Stimuli-responsive conjugated polymers. Synthesis and chiroptical properties of polyacetylene carrying L-glutamic acid and azobenzene in the side chain

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Abstract

A glutamic acid- and azobenzene-containing novel N-propargylamide, (S)-CH≡CCH$_2$NHCOCH(CH$_2$CH$_2$CO$_2$CH$_2$C$_6$H$_5$)NHCO$_2$CH$_2$CH$_2$–p–C$_6$H$_4$N=NC$_6$H$_5$ (**1**) was synthesized and polymerized with (nbd)Rh$^+$[η^6-C$_6$H$_5$B$^-$(C$_6$H$_5$)$_3$] as a catalyst to obtain the corresponding polymer [poly(**1**)] with the moderate number-average molecular weight of 12,200 in 93% yield. The chiroptical studies revealed that poly(**1**) took a helical structure in THF, CHCl$_3$, CH$_2$Cl$_2$ and toluene. Poly(**1**) underwent solvent and heat-driven helix–helix transition. The *trans*-azobenzene of the side chain isomerized into cis upon UV-irradiation, accompanying decrease in helicity. The *cis*-azobenzene moiety reisomerized into trans upon visible-light irradiation, while the polymer did not recover the original helicity.
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1. Introduction

Change and switching of chiroptical properties of polymers upon external stimuli are of great interest because of potential applications in data storage, optical devices, and liquid crystalline displays [1]. Heat, light, and change of medium conditions including polarity and pH are commonly employed as stimuli, since these stimuli are easily controllable and applicable to practical usage. The light-driven reversible isomerization between trans and cis forms of azobenzene makes azobenzene-containing polymers promising candidates for stimuli-responsive materials [2]. Several photo-responsive chiral polymers carrying azobenzene in the main chain or side chain have been studied. Ueno et al. [3a] and Ciardelli and coworkers [3b] have investigated the helix transition of azobenzene-containing polypeptides. Zentel and coworkers have investigated a series of chiral polyisocyanates, which serve as optical switches triggered by a small amount of azobenzene moieties [4]. Jaycox and coworkers have found

that azobenzene-modified polyaramides with atropisomeric 2,2′-binaphthyl linkages exhibit thermo- and photo-responsive chiroptical properties [5]. Rochon and coworkers have demonstrated the photo-induced chirality in thin films of achiral polymer liquid crystals containing azobenzene chromophores [6]. The photo-induced circular dichroism (CD) can be erased by heating the films above the clearing temperature of the polymer liquid crystals or by annealing the films. Nozaki and coworkers have synthesized optically active γ-polyketones with azobenzene side chains by the asymmetric alternating copolymerization of azobenzene-substituted α-olefins and carbon monoxide [7]. The polyketones change the conformation of the main chain upon trans–cis photoisomerization of the azobenzene moieties.

Polyacetylene derivatives exhibit unique properties such as semiconductivity, high gas permeability, nonlinear optical properties, and the ability to form a helical structure [8]. Substituted helical polyacetylenes belong to dynamic helical polymers. They undergo helix–helix or helix–coil interconversion due to the small energetic barriers to helical reversal [9].

We have reported the polymerization of a series of amino acid-derived acetylene monomers catalyzed with an Rh zwitterion complex [10]. The polymers possibly take helical structures stabilized by steric repulsion between the side chains, along with intramolecular hydrogen bonding between the side chains at the amide, hydroxy, and carbamate groups.
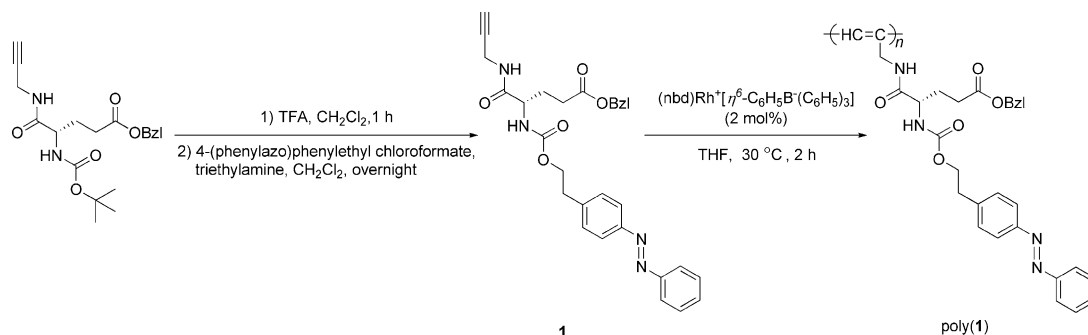
Scheme 1. Synthesis of poly (**1**)

Some of these polymers transform the helical sense and tightness by external stimuli such as heat [10d,j,k,l] solvent [10i,j,k,l] and pH [10i]. A copolymer of an L-alanine-derived *N*-propargylamide with an azobenzene-containing *N*-propargylamide forms a helical structure [10g]. The azobenzene moiety reversibly isomerizes between trans- and cis-forms upon UV and visible light irradiation. On the other hand, once the helix has transformed into random state, it does not recover the helical structure. In the course of our study concerning stimuli-responsive amino acid-based helical polyacetylenes, we have designed a novel chiral polyacetylene carrying L-glutamic acid and azobenzene in the side chain (Scheme 1). The present study deals with the transformation of its high order structure by solvent, temperature and photo irradiation.

2. Experimental section

2.1. Measurements

^{1}H and ^{13}C NMR spectra were recorded in chloroform-*d* (CDCl$_3$) on a JEOL EX-400 spectrometer. IR spectra were measured on a Shimadzu FTIR-8100 spectrophotometer. Elemental analysis was carried out at the Kyoto University Elemental Analysis Center. The number- and weight-average molecular weights (M_n and M_w) of the polymer were determined by gel permeation chromatography (GPC) using THF as an eluent calibrated by polystyrene standards at 40 °C. Melting point (mp) was measured on a Yanaco micro melting point apparatus. Specific rotations ([α]$_D$) were measured on a JASCO DIP-1000 digital polarimeter with a sodium lamp as a light source. CD and UV spectra were recorded in a quartz cell (thickness: 1 cm) using a JASCO J-820 spectropolarimeter. The photo irradiation was carried out in a quartz glass tube with a Fuji Glass HB-400 400-W high-pressure mercury lamp through Asahi Techno Glass UV-DS33S and L-42 filters to exclude the light of wavelengths other than 300 nm $< \lambda <$ 400 nm, and 420 nm $< \lambda$, respectively. A Pyrex glass filter was also used along with these filters.

2.2. Materials

THF was distilled over CaH$_2$ prior to use. (nbd)Rh$^+$[η^6-C$_6$H$_5$B$^-$(C$_6$H$_5$)$_3$] was prepared as reported [11]. 4-(Phenylazo)phenethyl alcohol was synthesized according to the

document [12]. 4-[4,6-Dimethoxy-1,3,5-triazine-2-yl]-4-methylmorpholinium chloride (TRIAZIMOCH) was supplied by Tokuyama Co. All other reagents were used as received without purification.

2.3. Synthesis of (S)-CH≡CCH$_2$NHCOCH(CH$_2$CH$_2$CO$_2$CH$_2$C$_6$H$_5$)NHCO$_2$C(CH$_3$)$_3$

N-(α-*tert*-Butoxycarbonyl)-L-glutamic acid γ-benzyl ester (10.0 g, 30 mmol) and propargylamine (1.7 g, 40 mmol) were dissolved in AcOEt (100 mL), and the resulting solution was stirred at room temperature for 10 min. TRIAZIMOCH (7.5 g, 40 mmol) was added to the solution, and the mixture was stirred at room temperature for 3 h. The mixture was subsequently washed with 1 N HCl aq, saturated NaHCO$_3$ aq and saturated NaCl aq, then dried over anhydrous MgSO$_4$, and concentrated by rotary evaporation. The crude product was purified by column chromatography eluted with *n*-hexane/AcOEt = 3/1. Yield 81%. Mp: 97.5–98.5 °C. [α]$_D$ $-5.8°$ (*c* = 0.1 g/dL in THF at RT). ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.43 [s, 9H, (CH$_3$)$_3$], 2.05 (m, 2H, CH$_2$CCH$_2$COO), 2.21 (s, 1H, C≡CH), 2.45 (m, 2H, CH$_2$COO), 3.93 (m, 2H, CH$_2$NH), 4.02 (s, 1H, CHNH), 5.12 (s, 2H, CH$_2$CH$_2$COOCH$_2$), 5.81 (s, 1H, NHCOO), 6.71 (s, 1 H, NHCO), 7.35 (s, 5H, C$_6$H$_5$). ^{13}C NMR (100 MHz, CDCl$_3$): δ 27.54 (CH$_2$CH$_2$COO), 27.97 (CH$_2$CH$_2$COO), 28.06 [(CH$_3$)$_3$], 30.17 (CH$_2$NH), 53.14 [CHNH], 66.38 (HC≡), 71.31 [C(CH$_3$)$_3$], 71.44 (CH$_2$CH$_2$COOCH$_2$), 80.00 (HC≡C), 127.91, 128.26, 135.30 (C$_6$H$_5$), 156.12 (NHCOO), 170.93 (CONH), 172.74 (COO). IR (cm^{-1}, KBr): 3389, 3241, 3061, 2983, 2125, 1730, 1687, 1651, 1520, 1368, 1232, 1174, 1068, 965, 694.

2.4. Synthesis of **1**

Triphosgene (1.0 g, 3.3 mmol) was added to a solution of 4-(phenylazo)phenethyl alcohol (2.3 g, 10 mmol) in THF (100 mL) at 0 °C. Then, triethylamine (1.51 g, 15 mmol) was added to the mixture slowly, and the resulting solution was stirred at room temperature for 3 h. It was filtered to remove triethylamine hydrochloride, and the organic layer was concentrated by rotary evaporation to give 4-(phenylazo)phenethyl chloroformate, which was used in the next step without further purification. Trifluoroacetic acid (10 mL, 30 mmol) was added to a solution of (*S*)-CH≡CCH$_2$NHCOCH

(CH$_2$CH$_2$CO$_2$CH$_2$C$_6$H$_5$)NHCO$_2$C(CH$_3$)$_3$ (3.6 g, 10 mmol) in CH$_2$Cl$_2$ (100 mL) at 0 °C, and then the resulting mixture was stirred at room temperature for 1 h. The reaction mixture was concentrated by rotary evaporation and dried in vacuo. The residual compound was dissolved in CH$_2$Cl$_2$ (100 mL), then the above obtained 4-(phenylazo)phenethyl chloroformate and triethylamine (2.0 g, 20 mmol) were added to the solution. After the mixture was stirred at room temperature overnight, it was subsequently washed with 1 M HCl (50 mL), saturated aqueous solution of NaHCO$_3$ (50 mL), and saturated aqueous solution of NaCl (50 mL). The organic layer was dried over anhydrous MgSO$_4$, filtered, and concentrated by rotary evaporation. The residue was purified by recrystallization from ethyl acetate to obtain the product in 42% yield. Mp: 152.5–154.0 °C. [α]$_D$+21° (c=0.1 g/dL in THF at RT). ^{1}H NMR (400 MHz, in CDCl$_3$): δ 1.71 (s, 2H, CH_2CH$_2$COOCH$_2$), 2.20 (s, 1H, HC≡), 2.44 (m, 2H, CH$_2$CH_2COOCH$_2$), 2.99 (m, 2H, CH_2CH$_2$COONH), 3.92 (s, 2H, CH_2NH), 4.01 (s, 2H, CH$_2$CH_2COONH), 4.30 (s, 1H, CHNH), 5.11 (s, 2H, CH_2COOCH$_2$CH$_2$CH), 5.57 (d, J=8.2 Hz, 1H NHCOO), 6.56 (s, 1H, NHCO), 7.33, 7.48, 7.90 (m, 14H, aromatic rings). ^{13}C NMR (100 MHz, CDCl$_3$): δ 28.18 (CH$_2$CH_2COOCH$_2$), 29.48 (CH_2CH$_2$COOCH$_2$), 30.62 (CH$_2$NH), 36.12 (CH_2CH$_2$ COONH), 54.5 (CHNH), 66.93 (CH_2COONH), 72.26 (HC≡), 78.10 (HC≡C), 122.98, 128.57, 129.26, 135.76, 141.26 (aromatic carbons), 171.01 (COOCH$_2$), 173.36 (NHCO). IR (cm^{-1}, KBr): 3294, 3041, 2940, 2130, 1733, 1658, 1474, 1418, 1283, 1176, 964, 768, 684, 524. Anal. Calcd for C$_{30}$H$_{30}$N$_4$O$_5$: C, 68.43; H, 5.74; N, 10.64. Found: C, 67.99; H, 5.79; N, 10.60.

2.5. Polymerization

Polymerization was carried out in a glass tube equipped with a three-way stopcock under nitrogen. (nbd)Rh$^+$[η^6-C$_6$H$_5$B$^-$(C$_6$H$_5$)$_3$] was added to a THF solution of **1** under dry nitrogen, and the resulting solution ([M]$_{total}$=1.0 M, [M]$_{total}$/[M]$_{cat}$=50) was kept at 30 °C for 2 h. The mixture was poured into a large amount of n-hexane to precipitate a powdery polymer. It was collected by filtration and dried in vacuo. Yield 93%.

2.6. Spectroscopic data of the polymer

IR (cm^{-1}, KBr): 3281, 3061, 2946, 2130, 1725, 1648, 1520, 1232, 1174, 1072, 969, 686. ^{1}H NMR (400 MHz, in CDCl$_3$): δ 1.7 (s, 2H, CH_2CH$_2$COOCH$_2$), 2.4 (broad, 2H, CH$_2$CH_2 COOCH$_2$), 2.8 (broad, 2H, CH_2CH$_2$COONH), 4.2 (broad, 5H, CH_2NH, CH$_2$CH_2COONH, CHNH), 4.9 (broad, 3H, CH_2 COOCH$_2$CH$_2$CH, NHCOO), 6.6 (broad, 2H, NHCO, –CH=C), 7.2, 7.4, 7.9 (m, 14H, aromatic rings).

3. Results and discussion

3.1. Synthesis and polymerization of **1**

Monomer **1** was synthesized by the reaction of 4-(phenylazo)phenethyl chloroformate with L-glutamic acid-derived

N-propargylamide in CH$_2$Cl$_2$ in presence of triethylamine as shown in Scheme 1. The structure of **1** was identified by ^{1}H, ^{13}C NMR, and IR spectroscopies besides elemental analysis. The polymerization of **1** was conducted in THF at 30 °C for 2 h catalyzed with (nbd)Rh$^+$[η^6-C$_6$H$_5$B$^-$(C$_6$H$_5$)$_3$] to obtain poly(**1**) with a moderate molecular weight (M_n 12,200; M_w/M_n=3.1). Poly(**1**) was soluble in THF, CHCl$_3$, CH$_2$Cl$_2$, toluene, acetone, DMF, and DMSO. The structure of poly(**1**) was examined by ^{1}H NMR and IR spectroscopies. It exhibited no proton signal and IR absorption based on ethynyl group, and exhibited reasonable spectroscopic patterns assignable to a polyacetylene structure in Scheme 1.

3.2. Conformation of poly(**1**) in solution

The conformation of poly(**1**) was examined by polarimetric, CD, and UV–vis spectroscopic methods. In contrast to **1** ([α]$_D$=+21°, c=0.1 g/dL, RT), poly(**1**) displayed large plus optical rotations in THF ([α]$_D$=+453°, c=0.1 g/dL, RT), CHCl$_3$ ([α]$_D$=+355°, c=0.1 g/dL, RT), large minus ones in CH$_2$Cl$_2$ ([α]$_D$=−240°, c=0.1 g/dL, RT) and toluene, ([α]$_D$=−195°, c=0.1 g/dL, RT). These data suggest that poly(**1**) takes a helical structure with predominantly one-handed screw sense in these solvents, and the sense depends on the solvent. Fig. 1 depicts the CD and UV–vis spectra of poly(**1**) measured in the given solvents at room temperature.
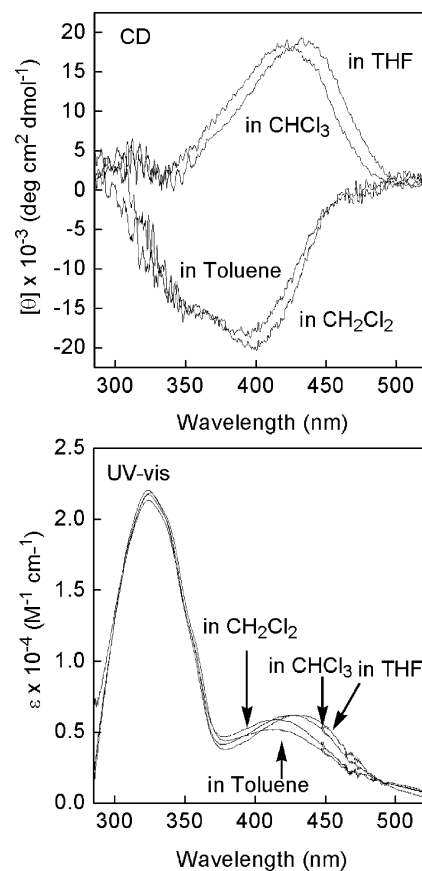

Fig. 1. CD and UV–vis spectra of poly(**1**) measured in various solvents at RT, c=1.0×10^{-4} M.
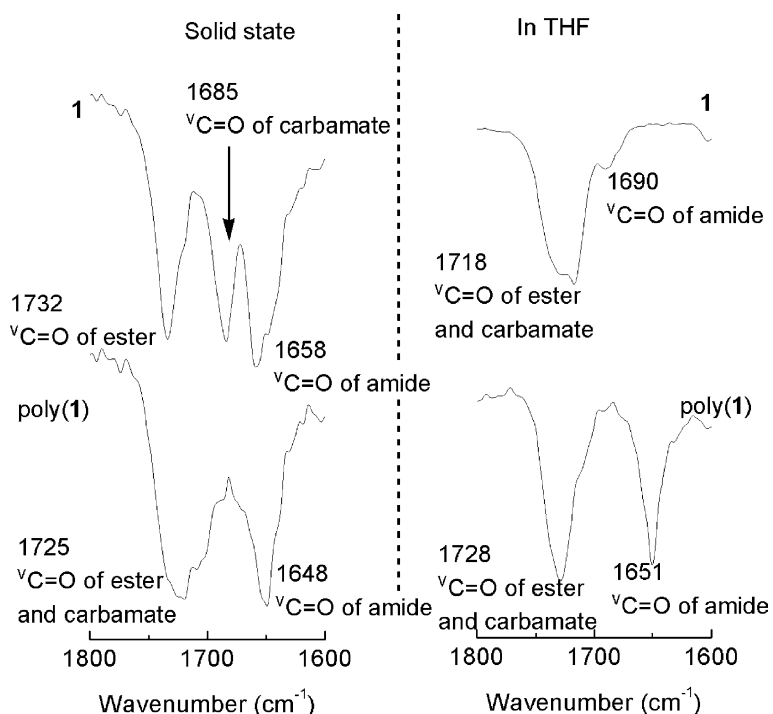
Fig. 2. IR spectra of **1** and poly(**1**) measured in solid state and in THF solution ($c = 20$ mM).

Poly(**1**) exhibited a large plus molar ellipticity [θ] in THF and CHCl$_3$ at 425 nm, while a large minus one at 400 nm in CH$_2$Cl$_2$ and toluene, respectively. In every case, a UV–vis absorption peak based on the polyacetylene main chain was observed at the same wavelength. At the same time, poly(**1**) displayed a strong UV–vis absorption band attributable to the π–π^* transition of the *trans*-azobenzene moiety at 325 nm similarly to **1**, but no CD signal at this wavelength. These results lead to a conclusion that the polyacetylene backbone of poly(**1**) takes a predominantly one-handed helical conformation, while the pendant azobenzenes form no regular strand. We have recently reported that the porphyrin side chains of helical poly(*N*-propargylamides) form externally ordered helical strands to show intense CD signals based on the porphyrin arrays [13]. Certain bulkiness seems to be necessary for the side chain chromophors to form regular external helical strands. Poly(**1**) showed opposite CD signs and optical rotations in THF and CHCl$_3$, compared to the cases in CH$_2$Cl$_2$ and toluene. This indicates that it forms helices with the opposite screw senses in the former two and the latter two solvents, respectively, because the CD signals do not come from the orientation of the side chains, but do from the conjugated polyacetylene main chain.

3.3. Solvent- and temperature-induced conformation change

Helical poly(*N*-propargylamides) stabilize the conformation by intramolecular hydrogen bonding between the amide groups in the side chains as well as steric repulsion. They deform the helical structure upon external stimuli such as heat and polar solvents. The solid- and solution-state IR spectra of **1** and poly(**1**) were measured to confirm the formation of hydrogen

bonding in poly(**1**) (Fig. 2). In the solid state, **1** and poly(**1**) exhibited the amide $\nu_{C=O}$ at 1658 and 1648 cm^{-1}, respectively, which indicates that the amide groups of both **1** and poly(**1**) intramolecularly and intermolecularly form hydrogen bonding since the monomer and polymer molecules are stacked in solid state. In THF, **1** and poly(**1**) exhibited the amide $\nu_{C=O}$ at 1690 and 1651 cm^{-1}, respectively. These results indicate that the amide groups of poly(**1**) form intramolecular hydrogen bonding in THF, which should promote the main chain to take a helical conformation.

Poly(**1**) forms a reverse-sensed helix in CH$_2$Cl$_2$ and toluene, compared to the cases in CHCl$_3$ and THF, judging from the optical rotations and CD signs in the solvents. We, therefore, attempted the helix inversion of poly(**1**) using the solvent pairs of CH$_2$Cl$_2$/CHCl$_3$ and toluene/CHCl$_3$ with various compositions. In CH$_2$Cl$_2$/CHCl$_3$, the minus CD signal decreased with the increase in the CHCl$_3$ composition (Fig. 3). The CD signal turned into a plus one when the CHCl$_3$ composition was raised to 40%, and it became larger by raising the CHCl$_3$ content further. When the CD spectra were measured in toluene/CHCl$_3$, the minus CD sign in toluene turned into plus only by adding 10% CHCl$_3$, and the intensity of CD sign increased by raising the CHCl$_3$ content. This large CD spectroscopic changes in CH$_2$Cl$_2$/CHCl$_3$ and toluene/CHCl$_3$ indicate that poly(**1**) transformed the conformation depending on the solvent composition. It is noteworthy that the helical sense is sensitive to the difference between CH$_2$Cl$_2$ and CHCl$_3$ as well as toluene and CHCl$_3$.

Fig. 4 depicts the temperature dependence of the CD spectra of poly(**1**) measured in THF, toluene and CHCl$_3$. In THF, the CD intensity decreased by raising the temperature from 0 °C, and became 75% of the original at 50 °C. Surprisingly, the CD
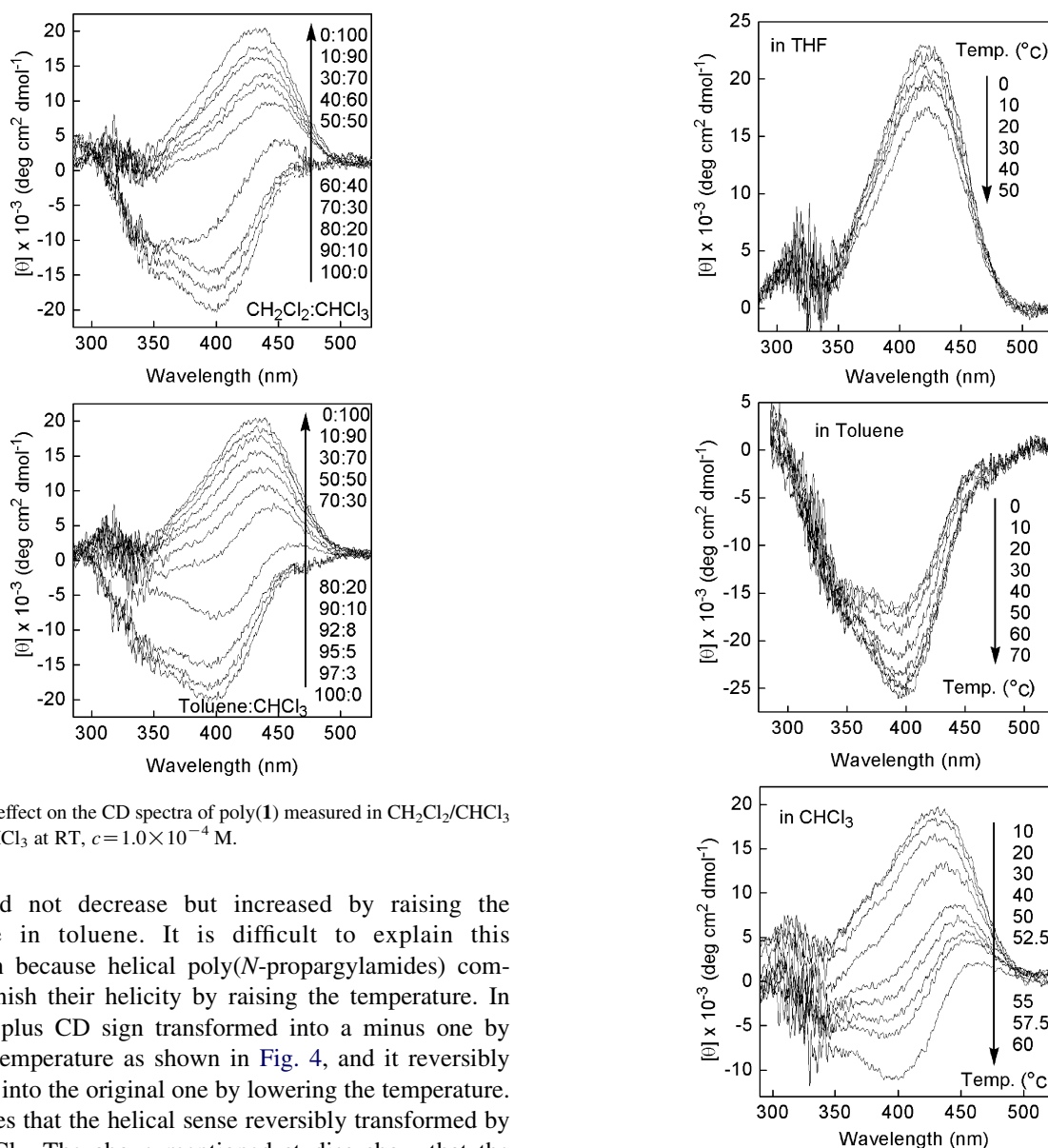
Fig. 3. Solvent effect on the CD spectra of poly(**1**) measured in CH$_2$Cl$_2$/CHCl$_3$ and toluene/CHCl$_3$ at RT, $c = 1.0 \times 10^{-4}$ M.

intensity did not decrease but increased by raising the temperature in toluene. It is difficult to explain this phenomenon because helical poly(*N*-propargylamides) commonly diminish their helicity by raising the temperature. In CHCl$_3$, the plus CD sign transformed into a minus one by raising the temperature as shown in Fig. 4, and it reversibly transformed into the original one by lowering the temperature. This indicates that the helical sense reversibly transformed by heat in CHCl$_3$. The above mentioned studies show that the chiroptical property of poly(**1**) is tunable by varying solvent compositions and temperature, and these helix–helix transitions are reversible.

3.4. Photophysical behavior in solution

Poly(**1**) displayed a strong absorption band attributable to the π–π* transition of the *trans*-azobenzene at 325 nm in THF as shown in Fig. 5. When a solution of poly(**1**) in THF was irradiated with a 400-W high pressure mercury lamp through glass filters to exclude the light of the wavelengths below 300 nm and above 400 nm, the absorption at 325 nm decreased with the irradiation time. The reduction of the absorption leveled off after 20 min. This data indicates that the *trans*-azobenzene moiety isomerized into the cis form upon irradiation of UV light with the wavelength of 300–400 nm. No apparent increase in the absorption attributable to the n–π* transition of *cis*-azobenzene could be observed

Fig. 4. Temperature dependence of the CD spectra of poly(**1**) measured in THF, toluene, and CHCl$_3$, $c = 1.0 \times 10^{-4}$ M.

around 470 nm during UV irradiation, probably because of its small ε value and overlap with the absorption of the polymer main chain. The CD signal at 425 nm based on the helical polyacetylene backbone decreased upon UV irradiation, and maintained 69% intensity after 20 min irradiation.

We next examined visible-light irradiation (420 nm < λ) to achieve isomerization of azobenzene from cis form to trans one (Fig. 6). As a result, the absorption at $\lambda_{max} = 325$ nm recovered 78% of the original value upon photoirradiation for 20 min [14]. On the contrary, the CD signal of the copolymer did not change clearly upon visible-light irradiation, which means that the polymer did not recover its original helicity. We continued visible-light irradiation for 1 h to find no clear change of the CD spectrum after 20 min.
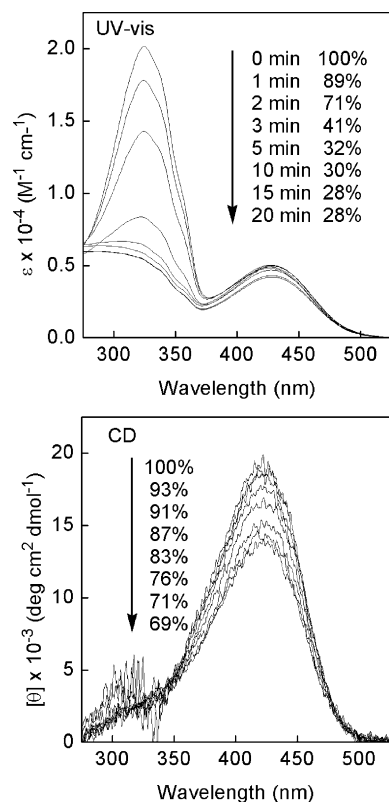
Fig. 5. Variation of the CD and UV–vis spectra of poly(**1**) with irradiation at $300 \, nm < \lambda < 400 \, nm$ in THF at RT, $c = 1.0 \times 10^{-4}$ M.
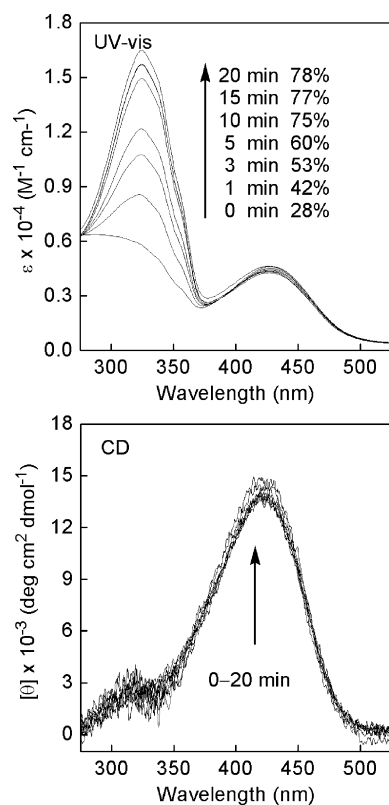

Fig. 6. Variation of the CD and UV–vis spectra of poly(**1**) with irradiation at $420 \, nm < \lambda$ in THF after irradiation for 20 min at $300 \, nm < \lambda < 400 \, nm$, $c = 1.0 \times 10^{-4}$ M.

4. Conclusions

In this article, we have demonstrated the synthesis of glutamic acid and azobenzene-containing novel polyacetylene [poly(**1**)], and examined the conformation changes in solution by changing solvent composition, heat, and phtoirradiation. CD spectroscopic and polarimetric analyses revealed that poly(**1**) took a helical structure in THF, CHCl$_3$, CH$_2$Cl$_2$ and toluene. The helical sense in THF and CHCl$_3$ was opposite to that in CH$_2$Cl$_2$ and toluene. Poly(**1**) underwent helix–helix transition induced by solvent compositions in CH$_2$Cl$_2$/CHCl$_3$ and toluene/CHCl$_3$. Poly(**1**) also underwent helix–helix transition in CHCl$_3$ by heat. The *trans*-azobenzene of the poly(**1**) side chain isomerized into cis upon UV irradiation, which was accompanied by decrease in helicity. The *cis*-azobenzene moiety reisomerized into trans upon visible-light irradiation, but the polymer did not recover the original helicity. It seems that the driving force of helix deformation is the increase in steric repulsion between the side chains resulting from the isomerization of the azobenzene moiety.

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