Communications to the Editor

Synthesis of Photoresponsive Organic−Inorganic Polymer Hybrids from Azobenzene-Modified Poly(2-methyl-2-oxazoline)

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Preparation of composite materials from organic and inorganic compounds has attracted much attention as they might show improved properties superior to those of the parent materials.[1−3] The sol−gel reaction of alkoxysilanes should be useful to prepare organic−inorganic hybrid materials. In the sol−gel process, a three-dimensional silica network is formed at relatively low temperature by hydrolysis and condensation reactions of alkoxysilanes.[4] Various kinds of organic compounds including polymers have been incorporated in the reaction mixture of the sol−gel reaction to obtain the organic−inorganic hybrid materials. Doping of low-molecular-weight organic molecules in silica matrix seems to have two objectives in general. One is to utilize them in the field of photo- or electrochemical applications such as optical recording media, chemical sensors, solid-state dye lasers, and nonlinear optics.[5−15] Another is to obtain information on the microscopic environment in the matrix and to clarify the interaction between the matrix and the doped molecules.[5,6,16−19] We have proposed organic−inorganic polymer hybrids, in which organic polymers and silica gel are dispersed at the molecular level, by utilizing the sol−gel reactions of alkoxysilanes in the presence of organic polymers. In particular, organic polymers containing hydrogen-bond accepting groups such as amide groups in their repeating units gave transparent and homogeneous polymer hybrids.[20,21]

As organic−inorganic polymer hybrids are transparent in the visible and near-ultraviolet region, it is interesting to investigate the photochemical/photophysical reaction in the polymer hybrids. Here we present an example of photochromic organic−inorganic polymer hybrids by using azobenzene-modified poly(2-methyl-2-oxazoline) as an organic polymer. It is well-known that the azobenzene chromophores photoisomerize from trans form to cis one by an irradiation of ultraviolet light, and the reverse process proceeds both thermally or by visible light irradiation.[22,23] Many studies have dealt with azobenzene chromophores incorporated into the backbone of polymer chain or into the pending groups, or doped in polymer matrices.[18,19,24−28] They reveal that the isomerization of azobenzene moieties can affect the physical and chemical properties of the polymers, and on the other hand, the isomerization behavior of azobenzene chromophores is affected by the polymer matrices.

Poly(2-methyl-2-oxazoline) (POZO) was prepared by the ring-opening polymerization of 2-methyl-2-oxazoline initiated by methyl tosylate. POZO was refluxed with an aqueous NaOH solution to give partially hydrolyzed POZO (H−POZO). Degree of hydrolysis could be controlled by the molar ratio of the amide groups to NaOH. Poly(2-methyl-2-oxazoline)s with various azobenzene contents (POZO-A) were prepared by the reaction of H−POZO with *p*-phenylazobenzoyl chloride in acetonitrile. Triethylamine or DBU was used to trap generated HCl. The results of the preparation of POZO-A are summarized in Table 1. It is confirmed that almost quantitative introduction of azobenzene moieties as pending groups into POZO could be achieved by this method. *N*,*N*-Diethyl-*p*-phenylazobenzamide was prepared by the condensation reaction of *p*-phenylazobenzoyl chloride with diethylamine and was used as a model compound for the isomerization reaction of azobenzene moieties.

A typical procedure for the preparation of organic−inorganic polymer hybrids is as follows. POZO-A and alkoxysilanes were dissolved into methanol, and aqueous HCl was added as a catalyst for the sol−gel reaction. Then the mixture was placed in air at room temperature. The results are summarized in Table 2. Transparent and homogeneous polymer hybrids were obtained when methyltrimethoxysilane (MeTMOS) and tetramethoxysilane (TMOS) were used as the alkoxysilanes. The feed ratio of the polymer to silicate (w/w) could be varied between $^1/_5$ and 2 without any influence in the homogeneity (runs 5−8). Differences of molecular weight and the content of azobenzene moieties up to 16 mol % also seem to have little effect on the homogeneity of polymer hybrids. According to the previous studies, it is known that stretching bands of amide carbonyl groups ($\nu_{C=O}$) are shifted to a lower wavenumber region in the polymer hybrid due to the hydrogen-bond formation between carbonyl groups and residual silanol groups. In POZO-A/MeTMOS polymer hybrid, $\nu_{C=O}$ shifted to lower wavenumbers region about 8 cm^{-1} compared with that of POZO-A. This result indicates that the hydrogen bond is formed in the same manner in the POZO-A/MeTMOS system, which is considered to be responsible for the molecular level homogeneity. In the cases where MeTMOS was used, the obtained polymer hybrids had no cracks after the complete removal of the solvent and they were flexible to some extent after completion of the condensation reaction of alkoxysilane, whereas in the case of TMOS, only cracked polymer hybrids were obtained. Therefore POZO-A/MeTMOS was used for further investigation as the film can be formed easily on a quartz substrate. On the other hand, ethyltrimethoxysilane (EtTMOS), isobutyltrimethoxysilane (*i*-BuTMOS) and phenyltrimethoxysilane (PhTMOS) gave only heterogeneous polymer hy-

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Table 1. Preparation of Azobenzene-Modified Poly(2-methyl-2-oxazoline) (POZO-A)

	POZO	H-POZO	POZO-A		
run	deg of polymerization[a]	deg of hydrolysis[a]	yield (%)	deg of modification UV[b]	deg of modification ^{1}H-NMR[c]
1	32	2.8	95	2.0	2.0
2	74	1.3	85	1.3	1.3
3	~100	1.7	85	1.2	1.2
4	32	19.2	~100	9.4	16.0
5	45	9.6	98	6.3	9.4

[a] Determined from ^{1}H-NMR spectra. [b] Calculated from UV spectra at λ_{max} = 328 nm (ϵ_{max} = 2.38 × 10^4). [c] Calculated from ^{1}H-NMR spectra (acetyl protons vs ring protons).

Table 2. Preparation of POZO-A/Alkoxysilane Polymer Hybrids[a]

run	POZO-A[b]	alkoxy-silane	ratio[c]	appearance	
1	1 (2.0)	MeTMOS	1/5	transparent, homogeneous	no cracks
2	2 (1.3)	MeTMOS	1/5	transparent, homogeneous	no cracks
3	3 (1.2)	MeTMOS	1/5	transparent, homogeneous	no cracks
4	4 (16.0)	MeTMOS	1/5	transparent, homogeneous	no cracks
5	5 (9.4)	MeTMOS	1/5	transparent, homogeneous	no cracks
6	5 (9.4)	MeTMOS	1/2	transparent, homogeneous	no cracks
7	5 (9.4)	MeTMOS	1/1	transparent, homogeneous	no cracks
8	5 (9.4)	MeTMOS	2/1	transparent, homogeneous	no cracks
9	3 (1.2)	TMOS	1/5	transparent, homogeneous	cracks
10	3 (1.2)	EtTMOS	1/5	turbid	
11	3 (1.2)	*i*-BuTMOS	1/5	turbid	
12	3 (1.2)	PhTMOS	1/5	turbid, phase separated	

[a] Methanol was used as a solvent and a drop of 0.1 N HCl_{aq} was added as a catalyst for the sol–gel reaction. [b] Degree of modification is shown in parentheses (calculated from ^{1}H-NMR spectra). [c] POZO-A/alkoxysilane (w/w).

brids under the same conditions.

The isomerization behavior of azobenzene moieties in solution was followed by absorption and ^{1}H-NMR spectra. The absorption maximum of the trans form was observed at 328 nm (ϵ_{max} = 2.38 × 10^4 M^{-1} cm^{-1}). This solution was irradiated with ultraviolet light at the wavelength between 300 and 400 nm by using a high-pressure Hg lamp. The photoisomerization of azobenzene moieties from trans form to cis one proceeded and reached to a photostationary state within 20 min. This could be indicated by a decrease of the absorption at 328 nm and an increase at 435 nm. ^{1}H-NMR spectra can also be employed to follow the reaction. The peaks for aromatic protons of the trans form were observed between 7.8 and 8.3 ppm. After the irradiation of ultraviolet light, new peaks corresponding to the cis form appeared between 7.1 and 7.7 ppm. From the integral of these protons, the ratio of trans and cis isomers in the photostationary state could be calculated to be 10:90. In the case of POZO-A in DMSO solution, the absorption maximum was at the same wavelength with the model compound, and the trans-to-cis ratio in the photostationary state turned out to be 15:85.

The photoisomerization reaction also took place in POZO-A film and POZO-A/MeTMOS hybrid. Figure 1 shows absorption spectra of POZO-A/MeTMOS hybrid. It was reported that the hydrogen-bond formation between azo groups and silanol groups was observed in the hybrid system consisting of monomeric azobenzene derivatives and TMOS.[18,19] The evidence for the formation of hydrogen bond is the change in absorption spectrum, that is, the shoulder absorption at the longer wavelength of the π–π* absorption. It was attributed to the blue shift of the n–π* transition. In our case, however, such a blue-shifted absorption was not observed. Moreover, there is no difference in the absorption maximum wavelength of POZO-A in solution, in film, and in the hybrid (Table 3). From these results, it can be said that the difference of the electronic interactions between azobenzene moieties and the surroundings can be ignored in our system. The trans-to-cis ratios in the photostationary state are also summarized in Table 3. In polymer film and polymer hybrid, the cis fraction in the photostationary state appeared to have smaller value than that in solution. This means the inhibition of the photoisomerization owing to a rather small free volume in the matrix compared with that in solution. Such inhibition of the isomerization of azobenzene was reported previously.[18,19]

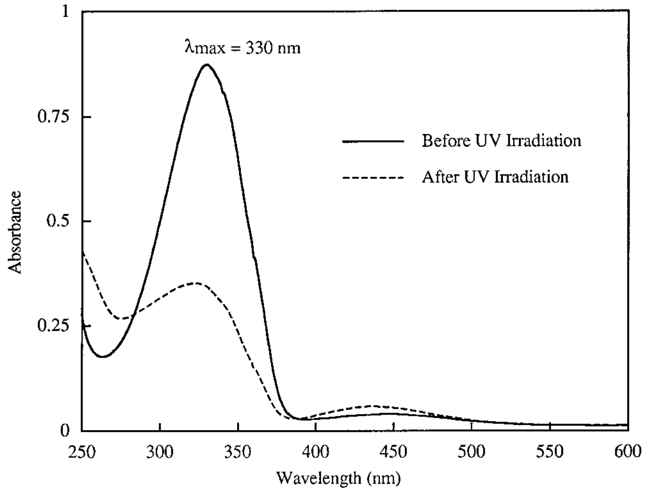

Figure 1. Absorption spectra of POZO–A/MeTMOS polymer hybrid film before and after irradiation with ultraviolet light. (POZO–A/MeTMOS = 1/20).

Table 3. Absorption Maximum Wavelength and Isomer Ratio in the Photostationary State of Each Sample

	λ_{max} (nm)	trans:cis
MODEL (in DMSO)	328	10:90
POZO-A (in DMSO)	330	15:85
POZO-A (film)	330	37:63
POZO-A/MeTMOS (film)	330	37:63

The reverse isomerization progressed both thermally and upon irradiation with visible light (436 nm). Compared with a thermal process at room temperature, a photochemical process proceeded much faster and reached to new photostationary equilibrium (trans:cis = 88:12).

In summary, we demonstrated here an example of the photoresponsive organic–inorganic polymer hybrids from azobenzene-modified poly(2-methyl-2-oxazoline). Transparent and homogeneous polymer hybrids could be obtained in a wide range of composition by the acid-catalyzed sol–gel reaction of alkoxysilanes in the presence of POZO-A. It is confirmed that both trans-to-cis photoisomerization and thermal or photochemical cis-to-trans reverse isomerization of azobenzene chromophores took place reversibly in POZO-A/MeTMOS polymer hybrid. Kinetic studies of thermal cis-to-trans isomerization is in progress to investigate the local environment around azobenzene moieties in the polymer hybrids.

References and Notes

(1) Novak, B. M. *Adv. Mater.* **1993**, *5*, 422.
(2) Schubert, U.; Hüsing, N.; Lorenz, A. *Chem. Mater.* **1995**, *7*, 2010.

(3) Judeinstein, P.; Sanchez, C. *J. Mater. Chem.* **1996**, *6*, 511.
(4) Brinker, C. J.; Scherer, G. W. *Sol–Gel Science, The Physics and Chemistry of Sol–Gel Processing*; Academic Press: Inc.: San Diego, CA, 1990.
(5) Dunn, B.; Zink, J. I. *J. Mater. Chem.* **1991**, *1*, 903.
(6) Avnir, D.; Levy, D.; Reisfeld, R. *J. Phys. Chem.* **1984**, *88*, 5956.
(7) Levy, D.; Einhorn, S.; Avnir, D. *J. Non-Cryst. Solids* **1989**, *113*, 137.
(8) Chaput, F.; Riehl, D.; Lévy, Y.; Boilot, J.-P. *Chem. Mater.* **1993**, *5*, 589.
(9) Costello, B. P. J. d. L.; Evans, P.; Ewen, R. J.; Honeybourne, C. L.; Ratcliffe, N. M. *J. Mater. Chem.* **1996**, *6*, 289.
(10) Panusa, A.; Flamini, A.; Poli, N. *Chem. Mater.* **1996**, *8*, 1202.
(11) Zhao, C. F.; Gvishi, R.; Narang, U.; Ruland, G.; Prasad, P. N. *J. Phys. Chem.* **1996**, *100*, 4526.
(12) Burzynski, R.; Casstevens, M. K.; Zhang, Y.; Ghosal, S. *Opt. Eng. (Bellingham, Wash.)* **1996**, *35*, 443.
(13) Lebeau, B.; Sanchez, C.; Brasselet, S.; Zyss, J.; Froc, G.; Dumont, M. *New J. Chem.* **1996**, *20*, 13.
(14) Chaput, F.; Riehl, D.; Boilot, J. P.; Cargnelli, K.; Canva, M.; Levy, Y.; Brun, A. *Chem. Mater.* **1996**, *8*, 312.
(15) Gvishi, R.; Bhawalker, J. D.; Kumar, N. D.; Ruland, G.; Narang, U.; Prasad, P. N.; Reinhardt, B. A. *Chem. Mater.* **1995**, *7*, 2199.
(16) Kaufman, V. R.; Levy, D.; Avnir, D. *J. Non-Cryst. Solids* **1986**, *82*, 103.
(17) Brik, M. E.; Titman, J. J.; Bayle, J. P.; Judeinstein, P. *J. Polym. Sci., B—Polym. Phys.* **1996**, *34*, 2533.
(18) Ueda, M.; Kim, H.-B.; Ikeda, T.; Ichimura, K. *Chem. Mater.* **1992**, *4*, 1229.
(19) Ueda, M.; Kim, H.-B.; Ikeda, T.; Ichimura, K. *J. Non-Cryst. Solids* **1993**, *163*, 125.
(20) Chujo, Y.; Saegusa, T. *Adv. Polym. Sci.* **1992**, *100*, 11.
(21) Chujo, Y. In *Organic/Inorganic Polymer Hybrids*; Salamone, J. C., Eds.; Polymeric Materials Encyclopedia; CRC Press: Boca Raton, FL, 1996; p 4793.
(22) Zimmerman, G.; Chow, L.-Y.; Paik, U.-J. *J. Am. Chem. Soc.* **1958**, *80*, 3528.
(23) Rau, H. In *Photochromism—Molecules and Systems*; Dürr, H., Bouas-Laurent, H., Eds.; Studies in Organic Chemistry 40; Elsevier: Amsterdam, 1990; p 165.
(24) Chen, D. T.-L.; Morawetz, H. *Macromolecules* **1976**, *9*, 463.
(25) Kim, Y. S.; Sung, C. S. P. *Macromolecules* **1996**, *29*, 462.
(26) Paik, C. S.; Morawetz, H. *Macromolecules* **1972**, *5*, 171.
(27) Barrett, C.; Natansohn, A.; Rochen, P. *Macromolecules* **1994**, *27*, 4781.
(28) Priest, W. J.; Sifain, M. M. *J. Polym. Sci., Part A-1* **1971**, *9*, 3161.

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