Solid-state Photosensitization to Generate Strong Acids to Formulate PAG-dispersed Photopolymers

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1. Introduction
A conventional photolithographic process consists of casting a photosresist solution dissolved in an organic solvent and image-wise exposure, followed by wet development. In order to meet with requirements for zero emission of volatile organic compounds in photolithography, one of the approaches is to use water as a safe and inexpensive solvent throughout the process. One of the problems in designing water-borne photopolymers is how to overcome the problem stemming from scarce water-solubility of conventional photoacid generators (PAGs).

Aqueous dispersions of nano-sized organic solids have attracting increasing interest not only because of their peculiar physico-chemical properties, but also because of solution-like behavior. This situation led us to study PAG-dispersed water-borne photopolymers based on the following key technologies. The first is to downsize PAG solids by milling to reduce light scattering to prepare thin films with reasonable optical quality. The second is to perform crystal-to-crystal photosensitization of PAG for versatile applications. We report here mechanical milling to provide aqueous sub-micron PAG dispersions and solid-state sensitization of PAG particles thus prepared to enable us to formulate a prototype of water-borne photopolymers.

2. Method
9,9'-Dipropoxyanthracene (DPA) as a sensitizer solid suspended in a 5 wt% aqueous solution of poly(vinyl alcohol) (PVA) of PD=500 were ground in absence or in the presence of bis[p-(imid-butyl)-phenyl]iodonium hexafluorophosphate (DPIP) or perfluorobutanesulfonate (DPI9F) with a planetary mill (Pulverisette 7; Fritsch) to give a milky-white dispersion containing 0.17 M of DPA. Particle size determination was made by dynamic light scattering using a Nano-Z (Sysmex). Aqueous dispersions of DPA or a mixture of DPA and PAG were exposed to >350 nm light to be subjected to UV-spectral measurements or alkaline titration to follow photo reaction. A dispersion of DPA and PAG was mixed with an aqueous solution of PVA of PD=1700 containing water-soluble 1,2-diglycidyloxyethane (DGGE) as an acid-sensitive crosslinker and cast on a glass plate to give a thin film. The film was exposed to 365 nm light, followed by heating at 120°C for 2 min and washed out with water to record film thickness on a surface profiler (KLA Tencor; Alpha-Step IQ).

Fig. 1 Solid-state photochemistry of a mixture of DPA and PAG in an aqueous dispersion.

3. Results and Discussion
Ball milling of organic crystals was conducted in
aqueous solutions of PVA as a binder polymer as well as a dispersion stabilizer to afford particles of ca. 300 nm – 600 nm diameters after optimizing milling conditions. It was found that a dilute aqueous dispersion of DPA displays UV-spectral changes upon photoirradiation even under anaerobic conditions due to solid-state transformation to anthraquinone (AQ). Co-milling with DPIP accelerated the photochemistry, suggesting that the photoreaction involves the generation of acidic species from the PAG. Accordingly, preparative irradiation was undertaken to estimate a chemical yield of an acid by alkaline titration. It was recognized that DPIP is not suitable for this purpose because an end point of the titration was not clear probably owing to the partial hydrolysis of HF six to give HF as an acidic extra. So, DPIP was replaced by DP19F liberating the stable sulfonic acid. Table 1 summarizes yields of AQ and the acid as a function of molar ratio of DPA and DP19F, suggesting that sensitized photoacid generation as a result of solid-state electron transfer competes with the transformation to AQ.

Table 1 Photolysis of aqueous dispersions of mixed crystals of DPA and DP19F

<table>
<thead>
<tr>
<th>Run</th>
<th>Molar ratio</th>
<th>Yield (%)</th>
<th>AO</th>
<th>H⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DPA:DP19F:AO</td>
<td>1:0:0</td>
<td>70</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>1:1:1</td>
<td></td>
<td>70</td>
<td>98</td>
</tr>
<tr>
<td>3</td>
<td>1:1:3</td>
<td></td>
<td>64</td>
<td>124</td>
</tr>
</tbody>
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In order to shed more light on solid-state electron transfer, fluorescence-quenching measurements were achieved for combinations of DPA as a donor and PAG as an acceptor. Dispersions containing DPA (0.17 M) was filled in a cell of a 3 mm depth to be excited with 375 nm light at a 45° incidence angle to capture emitted light from a surface layer at a 90° geometry. It was found that DPIP exhibits a higher quenching efficiency when compared with DP19F and that the fluorescence was thoroughly quenched by a two-molar amount of DPIP. Note here that DPA is essentially insoluble in water whereas saturated concentrations of DPIP and DP19F in water are 1.3 x 10⁻³ M and 4.1 x 10⁻⁵ M, respectively. Accordingly, PAG molecules dissolved in water plays a negligibly small contribution in the quenching. In other words, the electron transfer occurs from excited DPA to PAG at interfaces between donor and acceptor crystals through exciton diffusion in DPA crystals. To the authors’ knowledge, this is the first example of solid-state electron transfer generating strong acid.

A film of PAG-dispersed photopolymer comprising PVA and DGE was insolubilized by irradiation with 365 nm light and post-exposure baking, leading to acid-catalyzed crosslinking. Subsequent development with neutral water provided negative-type photoimages, which were relatively transparent. Fig. 2 shows photosensitivity characteristics of novel water-borne photopolymers dispersing 1:1 and 1:2 (mol/mol) mixtures of DPA and DPIP. The latter mixture gave high photosensitivity.

Fig. 2 Photosensitivity curves of PVA and DGE dispersing 1:1 (open circles) and 1:2 (closed circles) (mol/mol) mixtures of DPA and DPIP.

In summary, PAG-dispersed photopolymers processed solely with neutral water was developed based on solid-state sensitization through electron transfer to generate acidic species. We believe that further reduction of particle size of mixed crystals of a sensitizer and PAG enhances both of a sensitization efficiency for photoacid generation and optical quality of photosensitive films to suppress light scattering sufficiently.

References