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REVERSIBLE HELIX REVERSION INDUCED BY LIGHT IN POLYASPARTATES WITH SMALL AMOUNTS OF PHOTOCHROMIC SIDE CHAINS

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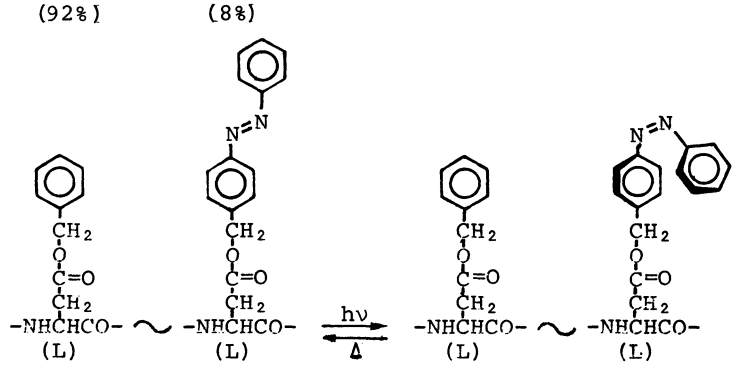
In mixed solvents of 1,2-dichloroethane and trimethyl phosphate, the copolymer 1 containing 8 mol % of azo groups exhibits a drastic conformational change from left-handed helix to right-handed helix by photoirradiation.

Azobenzene derivatives exhibit photoinduced *cis-trans* isomerism and can be used as chemical transducers of light energy to chemical functions.[1-3] Micelles,[4] membranes[5] and macromolecules[6] with both photoresponsive and functional moieties are also candidates of mediators for the conversion of light energy to chemical functions *via* structural changes. Much effort has been invested especially to perform light-induced conformational changes of polymers with vinyl polymers,[6-8] polypeptides[9-11] and others.[12,13] Polypeptides containing azobenzene residues in their side chains were first investigated by Goodman et al.[9] They found that photoisomerization of the side chains changes chiroptical properties of the polymers without variation in the backbone conformation.[9b] In 1977, we reported the first example of light-induced conformational changes of polypeptides with arylazo polyaspartates.[10a] In continuation of the work, we have performed several kinds of light-induced conformational changes occurring between left-handed helix and right-handed helix and between helix and coil.[10] Pieroni et al. recently added another kind of conformational change occurring between β-structure and coil with an azo-modified polyglutamate.[11b] Heretofore, the light-induced conformational changes were attained on the copolymers with large amounts of azobenzene residues. It is, however, desirable that small amounts of photochromic moieties can cause marked conformational changes in order to use such systems as effective chemical transducers or mediators. We wish to report here on the light-induced helix reversion of the copolymer 1 which contains small amounts of azo amino acid residues (8 mol %). This copolymer was previously reported to be insensitive to light in 1,2-dichloroethane (DCE),[10c] but has been found, in this work, to undergo a drastic conformational change in



1: left-handed helix right-handed helix

mixed solvents of DCE and trimethyl phosphate (TMP).[14]

The synthesis and analytical data of 1 were previously reported.[10c] Photoirradiation was carried out with a 500-W xenon lamp using a Corning 7-37 filter (320-390 nm), the *cis* per cent in the photostationary state being about 70. Circular dichroism (CD) measurements were undertaken on a JASCO CD-400X apparatus.

The CD spectra below 250 nm of 1 in mixed solvents of DCE and TMP are shown in Figure 1. In the peptide absorption region, the spectrum of the dark-adapted (*trans*) 1 in pure DCE is characteristic of the left-handed α-helix,[14] the molecular ellipticity $[\theta]_{222}$ being 37000. The spectrum changes on addition of TMP in the solvent range of 25-50% TMP, accompanying the reversion in the sign of $[\theta]$. The CD spectrum of *trans*-1 above 50% TMP is qualitatively similar to that usually associated with the right-handed α-helix, but the value of $[\theta]_{225}$ (about -60000) is greater than the standard value -40000.[15] This relatively small deviation from the optical property usually associated with the right-handed α-helix is not as large as the deviations reported by Goodman et al. for (phenylazo)phenylalanine polymers,[9] and probably arises because of slight differences in the backbone conformation between various right-handed α-helical polymers. The CD data after photoirradiation at various TMP contents are also shown in Figure 1. The effect of light is negligible below 20% TMP whereas remarkable above 25% TMP. A drastic change was observed at 28% TMP where the value of $[\theta]_{222}$ changes from 27000 to -25000. This marked conformational change is sur-

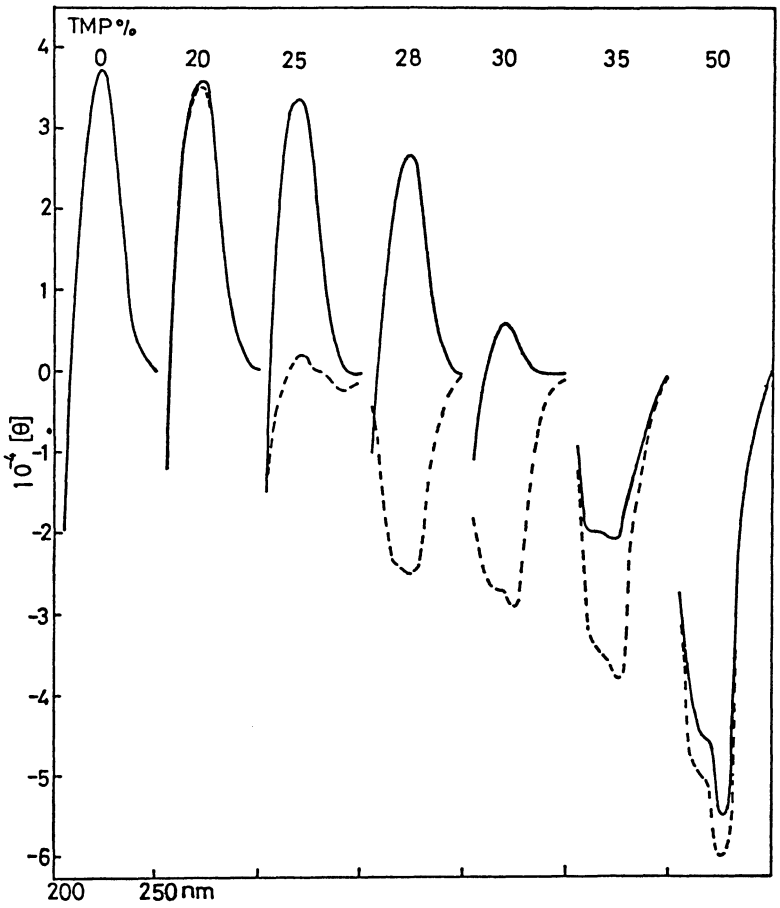


Fig. 1 CD spectra (200-250 nm) of 1 in mixed solvents of DCE and TMP before (——) and after (- - -) photoirradiation.

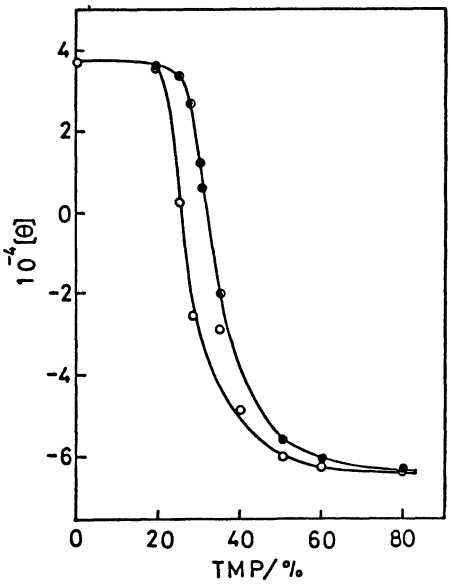


Fig. 2 Variation of $[\theta]_{222}$ of 1 induced by TMP before (●) and after (○) photoirradiation.

prising since $\underset{\sim}{1}$ contains only 8% azo amino acid residues and *trans-cis* isomerism is not perfect. The plotting of $[\theta]_{222}$ vs. TMP% indicates (Figure 2) that the conformational transition occurs with different TMP% for the dark-adapted sample (TMP 30%) and the irradiated one (TMP 25%). This means that the left-handed helix has different stability when azo units in $\underset{\sim}{1}$ are either all *trans* or 30% *trans* and 70% *cis*. Accordingly, this light-induced conformational change occurs in the narrow range of TMP. The isomerization process was completely reversible, enabling this system to operate as a "chemical switch".

The copolymer $\underset{\sim}{1}$ exhibits CD bands in the region of azobenzene n-π* and π-π* transitions (400-500 nm and 250-350 nm, respectively). It is an interesting problem how these side-chain CD bands are influenced by the conformational variation of the backbone. Figures 3 and 4 show the beahvior of these side-chain CD bands before and after photoirradiation when the content of TMP changes, the ellipticity being calculated based on the molar concentration of the azo amino acid residues. In the dark-adapted state, the sign of the side-chain n-π* CD band centered at 430 nm changes from positive to negative near 30% TMP on increasing TMP content, corresponding to the conformational change from left-handed helix to right-handed helix. On the other hand, the side-chain π-π* CD is negligible at low TMP contents, and appears with the extremum near 332 nm at the solvent range where the helix reversion begins.

The values of [θ] of both n-π* and π-π* side-chain CD bands increase on photoirradiation with a simultaneous blue shift of the π-π* CD band (Figure 3). The solvent dependencies of these bands are similar to those before photoirradi-

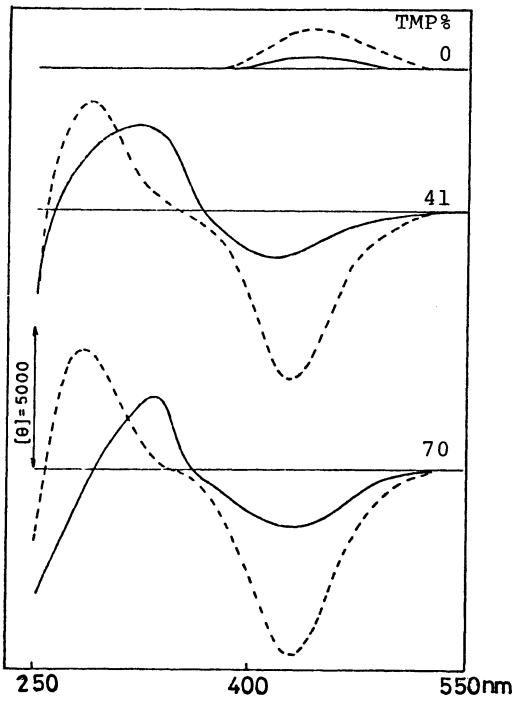


Fig. 3 CD spectra associated with the side-chain π-π* (250-350 nm) and n-π* (400-500 nm) transitions of $\underset{\sim}{1}$ before (——) and after (- - -) photoirradiation.

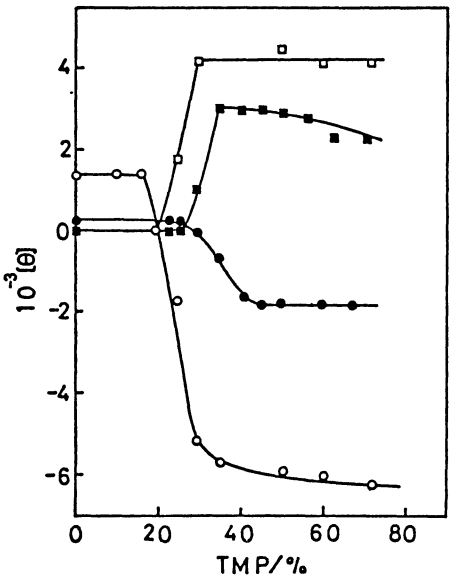


Fig. 4 Variation of [θ] of the side-chain n-π* (●,○) and π-π* (■,□) CD bands of $\underset{\sim}{1}$ before (●,■) and after (○,□) photoirradiation.

ation though the transitions occur at smaller TMP contents. The behavior of the side-chain CD bands before and after photoirradiation clearly indicates that the signs of the bands are determined by the screw sense of the polypeptide chain.

The present study establishes that small amounts of azobenzene residues are enough to cause a remarkable conformational change of the polypeptide chain. Functional units could thus be incorporated into the copolymer sequence other than the photoresponsive units, producing photoresponsive functional polymers in which chemical functions are photocontrolled in an "on-off" fashion. Several investigations along this line are now under way.

References and Notes

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