Colloid Polym Sci (2002) 280: 539–546
DOI 10.1007/s00396-002-0649-4

ORIGINAL CONTRIBUTION

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Photocontrol of polyion complex formation between polylysine and chondroitin sulfate in the presence of pararosaniline leucohydroxide

Received: 26 June 2001
Accepted: 6 December 2001
Published online: 10 April 2002

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Abstract The photocontrol of polyion complex formation between polylysine bromide (PlysBr, $M_w = 21{,}800$) and sodium chondroitin sulfate (NaChs, $M_w = 24{,}700$) in aqueous solution was examined in the presence of a photochromic dye, pararosaniline leucohydroxide (leuco(OH)), with special reference to its pH-dependence. Under pH conditions examined ($6 <$ pH < 12), NaChs was almost fully dissociated, while dissociation of PlysBr reduced with increasing pH, resulting in a random coil-to-α-helix transition at around pH 9.4. Thus, the complex formation clearly showed pH-dependence. On the other hand, leuco(OH) undergoes photodissociation to increase the solution pH. By coupling these processes, we aimed to control the complex formation by photoirradiation. Turbidimetry, dynamic light scattering and electrophoretic light scattering measurements showed that the optimum condition for the complex formation was at approximately pH 10.5, where the net charge of complex was nearly zero, for solutions of [NaChs] = 1.0 mM, [PlysBr] = 1.5 mM (in molalities of dissociable groups), at a salt concentration of 1.5 mM. In the presence of 0.5 mM leuco(OH), the variation of complex size was clearly observed by photoirradiation. The hydrodynamic radius of the complex stayed almost constant at pH < 9 and pH > 11, increased at $9 <$ pH < 10, and decreased at $10 <$ pH < 11. The observed trend could be reasonably explained in terms of the pH change due to photodissociation of leuco(OH). A photoinduced coil-to-α-helix transition of PlysBr in the presence of leuco(OH) was also reported.

Keywords Photoinduced complex formation · Photodissociation · Polyion complex · Helix-coil transition

Introduction

In recent years, much attention has been paid to the photocontrol of the conformation and organization of macromolecules [1]. In many biological photoreceptors, the photoinduced conformational change of biopolymers plays an essential role. Furthermore, in view of material science, photoresponsive systems could provide a variety of applications. Thus, extensive studies have reported on photoresponsive polymer systems as model biological photoreceptors [2, 3], as well as novel tunable materials, e.g. photocontrollable polymer gel [4], liquid crystal [5, 6, 7], membrane [8, 9] and colloidal crystal systems [10].

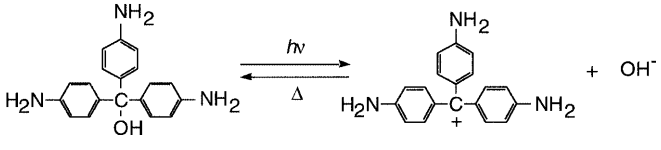
In the present study, we extended the photoregulation of the polymer association to polyion complex formation in aqueous solution, by using a photodissociable dye. The polyion complex is formed between two oppositely charged polyelectrolytes due to strong electrostatic attraction. Although photoinduced self-association of

polymers has been found in several systems, e.g. for amphiphilic block copolymers [11], to the best of our knowledge, there have been few studies on the photocontrol of polyion complex formation.

To control the complex formation in solution, a soluble complex is desired; polyion solubility is significantly reduced on complex formation owing to a decrease of both the net charge and the configurational entropy of the polymer chain, sometimes resulting in insoluble precipitates. Typical soluble complex systems are polyelectrolyte- and acid polysaccharide-protein complexes and acid polysaccharide-polypeptide complexes. So far, several studies have been reported concerning the formation and physicochemical properties of these complexes [12, 13, 14, 15, 16]. In our laboratory, the characteristics of the acid polysaccharide-protein complex, such as shape, phase behaviour and H-ion binding enhancement, have been studied using chondroitin sulfate-gelatin and hyaluronate-bovine serum albumin systems [17, 18].

Here we are concerned with the complex between an anionic polysaccharide, sodium chondroitin sulfate type-A (NaChs), and the cationic polypeptide polylysine bromide (PlysBr). Chs has strongly acidic sulfate and weakly acidic carboxylic groups, while Plys is a weak base. Thus, the complex formation between them is expected to show clear pH-dependence. Pararosaniline leucohydroxide (leuco (OH)) was used as the photochromic dye. As shown in Scheme 1, leuco(OH) undergoes photodissociation to give triallylmethyl cations and hydroxide ions, causing the pH of the solution to increase [19, 20, 21][1]. The dissociation is reversible, and it gradually returns to the undissociated form if kept in the dark. By coupling the pH-dependent complex formation between PlysBr and NaChs, with the photoinduced pH change by leuco(OH), we could successfully control the formation of the polyion complex by the photoirradiation.

The organization of this paper is as follows: after describing the experimental details, we show the photodissociation behaviour of leuco(OH) in aqueous solution. Next, we report the pH-dependence of the dissociation state and conformation of PlysBr. We then demonstrate the influence of pH on the complex formation in the absence of leuco(OH). After touching on a photoinduced conformational change of PlysBr, we finally describe the photoinduced complex formation between PlysBr and NaChs in the presence of leuco(OH).



Scheme 1. Photoinduced dissociation of leuco(OH)

[1]It was reported in the previous reference, i.e. Ref. 21, that photodissociations of the leuco derivatives takes place on UV irradiation. The light source we used had a strong emission in UV region, but also emitted visible light. An influence of visible light might not be ruled out for e.g. qualitative discussion on the photodecomposition rate.

Experimental section

Materials

NaChs was a kind gift from Seikagaku (Tokyo) and was purified by dialysis against Milli-Q water. The purified sample was passed several times through a column of cation and anion-exchange resin. The amounts of the loaded resin (Amberlite IR-120B and IRA-400, Organo, Tokyo) were five times and 1/4 time equivalent to the polyion, respectively. The acid form of chondroitin thus obtained was then neutralized with NaOH, and freeze-dried. PlysBr was purchased from Sigma (MO, USA) and used without further purification. Conductometric and potentiometric titration showed that 94% of the amino groups of the Ply was Br type, and 6% was protonated. Leuco(OH) was purchased from Aldrich (WI, USA).

Characteristics of the NaChs and PlysBr are presented in Table 1. The weight averaged molecular weight (M_w) and the polydispersity index (M_w/M_n) for PlysBr are the values reported by the producer, while those for NaChs were determined by using the gel permeation chromatography-multi angle laser light scattering (GPC-MALLS) method. The averaged pKa values of the dissociable groups ($\overline{\text{pKa}}$) for both polymers were determined by potentiometric titrations.

The sample solutions were prepared by mixing a 10 vol% MeOH/water solution of leuco(OH) and stock aqueous solutions of PlysBr (10 mM: concentration is the molality of the dissociable groups of the polymer) and NaChs (20 mM). [MeOH] in the sample solutions was 1 vol% (for [leuco(OH)] = 0.1 mM) or 5 vol% ([leuco(OH)] = 0.5 mM). The water used was purified by Milli-Q Simpli-Lab system (Millipore, MA, USA) and had an electrical conductivity of 0.4~0.6 μS cm^{-1}. The pHs of the solutions were adjusted by addition of 0.1 M NaOH or 0.1 M HCl. All the experiments were carried out at $6 < pH < 12$. NaCl was used as an added salt.

Method

The GPC-MALLS measurements were performed by using type TM600 high performance liquid chromatography (Waters, MA, USA) and DAWN-DSP light scattering system (Wyatt Technology, CA, USA).

The photoirradiation was carried out by using a 400 W Hg lamp (Type H400-P, Toshiba, Tokyo), with tube height 150 mm × tube diameter 18.5 mm, and an arc strength of 200 candela cm^{-2}.

Table 1 Characteristics of polymers used

Polymer	M_w	M_w/M_n	$\overline{\text{pKa}}$
NaChs	24,700[a]	1.10[a]	3.6[c] (sulfate) 4.3[c] (carboxylate)
PlysBr	21,800[b]	1.15[b]	8.6

[a]Determined by GPC-MALLS method
[b]Reported by producer
[c]Determined by potentiometric titration

It was placed in a lamp house equipped with a reflector. According to the producer, the energy spectrum of the lamp had a broad continuous emission region in 220–300 nm with sharp peaks at about 360, 400, 420, 550 and 590 nm. The lamp was used without any optical filter.

The sample solution was introduced into a quartz cell (width 10 × height 30 × optical path length 5 mm) and placed 10 cm away from the light source. The irradiation time was 3 min, unless stated otherwise.

The pH measurements were performed by using an F-13 pH meter (Horiba, Kyoto, Japan) equipped with a #6378-type electrode (Horiba).

Turbidity was measured with a UV-VIS spectrophotometer (UV-2400, Shimadzu, Kyoto, Japan) and a quartz cell with an optical path length of 10 or 1 mm at room temperature.

The circular dichroism (CD) spectra were measured with a 720 CD spectrometer (Jasco, Tokyo, Japan) with a thermostated quartz cell with a path length of 0.2 mm at 25 °C. The molar ellipticity at a wavelength $\lambda = 222$ nm, $[\theta]_{222}$, was estimated from the relationship $[\theta]_{222} = M\theta_{222}/10dc$, where M is the monomer molecular weight, θ_{222} the ellipticity at 222 nm, d the optical path length and c the concentration of polymers expressed in mg ml^{-1}.

Dynamic laser light scattering (DLS) measurements were carried out by using a model DLS-7000 light scattering apparatus (Otuska Electron, Tokyo, Japan) at 25 °C. As a light source, we employed a He-Ne laser having a wavelength of 633 nm, at which an absorbance of leuco(OH) was negligibly small (Fig. 1a). The hydrodynamic radius of the polyion complexes was estimated by applying the cumulant expansion method [22]. An electrophoretic laser light scattering apparatus, (type ELS-600, Otuska Electron, Tokyo, Japan) equipped with a He-Ne laser ($\lambda = 633$ nm) was used for the electrophoretic mobility measurements.

Results and discussion

Photodissociation of leuco(OH)

The dissociated form of leuco(OH) has a strong absorption band with a maximum wavelength (λ_{max}) of 540 nm in aqueous solution, due to the kinoid structure of the triallylmethyl cation [19]. We examined the photodissociation behaviour of leuco(OH) by UV-VIS spectroscopy.

Since leuco(OH) is weakly basic, its degree of dissociation (α) increases with decreasing pH. Figure 1a shows the variation of the absorption spectrum for aqueous solutions of 0.5 mM leuco(OH) at various NaOH and HCl concentrations.

On photoirradiation, absorption of the leuco(OH) solution was immediately increased within 1 min, and did not significantly change under the irradiation for 1∼5 min. However, on further irradiation, the absorbance was rather reduced, presumably due to the photodecomposition of leuco(OH). Figure 1b shows the absorbance at 540 nm (Abs_{540}) before and after the photoirradiation for 3 min, at various NaOH or HCl concentrations. In Fig. 1c, Abs_{540} was plotted against the pH before the photoirradiation. We denote this as pH_0, to distinguish it from the pH after the photoirradiation (pH*). The photodissociation behaviour of leuco(OH) was clearly observed, especially at $6 < pH_0$.

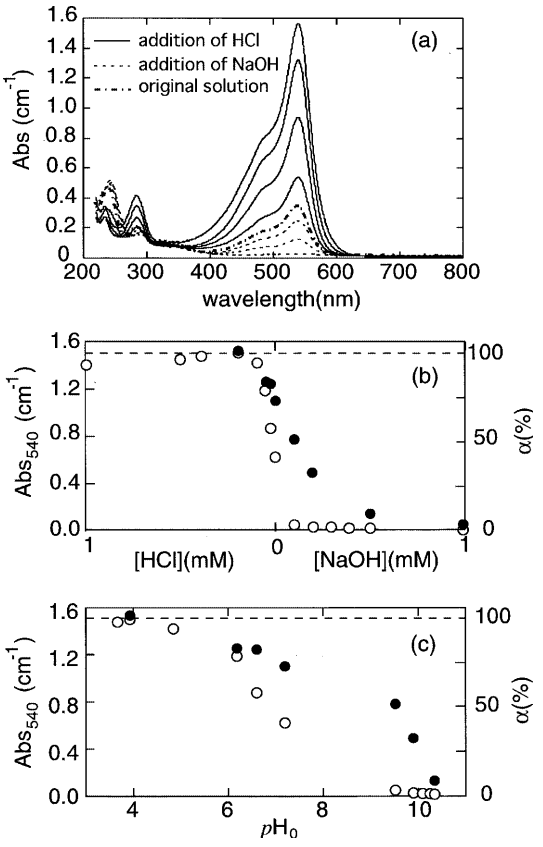


Fig. 1 **a** Variation of UV-VIS spectrum for leuco (OH) solution (0.1 mM in 1% MeOH/water) with changing HCl or NaOH concentrations. From the *top*, [HCl] = 0.65, 0.29, 0.10 and 0.02 mM; original solution; [NaOH] = 0.20, 0.48 and 2.0 mM. A strong adsorption band at $\lambda_{max} = 540$ nm is due to dissociation of leuco (OH). **b** Absorbance at $\lambda = 540$ nm, Abs_{540} and the degree of dissociation (α) for the leuco(OH) solution at various [NaOH] and [HCl] before (*open circles*) and after (*filled circles*) photoirradiation. **c** Abs_{540} and α plotted against pH before the irradiation (pH_0). Symbols are the same as those in Fig. 2b

At sufficiently high [HCl] and [NaOH], Abs_{540} levelled off, which could be regarded as $\alpha = 100$ and 0%, respectively. The molar absorption coefficient for the dissociated leuco(OH) at 540 nm (ϵ_{540}), which was estimated from Abs_{540} at a high [HCl] (9.35×10^{-5} M), was 8.26×10^4 cm^{-1} M^{-1}. The α values calculated from Abs_{540} and ϵ_{540} are also shown in Figs. 1b,c. The pKa of leuco(OH) determined from the pH-α plot in Fig. 1c was about 7.2, which was in rough agreement with the value reported previously by Goldacre et al. (7.57) [19]. The pKa under photoirradiation was about 9.5. We noted that a variation of acidity on photoirradiation has been observed for various organic compounds [23, 24]; this is due to a difference of electron energy levels between ground and photoexcited states. For example, the pKa of benzoic acid increases from 4.2 to 9.5 on photoirradiation [23]. Irie reported that an aqueous solution for 4,4′-bis(dimethylamino)triphenylmethane leucohydroxide,

which had a similar structure to the present photochromic dye, exhibited a large pH change (about 5.5–10) on irradiation [20].

pH-dependence of PlysBr's dissociation state and conformation

Under the pH conditions examined for complex formation ($6 < pH < 12$), we can safely assume that NaChs is fully dissociated, since its $\overline{pKa}$ values were sufficiently lower than the pH (Table 1). On the other hand, the degree of dissociation of PlysBr (α') should increase with pH, resulting in a clear pH effect for the complex formation.

Figure 2a shows the plot of α' against pH for the PlysBr calculated from potentiometric titration data (shown in an inset of Fig. 2a) at [PlysBr] = 1 mM (0.31 mg ml^{-1}) and under salt-free conditions. It is clear that PlysBr is almost undissociated at approximately pH > 10.

It is well known that Plys undergoes a random coil-to-α-helix transition by changing the pH [25]. We measured the CD spectrum for the PlyBr solution at various pHs. Typical CD spectra for random coil (pH 7.7) and α-helix (pH 11.1) structures are inset in Fig. 2b. Figure 2b shows the molar ellipticity at 222 nm ($[\theta]_{222}$) versus pH at [PlysBr] = 1.5 mM, under salt-free conditions[2]. $[\theta]_{222}$ has a small positive value for random coil conformations and is negative for α-helical structures. It is clear from Fig. 2b that the coil-to-helix transition starts at around pH 9.4, and thereafter the helix content increased with pH. The helix content at pH 11.1 was 68%, as estimated by using the method by Greenfield et al. [26].

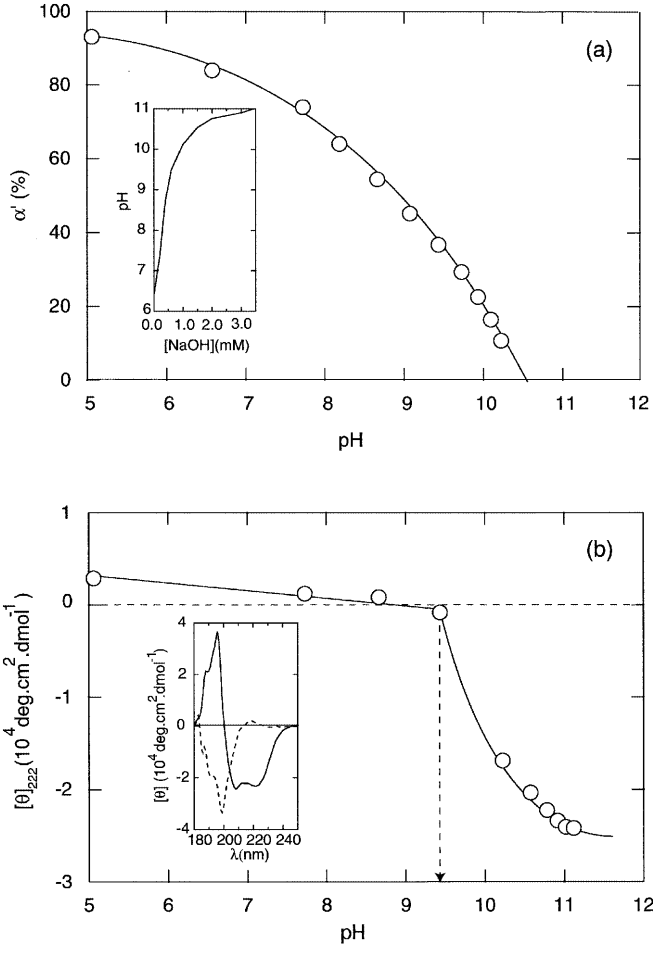


Fig. 2 **a** The degree of dissociation (α') versus pH plot for 1 mM PlysBr determined from potentiometric titration (*inset*). **b** The molar ellipticity at 222 nm ($[\theta]_{222}$) versus pH plot for 1 mM PlysBr, showing coil-to-helix transition at pH∼9.4. *Inset* shows a typical CD spectrum for random coil (*broken line*, pH 7.7) and helix (*solid line*, pH 11.1) states

Complex formation between PlysBr and NaChs

We examined the pH-dependence of the polyion complex formation between PlysBr and NaChs by applying turbidimetry and scattering methods.

Time and pH-dependence of turbidity

It should be noted that the size of the complex is generally time dependent. Figure 3 shows the time dependence of the turbidity (τ) at 700 nm, for aqueous solutions of 1.5 mM PlysBr and 1.0 mM (0.23 mg ml^{-1}) NaChs at various pHs. Salt concentration (C_s), which was calculated as a sum of concentrations of added NaCI and NaOH, was kept constant at 1.5 mM. The samples were prepared at time (t) = 0. At pH 6.44, 8.39 and 9.35, τ immediately increased after the preparation due to the complex formation, and thereafter did not largely vary with t. On the other hand, at pH 10.58 and 11.26, τ slowly increased with t, and precipitates were formed at t = 20 and 80 min, respectively. Thus, the complex formation process showed a marked pH-dependence.

Although graphical presentations are omitted, similar experiments in salt-free conditions showed that precipitation took place quite rapidly at pH > 10, while at higher C_ss, the complex formation rate was very much reduced in the low pH region. Thus, in all the following experiments, we adopted C_s = 1.5 mM, which enabled us to perform turbidity and scattering measurements in due time. Polymer concentrations were fixed at

[2] At $C_s = 0 \sim 1.0$ mM, pH at the transition point did not significantly vary. At $C_s = 0.1$ M, the transition point was approximately pH 10.5.

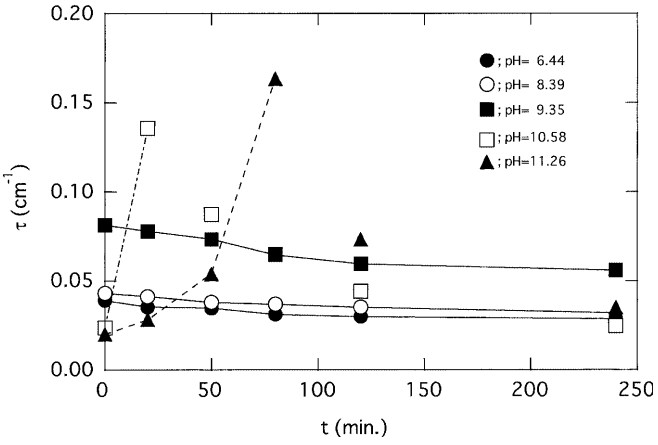


Fig. 3 The time evolution of turbidity (τ) for the solution of PlysBr-NaChs complex at various pHs. [Plys] = 1.5 mM, [NaChs] = 1.0 mM, C_s = 1.5 mM

[PlysBr] = 1.5 mM and [NaChs] = 1.0 mM, in the following complex formation experiments.

pH-dependence of hydrodynamic radius

The hydrodynamic radius (r_h) of the complex was measured by applying the DLS method. Figure 4a demonstrates the variation of r_h and τ value with pH at $t = 20$ min[3]. The value of r_h first increased with pH, passed through a maximum at around pH 10.5 and then decreased with further increase in pH. The observed trend showed a good correspondence with the pH-dependence of τ. The size distribution of the complex was relatively narrow. The normalized variance, which is a measure of the polydispersity [22], was 0.1∼0.3 and did not significantly depend of the pH.

pH-dependence of surface charge

Charged states of the complex were examined by ELS measurements. Figure 4b shows an electrophoretic mobility versus pH plot for the complex. The measurements were repeated three times at given pHs. The averaged values and the standard deviations are shown in Figure 4b. It is clear that the complexes had almost constant positive surface charges at pH < 9, took a zero net charge around pH∼10 and then were negatively charged at higher pH.

[3]DLS measurements started 5 min after the sample preparation, and approximately 15 min was needed for the data accumulation. The averaged data from $t = 5$ to 20 min were obtained.

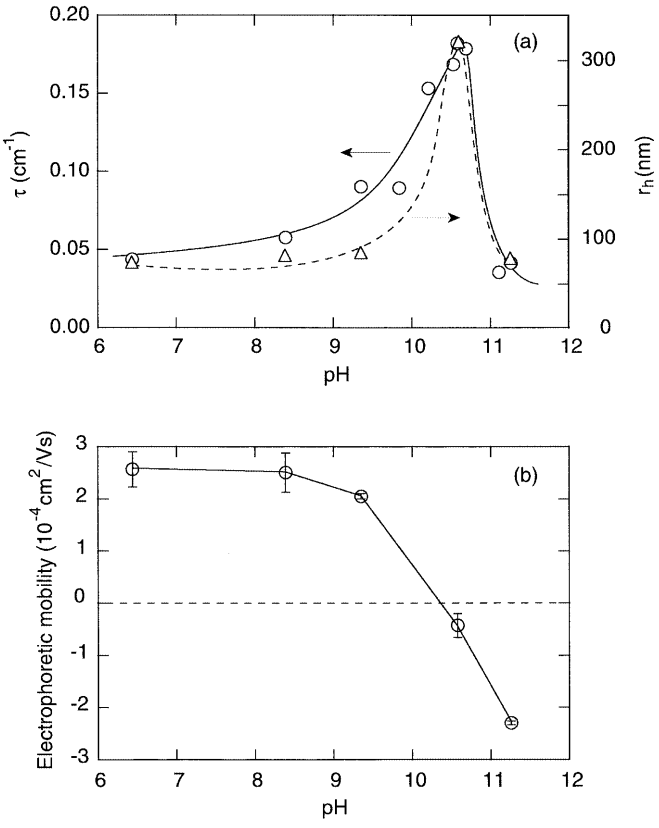
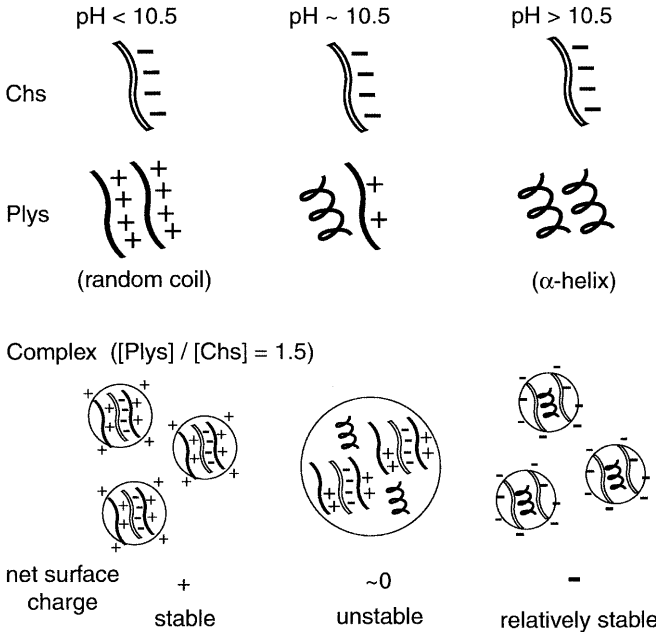


Fig. 4 pH-dependence of **a** the hydrodynamic radius (r_h) and τ, and **b** the electrophoretic mobility, for the PlysBr-NaChs complex. [Plys] = 1.5 mM, [NaChs] = 1.0 mM, C_s = 1.5 mM

Possible mechanism for the pH-dependence of the complex formation

From the experimental findings mentioned above, the pH-dependence of the complex formation appears to be accounted for in terms of the mechanism shown in Scheme 2. At pH < 10.5, both PlysBr and NaChs were sufficiently dissociated. Since a molar ratio for the dissociable groups on the polymers ([PlysBr]/[NaChs]) was chosen to be 1.5, it should be reasonable that the net surface charge of the complex was positive, due to the excess adsorption of cationic PlysBr. Under this condition, the individual complexes were electrostatically stabilized and consequently growth of the complex was restricted (Fig. 3), resulting in the small r_h (Fig. 4a). However, with increasing pH, the charge number of Plys became smaller. Then, the net surface charge of the complex approaches zero, and the solution should become unstable. In fact, at the optimum pH for the complex formation pH∼10.5 (Fig. 4a), the surface charge was nearly zero (Fig. 4b). At pH > 10.5, Plys was almost undissociated. Even then, however, the complex was formed between Plys



Scheme 2 Proposed model for pH-dependence of the PlysBr-NaChs complex structure

and NaChs[4]. In this case, the driving force for the complex formation should be non-electrostatic. In connection with this, it should be noted that Plys took a helical structure in this pH region, which is much hydrophobic than the random coil conformation. We assume that the enhanced hydrophobic interaction is a major driving force of the complex formation here. The importance of the hydrophobic interaction in the high pH region has also been suggested by Davidson et al. [12], who examined the polyadenylic acid-Plys complex system. The negative surface charge of the complex at pH > 10.5 (Fig. 4b) is accounted for in terms of the presence of excess NaChs. The system then becomes relatively stable, as seen from the smaller growth rate (Fig. 3) and r_h value (Fig. 4a) than those at pH~10.5.

Photoinduced helix-to-coil transition of PlysBr

We have demonstrated the pH-dependent conformational change of PlysBr and complex formation. Here, we examine the photoinduced helix-to-coil transition of PlysBr in the presence of leuco(OH). The photocontrol of the helix-to-coil transition has so far been reported for several photochromic polypeptide systems [27, 28].

[4]The turbidity of the 1.5 mM PlysBr solution was nearly zero at pH < 12 and at C_s = 1.5 mM. Thus, a salting-out effect of the Plys could be ruled out under the present conditions.

Figures 5a and b show CD spectra before and after the photoirradiation for solutions of 1.5 mM PlysBr in the presence of 0.5 mM leuco(OH) at C_s = 1.5 mM and pH_0 8.25 and 9.00. The random coil-to-α-helix transition of PlysBr took place at pH~9.4, as was mentioned above. Consequently, PlysBr had a random coil conformation before the photoirradiation, in both cases. On photoirradiation, pH values increased to pH* 8.88 and 9.62, respectively. The CD spectra show that Plys remained in the coil structure or underwent the coil-to-helix transition on photoirradiation, as expected, at the lower or higher pH_0, respectively.

Photoinduced complex formation between PlysBr and NaChs

By coupling the photoinduced pH change by leuco(OH) with the pH-dependent PlyBr-NaChs complex formation, we finally examined the photoinduced polyion complex formation in the presence of leuco(OH).

First, the change of pH for the PlysBr-NaChs solution on photoirradiation was measured in the presence of 0.5 mM leuco(OH) (Fig. 6). A marked increase of pH was observed especially at low [NaOH].

Figure 7 shows the variations in appearance of the sample on photoirradiation at three pH_0s. The pH changes examined were pH_0 7.64→pH* 8.40, 9.93→10.23 and 11.00→11.04. As mentioned above, the dis-

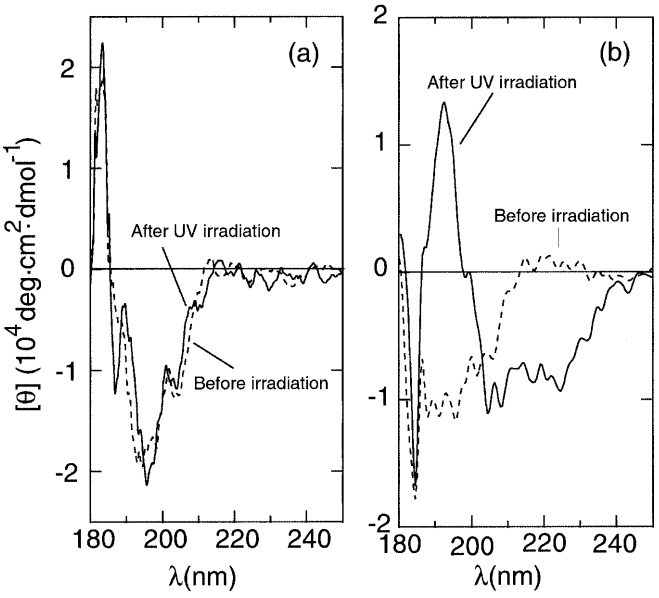


Fig. 5a,b CD spectra of 1.5 mM PlysBr in the presence of 0.5 mM leuco(OH) at **a** pH_0 8.25 and pH* 8.88, and at **b** pH_0 9.00 and pH* 9.62. pH* denotes the pH value after the photodissociation. C_s = 1.5 mM. In **b**, photoinduced coil-to-helix transition was observed

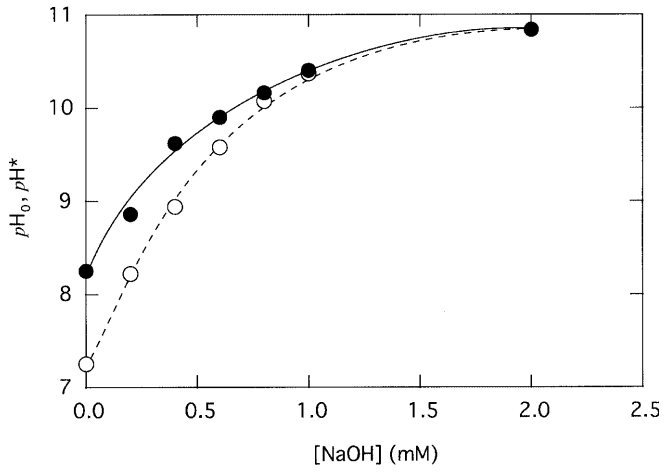


Fig. 6 Photoinduced pH for solutions of PlysBr and NaChs at various [NaOH]s, in the presence of leuco(OH). *Open circles* indicate pH_0, and *filled circles* indicate pH*. [Plys] = 1.5 mM, [NaChs] = 1.0 mM and [leuco(OH)] = 0.5 mM. C_s = 1.5 mM

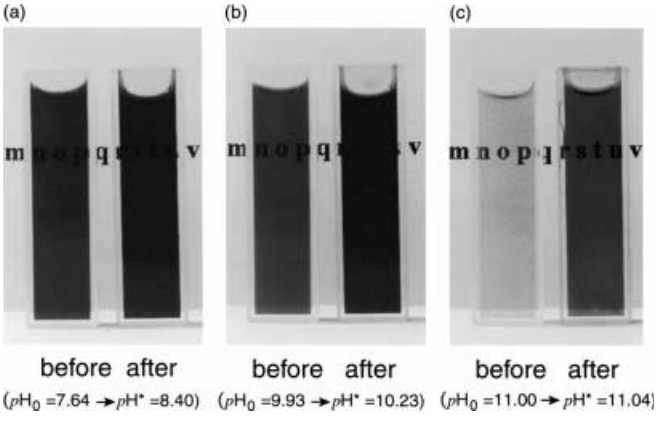


Fig. 7a–c Change in the appearance of the solutions of PlysBr and NaChs in the presence of leuco(OH) on photoirradiation with pH changes of **a** pH_0 7.64→pH* 8.40, **b** 9.93→10.23, and **c** 11.00→11.04. The variation in the colour was due to photodissociation of leuco(OH). In *b*, the sample became turbid on irradiation because of the complex formation

sociated form of leuco(OH) had a strong absorption band at 540 nm. Thus, the colour of the sample varied in all the cases, corresponding to the changes in the dissociation state. The turbidity of the sample did not markedly change at pH_0 7.64 and 9.93. However, at pH_0 10.20, a drastic increase of turbidity was observed on photoirradiation. This obviously indicates that the complex was formed by the photoirradiation under this pH condition.

The pH-dependence of the photoinduced complex formation was examined in detail by DLS measurement. Figure 8a shows the hydrodynamic radius of the complex at $t = 20$ min, plotted against pH_0. A characteristic pH-dependence was observed for the variation of the

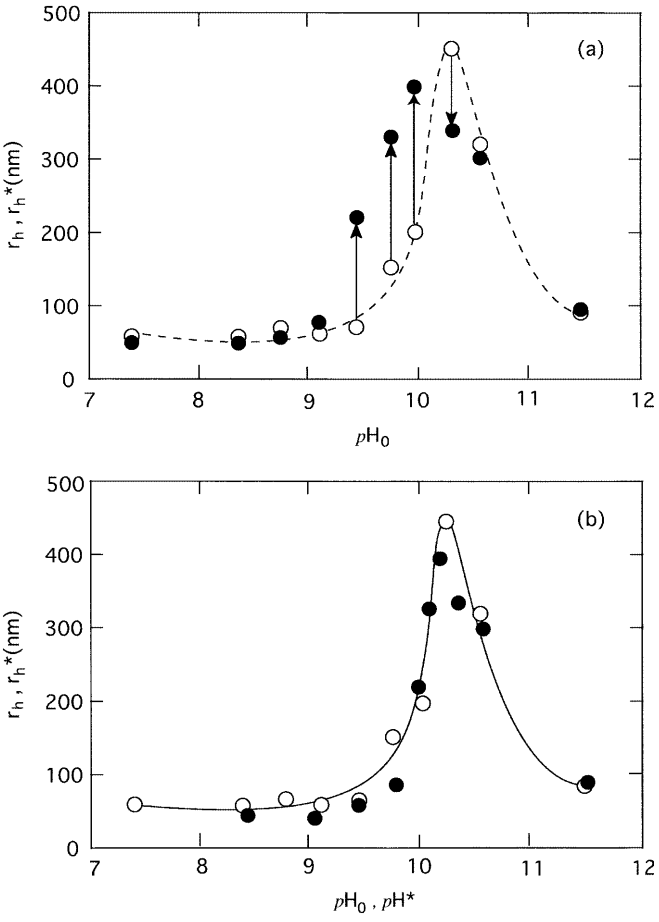


Fig. 8 **a** Changes in the hydrodynamic radius of the Plys-NaChs complex before (r_h, *open circles*) and after (r_h*, *filled circles*) the photoirradiation with pH_0. At $9 < pH < 10$, the hydrodynamic radius increased on photoirradiation, while at $10 < pH < 11$, it decreased. **b** r_h versus pH and r_h* versus pH* plots represented in an identical coordinate. The two plots could be represented by a single curve

complex size: at $pH_0 \leqq 9$ and $11 < pH_0$, the value of the hydrodynamic radius with photoirradiation (r_h*) was not significantly different from that without photoirradiation (r_h). At $9 < pH_0 \leqq 10$, however, r_h* was considerably larger than r_h, indicating a photoinduced complex formation. Furthermore, at $10 < pH_0 \leqq 11$, r_h* was rather smaller than r_h, indicating a decomposition of the complex by the photoirradiation.

To elucidate this pH-dependence, we plotted r_h* values against pH*, that is the pH value after the photoirradiation. In Fig. 8b, plots of r_h against pH and r_h* against pH* are presented in the same coordinate. Obviously, they can be represented by a single curve. This implies that the complex size was solely dependent an the pH value of the solution both in the absence and presence of the photoirradiation, and that the variation of complex size observed in Fig. 8a was caused by the pH change through the photodissociation of leuco(OH).

Thus, as described above, we could control the complex formation between PlysBr and NaChs by coupling it with the pH change due to photodissociation of leuco(OH). The present study appears to be extendable to photocontrol of many other pH-dependent phenomena.

Conclusion

In this paper, we examined the photocontrol of polyion complex formation between PlysBr and NaChs in aqueous solution, in the presence of leuco(OH).

Under the pH condition examined ($6 < pH < 12$), Chs was fully dissociated, while dissociation of Plys was reduced with increasing pH. Thus, the complex formation showed a clear pH-dependence, with an optimum condition at pH$\sim$10.5. By coupling the pH-dependent complex formation with the photoinduced pH change by leuco(OH), we could successfully control the complex formation by photoirradiation. The observed pH-dependence of the complex size on the photoirradiation was reasonably explainable in terms of the pH change due to photodissociation of leuco(OH).

Acknowledgements This work was generously supported by the Sasakawa Scientific Research Grant from The Japan Science Society (1999–2000).

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