Photoresponsive Peptide and Polypeptide Systems. VI.[1] Reversible Solubility Change of Azo Aromatic Lysine

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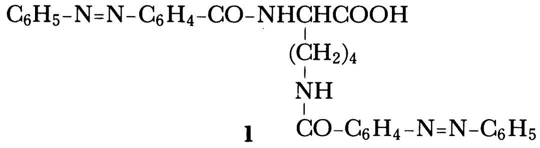
Synopsis. The reversible solubility change of azo aromatic lysines due to the trans-cis photoconversion of azo moieties was studied. On irradiation at different wavelengths, azo aromatic lysines are soluble under ultraviolet light (cis) and precipitate under visible light (trans). The dipole moments of the solvents used are considered to play a role in the solubility change.

The two conformers of azobenzene are known to have two different dipole moments (μ); that is, the μ values are 0.5D for the trans conformer and 3.1D for the cis conformer.[2] Recently, Irie et al.[3–5] reported on the photostimulated reversible solubility change of aggregated polystyrene and poly(glutamic acid) containing azobenzene. Our group has previously investigated the photoresponsive systems using cationic peptides and polypeptides[1,6–9] because of their relevance to the molecular mechanism of photoregulation in biological materials and process. One difficulty in studying such photoresponsive systems is, however, the subject of their solubilities, since azo aromatic peptides with high azo moieties are sparingly soluble in common solvents. This series of studies raises the question of whether or not azo aromatic amino acids undergo a rapid change in their solubilities upon the irradiation of light.

In this note azo aromatic lysine (compound **1**) will be described in order to increase knowledge regarding the photoresponsive change in azo aromatic peptide systems, giving a clue to its improved solubility.



$$\begin{array}{l} C_6H_5\text{-}N{=}N\text{-}C_6H_4\text{-}CO\text{-}NHCHCOOH \\ \qquad\qquad\qquad\qquad\quad |\\ \qquad\qquad\qquad\qquad (CH_2)_4 \\ \qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\ NH \\ \qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad CO\text{-}C_6H_4\text{-}N{=}N\text{-}C_6H_5 \end{array}$$

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Experimental

Bis[*p*-(phenylazo)benzoyl]-L-lysine (BPAZ-L-Lys, **1**) was prepared according to the usual Schotten-Baumann procedure using L-lysine hydrochloride and *p*-(phenylazo)benzoyl chloride in a mixed NaOH-1,4-dioxane solvent; yield, 72%; mp 229 °C, $[\alpha]_D^{23}=-128°$ (*c* 0.25, 1,4-dioxane). Found: C, 68.45; H, 5.32; N, 14.94%. Calcd for $C_{32}H_{30}N_6O_4$: C, 68.31; H, 5.37; N, 14.94%. D-Antipode was prepared by the same procedure; yield, 64%; mp 229°C, $[\alpha]_D^{23}=132°$ (*c* 0.25, 1,4-dioxane). The absorbance spectra were measured with a Jasco UVIDEC-1 spectrometer. The critical solubilities of trans BPAZ-L-Lys at 25 °C are 3.8×10^{-4} mol dm^{-3} in a 1,4-dioxane-water mixture (1 : 1.1 v/v) and 2.3×10^{-4} mol dm^{-3} in acetonitrile, while those of the cis isomer are 1.6×10^{-3} mol dm^{-3} in a 1,4-dioxane-water mixture (1 : 1.1 v/v) and 9.8×10^{-4} mol dm^{-3} in acetonitrile. The cis isomer is 4.3 times more soluble in solvents than is its trans isomer. The turbid solutions were prepared by adding water to a clear trans BPAZ-L-Lys solution in 1,4-dioxane (ca. 1 : 1 v/v) until the precipitated solute could be observed or by using solvents with a poor solubility to BPAZ-L-Lys. The concentrations of BPAZ-L- and D-Lys in solutions were in the 4.8×10^{-4}—1.5×10^{-3} mol dm^{-3} range.

The irradiation of the sample solutions was carried out at 25 °C with a mercury lamp (400W) filtered with narrow-band interference filters from Toshiba, Ltd. The light intensities, as determined by chemical actinometry, were 1.8×10^{19} photon cm^{-2} s^{-1} at 360 nm and 1.3×10^{19} photons cm^{-2} s^{-1} at 460 nm.

Results and Discussion

Figure 1 shows the changes in the absorption spectra of BPAZ-L-Lys in 1,4-dioxane on irradiation. Before irradiation (trans, in the dark), the BPAZ-L-Lys exhibits absorption bands at 217, 232, 258, 327, and 440 nm. The absorption bands exhibit photochromism when the trans conformer is converted to cis on irradiation at

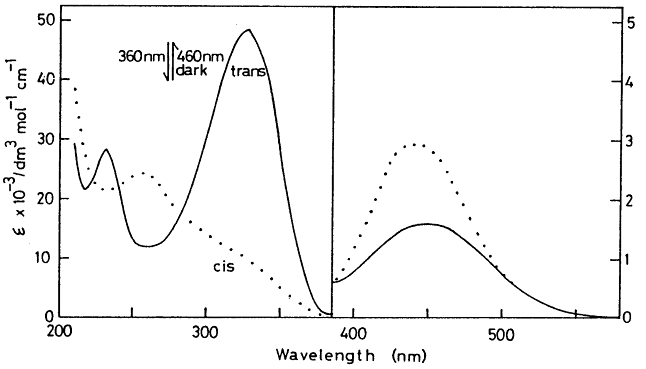

Fig. 1. Absorption spectra of BPAZ-L-Lys in 1,4-dioxane at 25 °C: —— trans, before irradiation and after reirradiation at 460 nm for 10 min; ······ cis, after irradiation at 360 nm for 10 min.

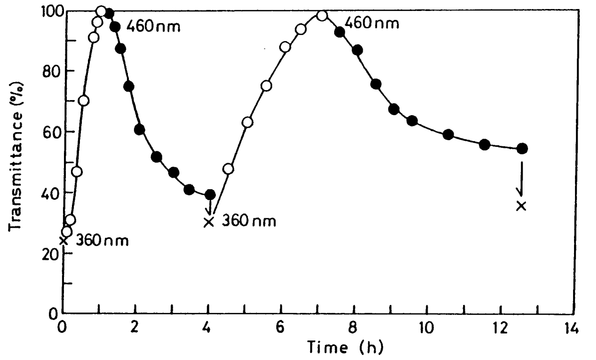

Fig. 2. Time dependence of the solubility change of BPAZ-L-Lys on irradiation at different wavelengths in 1,4-dioxane-water (1:1.1, v/v) at 25 °C: × dark adaptation. Transmittance at 650 nm; concentration 4.8×10^{-4} mol dm^{-3}.

360 nm (ultraviolet), whereas on the reirradiation of the irradiated solution at 460 nm (visible) the cis conformer returns to trans. The photoconversion from trans to cis on irradiation at ultraviolet and visible wavelengths is reversible.

Since the two conformers of azobenzene have the two different dipole moments of 0.5D (trans) and 3.1D (cis),[2] before irradiation we made turbid BPAZ-L-Lys solutions by mixing low- and high-dipole moment solvents or by cooling the heated solution to under the critical solubility. To a solution of trans BPAZ-L-Lys in 1 ml of 1,4-dioxane (μ, 0D), 1—1.1 ml of water (μ, 1.9D) was added to make it turbid. The turbid mixture becomes clear on irradiation at 360 nm for 1 h, accompanied by photoconversion to cis. On reirradiation at 460 nm, the clear solution becomes turbid again, as is shown in Fig. 2. Although this photoinduced solubility change due to the trans-cis isomerization of azo aromatic moieties is reversible, the time course to complete the first cycle (4 h) was much longer than is the case with the azo aromatic poly(glutamic acid) system.[5] Moreover, the second reversible cycle took 8 h, and bigger particles of the precipitated crystals were observed. Though not so marked, the dark adaptation (overnight) after irradiation at 460 nm further decreased the transmittance of the system. The reason for the rapid reversible change of the solubility on irradiation in the azo aromatic polymer system may be attributed to the solubilizing effect among azo aromatic moieties in the backbone chain, i.e., the polymeric effect.

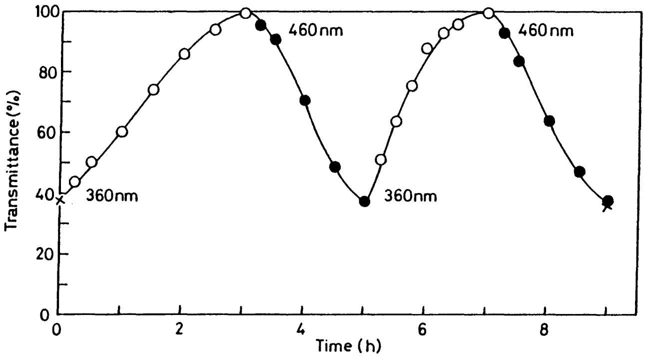

Fig. 3. Time dependence of the solubility change of BPAZ-L-Lys on irradiation at different wavelengths in acetonitrile at 25 °C: × dark adaptation. Transmittance at 650 nm; concentration 5×10^{-4} mol dm^{-3}.

Figure 3 shows the reversible solubility change of BPAZ-L-Lys in acetonitrile (μ, 3.8D). In the acetone (μ, 2.9D) and acetone-hexane (μ, 0.09D) mixed solvent the BPAZ-L-Lys photoresponded as in acetonitrile. D-Antipode, BPAZ-D-Lys, exhibited the same behavior as BPAZ-L-Lys. Thus, when their response times are improved, azo aromatic amino acids might be promising as physicochemical detective and sensory systems under controlled light conditions.

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