Synthesis and Photochemical Reaction of Self-Sensitized Photosensitive Polymer Containing Pendant Propargyl Moiety

Tadatomi Nishikubo, Katsumi Inomata and Tsutomu Shimokawa

Department of Applied Chemistry, Faculty of Engineering, Kanagawa University,
Rokkakubashi, Kanagawa-ku, Yokohama, 221

Hay et al.\(^1\) and Kato et al.\(^2\) have reported the photo-crosslinking reaction of polymers containing propargyl (PG) moieties, which are to be expected for new photosensitive group by photo-initiated cationic reaction. Recently, we synthesized\(^3\) poly(propargyl methacrylate) (PPMA) by the condensation reaction of poly(methacrylic acid) (PMA) with propargyl bromide (PGB) using DBU (1,8-diazabicyclo-[5,4,0]-7-undecene) in aprotic polar solvents, which is a new and conventional method for chemical modifications of polymers, and investigated the photo-sensitized crosslinking reaction with various photosensitizers or photon-generated cationic catalysts.

This communication reports the syntheses of self-sensitized photosensitive polymers containing pendant PG moiety as a photosensitive group and 2-methylanthraquinonyl (MAQ) moiety as photo-sensitizing group, and studies the photochemical properties of the resulting polymers.

A typical procedure for the synthesis of polymers containing PG ester and MAQ moiety was as follows: PMA [2.58 g (30 mmol)] (reduced viscosity; 0.69 dL/g, measured at 0.5 g/dL in DMF at 30 °C) and 4.57 g (30 mmol) of DBU was dissolved in 15 mL of DMSO, and then 0.45 g (1.5 mmol) of 2-bromomethylanthraquinone (BMAQ) in 20 mL of DMSO was added into the solution at room temperature. After the addition of BMAQ solution, the mixture was stirred at room temperature for 60 min. To the solution was added 5.36 g (45 mmol) of propargyl bromide, stirred at 60 °C for 60 min, precipitated into methanol, reprecipitated twice from THE into methanol, filtered, and dried in vacuo. Yield: 2.68 g. Degree of esterification was 100 % (determined by the titration of carboxylic acid and \(^1\)H NMR spectrum). Content of MAQ unit in the polymer was 3.4 mol-% (calculated from UV absorbance at 329 nm). IR (film): 3300 (=C-H), 2150 (C=C), 1740 (C=O), 1680 (C=O), and 1140 cm\(^{-1}\) (C-O-C). \(^1\)H NMR (CDCl\(_3\)): \(\delta\) = 0.9 (C-CH\(_3\)), 1.9 (C-CH\(_2\)), 3.5 (C=CH), 4.6 (O-CH\(_2\)-C), 5.2 (O-CH\(_2\)-Ar), and 7.0-
8.3 ppm (aromatic protons). The rate of photochemical reaction and practical photosensitivity of the resulting polymers were measured as reported previously\(^3\),\(^4\).

The condensation reaction of PMA or poly(acrylic acid) (PAA) with PGB and BMAQ to give the corresponding self-sensitized photosensitive polymers proceeded quantitatively using DBU as a base in DMSO or DMF under mild reaction conditions. The resulting polymers were soluble in various organic solvents, and were insoluble in water and methanol, when the esterification done with about 100 mol-%. Water soluble self-sensitized photosensitive polymers were also synthesized by partial esterification reaction of PMA or PAA with PGB and BMAQ, followed by neutralization of pendant carboxylic acid in the polymers with various tert-amines or potassium hydroxide.

As summarized in Table I, practical photosensitivity of the self-sensitized photosensitive polymer containing about 13 mol-% of pendant MAQ moiety was higher than the other polymers. On the other hand, the polymer only containing MAQ moiety did not show high photosensitivity. This result indicates that pendant PG moiety in the polymer works as excellent photosensitive group, and MAQ group in the polymer acts as photosensitizer for PG moiety.

Table I. Syntheses of the polymers containing PG and MAQ moieties and practical photosensitivities of the resulting polymers\(^a\).

<table>
<thead>
<tr>
<th>Polymer No.</th>
<th>BMAQ (mmol)</th>
<th>PGB (mmol)</th>
<th>Yield (g)</th>
<th>(\eta_{red}) (^b)</th>
<th>MAQ unit in copolymer (mol-%)</th>
<th>PG unit in copolymer (mol-%)</th>
<th>Insoluble step No. (^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-1</td>
<td>1.5</td>
<td>45</td>
<td>2.68</td>
<td>0.55</td>
<td>3.4</td>
<td>96.6</td>
<td>10</td>
</tr>
<tr>
<td>P-2</td>
<td>3.0</td>
<td>45</td>
<td>2.70</td>
<td>0.43</td>
<td>7.8</td>
<td>92.2</td>
<td>12</td>
</tr>
<tr>
<td>P-3</td>
<td>4.5</td>
<td>45</td>
<td>2.83</td>
<td>0.45</td>
<td>13.1</td>
<td>86.9</td>
<td>13</td>
</tr>
<tr>
<td>P-4</td>
<td>6.0</td>
<td>45</td>
<td>2.98</td>
<td>0.31</td>
<td>16.7</td>
<td>83.3</td>
<td>12</td>
</tr>
<tr>
<td>P-5</td>
<td>9.0</td>
<td>45</td>
<td>3.46</td>
<td>0.22</td>
<td>21.1</td>
<td>78.9</td>
<td>11</td>
</tr>
<tr>
<td>P-6</td>
<td>4.5</td>
<td></td>
<td>1.30</td>
<td>0.60</td>
<td>11.3</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>P-7</td>
<td>0.22</td>
<td></td>
<td>11.3</td>
<td>0(^d)</td>
<td>0</td>
<td>0(^e)</td>
<td>3</td>
</tr>
</tbody>
</table>

\(^a\) Carried out with 30 mmol of PMA and 30 mmol of DBU in DMSO. \(^b\) Measured at 0.5 g/dL in DMF at 30 °C. \(^c\) Exposed for 3 min by the chemical lamp and developed for 2 min by acetone. \(^d\) Containing 88.7 mol-% of pendant carboxylic acid. \(^e\) Containing 88.7 mol-% of the methyl ester moiety.

The practical photosensitivity of P-3 did not change by heating at 100 °C.
for 3 h, although the sensitivity of the mixture of PPMA with 2-methylanthraquinone (13.1 mol-%) depressed by heating for 30 min. This result means that the self-sensitized photosensitive polymer containing pendant PG and MAQ moieties have high photosensitivity and excellent thermal stability.

Self-sensitized polymers containing pendant carboxylic acid group became soluble in water by neutralization with bases, and the sensitivity of the neutralized polymers increased dramatically. Furthermore, it was found that the polymers prepared from the reaction of PAA have higher photosensitivity and higher rate of gel production than the polymers prepared from the reaction of PMA. This suggests that flexibility of the polymer chain affected strongly for the photo-crosslinking reaction of these polymers. Water soluble self-sensitized photosensitive polymers containing pendant PG and MAQ moieties also applied for the immobilization of enzyme.

References