Research Article

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Synthesis and characterization of a polyisocyanide with thioether pendant caused an oxidation-triggered helix-to-helix transition

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Abstract: Stimuli responsive helical polymers have attracted wide attention and many polymers responsive to the external stimuli have been synthesized. But, only a few examples have been reported regarding the redox-induced helicity inversion helical polymers. The polyisocyanide including thioether pendant (poly-MBTIP) was synthesized by polymerization of methyl (R)-3-(benzylthio)-2-isocyanopropanoate (MBTIP) monomer using $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ as catalytic agent in dry DCM. The chiroptical and oxidation properties of the poly-MBTIP are investigated. The poly-MBTIPs exhibit intense specific optical rotations and Cotton effects compared to the monomer, strongly suggesting a helical conformation of the polymer backbone. Additionally, the thioether pendant of poly-MBTIP backbone was oxidized to sulfoxide group by H_2O_2 . Interestingly, the specific optical rotations and Cotton effects of poly-MBTIP oxidized are reversed, probably suggesting a helical conformation inversion.

Keywords: helical polymer; helix-to-helix; oxidation-triggered; polyisocyanide; thioether

1 Introduction

The helix is the fundamental structural motif in biological macromolecules, which is of key importance for their elaborate functions in living systems. Not only to mimic biological helices and functions, but also for their potential applications in material science, many helical

polymers have been synthesized such as polyisocyanides (1-5), acetylenes (6-8) polypeptide polymers (9-13), polymethacrylates (14), polystyrenes (15), polyacrylamides (16), poly(α , β -unsaturated ketone) (17,18) and so on (19-22). The dynamic helical polymers including stimuli responsive helical polymers, possess a very low helix inversion barrier. Their one-handed helical conformation can be induced by chiral groups attached as side chains or as terminal groups, and be capable of responding to external stimuli by conformational changes. Therefore, stimuli responsive helical polymers can be served as chiroptical sensors and actuators (19,23,24). So, many polymers responsive to the external stimuli including chiral compounds, pH, light, solvents, metal ions, etc., have been extensively studied and prepared (24-28).

Among all the stimuli-responsive helical polymers, the redox-stimuli-responsive helical polymers are particularly attractive due to their controllability in the solid state, no bleaching reaction, easy integration and potential application in biosensor and targeted drug delivery (29,30). So far some of redox responsive helical polymers including different pendant group have been prepared, such as ferrocenyl groups (1), tetrathiafulvalene derivatives (3), riboflavin pendants (6,31), anthraquinone imide (7), viologens (8), and thioether (10-13), etc. (32). The helical polymers obtained are very sensitive to redox stimuli, most of which are the redox triggered chirality switching of optically active polymers, the CD signs of which are on/off, the conformation changes from helix to random coil (1,3,6-8,10,31). However, to the best of our knowledge, only a few examples have been reported regarding the redox-induced helicity inversion helical polymers (32).

The thioether group can be easily oxidized to sulfoxide and sulfone. Utilizing this feature, several redox responsive polymers containing thioether pendant have been synthesized (10,33,34). However, the redox responsive helical polymers with thioether group rarely have been reported (10-13). To the best of our knowledge, the polymer with a oxidation-triggered helix-to-helix

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transition hasn't been reported. Here, polyisocyanides with thioether pendant were synthesized. The helical structures and oxidation-responsive behavior of the polyisocyanides were checked. The phenomenon was found that the helix sense of polyisocyanide with thioether pendant was probably inversion when it was oxidized.

2 Experimental

2.1 Materials

L-cysteine ($[\alpha]_D^{25} = +9.2^\circ$ in H_2O) was purchased from Geao chemical technology Ltd. $NiCl_2 \cdot 6H_2O$ was purchased from J&K Scientific LTD. Anhydrous methanol was obtained from drying over Mg. Ether acetate was dried over anhydrous $MgSO_4$ overnight before use. Triethylamine was distilled over calcium hydride before use. Other chemicals were commercial analytic reagent, and used as received without further purification. The deionized water was obtained by distillation.

2.2 Measurements

NMR spectra were recorded on a BRUKER ARX400M Hz spectrometer using tetramethylsilane (TMS) as internal

standard and $CDCl_3$ as solvent. Elemental analyses were carried out with an Elementary Vario EL instrument. The number-average molecular weights (M_n) and polydispersity (PDI) were measured on a GPC KF-800 (Dalian elite Instrument Co., Ltd.) gel permeation chromatography (GPC) instrument with a set of HT3, HT4 and HT5. The μ -styragel columns used THF as the fluent (1.0 mL/min) at $38^\circ C$. The calibration curve was obtained with linear polystyrene as standards. Optical rotations (OR) were measured using a PolAAR 3005 polarimeter. Circular dichroism (CD) spectra were measured on Jasco J-810 CD instrument using $CHCl_3$ as solvent. The UV-vis spectra were obtained from a Perkin-Elmer Lambda 25 spectrometer using $CHCl_3$ as solvent. Fourier transform infrared (FT-IR) spectra were recorded on an IRAffinity-1 spectrophotometer system (Shimadzu, Japan) using KBr pellets at $25^\circ C$.

2.3 Synthesis of monomer

2.3.1 Synthesis of S-benzyl-L-cysteine

L-cysteine (2.42 g, 0.02 mol) and NaOH solution (2.0 mol/L, 40 mL) were added into a 100 mL three necked round flask. To the rapidly stirring solution, benzyl bromide (2.4 mL, 0.02 mol) was added slowly at $45^\circ C$. The water solution was neutralized to pH 5.4 by careful addition of acetic acid (20%) after 30 min. At the time, a large number

Scheme 1: The synthesis and oxidation of poly-MBTIP.

of white precipitate was formed immediately. The solids were collected by filtration, washed with water, and dried at 40°C *in vacuo* to obtain white power (4.14 g) in 98.1% yield. $[\alpha]_{589}^{25} = +26.0^\circ$ ($c = 0.4$ mol/L, 1 mol/L NaOH), m.p. = 215.5–216.4°C. ^1H NMR (400 MHz, $\text{D}_2\text{O} + \text{NaOH}$): δ 7.34 (s, 1H), 7.33 (s, 2H), 7.27 (dd, $J = 8.8, 4.5$ Hz, 1H), 3.71 (s, 2H), 3.31 (dd, $J = 6.6, 5.4$ Hz, 1H), 2.67 (qd, $J = 13.5, 6.0$ Hz, 2H). ^{13}C NMR (101 MHz, $\text{D}_2\text{O} + \text{NaOH}$): δ 181.00, 138.59, 128.97, 128.82, 127.28, 54.98, 36.49, 35.54. IR (KBr, cm^{-1}): 1619, 1568, 1493(Ar), 1394(C-N), 768(Ar-H), 698.

2.3.2 Synthesis of S-benzyl-L-cysteine methyl ester

To the solution of S-benzyl-L-cysteine (2.11 g, 10.00 mmol) in dry methanol (30.0 mL), thionyl chloride (1.10 mL, 15 mmol) was dripped slowly with stirring at -15°C under nitrogen atmosphere. The reaction solution stirred at the temperature until it became transparent, then the solution was stirred at room temperature for 4 h and was heated to reflux for 6 h. Removing the solvent by evaporation, the yellow oil was obtained. Fresh methanol (30.0 mL) was added to the oil, after the methanol was removed again, and the faint yellow solid was afforded after a time. The solid was the S-benzyl-L-cysteine methyl ester hydrochloride salt.

To the solution of hydrochloride salt obtained in dry methanol (40 mL), the triethylamine was dripped slowly until there was no white precipitate to appear. The mixture was continued to stir for 30 min, then sucked filtration. The filtrate was removed the solvent to obtain S-benzyl-L-cysteine methyl ester (2.23 g) in 95.3% yield. $[\alpha]_{589}^{25} = +25.5^\circ$ ($c = 0.01$ mol/L in acetic ether), ^1H NMR (400 MHz, CDCl_3) δ 7.36–7.19 (m, 5H), 3.74 (s, 2H), 3.68 (d, $J = 12.5$ Hz, 1H), 3.60 (dd, $J = 7.5, 4.8$ Hz, 1H), 2.83 (dd, $J = 13.5, 4.7$ Hz, 1H), 2.67 (dd, $J = 13.5, 7.5$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 174.41, 137.98, 128.90, 128.54, 127.15, 54.04, 52.15, 36.60, 36.43.

2.3.3 Synthesis of N-formoxyl-S-benzyl-L-cysteine methyl ester

After a mixture of anhydrous formic acid (3.00 mL, 79.7 mmol) and acetic anhydride (1.50 mL, 15.8 mmol) was stirred at room temperature for 2 h under a dry nitrogen atmosphere, the mixture was added to the solution of S-benzyl-L-cysteine methyl ester (2.25 g, 10.00 mmol) in dry ethyl acetate (30 mL) at 0°C. The dispersion solution was stirred at 0°C for 30 min, and then at room temperature for 2 h. After the solvent was removed by evaporation, the crude product was purified by column chromatography (silica gel, 50% CHCl_3 /ethyl acetate) to obtain faint yellow

solid (1.96 g, yield 79.0%). mp: 49.7–51.6°C. $[\alpha]_{589}^{25} = +46.9^\circ$ ($c = 0.0053$ g/mL in CHCl_3), IR (KBr, cm^{-1}): 1641(O=CNH), 1517(CON-H). ^1H NMR (400 MHz, CDCl_3): δ 8.12 (s, 1H), 7.38–7.27 (m, 5H), 4.92–4.85 (m, 1H), 3.76 (d, $J = 3.2$ Hz, 3H), 3.71 (d, $J = 2.3$ Hz, 2H), 2.93 (d, $J = 5.1$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ 170.86, 160.71, 137.77, 129.02, 128.75, 127.43, 52.84, 50.31, 36.80, 33.46.

2.3.4 Synthesis of methyl (R)-3-(benzylthio)-2-isocyanopropanoate (MBTIP)

Triethylamide (2.25 mL, 16.1 mmol) was added to a solution of N-formoxyl-S-benzyl-L-cysteine methyl ester (1.80 g, 7.08 mmol) in dry CH_2Cl_2 (30 mL). After the reaction mixture was stirred at 0°C for 10 min under a dry nitrogen atmosphere, a solution of triphosgene (BTC) (1.32 g, 4.43 mmol) in CH_2Cl_2 (10 mL) was added dropwise carefully to the mixture using CP. dropping funnel and finished for 30 min. The dispersion solution was stirred at room temperature for 2.5 h. At the time, a large number of white crystal was crystallized out, and then CH_2Cl_2 (30 mL) was added. After filtration, the solution was washed with aqueous NaHCO_3 (100 mL) and dried over anhydrous MgSO_4 . The solvent was removed by evaporation, and the crude product was purified by column chromatography (silica gel, light petroleum/ethyl acetate = 2:1, v/v) to obtain faint yellow liquid (0.51 g, yield 30.5%). IR (KBr, cm^{-1}): 2149 ($\text{C}\equiv\text{N}$). ^1H NMR (400 MHz, CDCl_3): δ 7.35 (s, 2H), 7.34 (s, 2H), 7.31–7.27 (m, 1H), 4.28 (dd, $J = 7.3, 5.2$ Hz, 1H), 3.85 (s, 2H), 3.82 (s, 3H), 2.99–2.85 (ddd, $J = 21.6, 14.3, 6.2$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.75, 161.67, 137.06, 129.04, 128.77, 127.55, 56.71, 53.61, 36.76, 33.30. Calcd for $\text{C}_{12}\text{H}_{14}\text{NO}_2\text{S}$ (236.1): C, 60.99; H, 5.97; N, 5.93; S, 13.57. Found: C, 61.01; H, 6.03; N, 5.90; S, 13.54.

2.3.5 Synthesis of methyl 3-(benzylsulfinyl)-N-formyl-L-alaninate

N-formoxyl-S-benzyl-L-cysteine methyl ester (1.06 g, 4 mmol) and 30% H_2O_2 (2.00 mL, 18 mmol) was stirred at room temperature (30°C) for 45 min. The progress was monitored by TLC and stopped until the raw was disappeared. The product was extracted with ethyl acetate (3 × 10 mL) and the combined organics was washed with brine (15 mL), and dried over anhydrous MgSO_4 . After the solvent was removed by evaporation, the crude product was purified by column chromatography (silica gel, 50% petroleum/ethyl acetate) to obtain white solid (0.96 g, yield 89.2%). mp: 93.5–95.6°C. $[\alpha]_{589}^{25} = +7.1^\circ$ ($c = 0.0054$ g/mL in CHCl_3), IR (KBr, cm^{-1}): 1035 (S=O). ^1H NMR (400 MHz,

CDCl_3) δ 8.09, 8.14 (s, 1H), 7.47 – 7.23 (m, 5H), 5.03 – 4.92 (m, 1H), 4.05 (s, 2H), 3.75 (s, 3H), 3.24 – 3.06 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) one group peaks: δ 170.04, 161.40, 130.25, 129.29, 129.09, 128.73, 58.52, 53.50, 52.04, 47.46; another group peaks: δ 169.96, 161.32, 130.25, 129.17, 129.03, 128.83, 58.86, 53.11, 51.09, 47.74.

2.3.6 Synthesis of methyl 3-(benzylsulfonyl)-N-formyl-L-alaninate

N-formoxyl-S-benzyl-L-cysteine methyl ester (1.06 g, 4 mmol) and 30% H_2O_2 (4.00 mL, 36 mmol) was stirred at room temperature (30°C) until the raw was disappeared by TLC. Then, the mixture was still stirred at 40°C for 8 h until the sulfoxide was disappeared. The product was extracted with ethyl acetate (3 $\times$ 10 mL) and the combined organics was washed with $\text{Na}_2\text{S}_2\text{O}_3$ (15 mL), and dried over anhydrous MgSO_4 . The methyl 3-(benzylsulfonyl)-N-formyl-L-alaninate was obtained by column chromatography (silica gel, 80% petroleum/ethyl acetate) to obtain white solid (yield 65.4%). mp: 122.7–125.9°C. $[\alpha]_{589}^{25} = +46.7^\circ$ ($c = 0.0053$ g/mL in CHCl_3), IR (KBr, cm^{-1}): 1124, 1352 (O=S=O). ^1H NMR (400 MHz, CDCl_3) δ 8.15 (s, 1H), 7.46 – 7.36 (m, 5H), 6.85 (d, $J = 7.3$ Hz, 1H), 5.04 – 4.96 (m, 1H), 4.27 (d, $J = 0.8$ Hz, 2H), 3.80 – 3.76 (m, 3H), 3.62 (dd, $J = 14.7, 5.2$ Hz, 1H), 3.51 (dd, $J = 14.7, 4.3$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3): δ 169.18, 161.09, 130.95, 129.50, 129.31, 127.27, 61.96, 53.51, 51.96, 46.89.

2.4 Polymer synthesis

A typical procedure is described below: a dry Schlenk flask was thoroughly purged with nitrogen for three cycles, then the solution of monomer, MBTIP (0.200 g, 0.85 mmol) in dry dichloromethane (DCM) (4.0 mL) and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.020 g, 0.085 mmol) in MeOH (10 wt%) was added via degassed syringes, respectively. At the time, the color of the solution was developed into puce immediately. The mixture was then stirred at 50°C for 24 h. The polymerization was quenched by cooling the reaction mixture to room temperature. The polymer was precipitated by adding a large amount of n-hexane and isolated by filtration three times and dried *in vacuo* at 40°C to a constant weight to obtain (0.111 g, yield 55.2%) and is denoted by poly-MBTIP.

2.5 Polymer oxidation

A poly-MBTIP was dissolved in a solution of 5% acetic acid, then the 30% H_2O_2 was dropped slowly at stirring.

The reaction solution was stirred sequentially at room temperature for 18 h. Drops of 1M sodium thiosulfate were added, and then the reaction solution was removed by evaporation. The residue was extracted with CHCl_3 , and the solution was dried over anhydrous MgSO_4 . After the solvent was removed by evaporation, the product was obtained (81.6% yield) and is denoted by poly-MBTIP-O.

3 Results and discussion

3.1 Synthesis and polymerization of thioether-bound isocyanide

The sulfoether-bound isocyanide monomer, was prepared according to the reported procedure for analogous compounds. The synthesis of methyl (R)-3-(benzylthio)-2-isocyanopropanoate (MBTIP) was performed a four-step synthetic route, the last step of which was the conversion of the formamide to the isocyanide by dehydration in dry CH_2Cl_2 with triphosgene. Treatment of MBTIP with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ as catalyst gave poly(isocyanide), poly-MBTIP. The chemical structures of monomer and the conversion of the monomer into the polymer were confirmed analytically by IR(infra-red spectra), ^1H -NMR and ^{13}C -NMR. The spectra of MBTIP and poly-MBTIP are given in Figure 1 and supporting material.

The IR spectra of MBTIP and poly-MBTIP are given in Figure S1 and S2. The IR spectrum of poly-MBTIP has signal disappear at 2149 cm^{-1} corresponding to the isocyanide moiety in MBTIP, and showed a broad band at approximately 1650 cm^{-1} from the imine groups attached to the polymer backbone. ^1H -NMR and ^{13}C -NMR spectra of the poly-MBTIP show broad resonances. These spectra confirm that the monomer was polymerized and the polyisocyanide (poly-MBTIP) was obtained. The number-average molecular weight (M_n) and polydispersity index (PDI) of poly-MBTIP were determined by GPC. By varying the molar ratio of the monomer to $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, poly-MBTIPs with different M_n were obtained, the detailed

Figure 1: The ^1H NMR of MBTIP and poly-MBTIP in the CDCl_3 .

Table 1: Polymerizations of MBTIP.^a

entry	$n_{\text{NiCl}_2 \cdot 6\text{H}_2\text{O}} / n_{\text{monomer}}$	Yield (%)	$M_n \times 10^{-3}$	Mw/Mn	$[\alpha]_D^{25}$
P-1 ^b	1/10	55.3	-	-	-
P-2	1/20	30.6	2.0	1.04	-80.0
P-3	1/60	29.2	2.8	1.10	-110.3
P-4	1/100	15.2	4.3	1.02	-350.2

^a $[\text{monomer}]_0 = 0.21 \text{ mol/L}$; solvent: DCM; polymerization temperature: 50°C; reaction time: 24 h.

^b M_n was unable to be detected by GPC.

results are summarized in Table 1. The yields go down and the M_n go up along with the molar ratio of the monomer to $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$. As a whole, the M_n of resultant polyisocyanides are low, the highest M_n is only 4.3×10^3 .

3.2 Chiroptical properties of thioether-bound isocyanide MBTIP and poly-MBTIPs

The chiroptical properties of monomer, MBTIP and the corresponding polymers, poly-MBTIPs are summarized in Table 1. The specific optical rotation ($[\alpha]_D^{25}$) of MBTIP is -5.83 ($c = 1.0 \text{ mg/mL}$, CHCl_3). All the resultant poly-MBTIPs show optical rotations quite different from the MBTIP. The $[\alpha]_D^{25}$ value of poly-MBTIPs are -80.00 , -110.53 , -350.21 , the M_n of which are 2.0×10^3 , 2.8×10^3 , 4.3×10^3 , respectively, far greater than the MBTIP. The large increase in specific optical rotation of poly-MBTIPs indicated that the most likely secondary helical structure of main chain had been formed (17,35). The increase interdependency in specific optical rotation of poly-MBTIPs with M_n is another evidence (36).

CD spectroscopy was applied to further investigate the optical property of poly-MBTIPs in solution. The CD of MBTIP and poly-MBTIPs are showed in Figure 2. Poly-MBTIPs show intense negative Cotton effect peaks at near 192 nm (Figure 2). These Cotton effect signals are caused by the helical backbone of the poly-MBTIPs rather than by the chirality of the side-chain pendant because MBTIP bears the same chiral pendant, but it shows no Cotton effect signal (Figure 2).

3.3 Redox properties of helical poly-MBTIPs and their model compounds

It is well known that thioether can be selectively oxidized into polar sulfoxide or sulfone groups (10,37). To study the redox property of poly(thioether-bound isocyanide), we performed the chemical oxidation of poly-MBTIP.

Figure 2: The CD spectra of monomer and polymers in CH_3OH at 25°C. Concentration: $3.6 \times 10^{-4} \text{ mol/L}$ (referred to one monomer unit). P-2, P-3 and P-4 are the poly-MBTIPs obtained in the Table 1, entry P-2, P-3 and P-4.

H_2O_2 was chosen as a model oxidant to oxidize the poly(thioether-bound isocyanide), P-4 (represent the poly-MBTIP obtained at the Table 1, entry P-4). The oxidized poly-MBTIP is denoted as P-4-O. It is well known that the structure confirmation of polymer is difficult. To study the structure of poly-MBTIP oxidized, methyl 3-(benzylsulfinyl)-N-formyl-L-alaninate and methyl 3-(benzylsulfonyl)-N-formyl-L-alaninate were synthesized as the model compound, respectively. Their structures are confirmed by ^1H NMR, ^{13}C NMR, IR and MS. The FTIR spectroscopy of model compound, methyl 3-(benzylsulfinyl)-N-formyl-L-alaninate shows an increase of infrared absorption band at 1035 cm^{-1} . Infrared absorption band at 1035 cm^{-1} is the characteristic absorption peak of $\text{S}=\text{O}$ (38,39). The FTIR spectroscopy of model compound, methyl 3-(benzylsulfonyl)-N-formyl-L-alaninate shows two types of new bands at 1124 cm^{-1} and 1352 cm^{-1} . They are the characteristic absorption peak of symmetric and asymmetric stretching of $-\text{SO}_2-$ groups (38,39).

FTIR spectroscopy and ^1H -NMR measurement were used for examining corresponding structures of polymers (Figure 3). FTIR data of P-4 and P-4-O show similar infrared absorption band at around 1220 cm^{-1} . But, FTIR data show an increase of infrared absorption band at 1030 cm^{-1} (Figure 3a, P-4-O) for P-4-O. It is near to the characteristic absorption peak of $\text{S}=\text{O}$ group of model compound, methyl 3-(benzylsulfinyl)-N-formyl-L-alaninate, which is at 1035 cm^{-1} ; away from the characteristic absorption peak of $\text{O}=\text{S}=\text{O}$ group of model compound, methyl 3-(benzylsulfonyl)-N-formyl-L-alaninate, which is at

1124 cm^{-1} and 1352 cm^{-1} . From the FTIR spectroscopy of model compounds, P-4 and P-4-O, the conclusion is that poly-MBTIP was oxidized by H_2O_2 to give S=O group.

Figure 3: (a) The FTIR spectra of P-4 and P-4-O in the solid state with the ranges of 900–1700 cm^{-1} , (b) ^1H -NMR spectra of P-4 and P-4-O in the CDCl_3 . P-4 is the poly-MBTIP obtained in the Table 1, entry P-4. P-4-O is the poly-MBTIP, oxidized P-4.

Figure 3b shows the ^1H -NMR spectra of P-4 and P-4-O. The ^1H -NMR spectra of P-4 have three broad peaks between $\delta = 1.28, 3.77$ and 7.28 . The ^1H -NMR spectra of P-4-O have four broad peaks between $\delta = 1.97, 3.73, 5.41$ and 7.33 . The chemical shift of ^1H -NMR spectra of P-4-O move downfield to the P-4. These data also indicate that the thioether group of poly-MBTIP was oxidized by H_2O_2 to give S=O group.

The UV-vis spectra of P-4 and P-4-O are given in the Figure 4a. The λ_{max} of P-4 is at near 206 nm. This strong absorption peak should be attributed to the $\pi\text{-}\pi^*$ transition of the N=C groups in the polymer backbone, is not due to the $n\text{-}\pi^*$ transition of the N=C groups in the polymer backbone which is responsible for the UV-vis spectra in the region 250–500 nm (40). The $\pi\text{-}\pi^*$ transition of the N=C group is allowable and blue shift to the $n\text{-}\pi^*$ transition of the N=C groups in the polymer backbone. So, the ϵ_{max} is large and easy to be characterized. From the diagram, there is no significant change in P-4 and P-4-O. The oxidized poly-MBTIP was investigated the secondary structures by specific optical rotations and CD spectroscopy. The specific optical rotation ($[\alpha]_D^{25}$) of P-4 is -350.2 . It is very interesting that the $[\alpha]_D^{25}$ of oxidized P-4, P-4-O is $+122.8$, is contrary to P-4. This phenomenon means that the helical direction of the poly-MBTIP chain is likely to change. The CD spectroscopy of P-4 and P-4-O are showed in Figure 4. It's obvious that P-4 shows intense negative Cotton effect peaks, and P-4-O shows positive Cotton effect peaks. Their Cotton effect peaks are contrary. So, the conclusion is probably that the helix sense of poly-MBTIP is inversion when it is oxidized.

Figure 4: (a) The UV-vis spectra of P-4 and P-4-O in CH_3OH at 25°C ; (b) CD spectra of monomer, P-4 and P-4-O in CH_3OH at 25°C . Concentration: 3.6×10^{-4} mol/L (referred to one monomer unit). P-4 is the poly-MBTIP obtained in the Table 1, entry P-4. The oxidized P-4 is P-4-O.

4 Conclusions

An oxidation-active single-handed helical polyisocyanide bearing thioether in the side chains was successfully prepared and studied for the chiroptical switching properties. The polyisocyanide was synthesized by polymerization of methyl (R)-3-(benzylthio)-2-isocyanopropanoate (MBTIP) monomer using $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ as catalytic agent in dry DCM. The poly-MBTIPs exhibit intense specific optical rotations and Cotton effects compared to the MBTIP, strongly suggesting a helical conformation of the polymer backbone. Additionally, the thioether pendant of poly-MBTIP backbone was oxidized to sulfoxide group by H_2O_2 . The specific optical rotations and Cotton effects of poly-MBTIP oxidized are reversed, probably suggesting a helical conformation inversion. So, a polyisocyanide with an oxidation-triggered helix-to-helix transition was probably synthesized.

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