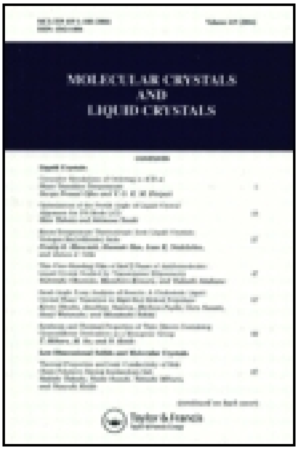

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Spiropyran-Containing Poly(L-Glutamic Acid). Photochromic and Conformational Behaviour in Acid Conditions

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Abstract. Poly(L-glutamic acid) containing spiropyran groups in the side chains was found to exhibit reverse photochromism in hexafluoro-2-propanol in the presence of trifluoroacetic acid, but the polypeptide conformation was not affected by the photoisomerization of the photochromic units. When appropriate amounts of methanol were added as a cosolvent, the system responded to light giving reversible coil → α-helix transitions whose extent depended on methanol concentration.

INTRODUCTION

In previous papers we have described the photochromic and conformational behaviour of poly(L-glutamic acid)[1] and poly(L-lysine)[2] containing spiropyran units in the side chains, and reported that exposure of hexafluoro-2-propanol (HFP) solutions to light and dark conditions induced reversible coil/α-helix conformational changes. Here we describe the behaviour of spiropyran-modified poly(L-glutamic acid) in the presence of trifluoroacetic acid (TFA) which converts the photochromic units to spiropyran salts. The photochromism of spiropyran salts involves different photoisomers with respect to the parent spiropyran compounds[3], therefore we may expect that spiropyran-modified polypeptides are affected by light in a different way, depending on whether they are irradiated in the absence or in the presence of acid.

EXPERIMENTAL PROCEDURE

Poly(L-glutamic acid) (M_v = 250,000) was reacted with 1-(ß-hydroxyethyl)-3',3'-dimethyl-6-nitrospiro-(indoline-2',2[2H-1] benzopyran), following the procedure already reported.[1] Two modified samples, containing 40 and 85 mol% spiropyran units were obtained by recovering the polymer after 24 and 144 h reaction time.

Solutions had concentrations in the range $1 \cdot 10^{-2} \div 6 \cdot 10^{-2}$ g/l. For the preparation of spiropyran salts, TFA ($1 \cdot 10^{-3}$ ml) was added to the HFP solutions (2 ml). The resulting solutions contained about 100 equivalents of acid with respect to the dye molar concentration.

Photoisomerizations were carried out by exposing the samples to sunlight or irradiating with a 100 W super pressure mercury lamp employing an interference filter with band-pass 450-550 nm.

RESULTS AND DISCUSSION

Photochromic Behaviour

Poly(Glu) containg 85 mol% spiropyran units in the side chains was dissolved in HFP and added of TFA. The concentration of the acid ($\approx 5 \cdot 10^{-4}$ g/ml) was in excess with respect to the molar content of photochromic units, but absolutely negligible with respect to the concentration needed to cause denaturation of the polypeptide conformation.

In these conditions the polymer exhibits reverse photochromism (Fig. 1). In the dark it gives yellow-coloured solutions due to the presence of the O-protonated merocyanine species I. Exposure to sunlight converts the species I to the colourless N-protonated spiro form II. Since spiropyrans are fairly strong bases in the open form, but are very weak bases in the closed spiro form, the charged species II can loose a proton and the neutral species III can be actually formed.

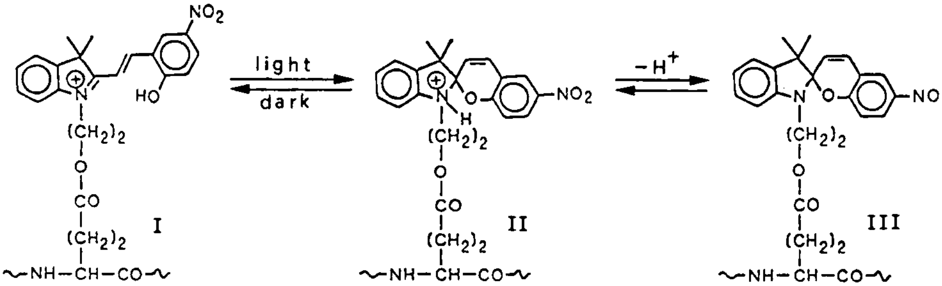

FIGURE 1 - *Reverse photochromism of poly(spiropyran-L-glutamate) in HFP/TFA.*

The absorption spectrum of the dark adapted sample exhibits one intense band at 415 nm and a weaker band at 310 nm : it corresponds exactly to the spectrum reported in literature[3] for the cationic species I. Exposure to visible light cancels the 415-nm band and the resulting spectrum shows only a broad band at 350 nm. When the sample is irradiated after addition of 10-40 % methanol, the spectrum shows absorption maxima at 350 and 272 nm and coincides with that of the sample irradiated in the absence of TFA. This suggests that also in the presence of TFA, the neutral species III is actually formed when irradiation is carried out in HFP/MeOH solvent mixture, while the charged species II is likely to be present when irradiation is carried out in HFP.

In the dark the original spectrum is reversibly restored, the curves monitored over time passing through an isosbestic point at 292 nm. The rate of appearance of the band at 415 nm slightly deviates from first order kinetics; however the time necessary to restore half of the original absorbance is about 6 h.

Photomodulation of Conformation

Differently from HFP solutions without TFA[1], poly(spiropyran-L-glutamate) does not give light-induced conformational changes in HFP in the presence of TFA, and the samples show the typical CD spectra of random coil polypeptides either when they are kept in the dark or exposed to light. When appropriate amounts of methanol are added as a cosolvent, the system responds to light giving coil → α-helix transitions.

The extent of the photoresponse depends on solvent composition (Fig. 2). In HFP/MeOH = 90/10 the CD spectra of the samples kept in the dark and exposed to light correspond respectively to the standard CD curves for random coil and α-helical polypeptides, indicating that light produces the full conversion from random coil to 100 % α-helix. The decay in the dark is accompanied by the progressive decrease of the helix content and recovery of the original disordered conformation.

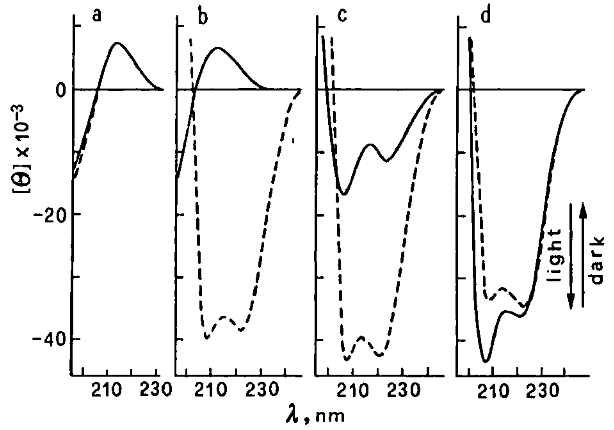

FIGURE 2 - *CD spectra before(——) and after (----) irradiation, in various HFP/MeOH solvent mixtures, in the presence of TFA ($5 \cdot 10^{-4}$ g/ml).*
MeOH % : a) 0-5 %; b) 10 %; c) 20 %; d) 40 %.

The conformational behaviour can be well explained on the basis of the photochromic reactions schematized in Fig. 1 and the above described absorption spectra.

In HFP/TFA the photochromic units are present as charged species either in darkness (species I) or in light conditions (species II), so the repulsive forces among the side chains make the macromolecules adopt an extended coil conformation in both conditions and no photoresponse is observed. Addition of methanol (> 10 %) should shift the equilibrium between the two colourless species II and III toward the neutral structure III, thus allowing the macromolecules adopt the α-helix structure. At sufficiently high methanol concentration (> 40 %) the macromolecules may stay in α-helix also when photochromic side chains are present as charged species (dark conditions), as occurring for other poly(α-aminoacid)s with salified side chains, such as sodium poly(L-glutamate)[4] and poly(L-lysine) hydrochloride[5], which are random coil in water and become helical upon addition of methanol.

The system described is particularly nice and attractive also because of the mild conditions in which it promptly responds to light. Indeed, exposure to sunlight for a few seconds is enough to induce the coil → helix transition of the polypeptide chains. The induced order-disorder cooperative transition is actually a mechanism of amplification and transduction of the primary photochemical event, so the system may be very promising for designing sensors and devices which can be photomodulated.

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