$\langle r^2\rangle_0/nl^2 = 25.3$ and $\langle \mu^2\rangle/xm^2 = 1.3$ for a perfectly isotactic chain ($P_{iso} = 1.0$).

Registry No. PVK, 25067-59-8; BCP, 102197-47-7.

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Photoinduced Conformational Transition of Polypeptide Membrane Composed of Poly(L-glutamic acid) Containing Pararosaniline Groups in the Side Chains

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ABSTRACT: Photoresponsive polypeptide membranes have been prepared by casting a dimethylformamide solution of poly(L-glutamic acid) (PGA) containing ca. 10 mol % pararosaniline (rose) groups in the polymer side chains (rose-PGA). The dark-adapted rose-PGA membranes in the aqueous solution exhibited a unique CD pattern with the pH dependence of the secondary structure, suggesting loss of α-helix structure at low and high pHs and formation of helix near weak alkaline pH. This behavior arises from the amphoteric nature of the rose-PGA side chains; i.e., the L-glutamic acid moiety is negatively charged at high pH, whereas the rose moiety is positively ionized at low pH. The light irradiation of the rose-PGA membranes produced changes in the secondary structure of the membranes, random coil to helix and helix to random coil transitions, depending on the pH at which the irradiation was carried out. The induced conformational transitions of the membrane can be explained in terms of the photoinduced changes in the balance of electrostatic interactions between oppositely charged side chains, based on a cooperative effect between the photodissociation of the rose moiety with production of a hydroxide ion and the induced acid dissociation of L-glutamic acid moiety accompanied by the increase in pH in the membrane phase on UV irradiation. After removal of the light, rose-PGA in the membrane returned to the initial conformation after 100 min in the dark.

Recently, many biological studies provide evidence that living cells have systems for information reception, intracellular transmission, and transduction and/or response along the route of signal transmission. It has been recognized, for example, that photoreceptors translate the information accepted by rhodopsin into transmembrane photoreceptor potentials resulting from conformational changes of channel proteins. In the vertebrate photosen-

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Table I
Poly(L-glutamic acids) Containing Pararosaniline Moieties in the Side Chains Obtained by the Modification of Poly(L-glutamic acid) with Pararosaniline

sample	reaction conditions			rose content, mol %
	R^a	temp, °C	duration, h	
rose-10.5-PGA	1.0	25	24	10.5
rose-15.5-PGA	1.0	25	48	15.5

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

sory system, the signals of the photoreception of rhodopsin are believed to be communicated to the channel proteins by means of the intracellular second messenger, *c*-GMP.[1,2] Investigations on external stimulus–responsive behavior in artificial systems are of major importance in understanding the mechanism by which specific signals are transferred through the membrane.

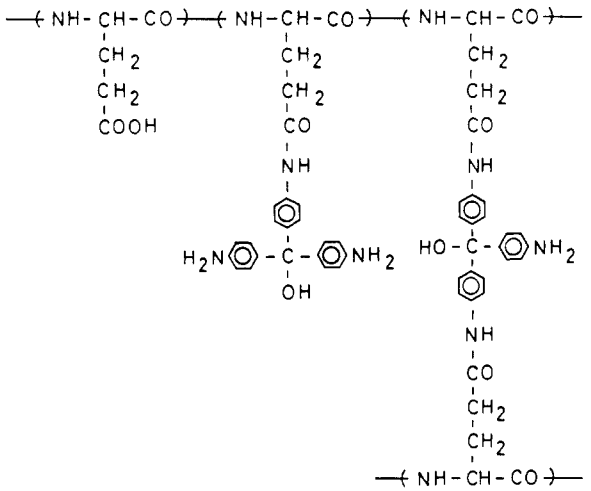
In previous studies,[3-5] we have investigated the photoresponsive behavior of a polypeptide membrane composed of poly(L-glutamic acid) containing azobenzene groups in the side chains. It was found that photoisomerization of side-chain azobenzene moieties resulted in changes in the membrane functions such as permeabilities and membrane potentials without variation in the backbone structure of the polypeptide.

We report here on the photoresponsive behavior of a polypeptide membrane composed of poly(L-glutamic acid) containing pararosaniline groups in the side chains. Light irradiation on the photoresponsive polypeptide membrane can induce changes in the backbone conformation of the polypeptide; i.e., the light signal is associated with the concentration change in hydroxy ion in the membrane phase via the photodissociation of the pararosaniline moieties and initiates acid dissociation of glutamic acid groups resulting in the conformational responses of the polypeptide. Preliminary results of the photocontrol of conformation of the rose-PGA membrane were reported previously.[6]

Experimental Section

Materials. The membrane of poly(L-glutamic acid) with incorporated pararosaniline groups in the side chains (rose-X-PGA, X is the mole percentage of the pararosaniline moieties) was prepared as follows.

Poly(L-glutamic acid) (PGA, $\bar{M}_v = 1.19 \times 10^5$) was obtained by saponification of poly(γ-methyl L-glutamate) (PMLG, $\bar{M}_v = 1.50 \times 10^5$) as previously reported.[7] The PGA was dissolved in dimthylformamide (DMF) at 0 °C. Pararosaniline (rose), *N*-hydroxybenzotiazole (HOBt), and 1-ethyl-3,3-(dimethylamino)-propylcarbodiimide hydrochloride (EDC·HCl) were added to the stirred DMF solution at 0 °C. After 1 h, the mixture was further stirred at 25 °C for 24 or 48 h (Table I). The bulk of the DMF was poured into methanol. Then the residues were reprecipitated 3 or 4 times until unreacted rose reagents could not be detected spectroscopically. The polymers obtained, rose-PGAs, were dried under vacuum. The rose content in the polymers was determined from the absorbance at λ_{max} (560 nm) of the DMF solution of rose-PGAs on the basis of the molar extinction coefficient of the model compound, 4-propionamido-4′,4″-diaminotriphenylcarbinol (pro-rose), at λ_{max} (560 nm). The conditions for the modification of poly(L-glutamic acid) and rose content, X, are summarized in Table I. The rose-PGAs were dissolved in DMF again, HOBt and EDC·HCl were added to the stirred DMF solution, and the solvent was evaporated gradually at 40 °C. The membranes obtained were washed with methanol for the purpose of the removal of unreacted reagents. Transparent stable polypeptide membranes of 3-μm thickness were obtained. The membrane obtained was no longer soluble in DMF or in aqueous solution of NaOH, indicating that some fraction of rose moieties with amino groups may act as a cross-linking agent in the concentrated solution of rose-PGA during the casting process.



4-Propionamido-4′,4″-diaminotriphenylcarbinol (pro-rose), the model compound for the photochromic side chain of rose-PGA, was synthesized as follows: propionic acid was dissolved in DMF, and the solution was cooled to 0 °C. Pararosaniline, rose, was added to the stirred solution followed by dicyclohexylcarbidiimide (DCC) and HOBt, and the mixture was allowed to warm to 25 °C for 24 h. The dicyclohexylcarbodiurea (DCUrea) precipitated was removed, and the solution was poured into alkaline water (pH 11.0). The obtained residues were redissolved in ethanol and crystallized by adding ether.

Measurement. Absorption and circular dichroism (CD) spectra of the membranes in aqueous solution were recorded on a Jasco UVIDEC 670 spectrophotometer and Jasco J 40C spectropolarimeter, respectively. The molar ellipticity, $[\theta]$, of the membrane was calculated by the following equation:

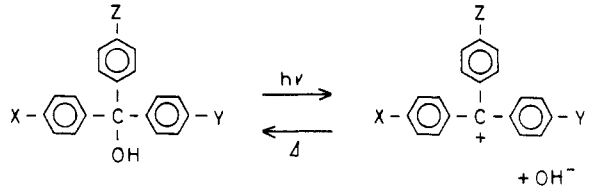
$$[\theta] = \frac{\theta \bar{M}_w}{dl}$$

where θ, $\bar{M}_w$, d, and l were ellipticity, average residual molecular weight, density of the membrane, and membrane thickness, respectively.

Irradiation. Irradiation of the membrane was carried out with a 500-W super-high-pressure mercury lamp (USHIO UVD500D) equipped with a Toshiba UV-D33s filter for ultraviolet light irradiation (250 nm < λ < 380 nm).

Results and Discussion

Photoinduced and pH-Induced Dissociation of Pararosaniline Groups. Triarylmethane leucohydroxide derivatives are known to dissociate into ion pairs under ultraviolet light irradiation with production of hydroxyl ions and colored triarylmethyl cations. And the ion pairs



dissociated thermally recombine again with each other in the dark.[8,9] Figure 1a shows the UV–visible absorption spectra of the dark-adapted and irradiated rose-15.5-PGA membrane in aqueous solution at pH 8.3. It is clear that the light irradiation produced a strong absorption band centered at 560 nm, which could be correlated with the formation of triarylmethyl cations. It was confirmed, therefore, that the rose moieties in the rose-15.5-PGA membrane can be dissociated by irradiation at pH 8.3, in a similar manner as the low molecular weight leuco dye, yielding hydroxyl ions in the membrane phase. The changes in the absorption spectra of the rose-15.5-PGA membrane effected by light irradiation (Figure 1a), therefore, suggest that the pH value in the membrane can

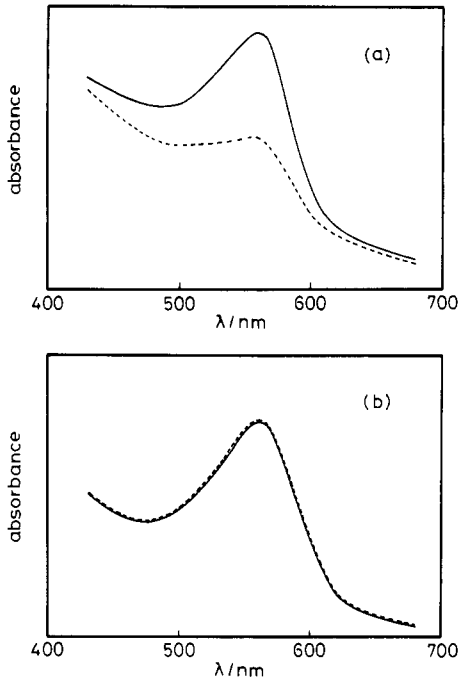


Figure 1. (a) Absorption spectra of a membrane of poly(L-glutamic acid) containing 15.5 mol % pararosaniline groups, before (---) and after (—) irradiation, in aqueous solution at 25 °C. The irradiation was carried out (a) at pH 8.3 and (b) at pH 6.5.

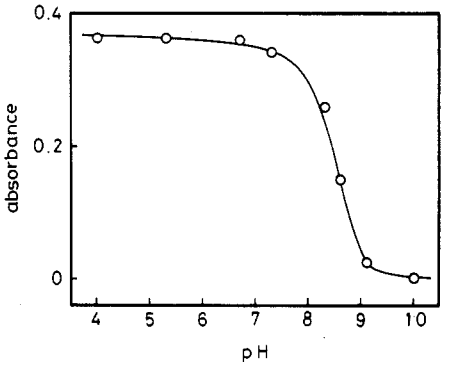
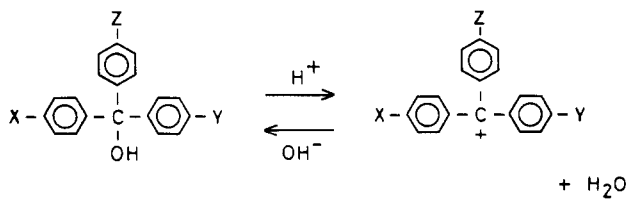


Figure 2. pH dependence of absorbance at 560 nm of a dark-adapted membrane of poly(L-glutamic acid) containing 15.5 mol % pararosaniline groups in aqueous solution at 25 °C.

be controlled by light irradiation resulting from the photodissociation of the rose moieties. It was also shown that, after removal of the light, the absorption band at 560 nm completely returned to the original value for 100 min in the dark at 25 °C.

On the other hand, Figure 2 shows the pH dependence of the absorbance of the rose-15.5-PGA membrane at 560 nm in the dark. The intensity of the absorbance at 560 nm was increased with decreasing aqueous pH value. As a result, below pH 7.0 the rose moieties were shown to be completely ionized in the membrane. The pK_a of the rose moiety in the rose-15.5-PGA membrane, estimated from Figure 2, was 8.6. Therefore, the degree of dissociation of the rose moieties in the membrane depends also on the aqueous pH in the dark, resulting from the neutralization reaction with proton ions.[10] This suggests that the mag-



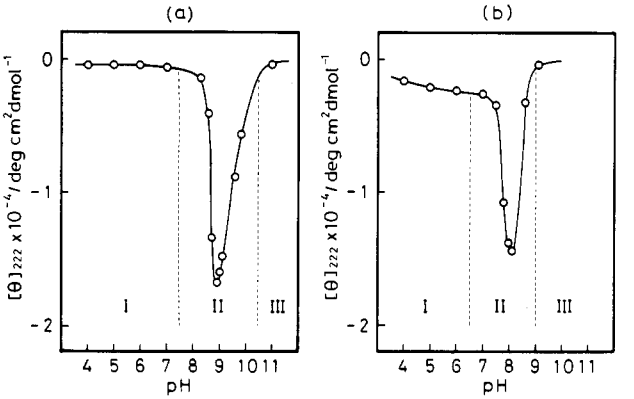


Figure 3. pH dependence of minimum ellipticity, $[\theta]_{222}$, of a dark-adapted membrane of poly(L-glutamic acid) containing (a) 15.5 mol % and (b) 10.5 mol % pararosaniline groups in aqueous solution at 25 °C.

nitude of the change in the dissociation degree of the rose moieties effected by light irradiation should be dependent on the pH at which the irradiation was carried out. As is expected, the irradiation at pH 6.5, where the rose moieties were fully ionized, did not induce any changes in the absorption spectra of the rose-15.5-PGA membrane (Figure 1b). These results established that the rose moiety, the photoreceptor site in the membrane, can be dissociated by light irradiation above pH 7.0 with production of a hydroxyl ion, which results in the creation of a second stimulation to the membrne, i.e., a pH increase in the membrane phase.

Conformation of the Dark-Adapted Rose-PGA in the Membrane. The backbone conformation of the rose-PGAs in the membrane was strongly dependent on the pH of the aqueous solution. Parts a and b of Figure 3 show the changes in the molar ellipticity at 222 nm, $[\theta]_{222}$, of rose-15.5-PGA and rose-10.5-PGA respectively. In both rose-PGAs, a similar pH dependence of $[\theta]_{222}$ was obtained, indicating loss of the α-helical structure at low pH and high pH regions (region I and region III, respectively) and formation of a α-helix at the weakly alkaline pH region (region II). This transition behavior arises from the amphoteric nature of the side chains in rose-PGA; i.e., the L-glutamic acid moiety is negatively ionized at high pH, whereas the rose moiety is positively ionized at low pH as described above (Figure 2). The repulsion forces among charged groups of the same sign, therefore, will disturb the formation of the α-helix structure of the membrane in regions I and III. On the other hand, in region II these charged side chains can be neutralized by the oppositely charged groups, which resulted in the formation of a α-helix structure in the rose-PGA membrane. The pK_a of the rose moiety in rose-15.5-PGA was shown to be ca. 8.6 (Figure 2). However, the transition region of the rose-15.5-PGA membrane seems to be shifted to a higher pH value, even though the pK_a of the L-glutamic acid group, which reduces the electrostatic repulsion between cationic rose moieties in the low pH region, was shown to be ca. 5.0 on pure poly(L-glutamic acid).[11] It is well-known that the hydrophobic environment around PGA effectively reduces the degree of dissociation of the side chain carboxyl groups, which results in a large shift of the pH of the helix to coil transition of the PGA toward higher values.[12,13] Therefore, the transition behavior of the rose-15.5-PGA membranes in Figure 3a can be explained in terms of the hydrophobic environment in the membrane provided by triarylmethane groups of the rose side chains around L-glutamic acid moieties; i.e., the rose groups with low dielectric constant may also produce a shift of the pK_a of

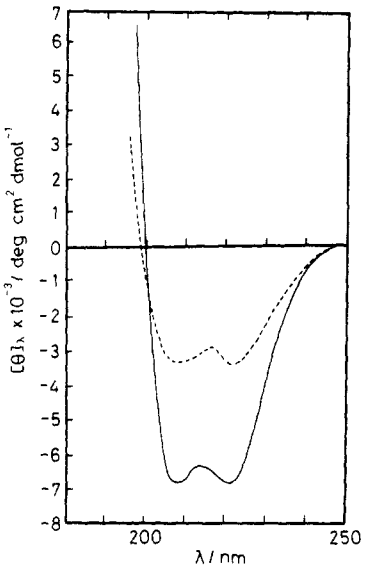


Figure 4. CD spectra of a membrane of poly(L-glutamic acid) containing 10.5 mol % pararosaniline groups, before (- - -) and after (—) irradiation, in aqueous solution at 25 °C. The irradiation was carried out at pH 7.5.

the COOH side chain toward higher values. It is also reasonable, therefore, that the helix formation pHs, region II, of the rose-10.5-PGA membrane with smaller amounts of the hydrophobic rose groups were shifted to lower pHs (Figure 3b), compared with that of the rose-15.5-PGA membrane.

Photoinduced Conformational Changes of Rose-PGA in the Membrane. Figure 4 shows the changes of circular dichroism (CD) spectra of the rose-10.5-PGA membrane upon ultraviolet light irradiation (250 nm < λ < 380 nm) at pH 7.5. Two negative bands at 222 and 208 nm characterized from the α-helical structure were strongly increased upon irradiation. During the irradiation, the molar ellipticity at 222 nm, $[\theta]_{222}$, of the membrane monotonously decreased from -3.40×10^3 to -6.84×10^3 deg·cm^2·dmol^{-1}. The rose moieties were shown to be dissociated into ion pairs by light irradiation at adequat pHs with production of a hydroxyl ion (eq 2 in Scheme I). According to this reaction, leucohydroxide functions as a light-induced OH^- ion emitter. This suggests that the pH value in the membrane can be controlled effectively by irradition as described above. This photoinduced α-helix formation, therefore, can be explained in terms of a cooperative effect between the photodissociation of the rose groups with the production of a hydroxyl ion and the induced acid dissociation of the neighboring L-glutamic acid moieties by an increase in pH in the membrane phase on the irradiation (Scheme I). This may indicate, therefore, that the photoirradiation is apparently equivalent to the replacement of the aqueous solution of pH 7.5 by that of pH 7.8 in the dark. Moreover, after removal of the light, CD bands at 222 and 208 nm gradually decreased again and returned to the initial value after 100 min in the dark.

Similar behavior could be observed for the rose-15.5-PGA membrane. Figure 5a shows the changes of the $[\theta]_{222}$ value of the rose-15.5-PGA membrane at pH 8.3 upon light irradiation and dark adaptation. This change was almost comparable with the changes of the absorbance of the membrane at 560 nm (Figure 5b). The photoinduced conformational change of the membrane (Figure 5a), however, was shown to respond more slowly than the spectral change (Figure 5b). The lag in the conformational change may correspond to the time taken to reach a uniform distribution of the hydroxyl ion, produced at the

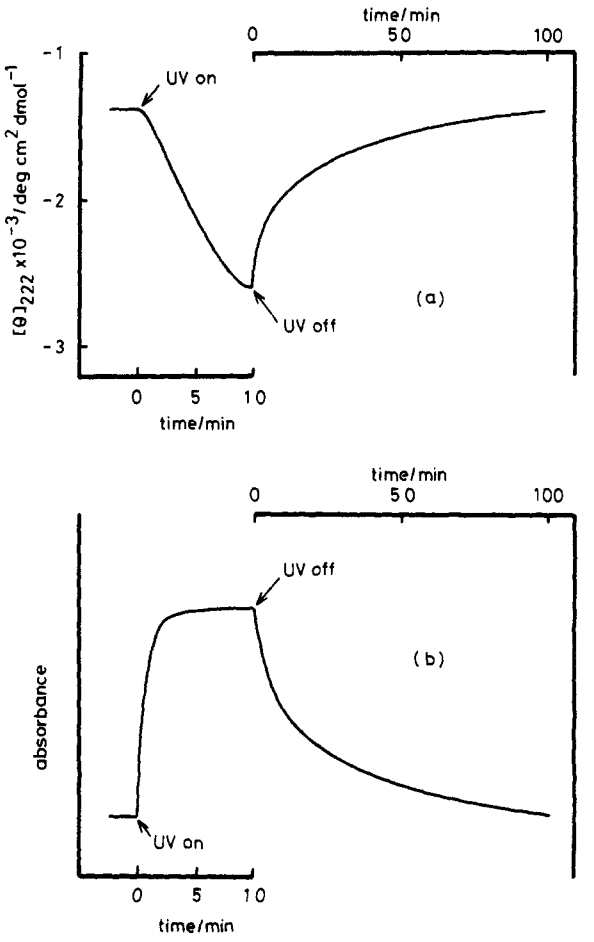


Figure 5. (a) Photoinduced changes in the minimum ellipticity, $[\theta]_{222}$, of a membrane of poly(L-glutamic acid) containing 15.5 mol % pararosaniline groups in aqueous solution at pH 8.3 and at 25 °C. (b) Photoinduced changes in the absorbance at 560 nm of a membrane of poly(L-glutamic acid) containing 15.5 mol % pararosaniline groups in aqueous solution at pH 8.3 and 25 °C.

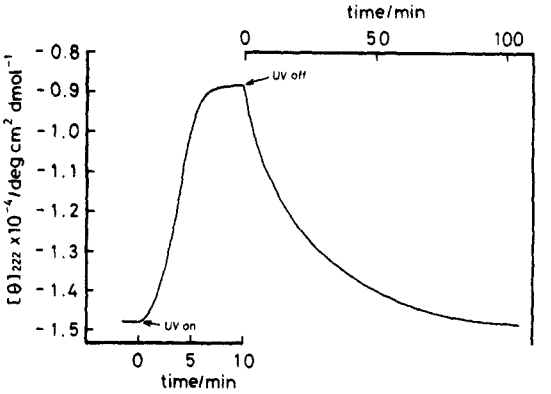
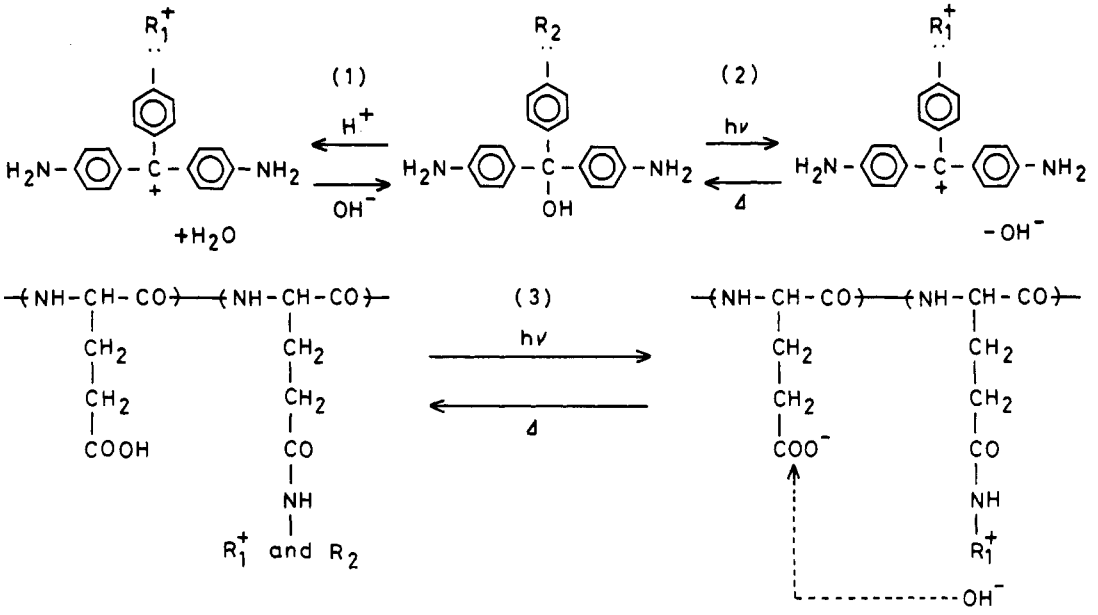


Figure 6. Photoinduced changes in the minimum ellipticity, $[\theta]_{222}$, of a membrane of poly(L-glutamic acid) containing 15.5 mol % pararosaniline groups in aqueous solution at 25 °C. The irradiation was carried out at pH 9.1.

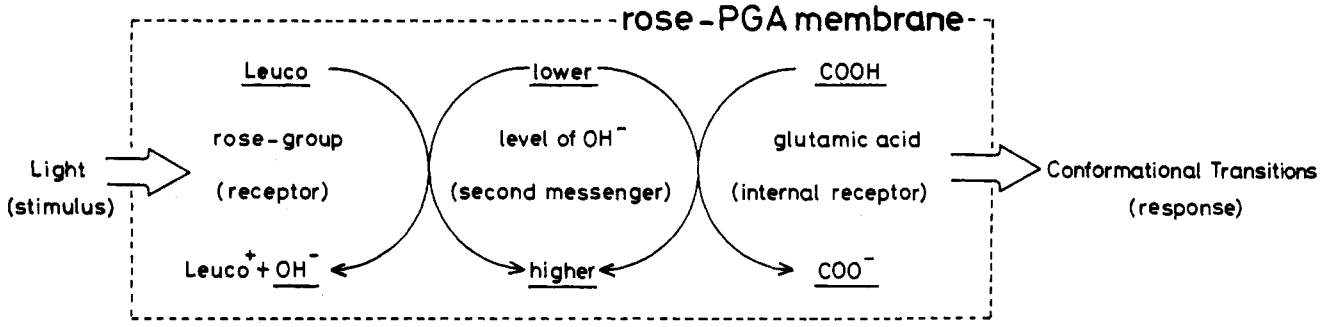
photoresponsive site, in the membrane.

On the other hand, the photoinduced conformational responses of the rose-15.5-PGA membrane were shown to be dependent on pH of the aqueous solution at which the irradiation was carried out. That is, the irradiation at pH 9.1, the transition point from α-helix to coil structure (Figure 3a), produced a decrease of the $[\theta]_{222}$ value (Figure 6); i.e., α-helix to coil transition of the rose-15.5-PGA membrane can be induced by the irradiation at pH 9.1. This result arises from the fact that the L-glutamic acid

Scheme I



Scheme II



moieties in the membrane could be dissociated in large excess at the higher pH resulting from the photoproduction of additional hydroxide ions from the rose moieties, which resulted in the formation of the coil structure. Figure 7a shows the degree of the variation of $[\theta]_{222}$, $\Delta[\theta]_{222} = [\theta]_{222}$ on UV irradiation $- [\theta]_{222}$ in the dark, associated with the photoinduced conformational changes of rose-15.5-PGA in the membrane at various pHs. It is clear that no effects have been observed upon light irradiation at lower and higher pH values. The former is the pH region (<7.5) where the conformation of the polypeptide was almost independent of the pH (Figure 3a) and the rose side chains were insensitive to light (Figure 2); the latter is the pH region (>10.5) where the polypeptide was kept in the random coil structure even though the rose side chains could be photodissociated. As a result, rose-PGA in the membrane was shown to have the pH-dependent conformational transitions (α-helix to coil and coil to α-helix structure) in the relatively narrow pH range upon light irradiation. This behavior was comparable with the pH dependence of the differential value of $[\theta]_{222}$ on pH, $d[\theta]_{222}/dpH$, (the values of $d[\theta]_{222}/dpH$ at every pH were calculated from the dependence of $[\theta]_{222}$ on pH in the dark in Figure 3a), as shown in Figure 7b. This suggests that the photoinduced conformational changes of the rose-PGA membrane are, in fact, due to the slight pH increase in the membrane phase on the irradiation at the adequate pHs.

The photoresponsive behavior of the rose-PGA membrane obtained in this study is summarized as follows (Scheme II). The light irradiation induced the dissociation of the rose moieties in the membrane with the production of hydroxyl ions (information reception). The hydroxyl

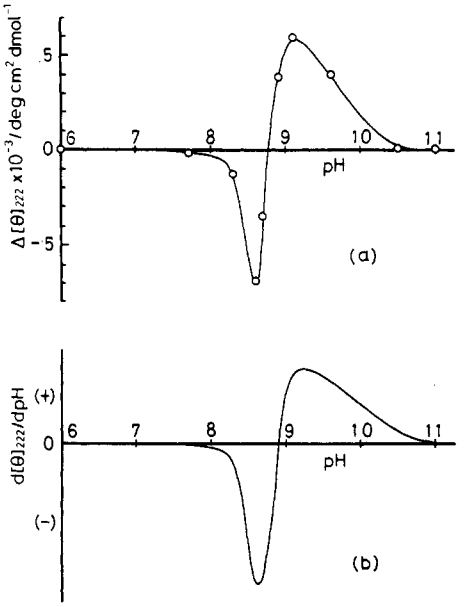


Figure 7. (a) pH dependence of $\Delta[\theta]_{222}$ (=$[\theta]_{222}$ on light irradiation $- [\theta]_{222}$ in the dark) of a membrane of poly(L-glutamic acid) containing 15.5 mol % pararosaniline groups in aqueous solution at 25 °C. (b) pH dependence of the differential value of $[\theta]_{222}$ on pH, $d[\theta]_{222}/dpH$, of a membrane of poly(L-glutamic acid) containing 15.5 mol % pararosaniline groups in aqueous solution.

ion produced, a so-called second messenger, increases pH in the membrane phase, resulting in the acceleration of dissociation of the glutamic acid moieties in the membrane (intramembrane signal transmission). Therefore, the re-

sulting dissociation of the internal receptor sites induces the pH-sensitive conformational transitions of the membrane (response).

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Thermoluminescence and NMR Studies of Segmented Poly(urethane ureas) in Relation to Phase Separation and Deformation

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ABSTRACT: Thermoluminescence (TL) and pulse NMR studies of segmented poly(urethane ureas) (SPUU) were conducted in relation to phase separation and deformation. The phase separation was controlled by changing the number-average molecular weights of poly(tetramethylene glycol) (PTMG) and the nitrogen content, and the effects of annealing and elongation on the extent of phase separation in samples having a fixed PTMG molecular weight and nitrogen content were also investigated. The TL glow curve of the original SPUU film exhibits a main peak (H) at around 430 K and a weak and broad peak (L) near 350 K. The H peak is related to the liberation of electrons trapped in the hard-segment domains, and the L peak is assigned to the molecular motions of the phase-mixed intermediate phase. The TL and NMR results show that either an increase in the PTMG molecular weight or a decrease in the 4,4′-methylenebis(phenyl isocyanate) content increased the peak intensity and shifted it to a higher temperature, thus indicating an improved phase separation. Annealing also increased the intensity of the H peak, implying that the phase separation is promoted by an increased degree of hydrogen bonding in the hard-segment domains. The changes in the TL glow due to an elongation of the SPUU films showed that the orientation, disintegration, and phase mixing of the hard-segment domains occurred in stages during elongation, and as a result, the intensity of the lower TL peak L increased considerably and the intensity of the H peak decreased accordingly in this process. The above TL results were strongly supported by the pulse NMR experiments.

Introduction

Many studies have been made of the synthesis, morphology, and properties of segmented poly(urethane ureas) (SPUU), and it is well-known that the spherulite texture organized with phase-separated domains is the most important morphological feature of the material, as revealed by small and wide X-ray diffraction,[1] small-angle light scattering,[2] small-angle neutron scattering,[3] IR spectroscopy,[4] DSC,[5] IR dichroism,[6] and NMR.[7]

Concerning NMR, particularly pulsed NMR, mention must be made of the work by Assink and Wilkes[7] on the domain structure of a series of linear and cross-linked polyurethanes. Assink and Wilkes showed that the difference between segmental mobilities of the hard and soft phases decreases with cross-linking, that the fraction of rigid segments decreases in two distinct steps as the temperature increases before cross-linking, and that the change is continuous after cross-linking. Their studies also showed that the sensitivity of the NMR method is high enough to follow changes of the segmental mobilities of different domains and phases.

In parallel with these investigations, considerable efforts have been made to gain an understanding of the phase separation, deformation mechanism, and mechanical properties of the material. Factors influencing the phase separation of SPUU include the polarity of the segments, the length of segments, the crystallinity of either segment, intra- and intersegment interactions such as hydrogen bonding, the overall composition, and the molecular weight. It is also known that phase separation can be promoted by annealing and destroyed by elongation.[8]

Over the past decades, thermoluminescence (TL) has become widely used as an approach for polymer characterization. This approach is even more sensitive than other techniques for the detection of molecular motions and structural changes in some polymers,[9] and a number of papers on the TL of polymers, both theoretical and experimental, have been published recently. The first theoretical approach to TL was made by Randal et al.[10,11] in 1939, dealing with the first-order process, and this was later developed and modified by Garlick and Gibson[12] and Pender and Fleming,[13] on the second-order process. Detailed experimental TL investigations of polymers were initiated by Nikol'skii and Buben[14] and Charlesby and Partridge[15,16] in the early 1960's, and these pioneering studies indicated a close correlation between TL and

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