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ABSOLUTE CONFIGURATION OF POLYPEPTIDE AND DYE COMPLEXES BY AN APPLICATION OF THE EXCITON CHIRALITY METHOD

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Absolute configurations of the poly(N^{ε}-alkyl-L-lysine) and alkylamino azo dye complexes have been examined by the exciton chirality method. Most complexes showed the S-chirality of the dipole transition moments of dyes. Increased hydrophobic property changed the chirality of dye from common S- to uncommon R-chirality.

The origin of induced circular dichroism (CD) between polypeptides having dissociable side-chains and dyes has been attributed to the chiral hydrophobic, hydrogen-bonding and electrostatic interactions, which contribute to complex formation. The skew dimeric methyl orange interacted with random coil poly(L-lysine) (PLL)[1,2] and the monomeric 2-p-toluidinonaphthalene-6-sulfonate with β-structure PLL.[3] Dye cations, either dimeric or monomeric, are arranged dissymmetrically on the polypeptide chains and induce CD. When a ε-amino group of PLL is changed to a ε-imino group by the substitution of alkyl groups, the interaction mode, at least hydrophobic property, will be affected.

Three analogous polypeptides, PLL, poly(N^{ε}-methyl-L-lysine) (PMLL) and poly(N^{ε}-ethyl-L-lysine) (PELL),[4] and three analogous azo dyes, 4'-aminoazobenzene 4-sulfonic acid sodium salt (AA), 4'-dimethylaminoazobenzene 4-sulfonic acid sodium salt (methyl orange, MO) and 4'-diethylaminoazobenzene 4-sulfonic acid sodium salt (ethyl orange, EO) were studied. To determine the absolute configuration of the chiral complex, the exciton chirality method was employed.[5,6] The ellipticity [θ] (degree cm^2 $dmol^{-1}$) and molar extinction coefficient ε were expressed on the basis of the dye concentration.

In the presence of PLL, PMLL and PELL, the positions of the peak and the band

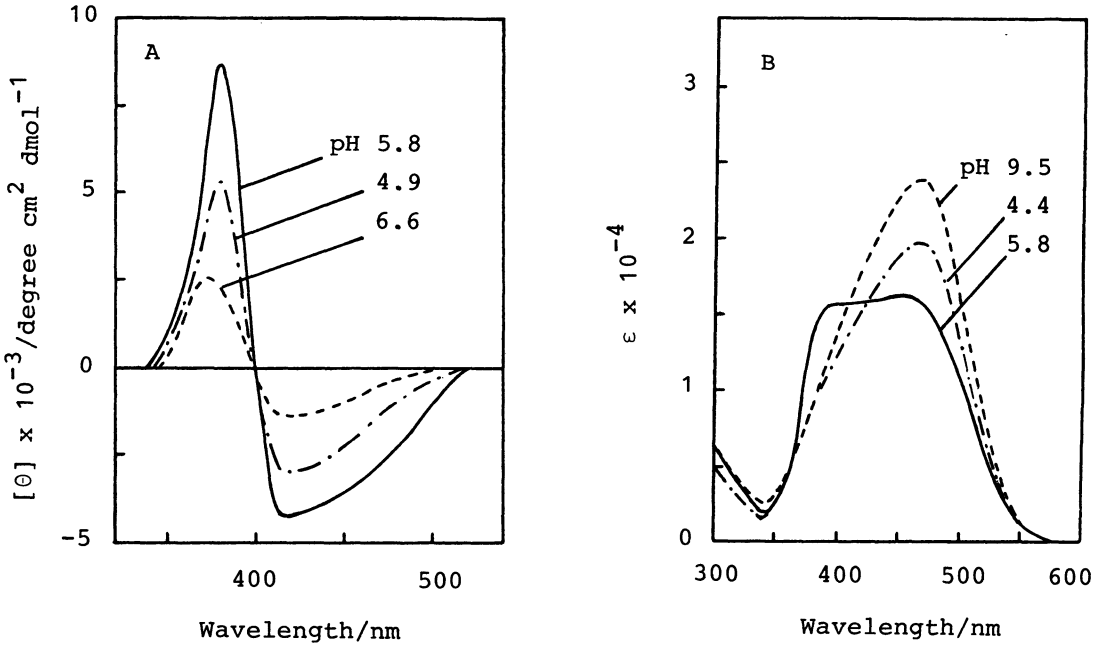

Fig. 1. Induced CD (A) and absorption (B) spectra of the PMLL-MO complex at R/D = 3.

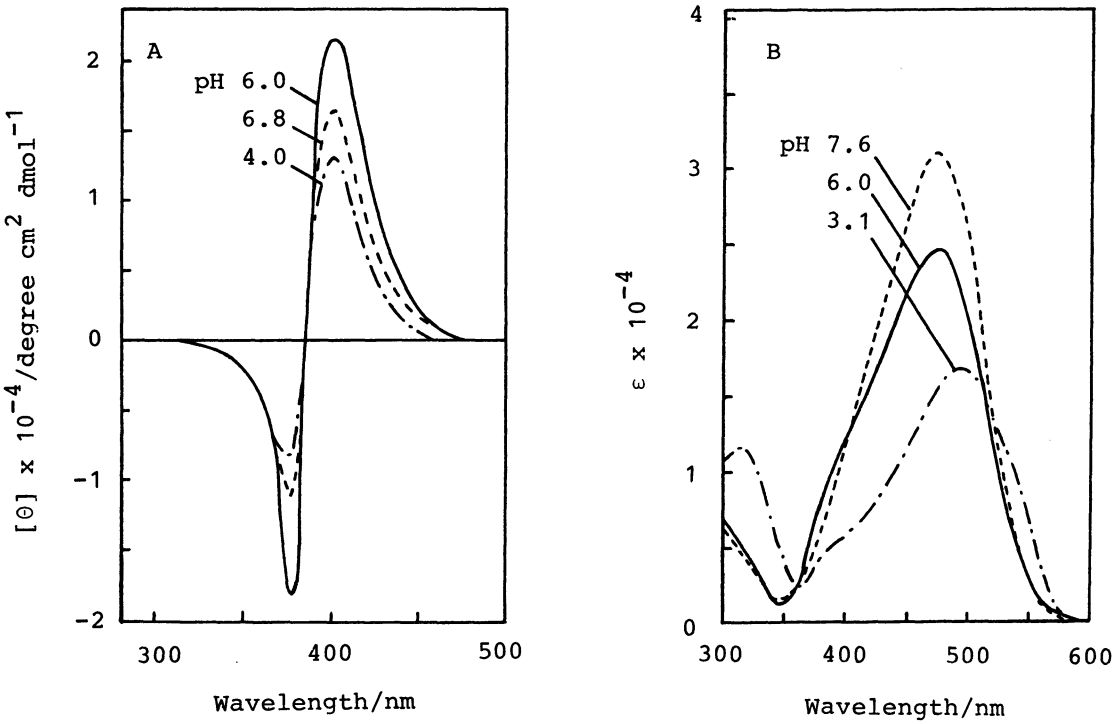

Fig. 2. Induced CD (A) and absorption (B) spectra of the PELL-EO complex at R/D = 0.3.

shapes in absorption spectra were changed in the cases of MO and EO, but no change was found in AA. Accordingly, MO and EO showed induced CD and AA showed no induced CD. Figure 1 shows the induced CD and absorption spectra of the PMLL-MO complex as a function of pH at residue/dye (R/D) ratio of 3. Two induced CD extrema were observed at 415 nm (negative) and at 380 nm (positive). Figure 2 shows the induced CD and absorption spectra of the PELL-EO complex as a function of pH at R/D ratio of 0.3. Two induced CD extrema were observed at 400 nm (positive) and at 377 nm (negative). Thus, increasing hydrophobicity from PLL to PELL and from MO to EO, when a complex was formed, the magnitudes of induced CD decreased and finally the most hydrophobic PELL-EO complex changed the sign from negative to positive at longer dichroic wavelengths. Table shows the results of induced CD in the polypeptide-dye complexes at their optimal pH 6 and R/D conditions. To characterize the transition at around 360-480 nm, a detailed three dimentional model for the polypeptide-azo dye complexes at varying R/D ratios is now studying by means of NMR.

Nakanishi et al. established the validity of the exciton chirality method for natural aromatic compounds[5,6] and, later, Hatano et al. drew a schematic illustration for the PLL-MO complex showing the S-chirality of the dipole transition moments of MO.[1] Since the L-enantiomeric α-carbon configuration was maintained for the three polypeptides presented in this work, the absolute configuration of the dipole transition moments of dyes was the S-chirality for the

Table. Characteristics of Induced CD in the Polypeptide-Dye Complexes.

Polypeptide	Dye	R/D	$[\theta]_{extrema}$ (nm) degree cm^2 $dmol^{-1}$		Chirality
PLL	MO	5	-170000 (370)	165000 (357)	S
	EO	5	-25200 (384)	23900 (370)	S
PMLL	MO	3	-4300 (415)	8700 (380)	S
	EO	3	-2800 (480)	4200 (400)	S
PELL	MO	0.3	-3000 (388)	3000 (370)	S
	EO	0.3	21500 (400)	-18300 (377)	R

PLL-MO, PLL-EO, PMLL-MO, PMLL-EO and PELL-MO complexes, and the R-chirality for the PELL-EO complex (see Table). An illustration is shown in Figure 3. Thus, the absolute configuration of the dye was dependent on the hydrophobic properties of both dye molecule and polypeptide side-chain. An increased hydrophobicity changed the chirality from common S- to uncommon R-chirality.

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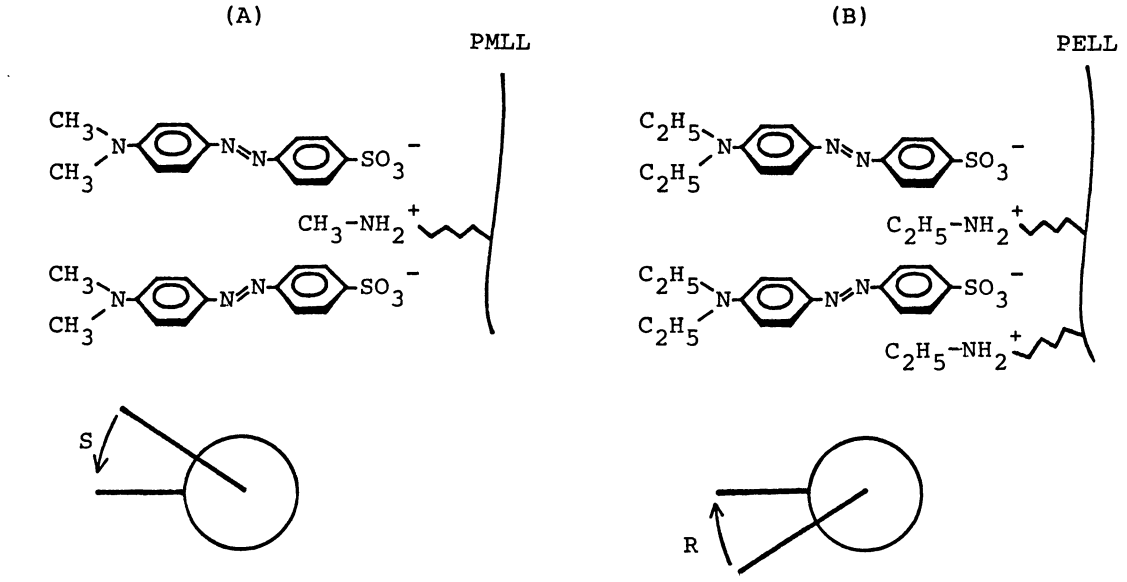

Fig. 3. Schematic illustrations for dyes bound to polypeptides: (A) dimeric MO bound to PMLL and the S-chirality of the dipole transition moments of MO; (B) monomeric EO bound to PELL and the R-chirality of EO.

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