

Photocontrol of Polypeptide Helix Sense by Cis-Trans Isomerism of Side-Chain Azobenzene Moieties

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Abstract: The effect of light on polypeptide conformation was investigated by circular dichroism measurements on a series of copolymers composed of β -benzyl L-aspartate and β -(*m*-phenylazo)benzyl L-aspartate, dissolved in the mixed solvents of 1,2-dichloroethane (DCE) and trimethyl phosphate (TMP). The dark-adapted (trans) copolymers are all left-handed helices in DCE and undergo a conformational change from a left-handed helix to a right-handed helix with an increase in the amount of TMP in the solutions. Photoisomerization of the side-chain azobenzene moieties from trans to cis isomers also causes helix reversal in these copolymers at adequate solvent compositions. These copolymers exhibit CD bands in the regions of azobenzene $n-\pi^*$ and $\pi-\pi^*$ transitions which change their CD signs corresponding to the helix reversal.

Photochromic substances which undergo reversible structural changes induced by light are candidates for chemical transducers or mediators of light energy to chemical functions as well as candidates for storage systems of light energy. Organisms on earth use photochromic systems such as rhodopsin in vision, phytochrome in regulation of life processes of plants, and others relating to various kinds of photomovements.^{1,2} Light-insensitive natural substances are also able to become photoresponsive by modification with photochromic moieties, and various chemical functions in biological systems have been photocontrolled with photoresponsive enzymes, membranes, and others.²⁻⁵

Photocontrol of chemical functions with artificial systems has recently been performed with azobenzene derivatives.⁵ Azobenzene derivatives undergo photoinduced cis-trans isomerism with large configurational change,⁶ and the substances with both azobenzene and functional moieties are suited as mediators between light energy and chemical functions via the structural change. On this basis, photocontrolled complexation was performed between azobenzene-capped cyclodextrin and various kinds of guest molecules,⁷ and also between azo-modified crown ethers and alkaline cations.⁸ Micelles,⁹ membranes,¹⁰ and macromolecules¹¹⁻¹⁵ with both photoresponsive and functional moieties are

also candidates for such photocontrol systems.

Much effort has been invested in effecting light-induced conformational changes of polymers with vinyl polymers,¹¹ polypeptides,¹²⁻¹⁴ and others.¹⁵ Investigations of photoresponsive polypeptides containing azobenzene moieties were first begun by Goodman et al. with (phenylazo)phenylalanine polymers.¹² They found that photoisomerization of the side-chain azobenzene moieties changed chiroptical properties of the polymers without variation in the backbone conformation.^{12b} We also investigated similar systems and showed the first example of light-induced conformational changes of polypeptides with polyaspartates containing azobenzene moieties in the side chains.^{13a} The design of these photoresponsive polypeptides was based on the conformational versatility of polyaspartates as shown by helix reversal induced by solvent¹⁶ or variations in ester components.¹⁷ Heretofore, we have found several kinds of conformational changes induced by light occurring between a left-handed helix and a right-handed helix and between a helix and a coil.¹³ Pieroni et al. recently reported another kind of light-induced conformational change occurring between a β structure and a coil with azo-modified polyglutamates.^{14b}

In the above photoresponsive polypeptides, large amounts of azobenzene moieties are necessary to attain significant conformational changes. It is, however, desirable for small amounts of photochromic moieties to cause marked conformational changes in order to use such systems as effective chemical transducers or mediators. We report here on the photoresponsive behavior of a copolymer series of β -benzyl L-aspartate and β -(*m*-phenylazo)benzyl L-aspartate. In this copolymer series, small amounts of azobenzene moieties are sufficient to cause photoinduced helix reversal when assisted by the solvent effect (Scheme I).

Experimental Section

Materials. The copolymers used in this work were prepared by polymerization of various ratios of β -benzyl L-aspartate and β -(*m*-phenylazo)benzyl L-aspartate *N*-carboxy anhydrides.^{13c} The copolymer compositions were estimated by using nitrogen contents of elemental analysis. Details in syntheses and characterization of these copolymers were reported previously.^{13c} As solvent for spectral measurements, 1,2-

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Scheme I

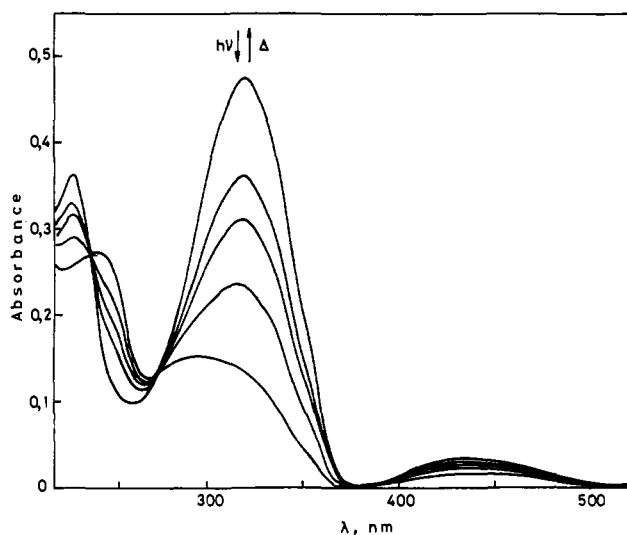
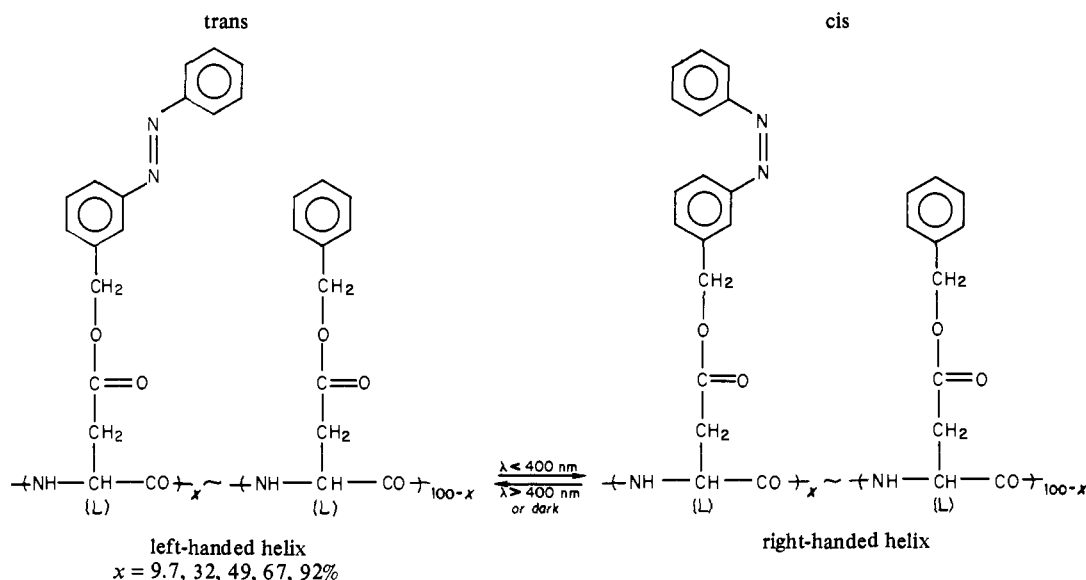


Figure 1. Absorption spectra of the copolymer containing 92% azo groups in the side chains ($c = 0.01$ g/L in DCE, path = 1 cm) at various cis contents (0, 24, 35, 50, and 70% from top to bottom at around 320 nm).

dichloroethane (DCE) and trimethyl phosphate (TMP) were used. The DCE was "Dotite Spectrosol" grade. The TMP was Tokyo Kasei extra pure grade and was purified by distillation.

Measurements and Isomerization. Ultraviolet-visible spectra were recorded on a Shimadzu-360 spectrophotometer. Circular dichroism (CD) measurements were made with a JASCO CD-400X apparatus at 25 °C. Calculated CD spectra for mixtures of left- and right-handed α -helices were obtained with the Data Processor DP-500 attachment. Molar ellipticities, $[\theta]$ in deg cm²/dmol, were calculated by means of the molar concentration of the amide group for the bands below 250 nm and by means of the molar concentration of the phenylazo residues for the side-chain CD bands. Photoisomerization from trans to cis isomers was carried out by irradiation with light of 320–390 nm from a 500W xenon lamp, using a Corning 7-37 filter. The cis isomers were thermally (40 °C) or photochemically (400–500 nm, Corning 3-74 and 7-59 filters) converted into the trans isomers. The cis percentages were calculated from the decrease in the absorbance around 320 nm, assuming that the absorbance of cis isomers is negligible in comparison with that of trans isomers. The values were 70–80 in the photostationary state.

Results and Discussion

The absorption spectra of the copolymers before irradiation resemble that of azobenzene, showing the absorptions associated with the π - π^* and n - π^* transitions of the side-chain azobenzene moieties around 320 and 450 nm, respectively, as exemplified in

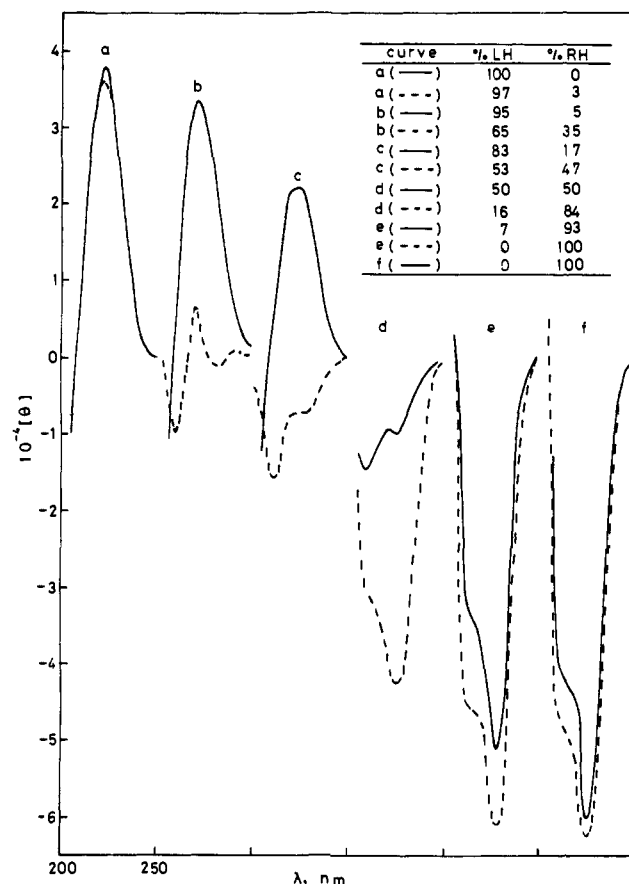


Figure 2. CD spectra below 250 nm of the copolymer containing 32% azo groups before (—) and after (---) irradiation in mixed solutions of DCE and TMP. TMP content: 20% (a); 40% (b); 50% (c); 55% (d); 60% (e); 70% (f). Percentages of left- and right-handed helices (%LH and %Rh, respectively) calculated for each spectrum are also shown.

Figure 1. Irradiation of the dark-adapted (trans) samples with light of 320–390 nm indicates the spectra which are very different from those before irradiation but have isosbestic points at 239, 273, and 380 nm, the intensity of the π - π^* absorption being markedly decreased and the n - π^* absorption being slightly increased and shifted to shorter wavelengths.

The CD spectra below 250 nm of the dark-adapted (trans) copolymer containing 32% azo groups exhibit various shapes and intensities depending on the solvent composition (Figure 2). The

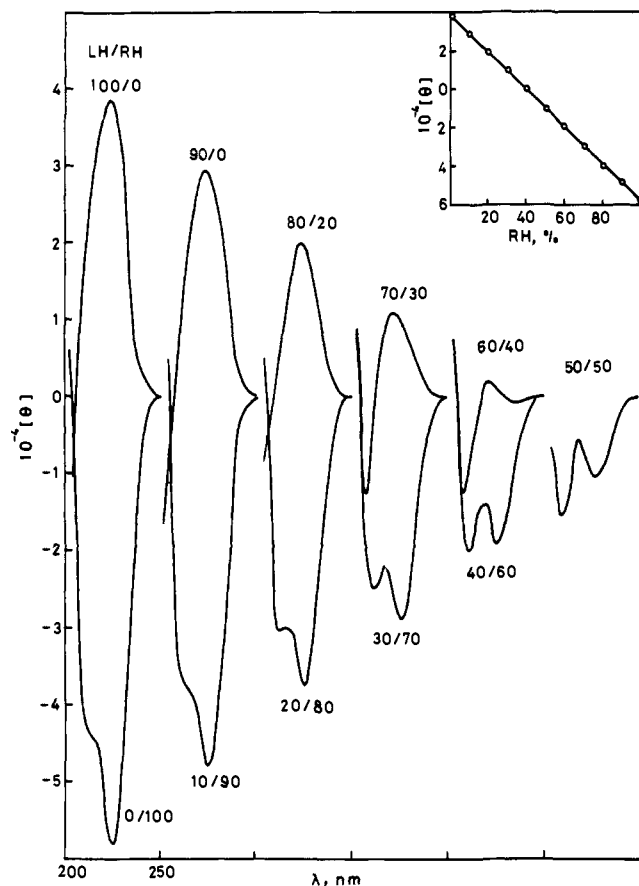


Figure 3. CD spectra computed for combination of left- and right-handed helices, using two limited spectra of the copolymer containing 32% azo groups.

spectrum in pure DCE is characteristic of the left-handed α -helix, having a positive maximum with $[\theta]$ of about 38 000 in the vicinity of 222 nm.^{16a,18} The CD spectrum changes with increasing TMP in the sample solutions accompanying the inversion in the sign of $[\theta]$ and finally giving the spectrum which is similar to that usually associated with the right-handed α -helix. The value of $[\theta]$ in the vicinity of 225 nm ($\sim -60\,000$) at high TMP contents is greater than the standard value ($-40\,000$) of the right-handed α -helix.¹⁹ This deviation cannot be ascribed to the side-chain chromophoric effect²⁰ of trans azobenzene moieties since it is not enhanced by an increase of azo groups on the copolymers (Figure 4). As similar deviation was reported for the right-handed helix of poly(*p*-chlorobenzyl L-aspartate),^{17f} it probably arises because of slight differences in the backbone conformation between various right-handed helical polymers. Conformational changes are also induced by irradiation (Figure 2), giving different CD spectra from those before irradiation.

The various CD spectra obtained for the polypeptide may be interpreted as a combination of two limited spectra corresponding to left- and right-handed α -helices. A family of calculated CD spectra are shown in Figure 3 to interpret every experimental spectrum, using the spectra of a left-handed helix (DCE 100%, $[\theta]_{222} = 38\,500$) and a right-handed helix (DCE/TMP = 20/80, $[\theta]_{226} = -58\,000$). When the maximum or minimum ellipticity at 222–226 nm is denoted by $[\theta]_m$, the plotting of $[\theta]_m$ vs. the percentage of right-handed helices gives a linear relationship (Figure 3), which may be used to evaluate the ratio of left-handed helices to right-handed helices (LH/RH ratio) from various CD spectra of this copolymer series. The LH/RH ratios obtained

by means of the relationship are given in Figure 2. The LH/RH ratios obtained by means of the relationship are given in Figure 2.

Other copolymers also exhibit similar behavior under the influence of solvent or light. Some features of the conformational transition can be deduced from the relations between $[\theta]_m$ and TMP% (Figure 4). The conformational transition occurs at different TMP percentages for the dark-adapted samples and the irradiated ones. This means that the left-handed helices have different stability when azo groups in the copolymers are either all trans or mixtures of trans and cis isomers. Accordingly, this light-induced conformational change occurs in the TMP range where the stability of the left-handed helix is different between both states before and after irradiation. The copolymers with smaller azo groups (9.7% and 32%) have narrow TMP ranges where the conformational change induced by light occurs. On the other hand, the copolymers with more azo groups exhibit the light-induced conformational change over wide ranges of TMP content. The TMP content needed to give an equal mixture of both helices ($[\theta]_m = -10\,000$) increased from 37% to 94% with increasing azo groups in the dark-adapted copolymers, whereas it is almost independent of the azo content after irradiation. This result may be explained in terms of trans-trans side-chain interactions which stabilize the left-handed helix but disappear upon irradiation.

The remarkable conformational changes observed in this work are shown in Figure 5. It should be noted that the CD patterns of the copolymers containing large amounts of azo groups are different, after irradiation, from the calculated ones as shown in Figure 3, the ellipticity in the vicinity of 210 nm being larger than that around 222 nm. This may arise from the side-chain chromophoric effect²⁰ of the *cis*-azobenzene moieties. The evaluation of LH/RH ratios from these perturbed spectra was carried out with the ellipticity at 222 nm. The most remarkable conformational change induced by light was observed with the copolymer containing 49% azo groups, the content of right-handed helices being changed from 14% to 100% by irradiation. It is also surprising that the copolymer containing azo groups of only 9.7% changes the content of right-handed helices from 9% to 74% at 25% TMP and also from 14% to 81% at 30% TMP by light. Such photoinduced helix reversal was also observed for para isomers of the copolymers,²¹ we showed that the copolymer composed of 8% β -(*p*-phenylazo)benzyl L-aspartate and 92% β -benzyl L-aspartate undergoes a marked conformational change induced by light in mixtures of DCE and TMP. These results established that small amounts (<10%) of azobenzene moieties are sufficient to cause a remarkable photoinduced conformational change in the polypeptide chain. The variations in $[\theta]_m$ ($>60\,000$) of these conformational changes are substantially larger than the value (<2000) reported by Pieroni et al.^{14b} for the light-induced $\beta \rightarrow$ coil transition of azo-modified polyglutamates, indicating the outstanding nature of this system in photoresponsibility. Such conformational versatility is essentially derived from the fact that the energy difference between both helices is very small^{17f} and is subject to perturbation so as to invert the helix sense. Although the photoinduced conformational change is limited to the helix reversal in solution, other kinds of conformational changes might be possible in the solid state since such polypeptides may be expected to take ω -helical conformation and the β -form other than right- and left-handed α -helices.²²

Another feature of the helix reversal may be obtained from detailed knowledge of the relation between the backbone conformation and the side-chain isomerization. The plotting of $[\theta]_m$ vs. cis % for the two copolymers containing 9.7% and 67% azo groups shows that the $[\theta]_m$ value changes linearly with increasing cis % although the value becomes almost constant at more than 50% cis for the copolymer containing 9.7% azo groups (Figure 6). This behavior is in contrast to that found for the copolymer composed of 41% β -benzyl L-aspartate and 59% β -(*p*-phenyl-

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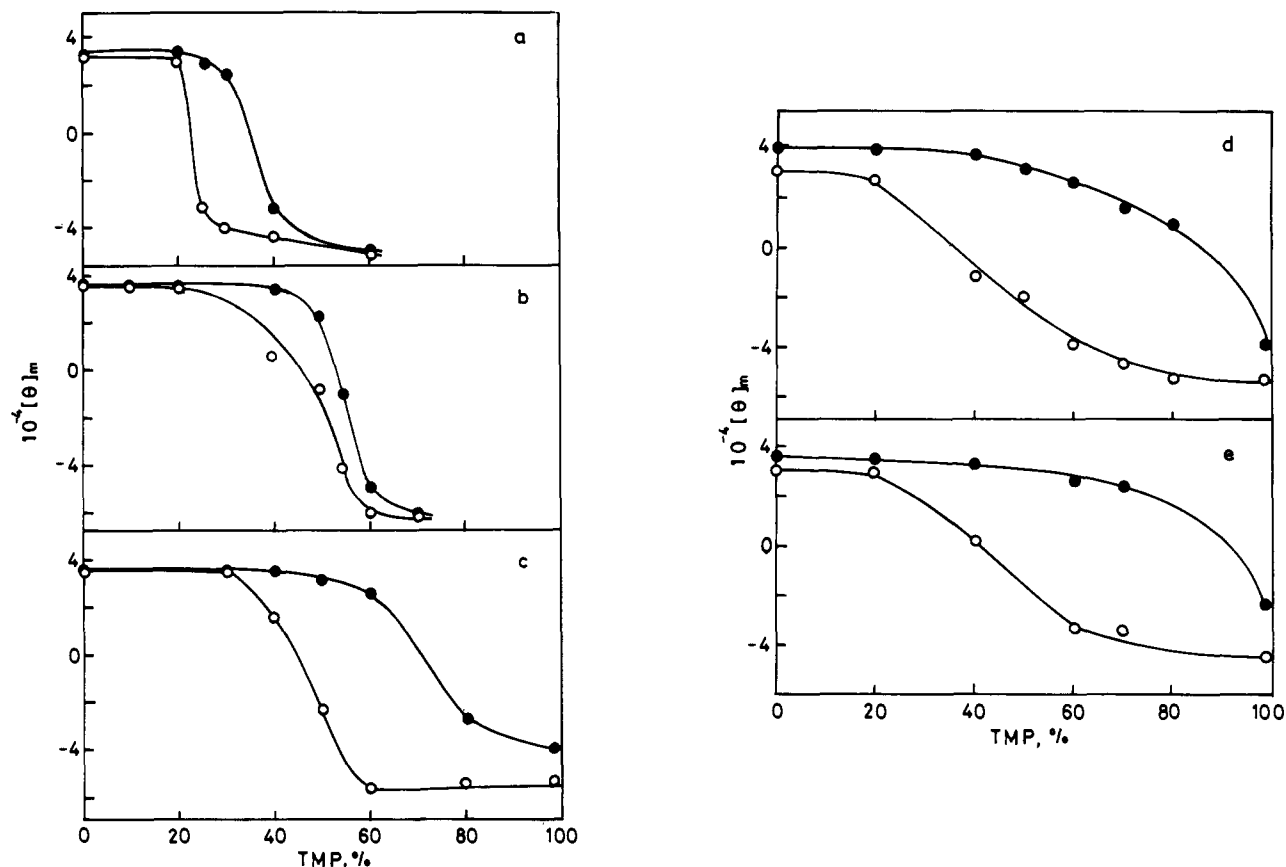


Figure 4. Dependence of the ellipticity of the amide $n-\pi^*$ CD band on TMP content before (●) and after (○) irradiation. Content of azo groups: 9.7% (a); 32% (b); 49% (c); 67% (d); 92% (e).

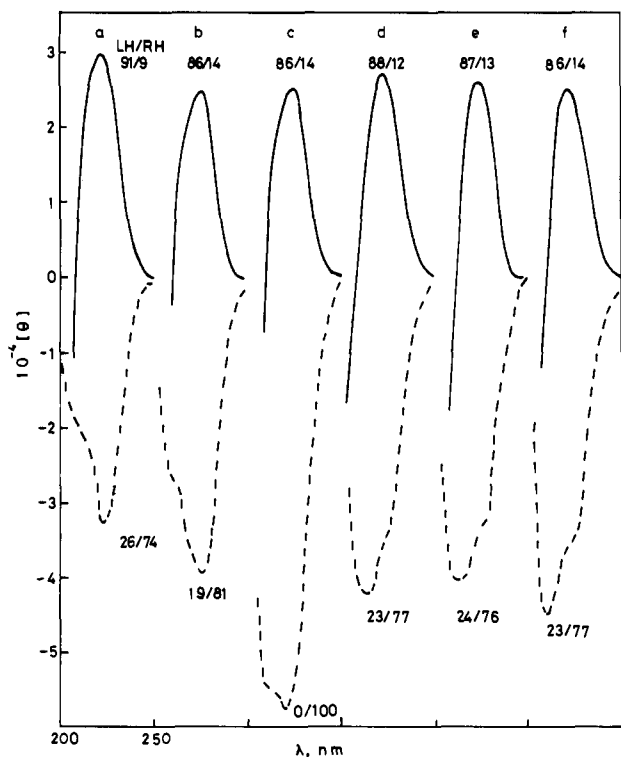


Figure 5. Remarkable changes in CD spectra induced by light in the copolymers. Content of azo groups: 9.7% (a, TMP 25%; b, TMP 30%); 49% (c, TMP 60%); 67% (d, TMP 60%); 92% (e, TMP 60%; f, TMP 70%). (—) Before irradiation; (---) after irradiation.

azo)benzyl L-aspartate, which undergoes a marked conformational change abruptly at more than 50% cis in DCE.^{13c} The different behavior may be due to the role of TMP in destabilizing the

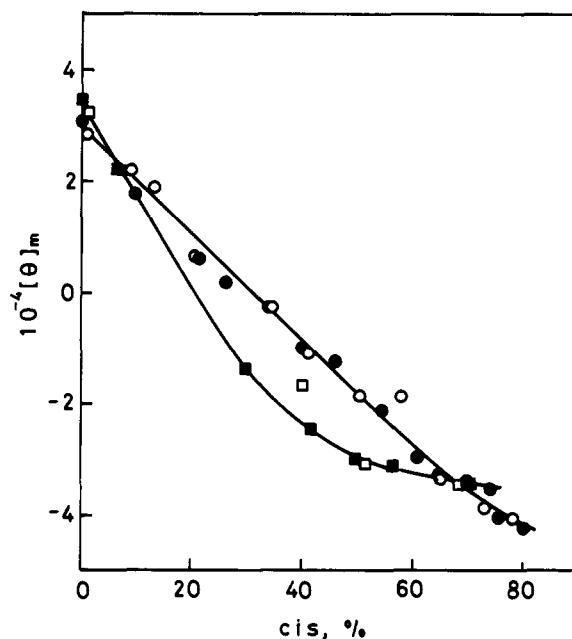


Figure 6. Variation in the ellipticity of the amide $n-\pi^*$ CD band in the course of photochemical isomerization of trans to cis (●, ■) and cis to trans (○, □) for the copolymers containing 9.7% (■, □; TMP 30%) and 67% (●, ○; TMP 60%) azo groups as a function of cis percent.

left-handed helix. The fact that 50% cis is sufficient to make a copolymer containing 9.7% azo groups fully photoresponsive indicates another important feature that such a marked conformational change can be brought about by trans-cis isomerization of only 5% of the units in the copolymer sequence.

The thermal decay from the cis to the trans form was examined in the dark in relation to the helix reversal. The thermal isom-

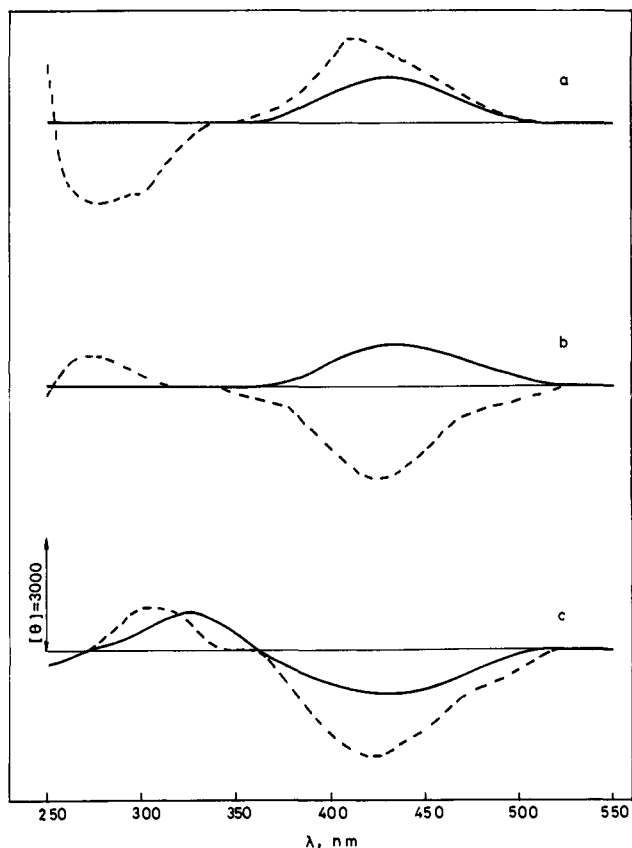
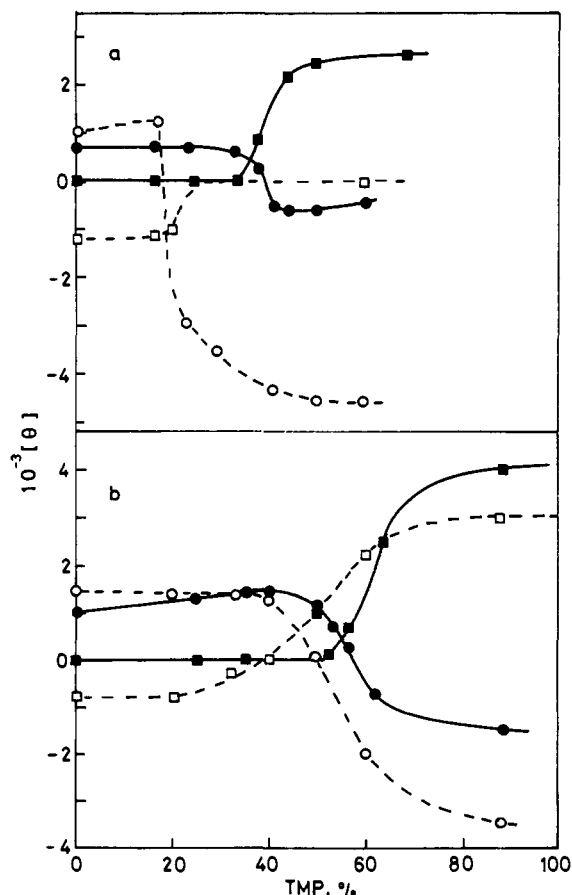


Figure 7. CD spectra associated with the side-chain transitions in the copolymer containing 49% azo groups before (—) and after (---) irradiation. TMP content: 0% (a); 60% (b); 87.5% (c).



erization of the copolymer containing 9.7% azo groups in the 30% TMP solution follows first-order kinetics with a half-life of 24 h at 40 °C and is not influenced by the helix reversal occurring during the decay process. The same feature was also observed for the copolymer containing 92% azo groups, the half-life being 21 h at 40 °C in the 60% TMP solution. These results suggest that the thermal cis to trans isomerization takes place at the same rates in both right- and left-handed helices.

The copolymers exhibit CD bands in the regions of azobenzene $n-\pi^*$ and $\pi-\pi^*$ transitions at 400–500 nm and 250–350 nm, respectively (Figures 7 and 8). The dark-adapted copolymers show, at smaller TMP contents, only a positive CD band associated with the azo $n-\pi^*$ and $\pi-\pi^*$ CD bands with a negative sign for the former and a positive sign for the latter (Figure 7c). The side-chain CD spectra of the irradiated copolymers are different, at smaller TMP contents, from those of the dark-adapted ones because of the appearance of a negative $\pi-\pi^*$ CD band (Figure 7a), whereas they are similar at larger TMP contents, although the $\pi-\pi^*$ CD band is blue shifted (Figure 7c). It is interesting how these side-chain CD bands are influenced by the conformational variation of the backbones.

Figure 8 shows the solvent dependencies of these bands. In the dark-adapted state, the sign of the side-chain $n-\pi^*$ band changes from positive to negative on increasing TMP% near the TMP range where the conformational change from a left-handed helix to a right-handed helix takes place. On the other hand, the side-chain $\pi-\pi^*$ CD is negligible at low TMP contents and appears with a positive extreme in the solvent range where the helix reversal begins. In the irradiated state, the behavior of the $n-\pi^*$ CD band is similar to that before irradiation, although the $[\theta]$ value is usually increased and the TMP percentage at which the sign of $[\theta]$ inverts is shifted to a smaller one. The inversion in the sign was also observed for the $\pi-\pi^*$ CD band after irradiation. The TMP percentages of the sign inversion of these bands are in the range of 40–50, except for the copolymer with the least azo groups, and

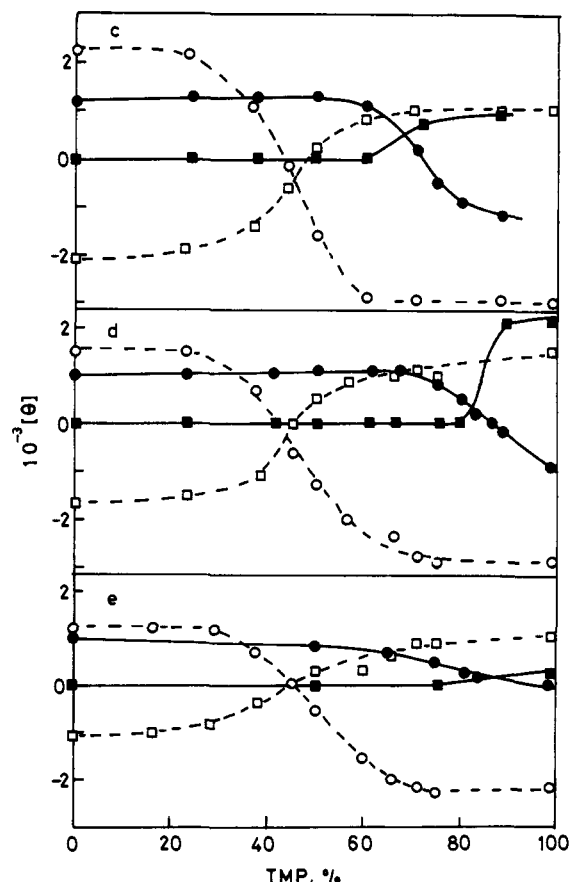


Figure 8. Dependence of the ellipticities of the side-chain $n-\pi^*$ (●, ○) and $\pi-\pi^*$ (■, □) CD bands before (●, ■) and after (○, □) irradiation on TMP content. Content of azo groups: 9.7% (a); 32% (b); 49% (c); 67% (d); 92% (e).

do not depend on the azo group content in the copolymers, being in good agreement with the transition behavior of the backbone conformation. These results of the side-chain CD bands before and after irradiation clearly indicate that the signs of the bands are determined by the screw sense of the polypeptide chain.

In conclusion, polypeptide helix sense can be inverted by light

on the basis of photoisomerization of the side-chain azobenzene moieties. This photoinduced reversible inversion in chirality might permit photocontrol in chiral recognition or chiral catalytic reactions when binding or catalytic functional groups are incorporated into the polypeptide sequence. Investigations along this line are now underway.

Absorption Spectra and Photochemical Rearrangements in Phenylalkene Cations in Solid Argon

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Abstract: Matrix photoionization experiments with phenylalkenes produced and trapped the parent molecular cations in solid argon at 20 K. In the substituted styrene cation cases, structure was resolved in red and ultraviolet absorption bands and assigned to Ph—C stretching and Ph—C=C bending modes. Molecular ion rearrangements were observed during sample formation and upon photolysis of the cold sample; allylbenzene cation rearranged to β -methylstyrene cation and indan cation with 290 nm irradiation. The matrix absorption bands were substantially sharper than photodissociation spectra, which suggests that excess internal energy may contribute substantially to the bandwidth of gaseous molecular ions produced by electron impact.

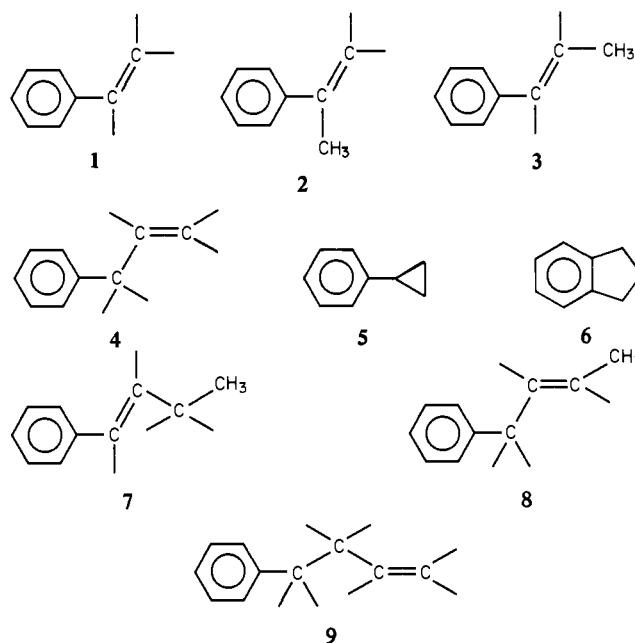
Styrene and substituted styrene radical cations are particularly interesting species owing to conjugation between the olefin and aromatic π systems. These ions have been produced in ion cyclotron resonance (ICR) experiments for extensive studies of photodissociation spectra (PDS).¹ The absorption spectrum of styrene cation in glassy matrices following γ -radiolysis exhibits strong bands at 630 and 342 nm.² The red band could not be characterized by PDS methods since this absorption energy lies below the one-photon dissociation threshold giving $C_6H_6^+$ and C_2H_2 .¹

Rearrangements of molecular ions have been of considerable interest to mass spectroscopists.³ The PDS of allylbenzene cation was identical with that of β -methylstyrene cation showing that double-bond migration into conjugation occurs under the conditions of the ICR experiment.¹ The matrix isolation technique has recently been used to trap molecular ions for observation of absorption spectra and molecular ion rearrangements. In a particularly interesting study, cycloheptatriene cation in solid argon was rearranged to toluene cation by visible photolysis.⁵ Quenching of internal energy by the matrix host makes photoisomerism a competitive process with photodissociation. Here follows a study of the absorption spectra, photochemistry, and rearrangements of phenylalkene and related cations in solid argon.

Experimental Section

The cryogenic and vacuum apparatus and windowless argon resonance lamps have been described previously.^{6,7} The experimental procedure and photolysis methods have been given in the cycloheptatriene ion report.⁵ Briefly, phenylalkene vapor was diluted to about 0.5% with argon and condensed at 20 ± 2 K on a sapphire substrate with argon at 150 μ m pressure flowing at about 1 mmol/h through a 3-mm i.d. orifice quartz discharge tube powered by microwave excitation. Assuming 1% photoionization of neutral molecules, an upper limit of approximately 10^{16} ions/cm² of sample surface may be trapped in a typical experiment. Absorption spectra were recorded on a Cary 17 spectrophotometer before and after photolysis with a high-pressure (1000 W) mercury arc, using glass wavelength cut-off filters. Photon flux from the mercury arc measured on a thermopile laser power meter arranged to match the sample configuration gave 5×10^{16} photons/(cm² s) in the 420–750 nm

Chart I



range, 8×10^{16} photons/(cm² s) at 290–420 nm, and 10×10^{16} photons/(cm² s) at 220–290 nm.

The phenylbutenes used here were obtained from ICN-K&K Laboratories, Inc.; all other samples came from Aldrich Chemical. After several freeze-thaw-pump cycles, the sample vapor was introduced di-

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