Formation of IPN organic-inorganic polymer hybrids utilizing the photodimerization of thymine

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Summary

Formation of an interpenetrating polymer network (IPN) composed of organic polymer gel and silica gel in the form of polymer hybrids was conducted by utilizing the photodimerization of thymine bases. Thymine-modified poly(2-methyl-2-oxazoline) (POZO-T) was synthesized by the condensation reaction of partially hydrolyzed polyoxazoline and 1-(2-carboxyethyl)thymine. Organic-inorganic polymer hybrids were prepared from POZO-T and tetramethoxysilane (TMOS). Transparent and homogeneous polymer hybrids could be obtained. The photodimerization and the reverse reaction of thymine in the polymer hybrids were monitored by the UV absorption spectroscopy.

Introduction

Organic polymers having strong hydrogen bond accepting groups, e.g., amide or urethane, can be dispersed homogeneously at a molecular level in a silica gel matrix by the sol-gel reaction of alkoxysilanes (1-4). Poly(2-methyl-2-oxazoline), poly(*N*-vinylpyrrolidone), and poly(*N,N*-dimethylacrylamide) are representatives of such polymers. The hydrogen bonding interactions between the silanol groups generated by the hydrolysis of alkoxysilane (5) and the hydrogen bond accepting groups in organic polymers are crucial for the formation of single-phase nanocomposites.

In these polymer hybrids, linear organic polymers are embedded in a three-dimensional silica network. This kind of structure is classified as a semi-interpenetrating polymer network (semi-IPN) (6). On the contrary, if both organic and inorganic phases are three-dimensionally cross-linked and they are interpenetrated each other, it is a complete IPN (6). Novak et al. have obtained a kind of IPN organic-inorganic nanocomposites via the synchronous formation of both the inorganic and organic components (7,8). This was accomplished by the sol-gel reaction of tetraalkenyl orthosilicates to form an inorganic SiO_2 matrix while simultaneously eliminating unsaturated alcohols which are polymerized in-situ using free-radical or metathesis techniques. A small amount of divinyl monomers was added to the reaction mixture

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prior to polymerization in order to cross-link the organic component. We have also proposed two methodologies to prepare the IPN polymer hybrids. One is by the in-situ polymerization method (9-13). The radical copolymerization of *N,N*-dimethylacrylamide or styrene and bifunctional cross-link agents was carried out simultaneously in-situ with the sol-gel reaction of alkoxysilane. The resulting IPN polymer hybrids showed excellent solvent resistance (9,10). The other is to introduce reactive functional groups in the side chain of organic polymers (14,15). The polymer hybrids prepared from these preformed polymers possess semi-IPN structure. The cross-linking reaction of organic polymers was then conducted by the photodimerization reaction of coumarin groups (14) or the Diels-Alder reaction of maleimide and furan groups (15). The reactions employed here were reversible, that is, the reproduction of coumarin groups or retro-Diels-Alder reaction was possible.

In this paper, the photodimerization of thymine bases was utilized to achieve the reversible IPN polymer hybrids. Thymine bases are known to photodimerize upon the irradiation above 270 nm and to revert back to thymine again upon the irradiation below 270 nm (Scheme 1) (16-20). In the case of coumarin, although the photodimerization reaction of coumarin in the polymer hybrids was found to be almost quantitative, the reproduction of coumarin upon the irradiation at 254 nm was not complete. It is expected that the reversible photodimerization of thymine bases accomplishes the improved reversibility.

Thymine bases were introduced in the side chain of poly(2-methyl-2-oxazoline)s (POZO-T), and the polymer hybrids were prepared from POZO-T and tetramethoxysilane. Reversible dimerization of thymine bases in the polymer hybrids was monitored by UV absorption spectroscopy.
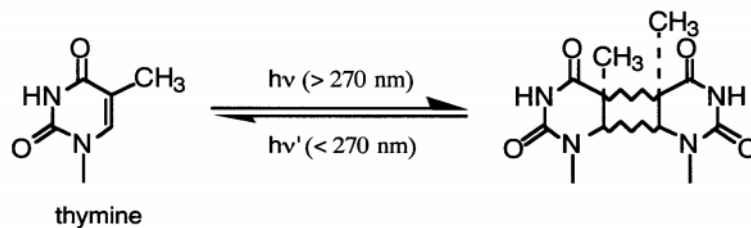
**Scheme 1.** Photocycloaddition reaction of thymine.

Experimental Section

General Procedure

^{1}H NMR spectra were recorded using a 270MHz JEOL-JNM-GX270 NMR spectrometer. Absorption spectra were obtained using a JASCO V-530 spectrophotometer. Thermogravimetric analysis (TGA) was performed using a TG/DTA6200, SEIKO Instruments, Inc., with a heating rate of 10 °C min^{-1} in air.

Materials

Methyl acrylate was distilled under reduced pressure. Methanol was dried and distilled from magnesium methoxide and stored under nitrogen atmosphere. 2-Methyl-

2-oxazoline was dried and distilled from KOH and stored under nitrogen. Methyl *p*-toluenesulfonate (MeOTs) was distilled under reduced pressure and stored under nitrogen. Acetonitrile was dried and distilled from CaH_2 and stored under nitrogen. Tetramethoxysilane (TMOS) was distilled and stored under nitrogen. Other chemicals are all used as received.
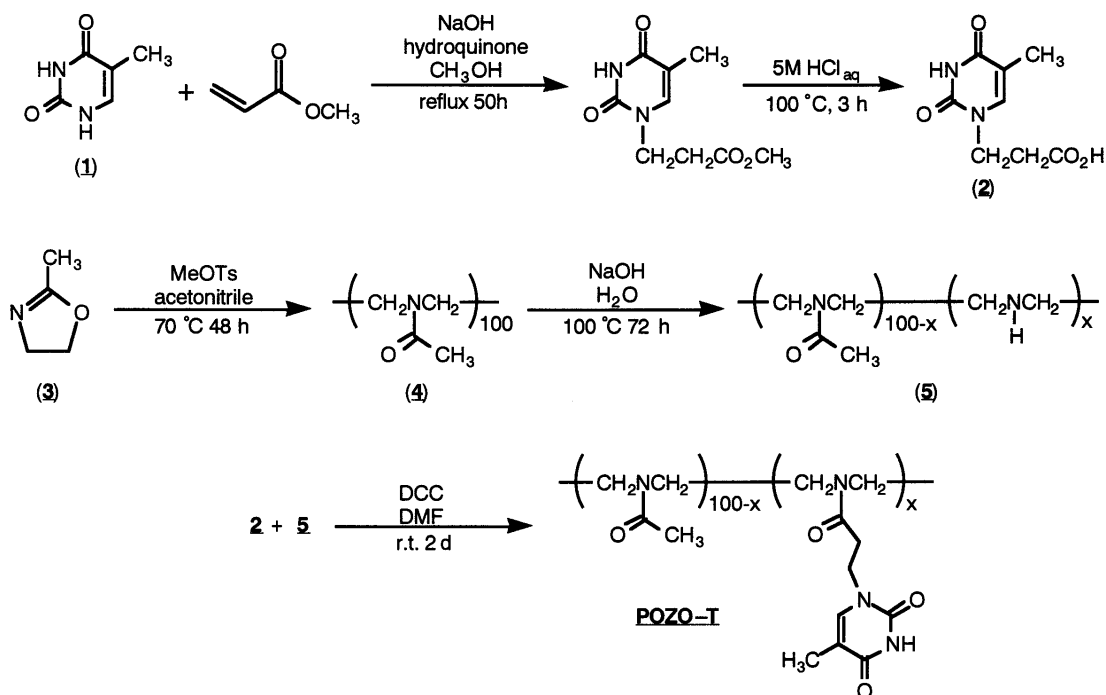
Scheme 2. Synthetic route of thymine-modified poly(2-methyl-2-oxazoline)s (POZO–T).

Synthesis of Thymine-Modified Poly(2-methyl-2-oxazoline)s (POZO-T)

      The synthetic route of POZO-T is shown in Scheme 2. 1-(2-Carboxyethyl)thymine (**2**) was prepared according to the literature (20). Poly(2-methyl-2-oxazoline) (**4**) was prepared by the ring-opening polymerization of 2-methyl-2-oxazoline (**3**) initiated by MeOTs (21). The feed ratio of monomer to initiator was set to be 100 (M_n = 8,500). Partial hydrolysis of polymer **4** in alkaline condition gives secondary amine unit in the main chain (**5**) (22). The degree of hydrolysis was calculated from ^{1}H NMR data to be 11.0 mol%. POZO-T was obtained by the condensation reaction of **2** and **5** in the presence of dicyclohexylcarbodiimide (DCC) as an activating agent. The obtained POZO-T was purified by reprecipitation from methanol into methyl *t*-butyl ether for 2 times. The UV absorption maximum was observed at 270 nm in methanol solution. Thymine derivative **2** was found to absorb at the same wavelength. The ^{1}H NMR spectrum of POZO-T is shown in Figure 1. The assignment of each peak is illustrated in the figure.

Preparation of Polymer Hybrids from POZO-T

      POZO-T and TMOS were dissolved in methanol and aqueous hydrochloric acid

(4 equivalents to TMOS) was added. The resulting mixture was stirred in a sealed bottle for 1 h before allowing the solvent to evaporate in air. After gelation and removal of the solvent, the polymer hybrids were obtained as glassy solids. Polymer contents were determined from TGA analysis. Polymer hybrid films for absorption measurement were prepared on quartz substrates by casting the reaction mixture.

Photo-Dimerization and Photo-Cleavage Reactions

Photo-dimerization of thymine groups was induced by the irradiation of light from 175W Xe lamp filtered with a Toshiba UV-D33S glass filter. Photo-cleavage reaction was carried out by the irradiation at 254 nm by a 10W low-pressure mercury lamp. Both reactions were performed at room temperature, and followed by the absorption spectroscopy.
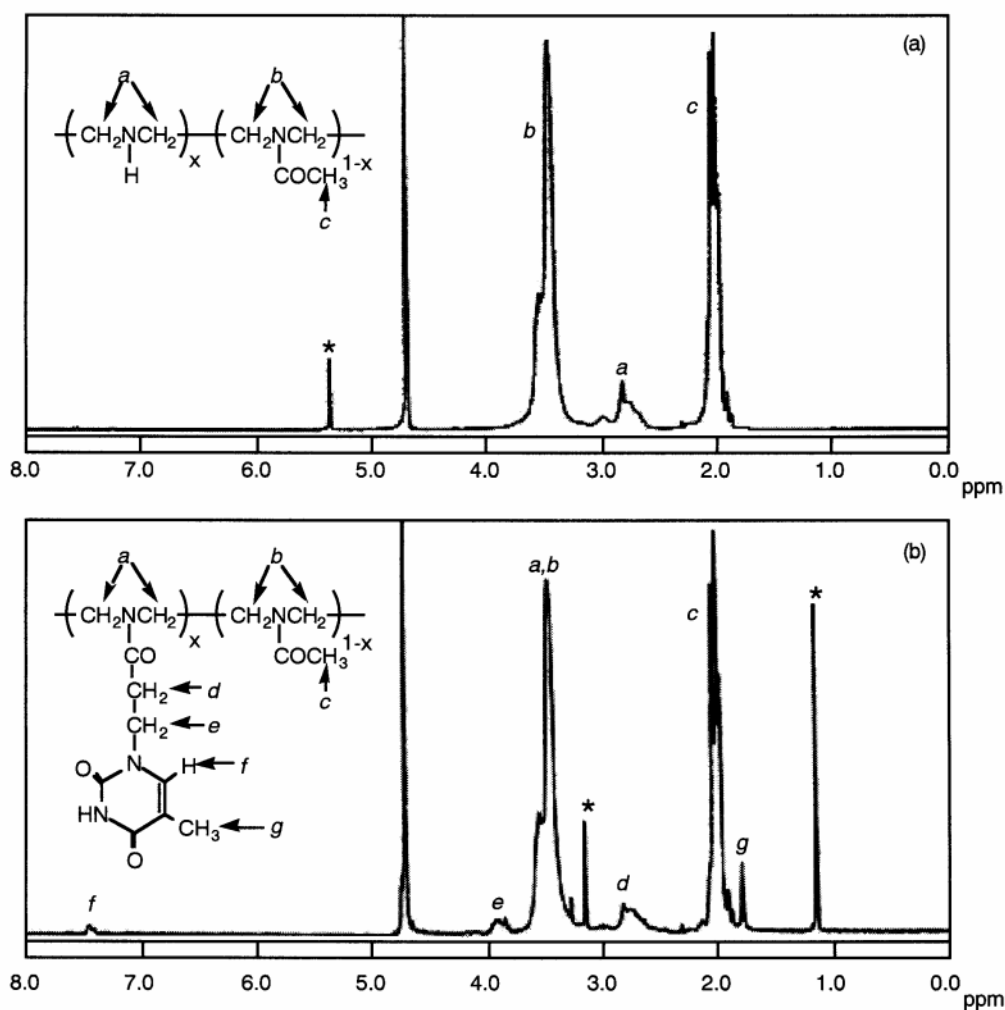
Figure 1. ^{1}H NMR spectra of (a) partially hydrolyzed poly(2-methyl-2-oxazoline) and (b) corresponding POZO–T (solvent D_2O). * depicts solvent contaminate.

Results and Discussion

Thymine-modified poly(2-methyl-2-oxazoline)s (POZO-T) were successfully synthesized by the condensation reaction of partially hydrolyzed poly(2-methyl-2-oxazoline) (**5**) and 1-(2-carboxyethyl)thymine (**2**) with DCC as an activating agent. The obtained polymer was found to have an absorption at 270 nm in methanol solution, indicating the introduction of thymine moieties on the side chain of the polymer. The quantitative evaluation of the degree of introduction was carried out by ^{1}H NMR spectroscopy. Figure 1 shows the ^{1}H NMR spectra of the partially hydrolyzed polyoxazoline (a) and the corresponding POZO-T (b). From the integral ratio of methylene protons adjacent to *N*-acetyl amide and secondary amine in Figure 1(a), the degree of hydrolysis was estimated to be 11.0 mol%. In Figure 1(b), new peaks corresponding to thymine moiety were observed (peaks *d*, *e*, *f*, *g*) and methylene protons adjacent to secondary amine group decreased. The degree of introduction of thymine groups calculated from Figure 1(b) was 10.6 mol%. The reaction efficiency of secondary amine on the polymer (**4**) and thus the degree of introduction of thymine groups was found to be almost quantitative from ^{1}H NMR data.

Polymer hybrids were prepared by the acid-catalyzed sol-gel reaction of TMOS in the presence of POZO-T. The results are summarized in Table 1. It was found that higher homogeneity was achieved by employing higher acid concentration (compare runs 2 and 3) and smaller amount of solvent (compare runs 4 and 5). Transparent polymer hybrids with polymer content as much as 67 wt % could be obtained by choosing appropriate conditions. Thymine moiety has rather poor miscibility in the reaction mixture and tends to aggregate. The tendency of aggregation of thymine moiety could be overcome by controlling the acid concentration and the amount of solvent. Both high acid concentration and small amount of solvent cause acceleration of the sol-gel reaction and hence faster gelation. This allows the better dispersion of thymine. The same trend was observed in the preparation of polymer hybrids from coumarin-modified polyoxazolines (14).

Table 1. Preparation of polymer hybrids from POZO–T.

run	POZO–T (mg)	TMOS (mg)	CH$_3$OH (mL)	HCl$_{aq}$^{a}	appearance	polymer content (wt%) calcd.	obsd.^{b}
1	50	1,000	5	0.1 M	transparent	-	-
2	50	500	5	0.1 M	translucent	-	-
3	50	500	5	1 M	transparent	20.0	26.5
4	100	500	10	1 M	translucent	-	-
5	100	500	1	1 M	transparent	33.3	39.5
6	100	250	10	1 M	turbid	-	-
7	100	250	1	1 M	transparent	50.0	50.2
8	100	125	1	1 M	transparent	66.7	67.0

^{a} Concentration of aqueous hydrochloric acid. ^{b} Polymer contents in the polymer hybrids were calcuated from TGA by charring the sample up to 900 °C in air.

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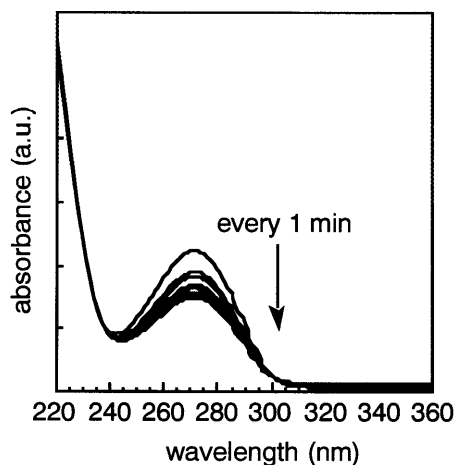
Figure 2. The change of absorption during irradiation of the polymer hybrid (run 5 in Table 1. POZO–T/silica=1/1).

Table 2. Reaction efficiency of photocycloaddition.

sample	efficiency (%)
run 3 (POZO–T:silica=1:4) hybrid	24.0
run 5 (POZO–T:silica=1:2) hybrid	36.4
run 7 (POZO–T:silica=1:1) hybrid	79.9
run 8 (POZO–T:silica=2:1) hybrid	80.8
POZO–T film	94.0
POZO–T:polyoxazoline (1:1) blend	86.8

Photoirradiation on the polymer hybrids was then carried out to induce the photodimerization of thymine. The films of polymer hybrids were prepared on quartz substrates. The changes of UV absorption during the photoirradiation were monitored. The absorption at 270 nm declined gradually, indicating the progress of photocycloaddition of thymine. A typical change of absorption spectra during the irradiation is shown in Figure 2. The reaction was saturated within 20 minutes. The photocycloaddition efficiencies estimated from the UV absorption spectra are listed in Table 2. Apparently the efficiencies in the polymer hybrids decreased with higher silica content. In the previous study of the polymer hybrids where coumarin-modified polyoxazolines were used instead of POZO-T (14), the photodimerization of coumarin took place quantitatively, even in the polymer hybrid whose polymer content was lower than 10 wt %. The lower photodimerization efficiency in the present POZO-T hybrid suggests that the less number of thymine groups are close enough to photodimerize. It is considered that this low efficiency is due to the hydrophilic nature of thymine group compared to coumarin group. It was found, however, that quite high efficiency around 80% was observed in

the polymer hybrids whose polymer content was 50% (run 7). This dimerization efficiency is high enough to improve the solvent resistance of the polymer hybrid.

To clarify the reason of the decline of the photodimerization efficiency in the polymer hybrids, a film of polymer blend composed of POZO-T and poly(2-methyl-2-oxazoline) (**4**) (1/1, w/w) was prepared. The efficiency of the photodimerization in the blend film was found to be 87%, which is lower than that of pure POZO-T film but higher than that of the polymer hybrid which has similar POZO-T content (run 7). This result indicates that the decline of the photodimerization efficiency in the polymer hybrids can partly be explained from a decrease of thymine concentration in the polymer hybrids. Additionally, the other reasons such as the rigidity or the acidity of the silica matrix should be considered.

Investigation on the photocleavage of thymine dimer was carried out by the irradiation at 254 nm from a low-pressure mercury lamp. It was found that ca. 17% of thymine dimer was converted to thymine monomer upon the irradiation. The progress of the photocleavage was, however, hardly observed in the polymer hybrids.

Conclusions

IPN polymer hybrids were prepared from thymine-modified polyoxazoline (**2**). Transparent and homogeneous polymer hybrids could be obtained by choosing the concentration of acid catalyst and the amount of solvent. The progress of the photodimerization of thymine in the polymer hybrids was confirmed by UV absorption spectroscopy. Unfortunately, the reverse reaction hardly took place upon the irradiation from a low-pressure mercury lamp at 254 nm.

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