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Photochromic organic-inorganic polymer hybrids from spiropyran-modified poly(*N*,*N*-dimethylacrylamide)

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Summary

Photochromic organic-inorganic polymer hybrids were prepared by the sol-gel reaction of tetramethoxysilane (TMOS) in the presence of spiropyran-modified poly(*N*,*N*-dimethylacrylamide) **3**. The obtained polymer hybrids were characterized by thermogravimetric analysis (TGA) and FT-IR, and photochromic behavior was followed by electronic absorption spectroscopy. Upon an irradiation of ultraviolet light, an absorption around 557 nm appeared in the visible region and the color of the hybrid turned to be violet. The effect of silica gel on the isomerization behavior seemed to be relatively small.

Introduction

Preparation of molecular composites of organic materials and inorganic ones has attracted much attentions in the field of materials science (1-5). Sol-gel technique of alkoxysilanes is widely employed to form silica gel at low temperature in the presence of organic compounds (6). The sol-gel reaction comprises the hydrolysis of Si-OR groups to Si-OH (silanol) groups and the condensation of the silanol groups into -Si-O-Si- linkages. Three-dimensional silica gel is constructed as a result.

We have investigated organic-inorganic polymer hybrids, where organic polymers were dispersed at the molecular level in a silica gel matrix (1,7). They are prepared by the sol-gel reaction of alkoxysilanes in the presence of organic polymers such as poly(2-methyl-2-oxazoline), poly (*N*-vinylpyrrolidone), and poly(*N*,*N*-dimethylacrylamide). It was found that the hydrogen bonding interactions between the silanol groups on the silica gel and the amide groups of the organic polymers play an critical role to achieve the molecular-level homogeneity.

On the other hand, photochromic materials have been investigated intensively so far from both scientific and applicational viewpoints (8-13). Spiropyran is one of the most well-known photochromic chromophore that photoisomerizes from spiropyran form to merocyanine structure by the irradiation of ultraviolet light (14). The reverse reaction

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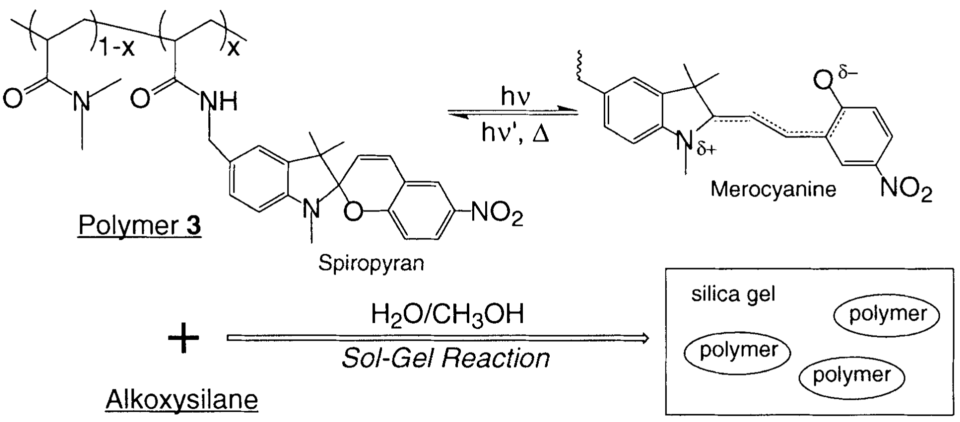
proceeds thermally or by visible light irradiation. The merocyanine is colored while the spiropyran is colorless. The photochromic band of merocyanine in the visible region is known to be solvatochromic, that is, the absorption shifts depending on the polarity of the solvent and the color changes.

Isomerization behavior of spiropyran in sol-gel matrices has been found to be somewhat complicated compared with that in solutions or in organic polymer films (15 - 19). The formation of the strong hydrogen bondings between $O^{\delta-}$ of merocyanine and the silanol groups of silica gels stabilizes the colored merocyanine form, and the reverse photochromism has been observed. It is of interest to investigate the isomerization behavior of spiropyran in the organic-inorganic polymer hybrids since they possess a unique morphology composed of organic polymer and silica gel. Little has been known about the microenvironment surrounding the dye in the polymer hybrids. As mentioned above, the absorption of the photochromic band of the chromophore is solvatochromic. Microscopic information around the chromophore can be estimated from this phenomena.

Here we demonstrate the synthesis and characterization of photochromic polymer hybrids from spiropyran-modified poly(*N*,*N*-dimethylacrylamide) **3** (Scheme 1).



Scheme 1. Preparation of Photochromic Polymer Hybrids via Sol-Gel Reaction

Experimental Section

Materials

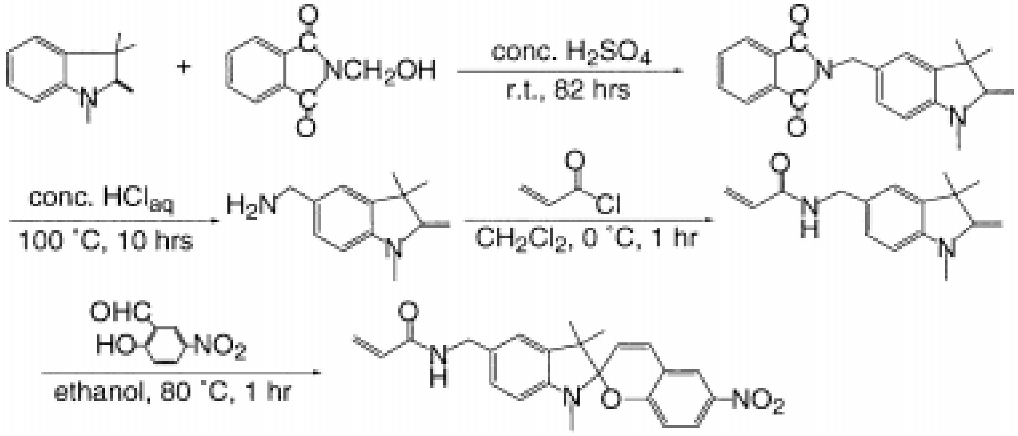
1,3,3-Trimethyl-2-methyleneindoline was distilled under reduced pressure. *N*-Hydroxymethylphthalimide and 5-nitrosalicylaldehyde were used as received. Acryloyl chloride and *N*,*N*-dimethylacrylamide were distilled under reduced pressure and stored under nitrogen atmosphere in a refrigerator. Dichloromethane, chloroform, and triethylamine were dried and distilled from CaH_2. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol below 30 °C. Tetramethoxysilane (TMOS) was distilled and stored under nitrogen atmosphere. Methanol was dried and distilled from magnesium methoxide and stored under nitrogen atmosphere.

General

^{1}H-NMR spectra were recorded on a 270 MHz JEOL-JNM-GX270 NMR spectrometer. IR spectra were obtained on a Perkin Elmer 1600 infrared spectrometer. Electronic absorption spectra were obtained on a JASCO V-530 spectrophotometer. Differential scanning calorimetry (DSC) thermograms were recorded with a DSC200, SEIKO Instruments Inc., with a heating rate of 10 °C min^{-1} under nitrogen atmosphere. Thermogravimetric analyses (TGA) were carried out on a TG/DTA6200, SEIKO Instruments, Inc., with a heating rate of 10 °C min^{-1} under air. Gel permeation chromatographic analysis (GPC) was conducted with a Tosoh TSKgel α-3000 column by using DMSO + LiCl (10mM) as an eluent at 50 °C after calibration with standard poly(oxyethylene).

Monomer Synthesis

Spiropyran monomer **1** was synthesized by following the route depicted in Scheme 2 according to a procedure described by Labsky et al. (20).



spiropyran monomer **1**

Scheme 2. Route to the Synthesis of Spiropyran Monomer **1**

Polymer Synthesis

Copolymer of *N,N*-dimethylacrylamide (**2**) and spiropyran monomer **1** was prepared by radical copolymerization initiated by AIBN. 2.4 g of **2** (24 mmol), 0.10 g of **1** (0.25 mmol), and 0.20 g of AIBN (1.2 mmol) were dissolved in 20 ml of chloroform under nitrogen atmosphere. The solution was heated at 60 °C for 24 h, and polymer was isolated by reprecipitation into hexane. The resulting polymer **3** was further purified by reprecipitation from chloroform into hexane for two times, and freeze-dried with benzene. Yield was 2.5 g. The structure was confirmed from ^{1}H-NMR, IR, and absorption spectra. The molecular weight was estimated by GPC to be M_w = 32,500, M_n = 8,600, M_w/M_n = 3.79. The spiropyran-content was calculated from the absorption spectrum to be 1.1 mol%, which corresponded well with the feed ratio of **1** and **2**.

Preparation of Polymer Hybrids from Polymer 3

Polymer **3** and TMOS were dissolved in methanol and water (4 equivalents to TMOS) was added. The resulting mixture was stirred at room temperature for 1 h in a sealed bottle. Then the mixture was placed in a polypropylene mold covered with a paper towel and left in air at room temperature. After removal of the solvent by evaporation, polymer hybrids were obtained as glassy solids. Polymer hybrid films for absorption measurement were prepared by casting the reaction mixture onto glass slides.

Measurements of Photochromism

A sample was irradiated with ultraviolet light at room temperature to induce the photoisomerization of spiropyran chromophores. 300W Xe lamp filtered with a Toshiba UV-D33S glass filter was employed as a source of ultraviolet light. The reaction was followed by absorption spectra.

Results and discussion

Spiropyran-modified poly(*N*,*N*-dimethylacrylamide) **3** was successfully synthesized by the radical copolymerization of *N*,*N*-dimethylacrylamide and spiropyran monomer **2**. Figure 1 shows the absorption spectra of polymer **3** in methanol before and after the irradiation of ultraviolet light. A new absorption band appeared after irradiation, indicating that the spiropyran chromophore was actually incorporated into polymer. This band showed solvatochromism, namely, the absorption maximum wavelength was 489 nm in water, 531 nm in methanol, and 566 nm in DMF. As the merocyanine form of the chromophore possesses high intrinsic polarity, the visible absorption maximum shifts shorter wavelengths in more polar solvents.

Photochromic polymer hybrids were then prepared via the sol-gel reaction of TMOS in the presence of polymer **3**. Acid catalyst was not employed for the sol-gel reaction since protonation on nitrogen atom of indoline ring of the chromophore changes the photochromic behavior. Thus polymer **3** and TMOS were dissolved in methanol, water of 4 equivalents to TMOS was added, stirred for 1 h in a sealed bottle to make the sol-gel reaction of TMOS proceeds to some degree, and the resulting mixture was left in air to dryness. The results of the preparation of polymer hybrids are summarized in Table I. The obtained polymer hybrids were optically transparent and homogeneous in all the examined weight ratios of polymer **3** to TMOS. Polymer contents observed by TGA were found to be somewhat larger than expected. Sol-gel reaction of TMOS without acid catalyst might be incomplete, though the weight ratio of polymer to silica

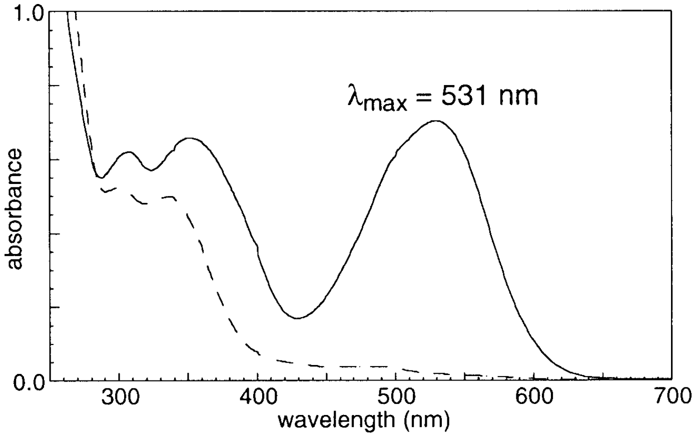


Figure 1. Absorption spectra of polymer **3** in methanol before (broken line) and after (solid line) UV irradiation.

Table 1. Polymer Hybrids from Polymer 3 and TMOS.[a]

run	polymer **3** (mg)	TMOS (mg)	appearance	polymer content (wt%)		T_{10}[c] (°C)	ν_{co}[d] (cm^{-1})
				calcd.	obsd.[b]		
1	200	250	transparent	66.9	72.1	335	1629
2	200	500	transparent	50.3	64.0	360	1632
3	200	1,000	transparent	33.6	43.6	372	1631
polymer **3**						356	1639

[a] 2 ml of methanol was used as a solvent. 4 equivalents of water (to TMOS) was added to the mixture. [b] Total weight loss by heating up to 1000 °C in air, observed by TGA. [c] 10 wt% weight loss temperature observed by TGA. [d] Wavenumbers of amide carbonyl stretching band observed by FT-IR.

gel could be varied widely. And the polymer hybrids with higher silica weight ratio showed higher thermal stability. The hydrogen bonding interactions between polymer and silica gel were confirmed by FT-IR. The stretching band of amide carbonyl group shifts to lower wavenumber region by hydrogen bonding interaction with silanol groups on silica gel. Polymer **3** has its original carbonyl peak at 1639 cm^{-1} and it shifts to about 1630 cm^{-1} by the formation of hydrogen bonding in the polymer hybrids. In the previous study, the degree of the shift of carbonyl vibration for poly(*N*,*N*-dimethylacrylamide)/TMOS polymer hybrids was found to be 18 cm^{-1} (1). In the present system, the hydrogen bonding interactions between polymer and silica gel seem to be weaker though the main chain structure is same. It might be the result from the fact that acid catalyst was not employed in this study.

Photochromic behavior of chromophore in the polymer hybrids was then examined. When spiropyran chromophore is doped in or adsorbed on silica gel, the color turns red (15-19). It can be attributed to the open merocyanine form of the chromophore. Moreover, this red color is thermally stable and disappears upon the irradiation of ultraviolet light. This reverse photochromism is considered to be the result from the formation of strong hydrogen bondings between merocyanine chromophores and silanols. All the polymer hybrids prepared were, however, found to be colorless. And the color turned violet upon

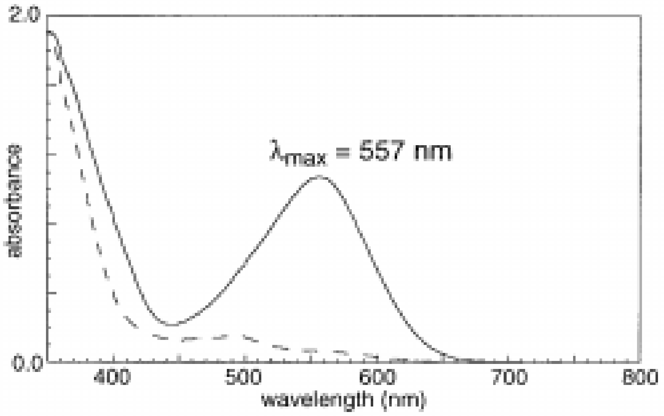


Figure 2. Absorption spectra of polymer hybrid (run 2) before (broken line) and after (solid line) UV irradiation.

the irradiation of the ultraviolet light. Absorption spectra of polymer hybrid before and after the irradiation of ultraviolet light are shown in Figure 2. The absorption maximum wavelengths were found to be 557 nm for the polymer hybrids (runs 1-3), and that for the polymer **3** itself in the film state was 559 nm. The color faded slowly when the sample was kept in the dark at room temperature, and the coloration-decoloration processes could be repeated. Therefore spiropyran chromophores in the polymer hybrids isomerize normally in spite of the presence of silica gels. From these results, the spiropyran chromophores in the polymer hybrids seem to be surrounded by organic polymer preferably, and the effect of silica gel on the photochromic behavior of the chromophore is relatively small. In our previous report, the solvatochromic chromophore was found to undergo the polymer-rich environment in the polymer hybrids where the domain size of the organic polymer was < 4 nm (21). In the current system, the same phenomena seem to occur. Further investigation on the isomerization actions, especially kinetics, will allow us better understandings on the correlation between the microenvironment around the chromophore and the photochromic behavior.

Conclusion

Poly(*N*,*N*-dimethylacrylamide) having spiropyran chromophores on the side chain (**3**) was synthesized by the radical copolymerization of *N*,*N*-dimethylacrylamide and spiropyran monomer **2**. Polymer **3** showed photochromic behavior upon the irradiation of the ultraviolet light. Photochromic organic-inorganic polymer hybrids were prepared by utilizing the sol-gel reaction of TMOS in the presence of polymer **3**. No acid catalyst was employed to avoid the protonation on the spiropyran chromophore. Transparent and homogeneous polymer hybrids could be obtained in all the weight ratios of polymer to silicate. The resulting polymer hybrids were characterized by TGA, FT-IR, and absorption spectra. Spiropyran chromophores in the polymer hybrids photoisomerize normally in spite of the existence of the silica gel. This might indicate the preferable solvation of the chromophore by organic polymer than by silica gel.

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