Effective Utilization of 366 nm-Light in Photo-Generation of Pendant Amino Groups Using Pendant Thioxanthone Groups

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INTRODUCTION

The effective utilization of light from light sources is an important factor in photochemical reactions in both basic and practical aspects. With the aim of improving the efficiency, greater molar absorption coefficient of chromophores is advantageous as well as higher quantum efficiency, because total efficiency depends on the both.

Conventional i-line (366 nm) from mercury lamps is a useful light in practical photochemical reactions. Thioxanthone moiety is one of good sensitizers that have strong absorption in this region of light.[1] However, the solubility of thioxanthone derivatives in organic solvents or polymer matrixes are poor in general. In order to overcome this problem, introduction of these groups into side-chain has been often applied.[2-4]

We have already reported that pendant aclyoxyimino (AOI) groups are transformed into primary amino groups on irradiation as shown in Scheme 1.[5,6] Triplet sensitizers such as aromatic ketones were very effective for the photo-transformation.[7,8] Furthermore, it was found that irradiated films became insoluble in THF after post-exposure bake (PEB) treatment.[9]

In this communication, we report preparation, photo-reactivity, and solubility change after PEB of copolymers bearing both AOI and sensitizing groups including thioxanthone moiety.

EXPERIMENTAL

Acetophenone O-acryloyloxime (AAPO),[6] 2-(acryloyloxy)thioxanthone (ATXT),[2] and 4-(acryloyloxy)benzophenone (ABP)[3] were obtained as described in literature. DMF and tetrahydrofuran (THF) were distilled under reduced pressure before use. Chloroform was obtained from Wako Chemical and used as received.

2-Acetonaphthone O-acryloyloxime (AANO) was obtained by adding 6.6 ml (80 mmol) of acryloyl chloride to the mixture of 10.0 g (54 mmol) of 2-acetonaphthone oxime and 15 ml (108 mmol) of triethylamine in dichloromethane below 5 °C. After refluxing for 5 h, the mixture was cooled and washed with 1.2 N-HCl, sat.NaHCO3 solutions, and water. After drying on sodium sulfate, the solvent was evaporated. The residue was purified by column chromatography on silica gel using dichloromethane as an eluent. Recrystallization from hexane yielded 9.3 g (72 %) of colorless solid, mp = 95-97 °C, 1H-NMR (CDCl3): δ = 2.53 (3H, s, CH3), 6.00 (1H, d, cis-CH2=), 6.35 (1H, dd, J = 10.5, 17.6 Hz, CH), 6.65 (1H, d, cis-CH2=), 7.49-8.02 (6H, m, 3,4,5,6,7,8-H), 8.19 (1H, d, 1-H). Calcd for C15H13O2N: C 75.35, H 5.48, N 5.85. Found: C 74.90, H 5.40, N 5.64.

Acryloyloxymethyl 2-naphthyl ketone (ANK) was obtained by adding 4.9 g (20 mmol) of α-bromoacetonaphthone to the mixture of 1.5 ml (22 mmol) of acryloyl acid, 3.1 ml (16 mmol) of 1,8-diazabicyclo[5,4,0]-7-undecene, and 50 ml of benzene below 10 °C. After stirring for 24 h at room temperature, the mixture was cooled and
washed with water. After drying on sodium sulfate, the solvent was evaporated. The residue was purified by column chromatography on silica gel using dichloromethane as an eluent. Recrystallization from ethanol yielded 2.88 g (61%) of colorless solid, mp = 65-66 °C, 1H-NMR (CDCl3): 5.58 (2H, s, CH2), 5.98 (1H, d, trans CH2=), 6.32 (1H, dd, J = 17.3, 11.1 Hz, CH), 6.61 (1H, d, cis CH2=), 7.55-7.67 (2H, m, 6,7-H), 7.78-8.02 (4H, m, 3,4,5,8-H), 8.45 (1H, s, 1-H). Calcd for C15H12O3: C 74.99, H 5.03. Found: C 74.61, H 4.87.

DMF solution containing 33-50 wt% of monomers and 0.3-0.8 wt% against monomers of α, α'-azobisisobutyronitrile was degassed and heated at 60 °C. The mixture was reprecipitated from methanol after dissolving in tetrahydrofuran (THF) or chloroform. The molar fractions of monomer incorporated in copolymers were determined by 1H-NMR and elemental analyses using a JEOL GX270 and a Yanako MT-3 CHN Corder, respectively. Number average molecular weights of polymers were measured by size exclusion chromatography (SEC) on a Jasco GPC equipment consisting of a PU-980 pump, an RI-930 and a Shodex KF806M column using polystyrene standards. Glass transition temperature (Tg) was obtained by a Rigaku 8230B differential scanning calorimeter at a heating rate of 10 K/min. Polymerization conditions and characterization of obtained polymers were listed in Table 1.

Polymer films were obtained by casting their THF or chloroform solution onto silicone plates, and pre-baked at 70 °C for 5 min. The thickness of films was ca. 1 µm, which was measured by a Nanometrics Nanospec/AFT M3000.

Irradiation was performed by 366 nm light obtained from an Ushio UM-102 medium-pressure mercury lamp (100 W) through a Toshiba UV-D1B.

Table 1. Characterization of Copolymer Samples

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Monomers in Feed (mol%)</th>
<th>P.T. (h)</th>
<th>Yield (%)</th>
<th>Mn (×10^4)</th>
<th>Mw/Mn</th>
<th>Tg (°C)</th>
</tr>
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<tbody>
<tr>
<td>AAPO(52)-ATXT</td>
<td>65 0 0 0 35</td>
<td>5</td>
<td>43.9</td>
<td>-</td>
<td>-</td>
<td>91</td>
</tr>
<tr>
<td>AAPO(57)-ABP</td>
<td>50 0 50 0 0</td>
<td>3</td>
<td>36.0</td>
<td>9.9</td>
<td>1.67</td>
<td>76</td>
</tr>
<tr>
<td>AAPO(49)-ABP(8)-ATXT</td>
<td>50 0 25 0 25</td>
<td>0.75</td>
<td>25.4</td>
<td>-</td>
<td>-</td>
<td>87</td>
</tr>
<tr>
<td>AANO(51)-ATXT</td>
<td>0 65 0 0 35</td>
<td>12</td>
<td>52.7</td>
<td>-</td>
<td>-</td>
<td>102</td>
</tr>
<tr>
<td>AANO(56)-ANK</td>
<td>0 50 0 50 0</td>
<td>12</td>
<td>39.8</td>
<td>3.1</td>
<td>2.02</td>
<td>91</td>
</tr>
<tr>
<td>AANO(55)-ANK(16)-ATXT</td>
<td>0 50 0 25 25</td>
<td>4.5</td>
<td>36.1</td>
<td>-</td>
<td>-</td>
<td>99</td>
</tr>
<tr>
<td>AANO(42)-St</td>
<td>0 30 0 0 0</td>
<td>8</td>
<td>36.5</td>
<td>6.0</td>
<td>2.43</td>
<td>100</td>
</tr>
</tbody>
</table>

a) Numbers in parentheses indicate molar fractions in polymers.
b) Polymerization Time.
c) From SEC with polystyrene standard.
d) Obtained from DSC.
e) Insoluble in THF.

Fig. 1. IR spectral changes for AAPO(52)-ATXT film on irradiation at 366 nm. 0 (solid line) and 1.2 J/cm² (dotted line) exposure.
filter at room temperature in air. Light intensity was measured by an Oric UV-M02 photometer to be ca 3 mW/cm² at 366 nm. Decomposed fraction of AOI groups was calculated based on the absorbance at 1760 cm⁻¹ in IR and assumed that the absorbance showing no change on further irradiation is the 100 %-decomposed point. PEB was carried out on a Koike Precision Instrument HM-15G hot plate at 150 °C for 10 min in air.

Development was performed by soaking the irradiated films in cast solvent for 10 min at room temperature. Normalized film thickness of polymer films was obtained from ratios of thickness before and after the development.

IR and UV spectra were obtained using a Jasco 410 and a Shimadzu 2400PC spectrometers, respectively.

RESULTS AND DISCUSSION

Thioxanthone moiety was successfully introduced into copolymers as a comonomer ATXT. Although copolymers of ATXT were insoluble in THF, they were dissolved in chloroform easily. All films investigated here were homogeneous and transparent.

Fig. 1 shows IR spectral changes for AAPO(52)-ATXT. A peak at 1760 cm⁻¹ due to C=O stretching band in AAPO units decreased on 366 nm-irradiation. Because AAPO unit has no absorption at 366 nm, it was clear that the photolyses of AOI groups were sensitized by thioxanthonyl groups that absorbed 366 nm light. Similar results were observed for copolymers of AAPO and ABP. The decomposed fractions of AOI groups in the copolymers were plotted against irradiation energy in Fig. 2. The degree of decomposition was in the order AAPO(49)-ABP(8)-ATXT > AAPO(52)-ATXT >> AAPO(57)-ABP. AAPO(52)-ATXT films having the highest absorbance at 366 nm were decomposed faster than AAPO(57)-ABP. However, AAPO(49)-ABP(8)-ATXT was faster than AAPO(52)-ATXT.

Fig. 3 shows the change of decomposed fraction for AOI groups in AANO copolymers. Because AANO absorbs 366 nm light, even copolymer with St was decomposed at 366 nm light. The behaviors of photo-decomposition of AANO copolymers were similar to AAPO copolymers, and these decomposition rates were in the order AANO(55)-ANK(16)-ATXT > AANO(51)-ATXT > AANO(56)-ANK >> AANO(56)-St. The effect of ATXT units was very similar to that observed in AAPO polymers. These results suggest that the great molar absorption coefficient of ATXT contributed to the faster decomposition of AOI groups. The reason of faster decomposition of AANO(55)-ANK(16)-ATXT than AANO(51)-ATXT is unknown at present.

It has been reported that copolymers bearing AOI groups turned insoluble into THF by PEB.[9] The insolubilization was also observed for copolymers of ATXT and AAPO or AANO. Fig. 4 shows the change of insoluble fraction of the copolymers in chloroform after PEB at 150 °C against irradiation time. In both copolymers, the order of insolubilization was the same as those observed in decomposition rates. That is, these
results show that the introduction of ATXT in the copolymers is very effective for the sensitization of their insolubilization. The above behaviors are consistent with the results of photo-initiated thermal insolubilization of AOI groups observed previously, suggesting the significant role of amino groups in the insolubilization by PEB.

In conclusion, thioxanthone moiety was successfully introduced into side-chain. By its great molar absorption coefficient at 366 nm, the decomposition of AOI groups and insolubilization into their casting solvent after PEB treatment was much sensitized.

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