Intercalation and Photochemical Behavior of Azobenzene Derivatives with Layered Polymer Crystals as the Organic Host

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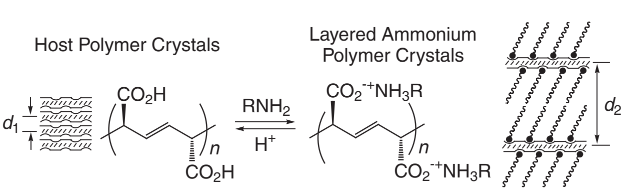
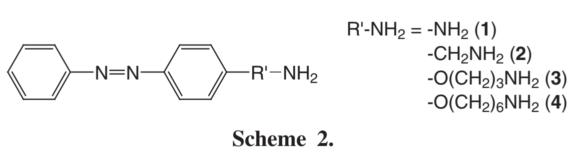
A photofunctional organic solid was fabricated by the intercalation of azobenzene derivatives containing an amino group into poly(muconic acid) as the layered polymer crystals. The organic intercalation and photoisomerization behaviors depended on the structure of the spacer between the azobenzene and amino groups of the guest.

Supramolecular materials including the photochromic moiety imply a possibility of application to novel photoresponsive materials and optical devices.[1] The intercalation of photoactive species into layered inorganic solids has been investigated in order to construct photofunctional intercalation compounds; for examples, the photochromic reactions of viologens, fulgide, spiropyrans, diarylethene, and azobenzene in the interlayer space of host materials.[2] In contrast, there is no example of constructing photoactive materials using layered organic materials coupled with any photochromic organic compounds.

Recently, we reported that poly(muconic acid) (PMA) functioned as a unique organic host compound for intercalation with various amines (Scheme 1).[3,4] The organic intercalation system consisting of layered organic polymers and guest amines has characteristics different from known intercalation compounds with an inorganic host. The former has a crystalline structure, in which carboxylic acids are orderly arranged along the polymer chain in a high density. A combination of the organic host crystal with organic guest molecules can induce any specific feature through not only host–guest but also guest–guest interactions. In this study, we carried out the intercalation of four kinds of azobenzene derivatives (**1**-**4**) containing different spacer groups between the azobenzene and amino groups (Scheme 2) to investigate the structure of the layers, the assembly of guest molecules, and the photochemical bahavior of the dyes intercalated into the PMA.



Scheme 1.



Scheme 2.

Table 1. Intercalation of azobenzene derivatives containing an amino group with PMA

Guest amine	Method[a]	Time/h	$[-NH_2]/[-CO_2H]$	Conversion /%	d/Å
1	A	2	10	0	—
1	B	0.5	10	0	—
2	A	36	3	81	26.5
2	B	0.5	1	48	—
3	A	48	4	93	36.0
4	B	0.5	>1	89	>44

[a] A: stirred in methanol as dispersant. B: ground in a mortar in the solid state.

Table 1 shows the conversion of the intercalation with various azobenzene derivatives. We first attempted the intercalation of **1** as a commercially available azobenzene by both dispersion and solid-state methods.[5] However, **1** was not incorporated into PMA due to the low basicity of the guest aniline (pKa = 4.6 for unsubstituted aniline). The intercalation of aniline derivatives with an electron-donating substituent such as methoxy and hydroxy groups was also attempted, but failed. Therefore, three azobenzene derivatives with a suitable spacer group were synthesized (**2**-**4**).[6]

From the diffraction peak at a low angle in powder XRD profiles for PMA intercalated with the azobenzene derivatives (**X**-PMAs) shown in Figure 1, the interlayer spacing (d) was evaluated. The d-value increased with an increase in the size of the guest, although the d-value for **4**-PMA could not be determined due to the diffraction at a lower angle. Considering the d-values and the size of the guest molecules, it is postulated that the azobenzene ammoniums are arranged in the interlayer space with a structure inclined to the PMA sheets, but not interdigitated (Figure 2). A similar inclined structure of the guests has also been formed for the intercalation with n-alkylamines, as previously reported.[4] The guest amines are regularly aligned along

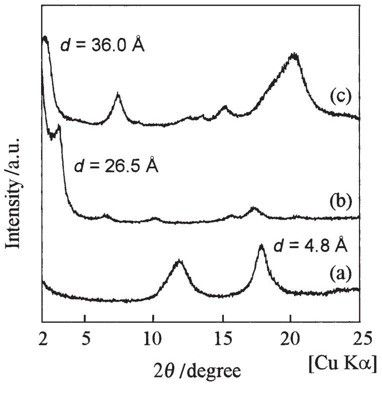


Figure 1. XRD diffraction profiles of PMA and **X**-PMAs. (a) PMA (before intercalation), (b) **2**-PMA, and (c) **3**-PMA.

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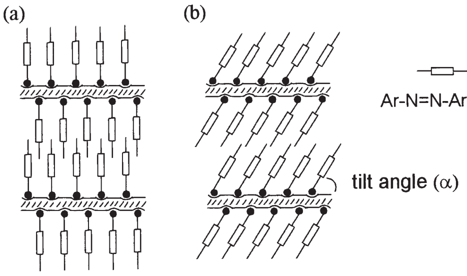

Figure 2. Models of stacking structure. (a) Interdigitated and (b) inclined structures.

the polymer chain at a stacking distance of 5 Å, and no interdigitated structure is observed. Tilt angles (α) are estimated to be 57 ° and 71 ° for **2** and **3**, respectively. According to the McRae and Kasha theory,[7] a blue shift is observed when an angle between the dipole direction of a dye molecule and the line which connects the center of an aggregating dye is greater than 54.7 ° (H aggregate). In fact, the absorption band due to the *trans*-azobenzene chromophore was observed at 314 and 316 nm for the **2**- and **3**-PMAs, respectively, which are shifted toward a shorter wavelength relative to that of a monomeric azobenzene in a dilute solution of the corresponding guests. These results suggest that the H-like aggregates of the azobenzene molecules are quite consistent with a tilt guest structure of the **2**- and **3**-PMAs.

The photochemical behavior of the **X**-PMAs was investigated under UV irradiation using a high-pressure Hg lamp. Figure 3 shows the change in the diffusion reflectance spectra of the **2**- and **4**-PMAs in the solid state. For both cases, an absorption intensity at around 450 nm due to the *cis*-isomer of the azobenzene moiety increased according to the photoirradiation time. It strongly indicates that the azobenzenes isomerize in the constrained interlayer spacing of the polymer crystals. However, the isomerization rate and the reversibility of the **2**- and **4**-PMAs were different from each other. In the case of **2**-PMA, the isomerization proceeded at a lower rate and the equilibrium was not yet achieved after a 1020-min irradiation. Furthermore, the original adsorption band due to the *trans* isomer was not recovered even after heating at 80 °C for 10 h or visible ray irradiation for 2 days. Thus, the E/Z isomerization of **2**-PMA proceeds very slowly and is apparently irreversible under these conditions. **3**-PMA also showed a photoreaction behavior similar to that of **2**-PMA. On the other hand, the isomerization of **4**-PMA was completed within 1-min of UV irradiation accompanying a slight change in the absorbance, and the photoreaction was reversible. The length of the spacer between the azobenzene and amino groups causes different behaviors of the azo group in the **X**-PMAs. **2** and **3** are strongly fixed near the carboxylate of the PMA sheets, while azobenzene as the photoreaction part is more flexible in **4**-PMA. As a result, the photoisomerization feature of **4**-PMA is similar to those observed for the azobenzene-containing polymer[8] and an azobenzene intercalated into inorganic layered materials.[2g,2h] No significant change in the interlayer spacing was observed for the **X**-PMAs upon photoirradiation under the conditions in this work. Further investigation is now continued.

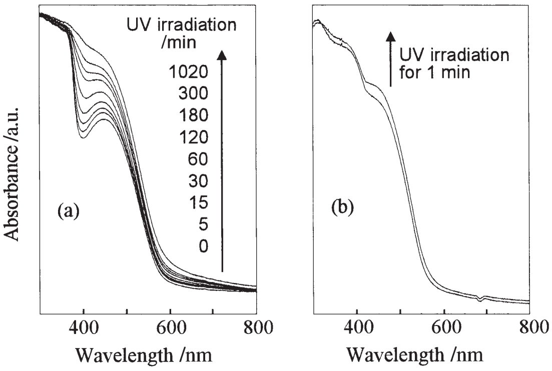

Figure 3. Changes in absorption spectra of **X**-PMAs in the solid state. (a) **2**-PMA during UV irradiation for 1020 min and (b) **4**-PMA during UV irradiation for 1 min.

In conclusion, we succeeded in the design of azobenzene derivatives as the guest suitable for organic intercalation with layered polymer crystals as the host. The intercalation of three kinds of azobenzene derivatives with an amino group through a spacer group into the interlayer space of poly(muconic acid) crystals occurs. It has been revealed that the azobenzene molecules form H-like aggregates in the interlayer space of the **2**- and **3**-PMAs. We also confirmed the different isomerization behaviors depending on the position of the azobenzene guest intercalated into the polymer sheets.

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6 **2**: 4-Phenylazobenzoyl chloride was reacted with ammonia, and then the resulting amide was reduced with $LiAlH_4$ to obtain **2**. mp 75 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.90 (m, 4H, Ar), 7.54-7.45 (m, 5H, Ar), 3.95 (s, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.61, 151.57, 146.39, 130.85, 129.05, 127.66, 123.07, and 122.74 (Ar), 46.18 (CH_2); UV (EtOH) $\lambda_{N=N}$ 323 nm ($\varepsilon = 22600$). **3**: 4-Phenylazophenol was reacted with a large excess of 1,3-dibromopropane, and then with sodium azide to obtain the corresponding azide, which was reduced with $LiAlH_4$ to obtain **3**. mp 88-90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.86 (m, 4H, Ar), 7.52-7.41 (m, 3H, Ar), 7.04-7.00 (m, 2H, Ar), 4.15 (t, $J = 6.0$ Hz, 2H, CH_2), 2.95 (t, $J = 6.8$ Hz, 2H, CH_2), 1.97 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.49, 152.74, 146.93, 130.33, 129.01, 124.73, 122.53, and 114.66 (Ar), 66.16, 39.12, and 32.97 (CH_2); UV (EtOH) $\lambda_{N=N}$ 344 nm ($\varepsilon = 19100$). **4**: 6-Bromo-*n*-hexanoic acid protected with 3,4-dihydro-2*H*-pyrane was reacted with 4-phenylazophenol.[9] After, removed the protecting group, the resulting azobenzene-containing carboxylic acid was reacted with thionyl chlorides. The following reactions were performed similarly to the method for **2**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.86 (m, 4H, Ar), 7.52-7.41 (m, 3H, Ar), 7.02-6.98 (m, 2H, Ar), 4.05 (t, $J = 6.4$ Hz, 2H, CH_2), 2.72 (t, $J = 7.2$ Hz, 2H, CH_2), 1.84 (m, 2H, CH_2), 1.55-1.22 (m, 6H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.54, 152.66, 146.73, 130.23, 128.93, 124.65, 122.43, and 114.58 (Ar), 68.10, 41.94, 33.43, 29.05, 26.55, and 25.81 (CH_2).

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