Photo Amphotheric Compound Generators for Environmentally-friendly Materials

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Photo amphotheric compound generators (PAmGs), which are onium salts used to generate 2-aminooethane-1-sulfonate (taurine) in photo decomposition, were prepared as a mixture and compared with the absorption spectra, photo generation of taurine, and photo pH changes in aqueous solution. One of these photo taurine generators (PtaurineGs) with bis(4-methoxyphenyl)iodonium was designed and prepared for environmentally-friendly photo-reactive materials. These PtaurineGs were water-soluble and photo-decomposable. The photo induced gelling of the aqueous solution drop including casein, which were derived from natural compounds, were demonstrated for stereolithography.

Keywords: Photo-initiator, Amphotheric compounds, Photo decomposition, Diphenyliodonium salts, Water-soluble, Environmentally friendly

1. Introduction

Photo-initiators are functional material to generate highly reactive intermediates, such as radicals, or catalytic compounds like super strong acids or bases from the excited states by absorbing photon energy. Photo-initiators are also called photo X generators (PXGs), for example, a photo acid generator (PAG), and a lot of characteristic compounds for PXGs have been developed and applied to the reactions of photo-curing materials, and photoresists [1-3]. However, there are few reports of photo amphotheric compound generators (PAmGs) [4-6] in comparison with PAGs, photo base generators (PBGs), or photo radical generators (PRGs).

For the realization of a sustainable society, environmentally-friendly materials or the processes of low environmental load are also required in photo-reactive materials. A famous concept is solar-induced photo-polymerization proposed by J. V. Crivello et al., utilization of a photosensitizer for diaryliodonium salts [7]. For a near infrared light source, various iodonium salts were also reported, which are electron acceptable from sensitizer molecules to generate radicals [8]. On the other hand, water-castable and water-developable photoresists have been studied for a long time to make the process to reduce environmental impact. Water-soluble photoresists derived from poly(vinyl alcohol) [9-11] are typical, which occur photo-dimerization reaction to crosslink polymers, and used for screen printing process [12], food packaging [13] or immobilization material for enzymes [14]. Photo-crosslinking of N-phenylamide groups was also applied as a water-developable negative photoresist [15]. Water-processable chemically amplified resists using PAGs were proposed as positive-tone resist [16], and negative-tone resist [17]. Water-soluble polymers and PAGs have important rolls in the materials.

In recent years, as 3D printers became popular, quick prototyping technologies are spreading in various fields and scenes. Thus, safe and environmentally-friendly materials are desirable in the technology, especially, for use in general household and early educational institutions. For example, photo curing materials initiated by visible light [18], near UV-curable acrylate based on natural phenolics [19], which are not derived from a petroleum source, were reported for stereolithography 3D printing.

In this report, we focused on PAmGs to generate 2-aminooethane-1-sulfonic acid (taurine). Taurine is a natural compound of plant and animal origin. Onium
salt type PAmGs based on a PAG structure are photo-decomposable base and water-soluble [6]. Therefore, during the photochemical reaction, these PAmGs are increasing \([H^+]\) in an aqueous solution. On the other hand, many natural macromolecules are known to be water-soluble and sensitive for pH circumstance. Casein is one of the natural products sensitive for pH and heat [20], and M. L. Picchio et al. proposed casein film for the pH triggered drug delivery system [21]. We demonstrated here the photo gelation of the photopolymer materials with the photo taurine generators (PtaurineGs) and casein.

2. Experimental

2.1. Materials

The onium salts, triphenylsulfonium 2-aminoethane-1-sulfonate (TPStaurine), diphenyliodonium 2-aminoethane-1-sulfonate (DPItaurine), and di(4-anisyl)iodonium 2-aminoethane-1-sulfonate (DAItaurine) were respectively prepared from triphenylsulfonium hydrogencarbonate (TPSHC), diphenyliodonium chloride (DPICl) and di(4-anisyl)iodonium bromide (DAIBr) with taurine or sodium-2-aminoethane-1-sulfonate. TPSHC, DPICl, DAIBr, and taurine were purchased from FUJIFILM Wako Pure Chemical Co. Their chemical structures of photo taurine generators (PtaurineGs) are shown in Fig. 1. TPStaurine and DPItaurine were prepared by the method described in a previous report [6].

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\begin{align*}
\text{TPStaurine} & \quad \text{DPItaurine} \\
\text{DAItaurine} & 
\end{align*}
\]

Fig. 1. Chemical structure of photo taurine generators (PtaurineGs).

DAItaurine was prepared as follows. In a 100 mL three-necked flask with a trap, 29.9 mg (0.356 mmol) of sodium hydrogen carbonate and 44.2 mg (0.356 mmol) of taurine were dissolved in 4 mL of distilled water. After the mixture was stirred vigorously at 60 \(^\circ\)C for 24 h with an oil bath, the solvent was removed to give a thick solution. The product (sodium 2-aminoethane-1-sulfonate) and 150 mg (0.356 mmol) of di(4-anisyl)iodonium bromide (DAIBr) were dissolved in 20 mL distilled water. After the mixture was stirred at room temperature for 24 h, the solvent was removed in a rotary evaporator. The solid product was dried and dissolved in dichloromethane again, and filtrated. After the solvent was removed from the filtrate and the solid product was dried in a vacuum overnight, a white solid was obtained. Yield 28.2 \%, \(^1\)H-NMR (DMSO-d\(_6\), 500 MHz): di(4-anisyl)iodonium part: 8.124-8.101 (d, 4H), 7.063-7.039 (d, 4H), 3.787 (s, 6H), 2-aminoethane-1-sulfonate part: 2.545-2.538 (t, 2H), 2.777-2.744 (t, 2H). Purity was 40.5 \%, determined on the signal intensity of NMR.

2.2. Measurements

The UV-vis absorption spectra were recorded on a Hitachi U-3000 spectrophotometer.

2.3. Observation of photo amphoteric compound generation by staining method using TBPBNa

A staining technique was used to estimate taurine generation, according the method to estimate acid generation [22]. The acetonitrile solution of PtaurineG (3 mL, DAItaurine 4.0×10^{-2} g L^{-1}) in a quartz cell was irradiated by a low-pressure mercury lamp (254 nm, 0.88 mJ cm^{-2} s^{-1}). After irradiation, the solution was mixed with 1 mL of acetonitrile solution of sodium salt of tetrabromophenol blue (TBPBNa, 5.0×10^{-5} mol dm^{-3}), and the absorption spectrum of the mixture solution was measured.

3. Results and discussion

3.1. Synthesis of PtaurineGs

In our preparations, purities of PtaurineGs were low because of the difficulty of separation from reactants, especially, in the onium salts with taurine. Comparing the purity on \(^1\)H-NMR, TPStaurine was 54.9 \%, DPItaurine was 40.8 \% and DAItaurine was 40.5 \% against the onium part. However, no other signals except reactants were observed. Then our materials are made into the mixture of onium 2-aminoethane-1-sulfonate and the reactant of onium salt. These PtaurineGs showed basic in water as noted later, thus, taurine was not free from the onium cation in these materials.

3.2. UV-Vis spectra of PtaurineGs

The UV-Vis absorption spectra of PtaurineGs in acetonitrile are shown in Fig. 2. It can be seen that
DAItaurine has specific absorption at 220-320 nm compared to TPStaurine and DPItaurine. It can be explained due to the electron donating effect of the methoxy group on diphenylidonium structure [23]. The di(p-anisyl)iodonium with the absorption in this wavelength area will be attractive as a photo-reactive block of PXGs. Figure 3 shows the changing of the absorption spectra of DAItaurine, which was exposed to a low-pressure mercury lamp (254 nm, 0.53 mJ cm\(^{-2}\) s\(^{-1}\)) in acetonitrile. Increases of absorption around 224-244 nm and decreases around 250-300 were observed, which is thought to be a product of and decomposition of the di(p-anisyl)iodonium part, respectively.

3.3. Photo generation of taurine

The staining method using TBPBNa makes clear if acidic or basic compounds are generated. Figure 4 shows changes of the absorption band of TBPBNa by the photo decomposition of DAItaurine. Before exposure, the absorption of TBPBNa was a bit higher than the reference without DAItaurine. However, after exposure, absorption was reduced due to the generation of acidic products generated from the photochemical reaction of DAItaurine. The changes of absorption band of TBPBNa can be compared to the calibration curve using taurine. Then, the concentration of taurine in the aqueous solution generated by irradiation for 6 s in this experimental condition can be estimated \(7.6 \times 10^{-6}\) mol L\(^{-1}\).

3.4. Photo pH control

PtaurineGs are basic material, and these compounds not only disappear but also generate acidic amphoteric compound in photo decomposition.

Figure 5 shows the pH curves of three types of Ptaurigne aqueous solution depending on exposure time. The pH of DAItaurine solution changed from 7.3 to 2.9, compared with TPStaurine (pH 8.8 → 4.2) and DPItaurine (pH 9.1 → 4.0) solutions. This difference is thought to be due to the lower purity and water solubility of DAItaurine. The concentration of TPStaurine aqueous solution was 3.0 g L\(^{-1}\), and that of DPItaurine solution was 3.2 g L\(^{-1}\), however, the concentration of DAItaurine was \(7.8 \times 10^{-1}\) g L\(^{-1}\), which was the maximum concentration in this.
experiment. This is influenced by the hydrophobicity due to methoxy group of DAItaurine. However, the light response of DAItaurine aq. was fastest among these PtaurineGs. It also shows that the photo-reactivity of DAItaurine was higher than TPStaurine and DPItaurine.

3.5. Demonstration of PtaurineG/casein photo sol-gel transformation.

These PtaurineGs are water-soluble and their photochemical reactions are available to control pH in an aqueous solution. Thus, we attempted to apply PtaurineGs to environmentally-friendly photo-polymer materials in combination with sodium caseinate, which is a water-soluble natural product, and pH sensible. Casein is a kind of protein to be included in milk. PtaurineG aqueous solutions (TPStaurine 3.0 g L\(^{-1}\), DPItaurine 3.2 g L\(^{-1}\), DAItaurine 7.8\(\times\)10\(^{-1}\) g L\(^{-1}\)) were prepared, then, casein was added to be 10 wt% in the solution, and a few drops that 0.25% aqueous ammonia to disperse sodium caseinate were added to the PtaurineGs/casein solution. After these solutions were stirred for one day, each of the PtaurineG/casein solutions were dropped on a glass plate, and it was irradiated by UV light for 30 min using a low-pressure mercury lamp (254 nm, 0.88 mJ cm\(^{-2}\) s\(^{-1}\)). The dropping and irradiation process were repeated, and the shapes of gelling drops were observed. Then the irradiated drop was subjected to a heat treatment (60 °C) for 30 min. These processes are shown in Fig. 6.

![Diagram showing the demonstration method of photo sol-gel transformation by PtaurineGs/casein (TPStaurine aq. 3.0 g L\(^{-1}\), DPItaurine aq. 3.2 g L\(^{-1}\), DAItaurine aq. 7.8\(\times\)10\(^{-1}\) g L\(^{-1}\) with casein 10 wt%).](image)

Fig. 6. Demonstration method of photo sol-gel transformation by PtaurineGs/casein (TPStaurine aq. 3.0 g L\(^{-1}\), DPItaurine aq. 3.2 g L\(^{-1}\), DAItaurine aq. 7.8\(\times\)10\(^{-1}\) g L\(^{-1}\) with casein 10 wt%).

The height of gelled PtaurineG/casein increased with the repeating of dropping and irradiation processes in all demonstrations as shown in Fig. 7. The shapes of dropped PtaurineG/casein after exposure, and after heating were observed to shrink.

![Fig. 7. Photograph of shape of dropped PtaurineG/casein aqueous solution, repeating of dropping and irradiation process, A1: TPStaurine/casein, B1: DPItaurine/casein, C1: DAItaurine/casein, and shape of dropped PtaurineG/casein before and after exposure, and after heating, A2: TPStaurine/casein, B2: DPItaurine/casein, C2: DAItaurine/casein.](image)

![Figure 8 shows the maximum values at each build-up process. One drop was around 0.080 mL. As shown in Fig. 8, the first gelled drop of DAItaurine was the highest in these PtaurineG. Repeating the dropping and irradiation process, the increased height of DAItaurine from the first drop to the fourth drop was larger than those of others. It would be explained from that, that the pH change by the photochemical reaction of DAItaurine was estimated to be faster than others in pH change as](image)
shown in Fig. 5. In Fig. 9, the weights of the dropped DAItaurine/casein were summarized. The decrease of weight means that the water in a gelled drop disappeared after exposure and after heating. That is to say that the PtaurineGs aqueous solution with casein turned into a dry state after heating.

This demonstration is a model process of stereolithography. Increases in height were observed by repeating the dropping and irradiation process. In the gelation of hydrosol, the height and weight of the gelling drop decreased after exposure and heating via the disappearance of water. However, it showed the possibility to make environmentally-friendly stereolithography 3D printing photo-gelation materials by pH changes induced by the generation of taurine from PtaurineGs.

4. Conclusion
We prepared some PAmGs material generating taurine. A new photo amphoteric compound generator, DAItaurine with di(p-anisyl)iodonium cation was designed and prepared. It showed a high efficiency of generation of taurine to give a faster pH change in an aqueous solution in comparison with triphenylsulfonium and diphenyliodonium salts. The photo decomposed products of the di(p-anisyl)iodonium part of DAItaurine is expected to reduce environmental load. A model process of 3D-lithography was demonstrated by the combination of those PtaurineGs and sodium caseinate, which is a natural product, for environmentally-friendly photo-reactive materials.

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