

Synthesis and properties of amino acid-derived optically active photo-responsive polymers

Hiromitsu Sogawa · Kayo Terada · Toshio Masuda · Fumio Sanda

Received: 17 December 2008 / Revised: 16 June 2009 / Accepted: 17 June 2009 /
Published online: 26 June 2009
© Springer-Verlag 2009

Abstract 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.

Keywords Azobenzene · Polymer · Photo-isomerization

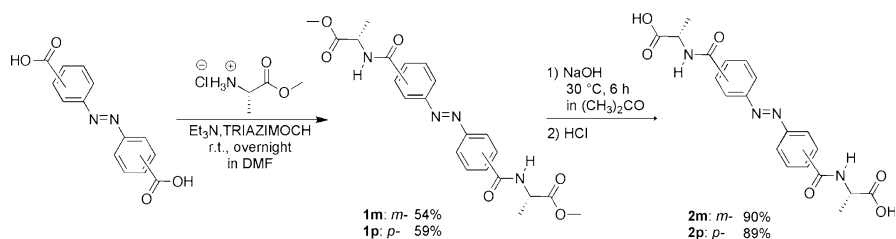
Introduction

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].

H. Sogawa · K. Terada · T. Masuda · F. Sanda (✉)
Department of Polymer Chemistry, Graduate School of Engineering,
Kyoto University, Kyoto 615-8510, Japan
e-mail: sanda@adv.polym.kyoto-u.ac.jp

Present Address:

T. Masuda
Department of Environmental and Biological Chemistry, Faculty of Engineering,
Fukui University of Technology, 3-6-1 Gakuen, Fukui 910-8505, Japan



Scheme 1 Synthesis of monomers

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 azobenzene dicarboxylic acids with diols and diamines, and the photo-isomerization behavior of the obtained polymers (Scheme 1).

Experimental

Measurements

^1H (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 **1m**

3,3'-Azobenedicarboxylic 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 (TRIAZIM-OCH, 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 CH₂Cl₂. The solution was washed with 0.5 M HCl, saturated NaHCO₃ aq., saturated NaCl aq., and then dried over anhydrous MgSO₄. 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, –CHCH₃–), 6.83 (d, 2H, –CHNH–), 7.95–8.01 (m, 8H, Ar). ¹³C NMR (100 MHz, CDCl₃): δ 18.7 (–CHCH₃–), 48.6 (–CHCH₃–), 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-*d*₆): δ 1.42 (d, *J* = 7.4 Hz, 6H, –CHCH₃–), 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, –CHCH₃NH–), 12.5 (s, 2H, –COOH). ¹³C NMR (100 Hz, CDCl₃): δ 16.9 (–CHCH₃–), 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'-azobenedicarboxylic acid and L-alanine methyl ester hydrochloride in a manner similar to **1m**. Yield 49%. Mp

231–233 °C. ^1H NMR (400 MHz, CDCl_3): δ 1.57 (s, 6H, $-\text{CHCH}_3-$), 3.82 (s, 6H, $-\text{OCH}_3$), 4.80–4.87 (m, 2H, $-\text{CHCH}_3-$) 6.83 (d, 2H, $-\text{CHNH}-$), 7.95–8.01 (m, 8H, Ar). ^{13}C NMR (100 MHz, CDCl_3): δ 18.7 ($-\text{CHCH}_3-$), 48.6 ($-\text{CHCH}_3-$), 123.2, 128.1, 136.1, 154.2 (Ar), 166.0 ($-\text{NHCO}-$), 173.6 ($-\text{COOCH}_3$).

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). $[\alpha]_D^{20} +120^\circ$ ($c = 0.100$ g/dL in DMF at room temperature). ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 1.42 (d, $J = 7.7$ Hz, 6H, $-\text{CHCH}_3-$), 4.39–4.48 (m, 2H, $-\text{CHCH}_3-$), 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, $-\text{CHCH}_3\text{NH}-$) 12.6 (s, 2H, $-\text{COOH}$). ^{13}C NMR (100 MHz, CDCl_3): δ 16.8 ($-\text{CHCH}_3-$), 48.3 ($-\text{CHCH}_3-$), 122.6, 128.8, 136.5, 153.3 (Ar), 165.3 ($-\text{NHCO}-$), 174.1 ($-\text{COOH}$). Anal. Calcd for $\text{C}_{20}\text{H}_{20}\text{N}_4\text{O}_6$: 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 NaHCO_3 aq. to precipitate a solid polymer. It was washed with 0.5 M NaHCO_3 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**) ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 1.44 (br, 6H, $-\text{CHCH}_3-$), 4.54 (br, 2H, $-\text{CHCH}_3-$), 5.20 (br, 4H, $-\text{CH}_2\text{O}-$), 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, $-\text{NHCO}-$). IR (cm^{-1} , KBr): 2,877 (CH), 1,744 (COO), 1,647 (C = O), 1,528 (NHCO), 1,303, 1,206, 1,157, 758, 691.

Poly(**2m-4**) ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 1.44 (br, 6H, $-\text{CHCH}_3-$), 4.54 (br, 2H, $-\text{CHCH}_3-$), 5.16 (br, 4H, $-\text{CH}_2\text{O}-$), 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, $-\text{NHCO}-$). IR (cm^{-1} , KBr): 2,987 (CH), 1,745 (COO), 1,653 (C = O), 1,527 (NHCO), 1,304, 1,205, 1,157, 691.

Poly(**2m-5**) ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 1.44 (br, 6H, $-\text{CHCH}_3-$), 4.54 (br, 2H, $-\text{CHCH}_3-$), 5.13 (br, 4H, $-\text{CH}_2\text{O}-$), 7.23–7.34 (br, 4H, Ar), 7.72 (br, 2H, Ar), 7.92–8.21 (br, 4H, Ar), 8.51 (br, 2H, Ar), 9.09 (br, 2H, $-\text{NHCO}-$). IR (cm^{-1} , KBr): 2,986 (CH), 1,744 (COO), 1,647 (C = O), 1,527 (NHCO), 1,306, 1,209, 1,157, 813.

Poly(**2m-6**) ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 1.30–1.72 (br, 8H, $-\text{CHCH}_3-$ bridge position), 2.20 (br, 2H, norbornene CH), 2.82–3.35 (br, 6H, norbornene CH, $-\text{CH}_2\text{O}-$), 4.46 (br, 2H, $-\text{CHCH}_3-$), 6.06 (br, 2H, $-\text{CH} = \text{CH}-$), 7.70 (br, 2H, Ar), 8.09–8.21 (br, 4H, Ar), 8.42 (br, 2H, Ar), 9.09 (br, 2H, $-\text{NHCO}-$). IR (cm^{-1} , KBr): 2,979 (CH), 1,746 (COO), 1,606 (C = O), 1,524 (NHCO), 1,302, 1,210, 1,156, 997.

Poly(**2m-7**) ^1H NMR (400 MHz, DMSO- d_6): δ 1.39–1.71 (br, 8H, $-\text{CHCH}_3-$ bridge position), 2.16 (br, 2H, norbornene CH), 2.82–3.35 (br, 6H, norbornene CH , $-\text{CH}_2\text{O}-$), 4.42 (br, 2H, $-\text{CHCH}_3-$), 6.09 (br, 2H, $-\text{CH} = \text{CH}-$), 7.72 (br, 2H, Ar), 8.09–8.21 (br, 4H, Ar), 8.42 (br, 2H, Ar), 9.08 (br, 2H, $-\text{NHCO}-$). IR (cm^{-1} , KBr): 2,980 (CH), 1,746 (COO), 1,647 (C = O), 1,536 (NHCO), 1,306, 1,209, 1,157, 813.

Poly(**2m-8**) ^1H NMR (400 MHz, DMSO- d_6): δ 1.41 (br, 6H, $-\text{CHCH}_3-$), 4.02 (br, 4H, $-\text{CH}_2\text{NH}-$), 4.55 (br, 2H, $-\text{CHCH}_3-$), 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, $-\text{CH}_2\text{NH}-$), 8.94 (br, 2H, $-\text{NHCO}-$). IR (cm^{-1} , KBr): 2,988 (CH), 1,640 (C = O), 1,536 (NHCO), 1,326, 1,218, 692.

Poly(**2m-9**) ^1H NMR (400 MHz, DMSO- d_6): δ 1.39 (br, 6H, $-\text{CHCH}_3-$), 4.11 (br, 4H, $-\text{CH}_2\text{NH}-$), 5.04 (br, 2H, $-\text{CHCH}_3-$), 7.14 (br, 4H, Ar), 7.71 (br, 2H, Ar), 8.11 (br, 4H, Ar), 8.46 (br, 4H, Ar), 8.81 (br, 2H, $-\text{NHCO}-$), 9.93 (br, 2H, $-\text{CH}_2\text{NH}-$). IR (cm^{-1} , KBr): 2,940 (CH), 1,651 (C = O), 1,526 (NHCO), 1,306, 758, 691.

Poly(**2m-10**) ^1H NMR (400 MHz, DMSO- d_6): δ 1.06–1.18 (br, 8H, $-\text{C}_6\text{H}_8\text{H}_2-$), 1.41 (br, 6H, $-\text{CHCH}_3-$), 1.72 (br, 2H, $-\text{C}_6\text{H}_8\text{H}_2-$), 4.45 (br, 2H, $-\text{CHCH}_3-$), 7.73 (br, 2H, Ar), 8.09 (br, 4H, Ar), 8.43 (br, 4H, Ar), 8.71 (br, 2H, $-\text{CH}_2\text{NH}-$), 9.09 (br, 2H, $-\text{NHCO}-$). IR (cm^{-1} , KBr): 2,938 (CH), 1,647 (C = O), 1,523 (NHCO), 1,304, 1,210, 1,157.

Poly(**2p-3**) ^1H NMR (400 MHz, DMSO- d_6): δ 1.44 (br, 6H, $-\text{CHCH}_3-$), 4.54 (br, 2H, $-\text{CHCH}_3-$), 5.17 (br, 4H, $-\text{CH}_2\text{O}-$), 6.67 (br, 2H, $-\text{NHCO}-$), 7.22–7.41 (br, 4H, Ar), 7.94 (br, 4H, Ar), 8.09 (br, 4H, Ar). IR (cm^{-1} , KBr): 2,960 (CH), 1,818 (COO), 1,647 (C = O), 1,604, 1,515 (NHCO), 1,250, 1,172, 1,087, 1,021.

Poly(**2p-4**) ^1H NMR (400 MHz, DMSO- d_6): δ 1.44 (br, 6H, $-\text{CHCH}_3-$), 4.54 (br, 2H, $-\text{CHCH}_3-$), 5.17 (br, 4H, $-\text{CH}_2\text{O}-$), 6.67 (br, 2H, $-\text{NHCO}-$), 7.22–7.41 (br, 4H, Ar), 7.94 (br, 4H, Ar), 8.09 (br, 4H, Ar). IR (cm^{-1} , KBr): 2,959 (CH), 1,818 (COO), 1,647 (C = O), 1,604, 1,516 (NHCO), 1,317.

Poly(**2p-5**) ^1H NMR (400 MHz, DMSO- d_6): δ 1.45 (br, 6H, $-\text{CHCH}_3-$), 4.46 (br, 2H, $-\text{CHCH}_3-$), 5.14 (br, 4H, $-\text{CH}_2\text{O}-$), 6.69 (br, 2H, $-\text{NHCO}-$), 7.27–7.30 (br, 4H, Ar), 8.00 (br, 4H, Ar), 8.12 (br, 4H, Ar). IR (cm^{-1} , KBr): 2,964 (CH), 1,818 (COO), 1,647 (C = O), 1,604, 1,514 (NHCO), 1,317.

Poly(**2p-6**) ^1H NMR (400 MHz, DMSO- d_6): δ 1.27–1.78 (br, 8H, $-\text{CHCH}_3-$ bridge position), 2.35 (br, 2H, norbornene CH), 2.71–3.35 (br, 6H, norbornene CH , $-\text{CH}_2\text{O}-$), 4.45 (br, 2H, $-\text{CHCH}_3-$), 6.06 (br, 2H, $-\text{CH} = \text{CH}-$), 6.63 (br, 2H, $-\text{NHCO}-$), 8.09 (br, 4H, Ar), 8.13 (br, 4H, Ar). IR (cm^{-1} , KBr): 2,984 (CH), 1,815 (COO), 1,604, 1,487 (NHCO), 1,177, 1,113.

Poly(**2p-7**) ^1H NMR (400 MHz, DMSO- d_6): δ 1.30–1.87 (br, 8H, $-\text{CHCH}_3-$ bridge position), 2.35 (br, 2H, norbornene CH), 2.71–3.35 (br, 6H, norbornene CH , $-\text{CH}_2\text{O}-$), 4.56 (br, 2H, $-\text{CHCH}_3-$), 6.12 (br, 2H, $-\text{CH} = \text{CH}-$), 6.57 (br, 2H, $-\text{NHCO}-$), 8.08 (br, 4H, Ar), 8.12 (br, 4H, Ar). IR (cm^{-1} , KBr): 2,964 (CH), 1,821 (COO), 1,647 (C = O), 1,604, 1,509 (NHCO), 1,317, 1,002.

Poly(**2p-8**) ^1H NMR (400 MHz, DMSO- d_6): δ 1.40 (br, 6H, $-\text{CHCH}_3-$), 4.02 (br, 4H, $-\text{CH}_2\text{NH}-$), 4.55 (br, 2H, $-\text{CHCH}_3-$), 7.26–7.42 (br, 4H, Ar), 7.65 (br, 2H, $-\text{NHCO}-$), 7.99 (br, 4H, Ar), 8.10 (br, 4H, Ar), 8.82 (br, 2H, $-\text{CH}_2\text{NH}-$). IR (cm^{-1} , KBr): 2,940 (CH), 1,642 (C = O), 1,530 (NHCO), 1,297, 1,159, 861.

Poly(**2p-9**) ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 1.53 (br, 6H, $-\text{CHCH}_3-$), 4.28 (br, 4H, $-\text{CH}_2\text{NH}-$), 4.54 (br, 2H, $-\text{CHCH}_3-$), 6.73 (br, 2H, $-\text{NHCO}-$), 7.19–7.48 (br, 4H, Ar), 8.01 (br, 4H, Ar), 8.36 (br, 4H, Ar), 8.80 (br, 2H, $-\text{CH}_2\text{NH}-$). IR (cm^{-1} , KBr): 2,983 (CH), 1,652 (C = O), 1,604, 1,527 (NHCO), 1,304, 1,177, 1,003.

Poly(**2p-10**) ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 1.06–1.18 (br, 8H, $-\text{C}_6\text{H}_8\text{H}_2-$), 1.42 (br, 6H, $-\text{CHCH}_3-$), 1.72 (br, 2H, $-\text{C}_6\text{H}_8\text{H}_2-$), 4.44 (br, 2H, $-\text{CHCH}_3-$), 6.72 (br, 2H, $-\text{NHCO}-$), 8.01 (br, 4H, Ar), 8.11 (br, 4H, Ar), 8.97 (br, 2H, $-\text{CH}_2\text{NH}-$). IR (cm^{-1} , KBr): 2,939 (CH), 1,653 (C = O), 1,604, 1,522 (NHCO), 1,487, 1,299, 1,007.

Photo-irradiation

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 $300\text{ nm} < \lambda < 400\text{ nm}$ or with an L-42 filter (Toshiba) for irradiation at $420\text{ nm} < \lambda$. 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.

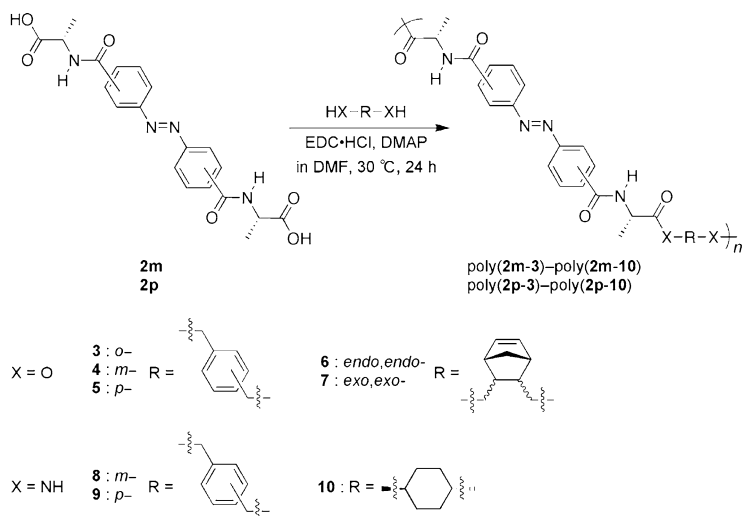
Results and discussion

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 $30\text{ }^\circ\text{C}$ for 24 h (Scheme 2). As summarized in Table 1, polymers with M_w 's of 3,300–33,700 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].

Photo-isomerization

Polymer solutions in DMF were irradiated with UV light at a wave length of $300 < \lambda < 400\text{ nm}$ at $20\text{ }^\circ\text{C}$. 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 Fig. 1, but the degree of isomerization was much lower. It



M_w 's of 3,300–33,700

Scheme 2 Polycondensation of **2m** and **2p** with diols **3–7** and diamines **8–10**

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 λ_{max} and band edge of the π - π^* transition band of poly(**2p-3**) appeared at 340, 20 nm longer than that of poly(**2m-3**). It presumed that this conjugation effects suppressed the photo-isomerization of *para*-linked polymer.

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.

Table 1 Polymerization of **1** and **2**

| Monomer | Polymer | | | |
|-----------------------|-----------------|----------------|----------------|----------------------|
| | Yield (%) | M_w^c | M_w/M_n^c | $[\alpha]_D^c$ (deg) |
| 2m + 3 | 89 ^a | 4,800 | 1.8 | 10 |
| 2m + 4 | 86 ^a | 7,500 | 1.7 | 6 |
| 2m + 5 | 86 ^a | 8,100 | 2.2 | 0 |
| 2m + 6 | 80 ^a | 6,600 | 1.8 | 2 |
| 2m + 7 | 70 ^a | 4,500 | 1.9 | 3 |
| 2m + 8 | 65 ^b | 3,300 | 1.4 | 4 |
| 2m + 9 | 95 ^b | 19,600 | 3.2 | 4 |
| 2m + 10 | 63 ^b | 7,600 | 1.5 | 8 |
| 2p + 3 | 86 ^a | 8,000 | 2.1 | 6 |
| 2p + 4 | 99 ^a | 20,400 | 4.5 | -1 ^f |
| 2p + 5 | 99 ^a | 13,100 | 2.6 | 33 ^f |
| 2p + 6 | 99 ^a | - ^d | - ^d | - ^d |
| 2p + 7 | 84 ^a | 33,700 | 6.4 | 3 ^f |
| 2p + 8 | 75 ^b | 3,500 | 1.5 | 55 |
| 2p + 9 | 78 ^b | 23,800 | 3.3 | 16 |
| 2p + 10 | 85 ^b | 8,200 | 2.5 | 15 |

Conditions: $[2\mathbf{m}]_0 = [2\mathbf{p}]_0 = [3-10]_0 = 0.5$ M, $[\text{EDC}\cdot\text{HCl}] = 1.1$ M, $[\text{DMAP}] = 0.1$ M in DMF at 30 °C for 24 h

^a NaHCO₃ aq.-insoluble part

^b 0.5 M HCl-insoluble part

^c Estimated by GPC based on polystyrene standard; eluent, LiBr solution in DMF (10 mM)

^d Not determined

^e Measured by polarimetry at room temperature, $c = 0.10$ g/dL in DMF

^f Measured in DMSO. $[\alpha]_D$ of monomers, **2m**: +80°, **2p**: +120°

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 fluorescence spectra of the monomers and polymers were also measured in the same conditions, but no emission was observed before and after the photo-irradiation.

Conclusion

In this article, we have demonstrated the polycondensation of optically active azobenzenedicarboxylic acids with various diols and diamines. The polymers

Table 2 Solubility of the polymers

| Polymer | Hexane | Toluene | CHCl ₃ | CH ₂ Cl ₂ | THF | MeOH | DMF | DMSO |
|-------------|--------|---------|-------------------|---------------------------------|-----|------|-----|------|
| Poly(2m-3) | – | – | + | ± | + | ± | + | + |
| Poly(2m-4) | – | – | + | ± | + | ± | + | + |
| Poly(2m-5) | – | – | ± | ± | + | ± | + | + |
| Poly(2m-6) | – | – | ± | ± | ± | ± | + | + |
| Poly(2m-7) | – | – | ± | ± | ± | ± | + | + |
| Poly(2m-8) | – | – | – | – | – | ± | + | + |
| Poly(2m-9) | – | – | – | – | ± | ± | + | + |
| Poly(2m-10) | – | – | ± | – | – | ± | + | + |
| Poly(2p-3) | – | – | – | – | + | – | + | + |
| Poly(2p-4) | – | – | ± | ± | + | ± | + | + |
| Poly(2p-5) | – | – | ± | ± | ± | ± | + | + |
| Poly(2p-6) | – | – | – | – | – | – | – | ± |
| Poly(2p-7) | – | – | – | – | – | – | + | + |
| Poly(2p-8) | – | – | – | – | – | ± | + | + |
| Poly(2p-9) | – | – | – | – | – | – | + | + |
| Poly(2p-10) | – | – | – | – | – | – | + | + |

+ Soluble, – insoluble, ± partly insoluble

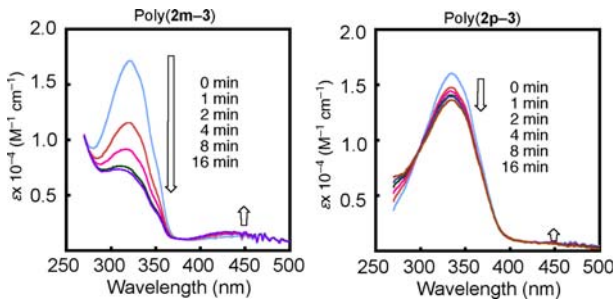


Fig. 1 UV–vis spectra of poly(2m-3) and poly(2p-3) with irradiation at $300 < \lambda < 400$ nm measured in DMF ($c = 0.05$ mM) at 20°C

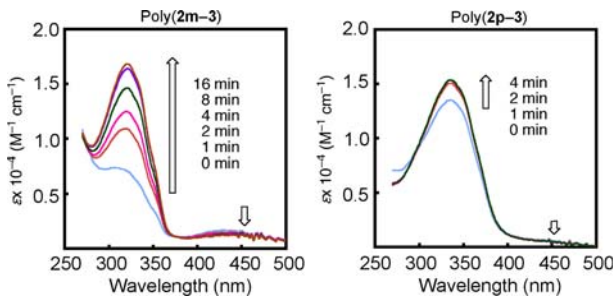


Fig. 2 UV–vis spectra of poly(2m-3) and poly(2p-3) with irradiation at $420 \text{ nm} < \lambda$, after irradiation at $300 < \lambda < 400$ nm for 32 min measured in DMF ($c = 0.05$ mM) at 20°C

obtained reversibly isomerized the azobenzene units from *trans* to *cis*, and *cis* to *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.

Acknowledgment This research was partly supported by Iketani Science and Technology Foundation.

References

1. Maeda Y, Yamauchi H, Fujisawa M, Sugihara S, Ikeda I (2007) Infrared spectroscopic investigation of poly(2-methoxyethyl vinyl ether) during thermosensitive phase separation in water. *Langmuir* 23:6561–6566
2. Gil ES, Hudson SM (2004) Stimuli-responsive polymers and their bioconjugates. *Prog Polym Sci* 29:1173–1222
3. Seki T (2007) Smart photoresponsive polymer systems organized in two dimensions. *Bull Chem Soc Jpn* 80:2084–2109
4. Kumar GS, Neckers DC (1989) Photochemistry of azobenzene-containing polymers. *Chem Rev* 89:1915–1925
5. Lim HS, Han JT, Kwak D, Jin M, Cho K (2006) Photoreversibly switchable superhydrophobic surface with erasable and rewritable pattern. *J Am Chem Soc* 128:14458–14459
6. Natansohn A, Rochon P (2002) Photoinduced motions in azo-containing polymers. *Chem Rev* 102:4139–4175
7. Irie M (2000) Diarylethenes for memories and switches. *Chem Rev* 100:1685–1716
8. Irie M (1990) Photoresponsive polymers. *Adv Polym Sci* 94:27–67
9. Smitha P, Asha SK, Pillai CKS (2005) Synthesis, characterization, and hyperpolarizability measurements of main-chain azobenzene molecules. *J Polym Sci Part A Polym Chem* 43:4455–4468
10. Acierno D, Amendola E, Bugatti V, Concilio S, Giorgini L, Iannelli P, Piotto SP (2004) Synthesis and characterization of segmented liquid crystalline polymers with the azo group in the main chain. *Macromolecules* 37:6418–6423
11. Moniruzzaman M, Sabey CJ, Fernando GF (2004) Synthesis of azobenzene-based polymers and the in-situ characterization of their photoviscosity effects. *Macromolecules* 37:2572–2577
12. Keum C, Ikawa T, Tsuchimori M, Watanabe O (2003) Photodeformation behavior of photodynamic polymers bearing azobenzene moieties in their main and/or side chain. *Macromolecules* 36:4916–4923
13. Wu S, Lu J, Zeng F, Chen Y, Tong Z (2007) Photoinduced formation of microscopic ordering and macroscopic pattern in spiropyran-containing polyacrylate–tetraoctylammonium bromide films. *Macromolecules* 40:5060–5066
14. Suzuki T, Kato T, Shinozaki H (2004) Photo-reversible Pb^{2+} -complexation of thermosensitive poly(*N*-isopropyl acrylamide-*co*-spiropyran acrylate) in water. *Chem Commun* 2036–2037
15. Berkovic G, Krongauz V, Weiss V (2000) Spiropyran and spirooxazines for memories and switches. *Chem Rev* 100:1741–1753
16. Nishi H, Kobatake S (2008) Photochromism and optical property of gold nanoparticles covered with low-polydispersity diarylethene polymers. *Macromolecules* 41:3995–4002
17. Kobatake S, Yamashita I (2008) Synthesis of photochromic diarylethene polymers for a write-by-light/erase-by-heat recording system. *Tetrahedron* 64:7611–7618
18. Kim E, Cho SY, Ahn K (2005) Photoswitching of diarylethene polymers synthesized by TEMPO mediated polymerization. *Mol Cryst Liq Cryst* 430:135–145
19. Kim E, Choi Y, Lee M (1999) Photoinduced refractive index change of a photochromic diarylethene polymer. *Macromolecules* 32:4855–4860

20. Sanda F, Takihana Y, Nomura R, Masuda T (2004) Synthesis and properties of novel metal-containing polymers having azobenzene units in the main chain. *Trans Mater Res Jpn* 29:19–22
21. Izumi A, Nomura R, Masuda T (2001) Design and synthesis of stimuli-responsive conjugated polymers having azobenzene units in the main chain. *Macromolecules* 34:4342–4347
22. Izumi A, Teraguchi M, Nomura R, Masuda T (2000) Synthesis of poly(*p*-phenylene)-based photo-responsive conjugated polymers having azobenzene units in the main chain. *Macromolecules* 33:5347–5352
23. Izumi A, Teraguchi M, Nomura R, Masuda T (2000) Synthesis of conjugated polymers with azobenzene moieties in the main chain. *J Polym Sci Part A Polym Chem* 38:1057–1063
24. Fujii T, Shiotsuki M, Inai Y, Sanda F, Masuda T (2007) Synthesis of helical poly(*N*-propargylamides) carrying azobenzene moieties in side chains. Reversible arrangement-disarrangement of helical side chain arrays upon photoirradiation keeping helical main chain intact. *Macromolecules* 40:7079–7088
25. Zhao H, Sanda F, Masuda T (2006) Stimuli-responsive conjugated polymers. Synthesis and chiroptical properties of polyacetylene carrying L-glutamic acid and azobenzene in the side chain. *Polymer* 47:2596–2602
26. Sanda F, Teraura T, Masuda T (2004) Synthesis of chiral polyacetylenes carrying amino acids and azobenzenes and transformation of the higher order structure by photoirradiation. *J Polym Sci Part A Polym Chem* 42:4641–4647
27. Nakai T, Karim SMA, Teraguchi M, Sanda F, Masuda T (2002) Synthesis and properties of polyacetylenes having substituted azobenzene pendant groups. *J Macromol Sci Pure Appl Chem* A39:935–951
28. Liu R, Shiotsuki M, Masuda T, Sanda F (2009) Synthesis and chiroptical properties of hydroxyphenylglycine-based poly(*m*-phenyleneethynylene-*p*-phenyleneethynylene)s. *Macromolecules*. doi: 10.1021/ma900910k
29. Terada K, Masuda T, Sanda F (2009) Synthesis and secondary structure of polyacetylenes carrying diketopiperazine moieties. The first example of helical polymers stabilized by *s*-cis-amide-based hydrogen bonding. *Macromolecules* 42:913–920
30. Mallakpour S, Rafiee Z (2008) Application of microwave-assisted reactions in step-growth polymerization: a review. *Iran Polym J* 17:907–935
31. Mallakpour S, Kolahdoozan M (2008) Room temperature ionic liquids as replacements for organic solvents: direct preparation of wholly aromatic polyamides containing phthalimide and S-valine moieties. *Polym J* 40:513–519
32. Mallakpour S, Khani M (2007) Novel optically active poly(amide-imide)s derived from *N*-trimethylylimido-*L*-isoleucine and different diisocyanates. *Polym Bull* 59:587–596
33. Maynard HD, Okada SY, Grubbs RH (2001) Inhibition of cell adhesion to fibronectin by oligopeptide-substituted polynorbornenes. *J Am Chem Soc* 123:1275–1279
34. Al-Muaiikel NS (2003) Synthesis and characterization of new unsaturated polyesters and copolyesters containing azo groups in the main chain. *Eur Polym J* 39:1025–1033
35. Moniruzzaman M, Talbot JDR, Sabey CJ, Fernando GF (2006) The use of ¹H NMR and UV-vis measurements for quantitative determination of trans/cis isomerization of a photo-responsive monomer and its copolymer. *J Appl Polym Sci* 100:1103–1112
36. Khan A, Hecht S (2006) Towards photocontrol over the helix-coil transition in foldamers: synthesis and photoresponsive behavior of azobenzene-core amphiphilic oligo(*meta*-phenylene ethynylene)s. *Chem Eur J* 12:4764–4774