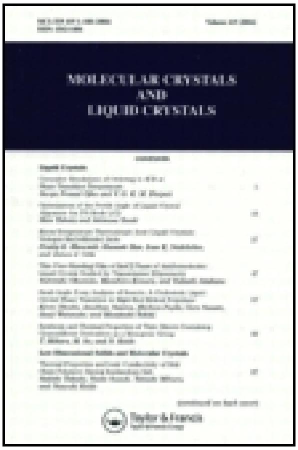

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Photochemical dimerization of acenaphthylene in hydrophobized graphite oxide

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PHOTOCHEMICAL DIMERIZATION OF ACENAPHTHYLENE IN HYDROPHOBIZED GRAPHITE OXIDE

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Photochemical dimerization of acenaphthylene was performed in various hydrophobized graphite oxide films. A large quantity of acenaphthyelene was intercalated into hydrophobized graphite oxide. The conversion of acenaphthyelene increased with the increase of acenaphthyelene contents in the intercalation compounds. Syn/anti ratio of acenaphthylene dimers increased with the increase of acenaphthylene contents and became larger in intercalation compounds containing alkyl amine with shorter alkyl chain probably because of the difference in diffusion rate of exited molecules.

Keywords: photochemical dimerization; acenaphthylene; graphite oxide

INTRODUCTION

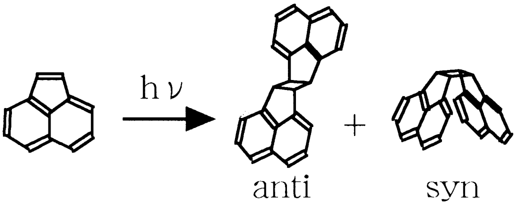
Recently, microporous solids such as zeolites, clay minerals, liquid crystals, etc have been used for reaction media with specific photochemical reactivity [1–8]. Layered compounds hydrophobized by alkyl amines are expected to be new types of reaction media because the substrates are introduced via hydrophobic interaction and accordingly, they would be free from a large electric field. Furthermore, the sizes and properties of the reaction cavity arising between amines can be modified very easily by changing the contents and sizes of alkyl amines. In this type of layered materials, it has been already reported that trans- to cis-photo isomerization of azobenzene, etc was observed [2,5–8], however, papers on photochemical reaction between two molecules are very few. In our previous letter, we have shown that a large amount of acenaphthylene was intercalated into surfactant-intercalated graphite oxide thin film and photochemical dimerization of acenaphthylene was observed. Spectroscopic and X-ray diffraction data suggested that the space available for the photochemical reaction between the surfactant ions was hydrophobic and flexible [9]. In this paper, photochemical dimerization of acenaphthylene in intercalation compounds with various sizes of available space and substrate loading levels was investigated.

EXPERIMENTAL

Graphite oxide was prepared from natural graphite powder by Brodie's method at 60°C [10]. From the elemental analysis data of carbon and hydrogen, $C_8O_{3.4}H_{2.3}$ was obtained for the composition. Octylamine ($C_8H_{17}NH_2$, henceforth abbreviated as C8, liquid), laurylamine ($C_{12}H_{25}NH_2$, C12, solid) hexadecylamine ($C_{16}H_{33}NH_2$, C16, solid)-intercalated GOs [11] were prepared by the direct reaction between amine and graphite oxide at room temperature. The compositions of the prepared intercalation compounds were $C8_{0.62}GO$ (Mw = 232.7), $C12_{0.62}GO$ (Mw = 267.4), $C16_{0.62}GO$ (Mw = 302.1) and $C16_{1.26}GO$ (Mw = 456.4).

Intercalation of acenaphthylene into hydrophobized GOs was performed as follows. Chloroform solution of acenaphthylene (4.67 mM, 2 mL) were mixed with various amounts of hydrophobized GO solutions (2.0 mg/mL in $CHCl_3$). The solvent was evaporated in order to obtain film-like sample at the bottom of the vial. The acenaphthylene/amine ratios varied between 1.5/1 and 0.25/1. The saturated amounts of acenaphthylene in the above intercalation compounds were determined from the X-ray diffraction data (Rigaku Rint-2100, CuKα) of the film samples. This is based on the fact that X-ray diffraction peak derived of crystallized acenaphthylene appears at $2\theta = 12.5°$, when the interlayer spacing is saturated by acenaphthylene. Photochemical dimerization of acenaphthylene in the resulting films of hydrophobized GO with various acenaphthylene/amine ratios was performed at room temperature. UV light (500 W ultra high pressure mercury lamp, Ushio BA-H500) was irradiated to the film sample through optical fiber for 80 min at room temperature. The acenaphthylene molecules undergo photochemical dimerization by irradiating UV light as shown in the Scheme 1 providing both syn- and anti-dimers.

The use of Corning CS 052 filter (cut off wavelength: 340 nm) prevented the excitation of syn- and anti-dimers at 313 nm. After the reaction, cyclohexane was poured into the vial, which allowed to extract the products from the intercalation compounds. The conversion of acenaphthylene monomer was calculated from the decrease of absorbance at 340 nm in UV-Vis. spectra (Hitachi UV-3010, in cyclohexane solution). Syn/anti ratios of dimers were determined from the ratio of the areas of ^1H NMR peaks ($CDCl_3$ solvent) at 4.84 ppm (syn, 4H) and 4.09 ppm (anti, 4H). Photochemical reaction of



SCHEME 1

acenaphthylene crystal was also performed as reference, and the conversion of 33% and syn-/anti ratio of 0.53 were obtained.

RESULTS AND DISCUSSIONS

Intercalation of Acenaphthylene into Amine-intercalated GO

Figure 1 shows the X-ray diffraction patterns of acenaphthylene-amine-intercalated GOs with various acenaphthylene/amine ratios. The diffraction peaks at $2\theta = 2.6$–$3.7°$ due to acenaphthylene-amine-intercalated GOs were observed and their interlayer spacings, I_c were calculated to be 2.43–3.35 nm. When the acenaphthylene contents increased and reached acenaphthylene/amine ratio of 1/0.5–1/1.5, a diffraction peak at $2\theta = 12.5°$ originating from excess acenaphthylene crystal deposited at the surface of the intercalation compound was observed. This means that the interlayer spacing of amine-intercalated GO was saturated by acenaphthyelene molecules. From these data, the maximum amounts of acenaphthylene intercalated into amine-intercalated GOs per GO unit were determined.

The concentrations of acenaphthylene in the samples can be calculated by using the unit cell volume of the acenaphthylene-amine-intercalated GOs and the number of acenaphthylene molecules in the unit cell, according to the following formula.

$$C = \frac{0.5 \times \mathrm{y}}{0.5 \times \mathrm{a_{GO}}^2 \times \sqrt{3} \times \mathrm{I_c} \times \mathrm{A} \times 10^{-24}} / \mathrm{M}$$

$\mathrm{a_{GO}}$(0.248 nm), $\mathrm{I_c}$: lattice parameters of intercalation compound

A: Avogadro constant (6.023×10^{23})

y: acenaphthylene content in intercalation compound

Since the structure of acenaphthylene-amine-intercalated GO has not been determined yet, we assumed hexagonal unit cell with $\mathrm{a_0} = 0.248$ nm

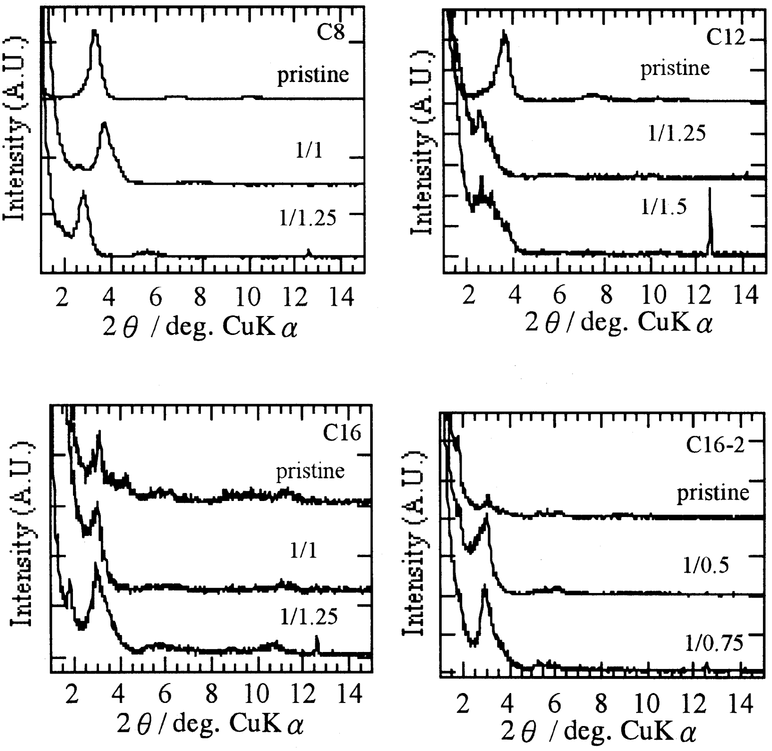


FIGURE 1 X-ray diffraction patterns of acenaphthylene-amine-intercalated GOs with various acenaphthylene/amine ratios. C8:C8$_{0.62}$GO, C12:C12$_{0.62}$GO, C16:C16$_{0.62}$GO and C16-2:C16$_{1.26}$GO.

(the same as that of GO) and $c_0 = I_c$, and stage 2 type structure of GO [12] in order to determine the number of acenaphthylene molecule per unit cell. The maximum amounts per unit GO and concentrations of acenaphthylene in intercalation compounds were summarized in Table 1. Note that if one

TABLE 1 Maximum Amounts per Unit GO and Concentrations of Acenaphthylene Adsorbed in Amine-Intercalated GOs, Together with I_c Values

Host	C8$_{0.62}$GO	C12$_{0.62}$GO	C16$_{0.62}$GO	C16$_{1.26}$GO
y in (acenaphthylene)$_y$Cn$_x$GO	0.62	0.78	0.62	0.63
I_c value/nm	2.43	3.35	2.91	2.93
concentration*/M	3.8	2.9	3.2	3.3

*Assuming stage 2 type structure of GO.

assumes stage 1 type structure of GO [13], the concentration of acenaphthylene becomes half of that obtained in Table 1. These values are much higher than those reported in zeolite and liquid crystals [14,15].

Photochemical Dimerization of Acenaphthylene in Various Amine-intercalated GO Films

Figure 2 show the conversion of acenaphthylene in various amine-intercalated GOs as a function of acenaphthylene contents. It increased with the increase of acenaphthylene contents except for that in C12GO, which indicates that the collisions between excited- and ground-state molecules became easier. Figure 3 shows the syn/anti ratio of acenaphthylene dimers determined from ^{1}H NMR data as a function of acenaphthylene contents. It varied in a wide range between 9.0 and 0.58, and roughly increased with the increase of acenaphthylene content, amine content and the decrease of alkyl chain length of amine.

It has been reported that the syn/anti ratio of acenaphthylene dimers varied drastically depending on the phase when acenaphthylene molecules are dimerized in liquid crystals [15]. The authors concluded that the difference of the diffusion rates in different directions was responsible for this behavior. In intercalation compounds with two dimensional structure, the diffusion of excited molecule is more anisotropic, therefore, the large difference in syn/anti ratio of dimers should be due to the that in diffusion rate between alkyl chains of amines and it would be in the order of $C8 < C12 \leqq C16$. The higher syn/anti ratio and lower conversion in $C16_{1.26}GO$ content would be also ascribed to the lower diffusion rate of exited molecules in densely packed alkylamines.

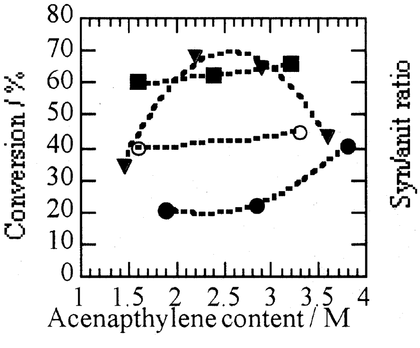


FIGURE 2 Conversion of acenaphthylene in ●: $C8_{0.62}GO$, ▼: $C12_{0.62}GO$, ■: $C16_{0.62}$ GO and ○: $C16_{1.26}GO$.

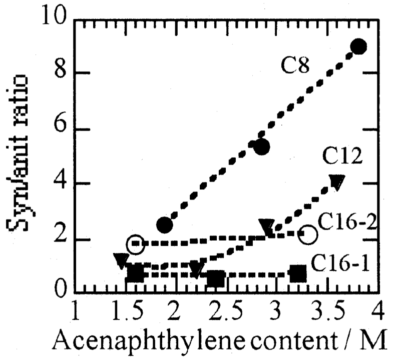


FIGURE 3 Syn/anti ratio of dimers prepared in ●: $C8_{0.62}GO$, ▼: $C12_{0.62}GO$, ■: $C16_{0.62}GO$ and ○: $C16_{1.26}GO$.

The data obtained in this study suggest that it would be possible to control photochemical reaction in intercalation compounds by changing the content and kind of hydrophobic molecule in them. Therefore, hydrophobized graphite oxides would be promising as reaction media for photo chemical reaction.

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