

Chiroptical Properties of Helical Poly(arylisocyanide)s Bearing *m*-Substituted Azobenzene Moiety

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Helical π -conjugated poly(arylisocyanide) copolymers bearing the *m*-substituted azobenzene moiety **A**, which slightly conjugates with the main chain in spite of its direct linkage to the main chain, were prepared. In the case of **A**-containing random copolymer, *random-M*₂₀**A**₁₀, an absorption band assigned to the *E*-azobenzene moieties was blue-shifted in comparison of *random-M*₂₀**A'**₁₀, of which the *p*-substituted azobenzene moiety strongly conjugates with the main chain. On the other hand, the intensity of negative Cotton effect assigned to helical main chain of *random-M*₂₀**A**₁₀ was smaller than that of *homo-M*₂₀, although the polymerization degree of *random-M*₂₀**A**₁₀ was higher than that of *homo-M*₂₀. These spectral features indicate that the conformation of the main chain in *random-M*₂₀**A**₁₀ was disordered in comparison with that of either *random-M*₂₀**A'**₁₀, *random-M*₂₀**A''**₁₀ or *homo-M*₂₀, and therefore *m*-substituted azobenzene moiety, such as **A**, induced disorders in the helical conformation. This was also supported by the high responsiveness of the azobenzene moiety introduced in the copolymers.

Key words: poly(arylisocyanide), *m*-substituted azobenzene, *E-Z* photoisomerization, helical conformation, living polymerization

1. INTRODUCTION

Much attention has been paid to the conformational control of helical π -conjugated polymers, since electronic structure of the π -conjugated system along the main chain depends on the twisted angles between p_z -orbitals of the neighboring sp^2 carbons.¹ The conformational change perturbs electronic structure and chiroptical property of the helical main chain. Thus, the helical conformational change of the main chain can be analyzed by UV-vis absorption band and their circular dichroism assigned to the π -conjugated main chain around visible region.

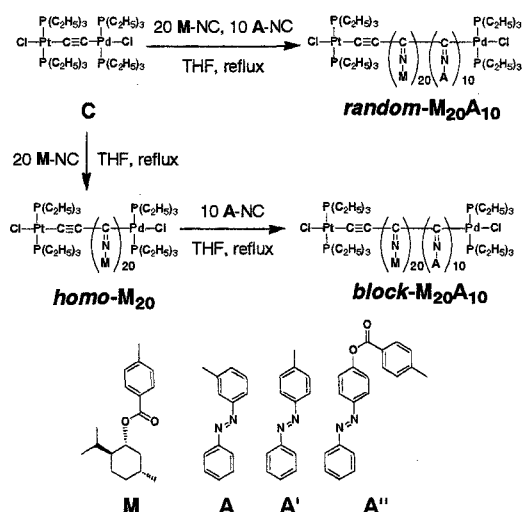
Poly(arylisocyanide) is predicted to a stable π -conjugated 4₁ helical conformation in solution from the investigation of the CD spectrum² and the molecular modeling calculations in combination with NMR studies.³ Poly(arylisocyanide) can be prepared by the living polymerization method with Pt-Pd μ -ethyndiyl initiator,⁴ and therefore any copolymer sequences including functional units along the helical main chain can be designed. In previous work, poly(arylisocyanide) copolymers bearing achiral azobenzene⁵ or nitrobenzene⁶ moieties as the functional units in a series of random and block copolymers with defined sequences were prepared, and their photoisomerization property of azobenzene moiety and redox one of nitrobenzene moiety were examined. The copolymer-sequence-dependent responsiveness of the azobenzene and nitrobenzene moieties in the side chain encouraged us to analyze the local conformational disorder in the helical main chain and to control the helical conformation

through the geometrical change of the azobenzene moiety and/or the formation of ion pair between the nitrophenyl anion radical and the electrolyte cation. However, in the case of *p*-substituted azobenzene moiety adjacent to the main chain (abbreviated by **A'** in Scheme 1), the photo-induced conformational change was significantly depressed because of the energy transfer from the excited state of azobenzene moiety to the ground state of helical conjugated main chain and the limited free volume around the azobenzene by the packing of side chains. On the other hand, in the case of *p*-substituted azobenzene moiety connected through the benzoate side chain **A''**, the photoisomerization was proceeded effectively but the conformational change was not observed since there are sufficient free volume but the azobenzene unit is distant from the helical main chain.

In this paper, for the purpose of the induction of more effective conformational change by the photoisomerization of the azobenzene moiety in the side chain, poly(arylisocyanide) copolymers containing the *m*-substituted azobenzene moiety **A**, which slightly conjugates with the main chain in spite of its direct linkage to the main chain were prepared and its photochemical properties were explored.

2. EXPERIMENTAL

General Methods. ¹H NMR spectra in CDCl₃ were recorded with a JEOL JNM-EX270 spectrometer. IR spectra were recorded with a Bio-rad FTS 3000 FT-IR spectrometer. The sample for IR spectra was cast film



Scheme 1. Living copolymerization of chiral and achiral isocyanides initiated by μ -ethynediyl Pt-Pd complex.

on Si wafer. Molecular weight and copolymer composition were derived from peak intensity of absorption bands assigned to ethynyl, imino, and ester groups. UV-vis absorption and CD spectra were recorded with a Shimadzu UV-2100S UV-visible spectrophotometer and a JASCO J-720z CD spectrophotometer, respectively, using a quartz cell with 1 mm optical path. Gel permeation chromatography (GPC) analysis was performed using a JASCO 880-PU HPLC pump equipped with an Erma Optical Works Co., Ltd. ERC-8710 UV detector, and THF was used as an eluent at 35°C. Two GPC columns, Shodex KF-802 and a JAI 3H-AF, were connected in series. The polydispersity (M_w/M_n) of the polymers was calculated on the basis of a polystyrene calibration. Photoirradiation experiment was performed using a Yamashita Denso XFL-150L Xenon lamp (150 W).

Chemicals and Materials. 4-(+)-(Menthoxycarbonyl)-phenyl isocyanide⁴ (abbreviated by **M** in Scheme 1), 4-(phenylazo)phenyl isocyanide⁷ (**A'-NC**), 4-{4-(phenylazo)phenoxy-carbonyl}phenyl isocyanide⁵ (**A''-NC**), and μ -ethynediyl Pt-Pd complex⁸ (**C**) 3-(phenylazo)phenylaniline⁹ were prepared by the methods reported previously. THF was dried over sodium with benzophenone and freshly distilled prior to use. CH_2Cl_2 was dried over CaH_2 and distilled. The following commercially available reagents were used without further purification. Nitrosobenzene and triphosgene were purchased from Tokyo Kasei. 3-Nitroaniline and acetic acid were purchased from Kanto Chemical. SiO_2 and Neutral Al_2O_3 for column chromatography were purchased from Merck. All other chemicals were purchased from Wako Pure Chemical.

3-(phenylazo)phenyl formamide. A 43.2 g (938 mmol) of formic acid and 15.4 g (166 mmol) of acetic anhydride were mixed and stirred 2 hr at 60 °C. A 2.0 g (10.1 mmol) of 3-(phenylazo)phenylaniline were added to the mixed solution and stirred 8 hr at room temperature. The reaction mixture was extracted with

hot benzene, neutralized, and dried by Na_2SO_4 . Orange needle crystal was obtained by recrystallization from benzene. Yield: 1.16 g (53 %). ¹H-NMR (270 MHz, CDCl_3): δ 8.46 (s, 1H, formyl-cis), 8.81 (d, $J = 10.8$ Hz, 1H, formyl-trans), 7.16-8.00 (m, 9H, aromatic). IR (KBr, cm^{-1}): 3241 (ν_{NH}), 1654 ($\nu_{\text{C=O}}$). MS (FAB, 3-nitrobenzylalcohol) m/z 226 $[\text{MH}]^+$. Elem. Anal. Calcd for ($\text{C}_{13}\text{H}_{11}\text{N}_3\text{O}$): C, 69.32; H, 4.92; N, 18.66. Found: C, 69.12; H, 5.01; N, 18.92.

3-(phenylazo)phenyl isocyanide (A-NC). A solution of 0.474 g (1.60 mmol) of triphosgene in 3 ml of CH_2Cl_2 was added to the a mixed solution of 0.278 g (1.23 mmol) of 3-(phenylazo)phenyl formamide and 0.376 g (3.69 mmol) of Et_2N in 15 ml of CH_2Cl_2 , 15 ml at 0 °C under nitrogen atmosphere with stirring. After 15 min 20 ml of saturated water solution of Na_2CO_3 was added to the mixed solution at room temperature and stirred 30 min. The reaction mixture was neutralized and dried by Na_2SO_4 . Orange solid was purified on column chromatography packed with neutral Al_2O_3 deactivated by 5 wt% water in CH_2Cl_2 eluent and washed with ethanol and dried under vacuum. Yield: 0.238 g (90 %). ¹H-NMR (270 MHz, CDCl_3): δ 7.16-8.00 (m, 9H, aromatic). IR (KBr, cm^{-1}): 2126 (ν_{CN}). Elem. Anal. Calcd for ($\text{C}_{13}\text{H}_9\text{N}_3$): C, 75.35; H, 4.38; N, 20.28. Found: C, 75.19; H, 4.11; N, 20.32.

Polymerization of isocyanide monomers Poly[4-(+)-(menthoxy-carbonyl)phenyl isocyanide] (**homo-M₂₀**), poly{[4-(+)-(menthoxy-carbonyl)phenyl isocyanide]-*ran*-[3-(phenylazo)phenyl isocyanide]} (**random-M₂₀A₁₀**), poly[4-(+)-(menthoxy-carbonyl)phenyl isocyanide]-*block*-poly[3-(phenylazo)phenyl isocyanide] (**block-M₂₀A₁₀**), poly{[4-(+)-(menthoxy-carbonyl)phenyl isocyanide]-*ran*-[4-(phenylazo)phenyl isocyanide]} (**random-M₂₀A'₁₀**), poly[4-(+)-(menthoxy-carbonyl)phenyl isocyanide]-*block*-poly[4-(phenylazo)phenyl isocyanide] (**block-M₂₀A'₁₀**), and poly{[4-(+)-(menthoxy-carbonyl)phenyl isocyanide]-*ran*-[4'-[4-(phenylazo)phenoxy-carbonyl]phenyl isocyanide]} (**random-M₂₀A''₁₀**) were prepared by the living polymerization procedure^{4,5} of chiral isocyanide **M** and achiral azobenzene-containing isocyanides **A-NC**, **A'-NC**, and **A''-NC** with μ -ethynediyl Pt-Pd complex **C**, respectively. The numbers of individual repeated units of the copolymers were given as the subscript numbers in **M₂₀**, **M₂₀A₁₀**, **M₂₀A'₁₀**, or **M₂₀A''₁₀**. (Scheme 1).

All the polymerizations proceeded to completely consume the feed monomers and to give the unimodal GPC traces of the copolymers with narrow polydispersity indexes (1.09-1.15). IR spectra of the resulting polymers show two characteristic absorption bands at 1650 cm^{-1} and 2090 cm^{-1} assigned to imino group of every repeated unit and ethyne group, respectively, which resulted from the catalyst and remained as one end of the polymer. Polymerization degrees of the resulting polymer were estimated from the intensity ratio of both absorption bands in the IR spectra, according to the previously established procedure.^{5,6}

Photochemical Measurements. *E-Z* Photoisomerization of the azobenzene moiety in the copolymers was achieved under UV irradiation with a 150 W Xe-lamp

through HOYA U340 and UV34 filters (optical window, $320 < \lambda < 380$ nm), while *Z-E* photoisomerization was achieved under visible light irradiation through a HOYA Y50 filter ($\lambda > 480$ nm). The photoisomerization was monitored by UV-vis absorption and CD spectra.

3. RESULTS AND DISCUSSION

Fig. 1 shows UV-vis absorption spectra of *random-M*₂₀*A*₁₀, *random-M*₂₀*A'*₁₀, and *random-M*₂₀*A''*₁₀ with *homo-M*₂₀ in CHCl₃. In the case of *homo-M*₂₀, an intense UV band at 255 nm and a weak broad band in 300-520 nm region are characteristic of poly(arylisocyanide). The former is assigned to π - π^* transition of the benzoate moiety, and the latter includes several electronic transitions such as π - π^* and n - π^* transitions of the imino moiety, having largely twisted π -bonding between sp^2 -carbons of the main chain, and their π -conjugated moieties. Strong circular dichroism was observed in the corresponding absorption region: a negative broad Cotton effect was observed in the region of 300-520 nm and a positive sharp Cotton effect appeared at 255 nm.⁴

In the UV-vis absorption spectra of azobenzene-containing random copolymers (Fig. 1), a strong absorption band assigned to π - π^* transition of the *E*-azobenzene moiety is superimposed on the 300-520 nm band. The absorption maxima at 325 nm is blue-shifted in comparison with the corresponding band of *random-M*₂₀*A'*₁₀ at 343 nm, and furthermore this absorption band of *random-M*₂₀*A*₁₀ is almost in agreement with that of *random-M*₂₀*A''*₁₀, of which azobenzene moiety does not conjugate with the main chain.⁵ These spectral features indicate that *m*-substituted azobenzene moiety in *random-M*₂₀*A*₁₀ slightly conjugates with the main chain in spite of its direct linkage to the main chain. In the case of *random-M*₂₀*A*₁₀, the contribution of the energy transfer from azobenzene moiety to the helical conjugated main chain may be reduced, and therefore, it should be expected that the photochemically excited azobenzene unit might be effectively isomerized without other deactivation paths.

In the CD spectra of azobenzene-containing random

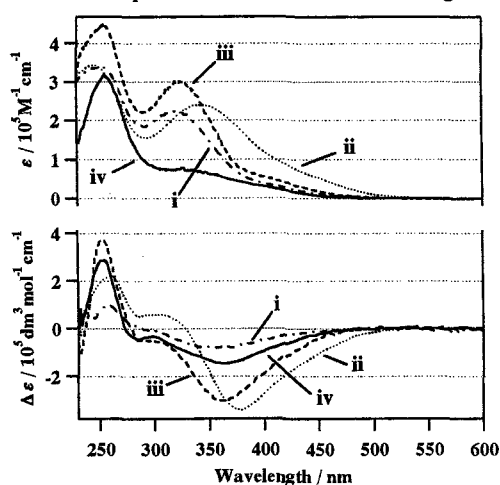


Fig. 1. UV-vis absorption (upper) and CD (lower) spectra of (i) *random-M*₂₀*A*₁₀, (ii) *random-M*₂₀*A'*₁₀, (iii) *random-M*₂₀*A''*₁₀ and (iv) *homo-M*₂₀ in CHCl₃.

copolymers (Fig. 1), a negative Cotton effect is observed in the 300-520 nm region of each copolymer, suggesting that these copolymers take a predominantly one-handed helical conformation in analogy with *homo-M*₂₀. On the other hand, a clear difference is also observed in the intensities of CD spectra of the copolymers: the CD spectrum of *random-M*₂₀*A'*₁₀ includes not only the negative broad dichroism characteristic of the helical main chain but also a large split Cotton effect assigned to an induced circular dichroism of the *E*-azobenzene moiety, caused by its regular arrangement along to prevailing helical direction.⁵ The CD spectrum of *random-M*₂₀*A''*₁₀ is similar to that of *homo-M*₂₀, suggesting that azobenzene moieties distant from main chain have little contribution to the helical conformation.⁵ Since the negative Cotton effects of these copolymers are larger than that of *homo-M*₂₀, the main chain attached to the azobenzene moieties in the copolymers would also preferentially take one-handed helical conformation. On the contrary, the negative Cotton effect of *random-M*₂₀*A*₁₀ is smaller than that of *homo-M*₂₀, although the polymerization degree of *random-M*₂₀*A*₁₀ is higher than that of *homo-M*₂₀. In addition, the intensity of the negative Cotton effect of *block-M*₂₀*A*₁₀ is similar to that of *homo-M*₂₀, suggesting that the negative Cotton effect of *block-M*₂₀*A*₁₀ is almost based on the contribution to *M*₂₀ block. These spectral features indicate that the conformation of the main chain of *random-M*₂₀*A*₁₀ is disordered in comparison with that of *homo-M*₂₀. This may arise from the lack of the symmetry around the bond connecting to the main chain in the *m*-substituted A unit, and therefore the copolymerization might proceed without keeping tacticity.

Fig. 2 shows UV-vis absorption spectral changes of *random-M*₂₀*A*₁₀ in CHCl₃ under UV light irradiation ($320 \text{ nm} < \lambda < 380 \text{ nm}$). The absorbance at 320 nm, attributable to π - π^* transition of *E*-azobenzene moiety, decreased and a weak band assigned to n - π^* transition of the *Z*-azobenzene moiety appeared around 440 nm. This spectral change was saturated within 20 min of the

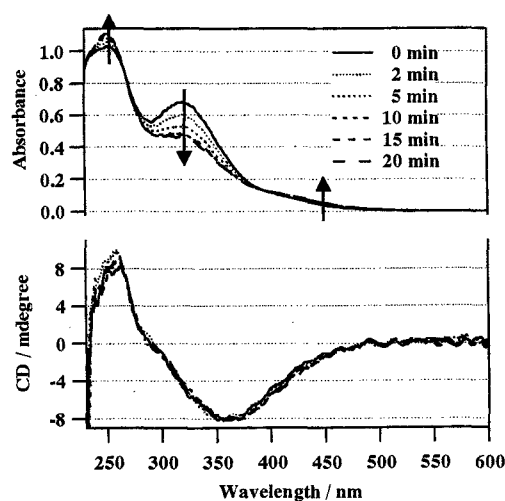


Fig. 2. UV-vis absorption (upper) and CD (lower) spectra of *random-M*₂₀*A*₁₀ in CHCl₃ using a 1 mm quartz cell under UV irradiation as a function of irradiation time. [polymer] = 3×10^{-5} M.

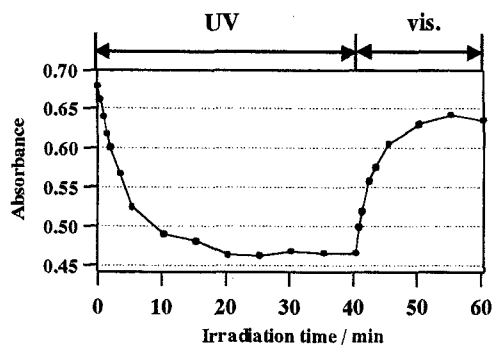


Fig. 3. Time course of the absorbance change at 320 nm in the UV-vis absorption spectra of **random-M₂₀A₁₀** in CHCl₃ in 1 mm quartz cell under the alternating UV and visible light irradiations. [polymer] = 3 × 10⁻⁵ M.

UV light irradiation, to reach a photostationary state. Upon visible light irradiation ($\lambda > 480$ nm), the spectrum went back to the original one, as shown in Fig. 3. These reversible changes are characteristic of well-established reversible *E-Z* photoisomerizations of azobenzene derivatives. Upon visible light irradiation, photo-stationary state was achieved, but the absorbance went back completely to the original value in the dark.

The *E-Z* photoisomerization of the azobenzene moieties in **random-M₂₀A₁₀** was reduced by 40 % of that of the corresponding monomer A-NC. On the other hand, more significant suppression in **random-M₂₀A[']₁₀** with 13 % and no suppression in **random-M₂₀A^{''}₁₀** were observed.⁵ In the case of **random-M₂₀A[']₁₀**, the suppression of the photoisomerization is based on limited free volume around the azobenzene moiety for the configurational change from planar *E*-isomer to non-planar *Z*-isomer, because the azobenzene moiety is packed in sterically congested side chains.⁵ On the contrary, the side chain of **random-M₂₀A^{''}₁₀** has sufficient free volume for the photoisomerization of azobenzene moiety apart from the helical main chain.⁵ These results imply that the side chains of **random-M₂₀A₁₀** are less sterically hindered than that of **random-M₂₀A[']₁₀** as a result of disordered local helical conformation induced by the introduction of A units.

Fig. 2 also shows the time courses of the negative Cotton effect change in the CD spectra of **random-M₂₀A₁₀** under the UV light irradiation. No CD change was observed during the *E-Z* photoisomerization of the azobenzene moiety, while the intensity of the positive and negative Cotton effects changed reversibly, synchronized with the *E-Z* photoisomerization of the azobenzene moiety in **random-M₂₀A[']₁₀**.⁵ On the other hand, the CD intensity in **block-M₂₀A[']₁₀** did not change in spite of more effective *E-Z* photoisomerization. Since the azobenzene moiety was loosely packed, the photoisomerization did not induce the conformational change.⁵ Therefore, no CD change during the *E-Z* photoisomerization of the azobenzene moiety in **random-M₂₀A₁₀** also indicates that the photoisomerization of azobenzene unit in **random-M₂₀A₁₀** may induce no or little perturbation on the helical conformation for its disordered structure around the A moieties.

The local conformation around the monomer unit

bearing azobenzene moieties can be analyzed through the electronic structure and chiroptical properties as well as photoresponsiveness of the azobenzene unit. In the case of the *p*-substituted azobenzene moieties, A' and A'', the random copolymerization relatively affords to keep helical conformation of poly(arylisocyanide), while *m*-substituted azobenzene monomer A can give disordered copolymer. Thus, the helical conformation of poly(arylisocyanide) strongly depends on the molecular structure and conformation of achiral azobenzene moiety in the side chain.

4. CONCLUSION

Poly(arylisocyanide) copolymers containing the azobenzene moiety A which slightly conjugate with the main chain in spite of its direct linkage to the main chain were synthesized by the living polymerization with Pt-Pd μ -ethynediyl complex as an initiator.

The helical conformation and photo-responsiveness of the azobenzene-containing copolymers strongly depended on the molecular structure and conformation of the achiral azobenzene moieties in side chain. The *m*-substituted azobenzene moiety A induced the disorder of the helical conformation of the main chain, while the *p*-substituted azobenzene moieties A' and A'' relatively kept the helical conformation of the random copolymers.

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