Photoinduced Conformational Transition of Polypeptides Containing Azobenzenesulfonate in the Side Chains

Morimasa Sato, Takatoshi Kinoshita,* Akira Takizawa, and Yoshiharu Tsujita

Department of Materials Science & Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466, Japan. *Received September 1, 1987*

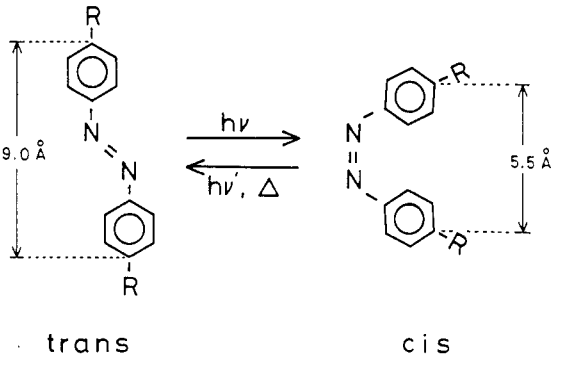
ABSTRACT: Photoresponsive polypeptides, poly(L-glutamic acids) containing 1.9, 9.3 and 46.3 mol % azobenzenesulfonate moieties in the side chains (azo-S-PGA), have been prepared by condensation reaction of poly(L-glutamic acid) (PGA, $\bar{M}_v = 1.19 \times 10^5$) with 4-amino-1,1′-azobenzene-4′-sulfonic acid sodium salt in dimethylformamide solution and the photoresponsive behavior of the copolypeptides obtained was investigated. The dark-adapted azo-S-PGAs containing 1.9 and 9.3 mol % azobenzenesulfonate (azo-S) moieties showed a pH-dependent α-helix to coil transition; however, the copolypeptide containing 46.3 mol % azobenzenesulfonate moieties was in the random coil conformation at any pH. Photoisomerization of the azobenzenesulfonate moieties from trans to cis forms induced by ultraviolet light resulted in α-helix to coil transition in the azo-S-PGA containing 9.3 mol % azobenzenesulfonate moieties at adequate pHs, indicating that the electrostatic repulsion between the sulfonate anions in the azo photochromic side chains and the neighboring glutamate anions was enhanced by the photoinduced changes in the geometry of the azo chromophores. It is also found, however, that the visible light irradiation or dark adaptation, cis to trans isomerization of azo photochromic moieties, did not induce any structural changes of the copolypeptide in the random coil conformation induced by the ultraviolet light. On the other hand, the conformations of the azo-S-PGAs containing 1.9 and 46.3 mol % azo sulfonate moieties were shown to be independent of the photoisomerization of the azo photochromic moieties at any pH.

It has been recognized that the essential part in the molecular mechanism of biological photoreceptors is the conformational change of a macromolecule resulting from the changes in the interaction between the macromolecule and its photochromic moiety upon exposure to light. Studies of photoresponsive synthetic macromolecules may not only be important to the understanding of the general mechanism of biological photoreceptors but may also form the basis of a molecular device for the foregoing information transfer system.

Because of a requirement that the receptors can exist in at least two different stable conformations, photochromic polypeptides, having typical conformational variations, were selected as useful models and their photoresponsive behavior has been investigated. For example, several kinds of conformational changes induced by light were first accomplished by Ueno et al.[1-10] with poly(β-benzyl L-aspartates) containing azobenzene moieties in the side chains depending on the solvent compositions and/or the amounts of the azobenzene moieties. Pieroni et al.[11-15] showed the example of photoinduced changes in conformation and aggregation of large amounts of azobenzene containing poly(L-glutamic acids) dissolved in the aqueous solution. We[16-18] investigated solid membrane systems of the azobenzene-containing poly(L-glutamic acids) and showed the photoregulation of several membrane functions. We[19] also showed the first example of the photocontrol of polypeptide conformation in the solid membrane using poly(L-glutamic acid) containing pararosaniline groups in the side chains.

On the basis of the observed photoresponsive effects with the azobenzene-containing polypeptides, it was demonstrated that the conformational changes of the polypeptide containing appropriate amounts of the azobenzene moieties at adequate solvent conditions can be induced by the photoisomerization of the azobenzene moieties from the trans to the cis form, involving changes in two important characteristics, geometry and polarity, of the photochrome, i.e., a change in the overall geometry of the azobenzene from planar to nonplanar, accompanying a decrease in the distance between para carbon atoms in the photochrome from 9.90 to 5.5 Å[20,21] and a increase in the dipole moment from 0.5 to 3.1 D.[22] That is, the change

Scheme I



in the geometry of the azobenzene moieties was shown to directly lead to the changes in the stability of polypeptide secondary structure such as α-helix, β-form, and helix sense. On the other hand, the increase in the polarity of the azobenzene moieties on light irradiation was shown to induce the changes in the physicochemical properties of the polypeptides, such as (i) a shift of pK_a of the neighboring weak acid moieties of the polypeptide yielding the changes in their ionization degree and (ii) a change in the balance of hydrophobic and hydrophilic interactions between the polypeptide and the environmental solvent, resulting in the structural change of the polypeptide.

We represent here an additional example of the photoinduced secondary structure changes of polypeptide with poly(L-glutamic acid) containing azobenzenesulfonate moieties based on the photoisomerization of the photochrome as a photoinduced geometry controllable site (Scheme I). That is, we extend the characterization of the photoinduced changes of polypeptide structure to the case in which the α-helix to coil transition can be effectively induced by an additional increase in the local charge density of the environment around the partially charged helical rod resulting from the photoinduced changes in the geometry of the azobenzene moieties carrying the sulfonate anion.

Experimental Section

Materials. Poly(L-glutamic acid) incorporated with azobenzenesulfonate groups (azo-S-*X*-PGA, *X* is the mole percent

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Scheme II

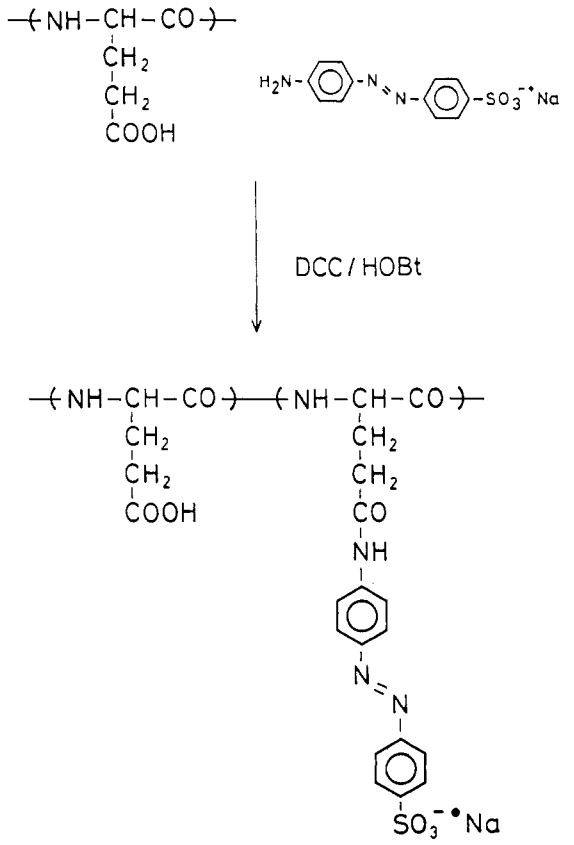


Table I
Poly(L-glutamic acids) Containing Azobenzenesulfonate Moieties in the Side Chains Obtained by the Modification of Poly(L-glutamic acid) with 4-Amino-1,1′-azobenzene-4′-sulfonic Acid Sodium Salt

sample	reactn conditions			azo cont/mol %
	R[a]	temp/°C	duration/h	
azo·S-1.9-PGA	0.5	25	24	1.9
azo·S-9.3-PGA	0.5	25	68	9.3
azo·S-46.3-PGA	3.0	25	24	46.3

[a] Azo reagent/γ-COOH groups molar ratio.

of the azobenzenesulfonate moieties) was synthesized by the coupling reaction as follows (Scheme II).

Poly(L-glutamic acid) (PGA, $\bar{M}_v = 1.19 \times 10^5$) was obtained by saponification of poly(γ-methyl L-glutamate) (PMLG) as previously reported.[23] The PGA dissolved in dimethylformamide (DMF) at 0 °C. 4-Amino-1,1′-azobenzene-4′-sulfonic acid sodium salt (azo·S), *N*-hydroxybenzotriazole (HOBt), and dicyclohexylcarbodiimide (DCC) were added to the stirred DMF solution at 0 °C. After 1 h, the mixture was further stirred for a given number of hours at 25 °C. Precipitated dicyclohexylcarbodiurea (DCUrea) (which is a side product of the reaction) was filtered out and the bulk of the DMF was pored into ether. Then the obtained residues were washed by extraction with methanol for 2 or 3 days for the purpose of removing any unreacted reagents. The polymers obtained, azo·S-PGAs, were dried under vacuum and were dissolved in water for spectroscopic measurements. The azobenzenesulfonate contents, *X*, in the polymers, which can be regulated by the molar ratio of azo·S to PGA and/or the reaction time in the coupling reaction, were determined from the absorbance at 366 nm of the DMF solutions of azo·S-PGAs on the basis of the molar extinction coefficient of the trans form of a model compound, 4-(propionamido)-1,1′-azobenzene-4′-sulfonic acid sodium salt (pro-azo·S; $\lambda_{max} = 365$ nm, $\epsilon_{max} = 2.59 \times 10^4$) in DMF solution. The conditions for the modification of poly(L-glutamic acid) and azo content, *X*, are summarized in Table I.

Azo·S-PGAs obtained were soluble in water; particularly azo·S-PGAs containing more than 9.3 mol % azobenzenesulfonate moieties were soluble in water below pH 3 in which the PGA homopolymer was precipitated.

4-(Propionamido)-1,1′-azobenzene-4′-sulfonic acid sodium salt (pro-azo·S), a low molecular weight model compound for the photoisomerizable moietiy of azo·S-PGA, was synthesized as follows: Propionic acid was reacted with 4-amino-1,1′-azobenzene-4′-sulfonic acid sodium salt in DMF as described above. The bulk of the DMF was pored into water and precipitates were filtered out. Then pro-azo·S was obtained by salting-out techniques and was confirmed by NMR spectra.

The data related to the characterization of azo·S, pro-azo·S, and azo·S-PGA are presented in Table II.

Table II
Spectroscopic Data of azo·S, pro-azo·S, and azo·S-PGA in DMF

sample	λ_{max}/nm	ϵ_{max}
azo·S	404	2.50×10^4
pro-azo·S	365	2.59×10^4
azo·S-PGA	366	2.59×10^4

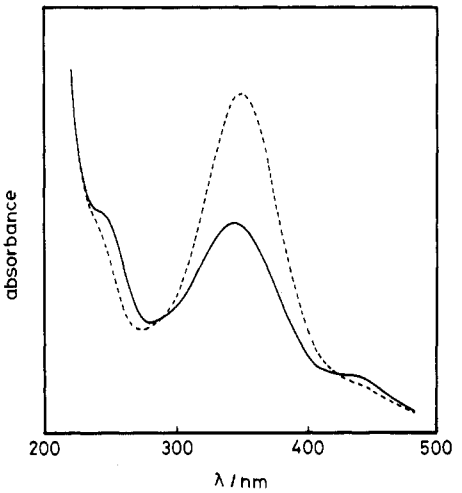


Figure 1. Absorption spectra of poly(L-glutamic acid) containing 9.3 mol % azobenzenesulfonate groups in aqueous solution, before (---) and after (—) ultraviolet light (250 nm < λ < 380 nm) irradiation at 25 °C. The irradiation was carried out for 5 min at pH 4.3.

Measurements. Absorption and circular dichrorism (CD) spectra of the samples were recorded on a Jasco UVIDEC 670 spectrophotometer and Jasco spectropolarimeter J 40C, respectively. The concentration of azo·S-PGA in aqueous solution was fixed to 1.92×10^{-4} g/cm^3. The pH of the solution was adjusted by the addition of HCl or NaOH.

For all the measurement, the polymer solutions were kept in the dark for a few days to ensure the all-trans form of azobenzene moieties at the begining of the measurements.

Irradiation. Irradiation of the sample was carried out with a 500-W superhigh-pressure mercury lamp (Ushio UVD 500) equipped with a Toshiba UV-D33s filter for UV irradiation or a Toshiba L-39 filter for visible light irradiation.

Results and Discussion

Photoisomerization of Azo·S-PGA in Aqueous Solution. Aromatic azobenzene compounds can be easily isomerized by light irradiation.[24] The irradiation in the region of the main absorption band (π–π^* transition) of the trans form creates a metastable, nonplanar, cis form, revealed by a strong decrease of a main absorption band. Figure 1 shows the photoinduced changes in the absorption spectra of azo·S-PGA containing 9.3 mol % azobenzenesulfonate moieties (azo·S-9.3-PGA) in aqueous solution at pH 4.3. The main absorption band at 354 nm decreased UV irradiation, indicating that the azobenzenesulfonate moieties in the side chains can be isomerized from the trans to the cis forms by irradiation. The extent of this isomerization can be estimated by the method as Ciardelli

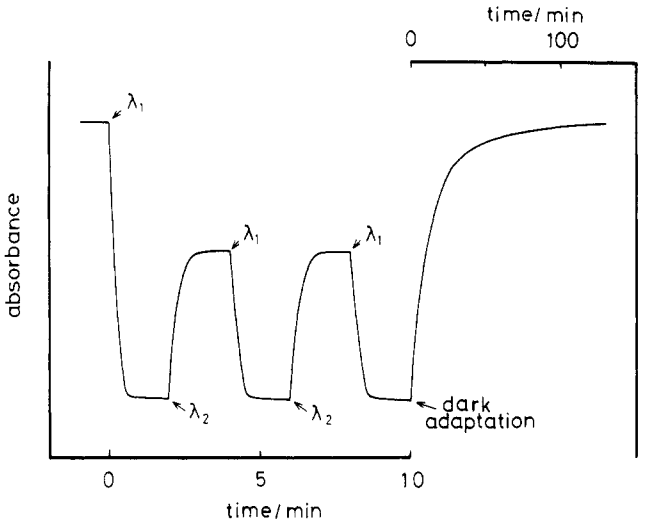


Figure 2. Changes in the absorbance at 354 nm of poly(L-glutamic acid) containing 9.3 mol % azobenzenesulfonate groups in aqueous solution at pH 4.3 on alternate irradiation with ultraviolet light (λ_1, 250 nm < λ_1 < 380 nm) and visible light (λ_2, λ_2 > 390 nm) or dark adaptation at 25 °C.

Table III
Photostationary Values of Percent Content of Cis Form and Reciprocal Values of the Half-Life Time, $(t_{1/2})^{-1}$, of the Thermal Cis to Trans Isomerization Reaction of Poly(L-glutamic acid) Containing 9.3 mol % Azobenzenesulfonate Groups in Aqueous Solution at Various pHs

pH	cis	$(t_{1/2})^{-1}$/min^{-1}	pH	cis	$(t_{1/2})^{-1}$/min^{-1}
3.0	52.5	1.82×10^{-1}	6.1	54.2	3.13×10^{-2}
4.1	53.5	1.33×10^{-1}	7.1	55.0	1.82×10^{-2}
5.0	54.0	7.41×10^{-2}	8.0	56.5	1.81×10^{-2}

et al. reported.[13] In our case, however, the molar extinction coefficient of the all-cis isomer (ϵ_{cis}) of azo-S-PGA in aqueous solution could not be obtained, so that the relative value of the conversion of the trans–cis isomerization of azo-S-PGA was calculated from the molar extinction coefficient of trans isomer ($\epsilon_{trans} = 2.11 \times 10^4$) of azo-S-PGA and the absorbance at 354 nm in aqueous solution. The photoconversion of this isomerization obtained was ca. 55% in aqueous solution at pH 4.3. It is also shown that the trans to cis photoisomerization in azo-S-9.3-PGA in aqueous solution were almost independent of pH conditions with a conversion of 53–56% (Table III). The result suggests, therefore, that the photoisomerization of the azobenzene in the azo-S-PGA is independent of the ionization degree of the neighboring L-glutamic acid side chains of the copolypeptide (Table III).

A succesive irradiation at different wavelengths induced the reversible photoisomerization from the cis to the trans form, but complete reversibility was obtained only when the samples were kept in the dark (Figure 2). It is noted here that the rate of the thermal isomerization of the azobenzenesulfonate moieties of the azo-S-9.3-PGA strongly depends on the pH of aqueous solution (Figure 3). Table III shows the reciprocal values of the half-life time, $(t_{1/2})^{-1}$, for cis to trans isomerization in the dark at various pHs. It is clear that the rate of isomerization decreases with increasing pH in the aqueous solution below neutral pH; e.g., the thermal isomerization reaction at pH 3.0 proceeds about 1 order of magnitude faster than that at pH 7.1. It may say, therefore, that the cis to trans isomerization reaction is catalyzed by the excess proton ions in the acid solution.

Conformations of Dark-Adapted Samples. It is well-known that the α-helix content of PGA markedly

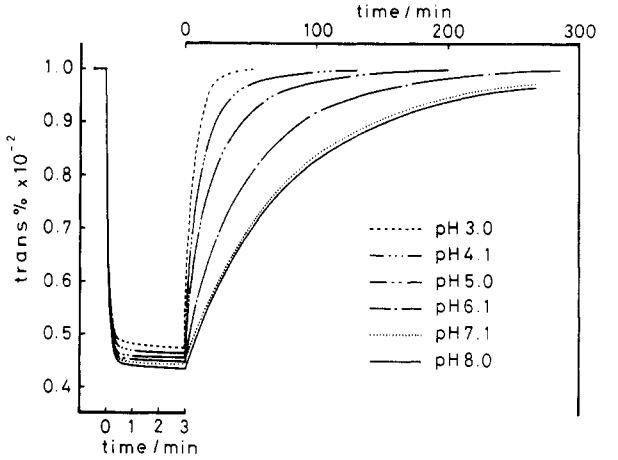


Figure 3. Changes in percent content of trans form, calculated from the absorbance at 354 nm, of azobenzenesulfonate moieties of poly(L-glutamic acid) containing 9.3 mol % azobenzenesulfonate groups in aqueous solution at various pHs by ultraviolet light (250 nm < λ < 380 nm) irradiation and by dark adaptation at 25 °C.

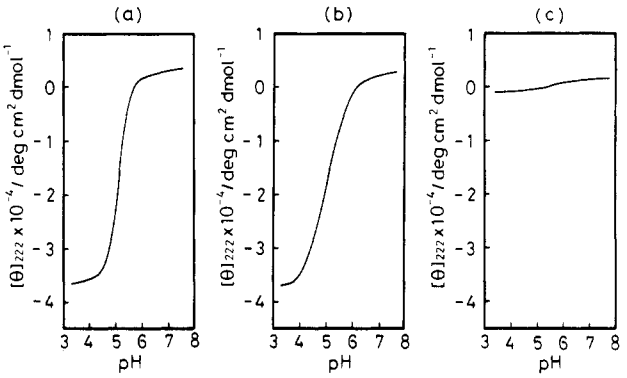


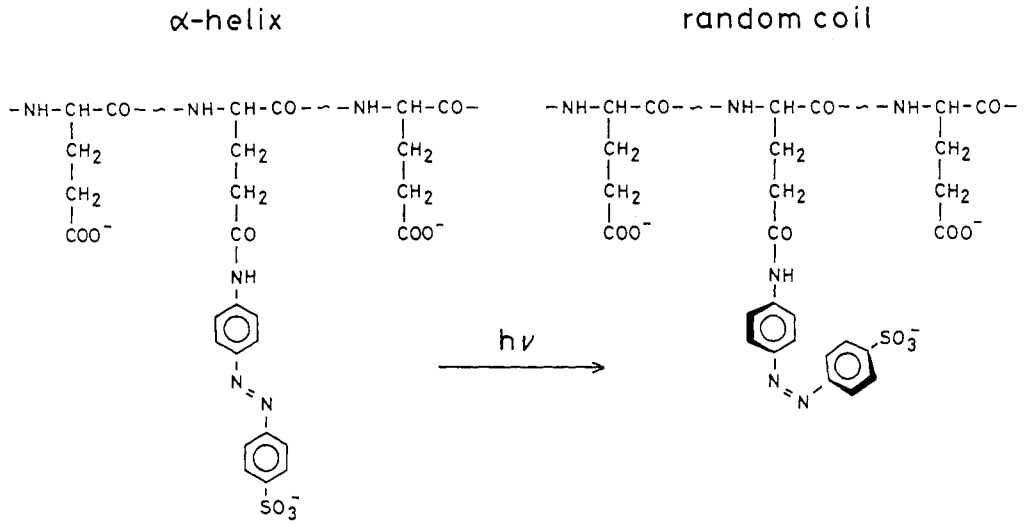
Figure 4. pH dependences of minimum ellipticity, $[\theta]_{222}$, of dark-adapted poly(L-glutamic acid) containing (a) 1.9 mol %, (b) 9.3 mol %, and (c) 46.3 mol % azobenzenesulfonate groups in aqueous solution at 25 °C.

depends on the pH of aqueous solution, i.e., the electrostatic repulsion forces between the dissociable L-glutamic acid side chains. It would also be predicted that the introduction of the azo sulfonate anions, a strong acid whose pK_a is below 1.0, to the PGA side chains may produce an additional electrostatic repulsion between the side chains in the copolypeptide to decrease the stability of the helix even in acid solution. The circular dichrorism (CD) spectra below 250 nm in aqueous solution of dark-adapted azo-S-PGAs showed that the helix stability of the copolypeptide, in fact, depends on the amounts of azobenzenesulfonate moieties, other than the aqueous pH value.

Figure 4 shows the pH dependence of molar ellipticity of the CD band at 222 nm, $[\theta]_{222}$, of azo-S-PGAs containing various amounts of azobenzenesulfonate moieties. The values of $[\theta]_{222}$, associated with the α-helix content, of azo-S-1.9-PGA and azo-S-9.3-PGA at pH 3.0, -3.71×10^4 and -3.62×10^4 deg cm^2 dmol^{-1}, respectively, correspond to the standard value[25] of the right-handed α-helical polypeptide. The result indicates that small amounts (< 10%) of azobenzenesulfonate moieties are insufficient to cause the conformational change in the copolypeptide chain. It is also clear that the conformation of both of the copolypeptides was changed from the stable α-helix in the acid solution to the random coil by increasing pH of the aqueous solution.

The value of $[\theta]_{222}$ of azo-S-46.3-PGA, however, is shown to be very small and is almost independent of pH value, indicating that the copolypeptide with a larger amount of

Scheme III



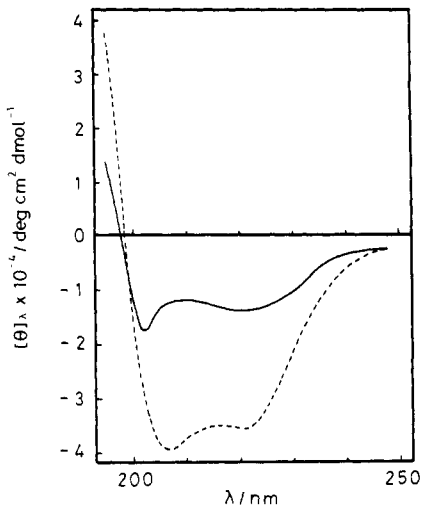


Figure 5. CD spectra of poly(L-glutamic acid) containing 9.3 mol % azobenzenesulfonate groups in aqueous solution, before (---) and after (—) ultraviolet light (250 nm < λ < 380 nm) irradiation at 25 °C. The irradiation was carried out for 5 min at pH 4.3.

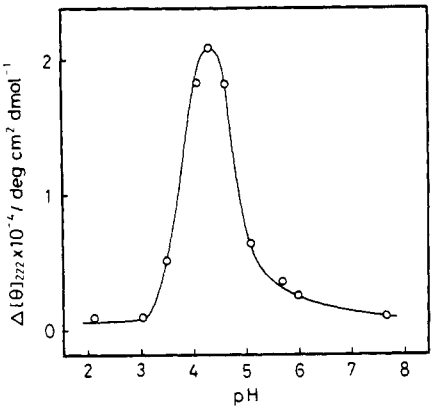


Figure 6. pH dependences of $\Delta[\theta]_{222}$ (=$[\theta]_{222}$ on UV irradiation − $[\theta]_{222}$ in the dark) of poly(L-glutamic acid) containing 9.3 mol % azobenzenesulfonate groups in aqueous solution. The irradiation was carried out for 5 min at 25 °C.

azo sulfonate moieites is always in the disordered structure in water. This different behavior is due to the role of the azo sulfonate anions in destabilizing the α-helix structure as noted above.

Photoinduced Conformational Changes of azo-S-PGA. The effects of light irradiation (250 nm < λ < 380 nm) of the dark-adapted copolypeptides were influenced by the amount of azobenzenesulfonate moieties. Irradiation of azo-S-1.9-PGA and azo-S-46.3-PGA did not induced any structural changes of their conformations at any pH values. The former ineffectiveness of the light irradiation may be attributed to the small amount of azo photochromic moieties (azo-S-1.9-PGA) and the latter one to no variations in the conformation of any pHs (azo-S-46.3-PGA). In constrast, azo-S-9.3-PGA exhibits remarkable conformational changes upon irradiation at adequate pH values. Figure 5 shows the photoinduced changes in CD spectra of azo-S-9.3-PGA at pH 4.3. Two negative bands at 222 and 208 nm connected with the α-helix structure are shown to be decreased by the irradiation. As a result, it can be estimated that the copolypeptide containing 9.3 mol % azobenzenesulfonate moieties changes the helix content from 96% to 45% at pH 4.3 by light. Ciardelli et al.[14] reported, on the other hand, that the α-helical structure of poly(L-glutamic acid) containing up to 16 mol % azobenzene moieties (without sulfonate anions) is independent of the light irradiation at any pH values. It may be said, therefore, that the trans to cis isomerization of the azobenzene itself does not produce any conformational variation of the polypeptides containing relatively small amounts of azobenzene moieties and the sulfonate anions in the azo photochromic moieties play an important role in the photoinduced conformational transition of the azo-S-9.3-PGA. These results established that the remarkable conformational change of azo-S-9.3-PGA induced by light at pH 4.3 arises from an additional increase in the local charge density of the environment around the partially charged helical rod at the fixed pH value, i.e., the increase in the electrostatic repulsion between sulfonate anions in the azobenzene side chains and carboxylate anions in the neighboring L-glutamic acid side chains resulting from a decrease in the distance between the para carbon atoms of the azobenzene moieties from 9.0 to 5.5 Å by light irradiation (Scheme III).

Figure 6 shows the variations in $[\theta]_{222}$ associated with the photoinduced conformational changes of azo-S-9.3-PGA, $\Delta[\theta]_{222} = [\theta]_{222}$ on UV irradiation − $[\theta]_{222}$ in the dark, at various pH values. It is clear that no effects have been observed upon irradiation at lower pH values (<3.0) where the neighboring L-glutamic acid moieties are in the undissociated state and at higher pHs (>7.0) where the copolypeptide is a completely random coil. As a result, the copolypeptide was shown to have a relatively narrow pH range where the photoinduced conformational transition occurs. It should also be noted that the pH (=4.3) at which

the maximum of photoinduced effects can be achieved is lower than that of the midpoint (pH = 5.1) of the α-helix to coil transition in Figure 4. This means that the photoinduced conformational change of the copolypeptide depends not only on the ionization degree of the neighboring acid moieties but also on the polypeptide secondary structure itself before UV irradiation. The most remarkable conformational change induced by light, therefore, can be achieved when the copolypeptide is in an α-helix structure carring adequately dissociated L-glutamic acid moieties, i.e., an unstable ordered structure.

It is also found that the opposite conformational change of azo-S-9.3-PGA from random coil to α-helix could not be induced by irradiating at $\lambda > 390$ nm or by dark adaptation in the pH range where the α-helix to coil transition induced by light occurs, thus confirming the irreversibility of the change. This result indicates that the isomerization of the azo chromophore from the cis to the trans forms does not affect the conformation of the copolypeptide in the disordered structure. We cannot find out, at present, the origin of this irreversibility of the change. However, it may be reasonable that, when the backbone is in the disordered structures, relative positional changes of the sulfonate anions resulting from the cis to trans isomerization of the azo moieties cannot induce a decrease in the local charge density of the environment around the polypeptide backbone to effectively reproduce the original ordered structure. The irreversibility of the photoinduced conformational change, including the local conformations of random coil polymer chains of the irradiated and dark-adapted samples, should be examined further.

In conclusion, α-helix to coil transitions to poly(L-glutamic acid) containing small amount of azobenzenesulfonate moieties (ca. 10 mol %) can be induced by light irradiation at adequate pH values on the basis of photoisomerization of the side-chain azobenzene chromophores from the trans to the cis forms. It is found that the photoinduced conformational transition is dependent on the azobenzenesulfonate content, ionization degree of the neighboring weak acid moieties, and polypeptide conformation itself; however, the main force of the conformational transition arises from a increase in the local charge density of the environment around the helical backborn owing to the change in the overall dimensions of the azobenzenesulfonate moieties at the fixed positions along the ordered helical axis. On the other hand, the opposite isomerization of the azo chromophores in the polypeptide in the random coil structure does not reform the original ordered structure.

The study of the photoinduced changes of the structure and functions of the azo-S-PGA membranes is in progress.

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Miscibility of Poly(vinyl methyl ether) with Styrene–Methyl Methacrylate Copolymers

Y. Y. Chien, Eli M. Pearce, and T. K. Kwei*

Department of Chemistry and Polymer Research Institute, Polytechnic University, Brooklyn, New York 11201. *Received December 1, 1987*

ABSTRACT: The miscibility of poly(vinyl methyl ether) (PVME) with a series of styrene–methacrylate copolymers was studied. It was found that the critical copolymer composition for achieving miscibility with PVME at room temperature was about 60 mol % styrene. The blends underwent phase separation at elevated temperatures, but the LCST passed through a maximum as the methyl methacrylate content of the copolymer was increased. The maximum value of LCST exceeded that of the PS–PVME pair. The significance of the observed miscibility window is discussed in terms of recent theories.

Introduction

The free energy of mixing of two polymers consists of three contributions:[1-3] (1) the combinatorial entropy of mixing, (2) intermolecular interaction, and (3) the "free volume" effect due to a mismatch of the equation of state parameters of the two polymers. In the context of the

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