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Effect of acid structure on deprotection of poly(2-trimethylsilyl-2-propyl methacrylate)

Jin-Baek Kim*, Hyunwoo Kim

Department of Advanced Materials Engineering, Korea Advanced Institute of Science and Technology, P.0. Box. 201, Cheongryang, Seoul 130-650, South Korea

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Abstract

Deprotection of poly(2-trimethylsilyl-2-propyl methacrylate) was studied for various photogenerated acids. Deprotection of 2-trimethylsilyl-2-propyl (TMSP) ester did not occur in a catalytic manner when the photogenerated acid possessing a fluoride ion source such as SbF_6^- or AsF_6^- was used. Because the cleaved product, α-methyl-α-(trimethylsilyl)ethyl cation, undergoes rearrangement through methyl migration from silicon to carbon with nucleophilic attack on the silicon by the fluoride ion, the acid was consumed in the reaction. Fortunately, when the counterion of the acid does not provide a fluoride ion, e.g. sulfonate, the carbonium ion undergoes elimination to produce 2,2,3-trimethyl-2-silabut-3-ene, and regenerates another acid. The thermal stability of TMSP ester was very similar to t-butyl ester, and acid catalyzed cleavage of the TMSP begins at 80°C. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Dry-developable resist; Chemically amplified resist; Silicon-containing polymer

1. Introduction

The design of positive 193 nm resists is a significant challenge. This emerging field has advanced remarkably in the past few years due to the efforts of resist designers around the world [1]. The majority of recently published work on 193 nm resists involves the design of new etch resistant polymers, focusing on new backbone polymer chemistry [2], alicyclic pendant groups [3], and acid labile protecting groups [4,5]. The acid labile protecting groups of the matrix polymer for chemically amplified resists (CARs) are various [6]. t-Butyl ester, tetrahydropyranyl ether and tetrahydrofuranyl ether are well-known protecting groups of the matrix polymers for 193 nm CARs.

We proposed a silicon-containing protecting group, 2-trimethylsilyl-2-propyl (TMSP) ester, for a dry-developable CAR [7]. TMSP ester groups were introduced as acid labile protecting groups into the methacrylate polymer, which is transparent in the deep UV region. Upon exposure and post-exposure bake (PEB), the silicon-containing groups were removed. Therefore the resist could be dry-developed by oxygen reactive ion etching utilizing the silicon content difference between the exposed and unexposed regions. We found that deprotection mechanism of the TMSP ester was much different from that of t-butyl ester in the presence of a certain type of photoacid generator (PAG). This paper describes mainly the effect of the PAG structure on the deprotection of the TMSP ester.

2. Experimental

2.1. Materials

Poly(2-trimethylsilyl-2-propyl methacrylate) (poly (TMSPMA)) was prepared using our previously published methods [7]. t-Butyl methacrylate was purchased from Aldrich Chemical Company. Triphenylsulfonium hexafluoroantimonate (TPSHFA) and diphenyliodonium hexafluoroarsenate (DPIHFA) were prepared as described in several publications [8–10]. Triphenylsulfonium triflate (TPSOTf), di(4-t-butylphenyl) iodonium triflate (DTBPIOTf), di(4-t-butylphenyl) iodonium camphorsulfonate (DTBICS), di (4-t-butylphenyl) iodonium hexafluoroantimonate (DTBPIHFA), and di(4-t-butylphenyl)iodonium perfluorobutanesulfonate (DTBPIPFBS) were given by Midori Kagaku Co., Ltd. The structures of the PAGs are given in Fig. 1. Poly(t-butyl methacrylate) (poly(TBMA)) was prepared and used as a model polymer. The number average molecular weight and polydispersity index were 18 000 and 1.9, respectively.

* Corresponding author. Tel.: +82-2-958-3514; fax: +82-2-958-3504.
E-mail address: kjb@cais.kaist.ac.kr (J.-B. Kim)

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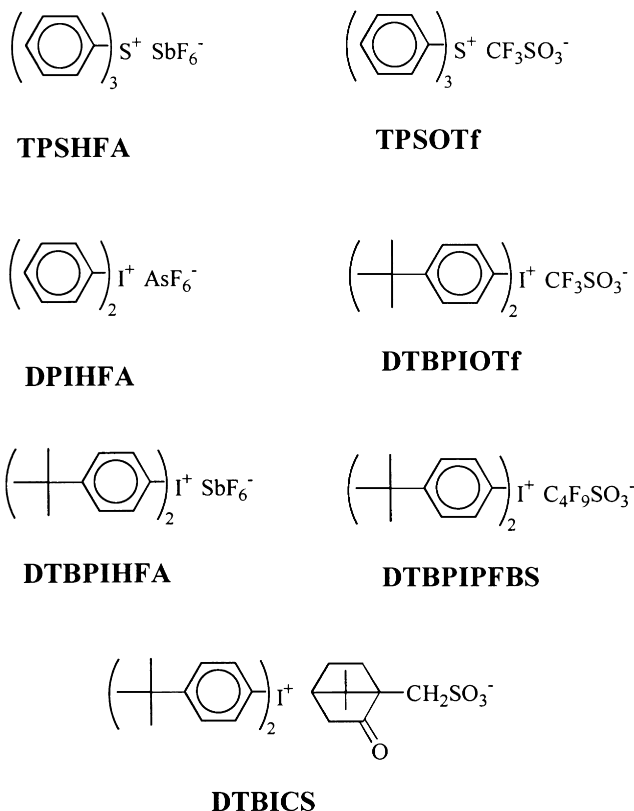

Fig. 1. Chemical structures of PAGS.

2.2. Measurements

Infrared spectra were recorded on a Bio-Rad FTS-165 spectrometer. The number-average molecular weights and polydispersities were determined in tetrahydrofuran by a Waters GPC-150C calibrated with polystyrene standards. Thermogravimetric analysis (TGA) data were obtained on a Perkin Elmer 7 series thermal analysis system. TGA measurements were taken at a heating rate of 10°C/min under nitrogen. A Headway photoresist spinner was employed for applying the photoresist solutions to silicon wafers. Deep-UV exposures were performed by contact printing using a 1000 W DUV illuminator (model 82531) from the Oriel corporation comprising a high pressure Hg(Xe) lamp with a shutter system, an intensity controller, and an exposure timer. Power density was measured using a radiant power energy meter (model 70260) from the Oriel corporation.

2.3. Preparation of resists

Resist solutions were prepared by dissolving poly (TMSPMA) or poly(TBMA) (12 wt%) in propylene glycol methyl ether acetate (PGMEA). The number average molecular weight and polydispersity index of poly(TMSPMA) were 15 000 and 2.01, respectively. TPSHFA, DPIHFA, TPSOTf, DTBPIOTf or DTBPIPFBS was mixed with each polymer solution as a PAG. In the case of DTBICS, cyclohexanone was used as the solvent because DTBICS did not dissolve in PGMEA. The resist solutions were filtered through a 0.2 μm millipore filter.

2.4. Acid catalyzed deprotection

Resist solutions were spin-coated at 1500–2000 rpm to obtain about 0.8 μm-thick films on silicon wafers for thermogravimetric analysis and on NACl plates for IR spectroscopy. The resist films were prebaked at 130°C for 2 min to remove residual solvent and exposed to produce photoacid. After exposure, the film on each wafer was peeled off and used for TGA.

3. Results and discussion

When the TPSHFA was used as a PAG, the thermograms of poly(TMSPMA) with and without photogenerated acid were as shown in Fig. 2. Upon heating to about 200°C, this polymer undergoes spontaneous thermolysis to liberate 2,2,3-trimethyl-2-silabut-3-ene in a clean and quantitative reaction (Fig. 2(A)). In the presence of the photogenerated acid the thermolysis begins around 50°C (Fig. 2(B)). However, the weight loss between 50 and 200°C in Fig. 2(B) was much less than the expected value (49%). Similar results were observed when DTBPIHFA or DPIHFA were used as the PAG, though enough energy (100 mJ/cm^2) was

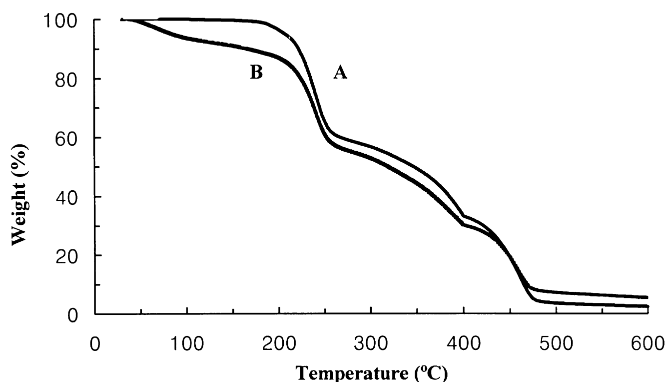

Fig. 2. TGA thermograms of the resist containing poly(TMSPMA) and 5 wt% of TPSHFA before (A) and after (B) UV exposure of 100 mJ/cm^2.

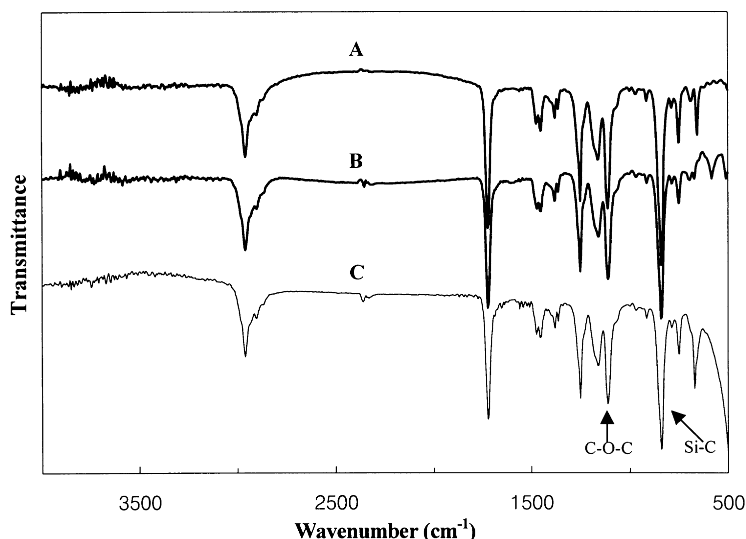

Fig. 3. IR spectra of the resists containing: (A) poly(TMSPMA) and 10 wt% of TPSHFA before exposure; (B) poly(TMSPMA) and 10 wt% of TPSHFA after exposure and PEB; and (C) poly(TMSPMA) and 30 wt% of TPSHFA after exposure and PEB (exposure and PEB conditions: 100 mJ/cm^2, 120°C for 5 min).

employed. Also IR spectra in Fig. 3 show that the Si–C stretching band at 840 cm^{-1} and C–O–C band of the TMSP ester at 1110 cm^{-1} were not changed significantly after exposure and PEB.

Olah et al. found the rearrangement process in the attempted ionization of diphenyl(trimethylsilyl)methyl alcohol [11]. Diphenyl(trimethylsilyl)methyl cation undergoes rearrangement through migration of a methyl group from silicon to an electron-deficient α carbon with immediate nucleophilic attack on silicon by counterion as shown in Fig. 4. They also found that dimethyl(trimethylsilyl)methyl alcohol gave similar rearranged products. By analogy with these findings, the deprotection of TMSP ester is not an acid catalyzed reaction when the PAG containing a fluoride ion source such as SbF_6^- or AsF_6^- was used, because acid is consumed in the reaction. In this case the cleavage reaction of the TMSP ester occurs as shown in Fig. 5. Nucleophilic substitution and elimination compete with each other, but the nucleophilic substitution is superior to the elimination. We expect that almost all the TMSP ester groups should be cleaved if an equivalent amount of TPSHFA was used. However, the loading of the PAG above 30 wt% (based on the polymer) causes severe problems such as opaqueness of the resist film, incompatibility with resin, and poor adhesion to substrate. Although the resist film was exposed at a high dose (100 mJ/cm^2), nearly the same FT-IR spectra were observed when TPSHFA, DTBPIHFA or DPIHFA were used as the PAG.

Fortunately, the TMSP ester was cleaved by an acid-catalyzed reaction (chemical amplification) when the anion of the PAG was a sulfonate which does not provide a fluoride ion. This is confirmed by TGA and FT-IR spectra as shown in Fig. 6 and Fig. 7. When DTBPIPFBS (Fig. 6(B)) or DTBPOTf (Fig. 6(C)) were used as the PAG, poly (TMSPMA) decomposed very rapidly in the temperature range between 80 and 125°C. Although a catalytic amount of PAG was used, nearly all the TMSP ester groups were cleaved in that temperature range. The same result was observed when TPSOTf was used as a PAG. The acid catalyzed cleavage reaction was confirmed by FT-IR analysis. As shown in Fig. 7, poly(TMSPMA) was converted to poly(methacrylic acid) by exposure (50 mJ/cm^2) and PEB (110°C for 5 min) in the presence of a catalytic amount of TPSOTf. Therefore the deprotection of poly(TMSPMA) is

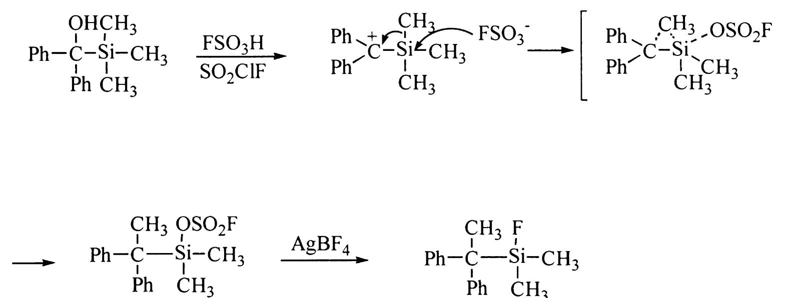

Fig. 4. Rearrangement of diphenyl(trimethylsilyl)methyl cation by methyl migration.

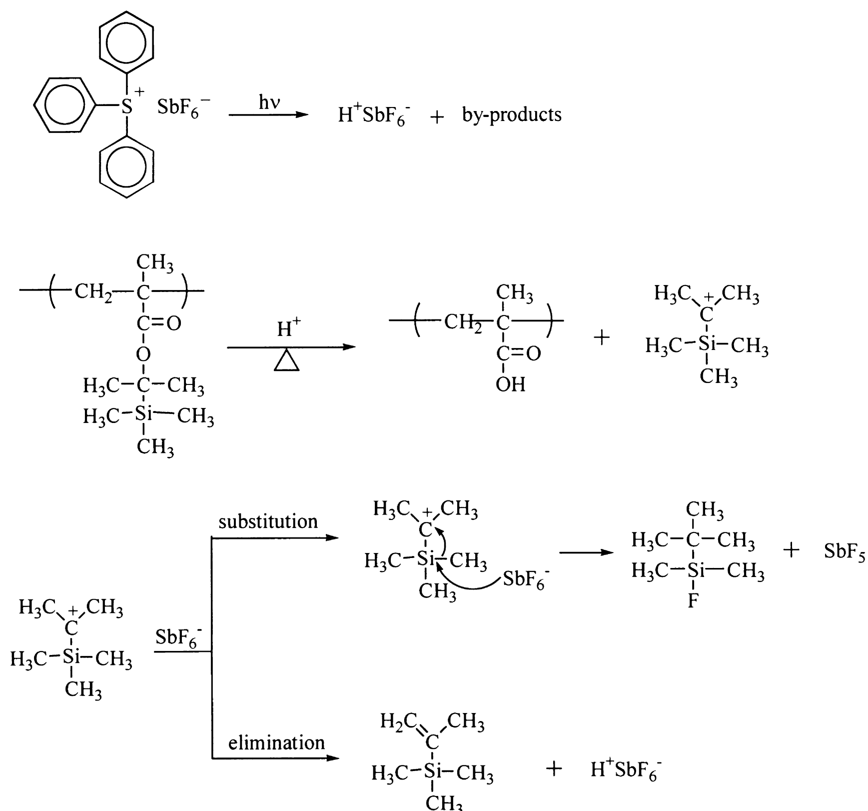

Fig. 5. Deprotection mechanism of the TMSP ester when the PAG containing SbF_6^- anion was used.

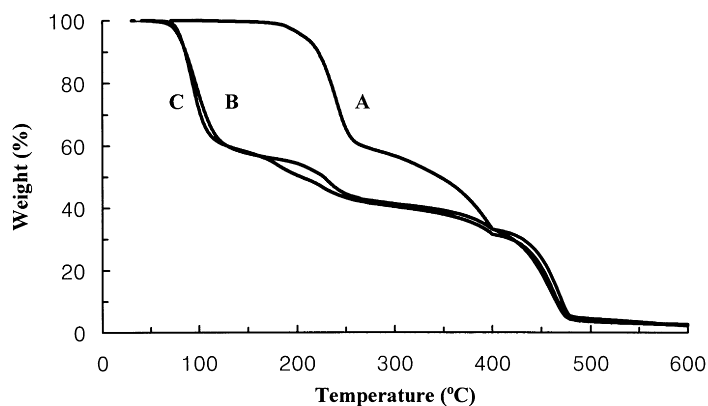

Fig. 6. TGA thermograms of: (A) poly(TMSPMA); (B) poly(TMSPMA) with 2 wt% of DTBPIPFBS; and (C) poly(TMSPMA) with 2 wt% of DTBPOTf ((B) and (C) after exposure of 50 mJ/cm^2).

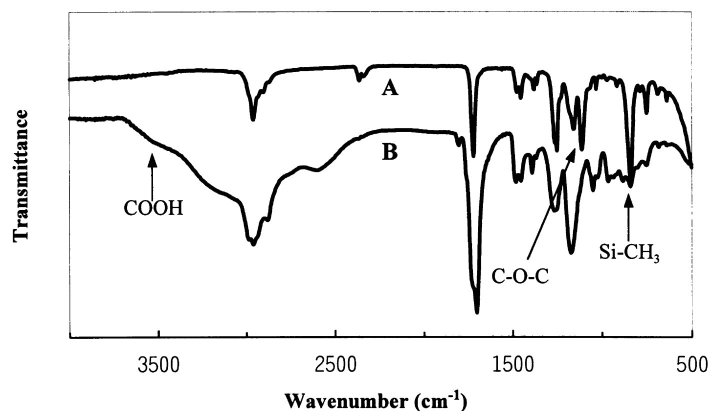

Fig. 7. IR spectral change of the resist containing poly(TMSPMA) and 2 wt% TPSOTf (A) before exposure and (B) after exposure and PEB (exposure and PEB conditions: 100 mJ/cm^2, 110°C for 5 min).

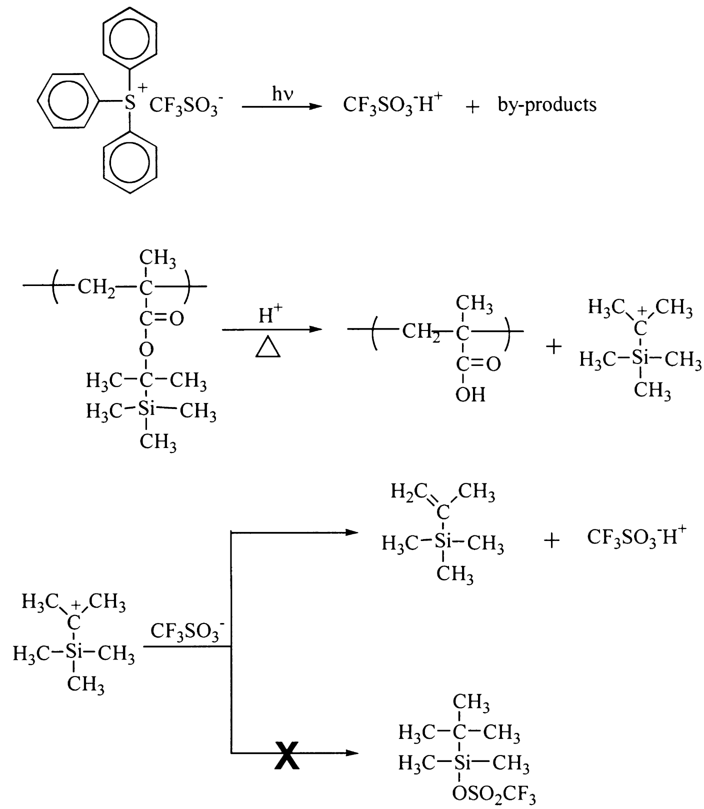

Fig. 8. Acid catalyzed deprotection of the TMSP ester protecting group.

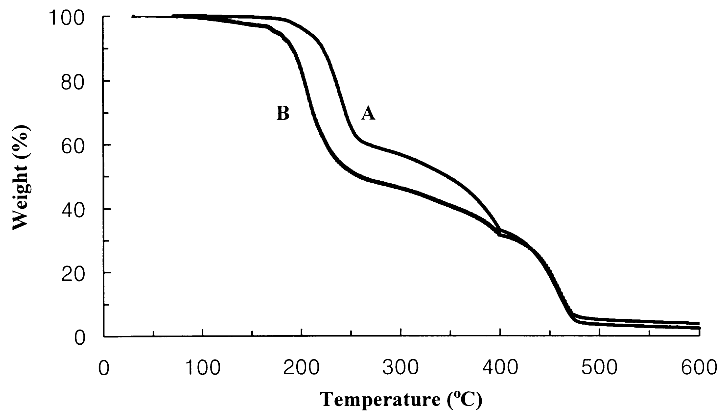

Fig. 9. TGA thermograms of the resist containing poly(TMSPMA) and 5 wt% of DTBICS before (A) and after (B) UV exposure of 100 mJ/cm^2.

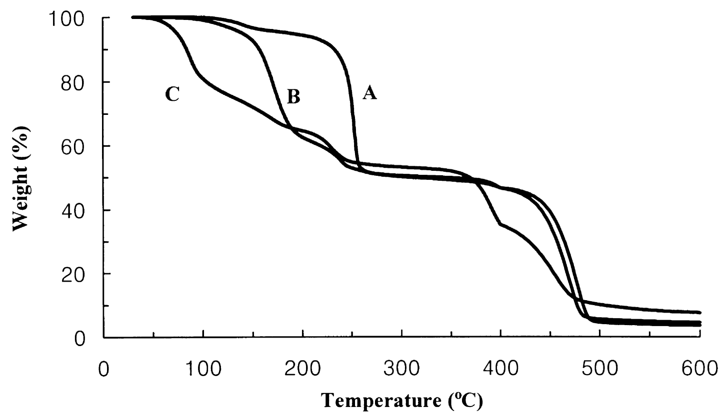

Fig. 10. TGA thermograms of: (A) poly(TBMA); (B) poly(TBMA) and 5 wt% DTBICS; and (C) poly(TBMA) and 5 wt% TPSOTf ((B) and (C) after exposure of 100 mJ/cm^2).

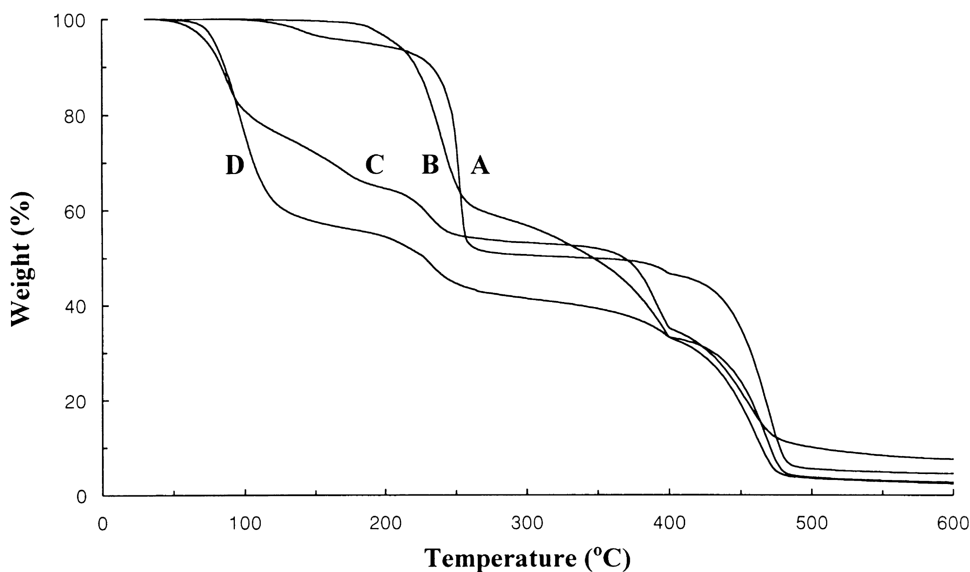

Fig. 11. TGA thermograms of: (A) poly(TBMA); (B) poly(TMSPMA); (C) poly(TBMA) and 2 wt% TPSOTf after exposure of 100 mJ/cm^2; and (D) poly(TMSPMA) and 2 wt% TPSOTf after exposure of 50 mJ/cm^2.

an acid catalyzed cleavage reaction, and the acid is not consumed in the reaction as shown in Fig. 8. Although $HSbF_6$ and CF_3SO_3H are both strong acids, CF_3SO_3H causes chemical amplification but $HSbF_6$ does not. This is caused by different reactivities of the anions to the silicon atom. The bond dissociation energy of the Si–F bond is 808 $kJ\ mol^{-1}$ and that of the Si–O bond is 531 $kJ\ mol^{-1}$ [12].

When the DTBICS was used as a PAG, the acid catalyzed cleavage reaction also occurred. However, the deprotection temperature was much higher compared with the temperatures found when DTBPIPFBS and DTBPOTf were used (Fig. 9). This result seems to be due to the different acidities of the photogenerated acids. Camphorsulfonic acid is much weaker in acidity than triflic acid or perfluorobutanesulfonic acid. Similar results were obtained when poly(TBMA) was used as the matrix polymer. When the DTBICS was used as a PAG, poly(TBMA) undergoes thermolysis at a higher temperature than that containing TPSOTf, as shown in Fig. 10.

TGA thermograms of poly(TMSPMA) and a typical model polymer, poly(TBMA), with and without a photogenerated acid are shown in Fig. 11. Both polymers gave similar deprotection temperatures. This indicates that the TMSP ester shows almost the same thermal reactivity as the t-butyl ester with and without the photogenerated acid which does not provide a fluoride ion.

Degrees of deprotection of the TMSP ester group in the presence of various photogenerated acids are shown in Table 1. The weight loss of poly(TMSPMA) below 200°C was converted to the degree of deprotection. PAGs containing a fluoride ion source such as SbF_6^- and AsF_6^- cannot perform acid catalyzed cleavage of the TMSP ester group, even though the high loading of the PAG increases the degree of deprotection. However, the PAGs which do not contain a fluoride ion source can cleave

Table 1
Degree of deprotection of TMSP ester group for various PAGs

PAG	PAG loading[a] (mol% (wt%))		Degree of deprotection[b] (mol%)
TPSHFA	3.0	(7.2)	10.5
TPSHFA	6.0	(9.7)	15
TPSHFA	12.0	(25.4)	19
DTBPIHFA	2.8	(8.3)	9.7
DPIHFA	2.8	(6.3)	9.3
TPSOTf	1.5	(3.0)	87.7
TPSOTf	3.0	(6.0)	96.5
DTBPIPFBS	1.5	(5.0)	85
DTBPIOTf	1.5	(4.0)	87.7

[a] PAG loading is based on the TMSPMA unit of poly(TMSPMA) in the resist.
[b] mol% Was calculated from weight loss that was measured with TGA after exposure (50 mJ/cm^2).

almost all the TMSP ester groups below 200°C in a catalytic manner.

4. Conclusions

Poly(TMSPMA) did not work properly as a matrix polymer of a CAR when an onium salt possessing a fluoride ion source such as SbF_6^- or AsF_6^- was used as the PAG. Because during deprotection of TMSP ester the migration of a methyl group from silicon to carbon occurs with nucleophilic attack on silicon by the fluoride ion, instead of elimination, the photogenerated acid was consumed in the deprotection reaction. When the anion of the onium salt does not provide a fluoride ion, e.g. sulfonate, the carbonium ion undergoes elimination to produce 2,2,3-trimethyl-2-silabut-3-ene, and regenerates another acid. The thermal stability of TMSP ester was very similar to t-butyl ester, and acid catalyzed cleavage of the TMSP begins at 80°C.

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