SHORT COMMUNICATIONS

# Functional Monomers and Polymers CXX. Photodimerization of Pendant Thymine Bases in Thymine Containing Isopoly-L-Lysine Derivative[†]

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In a series of our studies on nucleic acid models, their specific base-base interactions have been widely investigated.[1] In this concern, the photodimerization reaction of thymine bases in the thymine grafted polymer was studied in order to estimate the intramolecular interaction of thymine bases in excited states.[2–5] The effects of the conformation of polymer main chains on the photodimerization of the grafted thymine bases were comprehensively studied using polylysine derivatives in $\alpha$-helical structure in aqueous solution. Since the photodimerization of thymine bases proceeds along the $\alpha$-helix, the thymine base in an $\alpha$-helical polymer forms a photodimer faster than that in an extended coiled one.[6] The photodimer thus formed causes fixation of the helical structure of polymer main chains.[7] In this communication, the effects of $\beta$-sheet structure on the photodimerization of grafted thymine bases are reported using isopoly-L-lysine derivatives, which can exist in $\beta$-sheet structure.

Thymine containing isopoly-L-lysine used here was prepared according to the method reported elsewhere.[8] This compound is abbreviated as isopoly(Thy-L-lys) (Scheme 1). Its thymine base content was 84 mol% from NMR spectroscopic data. Photochemical reactions were carried out with a 10-mm pathlength quartz cell filled with 4 ml of a solution at 20°C. A Philips SP lamp (500-w super high pressure mercury lamp) filtered through a combination of glass filters was used as the light source ($\lambda > 280$ nm). Light intensity was determined by potassium ferrioxalate actinometry. The quantum yield for oxalic acid decomposition was 1.24 at 313 nm.[9] The concen-
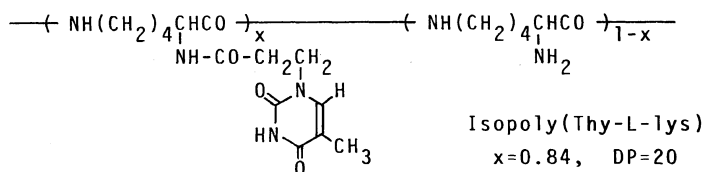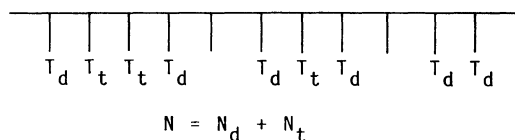


Scheme 1.

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[†] For Part CXIX. See Y. Suda, S. Fukunaga, Y. Inaki, and K. Takemoto, *J. Polym. Sci., Polym. Chem. Ed.,* in contribution.

tration of the thymine base derivatives was kept constant at $1 \times 10^{-4}$ mol l$^{-1}$ of the thymine unit in aqueous buffered solution (0.2 mol l$^{-1}$ of $Na_2CO_3$–$NaHCO_3$). In the case of the photolysis, only a cyclobutane type photodimer of the thymine base was formed intramolecularly.[6]

The quantum yields for the intramolecular photodimerization of the grafted thymine bases were 0.0033 at pH 10.4, 0.0022 at pH 10.8, and 0.0023 at pH 11.2. The quantum yield values were plotted according to eq 1, in which the effects of the sequence of the grafted thymine units and the singlet energy migration were involved[6]:

$$\Phi_{DF} = \phi_d + (gNt\phi_t - \phi_d)(Nt/N) \qquad (1)$$

where $Nt/N$ is the ratio of triad thymine units ($Nt$) to the thymine base content ($N$), which was obtained from the statistical calculation by the Monte Carlo method,[4] and $\phi_d$ and $\phi_t$ are the quantum yields for the photodimerization of the diad (Td) and triad (Tt) thymine unit, respectively, as shown in Scheme 2. The

$$N = N_d + N_t$$

**Scheme 2.**

slopes obtained, $gNt\phi_t - \phi_d$, were plotted against $Nt$ values (Figure 1). The $Nt$ value means the content of the triad thymine unit in the polymer and can be obtained from the $Nt/N$ values, that is, $Nt = Nt/N \times N$, where $N$ is the thymine base content in the polymer. In Figure 1, the data of polylysine derivatives[6] were also plotted for comparison. By extrapolation of the straight lines in Figure 1 to $Nt = 1$, quantum yield of the polymer with a 100% content of thymine base was estimated at each pH of the system (Table I).

It was reported in the previous paper that the difference in the estimated values of poly(Thy-D-lys)s or poly(Thy-L-lys)s and
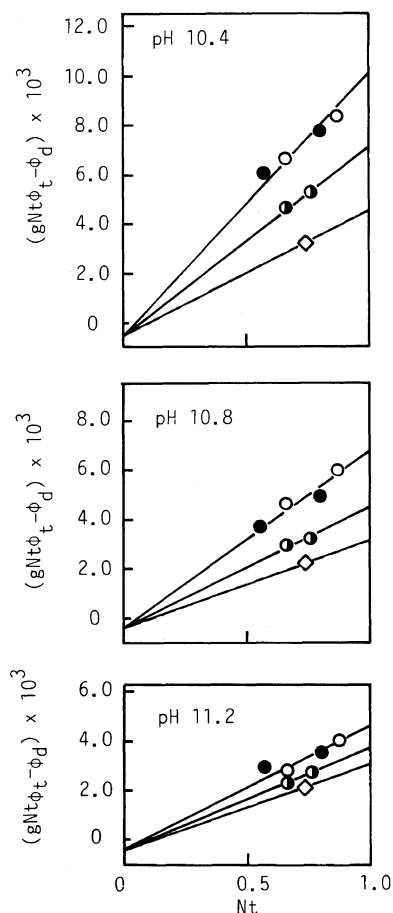
**Figure 1.** Relationships between $(gNt\phi_t - \phi_d)$ and $Nt$ values at each pH: isopoly(Thy-L-lys) ($\Diamond$); poly(Thy-DL-lys)s ($\ominus$); poly(Thy-D-lys)s ($\bullet$); poly(Thy-L-lys)s ($\bigcirc$).

**Table I.** Extrapolated quantum yields of the photodimerization of thymine bases in polymers at each pH[a]

| Compound | pH 11.2 | pH 10.8 | pH 10.4 |
|---|---|---|---|
| Isopoly(Thy-L-lys) | 0.0029 | 0.0027 | 0.0045 |
| Poly(Thy-DL-lys)s | 0.0037 | 0.0045 | 0.0071 |
| Poly(Thy-D-lys)s and Poly(Thy-L-lys)s | 0.0046 | 0.0068 | 0.0102 |

[a] From Figure 1, see the text.

poly(Thy-DL-lys)s was attributable to their conformational difference in the polymer main chains α-helical structure for poly(Thy-D-lys)s
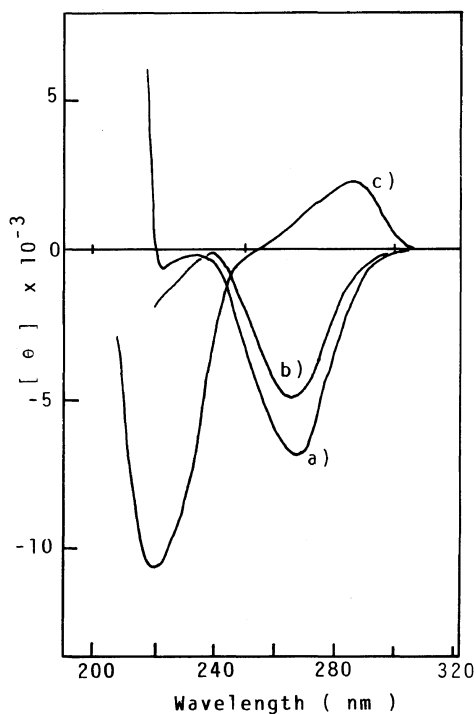
Figure 2. CD Spectra of isopoly(Thy-D-lys)-95 (ref 8) in ethyleneglycol–water mixed solvent at pH (a) 11.83, (b) 10.86, and (c) 10.31.



Figure 3. $\beta$-Sheet structure of isopoly(Thy-L-lys).

or poly(Thy-L-lys)s and an extended coiled conformation for poly(Thy-DL-lys)s.[6] The estimated value of isopoly(Thy-L-lys) in Table I was smaller than that of poly(Thy-DL-lys)s at each pH. The difference in the values increased with decreasing pH; pH = 11.2 < 10.8 < 10.4. At pH 11.2, isopoly(Thy-L-lys) is present in an extended coiled conformation because of the electrostatic repulsion among the anionized grafted thymine bases ($pK_a = 10.07$). The CD spectra of isopoly(Thy-L-lys) in ethylene glycol–water mixed solvent at higher pH (pH > 11) may support the extended coiled conformation (Figure 2).[8] Poly(Thy-DL-lys) may exist as an extended coil because of the racemic nature.[6] Therefore, almost no conformational difference between isopoly(Thy-L-lys) and poly(Thy-DL-lys)s at pH 11.2 may exist at pH 11.2. The small difference in the values at pH 11.2 (Table I) may be resulted from
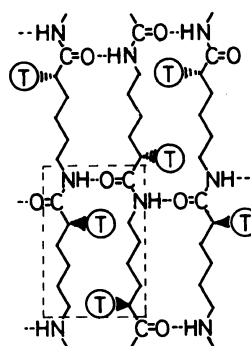
the structural characteristics of isopoly(Thy-L-lys); that is, the polymer has shorter side chains and longer distance between the side chains as compared with those of poly-lysine derivatives.[6]

In the CD spectra of isopoly(Thy-L-lys) (Figure 2), a crossover point near 260 nm and a large peak at 216 nm ($[\theta] = -10000$) were observed at pH 10.4. This suggests that isopoly(Thy-L-lys) exists in an ordered conformation, an antiparallel $\beta$-sheet conformation at lower pH in ethylene glycol–water mixed solvent. The $\beta$-sheet structure was reported for isopoly(L-lysine).[10]

Isopoly(Thy-L-lys) may exist thus in a $\beta$-sheet conformation in aqueous solution when pH of the system is low and the content of $\beta$-sheet may increase with decreasing pH of the system. Therefore, at pH 10.4, isopoly(Thy-L-lys) exists partially in an antiparallel $\beta$-sheet conformation as shown in Figure 3. In this conformation, the thymine bases of neighboring units are present on the opposite site of the $\beta$-sheet, and the nearest thymine bases are present on the neighboring chain. When these thymine bases form a photodimer, a strain may occur in the $\beta$-sheet structure, because the length of the side chain of isopoly(Thy-L-lys) is too small to form the photodimer of the grafted thymine bases with ease. This situation was supported from the CPK model for the antiparallel $\beta$-sheet structure of isopoly(Thy-L-lys). This strain may lower the quantum

yield for the photodimerization of thymine bases. The maximum conversion of the photodimer for isopoly(Thy-L-lys) was about 60% at pH 10.4, and the CD peak below 230 nm in aqueous solution at pH 10.4 decreased with an increase in the conversion of the photodimer. These facts support that the photodimerization of thymine bases in isopoly(Thy-L-lys) gives strain against the ordered $\beta$-sheet structure.

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