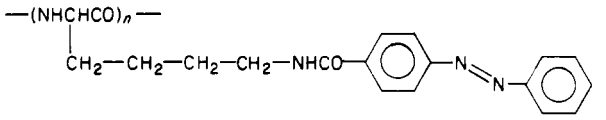
Light-Induced Reversible Conformational Changes in Poly(L-lysine) with Photochromic Side Chains

Photochromic polypeptides represent interesting systems because of their relevance to the molecular mechanism of photoregulation in biological processes.[1] Neutral polypeptides containing photoisomerizable azo aromatic chromophores were first investigated by Goodman et al.[2] More recently, two groups have studied reversible conformational properties induced by light, of anionic photochromic polyaspartates and polyglutamates containing azobenzene.[3,4] Although Atreyi et al.[5] reported a conformational study of cationic poly(L-lysine) containing azo aromatic groups, a photochemical approach has not yet been examined. In this communication we describe the synthesis and reversible photochromic properties of poly(N^{ϵ}-(phenylazobenzoyl)-L-lysine) (PPABLL).



PPABLL

PPABLL was synthesized from poly(L-lysine) hydrobromide (degree of polymerization 3260, 1 mmol) and *p*-(phenylazo)benzoic acid *p*-nitrophenyl ester (3 mmol) in the presence of triethylamine (1.2 mmol) in aqueous dimethylformamide; yield 97%. Anal. Calcd for $(C_{19}H_{20}N_4O_2)_n$ as 97 mol % azo moieties: C, 67.49; H, 6.09; N, 16.82. Found: C, 67.21; H, 6.03; N, 16.73. PPABLL is only soluble in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). Irradiations of the sample solutions were carried out at 25 °C with a mercury lamp (400 W) filtered with narrow-band interference filters. The light intensity was determined by chemical actinometry using potassium ferrioxalate and was found to be 2.7×10^{19} photons cm^{-2} s^{-1} at 360 nm and 2.1×10^{19} photons cm^{-2} s^{-1} at 460 nm. The spectral data were expressed in terms of mean residue ellipticity $[\theta]$ (deg cm^2 dmol^{-1}) and molar extinction coefficient ϵ (dm^3 mol^{-1} cm^{-1}).

The effect of solvent on the photoisomerization of azo dyes has been studied in detail.[6-8] Among nine azo dyes examined,[8] *p*-(phenylazo)benzoic acid in HFIP is capable of causing trans-to-cis photoisomerization upon irradiation at 360 nm, whereas the opposite occurs upon irradiation at 460 nm. The cis isomer of the azo dye returns to the trans form when kept in the dark. The absorption spectra of PPABLL in HFIP exhibit main absorption bands at 425, 318, and 230 nm. These three bands exhibit photochromism upon irradiation at 360 nm as depicted in Figure 1. Figure 2 shows the circular dichroism (CD) spectra of PPABLL in HFIP in the 200–520-nm wavelength region. Before irradiation, dichroic bands were observed at 435 nm with $[\theta]_{435} = 600$, at 340 nm with $[\theta]_{340} = -3100$, and below 240 nm with $[\theta]_{221} = -27\,600$ and $[\theta]_{207} = -29\,500$. The origin of the two longer wavelength dichroic bands at 435 and 340 nm arises from the dipole–dipole interaction between two transition dipoles of the azo aromatic chromophores under a chiral environment,[9,10] and the two negative dichroic bands below 240 nm are due to the peptide transitions. From the positions and magnitudes of the n–π^* and π–π^* peptide amide transitions, the backbone conformation of PPABLL in HFIP can be assigned to be the right-handed α-helix structure. In this connection, poly(L-lysine) containing 4.6 mol % *p*-(dimethylamino)azobenzene-*p*-carboxylic acid moieties was reported to exist in a β-structure in water.[5] However, direct comparison of the two different conformations reported by Atreyi et al.[5] and described here is difficult, since the mole percent of azo moieties in poly(L-lysine) and the solvents is so different.

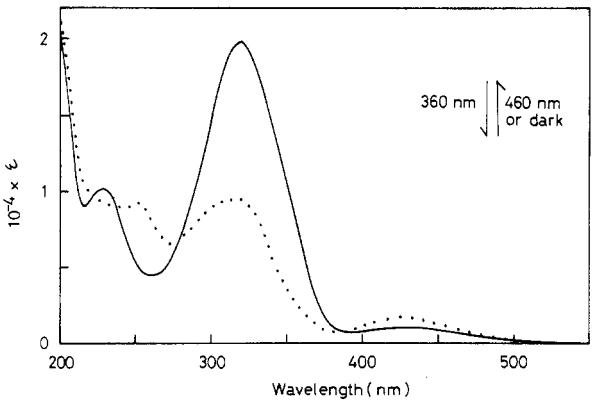


Figure 1. Absorption spectra of PPABLL in HFIP at 25 °C: (—) trans, before irradiation; (···) cis, after irradiation at 360 nm for 45 min.

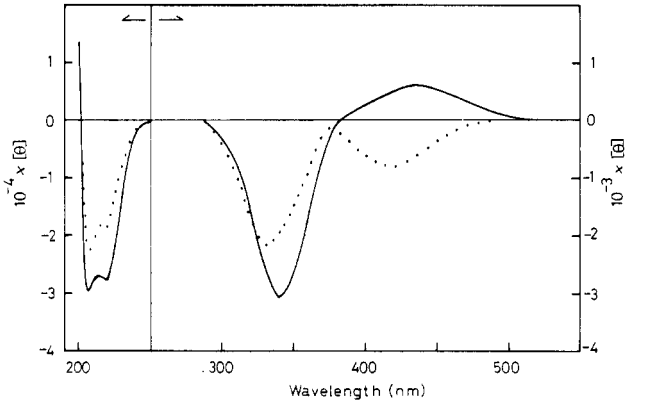


Figure 2. CD spectra of PPABLL in HFIP at 25 °C: (—) before irradiation; (···) after irradiation at 360 nm for 45 min.

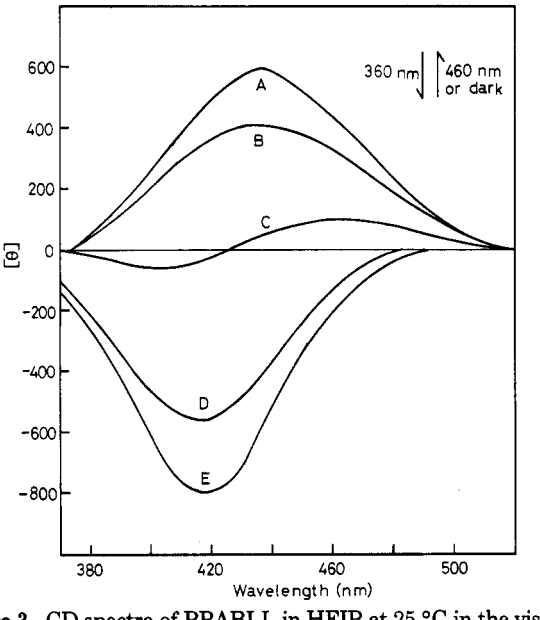


Figure 3. CD spectra of PPABLL in HFIP at 25 °C in the visible wavelength region. Irradiation time at 360 nm: (A) 0, (B) 5, (C) 15, (D) 30, and (E) 45 min.

Light produces a photochromism in the CD spectrum of PPABLL in HFIP. Upon irradiation at 360 nm, the positive band at 435 nm became negative at 418 nm within

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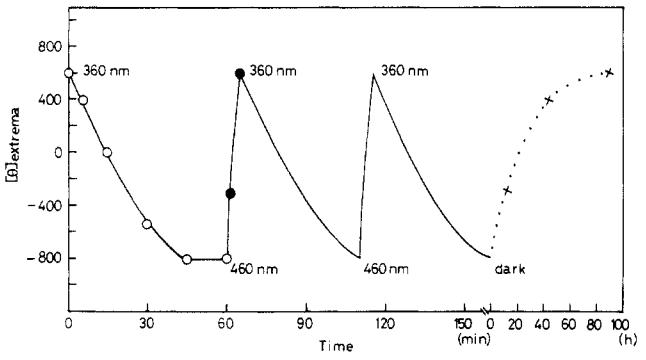

Figure 4. Azo-modified poly(L-lysine) in HFIP. Change of ellipticities at extrema as a function of irradiation time at different wavelengths and of the dark adaptation time.

45 min, and the negative bands at 340 nm and below 240 nm continued to decrease their ellipticities (up to 4 h). Reirradiation at 460 nm for 2 h at 25 °C does not cause a reverse photoconversion of the dichroic bands at 340 nm and below 240 nm. The dichroic band at 435 nm, however, exhibits a typical photochromism as depicted in Figures 3 and 4. The complete reversibility of the CD spectra in Figure 3 is due to the trans $\rightleftarrows$ cis photoisomerization (see Figure 1), which affects the interaction mode of the transition dipole moments of the azo dye covalently linked to poly(L-lysine). When the cis azo isomer of PPABLL with negative ellipticity at 418 nm was kept in the dark for 2 days, the cis conformer isomerized mostly to the trans isomer exhibiting positive ellipticity at 435 nm (see Figure 4). This is fundamentally the same observation as for *p*-(phenylazo)benzoic acid itself in HFIP.[8]

The results show the photochromism of poly(L-lysine) containing a high mole percent of azo aromatic chromophores and are the first reversible photochromism of visible CD of a cationic polypeptide. Like anionic polypeptides containing azobenzene, poly(L-lysine) with azo chromophores seems to have promise as a photoresponsive system.

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References and Notes

(1) See, for example: Lovrien, R.; Pesheck, P.; Tisel, W. *J. Am. Chem. Soc.* **1974**, *96*, 244. Van der Veen, G.; Hoguet, R.; Prins, W. *Photochem. Photobiol.* **1974**, *19*, 197.
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CORRECTIONS

E. Pefferkorn, A. Carroy, and R. Varoqui*: Adsorption of Polyacrylamide on Solid Surfaces. Kinetics of the Establishment of Adsorption Equilibrium. Volume 18, Number 11, November 1985, page 2252.

Equation 12 should read

$$-V\frac{d}{dt}\ln(1-\theta) - J_v \ln(1-\theta) + \theta K S N_{sm} = J_v K N_0 t, \qquad K \equiv K_3 \quad (12)$$

In eq 1 and 6, the last term $-J_v\sum_{i=1}^{n}A_i$ should be $-J_v\sum_{i=1}^{n}A_i\Delta t$. As Δt is equal to unity, this correction does not affect the results.