Photochromism of Spiropyrans-Clays Intercalation Compounds Cast Film

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Many studies have been reported [1] on the photochromism of spiropyrans (SPs) reversibly forming photomerocyanines (PMCs) probably because of their potential usefulness as photoresponsive materials, e.g., reversible light filters, ornaments and reversible optical recording media. In order to obtain a spiropyran having the photochromic properties required for applications systems, one of the most frequently employed approaches has been to modify its structure. On the other hand, as it has become clear that the photochromic properties of spiropyrans are greatly improved by changing the surrounding matrices, studies have increasingly concentrated on this aspect. Thus, the photochromic behavior of spiropyrans in polymer films [2], monolayer [3] and bilayer membranes [4,5], Langmuir-Blodgett multilayers [6], liquid crystals [7] and micelles [8] have been studied and useful information concerning the factors which stabilize photomerocyanines in these molecular assemblies is now available. Thus, as a part of our studies [9] on the photochromic behavior of spiropyrans, we studied their photochromism in clay-intercalated cast film.

Spiropyran (SP06Py12) bearing hexylpyridinium group at 1 position and alkanoyloxymethyl group at 8 position was prepared according to the usual method. Aqueous solution of SP06Py12 and clay (montmorillonite) were mixed at 70°C with vigorous stirring
for 2h. After standing at room temperature for several hours, the blue precipitate was collected by filtration, washed with MeOH and dried under vacuum to constant weight. The intercalation compound was then dissolved in chloroform and the resulting solution was cast onto a Pyrex plate. A cast film consisting of the SP incorporated into a bilayer intercalated into a clay was also prepared on a glass plate by slowly evaporating a solution of the SP and compound resulting from intercalation of didodecyldimethylammonium chloride (DDAC) into montmorillonite in CHCl₃. The film became strongly colored upon exposure to UV light from a 500 W high-pressure Hg lamp at room temperature and the color faded upon heating in the dark to reform the SP. The photochromic properties were conveniently studied in the usual way using UV spectroscopy: the thermal isomerization of PMC to SP in the film exhibited first-order kinetic. Computer generated correlations of plot of ln (Aₜ-A∞) vs. time were linear over at least half-lives with correlation coefficients r>0.99.

In Table 1, we summarize λ max values and the thermal decoloration rates (k) of PMC. For comparison, λ max observed in EtOH and CHCl₃ are also listed. The results show that the photochromic properties were highly dependent on the environments. Absorption maximum (λ max) of the PMC in the montmorillonite-based cast film is rather similar to that observed in CHCl₃ rather than in EtOH. This implies that the SP
is located at a nonpolar, hydrophobic portion of the molecular assemblies. The rate constant (k) for the thermal isomerization in the cast film is, however, noticeably smaller than that observed in CHCl₃. In homogenous solution, the absorption maximum of PMC shifts to blue and the rate constant (k) decreases as the polarity of the medium increases, and a linear correlation exists between lnk and λ_max. In the heterogenous medium, on the other hand, a large deviation from a linear correlation is often observed and usually the distinct lowering of the kinetics of ring closure as compared with that expected in a solvent of the same polarity parameter appears presumably as a result of increased fluidity of the field to restrict the rotative movement accompanied by the ring closure.

Another interesting point which is worthy to comment here is that, in the cast film consisting of SP06Py12-montmorillonite intercalation compounds, the first-order plots of the reaction showed strong deviation from linearity and were satisfactorily analyzed as being the sum of two first-order processes. Although we do not know the origin of the deviation, presumably nonhomogeneous steric restriction by matrix plays an important role in this case. Since such a deviation was not observed in

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**Table 1. Photochromic Properties of SP06Py12**

<table>
<thead>
<tr>
<th>Environments</th>
<th>λ_max/nm</th>
<th>10^4k/sec⁻¹(T°C)</th>
<th>rel.rate</th>
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<tbody>
<tr>
<td>CHCl₃</td>
<td>574</td>
<td>93.3 (37)</td>
<td>345</td>
</tr>
<tr>
<td>EtOH</td>
<td>548</td>
<td>30.2 (37)</td>
<td>157</td>
</tr>
<tr>
<td>DDAC-Mont⁴</td>
<td>570</td>
<td>8.5 (56)</td>
<td>4</td>
</tr>
<tr>
<td>SP-Mont⁵</td>
<td>566</td>
<td>28.3 (56)</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.1 (56)</td>
<td>1.0</td>
</tr>
</tbody>
</table>

uartation maximum of PMC.  b The first-order rate constants (k) for the thermal isomerization of PMC to SP at the indicated temperature.  c Relative rate for the thermal isomerization at 50°C.  d A cast film consisting of SP06Py12, DDAC, and montmorillonite.  e A cast film consisting of SP06Py12 and montmorillonite.
DDAC-Mont-SP film, where only "slow-decaying" process was apparent, addition of DDAC as a bilayer component must result in the extinction of the matrix site causing "fast-decaying" process.

References