolymers. On the other hand, synthetic helical polymers may find application in areas such as the development of circularly polarized photo- and electroluminescent materials and enantioselective sensors and/or catalysts. Among varieties of synthetic helical polymers, helical polyacetylenes have attracted much attention due to the ability to form regulated secondary structures and responsiveness to external stimuli^[1–5]. Yashima and coworkers have synthesized poly(phenylacetylene) derivatives containing alanine residues with long alkyl pendants and found that they showed liquid crystalline properties and formed helix^[6, 7]. Tang *et al.* have paid attention to helical poly(phenylacetylene) derivatives carrying amino acid, which exhibited self-assembling properties, formed helical conformation stabilized by hydrogen bonding^[8–12]. We have synthesized amino acid based poly(*N*-propargylamide)s^[13, 14] and poly(1-methylpropargyl esters)^[15–17] and found that they transformed the structure from a helix to a random coil or revert helical sense according to the external stimuli such as heat^[18, 19] and solvent^[20–22]. Hydrogen bonding involving N—H linkage plays an important role in stabilizing the helical conformation. For example, an glutamic acid based poly(*N*-propargylamide) takes a helical structure stabilized by hydrogen bonding at the amide-amide and carbamate-carbamate moieties^[23].

If we incorporate urea groups in the side chain of poly(phenylacetylene)s, it is expected to obtain a polymer conforming helix stabilized by hydrogen bonding and undergoing helix-coil transition caused by the addition of

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Reaction scheme showing the polymerization of monomer **1** to Poly(**1**) using Rh Cat in a solvent at 30 °C for 24 h.

Monomer **1** structure: A substituted styrene derivative with a 4-ethynylphenyl group, a methyl ester, and a 1-octylamino group.

Poly(**1**) structure: The corresponding polymer, where the monomer units are linked by the vinyl backbone, with the side chain containing the ester and octylamino groups.

EXPERIMENTAL

¹H-(400 MHz) and ¹³C-(100 MHz) NMR spectra were recorded on a Bruker Avance/DMX 400-MHz NMR spectrometer with chloroform-d as solvents and tetramethylsilane as an internal reference. IR spectra were measured using a Shimadzu FTIR-8100 spectrophotometer. Melting points (mp) were measured on a Yanaco micro-melting point apparatus. Elemental analysis was carried out on an Elementar Vario EL-III instrument. The number- and weight-average molecular weights (M_n and M_w) of polymers were determined by gel permeation chromatography (GPC) on a JASCO GULLIVER system (PU-980, CO-965, RI-930, and UV-1570) equipped with polystyrene gel columns (Shodex columns K804, K805, and J806) using tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 mL/min, calibrated by polystyrene standards at 40 °C. Specific rotations [α]_D were measured on a JASCO DIP-1000 digital polarimeter with a sodium lamp as a light source. CD and UV-Vis spectra were recorded in a quartz cell (thickness: 1 cm) at room temperature using a JASCO J-820 spectropolarimeter.

4-Indo-*L*-phenylalanine, thionyl chloride and bis(trimethylsilyl)acetylene were purchased from Aladdin. Isocyanic acid hexyl ester was purchased from TCI. Unless otherwise stated, reagents were purchased and used without purification. (s)-Methyl-2-amino-3-(4-iodophenyl)propanoate was synthesized according to the reference^[24], (nbd)Rh⁺(η^6 -C₆H₅B⁻(C₆H₅)₃), (nbd) = 2,5-norbornadiene, was prepared by the reaction of ((nbd)RhCl)₂ with NaB(C₆H₅)₄ as described in the literature^[25]. Solvents used for polymerization were purified by the standard methods. Tetra-*n*-butylammonium bromide (TBABr), and tetra-*n*-butylammonium fluoride (TBAF) were purchased from Sigma-Aldrich Chemical Co., Inc., and used as received.

(S)-Methyl 2-(3-hexylureido)-3-(4-iodophenyl)propanoate(2)

A 100 mL three-necked flask was equipped with a three-way stopcock and a magnetic stirring bar, and filled with dry nitrogen. C₆H₁₃NCO (6.22 mL, 48 mmol) was added into the solution of (*S*)-methyl 2-amino-3-(4-iodophenyl)propanoate (4.82 g, 16 mmol) in Et₃N (0.1 mL, 0.8 mmol) and CH₂Cl₂ (30 mL). The mixture was stirred at room temperature overnight. The resulting solution was concentrated with a rotary evaporator. Purification of the crude product by silica gel column chromatography eluted with hexane/ethyl acetate = 9:1 (volume ratio) provided (*S*)-methyl 2-(3-hexylureido)-3-(4-iodophenyl)propanoate as a white solid (yield 5.95 g, 86%). ¹H-NMR (300 MHz, CDCl₃, δ): 0.86–0.89 (m, 3H, CH₃), 1.27–1.48 (m, 8H, CH₂), 2.88–3.10 (m, 2H, CH₂), 3.12 (s, 2H, –NHCH₂), 3.30–3.44 (m, 2H, CH₂), 3.72 (s, 3H, –COOCH₃), 4.21 (s, 1H, NHCH), 4.35 (s, 1H, NH), 5.82 (s, 1H, NH), 7.14–7.16 (d, 2H, Ar), 7.43–7.45 (d, 2H, Ar). ¹³C-NMR (100Hz, CDCl₃, δ): 14.1, 23.1, 26.0, 27.8, 31.1, 36.7, 38.9, 41.2, 58.9, 94.3, 121.5, 129.4, 132.5, 157.1, 172.8.

(S)-Methyl 3-(4-ethynylphenyl)-2-(3-hexylureido)propanoate (1)

A 100 mL three-necked flask was equipped with a three-way stopcock and a magnetic stirring bar, and filled with dry nitrogen. (S)-Methyl 2-(3-hexylureido)-3-(4-iodophenyl)propanoate (5.19 g, 12 mmol), (trimethylsilyl)acetylene (2.1 mL, 14 mmol), bis(triphenylphosphine) palladium dichloride (82 mg, 0.2 mmol), triphenylphosphine (92 mg, 0.58 mmol), cuprous iodide (89 mg, 0.78 mmol), triethylamine (100 mL), and THF (20 mL) were fed into the flask. The mixture was stirred at room temperature overnight. The resulting solution was filtered, and the filtrate was concentrated with a rotary evaporator. Purification of the crude product by silica gel column chromatography eluted with hexane/ethyl acetate = 9:1 (volume ratio) provided (S)-methyl 2-(3-hexylureido)-3-(4-(2-(trimethylsilyl)ethynyl)phenyl)propanoate as a yellow solid (yield 3.672 g, 76%).

A 100 mL three-necked flask was equipped with a three-way stopcock and a magnetic stirring bar, and charged with dry nitrogen. A solution of tetrabutylammonium fluoride (TBAF, 1 mol·L⁻¹ solution in THF) (4 mL) in THF (10 mL) was added to a solution of (S)-methyl 2-(3-hexylureido)-3-(4-(2-(trimethylsilyl) ethynyl) phenyl) propanoate (3.63 g, 9 mmol) in THF (15 mL), and the mixture was stirred overnight at room temperature, then the reaction mixture was diluted with CHCl₃ (30 mL). The solution was washed subsequently with aqueous NH₄Cl, brine, and water. The organic layer was dried over anhydrous MgSO₄ and concentrated to afford a pale yellow solid. It was purified by silica gel column chromatography eluted with hexane/ethyl acetate 9:1 (volume ratio) to afford **1** as a white solid. Yield: 2.528 g (85%); mp = 95.8–98.9 °C. [α]_D = -14.1° (*c* = 0.1 g·dL⁻¹ in CHCl₃). ¹H-NMR (300 MHz, CDCl₃, δ): 0.86–0.89 (m, 3H, CH₃), 1.26–1.49 (m, 8H, CH₂), 2.89–3.08 (m, 2H, CH₂), 3.08 (s, 2H, NHCH₂), 3.12 (s, 1H, $\equiv$ CH), 3.32–3.47 (m, 2H, CH₂), 3.77 (s, 3H, CH₃), 4.23 (s, 1H, CH), 4.37 (s, 1H, NH), 5.79 (s, 1H, NH), 7.15–7.17 (d, 2H, Ar), 7.42–7.44 (d, 2H, Ar). ¹³C-NMR (100 Hz, CDCl₃, δ): 14.0, 22.6, 26.3, 27.9, 31.5, 37.7, 38.7, 40.8, 57.9, 77.7, 83.1, 121.4, 129.5, 132.5, 135.9, 157.2, 172.9. IR (KBr, cm⁻¹): 3331, 3274, 2927, 2856, 2363, 2108, 1922, 1753, 1704, 1615, 1578, 1504, 1458, 1425, 1362, 1303, 1251, 1218, 1181, 1115, 1082, 1033, 991, 941, 885, 848, 824, 763, 729, 696, 667, 604, 567, 514. Anal.Calcd for C₁₉H₂₆N₂O₃: C 69.59, H 7.96, N 8.46, O 14.52 Found: C 69.06, H 7.93, N 8.48, O 14.53.

Polymerization

All the polymerizations were carried out in a Schlenk tube equipped with a three-way stopcock under dry nitrogen. A typical experimental procedure for the polymerization of **1** by (Rh(nbd)Cl)₂ is given below.

Into a baked 20 mL Schlenk tube with a stopcock in the sidearm was added 66 mg (0.2 mmol) of **1**. The tube was evacuated under vacuum and then flushed with dry nitrogen three times through the sidearm. Freshly distilled THF (1 mL) was injected into the tube to dissolve the monomer. The catalyst solution was prepared in another tube by dissolving (Rh(nbd)Cl)₂ (0.004 mmol) in 1 mL of THF with 1 drop of TEA, which was transferred to the monomer solution using a hypodermic syringe. The solution was kept at 30 °C for 24 h. The polymerization mixture was then diluted with 2 mL of THF and poured into a large amount of MeOH to precipitate a polymer. The precipitate was collected by filtration and dried under vacuum at room temperature to a constant weight. The polymeric product was isolated as yellowish fibrous solid in a high yield (87%).

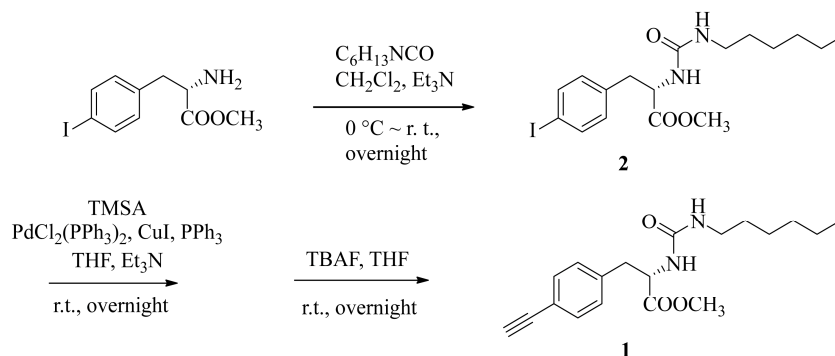
Spectroscopic Data of the Polymers

Poly(**1**): ¹H-NMR (CDCl₃, δ): 0.82–1.37 (br, 11H, CH₂CH₂CH₂CH₂CH₃), 2.97 (br, 2H, NHCH₂), 1.75 (br, 3H, NHCHCH₃), 3.42 (br, 5H, ArCH₂, COOCH₃), 4.37 (br, 1H, NHCH), 5.61 (br, 1H, C=CH), 6.74–7.21 (br, 4H, Ar). IR (KBr, cm⁻¹): 3374, 2981, 2935, 1716, 1511, 1454, 1369, 1253, 1169, 1061, 856, 783.

RESULTS AND DISCUSSION**Monomer Synthesis**

We designed molecular structure of phenylacetylene derivatives containing urea groups and elaborated reaction routes for their synthesis (Scheme 2). At first, the compound of (S)-methyl 2-(3-hexylureido)-3-(4-iodophenyl)propanoate was prepared by the reaction of (S)-methyl 2-amino-3-(4-iodophenyl)propanoate with isocyanatohexane in the present of the Et₃N and the CH₂Cl₂, and white solid was obtained in 86% yield. Monomer **1** was synthesized by the reaction of (S)-methyl 2-amino-3-(4-iodophenyl)propanoate with

(trimethylsilyl)acetylene, followed by desilylation using TBAF in 85% yield. The monomer was characterized by spectroscopic methods and satisfactory analysis data corresponding to the molecular structure were obtained.



Scheme 2 Synthesis of **1**

Polymerization

To polymerize the monomer, we tried different catalysts. We first attempted to polymerize **1** using $\text{Rh}^+(\text{nb})\text{d}(\eta^6\text{-C}_6\text{H}_5\text{B}^-(\text{C}_6\text{H}_5)_3)$, a good catalyst for polymerization of *N*-propargylamides. As can be seen from Table 1, the polymerizations of **1** catalyzed by $\text{Rh}^+(\text{nb})\text{d}(\eta^6\text{-C}_6\text{H}_5\text{B}^-(\text{C}_6\text{H}_5)_3)$ in THF, chloroform and toluene afford polymers with moderate molecular weights (5600–6100). Then, we check the polymerization of $(\text{Rh}(\text{nb})\text{d})\text{Cl}_2$. $(\text{Rh}(\text{nb})\text{d})\text{Cl}_2$ works well for the acetylene polymerization in THF/ Et_3N , chloroform/ Et_3N and toluene/ Et_3N , furnishing polymers with M_w up to 10200 in over 83% yields. Poly(**1**) was completely soluble in CH_2Cl_2 , CHCl_3 , THF, dioxane, toluene and DMF, and insoluble in MeOH, diethyl ether and *n*-hexane.

Table 1. Polymerization of **1**^a

Run	Catalyst	Solvents	Yield ^b (%)	M_n ^c	M_w/M_n ^c
1	$\text{Rh}^+(\text{nb})\text{d}(\eta^6\text{-C}_6\text{H}_5\text{B}^-(\text{C}_6\text{H}_5)_3)$	THF	79	6100	1.48
2	$\text{Rh}^+(\text{nb})\text{d}(\eta^6\text{-C}_6\text{H}_5\text{B}^-(\text{C}_6\text{H}_5)_3)$	CHCl_3	76	5900	1.50
3	$\text{Rh}^+(\text{nb})\text{d}(\eta^6\text{-C}_6\text{H}_5\text{B}^-(\text{C}_6\text{H}_5)_3)$	Toluene	78	4300	1.70
4	$(\text{Rh}(\text{nb})\text{d})\text{Cl}_2$	THF	87	12400	1.51
5	$(\text{Rh}(\text{nb})\text{d})\text{Cl}_2$	CHCl_3	83	10200	1.63
6	$(\text{Rh}(\text{nb})\text{d})\text{Cl}_2$	Toluene	86	11700	1.55

^a Conditions: $[\mathbf{1}]_0 = 0.1 \text{ mol/L}$, $[\mathbf{1}]/[\text{Rh}] = 50$, at 30 °C for 24 h;

^b MeOH-insoluble part;

^c Determined by GPC eluted with THF calibrated by polystyrene standards

Polymer Structure

The polymeric product was characterized by spectroscopic methods, and poly(**1**) gave satisfactory analysis data corresponding to its expected molecular structure. The IR spectrum of poly(**1**) is shown in Fig. 1, the spectrum of corresponding monomer is also given in the same figure for comparison. The monomer shows absorption bands at 3274 cm^{-1} and 2108 cm^{-1} associated with the $\equiv\text{C}-\text{H}$ and $-\text{C}\equiv\text{C}-$ stretching vibrations, respectively, while the polymers did not exhibit these peaks. It means that the acetylene triple bond of **1** has been consumed by the polymerization reaction.

Figure 2 shows the $^1\text{H-NMR}$ spectra of poly(**1**) and its monomer. The protons of the phenyl ring linked to the acetylene triple bond of **1** resonate at 3.12, which disappear in the spectrum of poly(**1**). The results clearly indicate that the acetylene polymerization took place to form polymers containing alternating single and double bonds along the main chain. Commonly, the Rh zwitterion complex efficiently catalyzes the polymerization of monosubstituted acetylenes by the insertion mechanism to give *cis*-stereoregular polyacetylenes^[26]. In the present study, the steric structure of the polymers is also the case; the *cis* contents ranged around 89%.

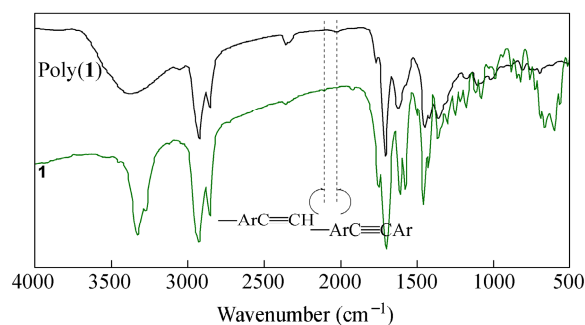


Fig. 1 IR spectra of **1** and poly(**1**)

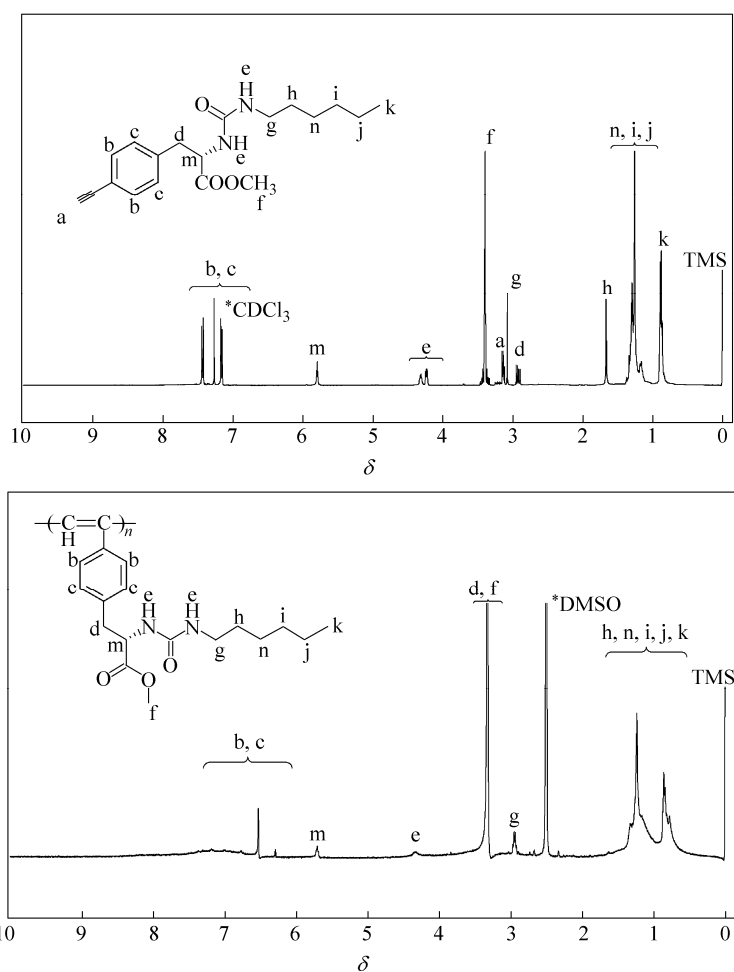


Fig. 2 The ^1H -NMR spectra of **1** and poly(**1**)

Secondary Structure of the Polymer

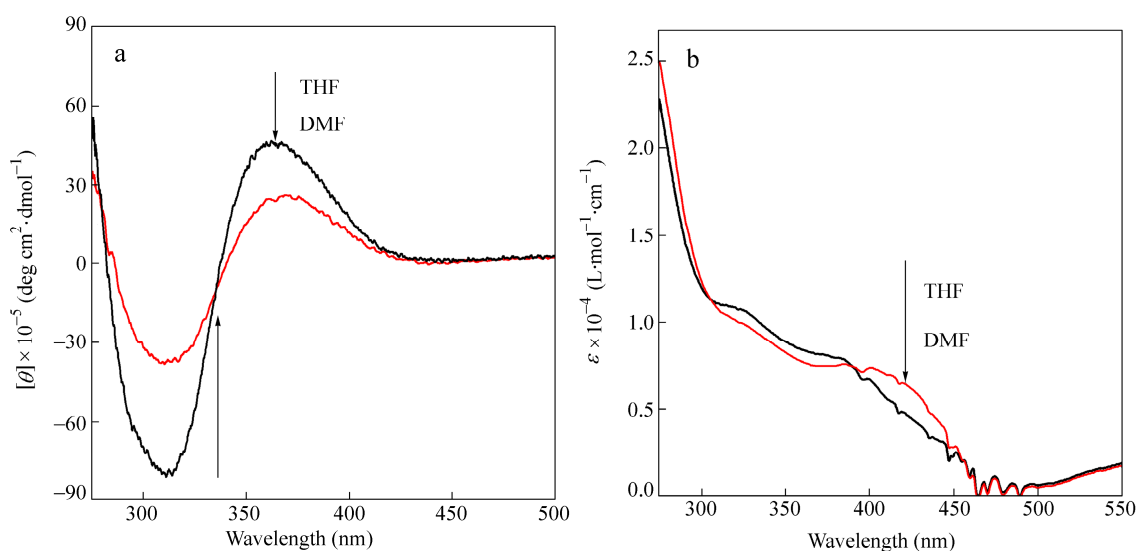
The secondary structure of poly(**1**) was examined by polarimetric, CD and UV-Vis spectroscopic methods. Table 2 summarizes the specific rotations ($[\alpha]_D$) of poly(**1**) along with the data of **1** measured in CHCl_3 , THF, CH_2Cl_2 , DMF, dioxane and toluene at room temperature. The $[\alpha]_D$ values of the polymer were much larger than those of **1** in all the solvents. This suggests that poly(**1**) takes a regulated higher order structure such as helix with an excess of preferred handedness.

Table 2. Specific rotations of **1** and poly(**1**)^a

Compounds	$[\alpha]_D^{25}$ (°)					
	CHCl ₃	THF	CH ₂ Cl ₂	DMF	Dioxane	Toluene
1	14.1	−9.2	−14.0	−13.5	−13.5	−13.7
poly(1)	+120	+134	+117	+41	+156	+108

^a Measured at room temperature ($c = 0.1 \text{ g} \cdot \text{dL}^{-1}$)

Figure 3 depicts the solvent dependence of CD and UV-Vis spectra of poly(**1**) measured in DMF and THF. Poly(**1**) exhibited plus CD signals around 368 nm and 363 nm in DMF and THF, based on the absorption of the conjugated polyacetylene backbone. It was confirmed that poly(**1**) took a helical conformation with an excess of one handedness in these solvents. Poly(**1**) also exhibited a bisignated CD signal at 310 nm, presumably due to exciton coupling of benzene moieties. The order of CD intensities of poly(**1**) was THF > DMF, which agreed with the order of specific rotations in these solvents as summarized in Table 2. The spectral pattern of poly(**1**) remains the same when its solvent is changed from THF to DMF, indicating that the same screw sense dominates in DMF and THF.

**Fig. 3** CD (a) and UV-Vis (b) spectra of poly(**1**) measured in DMF and THF at room temperature ($c = 1.34 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$)

The helical conformation of poly(*N*-propargylamide)s^[27–29] and poly(phenylacetylene)s carrying amide moiety^[30] was stabilized by intramolecular hydrogen bonding between the amide groups at the side chains and/or steric repulsion. The present polymer is also possibly form hydrogen bonding between urea group. Liquid-state IR spectroscopic study was carried out to obtain information on hydrogen bonding. Figure 4 depicts the partial IR spectra of **1** and poly(**1**) measured in solid state and in THF. As shown in Fig. 4, there was little difference between the urea $\nu_{\text{C=O}}$ peaks of **1** and poly(**1**) in solid state. On the other hand, poly(**1**) showed the urea absorption peak at 1616 cm^{-1} in THF, which was 25 cm^{-1} lower than that of **1**. These results indicate that the urea groups form hydrogen bonding, and it is an intramolecular one judging from the low reagent concentration ($30 \text{ mmol} \cdot \text{L}^{-1}$).

Temperature-induced Conformation Change of Poly(**1**)

As described above, poly(**1**) formed intramolecular hydrogen bonding, presumably contributing to the stabilization of the helical structure in a manner similar to previously reported amino acid-based poly(*N*-propargylamide)s^[31, 32]. If this assumption is operative, the helical structure should be sensitive to external stimuli such as heat. Figure 5 illustrates the temperature dependence of the CD and UV-Vis spectra of poly(**1**)

measured in THF in the range of 0–50 °C. Poly(**1**) reduced the intensity of the CD signal around 365 nm in THF as raising temperature. On the other hand, the UV-Vis spectra was almost the same irrespective of temperature. It is concluded that the decrease in the CD signal is not caused by transition from a helix to a random state but by depopulation of the helical conformation.

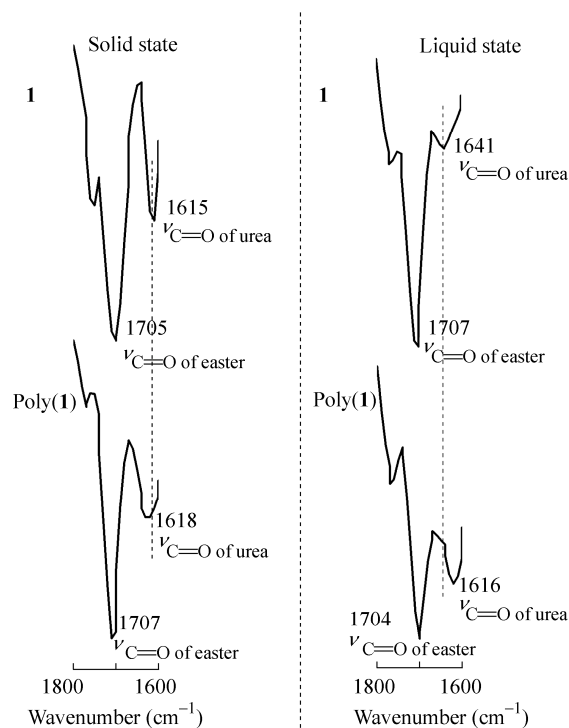


Fig. 4 IR spectra of **1** and poly(**1**) in various states (The liquid-states were measured in THF at a concentration of 30 mmol·L⁻¹.)

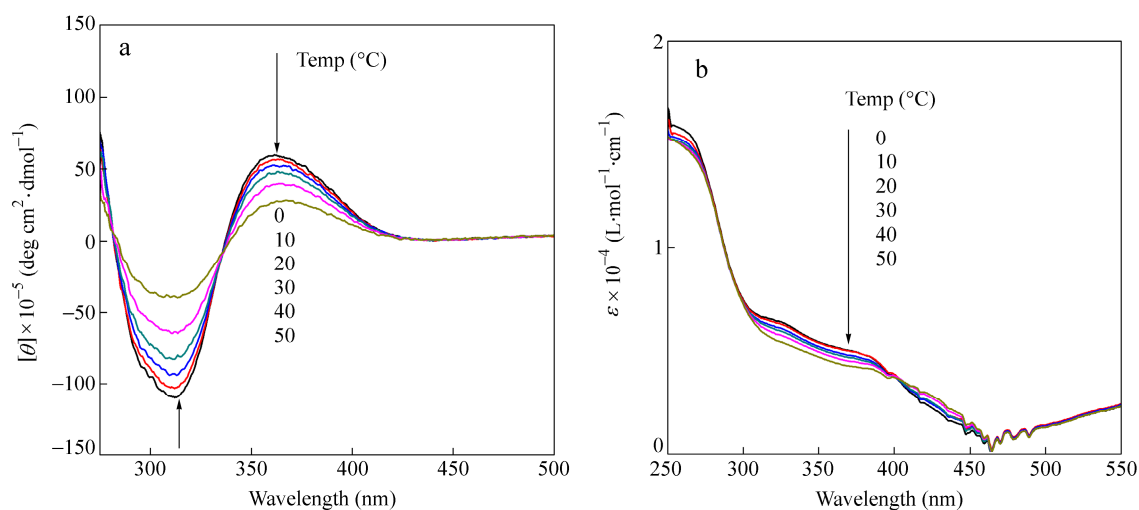


Fig. 5 Temperature-variable CD (a) and UV-Vis (b) spectra of poly(**1**) measured in THF ($c = 1.34 \times 10^{-4}$ mol·L⁻¹)

Anion-induced Conformation Change of Poly(**1**)

It is known that the urea moieties are able to bind with different anions^[33–36]. Thus, the urea moieties of poly(**1**) may be able to bind with anions, and as a result, the helical structure would be modulated. To provide a

preliminary insight into the influence of anion on the helicity of poly(**1**), F^- and Br^- were added to the solution of poly(**1**) in THF. Figure 6 depicts the CD and UV-Vis spectra upon addition 10 equiv of TBAF and TBABr to the solution of poly(**1**) in THF. As shown in Fig. 6, one equivalent of TBAF decreased the $[\theta]$ of poly(**1**) at 365 nm from +3642311 to +984253 $\text{deg cm}^2\cdot\text{dmol}^{-1}$ (−73%), while the same amount of TBABr decreased slightly. Hydrogen bonding may be one possible reason why F^- largely affected the helicity of the polymer. The urea moieties are able to bind with F^- ; thus, the intramolecular hydrogen bonding between the urea moieties would be disrupted in the presence of F^- , while keeps stable in presence of Br^- .

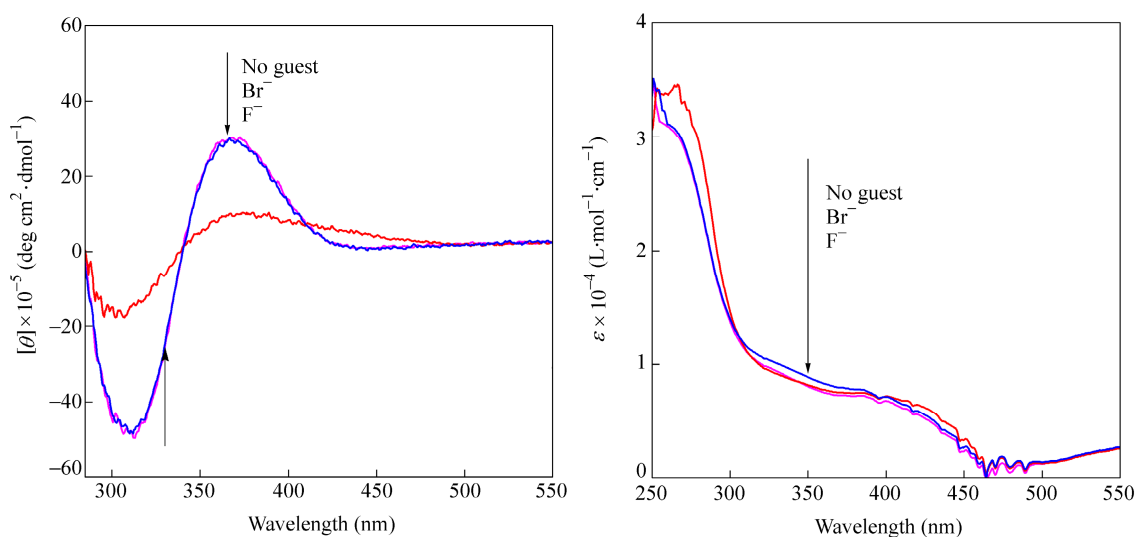


Fig. 6 CD (a) and UV-Vis (b) spectra of poly(**1**) upon addition with various anions measured in THF ($c = 1.34 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$)

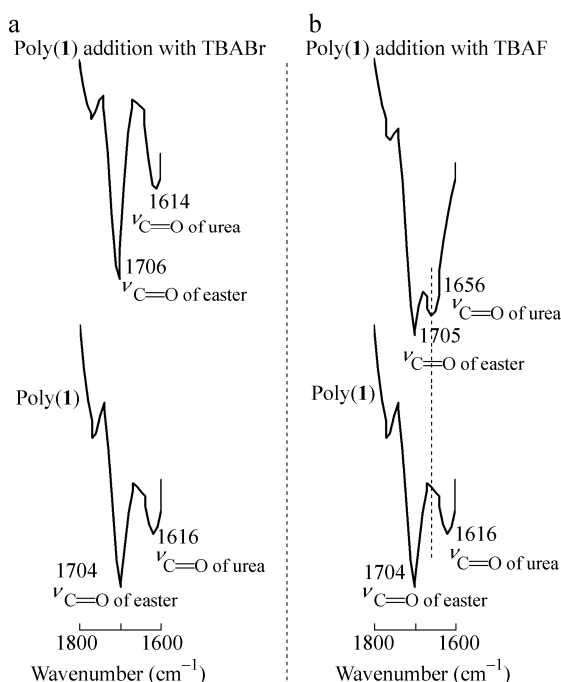


Fig. 7 IR spectra of poly(**1**) upon addition with TBABr and TBAF measured in THF at a concentration of $30 \text{ mmol} \cdot \text{L}^{-1}$

We measured the solution-state IR spectra of polymer with addition of F^- and Br^- . As shown in Fig. 7, the urea $\nu_{C=O}$ peaks of poly(**1**) shift from 1616 cm^{-1} to 1656 cm^{-1} after the addition of TBAF. On the other hand, poly(**1**) showed the urea absorption peak almost at same wavenumber upon addition of TBABr. It seems that the hydrogen bonding of poly(**1**) between urea groups was destroyed upon addition of F^- , while hydrogen bonding kept stable in presence of Br^- .

Figures 8 and 9 show the change of CD and UV-Vis spectra of poly(**1**) with addition of TBABr and TBAF in THF. As depicted in Fig. 8, poly(**1**) slightly decreased the intensity of the CD signals by the addition of TBABr. With addition of 1000 equiv of TBABr, the CD intensity kept 61% of that without addition of TBABr. As shown in Fig. 9, the CD spectroscopic pattern was very sensitive to F^- . The plus signed CD signal around 365 nm sharply decreased by raising the amount of TBAF, and disappeared by addition of 100 equiv of TBAF. It is concluded that the helical structure of poly(**1**) was more stable to Br^- than to F^- .

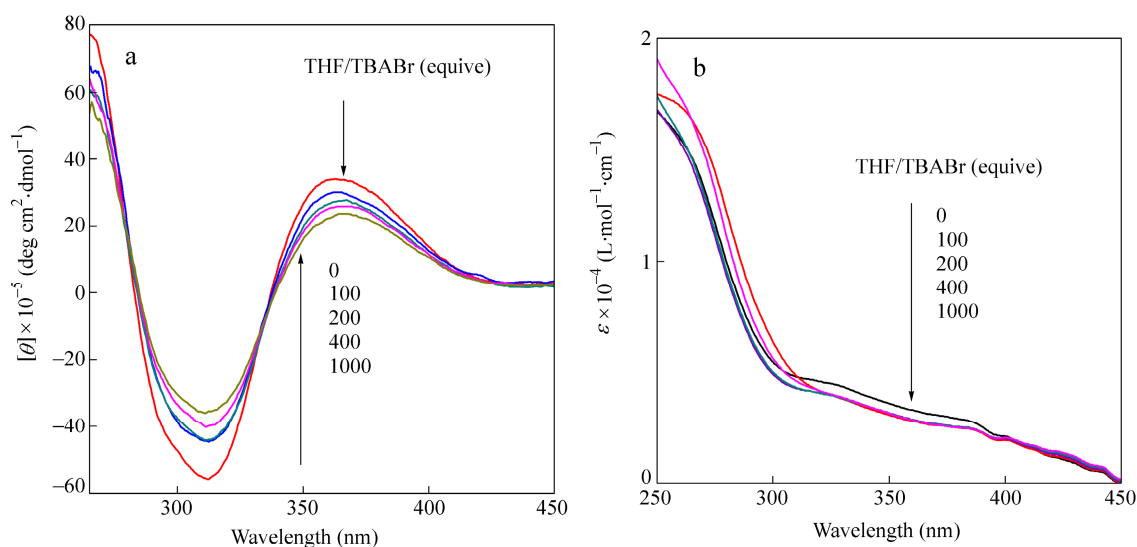


Fig. 8 CD (a) and UV-Vis (b) spectra changes of poly(**1**) upon addition of TBABr measured in THF ($c = 1.34 \times 10^{-4}\text{ mol}\cdot\text{L}^{-1}$) at room temperature

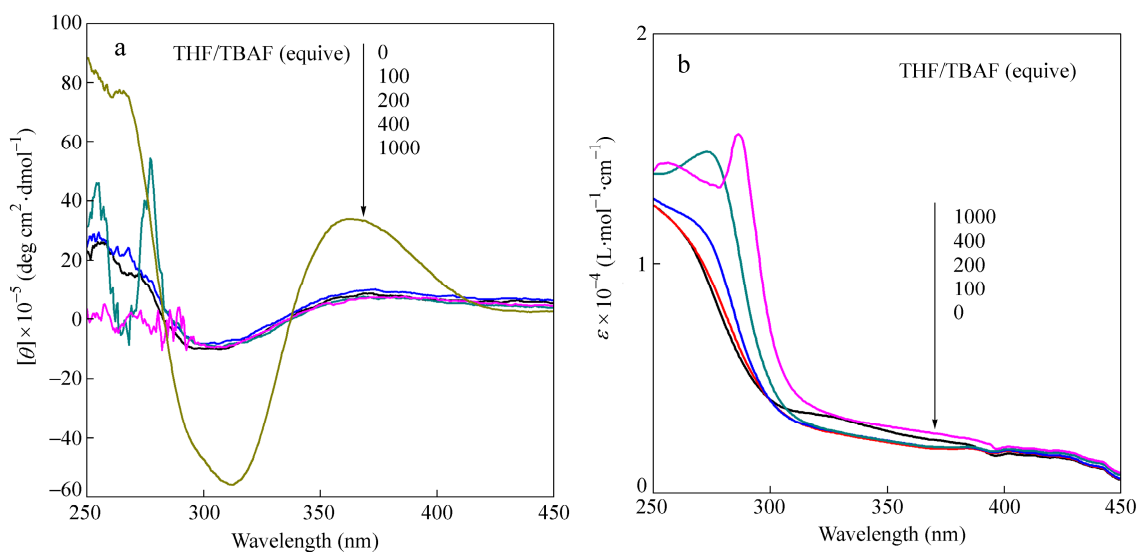


Fig. 9 CD (a) and UV-Vis (b) spectra changes of poly(**1**) upon addition of TBAF measured in THF ($c = 1.34 \times 10^{-4}\text{ mol}\cdot\text{L}^{-1}$) at room temperature

CONCLUSIONS

In this article, we have synthesized a poly(phenylacetylene) derivative bearing urea groups, and polymerized it to obtain poly(**1**) with moderate molecular weights in good yields. Large optical rotation and intense CD signals indicate the polymer took a helical conformation with predominantly one-handed screw sense. Liquid state IR spectroscopic measurements revealed that poly(**1**) took helical conformations stabilized by intramolecular hydrogen bonding at the urea-urea moieties. The helicity of poly(**1**) could be tuned by temperature and anion. The helical structure of polymer was stable against Br⁻ but susceptible to F⁻, presumably based on that the hydrogen bonding between urea groups was disrupted by F⁻.

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