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PHOTODIMERIZATION OF THYMINE-CONTAINING POLYMERS: APPLICABILITY TO REVERSIBLE PHOTORESISTS

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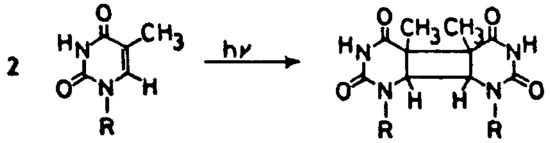
ABSTRACT

The intramolecular photodimerization of thymine bases present on the side chain of a variety of synthetic oligomers and polymers was studied in detail in various organic solvents, and particularly in the case of thymine-containing polylysines, over a wide range of pH. Effects of solvents, presence of the complementary base, and spacers on the photoreaction were examined, and the conformational changes of the polymers were discussed in relation to their functionalities. Intermolecular photodimerization was further studied, and its applicability to photoresists was shown.

INTRODUCTION

The photochemistry and photobiology of nucleic acids have received considerable attention in recent years. Exposure of the nucleic acids to UV irradiation both *in vivo* and *in vitro* lead to the formation of photodimers with the cyclobutane ring of thymine or other pyrimidine bases as shown below [1, 2]:



In this connection, detailed studies have been made both on the intramolecular photodimerization of thymine bases present on the side chains of the synthetic polymers and dimeric model compounds, and on the intermolecular photodimerization that causes crosslinking between oligomers and polymers. In the present paper, emphasis is focused on our systematic work on the photodimerization reaction of thymine-containing oligomers and polymers and their applicability to reversible photoresists.

INTRAMOLECULAR PHOTODIMERIZATION STUDY ON SYNTHETIC POLYMERS

Photodimerization of thymine bases present on the side chain of acryloyl and methacryloyl-type polymers was at first studied in DMSO, DMF, and DMSO-ethylene glycol (EG) mixtures. The preliminary work revealed that the quantum efficiencies for photodimerization and quenching with isoprene were influenced by the organic solvents used. The rate of the photodimerization was accelerated in the case of thymine-containing polymeric derivatives, and the reaction depended also on the sequence of thymine bases along the polymer chain. The self-association of thymine bases estimated from their UV spectra and intrinsic viscosity were related to the effect of the solvent [3, 4].

The photodimerization reaction was then also studied on dimeric model compound containing thymine bases, and the results were compared with those obtained for the polymers. The reaction both in the polymers and in the dimeric compound was found to be quenched by the addition of adenine derivatives. The quenching of the photodimerization of thymine bases in the presence of adenine derivatives was discussed in terms of the specific interaction between adenine and thymidine bases both in the ground state and in excited states [5].

The photodimerization of thymine-containing polymers was further studied in poly(methyl methacrylate) film. The quantum efficiency for the photodimerization of thymine bases of polyacrylate and polymethacrylate fixed in the poly(methyl methacrylate) film was measured, and the value for the film was higher than those measured in solution [6].

In relation to these studies, it is to be noted that Overberger and his coworkers have prepared poly(ethyleneimine) derivatives containing a series of nucleic acid bases and studied both intramolecular and intermolecular interactions of the polymers in detail [7-12]. We have also prepared a series of oligomer models of poly(ethyleneimine) derivatives having pendent thymine bases by the reaction of carboxyethyl derivatives of thymine with oligomeric amines using an activated ester method. In our case the hypochromicity values obtained from UV spectra and pK_a values obtained from spectrophotometric titrations depend on the chain length of the oligomers and the thymine content of the polymers [13].

EFFECT OF THE DEGREE OF POLYMERIZATION AND THE SPACERS

Another factor that may influence the photodimerization of thymine bases in the polymer structure is the degree of polymerization. The reaction was then studied by preparing a series of oligo- and poly(ethyleneimine) derivatives that contain pendent thymine bases in various amounts, in aqueous solution over a wide pH range and in DMF solution. The quantum efficiency of the pnotodimerization was found to be greater than that for the oligomers, and the value increased with increasing thymine content in the polymers and with increasing molecular weight of the oligomers (Table 1, Fig. 1). The result was discussed in terms of the effect of the nearest neighboring thymine units and singlet energy migration, particularly in the polymers [14].

The photodimerization was further studied for the thymine bases incorporated in the modified oligo- and poly(ethyleneimine), in which α-alanine or β-alanine units were inserted between the main chain and the thymine bases. The reaction was carried out in aqueous buffer solution and in DMSO solution. In this case the quantum yields for the photodimerization for the oligomers

TABLE 1. Quantum Efficiency for the Photodimerization of Thymine Derivatives in DMF Solution[a] [14]

Compound	$\Phi_{DF}{}^{\circ b}$
EI-T-3	0.0068
EI-T-5	0.0089
PEI-T-60	0.022
PEI-T-80	0.025
PEI-T-100	0.029

[a] All data were obtained for 0.1 mmol/L solutions of thymine units.
[b] Quantum efficiency.

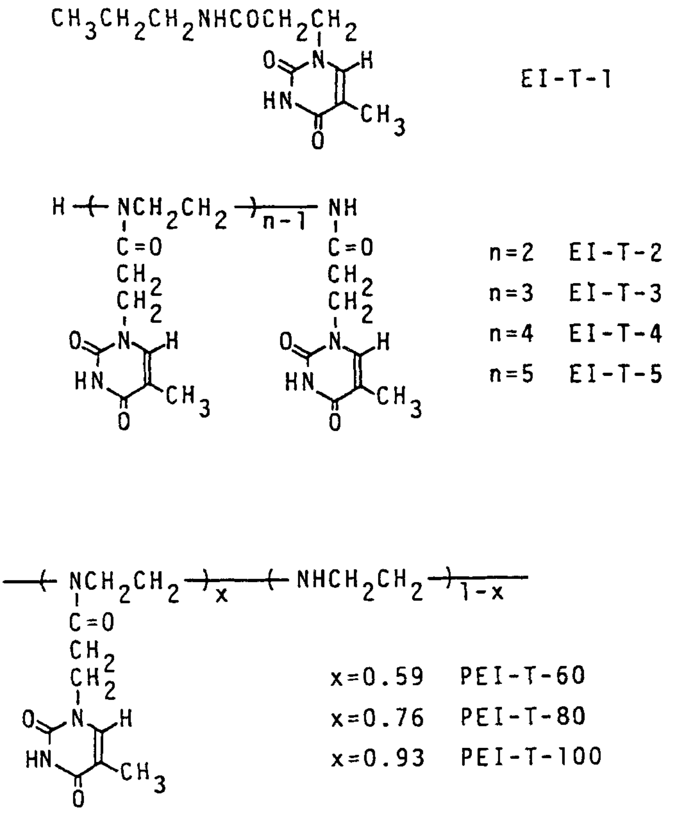
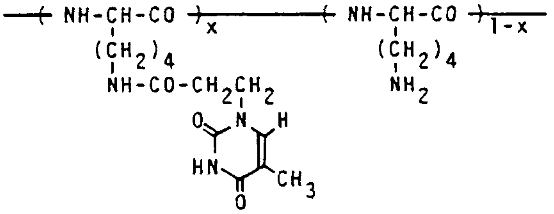


FIG. 1.

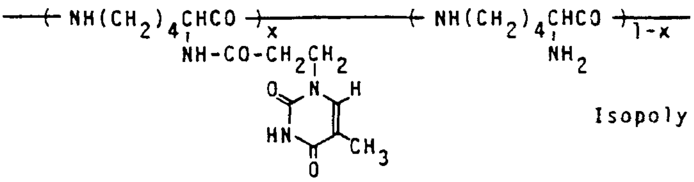
were closely related to the intramolecular interaction in the ground state, while those of the polymers were not related to the ground-state interaction. It was suggested that singlet energy migration was present in the case of the poly(ethyleneimine) derivatives. The result is also discussed in a way similar to the former reports [14, 15].

EFFECT OF THE CONFORMATIONAL CHANGES ON THE PHOTODIMERIZATION OF POLYAMINO ACIDS

The photodimerization of thymine bases incorporated in poly-*D*-, poly-*L*-, and poly-*D,L*-lysine and isopoly-*L*-lysine derivatives was next studied over a wide range of pH in aqueous buffered solutions. The polymers used here were prepared according to the earlier report [16], and their structures are shown in the following scheme:



Poly(Thy-D-lys)s .	$\overline{DP}$=500
Poly(Thy-L-lys)s	$\overline{DP}$=400
Poly(Thy-DL-lys)s	$\overline{DP}$=400



Isopoly(Thy-L-lys) $\overline{DP}$=20

From CD spectra it was found that the thymine-containing poly-*D*- and poly-*L*-lysine derivatives, that is, poly(Thy-*D*-lys) and poly(Thy-*L*-lys) can exist as α-helices at low and neutral pH. In the higher pH region, these polymers exist as extended charged coils because thymine bases present in the side chain are anionized. On the other hand, poly(Thy-*D,L*-lys) cannot exist as α-helices because of its racemic nature, but may exist as extended coils in solution over pH 10.

The quantum yield of the intramolecular photodimerization was found to be affected by the conformation of the polylysine derivatives in solution, that is, either α-helix or random coil. Detailed investigation revealed that the helical conformation is favorable for causing the photodimerization reaction.

The photodimerization of thymine containing poly-*D*- and poly-*L*-lysine derivatives caused an increase in the helix content of these polylysines because the photodimer structure of the thymine bases formed tend to force α-helical structure of the polymer main chain [17, 18]. The conformational change in the polymer chain was thoroughly studied in this respect [19].

On the other hand, thymine containing isopoly-*L*-lysine, that is, isopoly(Thy-*L*-lys), may exist in a β-sheet conformation in aqueous solution when the pH of the system is low, and the content of such a structure tends to increase with decreasing pH of the system. It was assumed that when these thymine bases form a photodimer, strain occurs in the β-sheet structure, and this strain may lower the quantum yield of the photodimerization [20].

INTERMOLECULAR PHOTODIMERIZATION STUDY AND ITS APPLICABILITY

In relation to the fundamental results obtained from intramolecular photodimerization, it can be assumed to be of interest that pyrimidine-containing polymers can possibly be applied as a new type of sensitive photoresist materials.

The photodimerization reaction of thymine bases has two characteristic features: 1) The reaction proceeds smoothly under the irradiation of deep UV light of about 270 nm wavelength, so that high resolution power could be expected; 2) the reaction is reversible in nature and can lead back to the original thymine bases by irradiating with UV light of about 250 nm wavelength.

First, a number of thymine-containing oligomers and polymers were prepared, and the reactivity for the photodimerization was studied in connection with their structure. From the reaction behavior in the film state, reversible photocrosslinking was clearly observed. The photoreaction products were analyzed for oligomers. Detailed study was made both on the photocrosslinking and polymerization type (negative type) and the photodegradation type (positive type) photoresists.

Among the compounds prepared, polyamides having thymine dimer structures showed resolution power as high as 0.5 to 0.3 μm, which corresponds to the value given by x-ray or electron beam resists. Condensation of thymine dimers with a variety of diamines also gave a new positive type of photoresist. The properties of the polymeric compounds, such as photodegradation and glass transition temperature, in relation to their main chain structure were studied.

Starting from thymine derivative **1**, the thymine photodimer **2** was derived by irradiating with UV light of about 270 nm wavelength. The compound was then converted to the activated ester form by reaction with pentachlorophenyl trichloroacetate and allowed to react further with five types of diamines (**a**–**e**) for 2 days, which afforded polyamide **4**, in which the thymine dimer structure is incorporated in the main chain. The photodegradation was carried out in the film state of these polymers by irradiating with deep UV light of about 250 nm wavelength. The photoscission of cyclobutane-type dimeric structure to revert to original thymine bases was confirmed by UV spectroscopy, and the decrease in molecular weight based on the decomposition was also ascertained by GPC. The tendency of photodecomposition of the five types of polymer was found to be about in the same order. Measurement of glass transition temperature was made for these polymers, which

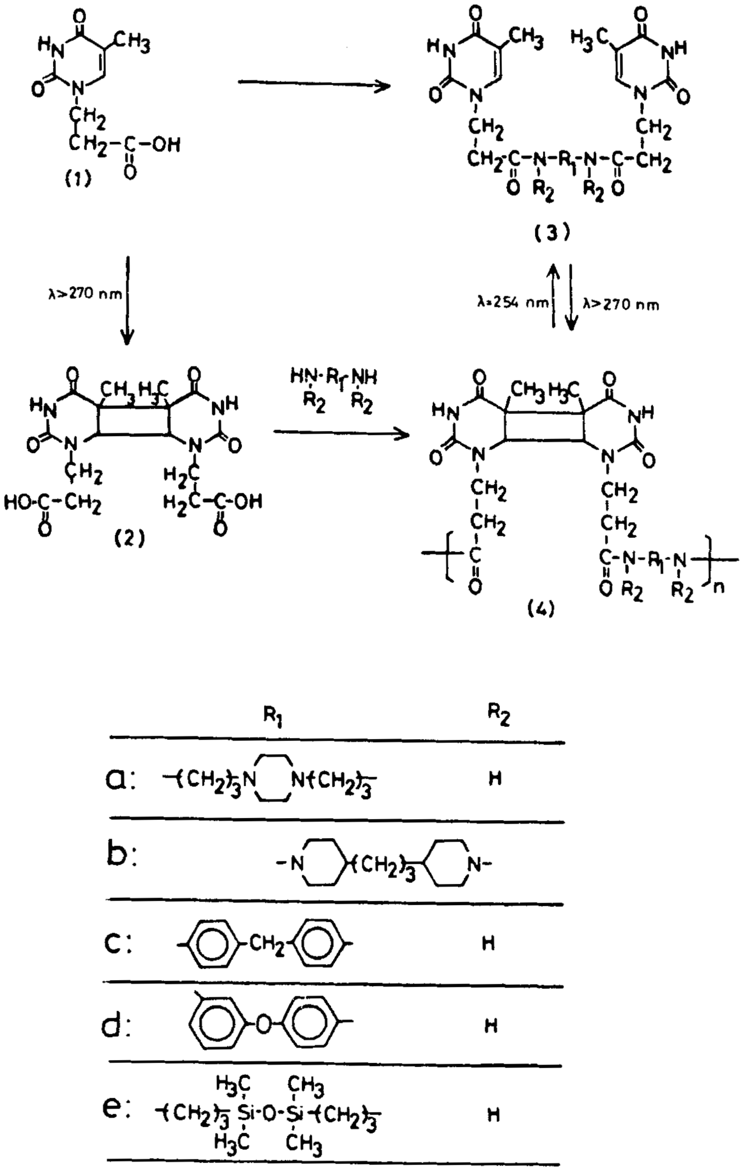


FIG. 2.

showed differences in each other, depending on their main-chain structure. For the evaluation of the resolution power in the image formation, polymer **C** showed the best result (Fig. 2).

Besides thymine base, other uracil derivatives were prepared for photodimerization study. Among them, 6-cyanouracil showed excellent photosensitivity to give its dimer in DMSO and in DMF solution. A polymethacrylate derivative containing 6-cyanouracil was also prepared, and its photochemical reaction was studied in detail. The photochemical reaction product was identified as a cyclobutane-type photodimer, and the quantum yield of the photodimerization of 6-cyanouracil derivative was greater than that of the thymine derivative. The photodimerization of the 6-cyanouracil derivative could not be quenched by the usual triplet quenchers, but it was found to be quenched by the polymeric derivative of adenine, suggesting a specific interaction [21].

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