# Synthesis and Photoisomerization of Optically Active 1,4-Polyketones Substituted by Azobenzene Side Chains

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*Received December 4, 2003; Revised Manuscript Received February 19, 2004*

ABSTRACT: Photoresponsive $\gamma$-polyketones substituted by azobenzene side chains were synthesized via asymmetric alternating copolymerization of the corresponding $\alpha$-olefins in the presence of the Pd-($R,S$)-BINAPHOS complex. $^{13}$C NMR of the polyketone having a tetramethylene spacer between the backbone and the azobenzene moiety disclosed that both ketone and spiroketal units existed in chloroform and that the spiroketal unit was transformed back to a ketone unit upon dissolution in 1,1,1,3,3,3-hexafluoro-2-propanol. Conformation of the polymer containing only ketone units was not affected by trans−cis photoisomerization of the side-chain azo chromophore, whereas the corresponding ketone/spiroketal polymer drastically changed its main-chain conformation upon trans-to-cis photoisomerization, as evidenced by increase of CD intensity by 70% at a carbonyl region.

## Introduction

Change in chiroptical properties of stimuli-responsive polymers is expected to find application in optical data storage materials and thus attracted much attention.[1] Recently, several responsive polymers have been recorded, such as polyisocyanates,[2,3] polyacetylenes,[4] polysilanes,[5] polymethacrylates,[6] polyisocyanides,[7] polyaramides,[8] and polypeptides.[9] These polymers change chiroptical properties by light irradiation, thermal treatment, chemical interaction, and/or electrical stimuli.

We previously reported that optically active $\alpha$-methyl-$\gamma$-polyketone, produced by asymmetric alternating copolymerization of propene and carbon monoxide,[10,11] has a relatively large mean radius of gyration and forms an extended and stiff structure.[12] Here, we introduce a stimuli-responsive side chain into the polyketone in lieu of a methyl group to observe change in chiroptical properties of the optically active polyketone upon the external stimulus. We employed an azobenzene group as the stimuli-responsive functional group.[13] Reversible trans−cis isomerization of azobenzenes is usually induced by alternating irradiation with UV and visible (blue) light. Azo $\pi-\pi^*$ excitation and azo n$-\pi^*$ excitation trigger trans-to-cis and cis-to-trans isomerization, respectively. The geometric change induced by isomerization of *trans*-azobenzene to *cis*-azobenzene brings in some cases drastic conformational changes of the polymer backbone, e.g., helical reversals.[2,6b,9]

Herein, we report synthesis of optically active $\gamma$-polyketones containing an azobenzene side chain via the asymmetric alternating copolymerization of azobenzene-substituted $\alpha$-olefins and carbon monoxide[14] and discuss chiroptical behavior of the polyketone by trans−cis photoisomerization of the side-chain azobenzene moiety.

## Results and Discussion

**Monomer Synthesis.** Monomers **1a**−**d**, 1-alkenes containing an azobenzene moiety, were synthesized as illustrated in Scheme 1. Each monomer was isolated in satisfactory yields with high purity and well-characterized by $^1$H and $^{13}$C NMR.

**Table 1. Copolymerization of Azobenzene-Substituted α-Olefins with Carbon Monoxide**

| run | alkene | yields (%) | $M_n$ | $M_w/M_n$ |
|---|---|---|---|---|
| 1 | **1a** | 68 | 13 300 | 1.67 |
| 2 | **1b** | 85 | 15 900 | 1.79 |
| 3 | **1c** | 28 | 10 600 | 1.63 |
| 4 | **1d** | 39 | 10 200 | 1.48 |

**Asymmetric Copolymerization of Azobenzene-Substituted α-Olefins with Carbon Monoxide Using Pd(II)-(*R,S*)-BINAPHOS Catalyst.** The azobenzene-substituted $\alpha$-olefin was subjected to asymmetric alternating copolymerization with carbon monoxide in the presence of a cationic Pd(II) complex of a chiral phosphine−phosphite, [PdMe($CH_3CN$){($R,S$)-BINAPHOS}][B{3,5-$(CF_3)_2C_6H_3$}$_4$] (**2**).[10] Monomer olefins **1a**−**d** were allowed to react with pressurized CO (20 atm) in the presence of **2** in an autoclave for 48 h at 25 °C (Scheme 2). Product polymers were purified by reprecipitation from $CHCl_3/CH_3OH$. The results are summarized in Table 1. Monomers with a methylene spacer ($m$ = 4 and 6) gave polymers in high yields, whereas those with a methylene spacer ($m$ = 3) gave the corresponding copolymer in lower yields due possibly to increased steric hindrance around the olefinic moiety and thus to slow polymerization.

**Conversion of Spiroketal Unit into Ketone Unit.** The structure of the copolymer derived from **1a** was examined by $^{13}$C NMR (Figure 1). In $CDCl_3$, signals of a ketone unit (212 ppm) and a spiroketal unit (114 ppm) were both observed (Figure 1a), suggesting most of the repeating unit in the polymer is a spiroketal as illustrated by **3a** in Scheme 2. In general, it is known that highly isotactic 1-alkene−CO polyketones exist in an equilibrium between polyketone and polyspiroketal (Scheme 3).[11a,15] The spiroketal form can be transformed to the ketone form either by heating[15a] or by dissolution in $(CF_3)_2CHOH$ (HFIP).[11a,15] Indeed, signals of the spiroketal unit in **3a** disappeared after 5 h by addition

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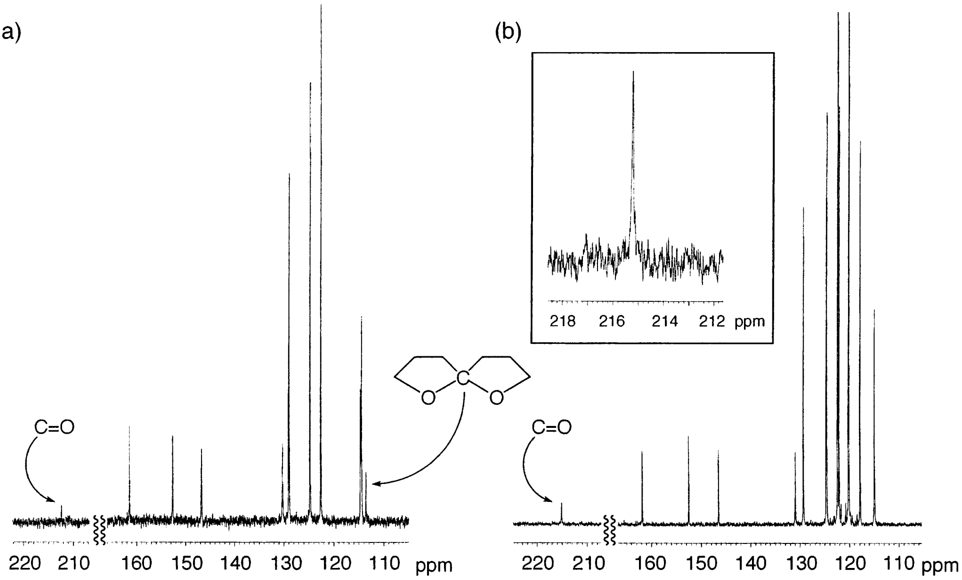
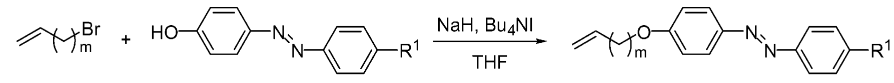


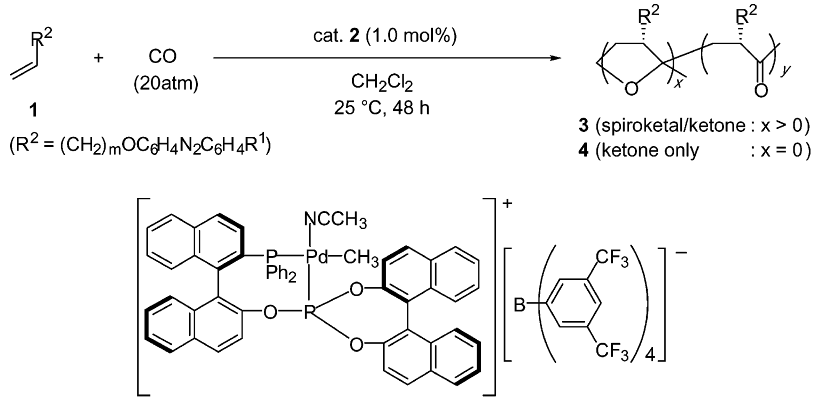
**Figure 1.** $^{13}$C NMR spectra of (a) **3a** in $CDCl_3$ and (b) **4a** in $CDCl_3/(CF_3)_2CDOD$ (3/1). Peaks at 212 and 114 ppm in (a) are assigned to ketone and spiroketal carbons, respectively. In (b), the peak at 114 ppm is missing to indicate complete conversion of the spiroketal unit into the ketone unit. Inset in (b): magnification of the carbonyl region.

**Scheme 1. Synthesis of Azobenzene-Substituted α-Olefin Monomers**



**1a** : m = 4 $R^1$ = H
**1b** : m = 6
**1c** : m = 3
**1d** : m = 3 $R^1$ = *t*-Bu

**Scheme 2. Asymmetric Alternating Copolymerization of Azobenzene-Substituted α-Olefins with Carbon Monoxide Catalyzed by Pd(II)-(*R*,*S*)-BINAPHOS (2)**



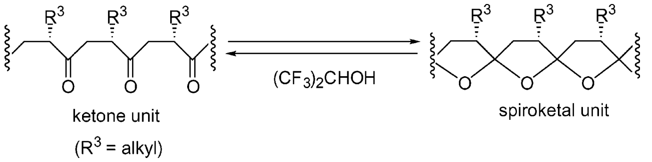
**1**

($R^2 = (CH_2)_mOC_6H_4N_2C_6H_4R^1$)

**3** (spiroketal/ketone : x > 0)
**4** (ketone only : x = 0)

**2**

**Scheme 3**



of $(CF_3)_2CDOD$ to a $CDCl_3$ solution of **3a** (Figure 1b), suggesting the resulting polymer structure to be polyketone **4a** shown in Scheme 2. High isotacticity of the keto form copolymer was confirmed by $^{13}$C NMR. In a carbonyl region, a sharp resonance at 215.2 ppm was observed, indicating high stereoregularity of the copolymer (Figure 1b, inset). On the basis of the stereochemical course of the propene–CO copolymer, the absolute configuration of the stereogenic center is analogously assumed to be *S*. This assumption is supported by the fact that a negative Cotton band is observed in a carbonyl region of CD spectrum of **4a** (vide infra).[12]

**CD Studies on Photochemical Isomerization of a Polyketone and a Polyketone/Spiroketal Substituted by Azobenzene Side Chain.** Photochemical isomerization of polyketone **4a** was studied by spectrometries. First, spiroketal/ketone polymer **3a** was dissolved in chloroform/HFIP to convert spiroketal units into ketone units, namely, **3a** into **4a**. After evaporation of the solvents, the residue was dissolved in chloroform ($2.0 \times 10^{-4}$ M). The isomerization of ketone into spiroketal is not probable in this solution because the ketone/spiroketal ratio in isotactic 1-heptene/CO copolymer was reported to be constant in $CDCl_3$ over 7 days.[11a] The polymer solution was irradiated for 4 h with a high-

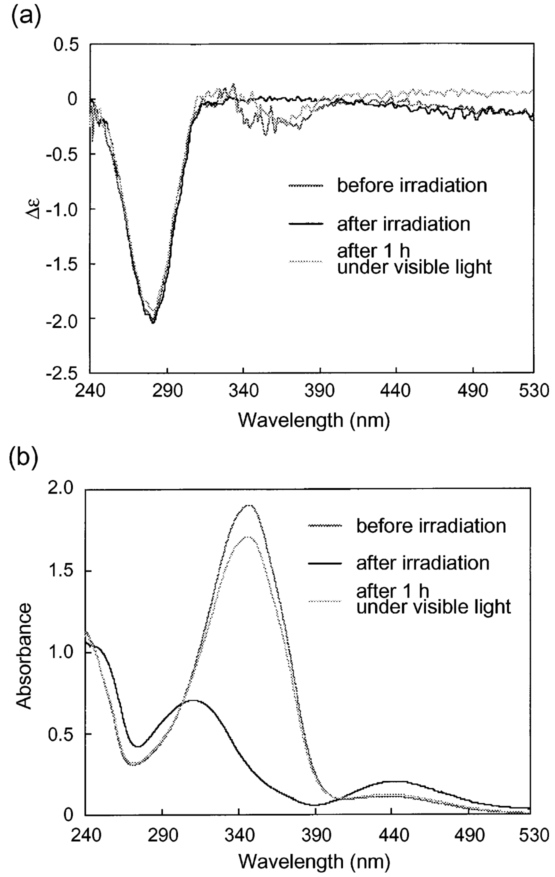
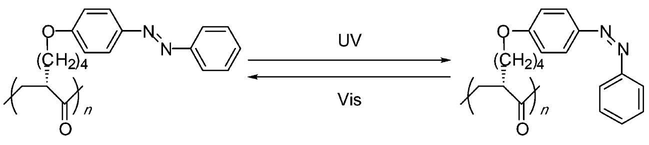


**Figure 2.** (a) CD and (b) UV spectra of **4a** before and directly after UV irradiation and after 1 h under visible light in chloroform (2.0 × $10^{-4}$ M).

**Scheme 4**



*trans*-**4a** *cis*-**4a**

pressure mercury lamp (320−420 nm) to induce trans−cis photoisomerization of the azobenzene side chain (Scheme 4).[16] Figure 2b shows UV spectral change of the solution during the photoisomerization process. After irradiation, the absorbance around 350 nm, $\pi-\pi^*$ transition of the trans component, decreased, indicating that the trans-to-cis isomerization indeed occurred. Then, the reverse process, cis-to-trans isomerization, occurred by standing under visible light for 1 h to reach a photochemical equilibrium. During the trans-to-cis and cis-to-trans photoisomerization, little intensity change was observed in CD of a negative Cotton band around 280 nm that corresponds to a $n-\pi^*$ transition of the main-chain carbonyl (Figure 2a). Thus, trans-to-cis isomerization of the side-chain azobenzene group likely induced only slight conformational change of the polymer main chain.

Photoisomerization of polymer **3a** containing ketone and spiroketal units (spiroketal/ketone ($x/y$) = 3/1) was next carried out (Scheme 5). It should be noted that, before isomerization, the split Cotton effect which was hardly detected for polyketone **4a** was observed in the *trans*-azobenzene region (Figure 3a). The band corresponding to the $\pi-\pi^*$ transition of the *trans*-azo chromophore splits into two bands with the opposite sign.

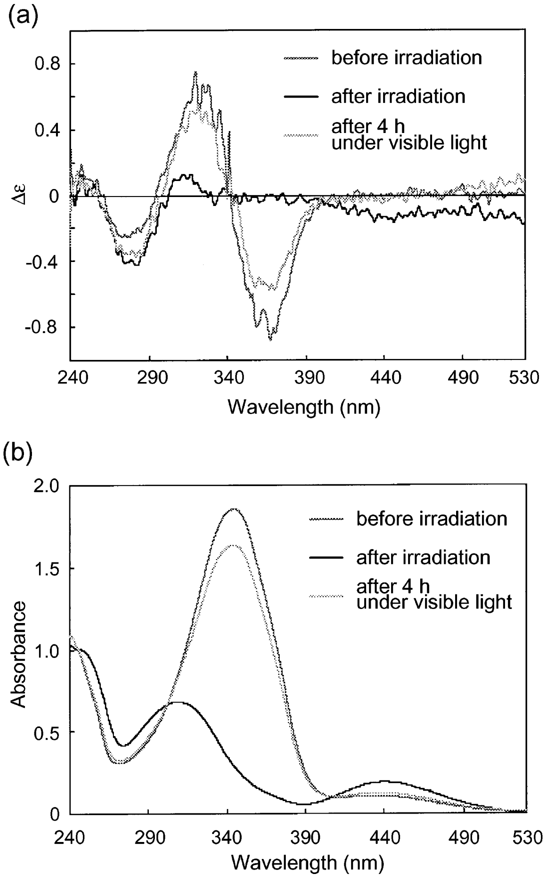


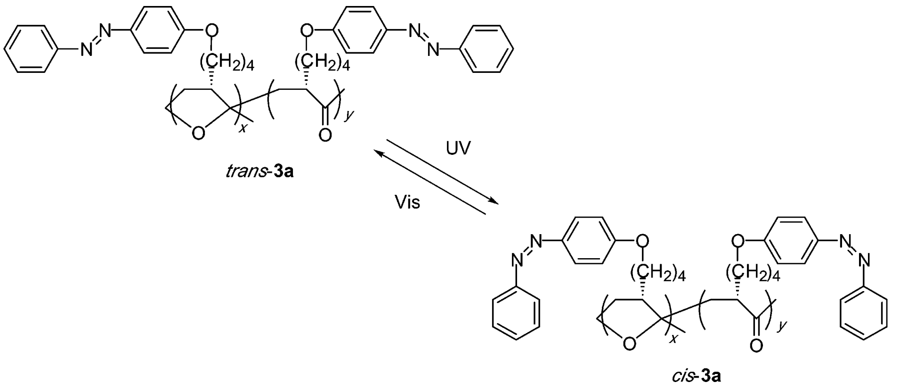
**Figure 3.** (a) CD and (b) UV spectra of **3a** before and directly after UV irradiation and after 4 h under visible light in chloroform (1.9 × $10^{-4}$ M).

After trans-to-cis photoisomerization of **3a** in chloroform (1.9 × $10^{-4}$ M, 4 h), the CD intensity in the carbonyl region increased by 70% (Figure 3a). Thus, the *cis*-azobenzene moiety isomerized back to trans in 1 h to reach a photochemical equilibrium as detected by CD and UV spectra, while the carbonyl group in **3a** took 4 h before reaching the equilibrium where CD intensity became constant.[17]

**Infrared Studies on Photoisomerization of Ketone/Spiroketal Polymer.** To exclude the possibility of transformation of spiroketal to carbonyl upon UV irradiation, which might have also caused the increase of CD intensity, we monitored the process by IR to detect the intensity change of carbonyl and spiroketal signals upon UV irradiation. Before UV irradiation, an absorption peak corresponding to C=O stretch of the ketone group in the backbone was observed at 1707 $cm^{-1}$ for *trans*-**3a** (Figure 4a), and an absorption peak derived from spiroketal unit was observed as a shoulder next to the strong absorption of an azophenoxy moiety at approximately 840 $cm^{-1}$ (Figure 4b). In general, absorptions of spiroketal units (C−O−C asymmetric stretching) appear around 830 $cm^{-1}$, and thus the assignment should be reasonable.

Photoisomerization of **3a** in a concentrated solution (1.5 × $10^{-2}$ M, cf. 1.9 × $10^{-4}$ M for CD experiment because of lower sensitivity of IR measurement) proceeded more slowly: UV irradiation for 6 h was required for the *trans*-to-*cis* photoisomerization and standing under visible light for 24 h for the *cis*-to-*trans* isomerization. Through the photoisomerization process, the intensity of carbonyl peaks did not change (Figure 4a),

**Scheme 5**



suggesting that isomerization of the spiroketal unit into the ketone unit did not occur upon UV irradiation. Therefore, it appears reasonable to consider that the increase of CD intensity in the carbonyl region, observed upon UV irradiation as mentioned above, should be attributed to the conformational change of the polymer main chain caused by *trans*-to-*cis and* the reverse isomerization of the side chain.

**Conformation of Azobenzene-Substituted Polyketones.** It is worthwhile to compare the difference between the conformational behavior of polymers **3a** and **4a** upon photoisomerization. Polymer **4a** containing only the ketone units may form an extended and stiff conformation like a planar zigzag or s(2/1) helical conformation in a manner similar to isotactic propene–carbon monoxide copolymer previously reported.[12] Herein, the side chain appears flexible, and thus the main-chain conformation is not likely influenced by the *trans*-to-*cis* photoisomerization.

In the case of **3a** which contains both the ketone and spiroketal units, helical conformation is suggested for the spiroketal units. Zentel has examined the conformation of polyisocyanates having a chiral azobenzene side chain and disclosed that the side-chain azo chromophore forms a chiral superstructure mediated by a helical structure of the polymer backbone.[2c] CD spectra of the spiroketal/ketone polymer in the present study and the polyisocyanate reported by Zentel have two points in common. First, split Cotton effect was observed for the absorption of $\pi-\pi^*$ transitions of the *trans*-azo chromophore. Second, the CD curves cross the wavelength axis (zero transition) at the wavelength of maximal absorption in UV spectra (344 nm for *trans*-**3a**). These phenomena were not observed for polyketone *trans*-**4a**. Therefore, the spiroketal moiety in *trans*-**3a** likely forms a helical structure. Herein, carbonyl groups may be incorporated partly into the spiroketal helical structure. After the *trans*-to-*cis* photoisomerization, large steric repulsion between *cis*-azobenzene side chains and the polymer backbone and/or the one between multiple side chains may possibly have driven the main-chain helical conformation to be more stable. This conformational change likely renders change of chiral environment of the main-chain carbonyl group to increase its CD intensity. Also, epimerization of the asymmetric spiro carbons may have occurred upon UV irradiation, causing the variation of the chiroptical properties of the polymer. The *cis*-to-*trans* photoisomerization seems to hardly affect the CD intensity of carbonyl region, which may be attributed to the fact that the stable main-chain conformation, once it is formed, does not return to the original conformation.

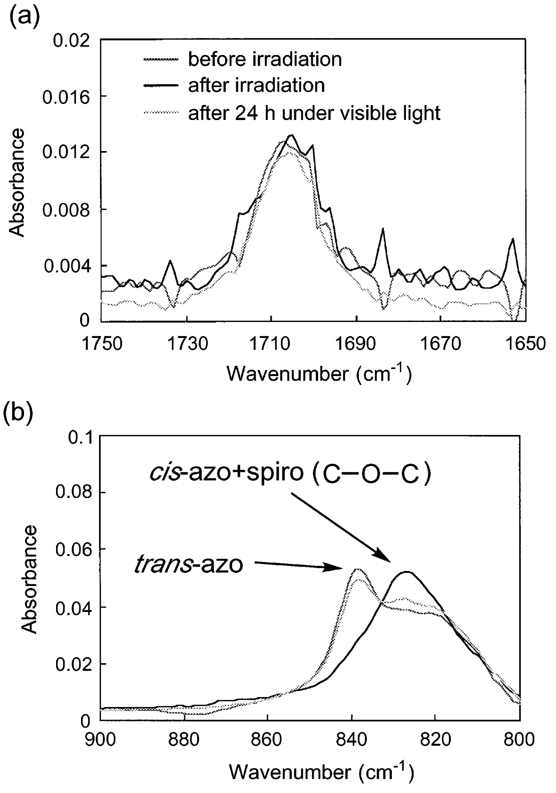


**Figure 4.** IR spectra of (a) ketone and (b) spiroketal moiety of **3a** before and directly after UV irradiation and after 24 h under visible light in chloroform ($1.5 \times 10^{-2}$ M).

## Conclusion

Asymmetric alternating copolymerization of azobenzene-substituted α-olefins and carbon monoxide provided optically active γ-polyketones with azobenzene side chain. Conformational change of the polyketone main chain is discussed upon *trans*–*cis* photoisomerization of the side-chain azobenzene moiety. Photoisomerization of polymer *trans*-**4a** containing ketone units isomerized by UV irradiation to induce little conformational change possibly due to the high flexibility of the side chain. On the other hand, drastic conformational change was observed for polymer *trans*-**3a** containing ketone and spiroketal units, the CD intensity of carbonyl group being increased by 70%. Observation of the split Cotton effect of the azobenzene moiety in *trans*-**3a** indicates formation of a helical conformation of spiroketal units in the main chain. In the environment of a rigid helical structure of the spiroketal unit, photoisomerization of the azobenzene side chain largely affected conformation of carbonyl group to change into more stable conformation and to increase the CD intensity of the carbonyl group.

## Experimental Section

**General Remarks.** All experiments were carried out using the standard Schlenk technique under an atmosphere of argon, which was purified by passing through a hot column packed with BASF catalyst R3-11. TLC analysis was carried out by means of Merck Kieselgel 60 F254. Silica gel column chromatography was performed using Wakogel C-200.

**Apparatus.** All NMR spectra were recorded at room temperature on a Varian Mercury 200 spectrometer ($^1$H NMR 200 MHz and $^{13}$C NMR 50 MHz), a JEOL EX-270 spectrometer ($^1$H NMR 270 MHz and $^{13}$C NMR 68 MHz), and a JEOL ECP-500 spectrometer ($^1$H NMR 500 MHz and $^{13}$C NMR 126 MHz) using tetramethylsilane as an internal standard, and coupling constants are given in hertz. CD and simultaneous UV−vis spectra were recorded using a JASCO J-820 spectropolarimeter (0.5 cm path length cell). Infrared spectra were recorded on a Shimadzu FTIR-8400 spectrometer. GPC was performed with a Shodex KF-804L chromatograph using THF as an eluent. A calibration curve was obtained with standard polystyrenes. Melting points were measured on a Yanagimoto-Seisakusho micro melting point apparatus, MP-500D. Elemental analyses were performed at the Microanalytical Center, Kyoto University.

**Chemicals.** Most of the reagents were purchased from Wako Pure Chemical Industries Ltd., Tokyo Kasei Kogyo Co., Ltd., Nacalai Tesque, Ltd., Kanto Chemical Co., Ltd. or Aldrich Chemical Co., Inc. All the solvents were purified by distillation under argon after drying over a suitable drying reagent. Carbon monoxide (99.9%) was purchased from Teisan Co.

**Preparation of Monomers: General Procedure. 4-(5-Hexenyloxy)azobenzene (1a).** To a suspension of sodium hydride (0.181 g, 60%, 4.5 mmol) in THF (20 mL) were added 4-phenylazophenol (0.81 g, 4.1 mmol) and tetrabutylammonium iodide (0.169 g, 0.46 mmol) under an argon atmosphere at 0 °C. Then, 6-bromo-1-hexene (0.60 mL, 4.5 mmol) was added to the mixture, and the resulting solution was stirred at 50 °C for 11 h. The reaction was quenched with 1 M HCl(aq) (50 mL) at 0 °C, and the mixture was extracted with ethyl acetate (50 mL). The aqueous layer was extracted repeatedly with ethyl acetate (3 × 50 mL). The combined organic layer was washed with saturated $NaHCO_3$(aq) (80 mL) and then with brine (80 mL), dried over anhydrous magnesium sulfate, filtered, and concentrated by a rotary evaporator. The residue was purified by silica gel column chromatography (hexane−dichloromethane = 5:2) to afford **1a** (1.01 g, 3.6 mmol, 88% yield) as an orange solid; mp 43.0−44.5 °C. $R_f$ 0.38 (hexane−dichloromethane = 5:2). $^1$H NMR ($CDCl_3$) $\delta$: 1.60 (quint, $J$ = 7.8 Hz, 2H), 1.84 (quint, $J$ = 6.9 Hz, 2H), 2.15 (dt, $J$ = 7.4, 6.9 Hz, 2H), 4.04 (t, $J$ = 6.4 Hz, 2H), 4.99 (dd, $J$ = 10.1, 1.4 Hz, 1H), 5.05 (dd, $J$ = 17.0, 1.4 Hz, 1H), 5.84 (ddt, $J$ = 17.0, 10.1, 6.4 Hz, 1H), 6.97−7.04 (m, 2H), 7.40−7.54 (m, 3H), 7.85−7.95 (m, 4H). $^{13}$C NMR ($CDCl_3$) $\delta$: 25.3, 28.6, 33.4, 68.1, 114.7, 114.8, 122.5, 124.7, 129.0, 130.3, 138.4, 146.9, 152.8, 161.6. IR ($CHCl_3$): 841 cm$^{-1}$. Anal. Calcd for $C_{18}H_{20}ON_2$: C, 77.11%; H, 7.19%. Found: C, 77.05%; H, 7.22%.

**4-(7-Octenyloxy)azobenzene (1b).** This was isolated in 84% yield as an orange solid; mp 47.9−48.9 °C. $R_f$ 0.70 (dichloromethane−hexane = 2:1). $^1$H NMR ($CDCl_3$) $\delta$: 1.34−1.54 (m, 6H), 1.83 (quint, $J$ = 6.9 Hz, 2H), 2.08 (dt, $J$ = 7.3, 6.9 Hz, 2H), 4.04 (t, $J$ = 6.5 Hz, 2H), 4.95 (dd, 10.1, 1.4 Hz, 1H), 5.01 (ddt, $J$ = 17.0, 1.9, 1.4 Hz, 1H), 5.82 (ddt, $J$ = 17.0, 10.1, 6.4 Hz, 1H), 6.98−7.05 (m, 2H), 7.41−7.55 (m, 3H), 7.85−7.96 (m, 4H). $^{13}$C NMR ($CDCl_3$) $\delta$: 25.8, 28.8, 28.8, 29.1, 33.7, 68.2, 114.3, 114.6, 122.5, 124.7, 130.0, 130.2, 138.9, 146.8, 152.7, 161.6. IR ($CHCl_3$): 840 cm$^{-1}$. Anal. Calcd for $C_{20}H_{24}ON_2$: C, 77.89%; H, 7.84%. Found: C, 78.09%; H, 7.77%.

**4-(4-Pentenyloxy)azobenzene (1c).** This compound was isolated in 97% yield as an orange solid; mp 61.7−62.5 °C. $R_f$ 0.42 (hexane−dichloromethane = 5:2). $^1$H NMR ($CDCl_3$) $\delta$: 1.94 (quint, $J$ = 6.5 Hz, 2H), 2.27 (dt, $J$ = 6.9, 6.9 Hz, 2H), 4.02 (t, $J$ = 6.3 Hz, 2H), 4.06 (t, $J$ = 6.4 Hz, 2H), 5.02 (d, $J$ = 10.1 Hz, 1H), 5.08 (dd, $J$ = 17.0, 1.4 Hz, 1H), 5.87 (ddt, $J$ = 17.0, 10.1, 6.9 Hz, 1H), 6.98−7.08 (m, 2H), 7.41−7.57 (m, 3H), 7.85−7.99 (m, 4H). $^{13}$C NMR ($CDCl_3$) $\delta$: 28.3, 30.0, 67.4, 114.7, 115.3, 122.5, 124.7, 129.0, 130.3, 137.6, 146.9, 152.7, 161.6. IR ($CH_2Cl_2$): 837 cm$^{-1}$. Anal. Calcd for $C_{17}H_{18}ON_2$: C, 76.66%; H, 6.81%. Found: C, 76.69%; H, 6.81%.

**4′-*tert*-Butyl-4-(4-pentenyloxy)azobenzene (1d).** This was isolated in 97% yield as an orange solid; mp 108.0−108.9 °C. $R_f$ 0.51 (hexanes−ethyl acetate = 7:1). $^1$H NMR ($CDCl_3$) $\delta$: 1.37 (s, 9H), 1.93 (quint, $J$ = 7.3 Hz, 2H), 2.27 (dt, $J$ = 6.9, 7.4 Hz, 2H), 4.05 (t, $J$ = 6.4 Hz, 2H), 5.02 (d, $J$ = 10.1 Hz, 1H), 5.08 (dd, $J$ = 17.0, 1.4 Hz, 1H), 5.87 (ddt, $J$ = 17.0, 10.1, 6.4 Hz, 1H), 7.00 (d, $J$ = 9.2 Hz, 2H), 7.51 (d, $J$ = 8.7 Hz, 2H), 7.81 (d, $J$ = 8.7 Hz, 2H), 7.89 (d, $J$ = 8.7 Hz, 2H). $^{13}$C NMR ($CDCl_3$) $\delta$: 25.3, 28.6, 33.4, 68.1, 114.7, 114.8, 122.5, 124.7, 129.0, 130.3, 138.4, 146.9, 152.8, 161.6. IR ($CH_2Cl_2$): 847 cm$^{-1}$. Anal. Calcd for $C_{21}H_{26}ON_2$: C, 78.22%; H, 8.13%. Found: C, 77.97%; H, 8.05%.

**Preparation of Polyketones: General Procedure. Asymmetric Alternating Copolymerization of 1a with CO Catalyzed by [Pd($CH_3$)($CH_3CN$){(*R,S*)-BINAPHOS}]·[B{3,5-($CF_3$)$_2$-$C_6H_3$}$_4$].** A solution of Pd(Me)(Cl){(*R*,*S*)-BINAPHOS} (9.4 mg, 0.010 mmol) in dichloromethane (2 mL) and a solution of NaB{3,5-($CF_3$)$_2$$C_6H_3$}$_4$ (9.6 mg, 0.011 mmol) in acetonitrile (1 mL) were mixed, and the resulting mixture was stirred at room temperature for 1 h. All the solvents were removed in vacuo to give [Pd(Me)($CH_3CN$){(*R*,*S*)-BINAPHOS}]·[B{3,5-($CF_3$)$_2$$C_6H_3$}$_4$]. This complex was dissolved in dichloromethane (2 mL), and the resulting solution was degassed three times by a freeze−thaw cycle. To the solution was charged with 4-(5-hexenyloxy)azobenzene (0.29 g, 1.0 mmol), and the mixture was stirred under CO (20 atm) at 25 °C for 48 h. To the solution were added dichloromethane (3 mL) and methanol (1.25 mL), and the mixture was stirred under CO (20 atm) at 25 °C for 1 h. The crude polymer was purified by reprecipitation from $CHCl_3$/$CH_3OH$ to give **3a** (0.21 g, 0.69 mmol, 68% yield). $M_n$ = 13 300; $M_w/M_n$ = 1.67. $^1$H NMR ($CDCl_3$) $\delta$: 1.10−1.83 (br m, 6H), 1.83−2.35 (br m, 2H), 2.57−3.10 (br m, 1H), 3.62−4.05 (br m, 2H), 6.65−7.10 (br, 2H), 7.35−7.60 (br, 3H), 7.67−7.95 (br, 4H). $^1$H NMR ($CDCl_3$/($CF_3$)$_2$CHOH) $\delta$: 1.21−1.88 (br m, 6H), 2.68−3.15 (br m, 3H), 3.83−4.07 (br m, 2H), 6.93 (d, $J$ = 8.7 Hz, 2H), 7.35−7.56 (m, 3H), 7.72 (d, $J$ = 6.9 Hz, 2H), 7.78 (d, $J$ = 7.3 Hz, 2H). $^{13}$C NMR ($CDCl_3$) $\delta$: 23.4, 25.0, 28.8, 29.1, 29.7, 31.1, 40.8, 43.8, 44.6, 45.1, 67.8 (O$CH_2$), 68.2 (O$CH_2$), 113.5 (O$C$O), 114.4 (Ar), 114.6 (Ar), 122.5 (Ar), 124.7 (Ar), 128.9 (Ar), 129.0 (Ar), 130.2 (Ar), 146.7 (Ar), 146.8 (Ar), 152.6 (Ar), 152.7 (Ar), 161.4 (Ar), 212.4 ($C$=O). $^{13}$C NMR ($CDCl_3$ /($CF_3$)$_2$CDOD) $\delta$: 23.5, 29.0, 31.0, 44.0 ($C$H), 45.7 (C(O)$C$H$_2$), 68.1 (O$C$H$_2$), 115.1 (Ar), 122.2 (Ar), 124.8 (Ar), 129.4 (Ar), 131.1 (Ar), 146.6 (Ar), 152.6 (Ar), 162.0 (Ar), 215.2 ($C$=O). IR ($CHCl_3$): 837, 1707 cm$^{-1}$. Anal. Calcd for $C_{19}H_{20}O_2N_2$: C, 74.00%; H, 6.54%. Found: C, 73.78%; H, 6.53%.

**Poly[4-(7-octenyloxy)azobenzene-*alt*-CO] (3b).** This polymer was isolated in 85% yield. $M_n$ = 15 900; $M_w/M_n$ = 1.79. $^1$H NMR ($CDCl_3$) $\delta$: 1.05−2.20 (br m, 11H), 2.56−3.18 (br m, 2H), 3.70−4.10 (br m, 2H), 6.70−7.05 (br m, 2H), 7.20−7.56 (br m, 3H), 7.60−8.05 (br m, 4H). $^1$H NMR ($CDCl_3$/($CF_3$)$_2$CDOD) $\delta$: 1.05−1.87 (br m, 10H), 2.62−3.15 (br m, 3H), 3.86−4.12 (br, 2H), 6.95 (d, $J$ = 8.7 Hz, 2H), 7.40−7.54 (m, 3H), 7.73 (d, $J$ = 7.3 Hz, 2H), 7.80 (d, $J$ = 7.3 Hz, 2H). $^{13}$C NMR ($CDCl_3$) $\delta$: 25.7, 26.1, 26.8, 28.5, 29.0, 29.2, 29.4, 30.1, 31.3, 44.8 ($C$H), 45.2 (C(O)$C$H$_2$), 68.1 (O$C$H$_2$), 113.6, 114.5 (Ar), 114.6 (Ar), 122.5 (Ar), 124.7 (Ar), 129.0 (Ar), 130.3 (Ar), 146.8 (Ar), 152.7 (Ar), 161.6 (Ar), 161.6 (Ar), 212.7 ($C$=O). $^{13}$C NMR ($CDCl_3$/($CF_3$)$_2$CDOD) $\delta$: 25.7, 26.9, 29.0, 29.3, 31.2, 44.2 ($C$H), 45.6 (C(O)$C$H$_2$), 68.5 (O$C$H$_2$), 115.1 (Ar), 122.2 (Ar), 124.8 (Ar), 129.4 (Ar), 131.0 (Ar), 146.7 (Ar), 152.7 (Ar), 162.1 (Ar), 215.6 ($C$=O). IR ($CHCl_3$): 839, 1705 cm$^{-1}$. Anal. Calcd for $C_{21}H_{24}O_2N_2$: C, 74.97%; H, 7.19%. Found: C, 74.25%; H, 7.07%.

**Poly[4-(4-pentenyloxy)azobenzene-*alt*-CO] (3c).** This polymer was isolated in 28% yield. $M_n$ = 10 600; $M_w/M_n$ = 1.63. $^1$H NMR ($CDCl_3$) $\delta$: 0.90−2.40 (br, 4H), 2.40−2.90 (br, 1H), 2.90−3.30 (br, 2H), 3.30−4.30 (br, 2H), 6.55−7.10 (br, 2H), 7.10−7.55 (br, 3H), 7.55−8.30 (br, 4H). $^{13}$C NMR ($CDCl_3$/($CF_3$)$_2$-

CHOH) $\delta$: 26.4, 27.8, 44.4 (*C*H), 45.2 (C(O)*C*H$_2$), 67.9 (O*C*H$_2$), 114.9 (Ar), 122.3 (Ar), 124.8 (Ar), 129.3 (Ar), 131.0 (Ar), 146.7 (Ar), 152.6 (Ar), 161.7 (Ar), 214.7 (*C*=O). IR (CH$_2$Cl$_2$): 839, 1709 cm$^{-1}$. Anal. Calcd for $C_{18}H_{18}O_2N_2$: C, 73.45%; H, 6.16%. Found: C, 70.57%; H, 5.95%.

**Poly[4′-*tert*-butyl-4-(4-pentenyloxy)azobenzene-*alt*-CO] (3d).** This polymer was prepared in 39% yield. $M_n$ = 10 200; $M_w/M_n$ = 1.48. $^1$H NMR (CDCl$_3$) $\delta$: 1.29 (s, 9H), 1.40−1.83 (br, 4H), 2.75−2.92 (br m, 1H), 2.96−3.17 (br m, 2H), 3.85−4.10 (br, 2H), 6.85−7.02 (br, 2H), 7.30−7.60 (br, 2H), 7.60−8.05 (br, 4H). $^{13}$C NMR (CDCl$_3$) $\delta$: 25.6, 26.5, 27.6, 27.8, 31.3 (*C*H$_3$), 34.9 ((CH$_3$)$_3$*C*), 40.4, 43.8, 44.8, 67.8 (O*C*H$_2$), 68.6 (O*C*H$_2$), 113.3 (O*C*O), 114.4 (Ar), 114.6 (Ar), 122.3 (Ar), 124.6 (Ar), 125.9 (Ar), 146.7 (Ar), 147.1 (Ar), 150.5 (Ar), 150.6 (Ar), 153.8 (Ar), 161.1 (Ar), 161.4 (Ar), 212.3 (*C*=O). $^{13}$C NMR (CDCl$_3$/(CF$_3$)$_2$CDOD) $\delta$: 26.5, 27.8, 31.0 (*C*H$_3$), 35.0 ((CH$_3$)$_3$*C*), 44.5 (*C*H), 45.3 (C(O)*C*H$_2$), 67.9 (O*C*H2), 115.0 (Ar), 122.0 (Ar), 124.7 (Ar), 126.4 (Ar), 146.8 (Ar), 150.6 (Ar), 155.1 (Ar), 161.7 (Ar), 214.8 (*C*=O). IR (CH$_2$Cl$_2$): 847, 1705 cm$^{-1}$. Anal. Calcd for $C_{22}H_{26}O_2N_2$: C, 75.40%; H, 7.48%. Found: C,74.88%; H, 7.42%.

**Photochemical Isomerization of Azobenzene-Substituted Polyketones.** In the CD study, polymer *trans*-**3a** (0.582 mg, $1.9 \times 10^{-3}$ mmol) or *trans*-**4a** (0.616 mg, $2.0 \times 10^{-3}$ mmol) was dissolved in chloroform (10 mL), and the solution was placed into a quartz cell (cell length = 1 cm). The polyketone solution was irradiated at 320−420 nm with a 100 W high-pressure mercury lamp through glass filters (Toshiba, UV-D36A + UV-35). Photochemical isomerization of *cis*-**3a** or *cis*-**4a** was performed with standing under visible light. CD measurement was carried out under the same concentration: **3a** ($1.9 \times 10^{-4}$ M) or **4a** ($2.0 \times 10^{-4}$ M). In the IR study, photoirradiation and IR measurement of **3a** were conducted in chloroform ($1.5 \times 10^{-2}$ M).

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(16) Although degradation of the polyketones by Norrish type I and II cleavage may be anticipated, the polymers were irradiated by UV light in the range of 320−420 nm, the light deviating from absorption of carbonyl n−$\pi^*$ transition (250−310 nm) that causes Norrish type I and II cleavage. We confirmed by GPC that the molecular weight of polyketones did not change after photoisomerization.

(17) We confirmed that it takes 10 min upon UV irradiation for the *trans*-to-*cis* isomerization and 60 min under visible light for the *cis*-to-*trans* isomerization (**3a** in chloroform, $1.9 \times 10^{-4}$ M).

MA0358430