Trioxane Derivative as an Acid Amplifier Exhibiting a Non-linear Organic Reaction

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(Received May 15, 1998; CL-980378)

2,4,6-Tris[2-(*p*-toluenesulfonyloxy)ethyl]-1,3,5-trioxane was prepared to be subjected to the acid-catalyzed decomposition to release three *p*-toluenesulfonic acid molecules which were able to act as an acid amplifier to enhance the photosensitivity of a chemically amplified photoresist.

We proposed a novel concept of acid proliferation reactions comprised of acid-sensitive compounds which display autocatalytic fragmentation to give rise to sulfonic acid with an acidity strong enough to lead to the decomposition of parent molecules. We have so far developed this kind of acid-labile compounds, which are referred to as acid amplifiers, including acetoacetate derivative,[1-3] β-sulfonyloxyketals,[4] and diol monosulfonates.[5,6] Each molecule of them gives birth to one new-borne acid molecule. It was further revealed that the addition of acid amplifiers to chemically amplified photoresists, which consist of a photoacid generator and an acid-labile polymer, results in the improvement of photosensitivity in some extent.[1-6] However, the level of the photosensitivity enhancement was not so high, whereas acid proliferation reactions proceed smoothly in solutions to give sigmoidal conversion curves, confirming the involvement of autocatalytic processes. This may be due to the fact that the efficiency of acid proliferation is determined by the diffusion rate of acid molecules in polymer solids.[7] Since the efficiency of acidolysis is influenced by some factors including the concentration of an acid catalyst, the rate of an acid proliferation reaction in a polymer solid may result from the increase in acid concentrations. In this context, if an acid amplifier is decomposed autocatalytically to release more than two acid molecules simultaneously, it would be anticipated that the addition of the acid amplifier to a chemically amplified photoresist leads to the improvement of photosensitivity because of the enhancement of the efficiency of an acid proliferation reaction. We report here that 2,4,6-tris[2-(*p*-toluenesulfonyloxy)ethyl]-1,3,5-trioxane (**1**) undergoes the acidolysis fragmentation to give three-molar amount of *p*-toluenesulfonic acid (TsOH), leading to the photosensitivity enhancement of chemically amplified photoresists.

We designed **1**[8] as an acid amplifier, taking notice of the fact that a trioxane ring suffers readily from the acidolysis to give the corresponding three-molar aldehyde which undergoes the β-elimination when the aliphatic aldehyde is substituted with an eliminating group such as a tosyloxy residue at the β-position. **1** was synthesized in a 3.6% overall yield by the oxidation of 3-benzyloxy-1-propanol with pyridinium chlorochromate (PCC) to give 3-benzyloxypropanal which was trimerized with 12-phosphomolybdic acid,[9] followed by the deprotection by the hydrogenation with palladium/carbon and by the subsequent tosylation in the presence of triethylamine and 4-dimethylaminopyridine.

The thermal decomposition behavior of **1** was studied by NMR spectroscopy. A solution of **1** (70 mmol dm^{-3}) in a 3 : 1 mixture of diphenyl ether and toluene-d$_8$ was heated at 100 °C. No change in a ^{1}H-NMR spectrum was observed in the absence of TsOH whereas the decomposition of **1** was induced by the addition of 16 mmol dm^{-3} of TsOH at the same temperature. The fragmentation reaction of **1** was followed by monitoring the decrease of the proton signal due to the methine with use of tetramethylsilane as an internal standard. Figure 1 shows that the consumption of **1** takes place quite abruptly to display a sigmoidal time conversion course, indicating that the fragmentation of **1** proceeds autocatalytically to lead to the proliferation of the acid molecules. As stated in our previous papers, an acid amplifier should fulfill the following requirements.[1-6] An acid amplifier should undergo readily an acidolysis to liberate a strong acid which is capable of catalyzing the decomposition of both of itself and of subsequent acidolysis transformation to result in a non-linear chemistry and be thermally stable under the conditions for these acidolysis reactions. The results obtained above support that **1** fulfills the requirements at least in solution.

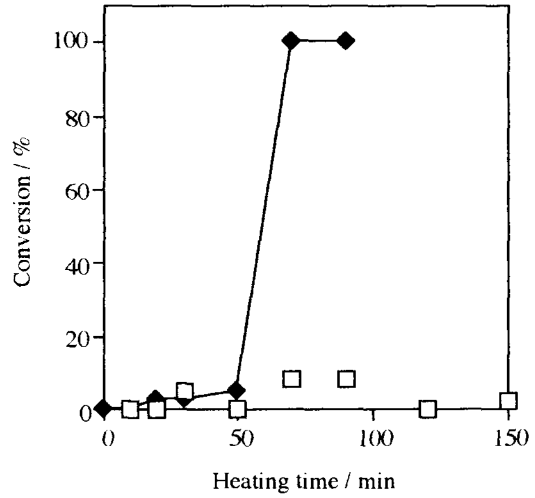
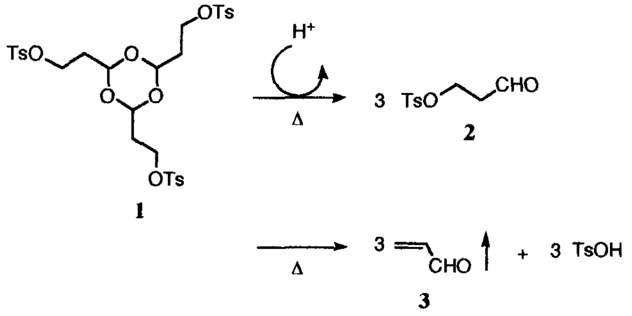


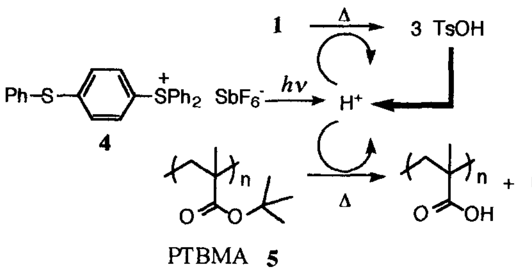
Figure 1. Time courses of the consumption of **1** in the presence of 16 mmol dm^{-3} *p*-toluenesulfonic acid (◆) and of the conversion of **1** in the absence of the sulfonic acid (□) in a 3 : 1 mixture of diphenyl ether and toluene-d$_8$ at 100 °C.

The acidolysis reaction of **1** proceeds as shown in Scheme 1. The heat treatment of **1** at an elevated temperature gives the β-tosyloxypropionaldehyde (**2**), which shows β-elimination to generate TsOH and acrolein (**3**) owing to the presence of electron-withdrawing formyl group. It is well known that the depolymerization of polymers of acetaldehyde and propionaldehyde occurs due to a low ceiling temperature which is lower than room temperature.[10] It follows that **1** is readily depolymerized to release acid molecules through a single process of the scission of the ring of **1**.



Scheme 1.

In order to confirm the applicability of **1** to a chemically amplified photoresist system, **1** was coupled with poly(*tert*-butyl methacrylate) (PTBMA) **5** as an acid-labile polymer and diphenyl-(4-phenylthiophenyl)sulfonium hexafluoroantimonate **4** as a photoacid generator (Scheme 2).[11] The acid proliferation as a result of the acid-catalyzed decomposition of **1** in a polymer film was monitored by the use of a film of PTBMA doped with 10-30 wt% of **1** in the presence of 5.5 wt% of **4** which generates $HSbF_6$ as a strong acid upon UV-irradiation. Thickness of resist films of 0.28 μm was adjusted by spin-coating on silicon wafers. The films were irradiated with 313 nm light by using a Hg-Xe lamp. The photosensitivity determination was performed here by monitoring the film reduction after post-exposure baking due to the elimination of isobutene from PTBMA in the presence of 10 wt% of **1**, since the development with an alkaline solution was insufficient probably because of the polymerization of acrolein.



Scheme 2.

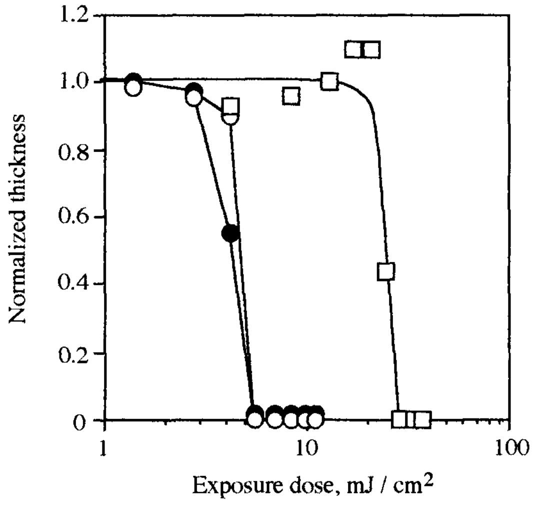


Figure 2. Photosensitivity curves of films of PTBMA containing 5.5 wt% of the photoacid generator (**4**) in the absence of (□) and in the presence of 20 wt% (○) and 30 wt% of **1** (●).

Figure 2 shows the photosensitivity characteristics of PTBMA films consisting of a photoacid generator **4** and an acid amplifier **1**. The addition of the acid amplifier **1** to the photoresist gave rise to the improvement of photosensitivity in the presence of 20 and 30 wt% of **1**. These suggest that the sensitivity enhancement reflects the proliferation of acid molecules by decomposition of the novel acid amplifier **1** in a resist film.

Finally, we would like to stress that the acid proliferation belongs to a novel category of organic reactions since it involves non-linear chemistry. In this respect, the presentation of scope and limitation of this type of non-linear organic reactions is of very importance.

References and Notes

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7 H. Ohmori, K. Arimitsu, K. Kudo, Y. Hayashi, and K. Ichimura, *J. Photopolym. Sci. Technol.*, **9**, 25 (1996).
8 Colorless crystals of mp=78~79 ℃. ^{1}H-NMR: (90 MHz, $CDCl_3$) δ (ppm): 1.89 (q, *J*=6.2 Hz, 6H, -CH_2-), 2.43 (s, 9H, Ar-CH_3), 4.07 (t, *J*=6.2 Hz, 6H, -CH_2OSO_2-), 4.82 (t, *J*=6.2 Hz, 3H, -CH-), 7.37 (d, *J*=7.7 Hz, 6H, Ar-H), 7.78 (d, *J*=7.7 Hz, 6H, Ar-H). IR (KBr) (cm^{-1}): 2979, 1598, 1360, 1179, 1143, 938. Found: C: 52.92; H: 5.53; S: 13.42%. Calcd. for $C_{30}H_{36}S_3$: C: 52.61; H: 5.30; S: 14.05%.
9 2,4,6-Tris(2-benzyloxyethyl)-1,3,5-trioxane as an oily substance. ^{1}H-NMR: (90 MHz, $CDCl_3$) δ (ppm): 1.96 (q, *J*=5.9 Hz, 6H, -CH_2-), 3.55 (t, *J*=5.9 Hz, 6H, OCH_2), 4.45 (s, 6H, $PhCH_2O$), 5.07 (t, *J*=5.9 Hz, 3H, -OCHO-), 7.29 (s, 15H, Ar-H). IR (neat) (cm^{-1}): 2862, 1415, 1367, 1144, 1089, 1027, 738, 698. Found: C: 73.05; H: 7.40%. Calcd. for $C_{30}H_{36}O_6$: C: 73.15; H: 7.37%. MS (FABMS): m/e 493 (MH^+).
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