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Spiropyran Derivative of an Elastin-like Bioelastic Polymer: Photoresponsive Molecular Machine to Convert Sunlight into Mechanical Work

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Photoresponsive polymers are able to respond to light, giving reversible variations of their structure and conformation that are accompanied by variations of their physical properties[1] that could be exploited in many future technological developments. One of the most important group of photoresponsive polymers is poly(α-amino acids) conjugated with photochromic side chains.[1] These polymers respond to light, giving reversible coil−α-helix (or β-sheet) transitions.[1]

However, these materials display these properties in suitable solvents that invariably have a bad environmental consideration. Furthermore, their efficiency is intrinsically low, since the number of attached photochromic moieties needed to yield a significant coil−α-helix transition is always high.[1] Fortunately, these two main drawbacks could be overwhelmed by the use of a new family of synthetic polypeptides, the bioelastic elastin-like polymers as substitutes of the conventional poly(α-amino acids). This has been demonstrated by a pioneer work from Strzegowski et al. on an azo derivative of this kind of polypeptide.[2]

The inverse temperature transition showed by bioelastic polymers is a molecular transition from a relatively extended and disordered chain to a regularly folded β-spiral that takes places in water solutions and hydrogels of these polymers[3] on raising the temperature. The term “molecular machines” can be applied to these polymeric molecules because of their exclusive ability to convert many types of energy into useful mechanical work on folding;[3,4] an ability that, in the limit, can be displayed by a single molecule.[4]

Following the path open by Strzegowski et al.,[2] we report herein the photomodulation of the inverse temperature transition of a modified bioelastic polypeptide that is able to respond to sunlight−darkness or, alternatively, sunlight−UV cycles. This polymer provides a route to photoresponsive materials capable of sunlight photomechanical transduction without the need for either solvents other than water or UV radiation and with a high efficiency.

The copolypeptide used in this work was prepared in the following manner. The random copolypeptide poly[0.74(VPGVG), 0.26(VPGEG)] was synthesized as described by Gowda.[5] Stoichiometry and purity were routinely checked by ^{13}C and ^{1}H NMR, elemental and amino acid analysis, and chromatographic methods. The mole fraction of both pentamers was determined by amino acid analysis. Some of the physical properties of the final polymer were also checked. The inverse temperature transition (T_t) for this polymer takes place at 32 °C (result not shown).

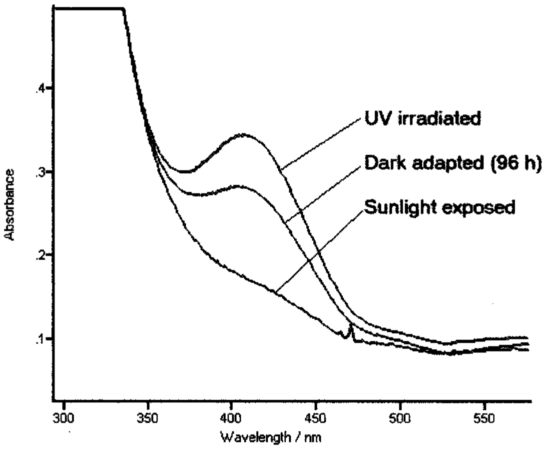

Figure 1. UV−vis absorption spectra of the conjugated polymer after sunlight and UV exposition and dark adaptation.

The spiropyran photochromic compound 1-(β-hydroxyethyl)-3,3-dimethyl-6′-nitrospiro-(indoline-2,2′[2*H*-1]benzopyran) (Sp-OH) was synthesized following the method of Zaitseva.[6] Finally, for conjugation of the photochromic molecule to the polymer, 55 mg of the copolymer (0.034 mmol of glutamic acid residues) was dissolved in 1 mL of *N,N*′-dimethylformamide. To this solution were added 5.5 mg (0.037 mmol) of pyrrolidinopyridine, 44 mg (0.214 mmol) of dicyclohexylcarbodiimide, and 76 mg (0.214 mmol) of Sp-OH. Sp-OH and the carbodiimide were added in excess to increase the yield of the conjugation reaction.[7] The solution was stirred at room temperature for 3 days. One drop of 1 M acetic acid was added to facilitate precipitation of the dicyclohexyl urea byproduct. The precipitate was removed by precipitation into excess diethyl ether, washed repeatedly with ether, and dried in air at room temperature. The yield was 42 mg (ca. 76%). Thin-layer chromatography revealed no contamination by unconjugated Sp-OH. Conjugation reached the 45% of the glutamic acid side chains, as revealed by UV−vis spectroscopy.[7]

Figure 1 shows the changes in the UV−vis absorption spectrum of a 5 mg/mL solution of the conjugated polymer in 0.01 N phosphate buffer (pH = 3.5) for the dark-adapted and the UV-exposed sample (250−400 nm from a 500 W Hg lamp equipped with a CVI Laser Corp. SUG-11-1.00 band-pass filter) and for the sunlight-exposed sample. The sunlight-exposed sample showed the pattern of the relatively apolar spiro form, while the dark-adapted and the UV-radiated polymer showed the expected absorption features of the merocyanine form, which is of higher polarity but is not zwitterionic in acid media (see Figure 2). According to the literature, irradiation with UV light restores the open merocyanine structure of the spiro compounds and has the same effect as the dark adaptation but with a higher rate.[7]

Figure 3 shows that the inverse temperature transition is sensitive to the state of the spiropyran chromophore. When buffered at pH 3.5, phase separation

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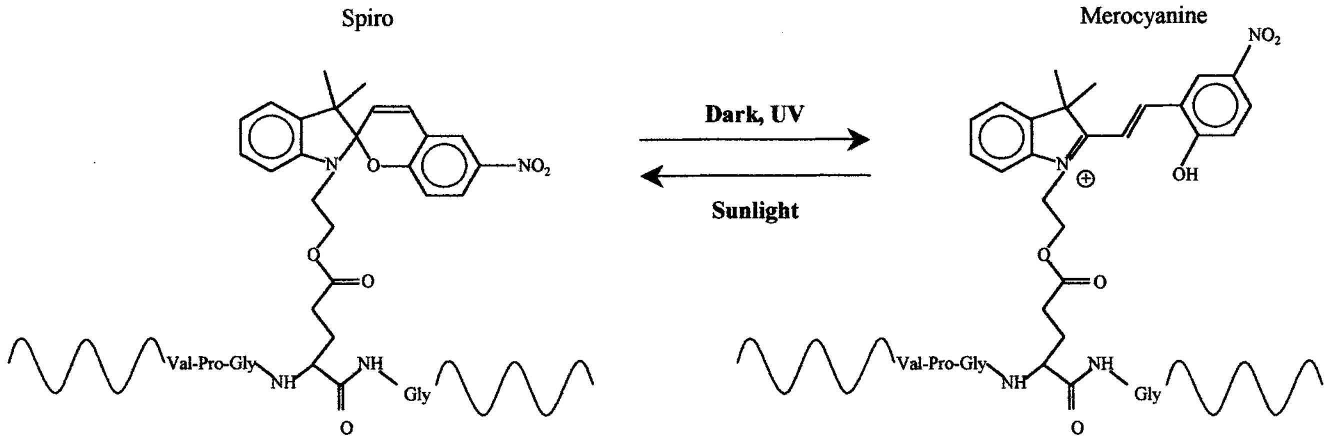

Figure 2. Photochemical reaction responsible for the photochromic behavior of the spiropyran derivative used in this work.

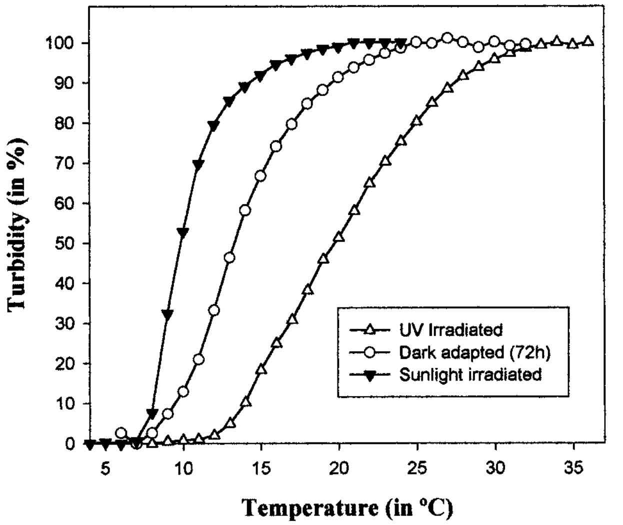

Figure 3. Temperature profiles of aggregation of 20 mg mL^{-1} phosphate-buffered (0.01 N, pH 3.5) water solutions of the photoresponsive polymer under different illumination regimens. The correspondence between each profile and its illumination condition is indicated in the plot. The transition temperature is considered as the temperature at which the relative turbidity reaches 50%. Turbidity was calculated from the absorbance values obtained at 600 nm on Cary 50 UV–vis spectrophotometer equipped with a thermostatized sample chamber.

of the polymer, as reported by an abrupt increase in the turbidity of the sample, occurs at ca. 10 °C for the sunlight-exposed sample (spiro form) while for the polymer having a complete transformation of the chromophore to the open merocyanine form (UV-radiated sample) T_t increases up to 20 °C. T_t is about 13.5 °C for the dark-adapted sample (72 h), which exhibits a partial transformation of the chromophore, as can be seen in its UV–vis absorption spectrum (Figure 1). Elevation of the transition temperature upon interconversion between the spiro and the merocyanine form is consistent with the increased polarity of the merocyanine form and with the established correlation between the polarity of the side chain and the temperature at which phase separation is observed in this family of bioelastic polymers.[2,3]

The shift in T_t upon spiro–merocyanine interconversion found in the sunlight- and UV-exposed samples opens a window, near 14 °C for isothermal photomodulation of the transition at a pH of 3.5. Figure 4A illustrates this fact. At 14 °C, the relatively hydrophobic

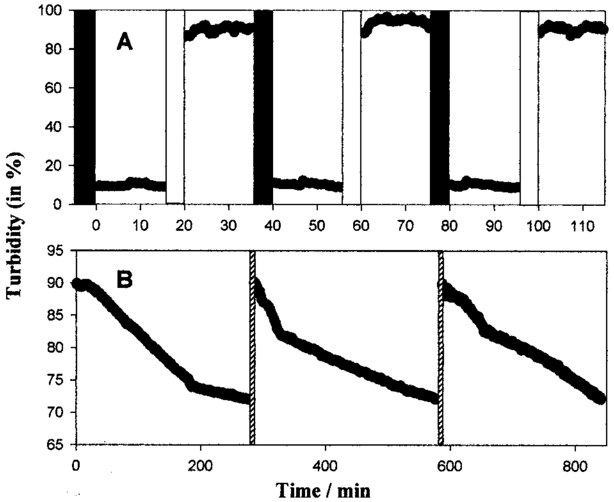

Figure 4. Photomodulation of phase separation of 5 mg mL^{-1}aqueous samples of the photochromic polymer (T = 14 °C, 0.01 N phosphate buffer at pH = 3.5). (A) UV–sunlight cycles. Boxes in the subplot represent periods of irradiation: UV, black boxes; sunlight, white boxes. (B) Darkness–sunlight cycles. Boxes in the subplot represent periods of sunlight irradiation.

spiro form of the polymer affords turbid biphasic suspensions. UV irradiation results in a fast conversion to the merocyanine form, with corresponding dissolution of the polymer and decreasing sample turbidity. Further sunlight exposition restores the hydrophobic spiro form and drives a second cycle of phase separation. The process appears to be fully reversible under these experimental conditions. The same behavior can be observed when UV radiation is substituted by dark adaptation of the sample (Figure 4B), although the slow rate of merocyanine conversion, under the conditions used in this work, yields an evident but moderate redissolution of the sample during the assayed time.

These results also illustrate the effectiveness of these photoresponsive polymers, since the attachment of 2.3 spiropyran chromophores per 100 amino acid residues in the polymer backbone is sufficient to render a clear photomodulation of their inverse temperature transition. Extension to cross-linked hydrogels and some supramolecular assemblies is being pursued. Furthermore, since several possible applications of these polymers would be in the sunlight energy use, some promising strategies to increase the slow conversion rate of the dark-adapted samples are also under consideration.

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References and Notes

(1) Some fine reviews dealing with various aspects of photochromic polymers have appeared in the past few years: Pieroni, O.; Ciardelli, F. *Trends Polym. Sci.* **1995**, *3*, 282−287. Cooper, T. M.; Natarajan, L. V.; Crane, R. L. *Trends Polym. Sci.* **1993**, *1*, 400−412. Pieroni, O.; Fissi, A.; Popova, G. *J. Prog. Polym. Sci.* **1998**, *23*, 81−123.

(2) Strzegowski, L. A.; Bueno Martinez, M.; Gowda, D. C.; Urry, D. W.; Tirrell D. A. *J. Am. Chem. Soc.* **1994**, *116*, 813−814.

(3) Urry, D. W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 819−841.

(4) Urry, D. W. *J. Phys. Chem. B* **1997**, *101*, 1007−11028.

(5) Gowda, D. C.; Parker, M. T.; Harris, R. D.; Urry, D. W. In *Peptides: Design, Synthesis and Biological Activity*; Basava, C., Anantharamaiah, G. M., Eds.; Birkhäuser: Boston, 1994.

(6) Zaitseva, E. L.; Prokhoda, A. L.; Kurkovskaya, L. N.; Shifrina, R. P.; Kardash, N. S.; Drapkina, N. A.; Krongauz, V. A. *Khim. Geterotsikl. Soedin.* **1973**, *10*, 1362−1369.

(7) Ciardelli, F.; Fabbri, D.; Pieroni, O.; Fissi, A. *J. Am. Chem. Soc.* **1989**, *111*, 3470−3472.

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