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<td>Sogawa, Hiromitsu; Terada, Kayo; Masuda, Toshio; Sanda, Fumio</td>
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<tr>
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Kyoto University
Synthesis and Properties of Amino Acid-derived Optically Active Photo-responsive Polymers

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Summary
Optically active azobenzenedicarboxylic acids were synthesized from L-alanine, and the polycondensation of the diacids with o-, m-, p-xylylenediols, 5-norbornene-2,3-endo,endo- and exo,exo-dimethanols, m-, p-xylylenediamines, and trans-1,4-cyclohexanediamine was carried in N,N-dimethylformamide. Polymers with weight-average molecular weights of 3,300–33,700 were obtained in 63%–quantitative yields. All the polymers reversibly isomerized the azobenzene units from trans to cis and vice versa upon UV- and visible-light irradiations. The polymers exhibited no evidence for the formation of a chiral secondary structure.

Introduction
Polymers that transform the structures by external stimuli such as temperature [1], pH [2], and light [3,4] gather much interest. Especially, photo-responsive polymers enable the design of highly sensitive photo-functional materials because of easy control over the irradiation wavelength, time, and intensity. Conformational changes of polymers induced by the isomerization of photochromic groups lead to the changes of physical and chemical properties including viscosity, conductivity, solubility, wettability, morphology, and so on [3–8].

Many attempts have been made to synthesize well-defined photo-responsive polymers, where azobenzene [9–12], spiropyran [13–15], and diarylethene [16–19] are commonly introduced as a photo-responsive chromophore at the main chain or side chain. For example, trans-azobenzene absorbs light around 320 nm based on the π−π* transition to transform into cis-azobenzene, and the cis-isomer absorbs light based on the n−π* transition around 430 nm to transform into trans-one reversibly, accompanying large changes of conformation and dipole moment. The cis-form also isomerizes into trans-one upon heating due to the low activation energy from cis to trans. We have previously synthesized conjugated polymers bearing azobenzene moieties in the main chain [20–23], some of which reversibly undergo cis-trans isomerization in spite of the rigid structures. We have also synthesized polyacetylenes substituted with azobenzene at the side chains [24–27]. Among them, chiral polymers form a helical structure with predominantly one-handed screw sense, and the photo-isomerization of the azobenzene moieties triggers the transformation of the secondary
structure to alternate the chiroptical properties. Amino acids are the useful biological chiral resources. Polymers containing amino acids attract attention due to their optical and biological activities [28–33]. In the course of our study on azobenzene-containing conjugated polymers, we have designed novel optically active amino acid-based polymers containing azobenzene moieties in the main chain, expecting the changes of chiroptical properties upon photo-irradiation. This article deals with the polycondensation of optically active azobenzenedicarboxylic acids with diols and diamines, and the photo-isomerization behavior of the obtained polymers (Scheme 1).

![Scheme 1. Synthesis of monomers](image)

**Experimental**

**Measurements**

$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra were recorded on a JEOL EX-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. Specific rotations ($[\alpha]_D$) were measured on a JASCO DIP-100 digital polarimeter with a sodium lamp as a light source. Elemental analysis was done at the Microanalytical Center of Kyoto University. Number- and weight-average molecular weights ($M_n$ and $M_w$) of polymers were determined by gel permeation chromatography (GPC) on TSK gel α-3000, using a solution of LiBr (10 mM) in $N,N$-dimethylformamide (DMF) as an eluent at a flow rate of 1.0 mL/min, calibrated by polystyrene standards at 40 °C. UV–vis absorption spectra were recorded on a JASCO J-820 spectropolarimeter.

**Materials**

All the reagents and solvents were used as purchased without purification.

**Synthesis of $\text{1m}$**

3,3'-Azobenzenedicarboxylic acid (1.08 g, 4.00 mmol) was dissolved in DMF (12 mL), and triethylamine (1.23 mL, 8.80 mmol) was added to the solution at room temperature. L-Alanine methyl ester hydrochloride (1.23 g, 8.80 mmol) and 4-[4,6-dimethoxy-1,3,5-triazin-2-yl]-4-methylmorpholinium chloride (TRIAZIMOCH, Tokuyama Co., 2.86 g, 8.80 mmol) were added to the mixture, and the resulting mixture was stirred at room temperature overnight. DMF was then distilled off using a rotary evaporator, and the residue was dissolved in CH$_2$Cl$_2$. The solution was washed with 0.5 M HCl, saturated NaHCO$_3$ aq., saturated NaCl aq., and then dried over anhydrous MgSO$_4$. The residue was purified by recrystallization with methanol/ethyl
acetate to obtain 1m as orange solid in 54%. Mp 192–194 °C. [α]D +40° (c = 0.100 g/dL in DMF at room temperature). 1H NMR (400 MHz, CDCl3): δ 1.57 (s, 6H, -CHCH3-), 3.82 (s, 6H, -OCH3), 4.80-4.87 (m, 2H, -CHCH2-), 6.83 (d, 2H, -CHNH-), 7.95-8.01 (m, 8H, Ar). 13C NMR (100 MHz, CDCl3): δ 18.7 (-CH2), 48.6 (-CHCH2-), 123.2, 128.1, 136.1, 154.2 (Ar), 166.0 (-NHCO-), 173.6 (-COOCH3). Anal. Calcd for C22H24N4O6: C, 59.99; H, 5.49; N, 12.72. Found: C, 59.71; H, 5.41; N, 12.76.

Synthesis of 2m
0.5 M NaOH aq. (8.00 mL, 4.00 mmol) was added to a suspension of 1m (0.805 g, 1.81 mmol) in acetone (40 mL), and the mixture was stirred at 30 °C for 6 h. 0.5 M HCl aq. (8.00 mL, 4.00 mmol) was added to the resultant mixture, and it was concentrated on a rotary evaporator. The residual solid was washed with ethyl acetate to obtain 2m as orange solid in 86% yield. Mp 256–257 °C. [α]D +80° (c = 0.100 g/dL in DMF at room temperature). 1H NMR (400 MHz, DMSO-d6): δ 1.42 (d, J = 7.4 Hz, 6H, -CHC3-), 4.42-4.49 (m, 2H, -CHCH3-), 7.73 (t, J = 7.8 Hz, 2H, Ar), 8.09 (d, J = 7.6 Hz, 4H, Ar), 8.44 (s, 2H, Ar), 8.94 (d, J = 7.1 Hz, 2H, -CHCH2NH2-), 12.5 (s, 2H, -COOH). 13C NMR (100 Hz, CDCl3): δ 16.9 (-CHC3-), 48.3 (-CHCH3-), 121.4, 125.4, 129.7, 130.6, 135.3, 151.7 (Ar), 165.3 (-NHCO-), 174.1 (-COOH). Anal. Calcd for C20H20N4O6: C, 58.25; H, 4.89; N, 13.59. Found: C, 57.96; H, 4.91; N, 13.48.

Synthesis of 1p
The title compound was synthesized from 4,4'-azobenzenedicarboxylic acid and L-alanine methyl ester hydrochloride in a manner similar to 1m. Yield 49%. Mp 231–233 °C. 1H NMR (400 MHz, CDCl3): δ 1.57 (s, 6H, -CHCH3-), 3.82 (s, 6H, -OCH3), 4.80-4.87 (m, 2H, -CHCH2-), 6.83 (d, 2H, -CHNH-), 7.95-8.01 (m, 8H, Ar). 13C NMR (100 MHz, CDCl3): δ 16.9 (-CHCH2-), 48.3 (-CHCH2-), 123.2, 128.1, 136.1, 154.2 (Ar), 166.0 (-NHCO-), 173.6 (-COOCH3).

Synthesis of 2p
The title compound was synthesized from 2p in a manner similar to 2m. Yield 98%. No mp was observed up to 281 °C (decomposition). [α]D +120° (c = 0.100 g/dL in DMF at room temperature). 1H NMR (400 MHz, DMSO-d6): δ 1.42 (d, J = 7.7 Hz, 6H, -CHCH3-), 4.39-4.48 (m, 2H, -CHCH2-), 8.00 (d, J = 8.3 Hz, 4H, Ar), 8.11 (d, J = 8.3 Hz, 4H, Ar), 8.88 (d, J = 7.1 Hz, 2H, -CHCH2NH2-), 12.6 (s, 2H, -COOH). 13C NMR (100 MHz, CDCl3): δ 16.8 (-CHCH2-), 48.3 (-CHCH2-), 122.6, 128.8, 136.5, 153.3 (Ar), 165.3 (-NHCO-), 174.1 (-COOH). Anal. Calcd for C20H20N4O6: C, 58.25; H, 4.89; N, 13.59. Found: C, 57.89; H, 4.86; N, 13.38.

Polycondensation: A typical procedure
A solution of 2m (166 mg, 0.402 mmol), 3 (56 mg, 0.405 mmol), 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (EDC•HCl, 162 mg, 0.845 mmol), and 4-(dimethylamino)pyridine (DMAP, 10 mg, 0.081 mmol) in DMF (0.8 mL) was stirred at 30 °C for 24 h. The resulting mixture was poured into a large amount of 0.5 M NaHCO3 aq. to precipitate a solid polymer. It was washed with 0.5 M NaHCO3 aq., separated by filtration with a membrane filter (pore size 0.2 μm), and dried in vacuo.
Spectroscopic Data of the Polymers

Poly(2m-3) $^1$H NMR (400 MHz, DMSO-$_d_6$): $\delta$ 1.44 (br, 6H, -CHCH$_3$), 4.54 (br, 2H, -CHCH$_3$), 5.20 (br, 4H, -CH$_2$O), 7.23-7.40 (br, 4H, Ar), 7.72 (br, 2H, Ar), 8.09 (br, 4H, Ar), 8.42 (br, 2H, Ar), 9.09 (br, 2H, -NHCO). IR (cm$^{-1}$, KBr): 2877 (CH), 1744 (COO), 1647 (C=O), 1528 (NHCO), 1303, 1206, 1157, 758, 691.

Poly(2m-4) $^1$H NMR (400 MHz, DMSO-$_d_6$): $\delta$ 1.44 (br, 6H, -CHCH$_3$), 4.54 (br, 2H, -CHCH$_3$), 5.16 (br, 4H, -CH$_2$O), 7.23-7.30 (br, 4H, Ar), 7.72 (br, 2H, Ar), 8.08 (br, 4H, Ar), 8.50 (br, 2H, Ar), 9.09 (br, 2H, -NHCO). IR (cm$^{-1}$, KBr): 2987 (CH), 1745 (COO), 1653 (C=O), 1527 (NHCO), 1304, 1205, 1157, 691.

Poly(2m-5) $^1$H NMR (400 MHz, DMSO-$_d_6$): $\delta$ 1.44 (br, 6H, -CHCH$_3$), 4.54 (br, 2H, -CHCH$_3$), 5.13 (br, 4H, -CH$_2$O), 7.23-7.34 (br, 4H, Ar), 7.92-8.21 (br, 4H, Ar), 8.51 (br, 2H, Ar), 9.09 (br, 2H, -NHCO). IR (cm$^{-1}$, KBr): 2986 (CH), 1744 (COO), 1647 (C=O), 1527 (NHCO), 1306, 1209, 1157, 813.

Poly(2m-6) $^1$H NMR (400 MHz, DMSO-$_d_6$): $\delta$ 1.30-1.72 (br, 8H, -CHCH$_3$-$\text{bridge}$ position), 2.20 (br, 2H, norbornene CH$_2$), 2.82-3.35 (br, 6H, norbornene CH, -CH$_2$O), 4.46 (br, 2H, -CHCH$_3$), 6.06 (br, 2H, -CH=CH$_2$), 7.70 (br, 2H, Ar), 8.09-8.21 (br, 4H, Ar), 8.42 (br, 2H, Ar), 9.09 (br, 2H, -NHCO). IR (cm$^{-1}$, KBr): 2979 (CH), 1746 (COO), 1606 (C=O), 1524 (NHCO), 1302, 1210, 1156, 997.

Poly(2m-7) $^1$H NMR (400 MHz, DMSO-$_d_6$): $\delta$ 1.39-1.71 (br, 8H, -CHCH$_3$-$\text{bridge}$ position), 2.16 (br, 2H, norbornene CH$_2$), 2.82-3.35 (br, 6H, norbornene CH, -CH$_2$O), 4.42 (br, 2H, -CHCH$_3$), 6.09 (br, 2H, -CH=CH$_2$), 7.72 (br, 2H, Ar), 8.09-8.21 (br, 4H, Ar), 8.42 (br, 2H, Ar), 9.08 (br, 2H, -NHCO). IR (cm$^{-1}$, KBr): 2980 (CH), 1746 (COO), 1647 (C=O), 1536 (NHCO), 1306, 1209, 1157, 813.

Poly(2m-8) $^1$H NMR (400 MHz, DMSO-$_d_6$): $\delta$ 1.41 (br, 6H, -CHCH$_3$), 4.02 (br, 4H, -CH$_2$NH), 4.55 (br, 2H, -CHCH$_3$), 7.14-7.37 (br, 4H, Ar), 7.72 (br, 2H, Ar), 8.08 (br, 4H, Ar), 8.52 (br, 2H, Ar), 8.58 (br, 2H, -CH$_2$NH), 8.94 (br, 2H, -NHCO). IR (cm$^{-1}$, KBr): 2988 (CH), 1640 (C=O), 1536 (NHCO), 1326, 1218, 692.

Poly(2m-9) $^1$H NMR (400 MHz, DMSO-$_d_6$): $\delta$ 1.39 (br, 6H, -CHCH$_3$), 4.11 (br, 4H, -CH$_2$NH), 5.04 (br, 2H, -CHCH$_3$), 7.14 (br, 4H, Ar), 7.71 (br, 2H, Ar), 8.11 (br, 4H, Ar), 8.46 (br, 4H, Ar), 8.81 (br, 2H, -NHCO), 9.93 (br, 2H, -CH$_2$NH). IR (cm$^{-1}$, KBr): 2940 (CH), 1651 (C=O), 1526 (NHCO), 1306, 758, 691.

Poly(2m-10) $^1$H NMR (400 MHz, DMSO-$_d_6$): $\delta$ 1.06-1.18 (br, 8H, -C$_6$H$_3$-), 1.41 (br, 6H, -CHCH$_3$), 1.72 (br, 2H, -C$_6$H$_3$-), 4.45 (br, 2H, -CHCH$_3$), 7.73 (br, 2H, Ar), 8.09 (br, 4H, Ar), 8.43 (br, 4H, Ar), 8.71 (br, 2H, -CH$_2$NH), 9.09 (br, 2H, -NHCO). IR (cm$^{-1}$, KBr): 2938 (CH), 1647 (C=O), 1523 (NHCO), 1304, 1210, 1157.

Poly(2p-3) $^1$H NMR (400 MHz, DMSO-$_d_6$): $\delta$ 1.44 (br, 6H, -CHCH$_3$), 4.54 (br, 2H, -CHCH$_3$), 5.17 (br, 4H, -CH$_2$O), 6.67 (br, 2H, -NHCO), 7.00-7.41 (br, 4H, Ar), 7.94 (br, 4H, Ar), 8.09 (br, 4H, Ar). IR (cm$^{-1}$, KBr): 2960 (CH), 1818 (COO), 1647 (C=O), 1604, 1515 (NHCO), 1250, 1172, 1087, 1021.

Poly(2p-4) $^1$H NMR (400 MHz, DMSO-$_d_6$): $\delta$ 1.44 (br, 6H, -CHCH$_3$), 4.54 (br, 2H, -CHCH$_3$), 5.17 (br, 4H, -CH$_2$O), 6.67 (br, 2H, -NHCO), 7.00-7.41 (br, 4H, Ar), 7.94 (br, 4H, Ar), 8.09 (br, 4H, Ar). IR (cm$^{-1}$, KBr): 2959 (CH), 1818 (COO), 1647 (C=O), 1604, 1516 (NHCO), 1317.
Photo-irradiation was carried out with a 400 W high-pressure mercury lamp equipped 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 nm < \( \lambda \) < 400 nm or with an L-42 filter (Toshiba) for irradiation at 420 nm < \( \lambda \). Sample solutions were fed in a quartz cell, and it was placed 20 cm apart from the lamp. The photo-isomerization was monitored by UV–vis absorption spectroscopy.

**Results and discussion**

**Polycondensation**

The polycondensation of 2m and 2p with diols 3–7 and diamines 8–10 was carried out using EDC•HCl as a condensation agent in the presence of DMAP in DMF at 30 °C for 24 h (Scheme 2). As summarized in Table 1, polymers with \( M_w \)’s of 3,300–33,700.
Scheme 1. Polycondensation of 2m and 2p with diols 3–7 and diamines 8–10

Table 1. Polymerization of 1 and 2a

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Polymer</th>
<th>Yield (%)</th>
<th>$M_w^d</th>
<th>M_w/M_n^d</th>
<th>[\alpha]_D^f (deg)</th>
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<tr>
<td>2m+3</td>
<td></td>
<td>89b</td>
<td>4,800</td>
<td>1.8</td>
<td>10</td>
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<tr>
<td>2m+4</td>
<td></td>
<td>86b</td>
<td>7,500</td>
<td>1.7</td>
<td>6</td>
</tr>
<tr>
<td>2m+5</td>
<td></td>
<td>86b</td>
<td>8,100</td>
<td>2.2</td>
<td>0</td>
</tr>
<tr>
<td>2m+6</td>
<td></td>
<td>80b</td>
<td>6,600</td>
<td>1.8</td>
<td>2</td>
</tr>
<tr>
<td>2m+7</td>
<td></td>
<td>70b</td>
<td>4,500</td>
<td>1.9</td>
<td>3</td>
</tr>
<tr>
<td>2m+8</td>
<td></td>
<td>65c</td>
<td>3,300</td>
<td>1.4</td>
<td>4</td>
</tr>
<tr>
<td>2m+9</td>
<td></td>
<td>95c</td>
<td>19,600</td>
<td>3.2</td>
<td>4</td>
</tr>
<tr>
<td>2m+10</td>
<td></td>
<td>63c</td>
<td>7,600</td>
<td>1.5</td>
<td>8</td>
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<tr>
<td>2p+3</td>
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<td>8,000</td>
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<td>_c</td>
<td>_c</td>
<td>_c</td>
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<td>3,500</td>
<td>1.5</td>
<td>55</td>
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<td>2p+9</td>
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<td>78c</td>
<td>23,800</td>
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<tr>
<td>2p+10</td>
<td></td>
<td>85c</td>
<td>8,200</td>
<td>2.5</td>
<td>15</td>
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aConditions: [2m]_0 = [2p]_0 = [3–10]_0 = 0.5 M, [EDC•HCl] = 1.1 M, [DMAP] = 0.1 M in DMF at 30 °C for 24 h. bNaHCO₃ aq.-insoluble part. c0.5 M HCl-insoluble part. dEstimated by GPC based on polystyrene standard; eluent, LiBr solution in DMF (10 mM). eNot determined. fMeasured by polarimetry at room temperature, c = 0.10 g/dL in DMF. gMeasured in DMSO. [\alpha]_D of monomers, 2m: +80 deg, 2p: +120 deg.
were obtained in 63–99% yields. Except for poly(2p-6), the polymers were soluble in DMF and DMSO while insoluble in hexane and toluene (Table 2). Poly(2p-6) became insoluble in DMF after isolation even though it was soluble during the polycondensation. The para-azobenzene-derived polymers tended to be less soluble than the meta-counterparts, presumably due to the larger stiffness of the para-linked backbone [34].

Table 2. Solubility of the polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Hexane</th>
<th>Toluene</th>
<th>CHCl3</th>
<th>CH2Cl2</th>
<th>THF</th>
<th>MeOH</th>
<th>DMF</th>
<th>DMSO</th>
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</thead>
<tbody>
<tr>
<td>Poly(2m-3)</td>
<td>−</td>
<td>−</td>
<td>+</td>
<td>±</td>
<td>+</td>
<td>±</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Poly(2m-4)</td>
<td>−</td>
<td>−</td>
<td>+</td>
<td>±</td>
<td>+</td>
<td>±</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Poly(2m-5)</td>
<td>−</td>
<td>−</td>
<td>±</td>
<td>±</td>
<td>±</td>
<td>±</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Poly(2m-6)</td>
<td>−</td>
<td>−</td>
<td>±</td>
<td>±</td>
<td>±</td>
<td>±</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Poly(2m-7)</td>
<td>−</td>
<td>−</td>
<td>±</td>
<td>±</td>
<td>±</td>
<td>±</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Poly(2m-8)</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>±</td>
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<tr>
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<td>−</td>
<td>−</td>
<td>−</td>
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<td>±</td>
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<tr>
<td>Poly(2p-3)</td>
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<tr>
<td>Poly(2p-4)</td>
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<td>−</td>
<td>±</td>
<td>±</td>
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<td>±</td>
<td>+</td>
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<tr>
<td>Poly(2p-9)</td>
<td>−</td>
<td>−</td>
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<td>−</td>
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<tr>
<td>Poly(2p-10)</td>
<td>−</td>
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*Symbols: +, soluble; −, insoluble; ±, partly insoluble.

Photo-isomerization

Polymer solutions in DMF were irradiated with UV light at a wave length of 300 nm < λ < 400 nm at 20 °C. The isomerization of azobenzene unit was monitored by UV–vis absorption spectroscopy. As shown in Figure 1, poly(2m-3) strongly absorbed light at 320 nm, which is attributable to the π–π* transition band of trans-azobenzene units. This absorption remarkably decreased the intensity upon UV-light irradiation. Simultaneously, a weak absorption attributable to the n–π* transition band of cis-azobenzene units appeared around 440 nm, and increased the intensity. Poly(2p-3) also exhibited the photo-isomerization in a manner similar to poly(2m-3) as shown in Figure 1, but the degree of isomerization was much lower. It was estimated that the trans/cis contents of azobenzene units of poly(2m-3) and poly(2p-3) were 41/59 and 83/17, respectively, after UV-light irradiation in DMF for 32 min, based on the assumption that all azobenzene units existed in trans form at the initial state, and the
absorption around 320–340 nm was derived from trans-azobenzene units [35]. Also the monomer 2m and 2p had 23/77 and 40/60 of trans/cis contents, respectively, after 32 min UV-light irradiation in the same conditions. It is likely that para-linked azobenzene units are unfavorable to photo-isomerization compared with meta-linked ones, and seem to be amplified by becoming the polymer. This is because para-linked azobenzene units in the trans-form are more conjugated than meta-linked ones. In fact, the $\lambda_{\text{max}}$ and band edge of the $\pi-\pi^*$ transition band of poly(2p-3) appeared at 340 nm, 20 nm longer than that of poly(2m-3). It presumed that this conjugation effects suppressed the photo-isomerization of para-linked polymer.

![Figure 1](image1.png)

**Figure 1.** UV–vis spectra of poly(2m-3) and poly(2p-3) with irradiation at 300 < $\lambda$ < 400 nm measured in DMF ($c = 0.05$ mM) at 20 °C.

Poly(2m-4)–poly(2m-10) exhibited UV–vis spectroscopic changes in a manner similar to poly(2m-3), and poly(2p-4)–poly(2p-10) did similarly to poly(2p-3). The absorption around 320 nm decreased to 12–64% of the initial state to reach a constant value by UV-light irradiation for 32–48 min. These spectral changes clearly show that trans-to-cis photo-isomerization of azobenzene moieties took place at the polymer main chain.

Next, the UV-light irradiated samples were further irradiated with visible light to check the reversibility of photo-isomerization of the azobenzene units. As shown in Figure 2, poly(2m-3) and poly(2p-3) gradually increased the absorption around 320–340 nm and decreased that around 440 nm as visible-light irradiation. After 8–32 min, the polymers recovered the UV–vis absorption at the pre-irradiation state. These spectral changes indicate the proceeding of reversible cis-to-trans photo-isomerization of azobenzene moieties in the polymers without degradation. As described above, the para-linked polymers, poly(2p-3)–poly(2p-10), isomerized the azobenzene units from trans to cis (12–40%) less than the meta-linked counterparts, poly(2m-3)–poly(2m-10) (55–65%) upon UV-light irradiation.

The CD spectra of the polymers were measured in DMF ($c = 0.05$ mM) at 20 °C with UV- and visible-light irradiations to obtain information on the chiroptical property. Unfortunately however, no CD signal was observed before and after the photo-irradiation, indicating that these polymers did not form a higher order structure.
The fluorescene spectra of the monomers and polymers were also measured in the same conditions, but no emission was observed before and after the photo-irradiation.

**Figure 2.** UV–vis spectra of poly(2m-3) and poly(2p-3) with irradiation at 420 nm < \( \lambda \), after irradiation at 300 < \( \lambda \) < 400 nm for 32 min measured in DMF (c = 0.05 mM) at 20 °C.

**Conclusion**

In this article, we have demonstrated the polycondensation of optically active azobenzenedicarboxylic acids with various diols and diamines. The polymers obtained reversibly isomerized the azobenzene units from \textit{trans} to \textit{cis}, and \textit{cis} to \textit{trans} upon UV- and visible-light irradiations, which were confirmed by UV–vis absorption spectroscopy. CD spectroscopic study revealed that the polymers did not form a higher-order structure before and after the photo-irradiation. A stiffer main chain such as phenyleneethynylene seems to be necessary to accomplish the preparation of photo-responsive polymers with a regulated secondary structure [36]. Further study on molecular design of photo-responsive optically active polymers is now under progress.

**Acknowledgement**

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**References**