Autocatalytic Fragmentation of Acetoacetate Derivatives as Acid Amplifiers to Proliferate Acid Molecules

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Abstract: A novel concept of acid proliferation to improve the photosensitivity of chemically amplified photoresist materials is described by presenting the autocatalytic fragmentation of acetoacetates having a (sulfonyloxy)methyl residue to liberate the corresponding sulfonic acid. 2-Methyl-2-((methane- or *p*-toluenesulfonyloxy)methyl)acetoacetates were designed to be subjected to the acid-catalyzed fragmentation through the corresponding acetoacetic acids which are readily decarboxylated and undergo the subsequent β-elimination to give a sulfonic acid which can act as the autocatalyst to lead to the increment of acid concentration in geometric progression. Among the acetoacetates tested, *tert*-butyl 2-methyl-2-((*p*-toluenesulfonyloxy)methyl)acetoacetate was the most suitable reagent for the present purpose because of its reasonable thermal stability. A nonlinear generation of the sulfonic acid was confirmed in the acidolytic transformation of the acetoacetate in nonpolar solvents and in a film of poly[4-((*tert*-butoxycarbonyl)oxy)styrene] (PBOCSt), respectively. It was found that the addition of the acetoacetate to a film of PBOCSt doped with a photoacid generator enhances the photosensitivity characteristics.

A catalyst is defined as a chemical species which initiates and/or accelerates a thermodynamically favorable reaction without any change of its concentration during the chemical transformation. One class of important catalysts is unequivocally acidic substances which enhance rates of versatile organic reactions including hydrolytic reactions, rearrangements, and eliminations. If an acid can be produced by an acid-catalyzed transformation of a precursor substrate to result in the increment of the amount of acidic species in a manner of geometric progression, subsequent acidolytic reaction rates should be enhanced exponentially, being essentially different from the kinetics of ordinary acidolytic reactions. This idea led us to carry out the molecular design and the synthesis of an acid precursor which is reasonably called an acid amplifier since the compound creates acid molecules more than it reacts with. Acid amplification processes can be coupled with versatile acidolytic reactions to develop various types of nonlinear chemical transformations. Our particular interest is the combination of a photoacid generator with an acid amplifier since a tiny amount of a photogenerated strong acid may be bred to result in the drastic enhancement of a subsequent acidolytic reaction by the autocatalytic decomposition of the acid amplifier. This leads to the improvement of photosensitivity of chemical amplification type photoimaging materials triggered by photogenerated acids.[1]

Our efforts have been focused on the development of acid amplifiers which should fulfill the following requirements. First, an acid amplifier should be readily subjected to an acid-catalyzed decomposition to liberate a strong acid which is capable of catalyzing the decomposition of itself. Second, an acid amplifier should be thermally stable in the absence of an acid at least under the reaction conditions to advance the autocatalytic decomposition and a subsequent acid-catalyzed reaction. Third, a liberated acid should be strong enough to catalyze subsequent chemical reaction(s) to display a nonlinear chemical transformation. The major concerns of this paper are to present acetoacetate derivatives which meet these requirements and to show that a novel photoimaging system is realized by the combination of the acid amplifier with a photoacid generator and an acid-labile polymer.[2] Other acid amplifiers with different chemical structures have been developed and reported elsewhere.[3,4]

Results

Molecular Design and Synthesis. An acid formed by the autocatalytic decomposition of an acid amplifier should be strong enough to trigger a conjugated acidolytic reaction. We employed sulfonates as acid precursors, taking the following into account: sulfonic acids are of sufficiently strong acidity to catalyze diversified organic reactions and are readily available by the esterification of alcohols. It has been well established that acidic molecules are liberated with ease as a result of β-elimination when the β-carbon is activated by electron-withdrawing group(s). This suggests reversely that the β-elimination may be suppressed effectively by the absence of hydrogen atoms at the β-carbon. This had led us to an idea to

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[⊗] Abstract published in *Advance ACS Abstracts*, December 15, 1997.

(1) Reichmanis, E. In *Polymers for Electronic and Photonic Applications;* Wong, C. P., Ed.; Academic Press: San Diego, 1993; p 67.

(2) A preliminary report: Ichimura, K.; Arimitsu, K.; Kudo, K. *Chem. Lett.* **1995**, 491.

(3) Kudo, K.; Arimitsu, K.; Ichimura, K. *Mol. Cryst. Liq. Cryst.* **1996**, *280*, 307.

(4) (a) Noguchi, S.; Arimitsu, K; Ichimura, K.; Kudo, K; Ohfuji, T.; Sasago, M. *J. Photopolym. Sci. Technol.* **1997**, *10,* 315. (b) Ohfuji, T.; Takahashi, M., Sasago, M.; Noguchi, S.; Ichimura, K. *J. Photopolym. Sci. Technol.* **1997**, *10,* 551.

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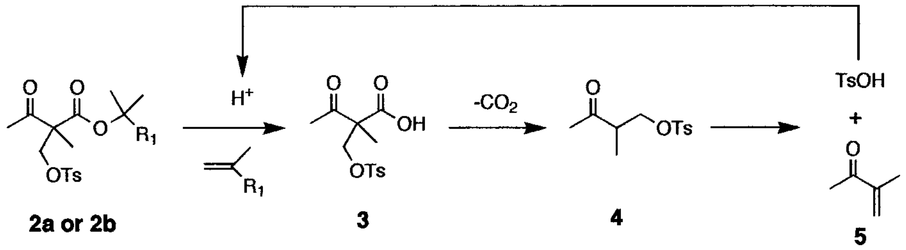
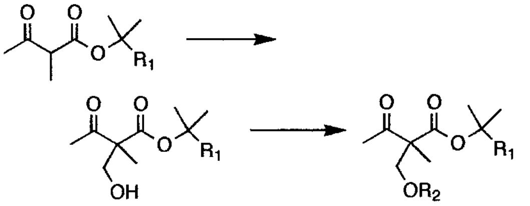
Scheme 1. Autocatalytic Fragmentation of **2a**



Scheme 2. Preparation of Acid Amplifiers



1 a: $R_1 = CH_3$
b: $R_1 = C_6H_5$

2 a: $R_1 = CH_3$, $R_2 = p\text{-}CH_3C_6H_4SO_2$
b: $R_1 = C_6H_5$, $R_2 = p\text{-}CH_3C_6H_4SO_2$
c: $R_1 = CH_3$, $R_2 = \text{-}CH_3SO_2$
d: $R_1 = C_6H_5$, $R_2 = CH_3SO_2$
e: $R_1 = CH_3$, $R_2 = Cl_2CHCO$
f: $R_1 = C_6H_5$, $R_2 = Cl_2CHCO$
g: $R_1 = CH_3$, $R_2 = C_6H_5CO$

protect β-hydrogen with a suitable acid-labile group like a (*tert*-alkylcarbonyloxy) residue. We consequently designed *tert*-alkyl 2-methyl-2-((sulfonyloxy)methyl)acetoacetates (**2a**−**d**) as acid amplifiers. The sulfonates possesses no hydrogen atom at the β-carbon so the thermal reaction is expected to be retarded. On the other hand, the action of acid causes the decomposition of the ester group, accompanied by the elimination of the corresponding olefin and carbon dioxide, to yield a β-ketosulfonyloxy compound which readily undergoes the β-elimination of sulfonic acid owing to the acetyl residue (Scheme 1).

The acetoacetates (**2**) were prepared according to Scheme 2. *tert*-Alkyl acetoacetate was monomethylated, followed by the hydroxymethylation with formalin under an alkaline condition to give hydroxylated derivatives (**1**).[5] Four derivatives were prepared from **2** with the esterification with *p*-toluenesulfonyl chloride and methanesulfonyl chloride, respectively. For comparison, three carboxylates (**2e**−**g**) were prepared by the esterification of **1** with dichloroacetyl chloride and benzoyl chloride, respectively. They were purified by column chromatography. Among the compounds thus prepared, the acetoacetates substituted with *p*-toluenesulfonyloxy (TsO) (**2b**: R = C_6H_5, X = TsO) and methanesulfonyloxy (MsO) (**2c**: R = CH_3, X = MsO and **2d**: R = C_6H_5, X = MsO) turned black in color abruptly with the complete consumption of the actoacetates to form the corresponding acid during the course of storage in a neat state for few days at room temperature. This sudden degradation suggests that it proceeds in a nonlinear manner. They were stored in a refrigerator for relatively longer terms.

Thermal Decomposition in Solutions. The acidolytic behavior of **2** in a 3:1 mixture of diphenyl ether and toluene-d_8 solution at an elevated temperature was followed by NMR spectroscopy. The formulation and experimental results are summarized in Table 1. Because of the hard solubility of *p*-toluenesulfonic acid (TsOH) in hydrocarbon solvents such as toluene, the mixture was employed as a solvent. No change in an NMR spectrum of **2a** was observed upon heating of a solution at 100 °C for 2 h in absence of TsOH (run 1). On the other hand, the decomposition of **2a** was induced by TsOH at the same temperature (run 2). The acid-catalyzed fragmentation of **2a** was followed by monitoring the decrease of the proton signals due to *tert*-butyl ($\delta = 1.28$) and β-methyl ($\delta = 1.28$) groups while the formation of the unsaturated ketone (**5**) was checked by the proton signal due to its vinyl group ($\delta = 5.50$) with the use of 2-methoxynaphthalene as an internal standard. Figure 1 shows that both the consumption of **2a** and the formation of **5** take place abruptly to display a sigmoidal time course, indicating that the fragmentation proceeds autocatalytically to lead to the proliferation of the acid. As seen in Figure 1, no quantitative formation of **5** was observed. The reduction of the yield of **5** may be ascribable to a partial loss due to radical polymerization. The figure indicates also that the rate of formation of **5** coincides with that of the consumption of **2a**. This reflects probably that the decarboxylation of the acetoacetic acid **3** and the subsequent β-elimination of β-tosyloxy ketone **4** take place reasonably fast though no identification of these intermediates was achieved because of complicated NMR signals of a reaction mixture (Scheme 2). The almost quantitative formation of TsOH in a 98% yield was confirmed separately by the titration of a reaction mixture of **2a** in a THF solution after 3 h of heating under reflux in the presence of TsOH.

Table 1. Acid-Catalyzed Decomposition of the Acetoacetates **2**

			concentration (mmol dm^{-3})			
run	AA[a]	acid[b]	AA[a]	acid	solvent[c]	remarks
1	**2a**	none	70	0	DE-TL	Figure 1
2	**2a**	TsOH	70	25	DE-TL	Figure 1
3	**2a**	none	65	0	DE-TL/MeOH	Figure 2
4	**2a**	TsOH	65	2.0	DE-TL/MeOH	Figure 2
5	**2a**	TsOH	65	28	DE-TL/MeOH	Figure 2
6	**2a**	none	58	0	TL	Figure 3
7	**2a**	TsOH	70	85	DO	no reaction
8	**2a**	TsOH	290	29	DO	no reaction
9	**2c**	none	83	0	TL	Figure 4
10	**2c**	MsOH	76	23	TL	Figure 4
11	**2e**	DCA	80	9.3	DT	no reaction
12	**2e**	DCA	78	9.8	TL	no reaction
13	**2f**	none	73	0	TL	Figure 5
14	**2f**	DCA	73	23	TL	Figure 5
15	**2f**	DCA	80	63	DO	no reaction
16	**2f**	TsOH	110	8.8	DO	negligible reaction

[a] AA, acetoacetate (**2**). [b] TsOH, *p*-toluenesulfonic acid; MsOH, methanesulfonic acid; DCA, dichloroacetic acid. [c] TL, toluene; DE-TL, a 3:1 (v/v) mixture of diphenyl ether and toluene; MeOH, methanol; DO, dioxane.

The thermal behavior of **2a** displayed considerable solvent dependence. When methanol was added to a mixed solvent of diphenyl ether and toluene-d_8 to enhance the solubility of TsOH, no degradation of **2a** was caused by heating at 100 °C in the

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[5] (a) Hiroi, K.; Abe, J. *Chem. Pharm. Bull.* **1991**, *39*, 616. (b) Wilson, B. D. *J. Org. Chem.* **1963**, *28*, 314.

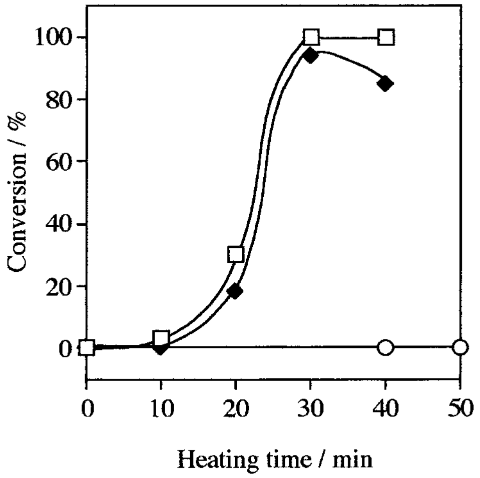

Figure 1. Time courses of the consumption of **2a** (□) and the formation of methyl isopropenyl ketone (◆) in the presence of 25 mmol dm^{-3} *p*-toluenesulfonic acid and of the conversion of **2a** in the absence of sulfonic acid (○) in a 3:1 mixture of diphenyl ether and toluene-d_8 at 100 °C.

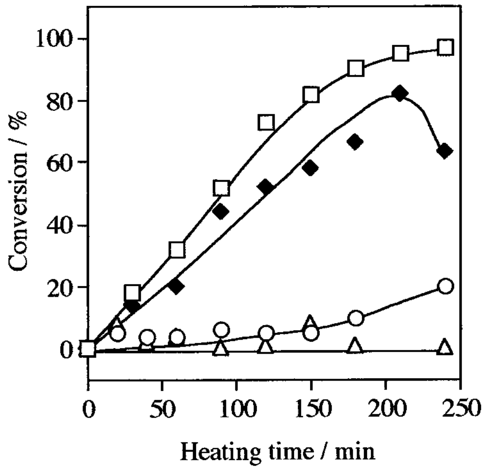

Figure 2. Time courses of the consumption of **2a** in the absence of (△) and in the presence of 2.0 mmol dm^{-3} (○) and 28 mmol dm^{-3} (□) *p*-toluenesulfonic acid and the formation of methyl isopropenyl ketone (◆) in the presence of 28 mmol dm^{-3} of the acid in a 3:1 mixture of diphenyl ether and toluene-d_8 containing 7.5 v/v % of methanol-d_4 at 100 °C.

absence and in the presence of a small amount of TsOH (runs 3 and 4 in Table 1). Although a large amount of TsOH results in the consumption of **2a** leading to the formation of **5**, no sigmoidal curve was observed (run 5) (Figure 2). In a sharp contrast to these results, **2a** displayed an abrupt decomposition with a sigmoidal time conversion curve when the compound was heated in toluene-d_8 as a nonpolar solvent at 100 °C even in the absence of TsOH (run 6), as shown in Figure 3. The result suggests that **2a** suffers from a pyrolytic decomposition to give TsOH, which accelerates the fragmentation reaction. These results all imply that **2a** itself is subjected to monomolecular fragmentation reaction upon prolonged heating at an elevated temperature to produce TsOH and that the acidolytic deprotection of **2a** is considerably suppressed by solvents such as methanol in diphenyl ether which act as weak bases. In fact, it was confirmed that **2a** was quite thermally stable in dioxane-d_8 (runs 7 and 8) even though the solution was contaminated with TsOH. Dioxane acts as proton acceptor so effectively that the acid-catalyzed deprotection of *tert*-butyl ester is severely retarded.

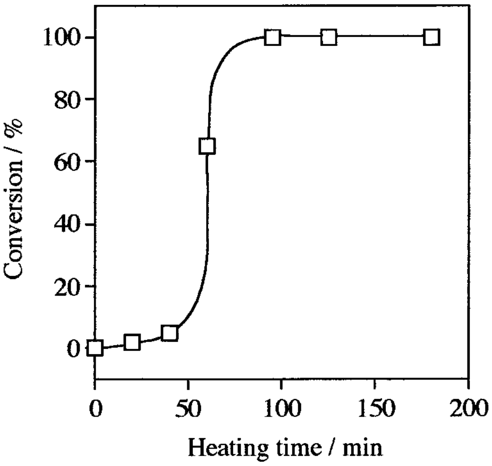

Figure 3. Time course of the consumption of **2a** in toluene-d_8 at 100 °C.

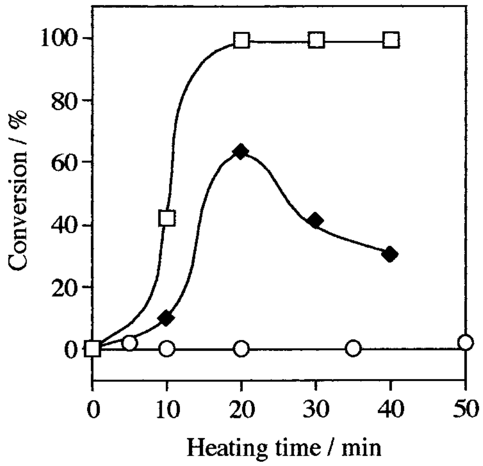

Figure 4. Time courses of the consumption of **2c** (□) and the formation of methyl isopropenyl ketone (◆) in the presence of 23 mmol dm^{-3} methanesulfonic acid and of the conversion of **2c** in absence of the sulfonic acid (○) in toluene-d_8 at 100 °C.

It was found that **2c** shows no degradation even at 100 °C for a while in toluene in absence of methanesulfonic acid (MsOH) (run 9). A sigmoidal increase in the conversion was induced when a toluene solution was heated in the presence of MsOH, as given in Figure 4. Methyl isopropenyl ketone (**5**) demonstrated a maximum yield during heating, followed by a decrease in the yield, probably again because of the polymerization.

The *tert*-butyl acetoacetate having a dichloroacetoxy residue (**2e**) was quite thermally stable even in the presence of dichloroacetic acid, indicating that this ester cannot serve as an acid amplifier (runs 11 and 12). It follows that 2-phenyl-2-propylacetoacetate with a dichloroacetoxy group (**2f**) was subjected to the determination of acidolytic reaction in toluene since the deprotection of the ester proceeds much faster than the *tert*-butyl ester (runs 13 and 14).[6] As shown in Figure 5, **2f** displays an abrupt increase in the conversion in the presence of dichloroacetic acid, indicating that the disappearance of the acetoacetate proceeds in a nonlinear manner though the rate was much slower.

Thermal Behavior of the Acetoacetates in Polymer Films. In order to confirm the third requirement for an acid amplifier, acetoacetate **2a** was coupled with a polystyrene substituted with (*tert*-butoxycarbonyl)oxy (*t*-BOC) residues (PBOCSt) (**6**) as an

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[6] Sieber, P.; Iselin, B. *Helv. Chim. Acta* **1968**, *51*, 614.

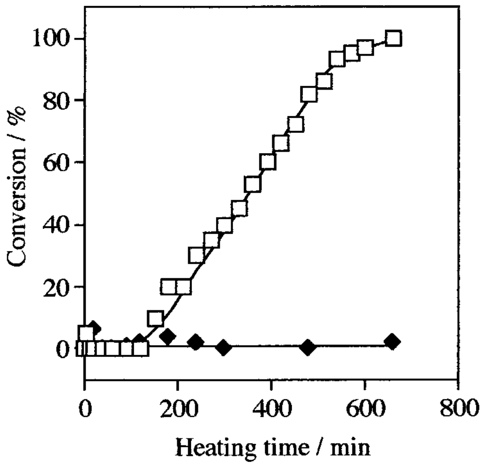

Figure 5. Time courses of the consumption of **2f** in the absence of (◆) and in the presence of (☐) 23 mmol dm^{-3} dichloroacetic acid in toluene-d_8 at 100 °C.

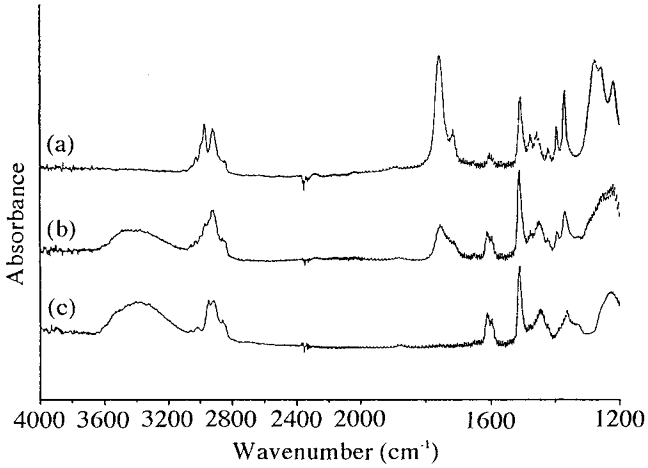

Figure 6. IR spectral change of a film of PBOCSt containing 10 wt % of **2a** (a) before and after heating at 100 °C for (b) 105 and (c) 120 min.

acid-labile polymer.[7] A thin film of PBOCSt containing 10 wt % of **2a** was spin-coated on a silicon wafer and heated at 100 °C. No essential change in IR spectra of the film was observed at the early stage of heating. But upon prolonged heating, the C=O stretching vibration due to the carbonyl residue of **2a** at 1719 cm^{-1} and that due to carbonate of PBOCSt at 1762 cm^{-1} disappeared quite suddenly, accompanied by the abrupt appearance of a broad absorbance at *ca.* 3400 cm^{-1} ascribable to phenolic OH, supporting the deprotection of the *t*-BOC residues (Figure 6). This shows that **2a** decomposes thermally in a polymer matrix just as in the case of a toluene solution upon prolonged heating and that the acid thus formed initiates acid amplification as a result of autocatalytic transformation of **2a**. This situation is visualized by plotting peak heights of C=O vibrations of both of PBOCSt and **2a** as a function of heating period, as given in Figure 7. **2a** showed no marked alteration of an IR absorption spectrum at least for *ca.* 1 h. The carbonyl absorption band decreased abruptly after prolonged heating for about 80 min, accompanied by the decrease in the absorption band due to the carbonate group of the acid-labile polymer. These results indicate clearly that the thermal decomposition of **2a** liberates TsOH, which catalyzes both the self-decompsition of **2a** and the deprotection of PBOCSt.

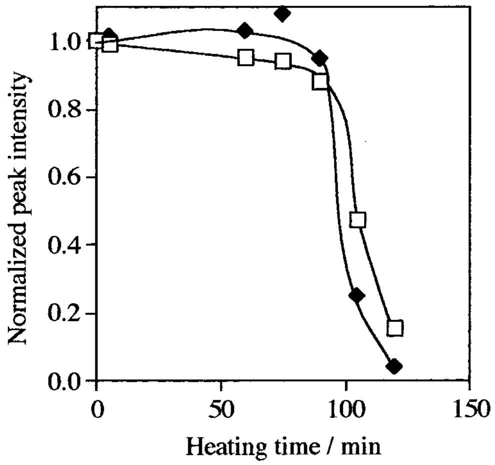

Figure 7. Time courses of the consumption of 10 wt % of **2a** (☐) and the deprotection of PBOCSt (◆) in a film.

Pyrolytic behavior of the other acetoacetates was determined in PBOCSt films. **2b** having a more acid-labile 2-phenyl-2-propyl ester group decomposed more rapidly in a film of the polymer. The C=O bands of both **2b** and the polymer disappeared completely after heating for 3 min at 100 °C, indicating that this compound is so thermally labile that it is hard to apply to photoimaging materials, as mentioned below. On the contrary, the *tert*-butyl ester having a mesyloxy group (**2c**) exhibited different behavior in a polymer film. The heat treatment of a PBOCSt film containing 100 mol % of **2c** at 100 °C resulted in the gradual reduction of the C=O band due to the ketone of **2c** whereas no alteration was observed in the C=O absorption bands of the polymer. This means evaporation of the acetoacetate from a polymeric film during heating without any thermal decomposition. The acetoacetates bearing dichloroacetoxy group (**2e** and **2f**) gave similar results when they were doped in polymer films. Being judged from these data, it was concluded that **2a** fulfills all requirements for the present purpose to achieve acid proliferation.

Acid Proliferation in Photosensitive Polymer Films. The phototriggered acid proliferation as a result of autocatalytic fragmentation was determined by the use of a film of PBOCSt doped with 30 wt % of **2a** in the presence of 3.6 wt % of (tosyloxy)methylated benzoin (**7**) which generates TsOH upon UV irradiation.[8] A thin film of PBOCSt containing **2a** and **7** was spin-cast on a silicon wafer. Film thickness was adjusted to *ca.* 0.30 μm so that films are put in color due to the interference of light. In this way, the progress of the acid-catalyzed polymeric reaction was monitored in real time during heat treatment after UV irradiation simply by observing the interference color changes due to the film thickness being markedly reduced bcause of the elimination of isobutene and carbon dioxide (Scheme 3). When a film was heated on a hot plate at 100 °C after UV irradiation through a circular window of a 3 mm diameter, a rapid color change took place exclusively at an irradiated area within a few seconds.

Surprisingly, prolonged heating of the film gave birth to the gradual enlargement of the circle in a concentric manner as a result of the lateral expansion of the color change to unexposed areas, as given in Figure 8 when 30 wt % of **2a** was added. Other photoacid generators which genenerate strong acids other than TsOH resulted in a similar phenomenon. Figure 9 shows the concentric expansion of color-changed circles as a function of heating time when diphenyl (4-phenylthiophenyl)sulfonium

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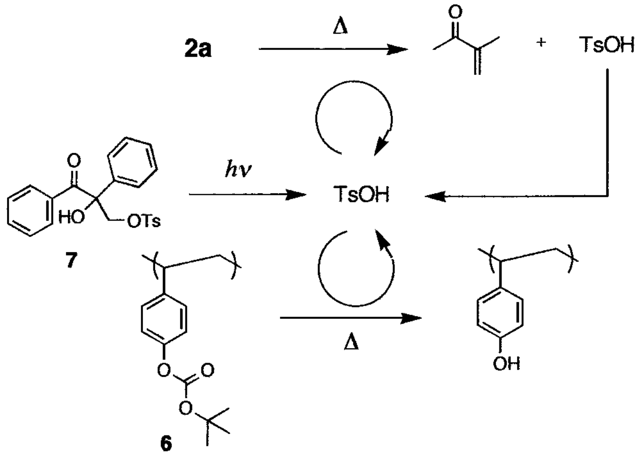
[7] Ito, H.; Willson, C. G.; Fréchet, J. M. J. *Digest of Technical Papers of 1982 Symposium on VLSI Technology*, **1982**, 86.

[8] Röschert, H.; Eckes, Ch.; Pawlowski G. *SPIE* **1993**, *1952*, 342.

Scheme 3. Working Principle of an Acid Proliferation-Type Photopolymer System



hexafluoroantimonate (**8**) was employed as a photoacid generator. In the case of a lower concentration of 10 wt % of the acetoacetate (**2a**), the expansion of color-bleached area slowed down upon prolonged baking, probably because of the gradual evaporation of the acid amplifier from a film. In order to check a plasticizing effect of **2a**, a system containing 29 wt % of a related compound, *tert*-butyl 2-methyl-2-((benzoyloxy)methyl)-acetoacetate (**2g**) was examined. This compound liberates benzoic acid with much weaker acidity and hence cannot act as an acid amplifier. It was confirmed that no area expansion is induced at all. These mean that the area expansion of the polymer decomposition reflects the proliferation of TsOH in a polymer matrix and is not due to the plasticizing effect.

The effect of addition of **2a** on the performances of the so-called chemically amplified photoresists was examined by using a typical chemically amplification photoresist consisting of poly(*t*-BOC-styrene) (**6**)[7] and tosyloxylated benzoin (**7**).[8] The results are shown in Figure 10. Thin films of polymers doped with the photoacid generator in absence or in the presence of 10 wt % of **2a** were exposed to UV light for various periods, followed by heat treatment as a postexposure baking. The extent of acid-catalyzed deprotection of *t*-BOC side chains was estimated by measuring film thickness, because the thickness is reduced up to *ca.* 60% as a result of the elimination of *t*-BOC residues. Although the addition of **2a** displays no effect on the photosensitivity characteristics upon heating for 1 min (Figure 10a), the postexposure baking for 3 min results in an abrupt decrease in the film thickness at UV exposure period of 200 s or longer, as seen in Figure 10c. The abrupt changes in IR spectra of films were also observed to support the deprotection of *t*-BOC residues.

Discussion

There have been only few reports on the autocatalytic generation of a strong acid. It was mentioned by Winstein et al. in a series of their systematic studies on solvolytic reactions without any experimental support that the reaction of a *p*-methoxyneophyl toluenesulfonate proceeds autocatalytically in benzene.[9] On the other hand, Nenitzescu et al. suggested that a cycloalkyl benzenesulfonate demonstrates autocatalytic elimination reaction to produce a cycloalkene and benzenesulfonic acid which adds to the cycloalkene again to result in a reversible elimination/addition process.[10] The time conversion curve of this process is sigmoidal, implying an autocatalytic reaction. As seen in Figure 1, the acid-catalyzed reaction of the acetoacetate substituted with a tosyloxy residue (**2a**) proceeds in a sigmoidal manner, indicating that the consumption of **2a** takes place autocatalytically. The unsaturated ketone **5** as a product is formed in a nonlinear manner in line with the disappearance of **2a**. This implies that the intermediates such as the deprotected acetoacetic acid (**3**) and the β-tosyloxy ketone (**4**) are short-lived in the present reaction conditions.

The marked solvent dependence of the autocatalytic process is interpreted as follows. The deprotection of **2a** is initiated by the protonation of an acidic catalyst at an oxygen atom of the ester residue so that any solvent molecules having oxygen atom(s) compete with **2a** in the protonation. The level of suppression of the acidolytic fragmentation of **2a** is determined by the basicity of solvents. As summarized in Table 1, dioxane quenches completely the acidolytic reaction. Methanol is also an effective quencher. These results arise from the basicity of these solvents, pK_a's of conjugated acids of dioxane and methanol are -2.92[11] and -2.2,[12] respectively, whereas ester groups have a pK_a of *ca.* -6.0.[13] Besides, these systems involve a large excess amount of solvent molecules so that even pyrolytic decomposition of **2a**, leading to the formation of TsOH, has essentially no role in the acidic catalysis. On the other hand, the autocatalytic fragmentation proceeds in a mixture solvent of diphenyl ether and toluene-d_8 due to the lower bacisity of the aromatic ether. Figures 3 and 4 demonstrate the sigmoidal consumption of the corresponding acetoacetates since toluene molecules are hardly protonated by TsOH and MsOH. In other words, the behavior of both acetoacetates in toluene reflects their inherent thermal lability and autocatalytic processes, respectively. It is safe to say that both *tert*-butyl esters bearing tosyloxy and mesyloxy residues (**2a** and **2c**) are not deteriorated upon heating at 100 °C for 50 min or more. This is important information concerning their applicability to the acid proliferation coupled with acidolytic reactions of polymer side chains to provide a novel photoimaging materials such as chemically amplified photoresists.

The results shown in Figure 7 demonstrate unequivocally that the autocatalytic fragmentation of **2a** is brought about even in polymeric films and that the acid-generated TsOH catalyzes the deprotection of *tert*-butyl carbonate residues. The unique features of this system are brought into relief by the results shown in Figures 8 and 9. The area, where *tert*-butyl carbonate side chains are deprotected by TsOH, increases upon heat treatment in a manner of geometrical progression. Therefore, it is reasonable to refer the autocatalytic acid generation as the acid proliferation reaction. **2c** does not meet the requirements for the acid proliferation in polymeric films because of the volatility leading to the escape during heat treament. However, as Figure 4 shows, this mesyloxylated acetoacetate seems to be a good candidate for acid proliferation systems if the suppression of the volatility is enhanced, taking into account the faster fragmentation, when compared with the tosyloxylated counterpart shown in Figure 3. The suppression of the volatility should be overcome by suitable ways, including the increase in the molecular weight of a mesyloxylated acetoacetate.

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(9) Smith, S. G.; Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1961**, *83*, 618.

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(11) Arnett, M.; Wu, C. Y. *J. Am. Chem. Soc.* **1960**, *82*, 4999.

(12) Gold, V.; Laali, K.; Morris, K. P.; Zdunek, L. Z. *J. Chem. Soc., Parkin Trans. 2* **1985**, 865.

(13) Bagno, A.; Scorrano, G.; Lucchini, V. *Gazz. Chim. Ital.* **1987**, *117*, 475.

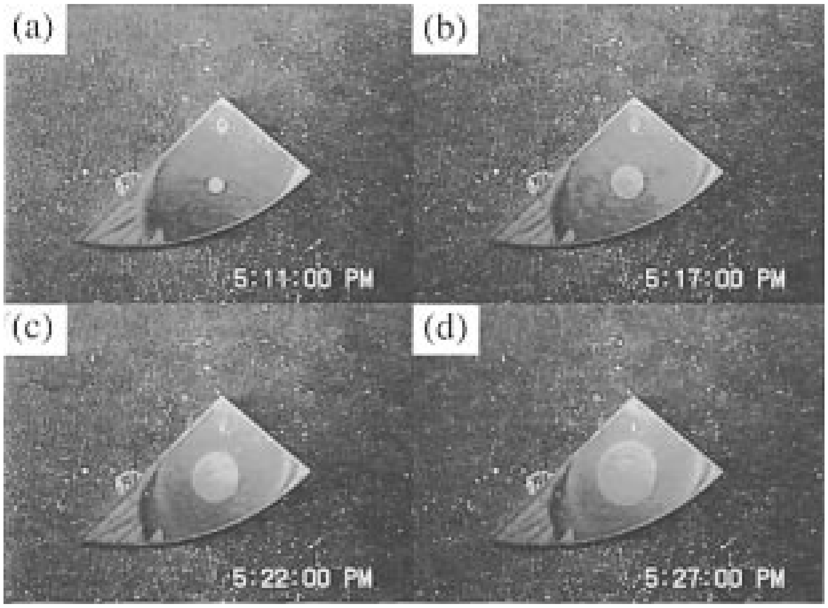

Figure 8. Photographs of a silicon wafer spin-cast with a 0.3 μm thick film of PBOCSt containing 3.6 wt % of the photoacid generator (**7**) and 30 wt % of **2a** upon heating at 100 °C for (a) 4, (b) 10, (c) 15, and (d) 20 min after UV irradiation through a circular window of 3 mm diameter.

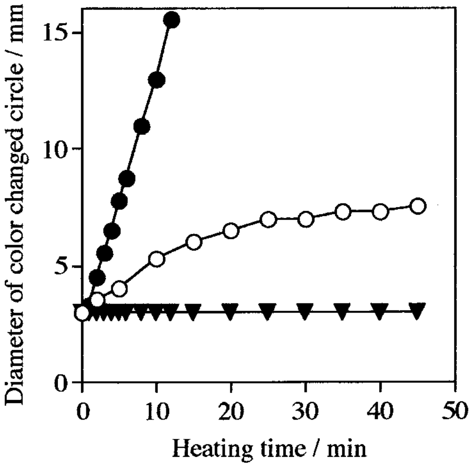

Figure 9. Expansion of the diameter of circular deprotected area of a film of PBOCSt containing 5.5 wt % of diphenyl (4-(phenylthio)-phenyl)sulfonium hexafluoroantimonate as a photoacid generator in the absence of (▼) and in the presence of 10 wt % (○) and 30 wt % (●) of **2a** upon heataing at 100 °C.

From a practical viewpoint, the drastic expansion of acidolytic areas upon heating as shown in Figures 8 and 9 is a fatal drawback when this system is applied to microphotopatterning owing to the considerable decrease in the resolution power. On one hand, it was reported that photogenerated acid molecules migrate within a sphere representing a diffusion range in polymer matrices.[14−17] On the basis of a chain length of the acidolytic deprotection of *t*-BOCSt polymer, the radius of this sphere was estimated to be approximately 5 nm when resist films are heated for 1 min.[14] On the other hand, it was described that the diffusion range of an acid photogenerated in a Novolak resin film into another fresh acid-labile polymer film is markedly influenced by the size of acidic species and comes to less than 100 nm for TsOH upon heating for 60 min.[15] It was also mentioned that a remaining solvent in a chemically amplified photoresist enlarges the diffusion range of an acidic species; a diffusion range is *ca.* 200 nm when 1 wt % of a solvent remains.[16] These values are too small when compared with the extent of the lateral expansion shown in Figure 9. This implied that the area expansion of acidolytic deprotection occurs through a phenomenon quite different from the diffusion in polymer solids.

It was found that the lateral expansion is practically prohibited by covering a photosensitive polymer film with a spin-cast Novolak film or simply with a glass slide. These facts support that the theory that the marked lateral expansion of the present system does not arise from the diffusion of TsOH within a polymer matrix but from the evaporation from and landing of acid molecules on a film surface, leading to the “air infection”. Although the evaporation of a photogenerated acid from a polymeric layer has been detected and discussed in connection with the improvement of performances of photoresists,[18,19] it is evident that the evaporation mechanism of the present system is quite different from that of chemically amplified photoresists. As seen in Figure 9, no expansion of the area was observed on a millimeter scale when no acid amplifier was added to give a conventional chemically amplified photoresist.

Although the effect on the photosensitivity characteristics of a chemically amplified photoresist was observed as seen in Figure 10, the level of amplification by autocatalytic acid generation is not so remarkable. Three possilibities should be considered. The first one is that the acid-calalyzed deprotection of *t*-BOC side chain takes place much faster than the acid-catalyzed fragmentation of **2a** so that no marked enhancement in photosensitivity is realized. This is not the case as revealed by IR spectral changes of a film doped with **2a** (Figure 6). Both *t*-BOC and **2a** disappear suddenly upon heating, indicating that there is no marked difference in the deprotection rate between *t*-BOC residues and **2a**. The second possibility is that **2a** acts

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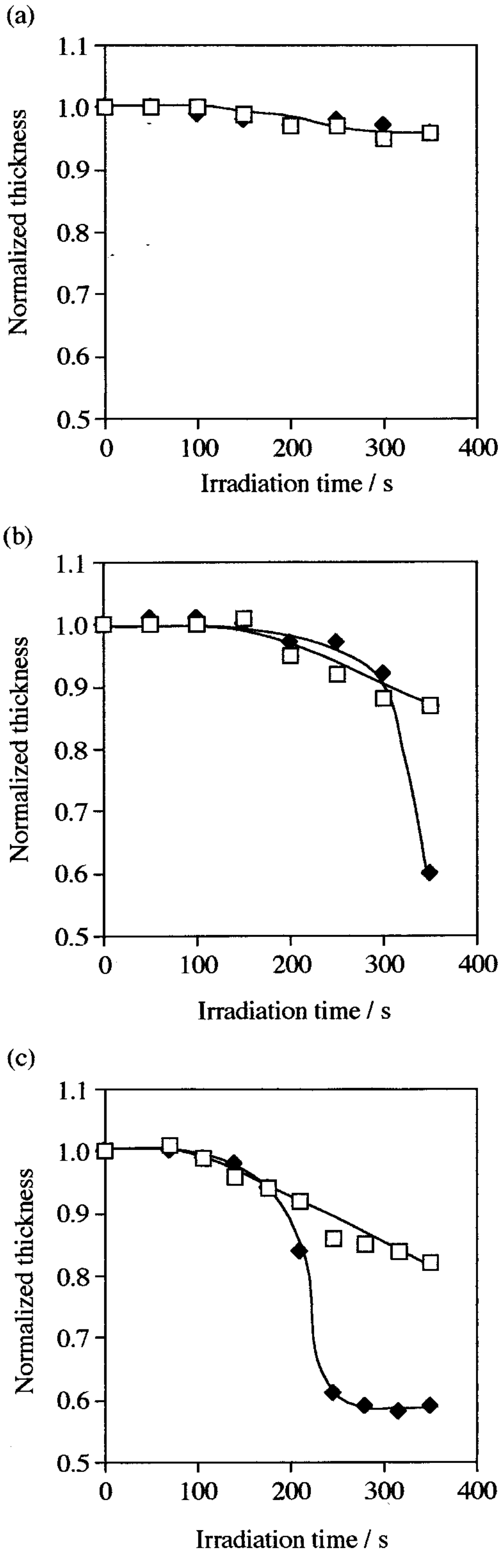

Figure 10. Photosensitivity curves of films of PBOCSt containing 3.6 wt % of the photoacid generator (**7**) in the absence of (□) and in the presence of 10 wt % of **2a** (◆). The films were exposed to UV light, followed by heating at 100 °C for (a) 1, (b) 2, and (c) 3 min, respectively.

as a quencher of excited state(s) of a photoacid generator. It seems to be likely that triplet energy transfer occurs in solid films. This is also not feasible, however, because both **2a** and a photoacid generator (**7**) bear a common aliphatic $C{=}O$ chromophore so that the specific quenching of triplet excited state of **7** by **2a** takes place only scarcely. Another possibility is based on the entrapment of a generated acid species by some kind of proton acceptor(s) in polymer films. In fact, as given in Table 1, solvent molecules having proton acceptor site(s) such as dioxane and methanol suppress critically the autocatalytic fragmentation. In the present polymeric systems, there seem to be many trapping sites capable of protonation by TsOH including *t*-BOC side chains, phenolic OH residues as a deprotected functional residue, and some degradation products derived from **2a**. Although detailed investigation is required, it is very likely that the acid proliferation is suppressed by this mechanism. In other words, an appropriate choice of acid-labile polymers with much lower basicity may exhibit the marked enhancement of photosensitivity in the presence of an acid amplifier. Endeavor to boost the photosensitivity of chemically amplified photoresist systems has been concentrated so far predominantly on the improvement of quantum efficiency of photoacid generation and the optimization of chemical structures of acid-labile polymers. We anticipate that the concept of acid prolifieration coupled with acidolytic reactions of polymer systems provides a novel way to improve the performances of photopolymers.[20] It is worthy to mention that an acid amplifier is practically applicable to 193 nm microphotolithography to enhance performances including superfine resolution of a chemically amplified photoresist.[4b]

Conclusion

Some of acetoacetate derivatives having (tosyloxy)methyl as well as (mesyloxy)methyl residues are subjected to the autocatalytic fragmentation to produce TsOH or MsOH which subsequently catalyzes the deprotection of *tert*-butyl carbonate side chains attached to polystyrene. This type of reaction is reasonably called the acid proliferation on account of the generation of catalytic acids in a manner of geometrical progression. Among the compounds tested, **2a** meets the requirements for the application to chemically amplified photoimaging materials because of its reasonable thermal stability and the ability to generate TsOH which possesses enough acidity to catalyze subsequent acidolytic reactions such as deprotection of polymer side chains. The addition of **2a** to a conventional chemically amplified photoresist consisting of *t*-BOC-styrene and a photoacid generator results in the enhancement of photosensitivity characteristics.

Experimental Section

Materials. *tert*-Butyl 3-ketobutanoate was commercially available while 2-phenyl-2-propyl ketobutanoate was prepared according to a literature.[21] Diphenyl (4-phenylthiophenyl)sulfonium hexafluoroantimonate was a gift from Midori Chemicals Co., Ltd. Poly(4-((*tert*-butoxycarbonyl)oxy)styrene) (PBOCSt)[7] and (tosyloxy)methylated benzoin[8] were prepared according to literatures.

***tert*-Butyl 2-Methyl-2-(hydroxymethyl)-3-ketobutanoate (1a).** To a suspension of sodium hydride (20 g; 0.51 mol) in 140 mL of THF was added *tert*-butyl acetoacetate (70 mL; 0.42 mol) dropwise under ice cooling, followed by stirring for 1 h. A solution of methyl iodide (31 mL; 0.5 mol) in 140 mL of THF was added to the reaction mixture under ice cooling, and the mixture was stirred for 2 days at room temperature. After the conventional workup, a colorless oil of bp_7 60 °C was obtained and weighed 54 g. Gas chromatography revealed that the product was a 2:1 mixture of monomethylated and dimethylated esters. The esters (24 g) were treated with 7.2 mL of formalin and 0.14 g of potassium hydroxide in 12 mL of ethanol. After 6 days of stirring at room temperature, the mixture was neutralized with dilute

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hydrochloric acid and extracted with benzene. An organic layer was washed with water, dried over magnesium sulfate, and subjected to column chromatography on silica gel to yield a yellowish oil weighing 7.6 g (20% yield). ^{1}H-NMR (CDCl$_3$): δ (ppm) 1.37 (s, 3H, C(CH$_3$)CO), 1.50 (s, 9H, C(CH$_3$)$_3$), 2.24 (s, 3H, CH$_3$CO), 2.89 (br t, J = 6 Hz, 1H, OH), 3.82 (br d, J = 6 Hz, 2H, CH$_2$O). IR (neat, cm^{-1}): 3502 (OH), 1725 ($>$C=O of ester), 1711 ($>$C=O). Anal. Found: C, 58.92; H, 9.23. Calcd for $C_{10}H_{18}O_4$: C, 59.39; H, 8.97.

2-Phenyl-2-propyl 2-Methyl-2-(hydroxymethyl)-3-ketobutanoate (lb). To a suspension of sodium hydride (4.72 g; 0.118 mol) in 40 mL of THF was added 2-phenyl-2-propyl 3-ketobutanoate (22 g; 0.099 mol) in 20 mL of THF dropwise under ice cooling, followed by stirring for 1 h. Subsequently, a solution of methyl iodide (6.1 mL; 0.098 mol) in 20 mL of THF was added to the mixture under ice cooling. The mixture was stirred for 22 h at room temperature, followed by dilution with ether and neutralization with dilute hydrochloric acid, followed by washing with a saturated aqueous solution of sodium hydrogen sulfite, a sodium bicarbonate solution, and a sodium chloride solution. The organic layer was dried over anhydrous sodium sulfate and evaporated to dryness to give 23 g of a crude methylated ester. The product was dissolved in 10 mL of ethanol and mixed with 7.8 mL of formalin and 0.1 g of potassium hydroxide. After stirring for 41 h at room temperature, benzene was added to the reaction mixture to be washed with dilute hydrochloric acid, a sodium bicarbonate solution, and a saturated sodium chloride solution. After the mixture was dried over anhydrous sodium sulfate, the solvent was evaporated off and an oily residue was purified by column chromatography on silica gel with a 10:1 mixture of hexane and ethyl acetate as an eluent to give 9.0 g (23% yield) of a yellowish oil. ^{1}H-NMR (CDCl$_3$): δ (ppm) 1.32 (s, 3H, C(CH$_3$)CO), 1.76 (s, 3H, OC(CH$_3$)$_2$), 1.80 (s, 3H, (CH$_3$)$_2$), 2.20 (s, 3H, CH$_3$CO), 2.70 (t, J = 7.0 Hz, 1H, OH), 3.80 (d of AB q, J = 7.0, 13 Hz, 2H, CH$_2$O), 7.30 (s, 5H, Ar-H). IR (neat, cm^{-1}): 3500 (OH), 1731 ($>$C=O of ester), 1711 ($>$C=O). Anal. Found: C, 66.32; H, 7.49. Calcd for $C_{14}O_{20}O_4$: C, 66.65, H, 7.99.

***tert*-Butyl 2-Methyl-2-((*p*-toluenesulfonyloxy)methyl)-3-ketobutanoate (2a).** To 20 mL of dichloromethane was added 4.5 g (24 mmol) of *p*-toluenesulfonyl chloride, 2.4 g (24 mmol) of triethylamine, and 1.2 g (10 mmol) of 4-(dimethylamino)pyridine, followed by stirring for 15 min at room temperature. A solution of 4.0 g of *tert*-butyl 2-methyl-2-(hydroxymethyl)-3-ketobutanoate (**1a**) in 15 mL of dichloromethane was added dropwise to the reaction mixture and heated for 8.5 h under reflux. The mixture was diluted with ether, washed with a saturated aqueous solution of copper sulfate and sodium chloride solution, and dried over magnesium sulfate to evaporate the solvent. An oily residue was purified by column chromatography on silica gel with a 10:1 mixture of hexane and ethyl acetate to afford 3.6 g (51% yield) of colorless crystals melting at 52−53 °C. ^{1}H-NMR (CDCl$_3$): δ (ppm) 1.38 (s, 3H, C(CH$_3$)CO), 1.40 (s, 9H, OC(CH$_3$)$_3$), 2.15 (s, 3H, CH$_3$CO), 2.47 (s, 3H, Ar-CH$_3$), 4.28 (AB q, J = 10 Hz, 2H, CH$_2$OSO$_2$), 7.38 (d, J = 7.7 Hz, 2H, Ar-H), 7.77 (d, J = 7.7 Hz, 2H, Ar-H). IR (KBr, cm^{-1}): 1738 ($>$C=O of ester), 1719 ($>$C=O). Anal. Found: C, 57.18; H, 6.90; S, 8.84. Calcd for $C_{17}H_{24}O_6S$: C, 57.29; H, 6.79; S, 9.00.

2-Phenyl-2-propyl 2-Methyl-2-((*p*-toluenesulfonyloxy)methyl)-3-ketobutanoate (2b). This was prepared in a similar manner in a 69% yield as a yellowish oil by the reaction of 2-phenyl-2-propyl 2-methyl-2-(hydroxymethyl)-3-ketobutanoate (**1b**) with *p*-toluenesulfonyl chloride. ^{1}H-NMR (CDCl$_3$): δ (ppm) 1.39 (s, 3H, C(CH$_3$)CO), 1.75 (s, 3H, OC(CH$_3$)$_2$), 1.79 (s, 3H, OC(CH$_3$)$_2$), 2.12 (s, 3H, CH$_3$CO), 2.44 (s, 3H, Ar-CH$_3$), 4.30 (AB q, J = 14 Hz, 2H, CH$_2$OSO$_2$), 7.30 (s, 5H, Ar-H), 7.35 (d, J = 8.7 Hz, 2H, Ar-H), 7.74 (d, J = 8.7 Hz, 2H, Ar-H). IR (neat, cm^{-1}): 2983, 1738 ($>$C=O of ester), 1716 ($>$C=O). Anal. Found: C, 62.98; H, 6.48; S, 6.76. Calcd for $C_{22}H_{26}O_6S$: C, 63.14; H, 6.26; S, 7.66.

***tert*-Butyl 2-Methyl-2-((methanesulfonyloxy)methyl)-3-ketobutanoate (2c).** To a solution of 0.90 g (4.5 mmol) of *tert*-butyl 2-methyl-2-(hydroxymethyl)-3-ketobutanoate (**1a**) and 0.52 g (5.1 mmol) of triethylamine in 2 mL of dichloromethane was added 0.51 g (4.5 mmol) of methanesulfonyl chloride in 2 mL of dichloromethane dropwise under ice cooling. After 1.5 h of stirring at room temperature, the reaction mixture was diluted with dichloromethane and washed with a saturated sodium bicarbonate solution and a sodium chloride solution. Drying over magnesium sulfate and evaporation of the solvent gave an oily residue which was purified by column chromatography on silica gel with benzene as an eluent. A viscous yellowish oily product weighed 1.2 g (97% yield). ^{1}H-NMR (CDCl$_3$): δ (ppm) 1.50 (s, 12H, C(CH$_3$)$_3$, C(CH$_3$)CO), 2.22 (s, 3H, CH$_3$CO), 3.05 (s, 3H, OSO$_2$CH$_3$), 4.50 (s, 2H, CH$_2$OSO$_2$). ^{13}C-NMR (CDCl$_3$): δ (ppm) 17.2 (CH$_3$), 27.2 (CH$_3$), 27.5 (CH$_3$), 36.9 (CH$_3$), 59.9 ($>$C$<$), 71.1 ($>$C$<$), 83.1 (CH$_3$), 168.3 (C=O), 202.7 (C=O). IR (neat, cm^{-1}): 2981, 1738 ($>$C=O of ester), 1714 ($>$C=O). Anal. Found: C, 47.33; H, 7.45; S, 10.3%. Calcd for $C_{11}H_{20}O_6S$: C, 47.13; H, 7.19; S, 11.44.

2-Phenyl-2-propyl 2-Methyl-2-((methanesulfonyloxy)methyl)-3-ketobutanoate (2d). This was prepared in a similar way in a 71% yield as a yellowish oil by the reaction of 2-phenyl-2-propyl 2-methyl-2-(hydroxymethyl)-3-ketobutanoate (**1b**) with methanesulfonyl chloride. ^{1}H-NMR (CDCl$_3$): δ (ppm) 1.49 (s, 3H, C(CH$_3$)CO), 1.75 (s, 3H, OC(CH$_3$)$_2$), 1.80 (s, 3H, O(CH$_3$)$_2$), 2.20 (s, 3H, CH$_3$CO), 2.90 (s, 3H, OSO$_2$CH$_3$), 4.48 (dd, J = 13 Hz, 2H, CH$_2$OSO$_2$), 7.30 (s, 5H, Ar-H). IR (neat, cm^{-1}): 2985, 1738 ($>$C=O of ester), 1714 ($>$C=O).

***tert*-Butyl 2-Methyl-2-((dichloroacetoxy)methyl)-3-ketobutanoate (2e).** A solution of 0.73 g (5.0 mmol) of dichloroacetyl chloride in 5 mL of THF was added dropwise to a solution of 1.0 g (4.9 mmol) of *tert*-butyl 2-methyl-2-(hydroxymethyl)-3-ketobutanoate (**1a**) and 0.53 mL (5.0 mmol) of 2,6-lutidine in 5 mL of THF under ice cooling and stirred for 3 h at room temperature. The reaction mixture was diluted with ether, washed with dilute hydrochloric acid, saturated sodium bicarbonate solution, and saturated sodium chloride solution, and dried over sodium sulfate. Evaporation of the solvent gave an oil which was subjected to column chromatography on silica gel with hexane as an eluent to give 0.28 g (18% yield) of the ester as a yellowish oil. ^{1}H-NMR (CDCl$_3$): δ (ppm) 1.45 (s, 12H, C(CH$_3$)$_3$, C(CH$_3$)CO), 2.20 (s, 3H, CH$_3$CO), 4.56 (s, 2H, CH$_2$OCO), 5.92 (s, 1H, CHCl$_2$). IR (neat, cm^{-1}): 2981, 1755 ($>$C=O of ester), 1713 ($>$C=O). Anal. Found: C, 46.09; H, 5.97; Cl, 22.84. Calcd for $C_{12}H_{18}O_5Cl_2$: C, 46.02; H, 5.79; Cl, 22.64.

2-Phenyl-2-propyl 2-Methyl-2-((dichloroacetoxy)methyl)-3-ketobutanoate (2f). This was synthesized in a similar way in a 77% yield as colorless crystals melting at 37−39 °C. ^{1}H-NMR (CDCl$_3$): δ (ppm) 1.47 (s, 3H, COC(CH$_3$)CO), 1.80 (s, 6H, OC(CH$_3$)$_2$), 2.20 (s, 3H, CH$_3$CO), 4.62 (s, 2H, CH$_2$OCO), 5.90 (s, 1H, CHCl$_2$), 7.30 (s, 5H, Ar-H). IR (KBr, cm^{-1}): 2985, 1770 ($>$C=O of ester), 1753 ($>$C=O of ester), 1714 ($>$C=O). Anal. Found: C, 53.88; H, 5.29; Cl, 19.79. Calcd for $C_{17}H_{20}O_5Cl_2$: C, 54.41; H, 5.37; Cl, 18.90.

***tert*-Butyl 2-Methyl-2-((benzoyloxy)methyl)-3-ketobutanoate (2g).** In a similar manner, benzoyl chloride instead of dichloroacetyl chloride was treated with *tert*-butyl 2-methyl-2-(hydroxymethyl)-3-ketobutanoate (**1a**) to give the ester in 52% yield as colorless crystals of mp 42−43 °C. ^{1}H-NMR (CDCl$_3$): δ (ppm) 1.40 (s, 9H, C(CH$_3$)$_3$), 1.48 (s, 3H, C(CH$_3$)CO), 2.25 (s, 3H, CH$_3$CO), 4.65 (s, 2H, CH$_2$OCO), 7.30−7.60 (m, 3H, Ar-H), 7.90−8.07 (m, 2H, Ar-H). IR (KBr, cm^{-1}): 2981, 1726 ($>$C=O of ketone, $>$C=O of ester). Anal. Found: C, 66.31; H, 7.33. Calcd for $C_{17}H_{22}O_5$: C, 66.65; H, 7.24.

Thermal Decomposition in Solutions. A 3-ketobutanoate (**2**) and 2-methoxynaphthalene as an internal standard were dissolved in a solvent containing a small amount of tetramethylsilane. The solution placed in an NMR tube was heated at 100 °C in an oven to be subjected to intermittent NMR measurement using a JEOL FX-90 NMR spectrometer to monitor the thermal stability of **2**. When no alteration in the NMR spectra was observed upon prolonged heating, *p*-toluenesulfonic acid monohydrate was added to a fresh solution to follow the acidolysis of the ester by means of NMR spectra. The compositions for the evaluation of thermal stability are summarized in Table 1. Since *p*-toluenesulfonic acid monohydrate was hardly soluble in toluene-d_8 and a 3:1 mixed solvent of diphenyl ether and toluene-d_8, 7.5 v/v % of methanol-d_4 was added to the 3:1 mixed solvent to enhance the solubility. The consumption of the *tert*-butyl esters and 2-phenyl-2-propyl esters was followed by monitoring the decrease of peak height of proton signals due to CO(CH$_3$)CO and *tert*-butyl and that due to COOC(CH$_3$)$_2$Ph with the use of the methyl protons of 2-methoxynaphthalene as an internal standard while the formation of a fragmentation product, methyl isopropenyl ketone, was traced by the increment of peak height of vinyl protons.

Evaluation of Thermal Stability in Polymeric Films. A 4 wt % solution of PBOCSt in chloroform containing 100 mol % of an acetoacetate ester was spin-coated on a silicon wafer to give a thin film which was dried in vacuo for 20 min. The wafer was placed on a hot stage to heat at 100 °C and was subjected to IR absorption measurement using a JEOL JIR-3505 spectrometer at intervals.

Deprotection of PBOCSt by 2a. A solution of 4 wt % PBOCSt in chloroform containing the (tosyloxy)methyl ester (10 wt % relative to the polymer) (**2a**) was spin-coated on a silicon wafer and dried *in vacuo* at room temperature. A thin film was heated at 100 °C on a hot stage to be subjected to IR absorption spectral measurement.

Observation of Expansion of Areas Displaying the Reduction of Film Thickness. A cyclohexanone solution containing PBOCSt, a photoacid generator, and an acid amplifier was spin-coated on a silicon wafer to give a thin film of *ca.* 0.3 μm thickness. After being prebaked for 1 min at 100 °C, the film showing violet interference color was irradiated with a 500 W super-high-pressure mercury arc through a circular window of a 3 mm diameter and subsequently heated at 100 °C on a hot stage. The color of the irradiated area was bleached immediately, followed by the gradual expansion of the bleached circular area which was monitored with a video camera.

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