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# Synthesis and Photoresponse of Helically Folded Poly(phenyleneethynylene)s Bearing Azobenzene Moieties in the Main Chains

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**Supporting Information** 

**ABSTRACT:** Novel optically active poly-(phenyleneethynylene)s bearing azobenzene moieties in the main chains [poly(1-2m), poly(1-2p)] were synthesized by the Sonogashira-Hagihara coupling polymerization of 3',5'diiodo-4'-hydroxy-*N*- $\alpha$ -tert-butoxycarbonyl-D-phenylglycine hexylamide (1) with 3,3'-diethynylazobenzene (2m) and 4,4'diethynylazobenzene (2p). The corresponding polymers [poly(1-2m), poly(1-2p)], with number-average molecular weights of 10700 and 9400, were obtained in 70% and 86% yields, respectively. CD and UV-vis spectroscopic analyses revealed that poly(1-2m) and poly(1-2p) formed predom-



inantly one-handed helically folded structures in  $CHCl_3/THF$  mixtures. Poly(1-2m) underwent a reversible conformational change between folded and unfolded structures upon UV and visible irradiation, as a result of *trans-cis* isomerization of the azobenzene moieties. On the other hand, poly(1-2p) showed very little conformational transformation or azobenzene isomerization. The formation of helical structures was supported by conformational analysis based on the molecular mechanics (MM), semiempirical molecular orbital (MO), and density functional theory (DFT) methods.

# ■ INTRODUCTION

Photoresponsive materials are attracting interest because of their applicability to optical memories,<sup>1–4</sup> molecular machines,<sup>5,6</sup> recognition materials,<sup>7–11</sup> catalysts,<sup>12–14</sup> actuators,<sup>15–18</sup> etc. Azobenzene is the most widely used photoresponsive compound due to its highly efficient reversible *cis/trans* photoisomerization.<sup>19</sup> The more stable *trans*-azobenzene undergoes isomerization upon UV irradiation to *cis*-azobenzene, and the isomerization is reversed by visible irradiation or heat. This occurs reversibly with high quantum yields with change in molecular shape from extended coplanar (trans) to twisted (cis) forms and resulting dipole moment change from 0 to 3 D, respectively.

Azobenzene units are often incorporated into main chains of oligomers/polymers to control the higher order structures.<sup>20–24</sup> Besides this, control over higher order structures of conjugated polymers by external stimuli is also gaining considerable attention, because of the possibility for development of stimuli-responsive photoelectrically functional materials.<sup>25</sup> There are various reports about the synthesis of conjugated polymers with photocontrollable higher order structures containing azobenzene moieties, either on the side chains<sup>26–33</sup> or the main chains.<sup>34–37</sup> Among various conjugated polymers, *ortho-* and *meta*-phenyleneethynylene derivatives are representative polymers that form folded helical structures by amphiphilic balance.<sup>38–48</sup> Recently, we synthesized a series of D-hydroxyphenylglycine-/L-tyrosine-derived poly(*m*-phenylenee-

thynylene-p-phenyleneethynylene)s, 33,49-51 and examined their secondary structures. These polymers form folded helical structures in nonpolar solvents such as CHCl<sub>3</sub>, as a result of the amphiphilicity afforded by the hydrophobic exterior (alkyl chains and phenyleneethynylene main chain) and hydrophilic interior (hydroxy groups). It should be noted that the amphiphilic balance is opposite from that of typical poly-(phenyleneethynylene) derivatives reported so far.<sup>52</sup> We further synthesized poly(*m*-phenyleneethynylene)s containing sidechain azobenzene moieties that are helically folded in nonpolar solvents.<sup>33</sup> The higher order structures of the polymers collapsed to some extent by UV irradiation and were reconstructed by visible irradiation, caused by photoisomerization of the azobenzene moieties. The degree of change of higher order structure was not large, probably because the cistrans isomerization of the azobenzene units did not directly twist the main chain.

Herein we report the synthesis of D-hydroxyphenylglycinederived novel optically active poly(pheyleneethynylene)s containing azobenzene moieties in the main chains with m,m'- and p,p'-linkages by the Sonogashira–Hagihara coupling polymerization of the corresponding monomers (Scheme 1). Photoinduced large conformational changes are expected

Received: February 8, 2013 Revised: May 12, 2013 Scheme 1. Sonogashira–Hagihara Coupling Polymerization of D-Hydroxyphenylglycine-Derived Diiodophenylene Monomer 1 with 3,3'- and 4,4'-Diethynylazobenzene Monomers 2m and 2p



because the azobenzene units are completely contained in the main chains instead of the side chains as in our previous polymers.<sup>33</sup> We discuss the chiroptical and photoresponsive properties of the polymers based on CD and UV–vis spectroscopic analysis, as well as MM, semiempirical MO and DFT calculations.

# EXPERIMENTAL SECTION

**Measurements.** Proton (400 MHz) and  ${}^{13}$ C (100 MHz) NMR spectra were recorded on a JEOL EX-400 or a JEOL AL-400 spectrometer. IR spectra were measured on a JASCO FT/IR-4100 spectrophotometer. Melting points (mp) were measured on a Yanaco micro melting point apparatus. Mass spectra were measured on a JEOL JMS-SX102A mass spectrometer. Number- and weight-average molecular weights ( $M_n$  and  $M_w$ ) of polymers were determined by size exclusion chromatography (SEC, Shodex columns KF805 × 3) eluted with tetrahydrofuran (THF) calibrated by polystyrene standards at 40 °C. CD and UV–vis absorption spectra were recorded on a JASCO J-820 spectropolarimeter. Dynamic light scattering (DLS) measurements were performed using a Malvern Instruments Zetasizer Nano ZS at 25 °C. The measured autocorrelation function was analyzed using a cumulant method. The hydrodynamic radii ( $R_h$ ) of the polymers were calculated from the Stokes–Einstein equations.

**Materials.** Unless stated otherwise, reagents and solvents were purchased and used without purification. Trimethylsilylacetylene was provided as a gift from Shin-Etsu Chemical Co., Ltd. 3,3'-Dibromoazobenzene<sup>53</sup> and 4,4'-diethynylazobenzene<sup>54</sup> (**2p**) were synthesized according to the literature reports. Et<sub>3</sub>N and *N*,*N*dimethylformamide (DMF) used for polymerization were distilled prior to use.

**Photoirradiation.** Photoirradiation was carried out with a 400 W high-pressure mercury lamp with a power source (HB-400, Fuji Glass Work) at room temperature. The appropriate wavelengths were selected either with a Pyrex glass and a UV-D33S filter (Toshiba) for irradiation at 300 <  $\lambda$  < 400 nm or with an L-42 filter (Toshiba) filter for irradiation at 420 nm <  $\lambda$ . The sample solution was held in a quartz cell (10 mm width) placed 20 cm from the lamp.

Synthesis of 3,3<sup>2</sup>-Diethynylazobenzene (2m). 3,3<sup>2</sup>-Dibromoazobenzene (3.40 g, 10.0 mmol),  $PdCl_2(PPh_3)_2$  (0.168 g, 0.24 mmol), PPh<sub>3</sub> (0.252 g, 0.96 mmol), and CuI (0.274 g, 1.44 mmol) were fed into a two-neck flask, which was flushed with dry nitrogen. THF (20 mL) and Et<sub>3</sub>N (15 mL) were added to the solution, and then trimethylsilylacetylene (3.30 mL, 23.9 mmol) was added dropwise to the solution. The mixture was stirred at 50 °C for 72 h. The resulting mixture was concentrated in vacuo and the residual mass was washed with Et<sub>2</sub>O to extract the product. The organic phase was washed with 1.0 M HCl, and saturated NaCl aq., dried over anhydrous MgSO<sub>4</sub>, and then filtered. The filtrate was concentrated, and the residual mass was purified by silica gel column chromatography eluted with hexane/ EtOAc = 9/1 (v/v) to obtain crude 3,3'-bis(trimethylsilylethynyl)- azobenzene. After that, it was dissolved in THF (5 mL), and 1.0 M solution of tetrabutylammonium fluoride in THF (25 mL) was added to the solution. The resulting mixture was concentrated in vacuo, and the residual mass was dispersed in CHCl<sub>3</sub> and water. The organic layer was washed with 1.0 M HCl and saturated NaCl(aq), dried over anhydrous MgSO<sub>4</sub>, and then filtered. The filtrate was concentrated, and the residual mass was purified by silica gel column chromatography eluted with hexane/CHCl<sub>3</sub> = 19/1 (v/v) to obtain **2m** as an orange solid in 28%. Mp 156–158 (lit.<sup>55</sup> 157–159 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.13 (s, 2H, –C=CH), 7.47 (t, *J* = 7.2 Hz, 2H, Ar), 7.59 (d, *J* = 7.6 Hz, 2H, Ar), 7.89 (d, *J* = 7.6 Hz, 2H, Ar), 8.03 (s, 2H, Ar). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  78.06 (–C=CH), 82.83 (–C=CH), 123.1, 123.5, 126.3, 129.1, 134.5, 152.1 (Ar). HRMS (*m*/*z*): [M + H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>11</sub>N<sub>2</sub>, 231.0922; found, 231.0919.

**Polymerization.** All the polymerizations were carried out in a glass tube equipped with a three-way stopcock under nitrogen. A typical experimental procedure for polymerization **1** with **2m** is given. A solution of **1** (218 mg, 0.400 mmol), **2m** (92.0 mg, 0.400 mmol),  $Pd(PPh_3)_2Cl_2$  (14.4 mg, 0.020 mmol),  $PPh_3$  (10.4 mg, 0.040 mmol), CuI (11.4 mg, 0.060 mmol), and Et<sub>3</sub>N (0.8 mL) in DMF (1.2 mL) was stirred at 80 °C for 24 h. The resulting mixture was poured into MeOH/acetone [9/1 (v/v), 300 mL] to precipitate the polymer. It was separated by filtration using a membrane filter (ADVANTEC H100A047A) and dried under reduced pressure.

Spectroscopic Data for the Polymers. Poly(1–2m). IR (KBr): 3421, 3331, 3064, 2952, 2926, 2857, 2215, 1671, 1476, 1366, 1160, 798, 687, 519. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.82–1.79 [br, 20H, –CONHCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>, –NHCOOC(CH<sub>3</sub>)<sub>3</sub>], 3.08–3.53 [br, 2H, –CONHCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>], 5.03–5.38 (br, 1H, –CHCONH–), 5.52–6.88 [br, 3H, –CONHCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>, –NHCOOC(CH<sub>3</sub>)<sub>3</sub>, –OH], 7.10–8.38 (br, 10H, Ar). Poly(1–2p): IR (KBr): 3422, 3339, 3060, 2956, 2928, 2857, 2204, 1676, 1491, 1366, 1260, 1228, 1161, 849, 804, 490 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.82–1.79 [br, 20H, –CONHCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>, –NHCOOC(CH<sub>3</sub>)<sub>3</sub>], 3.08–3.53 [br, 2H, –CONHCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>], 5.03–5.38 (br, 1H, –CHCONH–), 5.52–6.88 [br, 3H, –CONHCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>, –NHCOOC(CH<sub>3</sub>)<sub>3</sub>, –OH], 7.10–8.38 (br, 10H, Ar).

**Computation.** The MM calculations were carried out using the Merck molecular force field<sup>56</sup> (MMFF94) with Wave function, Inc., Spartan '10 version 1.1.0, running on a Macintosh computer. The semiempirical MO calculations (PM6,<sup>57</sup> ZINDO/S) and DFT<sup>58</sup> calculations were performed with the GAUSSIAN 09 program,<sup>59</sup> EM64L-G09 Rev C.01 running on the supercomputer system, Academic Center for Computing and Media Studies, Kyoto University. Theoretical CD and UV–vis spectra were simulated by the ZINDO/S method<sup>60–64</sup> in the GAUSSIAN 09 program. The low-energy transition states of 20 were predicted under the condition of a CI number of  $20 \times 20$ , including each oscillator strength (f) and rotatory strength ( $R_{vel}$ ) in velocity form. The simulated CD and UV–vis spectra were produced by using the  $R_{vel}$ – and f–wavelength data with

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a wavelength-based Gaussian function of 14 nm tentatively used for a half of 1/e-bandwidth, respectively.

# RESULTS AND DISCUSSION

**Polymerization.** The Sonogashira–Hagihara coupling polymerizations of 1 with diethynylazobenzenes 2m and 2p were performed to obtain the corresponding polymers with azobenzene chromophore in the main chains. Poly(1-2m) and poly(1-2p) with  $M_n$ 's of 10,700 and 9,400 were obtained in 70 and 86% yields, respectively (Table 1). Polymers with almost

Table 1. Sonogashira–Hagihara Coupling Polymerization of 1 with 2m and  $2p^a$ 

		polymer		
monomer		yield <sup>b</sup> (%)	$M_n^c$	$M_{\rm w}/M_{\rm n}^{\ c}$
1 + 2m	poly(1-2m)	70	10700	1.7
1 + 2p	poly(1-2p)	86	9400	1.8
<sup><i>a</i></sup> Conditions:	$[1]_0 = [2m]_0 = [2m]_0$	$[2p]_0 = 0.20 \text{ M}, [$	PdCl <sub>2</sub> (PPh	$_{3})_{2}] = 0.010$
$M, [PPh_3] =$	0.020 M, [CuI] =	0.030 M, DMI	$F/Et_3N = 3/$	/2 (v/v), 80
°C. 24 h. <sup>b</sup> In	soluble part in M	eOH/acetone =	= 9/1 (v/v)	. <sup>c</sup> Estimated

by SEC measured in THF, polystyrene calibration.

the same  $M_n$ 's were obtained irrespective of the way of substitution. The DP's of poly(1–2m) and poly(1–2p) are calculated to be 18 and 16 from the  $M_n$ 's and formula weights of the monomer units. The helix turns are estimated to be 2–3 (6–1 helix).<sup>49</sup> The solubilities of the two polymers were different. Poly(1–2m) and poly(1–2p) were soluble in CHCl<sub>3</sub>, THF and DMF. Poly(1–2m) was soluble in CH<sub>2</sub>Cl<sub>2</sub> and toluene as well, while poly(1–2p) was not. The solubility of poly(1–2m) was comparatively higher than that of poly(1– 2p), presumably because the main chain of poly(1–2m) is less stiff than that of poly(1–2p). This will be discussed later in this paper.

**Chiroptical Properties of the Polymers.** The CD and UV–vis spectroscopic analysis was performed to obtain information about higher order structures of the polymers. As shown in Figure 1, poly(1-2m) showed intense split-type CD signals in the absorption region of the main chain chromophore in CHCl<sub>3</sub>/THF = 7/3 mixture, while the polymer did not show such intense peaks in either CHCl<sub>3</sub> or THF alone. On the other



Figure 1. CD and UV–vis spectra of poly(1-2m) measured in CHCl<sub>3</sub>, THF, and CHCl<sub>3</sub>/THF = 7/3 (c = 0.03 mM) at 20 °C.

hand, poly(1-2p) exhibited intense CD signals both in CHCl<sub>3</sub> and THF, and in CHCl<sub>3</sub>/THF mixtures with various compositions (Figure 2 and Figure S4, Supporting Informa-



Figure 2. CD and UV–vis spectra of poly(1-2p) measured in CHCl<sub>3</sub> and THF (c = 0.03 mM) at 20 °C.

tion). The CD and UV–vis signals of the polymers did not change over the concentration range of 0.03–0.3 mM or after filtration using a membrane filter with a pore size of 0.45  $\mu$ m.<sup>65</sup> Dynamic light scattering (DLS) measurements of the sample solutions showed no signal assignable to polymer aggregates. These results indicate that the CD signals do not originate from chiral aggregation but from unimolecularly folded helical structures with predominantly one-handed screw sense.<sup>66</sup> The  $\lambda_{\rm max}$  of poly(1–2p) at 390 nm is 76 nm longer than that of poly(1–2m) likely due to the p,p'-linked acobenzene units. The CD intensities of poly(1–2m) varied according to the composition of CHCl<sub>3</sub>/THF mixtures. Figure 3 shows the plot



Figure 3. Plot of g-values of poly(1-2m) at the  $[\theta]_{max}$  wavelengths measured in CHCl<sub>3</sub>/THF mixtures with various compositions (c = 0.03 mM) at 20 °C.

of the Kuhn dissymmetry factor  $g (=\Delta \varepsilon/\varepsilon$ , in which  $\Delta \varepsilon = [\theta]/3,298)^{67}$  of poly(1–2m) observed in CHCl<sub>3</sub>/THF with various compositions at the  $[\theta]_{max}$  wavelengths. The *g*-values give quantitative information associated with the degree of preferential screw sense.<sup>68</sup> As shown in Figure 3, the *g*-value reached a maximum at a ratio of CHCl<sub>3</sub>/THF = 7/3. Poly(1–2p) exhibited the similar trend, although it showed intense CD signals both in CHCl<sub>3</sub> and THF (Figure S4, Supporting

Information). As listed in Table 2, the g-values of poly(1-2p) were almost five times larger than those of poly(1-2m) at the

Table 2.	Absolute	g-Values	of Poly	(1–2m)	and P	Poly(1	1–2p)
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	$ g  \times 10^4$					
polymer	first Cotton	second Cotton				
$poly(1-2m)^a$	5.07	2.49				
$poly(1-2p)^b$	25.1	11.7				
<sup>a</sup> Measured in CHCl <sub>3</sub> /TI	HF = 7/3 ( $c = 0.0$	3 mM). <sup>b</sup> Measured in				
$CHCl_3/THF = 6/4$ (c =	0.03 mM).					

wavelengths of both the first and second Cotton effects. It is considered that the one-handedness is more predominant in the poly(1-2p) helix than in the poly(1-2m) helix.<sup>69</sup> The CD intensities of oligomeric phenyleneethynylene foldamers significantly depend on molecular weights.<sup>70</sup> As mentioned above, the *DP* of poly(1-2p) is smaller than that of poly(1-2m), while the *g*-values of poly(1-2p) are larger than those of poly(1-2m).<sup>71</sup> It is likely that the helix-forming ability of poly(1-2p) is higher than that of poly(1-2m).

Intramolecular hydrogen bonds and  $\pi$ -stacking are the key factors for stabilizing helically folded structures of some poly(phenyleneethnylene)s, in a fashion similar to that of other artificial helical polymers, including polyisocyanide, polyisocyanate, polyacetylene, etc.<sup>33,49,72–74</sup> Solution-state IR spectra of poly(**1–2m**), poly(**1–2p**), and monomer **1** were measured in CHCl<sub>3</sub>/THF = 7/3 and CHCl<sub>3</sub> under diluted conditions (20 mM) to determine the presence/absence of intramolecular hydrogen bonding (Table 3). All the com-

Table 3. Solution-state IR Spectroscopic Data (C=O Absorption Peaks) of the Monomer and Polymers<sup>a</sup>

		wavenumber $(cm^{-1})$		
solvent	compound	carbamate	amide	
$CHCl_3/THF = 7/3$	1	1709	1678	
	poly(1-2m)	1703	1671	
CHCl <sub>3</sub>	1	1701	1677	
	poly(1-2p)	1700	1652	
$^{a}c = 20 \text{ mM}.$				

pounds exhibited two strong absorption peaks assignable to C=O stretching vibrations of the amide and carbamate groups. Poly(1-2m) exhibited the carbamate and amide C=O peaks at 1703 and 1671  $\text{cm}^{-1}$ , which were lower by 6 and 7  $\text{cm}^{-1}$ compared with those of 1, respectively. On the other hand, the carbamate C=O peak of poly(1-2p) was observed at only 1  $cm^{-1}$  lower wavenumber than that of 1, while the amide C=O peak was observed at 25 cm<sup>-1</sup> lower than that of 1. The sample solutions were sufficiently dilute to avoid intermolecular interaction as mentioned above.75 These results indicate that poly(1-2m) forms intramolecular hydrogen bonds between the carbamate and amide groups in  $CHCl_3/THF = 7/3$ mixture. The hydrogen bonds in poly(1-2p) involve amideamide interactions in CHCl<sub>3</sub>. It is assumed that the way of hydrogen bonding affects the helix forming ability of the polymers. More detailed information about the hydrogen bonding will be discussed in the Conformational Analysis part below.

The CD and UV-vis spectra of the polymers were measured upon photoirradiation to examine the photoisomerization behavior. A solution of poly(1-2m) in  $CHCl_3/THF = 7/3$  [the composition at which poly(1-2m) exhibited the largest CD intensities] was irradiated with UV-light through a suitable transmission filter using a high pressure mercury lamp. The intensities of the CD signals gradually decreased upon UV irradiation, and approached a minimum after 16 min (Figure 4). The intensity of the UV-vis signal around 315 nm also



**Figure 4.** CD and UV–vis spectra of poly(1–2m) upon UV-light irradiation ( $300 < \lambda < 400$  nm) for 16 min measured in CHCl<sub>3</sub>/THF = 7/3 (*c* = 0.03 mM) at 20 °C.

decreased, apparently due to the decrease of absorption based on the  $\pi - \pi^*$  transition band of the *trans*-azobenzene units. Although no increase was observed corresponding to the  $n-\pi^*$ of cis-azobenzene, it appears that the trans-azobenzene moieties isomerized into the cis-form, weakening the chirality of the polymer molecule. In helical polymers, the decrease of CD intensity represents the transformation of a helix into a random structure and/or loss of predominance of one-handedness while keeping the total helix content constant. In the present case, it is likely that the decrease of CD intensities is caused by the collapse of helically folded structures. It has been reported that the trans-to-cis photoisomerization of azobenzene units in the main chains of oligo(phenyleneethynylene) derivatives disorders the helically folded structures due to the loss of  $\pi$ -stacking interactions between the folded main chains induced by loss of planarity.<sup>34,36,37</sup> This is predictable from the fact that *trans*azobenzene is linear and planar, while cis-azobenzene is bent. In the present study, the CD intensities of poly(1-2m) decreased by as much as 71% after UV irradiation for 16 min. This is a much larger effect than that of the analogous polymer (10%) with azobenzene moieties on the side chains under the same conditions.<sup>33</sup> This remarkable difference is caused by introducing the azobenzene moieties into the main chain.

Subsequent irradiation with visible light resulted in almost full recovery of the initial CD and UV-vis spectra (Figure S6, Supporting Information), indicating that poly(1-2m) refolded into a helix with isomerization of azobenzene units from *cis* to *trans*. Further reversibility was confirmed upon repeated UVand visible irradiation. As shown in Figure 5, the CD and UVvis intensities were reversible upon alternating UV and visible irradiation for 16-min intervals without remarkable decomposition. This indicates that the folded helical structure was repeatedly deformed and reformed even after 8 cycles of alternating UV and visible irradiation. On the contrary, UV



**Figure 5.** Plot of  $[\theta]_{\text{max}}$  and  $\varepsilon_{\text{max}}$  after repeated photoirradiation cycles: UV (300 <  $\lambda$  < 400 nm) 16 min; then visible (420 nm <  $\lambda$ ) 16 min repeated 8 times; measured in CHCl<sub>3</sub>/THF = 7/3 (*c* = 0.03 mM) at 20 °C.

irradiation did not induce CD or UV-vis spectral changes in poly(1-2p) (Figure 6). After UV irradiation for 16 min, the



**Figure 6.** CD and UV–vis spectra of poly(1-2p) upon UV irradiation (300 <  $\lambda$  < 400 nm) for 16 min measured in CHCl<sub>3</sub> (c = 0.03 mM) at 20 °C.

intensities of the CD and UV–vis signals decreased by only 17% and 1%, respectively. Monomer **2p** was photoisomerized upon UV and visible irradiation; the UV–vis absorption at the  $\lambda_{\text{max}}$  decreased 51% upon UV irradiation for 8 min compared with its initial state (Figure S8, Supporting Information).

The large difference in photoresponse between poly(1-2p)and 2p is explained by an extended azobenzene chromophore of poly(1-2p) due to the *para*-connected phenyleneethynylene unit, which has a lower efficiency of isomerization.<sup>34</sup> This linear repeating unit has a much stronger tendency to  $\pi$ -stack (ideally with itself) that introduces a higher barrier for its isomerization. When azobenzene is incorporated into the main chain of a conjugated polymer at the *p*,*p*'-positions, the  $\pi$ -electrons of azobenzene are delocalized through the conjugated main chain. As a result, the efficiency of the UV-induced  $\pi - \pi^*$  transition localized at azobenzene is decreased in conjunction with the enhanced stiffness of the main chain by extension of conjugation involving azobenzene.<sup>76–78</sup> Azobenzene-containing oligo(phenyleneethynylene)s undergo photoisomerization more efficiently when they take random coil structures compared with helically folded structures because the below and above conjugated plane of unimolecular polymer chain in helix state were strongly interacted in dilute concentration.<sup>37</sup> Consequently, poly(1-2p) hardly undergoes photoisomerization, while poly(1-2m) easily does. It is possible to estimate the photoisomerization ratio of trans-azobenzene moieties from the decrease in the ratio of  $\pi - \pi^*$  absorption.<sup>79</sup> In the present study, however, this measurement was complicated by the overlap of absorption peaks of the azobenzene units and the conjugated main chain. We tried to determine the isomerization ratio by <sup>1</sup>H NMR spectroscopy and SEC measurement, but unfortunately we failed to obtain clear information.

Conformational Analysis. There are several reports regarding the conformational analysis of poly-(phenyleneethynylene)s using the  $MM^{33,49}$  and molecular dynamics simulations.<sup>80–82</sup> In the present study, the geometries were optimized first with the MM method using the MMFF94,<sup>56</sup> second with the semiempirical MO method using the PM6 Hamiltonian, and finally with the DFT method at the M06-2X/6-31G\* level for selected conformers. The M06-2X functional was employed because it is superior compared to the commonly used B3LYP functional in estimating noncovalent interactions including  $\pi$ -stacking and hydrogen bonding,<sup>83,84</sup> both of which are essential for stabilizing the helically folded structures of the present poly(phenyleneethynylene) derivatives. Charts 1-3 summarize the possible stereoregular right- and left-handed helical conformers of poly(1-2m) and poly(1-2p) (12-mer), both of whose chain ends are terminated with hydrogen atoms. The hexyl groups are replaced with methyl groups to save CPU time. Trans zigzag conformers (Chart 4) were also calculated for comparison. The torsional angles of the main chains of right- and left-handed helices were set to  $+6^{\circ}$  and  $-6^{\circ}$  per phenylene unit, respectively, and the azobenzene units were set to a planar structure in the initial geometries.

As shown in Chart 1, poly(1-2m) forms helices with short diameters when the two ethynylene groups at the 3,3'-positions of the azobenzene moiety adopt the "cis" geometry. (Note that the azobenzene moieties are always in the "trans" configurations in these optimized geometries.) One turn consists of two monomer units (denoted 2-1 in Chart 1). In the chart, symbols "R" and "L" represent right- and left-handed helices, respectively. Four stereoregular conformers are possible as right-handed helices considering the directions of the azobenzene and amide/carbamate moieties. Symbols "O" and "I" represent the directions of the azobenzene moieties along the conjugated plane of the main chain, corresponding to bending outside and inside viewed from the top positions. Symbols "A" and "B" represent the two possible directions of the amide/carbamate moieties. In a similar way, four stereoregular conformers are possible as left-handed helices. After geometry optimization by the MMFF94 method using the constraints described above, the amide and carbamate N-H groups of a monomer unit formed stereoregular intramolecular hydrogen bonds with the C=O groups of the amide and carbamate groups two units earlier  $(i + 2 \rightarrow i \text{ N-H} \cdots \text{O} = C$ hydrogen bonding), respectively. Next, the geometries were fully optimized without any constraints by the PM6 method. In

# Chart 1. Possible Regulated 2-1 Helical Conformers of 12-mers of $Poly(1-2m)^a$



"Ten monomer units are omitted at the wavy lines. The torsional angles of the main chains of right- and left-handed helices were set to  $+6^{\circ}$  and  $-6^{\circ}$  per phenylene unit, respectively, and the azobenzene units were set to a planar structure in the initial geometries.

Chart 2. Possible Regulated 6-1 Helical Conformers of 12-mers of  $Poly(1-2m)^a$ 



"Six monomer units are omitted at the wavy lines. The torsional angles of the main chains of right- and left-handed helices were set to  $+1^{\circ}$  and  $-1^{\circ}$  per phenylene unit, respectively, and the azobenzene units were set to a planar structure in the initial geometries.

# Chart 3. Possible Regulated 6-1 Helical Conformers of 12-mers of $Poly(1-2p)^{a}$



<sup>a</sup>Six monomer units are omitted at the wavy lines. The torsional angles of the main chains of right- and left-handed helices were set to  $+1^{\circ}$  and  $-1^{\circ}$  per phenylene unit, respectively, and the azobenzene units were set to a planar structure in the initial geometries.

Chart 4. Trans Zigzag Conformers of 12-mers of Poly(1-2m) and Poly(1-2p)



every case, the regulated  $i + 2 \rightarrow i$  N–H•••O=C hydrogen bonding strands were intact after the semiempirical calculations.

On the other hand, poly(1-2m) forms helices with long diameters when the two ethynylene groups at the 3,3'-positions of the azobenzene adopt the "*trans*" geometry, as shown in Chart 2.

The torsional angles of the main chains of right- and lefthanded helices were set to  $+1^{\circ}$  and  $-1^{\circ}$  per phenylene unit, respectively, and the azobenzene units were set to a planar structure in the initial geometries. One turn consists of six monomer units (denoted 6–1 helices in Chart 2). There are four possible stereoregular conformers according to the directions of the azobenzene and amide/carbamate moieties in right-handed helices, and four left-handed helices as well. The symbols "R/L", "O/I" and "A/B" are employed in the same manner as with the 2-1 helices mentioned above. Stereoregular hydrogen-bonding strands were formed after geometry optimization with constraints described above by the MMFF94 method; the amide and carbamate N-H groups of a monomer unit formed stereoregular intramolecular hydrogen bonds with the C=O groups of the amide and carbamate groups six units earlier  $(i + 6 \rightarrow i \text{ N-H} \cdots \text{O} = C \text{ hydrogen}$ bonding), respectively. The hydrogen bonding strands were intact after full geometry optimization without any constraints by the PM6 method in a fashion similar to the 2-1 helices mentioned above. Judging from the relative energy values calculated by the PM6 method (Table 4), 2-1 helical conformer m-2-1-R-I-A is most likely among the 16 possible stereoregular conformers for poly(1-2m). The geometries of stable conformers were further optimized by the DFT method at the M06-2X/6-31G\* level to confirm the similar trend with the PM6 method. Although PM6 is a semiempirical method, and therefore it is exempt from long CPU time compared with DFT, PM6 is reliable enough for preliminarily estimating the stable conformers of the present polymers involving  $\pi$ -stacking and hydrogen bonding.85 The right-handed helical structure of m-2-1-R-I-A coincides with the first-positive and secondnegative exciton coupling observed in the CD spectra of poly(1-2m) shown in Figure 1. The helical pitch after full optimization with DFT was 3.8 Å, which is consistent with the turns of the helix being near van der Waals contact and comparable to  $\pi$ -stacking between aromatic rings.<sup>86</sup> The trans zigzag conformer was unstable compared with m-2-1-R-I-A by as much as 132.6 kJ/(mol·unit) at the M06-2X/6-31G\* level,

	Table 4.	Relative	Energies	for the	Possible	Conformers	of 12-mer	rs of Poly	(1 - 2m)	and P	oly(1-	-2p)
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	relativ (1	ve energy [kJ/ mol·unit)]	relative energy [kJ/ (mol·unit)]			relative energy [kJ/ (mol·unit)]		
conformer of poly(1-2m)	PM6 <sup>a</sup>	M06-2X/6- 31G* <sup>b</sup>	conformer of poly(1-2m)	PM6 <sup>a</sup>	M06-2X/6- 31G* <sup>b</sup>	conformer of poly(1-2p)	PM6 <sup>a</sup>	M06-2X/6- 31G* <sup>b</sup>
<i>m</i> -trans zigzag	40.2	132.6				p-trans zigzag	59.1	153.9
m-2-1-R-O-A	4.6	С	<i>m</i> -6–1-R-O-A	14.8	с	p-R-O-A	32.7	80.7
m-2-1-R-O-B	2.2	6.4	<i>m</i> -6–1-R-O-B	11.7	44.0	<i>p</i> -R-О-В	33.9	с
<i>m</i> -2–1-R-I-A	0.0	0.0	<i>m</i> -6–1-R-I-A	13.2	с	p-R-I-A	33.2	81.8
m-2-1-R-I-B	6.2	с	<i>m</i> -6–1-R-I-B	10.7	47.4	p-R-I-B	33.7	с
m-2-1-L-O-A	11.8	с	<i>m</i> -6–1-L-O-A	15.4	с	p-L-O-A	47.5	101.0
m-2-1-L-O-B	4.1	13.1	m-6-1-L-O-B	9.6	44.7	<i>p</i> -L-О-В	50.6	с
m-2-1-L-I-A	10.1	С	<i>m</i> -6–1-L-I-A	13.2	41.8	p-L-I-A	50.1	с
m-2-1-L-I-B	5.7	13.9	<i>m</i> -6–1-L-I-B	15.5	с	p-L-I-B	28.7	72.3
<sup>a</sup> Converted using the va	alue of <i>m</i> -	2–1-R-I-A [66.	6 kJ/(mol·unit)] as zero.	<sup>b</sup> Conver	ted using the val	ue of <i>m</i> -2–1-R-I-A [–4	405952.4	kJ/(mol·unit)]

as zero. <sup>c</sup>Not calculated.

definitely due to the absence of  $\pi$ -stacking and hydrogen bonding.

In contrast to poly(1-2m), poly(1-2p) cannot form 2–1 helices because of the geometrical restriction. Poly(1-2p)possibly forms the 6–1 helices presented in Chart 3. The symbols "R/L", "O/I", and "A/B" are used as described above for poly(1-2m) helices. Among the possible eight helical structures, *p*-L-I-B seems to be most stable based on the relative energies calculated by the PM6 and M06-2X/6-31G\* method. However, the left-handed helical structure does not coincide with the exciton coupling of the CD spectra shown in Figure 2.

The CD and UV-vis spectra of the polymers were theoretically simulated by the ZINDO/S method to obtain more structural information. Among the conformers listed in Table 4, *p*-R-I-A successfully gave theoretical CD and UV-vis spectra (Figure 7) that agree well with the observed ones (Figure 2). The theoretical CD spectrum shows the positive first and negative second CD signals assignable to exciton coupling based on the main chain chromophore twisted in right-handed helices. Thus, it is likely that poly(1-2p) adopts a stereoregular 6–1 helically folded conformation like *p*-R-I-A, as



**Figure 7.** CD and UV–vis spectra of *p*-**R**-**I**-**A**. One possible conformer of poly(1–2*p*) simulated by the ZINDO/S ( $n_{\text{states}} = 20$ ) method using the geometries optimized by M06-2X/6-31G<sup>\*</sup>. The red lines indicate  $R_{\text{vel}}$  and *f* values.  $\varepsilon$ ,  $\Delta \varepsilon$ ,  $R_{\text{veb}}$  and *f* of the polymer molecule are divided by 12 as the values per monomer unit.

shown in Figure  $8.^{87}$  We can say that the geometry optimization by PM6 followed by the DFT calculation



Figure 8. Conformation of *p*-R-I-A after geometry optimization by M06-2X/6-31G\*.

reasonably predicts the conformations of the present polymers, and the ZINDO/S method is effective for simulating the CD and UV–vis spectra. We also tried time-dependent DFT calculations but could not obtain the results within the acceptable CPU time.<sup>88</sup>

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In the present study, we have synthesized novel optically active poly(phenyleneethynylene)s containing azobenzene moieties in the main chains [poly(1-2m) and poly(1-2p)] by the Sonogashira-Hagihara coupling polymerization of D-hydroxyphenylglycine-derived monomer 1 with 3,3'- and 4,4'diethynylazobenzenes (2m, 2p). Poly(1-2m) was folded into a predominantly one-handed helix in  $CHCl_3/THF = 7/3$ , but the helix structure is less predominant in CHCl<sub>3</sub> and THF. On the other hand, poly(1-2p) was folded into a helix both in CHCl<sub>3</sub> and THF, and their mixtures. The  $\lambda_{max}$  of poly(1–2p) occurs at a longer wavelength than that of poly(1-2m). Solution state IR measurements revealed the existence of intramolecular hydrogen bonds between the amide and/or carbamate groups at the side chains, and higher hydrogenbonding strength in poly(1-2p) than that in poly(1-2m), in agreement with the higher helicity of poly(1-2p). The folded structure of poly(1-2m) was disrupted upon UV irradiation, which induced the photoisomerization of the azobenzene units

from the planar trans-form to the bent cis-form. The deformed poly(1-2m) refolded into a helix upon visible irradiation as a result of isomerization of the azobenzene units from the cisform to the trans-form. This reversible photoinduced conformational change of poly(1-2m) was further confirmed by cycles of alternating UV and visible irradiation. Thus, incorporation of  $m_{i}m'$ -linked azobenzene units in the main chain is effective in achieving reversible photoresponsive conformational changes of poly(phenyleneethynylene)s. Interestingly, poly(1-2p)showed very little cis-trans photoisomerization of the azobenzene units and polymer conformation. This is explainable from the stiff main chain, which is more strongly stabilized by hydrogen bonding and extended conjugation through  $p_{,p'}$ linked azobenzene units compared with the m,m'-counterpart [poly(1-2m)]. Conformational analysis of the polymers using the MM, semiempirical MO and DFT methods confirmed that the folded helical structures are energetically more stable than the extended trans zigzag structures due to the contribution of  $\pi$ -stacking and hydrogen bonding. At the moment, we could not obtain clear evidence of liquid crystalline properties in these polymers,<sup>89</sup> presumably due to their relatively low molecular weights. Further research to increase the molecular weights is ongoing and may eventually lead to the application of the present polymers as photoswitchable functional materials.

# ASSOCIATED CONTENT

# **S** Supporting Information

SEC, <sup>1</sup>H NMR, and IR spectra of poly(1-2m) and poly(1-2p)(Figures S1–S3), plot of g value of poly(1-2p) measured in various compositions of CHCl<sub>3</sub>/THF (Figure S4), temperature dependence of g values of poly(1-2m) and poly(1-2p)(Figure S5), CD and UV–vis spectra of poly(1-2m) measured in CHCl<sub>3</sub>/THF = 7/3 upon visible irradiation (Figure S6), UV–vis spectra of **2m** and **2p** upon UV and visible irradiation (Figures S7 and S8), and Cartesian coordinates for conformers optimized by the M06-2X/6-31G\* listed in Table 4. This material is available free of charge via the Internet at http:// pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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- (88) We first tried to examine the conformation of 18- and 24-mers but we could not complete the calculations. We therefore calculated 12-mers to save CPU time.
- (89) Poly(1–2m) did not show any liquid crystal texture in CHCl<sub>3</sub>/ THF = 19/1 mixture (up to 25 wt %). Such concentrated solutions of poly(1–2p) could not be prepared due to the lower solubility.