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Haichao Zhao^a; Fumio Sanda^a; Toshio Masuda^a

^a Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura Campus, Kyoto, Japan

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Synthesis and Chiroptical Properties of L-Serine-Based Poly(phenylacetylenes)

HAICHAO ZHAO, FUMIO SANDA, and TOSHIO MASUDA

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura Campus, Kyoto, Japan

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L-Serine-based hydroxy group-containing phenylacetylene, *N*-(α -*tert*-butoxycarbonyl)-L-serine 4-ethynylphenylamide (**1**), and the hydroxy group-protected counterpart, *N*-(α -*tert*-butoxycarbonyl)-*O*-trimethylsilyl-L-serine 4-ethynylphenylamide (**2**) were polymerized with (nbd)Rh⁺[η^6 -C₆H₅B⁻(C₆H₅)₃] as a catalyst to obtain the corresponding polymers [poly(**1**) and poly(**2**)] with moderate molecular weights in good yields. The polarimetric and CD spectroscopic data indicated that poly(**1**) existed in a helical conformation in DMF, MeOH, and THF; and that poly(**2**) also took a one-handed helical structure in CHCl₃ and toluene in addition to these solvents. The helical tightness of poly(**2**) depended on the polarity of the solvents. Upon heating, poly(**1**) and poly(**2**) slightly decreased the CD intensity in DMF, MeOH and THF, while poly(**2**) increased it in toluene. The helical conformation of poly(**1**) and poly(**2**) was stable by adding cyclohexane to THF.

Keywords: L-serine; poly(phenylacetylene); helix

1 Introduction

Incorporation of amino acid residues into synthetic polymers is of interest because these combinations may create new nonbiological macromolecules with biomimetic structures and properties, and thus have many potential applications, such as polyelectrolytes, optical resolution, photochromic materials, controlled release systems, biologically active materials and stimuli-responsive materials (1). Endo and coworkers (2–7), and Xie et al. (8, 9) have synthesized a variety of amino acid- and peptide-carrying poly(methacrylates), poly(acrylamides), and poly(methacrylamides) by radical polymerization. North et al. have prepared serine-based poly(acrylates), where serine is attached to polymer backbone at the hydroxy group (10, 11). Grubbs and coworkers (12, 13) and North and coworkers (14) have synthesized poly(norbornenes) bearing amino acids and peptides by ring-opening metathesis polymerization. Wagener and coworkers have synthesized amino acid- and dipeptide-branched polyolefins by acyclic diene metathesis polycondensation (15–17).

Among varieties of amino acid-containing synthetic polymers, amino acid-substituted poly(acetylenes) have drawn

much attention due to the regulated secondary structures. Yashima and coworkers have synthesized novel sets of stereoregular poly(phenylacetylenes) bearing D-, L-, and racemic DL-alanine residues with long alkyl pendants to find that they form well-defined lyotropic cholesteric or nematic liquid crystals as evidenced by their indisputably clear fingerprint and Schlieren textures (18). Tang and coworkers have focused on helical poly(phenylacetylene) derivatives carrying amino acids moieties, which exhibit unique properties including self-assembling, formation of superhelical fibers, chirality transcription, and change of helicity by pH change (19). We have reported a series of helical poly(*N*-propargylamides) containing alanine (20), serine (21), aspartic acid (22, 23), and glutamic acid moieties (24), some of which undergo inversion of helical sense reversibly upon external stimuli such as heat and solvent.

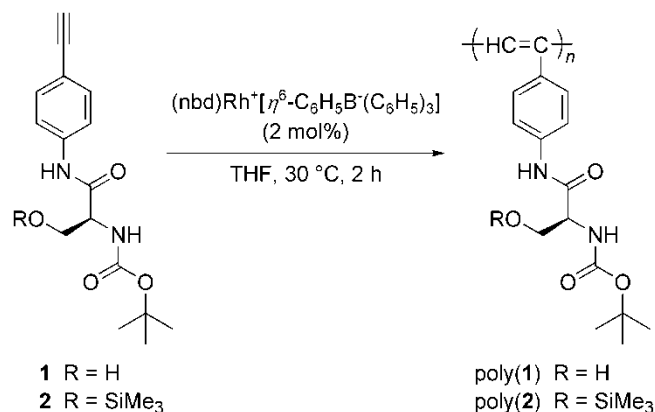
In this article, we report the synthesis of L-serine-based novel poly(phenylacetylenes), and examination of the effect of hydroxy group on the helical conformation (Scheme 1).

2 Experimental

2.1 Materials

THF was distilled over CaH₂ prior to use. (nbd)Rh⁺[η^6 -C₆H₅B⁻(C₆H₅)₃] was prepared as reported (25). 4-[4,6-Dimethoxy-1,3,5-triazine-2-yl]-4-methylmorpholinium chloride (TRIAZIMOCHE) was supplied by Tokuyama Co. All other reagents were used as received without purification.

Address correspondence to: Fumio Sanda and Toshio Masuda, Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura Campus, Kyoto 615-8510, Japan. Tel.: +81-75-383-2589; Fax: +81-75-383-2590; E-mail: sanda@adv.polym.kyoto-u.ac.jp; masuda@adv.polym.kyoto-u.ac.jp



Sch 1. Polymerization of L-serine-based phenylacetylene.

2.2 Synthesis of [N-(α-tert-butoxycarbonyl)-L-serine]-4-ethynylphenylamide (**1**)

N-(α-tert-Butoxycarbonyl)-L-serine (4.1 g, 20 mmol) and *p*-ethynylaniline (2.3 g, 20 mmol) were dissolved in AcOEt (100 mL), and the resulting solution was stirred at room temperature for 10 min. TRIAZIMOXH (4.9 g, 20 mmol) was added to the solution, and the resulting mixture was stirred at room temperature overnight. The mixture was subsequently washed with 1 N HCl aq, saturated NaHCO₃ aq and saturated NaCl aq, then dried over anhydrous MgSO₄, and concentrated by rotary evaporation. The residue was purified by silica gel column chromatography eluted with AcOEt to obtain **1** in 89% yield. Mp 152 – 153.5°C. $[\alpha]_D = -41^\circ$ ($c = 0.1$ g/dL, in THF, r.t.). ¹H-NMR (400 MHz, CDCl₃): δ 1.49 (s, 9H, C(CH₃)₃), 2.01 (s, 1H, OH), 3.05 (s, 1H, –C≡CH), 4.14 (d, $J = 12$ Hz, 1H, CH), 4.30 (s, 1H, NHCOO), 5.78 (s, 1H, NHCO), 7.44, 7.47, 7.49 (m, 4H, C₆H₄).

¹³C-NMR (100 MHz, CDCl₃): 28.25 (C(CH₃)₃), 62.46 (CH₂), 55.51 (CH), 80.36 (C≡CH), 83.25 (C≡CH), 118.01, 132.91 (C₆H₄), 137.86 (NHCOO), 169.70 (NHCO). IR (cm⁻¹, KBr): 3358, 2983, 2112, 1686, 1594, 1496, 1409, 1392, 1370, 1298, 1081, 836, 594. Anal. Calcd. for C₁₆H₂₀N₂O₄: C, 63.14; H, 6.62. Found: C, 62.97; H, 6.65.

2.3 N-(α-tert-butoxycarbonyl)-O-trimethylsilyl-L-serine 4-ethynylphenylamide (**2**)

Trimethylsilyl chloride (1.2 g, 12 mmol) was added to a solution of **1** (3.1 g, 10 mmol) and imidazole (0.8 g, 12 mmol) in *N,N*-dimethylformamide (DMF, 30 mL) at room temperature. The reaction mixture was stirred overnight, and then water (200 mL) was added to the mixture. It was extracted with ether (200 mL), and the combined organic phase was dried over MgSO₄. It was concentrated by rotary evaporation, and the obtained mass was purified by silica gel column chromatography eluted with hexane/AcOEt (6/1, volume ratio) to obtain **2** in 48% yield. Mp 44.5 – 45.5°C. $[\alpha]_D = -30^\circ$ ($c = 0.1$ g/dL, in THF, r.t.). ¹H-NMR (400 MHz, CDCl₃): δ 0.05 (s, 9H, Si(CH₃)₃), 1.29 (C(CH₃)₃), 2.01 (s, 1H, OH), 2.91 (s, 1H, –C≡CH), 3.59 (m, 1H, CH), 3.93 (m, 2H, CH₂), 4.12 (s, 1H, NHCOO), 5.32 (s, 1H, NHCO), 7.12, (m, 4H, C₆H₄). ¹³C-NMR (100 MHz, CDCl₃): 0 (Si(CH₃)₃), 28.92 (C(CH₃)₃), 63.04 (CH₂), 55.51 (CH), 79.96 (C≡CH), 84.31 (C≡CH), 119.89, 133.62 (C₆H₄), 138.65 (NHCOO), 169.99 (NHCO). IR (cm⁻¹, KBr): 3306, 3053, 2977, 2180, 1673, 1601, 1530, 1406, 1392, 1367, 1295, 1252, 1163, 1112, 1046, 1016, 966, 870, 840, 753, 684, 537. Anal. Calcd. for C₁₉H₂₈N₂O₄Si: C, 60.61; H, 7.50. Found: C, 60.42; H, 7.43.

2.4 Polymerization (Typical Procedure)

Polymerizations were carried out in a glass tube equipped with a three-way stopcock under nitrogen. (nbd)Rh⁺[η⁶-C₆H₅B⁻(C₆H₅)₃] was added to a THF solution of **1** or **2** under dry nitrogen, and the resulting solution ($[M]_0 = 1.0$ M, $[M]_0/[Rh] = 50$) was kept at 30°C for 2 h. The mixture was poured into a large amount of *n*-hexane (poly(**1**)) or H₂O (poly(**2**)) to precipitate a powdery polymer. It was collected by filtration and dried *in vacuo*.

2.5 Spectroscopic Data of the Polymers

Poly(**1**): IR (cm⁻¹, KBr): 3381, 2975, 2112, 1687, 1599, 1510, 1496, 1368, 1312, 1250, 1165, 1060, 838, 661.

Table 1. Polymerization and properties of the polymers

Polymer	Yield (%)	M_n^d	M_w/M_n^d	$[\alpha]_D^e$ (deg)				
				DMF	THF	MeOH	CHCl ₃	Toluene
Poly(1)	91 ^b	15000	1.67	-418	-472	-442	- ^f	- ^f
Poly(2)	70 ^c	40800	1.97	-508	-382	-391	-553	-245

^aCatalyst: (nbd)Rh⁺[η⁶-C₆H₅B⁻(C₆H₅)₃], nbd = norbornadiene, time 2 h.

^b*n*-Hexane-insoluble part.

^cWater-insoluble part.

^dDetermined by GPC calibrated by polystyrene standards; eluent: THF.

^eMeasured by polarimetry at room temperature, $c = 0.10$ g/dL.

^fNot measured due to poor solubility.

$^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$): δ 1.35 (s, 9H, $\text{C}(\text{CH}_3)_3$), 3.63 (s, 1H, OH), 4.16 (s, 1H, CH), 4.84 (s, CH_2), 5.72 (s, 1H, NHCOO), 6.67 (b, 1H, NHCO), 7.32 (b, 4H, C_6H_4). Poly(2): IR (cm^{-1} , KBr): 3317, 2959, 1686, 1600, 1509, 1496, 1367, 1251, 1169, 1110, 843, 606. $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$): δ 0.12 (s, 9H, $\text{Si}(\text{CH}_3)_3$), 1.50 (s, 9H, $\text{C}(\text{CH}_3)_3$), 4.16 (b, 2H, CH, NHCOO), 4.37 (b, CH_2), 5.72 (s, 1H, NHCOO), 5.58 (b, 1H, NHCO), 7.26 (b, 4H, C_6H_4).

2.6 Measurement

^1H and $^{13}\text{C-NMR}$ 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 polymers were determined by gel permeation chromatography (GPC) on a JASCO Gulliver system using THF as an eluent, calibrated by polystyrene standards at 40°C . Specific rotations ($[\alpha]_D$) 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) using a JASCO J-820 spectropolarimeter.

3 Results and Discussion

3.1 Monomer Synthesis and Polymerization

L-Serine-based phenylacetylene monomer **1** was synthesized by the condensation of BOC-L-serine with *p*-ethynylaniline

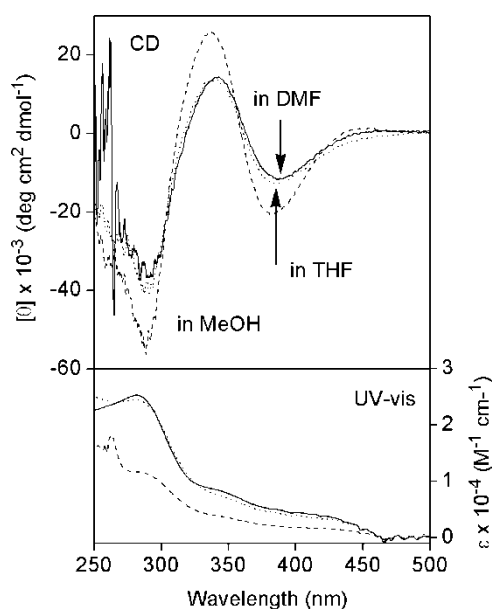


Fig. 1. CD and UV-vis spectra of poly(1) measured in DMF, THF, and MeOH at rt, $c = 2.0 \times 10^{-4}$ M.

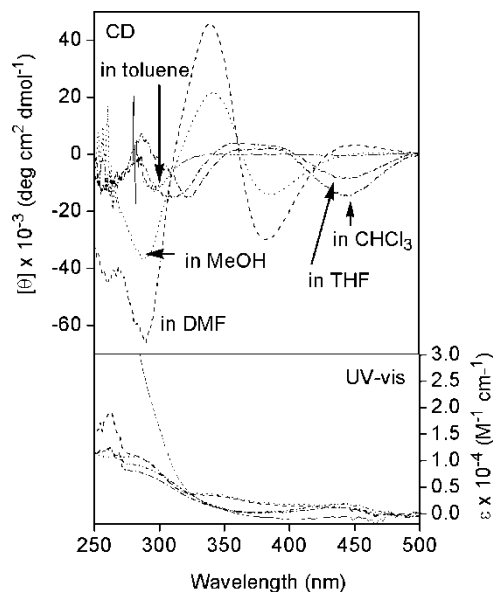


Fig. 2. CD and UV-vis spectra of poly(2) measured in DMF, THF, MeOH, CHCl_3 , and toluene at rt, $c = 2.0 \times 10^{-4}$ M.

using TRIAZIMOXH as a condensation agent. Hydroxy group-protected monomer **2** was obtained by *O*-silylation of **1** in DMF in the presence of imidazole. The structures of the monomers were confirmed by ^1H , $^{13}\text{C-NMR}$, and IR spectroscopies besides elemental analysis. The polymerization of **1** and **2** were conducted in THF at 30°C for 2 h, catalyzed with $(\text{nbdrh})^+[\eta^6\text{-C}_6\text{H}_5\text{B}^-(\text{C}_6\text{H}_5)_3]^-$ as summarized in Table 1. The monomers satisfactorily underwent polymerization to afford the corresponding polymers with moderate molecular weights in good yields. Poly(1) was soluble in DMF, MeOH and THF, partly soluble in CHCl_3 and toluene, while poly(2) was soluble in all the above

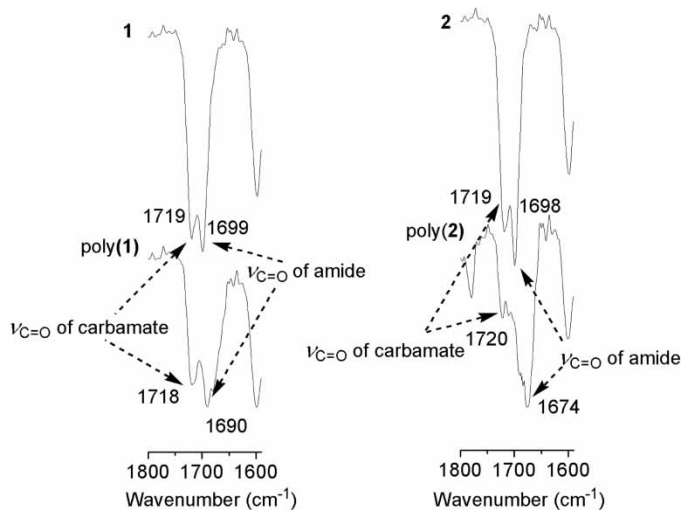


Fig. 3. IR spectra of **1**, **2** and the corresponding polymers measured in THF (50 mM).

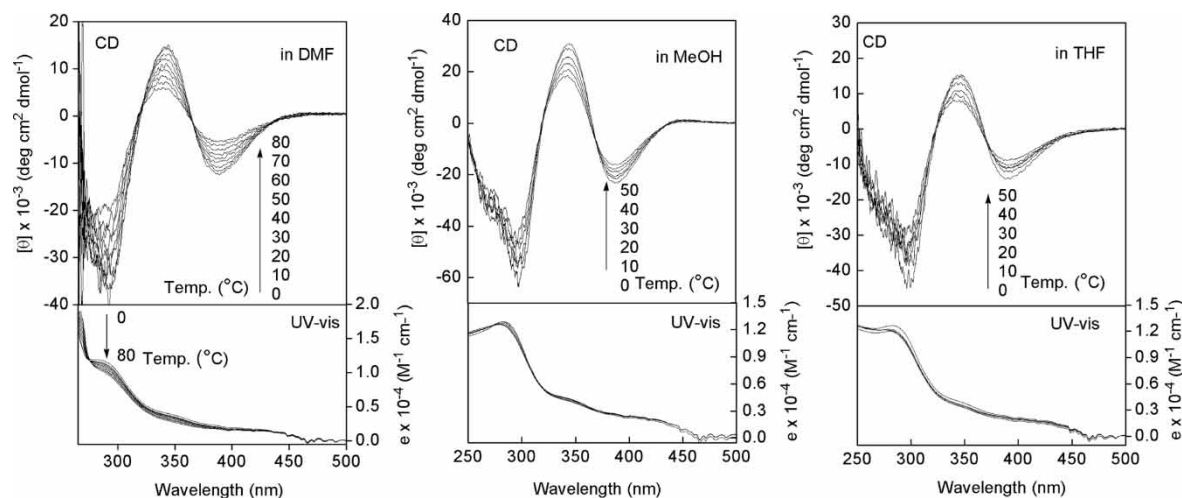


Fig. 4. Temperature dependence on the CD and UV-vis spectra of poly(**1**) measured in DMF, THF and MeOH, $c = 1.0 \times 10^{-4}$ M.

mentioned solvents, as expected from the low polarity due to the Si-protected hydroxy group.

3.2 Secondary Structure of the Polymers

The secondary structure of the polymers was examined by polarimetry, CD, and UV-vis spectroscopies. As shown in Table 1, poly(**1**) showed large minus rotations in DMF (-418°), MeOH (-442°), and THF (-472°), which were ca. ten-fold larger than that of monomer **1** (-41°). Poly(**2**) showed larger minus rotations in DMF (-508°), MeOH (-391°), THF (-382°), CHCl_3 (-553°), and toluene (-245°) compared to that of **2** (-30°). These data strongly suggest that both poly(**1**) and poly(**2**) take a predominantly one-handed helical conformation in these solvents.

Figures 1 and 2 display the CD and UV-vis spectra of poly(**1**) and poly(**2**) in different solvents. Poly(**1**) showed

intense CD signals in DMF, MeOH and THF at 290, 340 and 380 nm, which were similar irrespective of the solvent. The observed strong CD signals at 350 and 390 nm should be associated with the polymer backbone, confirming that poly(**1**) takes a helical structure with a predominant one-handed screw sense. Meanwhile, poly(**2**) showed the CD signals in different ways according to the solvents as shown in Figure 2. In polar solvents such as DMF and MeOH, poly(**2**) exhibited strong CD signals at 290, 340, and 380 nm, which were similar to those of poly(**1**) in DMF, MeOH, and THF. Poly(**2**) showed large minus CD signs at 320 and 450 nm in less polar solvents such as THF and CHCl_3 , while it displayed only one small CD signals at 320 nm in toluene. These results indicate that the helicity of poly(**2**) changed in accordance with the solvents.

We have previously obtained L-serine-based helical poly(*N*-propargylamide), whose helical structure was stabilized

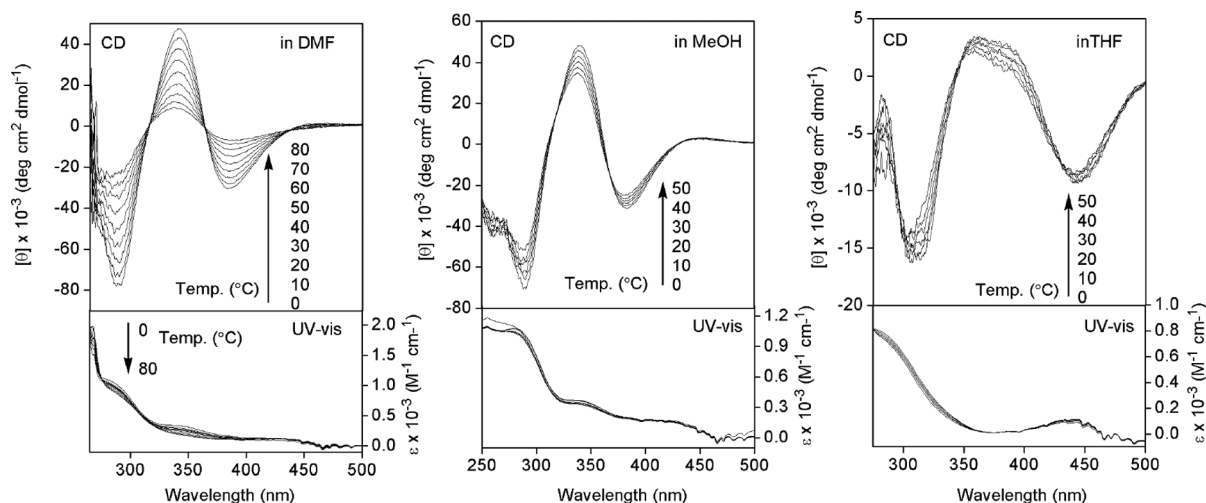


Fig. 5. Temperature dependence on the CD and UV-vis spectra of poly(**2**) measured in DMF, THF and MeOH, $c = 2.0 \times 10^{-4}$ M.

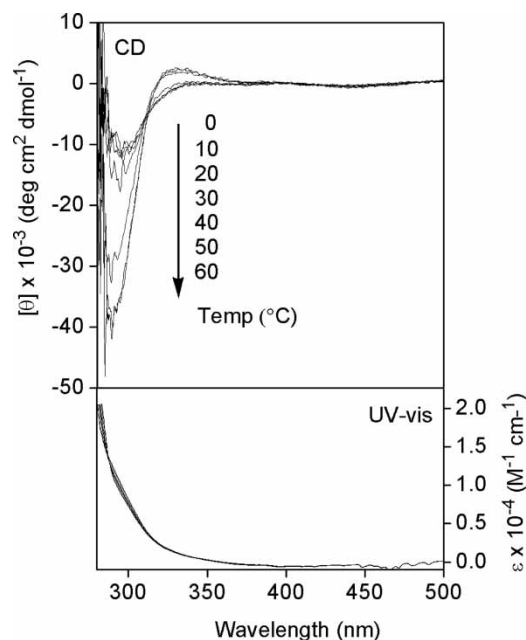


Fig. 6. Temperature dependence on the CD and UV-vis spectra of poly(2) measured in toluene, $c = 2.0 \times 10^{-4}$ M.

by intramolecular hydrogen bonding among amide and/or hydroxy groups (21). We examined whether hydrogen bonding played an important role for the L-serine-based poly(phenylacetylenes) to form helix by solution state IR spectroscopic measurement (Figure 3). **1** and poly(**1**) exhibited the amide $\nu_{\text{C=O}}$ peaks at 1699 and 1690 cm^{-1} in THF (50 mM), respectively, indicating that the amide groups are hardly hydrogen bonded. On the other hand, poly(**2**)

showed the amide absorption peak at 1674 cm^{-1} , which was 24 cm^{-1} lower than that of **2**. Judging from the low reagent concentration (50 mM), it is concluded that poly(**2**) forms weak intramolecular hydrogen bonding between the amide groups.

3.3 Conformation Change on External Stimuli

The helical conformation of polyacetylenes is dynamic and susceptible to external stimuli such as heat and solvent. We first examined the stability of helical conformation of poly(**1**) and poly(**2**) by heating. Figure 4 depicts the CD and UV-vis spectra of poly(**1**) measured in DMF, MeOH, and THF at various temperatures. The intensity of CD signals of poly(**1**) gradually decreased in DMF accompanying the decrease of the UV-vis absorption, upon raising temperature. The intensity of CD signals of poly(**1**) also weakened upon heating in MeOH and THF. The spectroscopic change was somewhat larger in DMF than that in MeOH and THF, but the difference between these three solvents was not remarkable. A similar tendency was observed in the temperature-valuable CD and UV-vis spectra of poly(**2**) in these solvents as shown in Figure 5. In this case, the change in DMF was more apparent compared to that of poly(**1**).

Surprisingly, poly(**2**) increased the CD intensity in toluene at 280 nm by heating as shown in Figure 6. It seems that a higher temperature is favorable for poly(**2**) to form a helical structure in toluene. This is completely different from the behavior of common helical polymers, as well as from that of poly(**1**) and poly(**2**) in DMF, MeOH and THF, but the concrete reason is unclear.

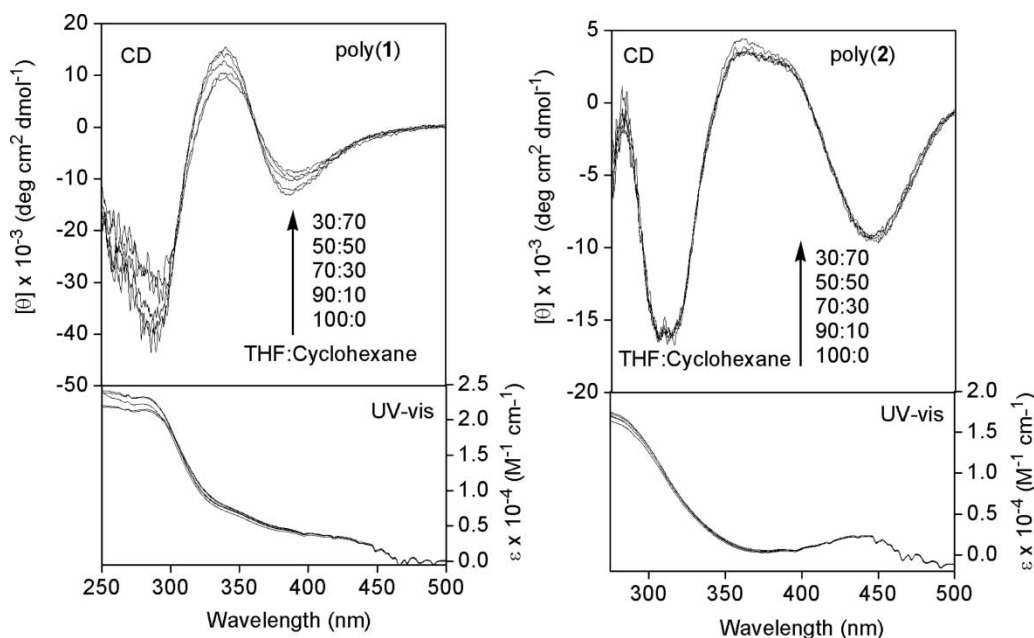


Fig. 7. Effect of THF/cyclohexane composition on the CD and UV-vis spectra of poly(**1**) and poly(**2**) measured at rt, $c = 2.0 \times 10^{-4}$ M.

Both poly(1) and poly(2) take a helical conformation in polar solvents such as DMF, MeOH and THF. We examined the effect of addition of nonpolar cyclohexane to THF on the conformation of the polymers. Figure 7 depicts the CD and UV-vis spectra of the polymers measured in THF/cyclohexane with various compositions. Poly(1) slightly decreased the CD intensity by raising the cyclohexane content, and poly(2) almost kept the same CD intensity. It was confirmed that the helical structures of poly(1) and poly(2) were stable to the increase of hydrophobicity of the solvent.

4 Conclusions

In this article, we have demonstrated the synthesis and chiroptical properties of L-serine-based poly(phenylacetylenes) bearing free and protected hydroxy groups, poly(1) and poly(2). Poly(1) adopted a helical conformation with predominantly one-handed screw sense in DMF, MeOH, and THF, and poly(2) did it also in CHCl₃ and toluene. Poly(1) and poly(2) slightly decreased the one-handed helicity in MeOH and THF, and somewhat largely in DMF upon heating. On the other hand in toluene, poly(2) unexpectedly increased the helicity upon heating.

5 Acknowledgement

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