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Acid Formation in Polymer Solids by Radiation-Induced Chain Reactions of Diphenyliodonium Salts

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Abstract

In order to develop chemically amplified radiation resist having ability of acid multiplication, acid formation in γ -irradiated polymer films and solutions of acetal compounds containing diphenyliodonium salt has been studied. Acids were generated in the films and solutions by chain reactions in large G-value. The G-value depends on the chemical structure of the polymers and acetal compounds. Compounds containing cyclic acetal structure give large G-values. This dependence can be explained by difference in the possibility of the electron transfer from radicals of the polymers and acetal compounds to diphenyliodonium salt. Polyvinyl acetals will be a candidate for the dually amplified resist.

Keywords: iodonium salt, γ -radiation, acetals, polyvinyl acetals, chemically amplified resists

1. Introduction

Chemically amplified resists have been widely used in current lithography processes(Ito and Willson 1983). Change in the solubility of the resists is induced by acid catalytic reactions during post exposure bake (PEB): an acid generated from the acid generators, such as sulfonium and iodonium salts, reacts with the base polymers many times. The high sensitivity of the chemically amplified resists is thereby attained.

The mechanism of acid formation in the radiolysis of polymers containing the onium salts is different from that in their photolysis. In the photolysis, photons are selectively absorbed by the onium salts. The excited molecules undergo dissociation to generate pairs of aryl cations and diarylsulfides or aryl iodides within solvent cages. The pairs are converted to protonic acids through cage-recombinations or cage-escape processes(Crivello 1993). In the radiolysis, radiation energy is primarily absorbed by the polymers. The cations of the polymers and electrons are generated by the ionization. The electrons cause dissociative electron attachment to the onium salts to generate protonic acids(Kozawa et al. 1992; Yamamoto et al. 2005).

Chain reactions are induced by the radiolysis or photolysis of alcohol or ether solutions of diphenyliodonium salts.(Hennig et al. 2001; Koizumi et al. 2002; Ma et al. 1988) Protonic acids are generated with high yields by the chain reactions. If we can utilize the chain reactions for the acid generation in the chemically amplified resists, the sensitivity of the resists will be much improved due to the amplifications by the catalysis and the chain reactions.(Nagahara et al. 2000)

In order to develop this dually amplified resist, we have examined acid formation in polymer solids by the radiation-induced chain reactions. We examined if the chain reactions actually occur even in polymer solids, and what kind of chemical structures of polymers is suitable for the acid generation. We have demonstrated that the chain reactions occur even in solid polymers, and found that the yield of the chain reactions is determined mainly by efficiency in electron transfer from radicals of the polymers to the iodonium salt.

2. Experimental and computational details

Diphenyliodonium trifluoromethanesulfonate (stated purity >98%) was supplied by Tokyo Kasei Kogyo Co., Ltd. The recrystallization of the iodonium salt from ethanol-water mixture had no effect on the experimental results. The iodonium salt was therefore used as received. Dimethoxymethane (>98.0 %), acetone dimethyl acetal (>98.0%), 1,3-dioxane (>98.0%), 4-methyl-1,3-dioxane (>99.0%), 2,4-dimethyl-1,3-dioxane (>98.0%) were supplied by Tokyo Kasei Kogyo Co. Ltd.. Acetaldehyde dimethyl acetal (>95%) and formaldehyde diethyl acetal (>99.0%) were supplied by Aldrich. Tetrahydrofuran (THF, >99.8%, without stabilizers) was supplied by Junsei Chemical Co., Ltd.. The acetal compounds and THF were used without further purification.

Diphenyliodonium solutions in THF and in mixtures of acetone and acetal compounds were degassed by freeze-pump-thaw cycles with a vacuum line. They were sealed in glass ampoules. The solutions were irradiated with γ -rays from a ^{60}Co source at Hokkaido University. The acid concentrations in the irradiated solutions were obtained by titrations with an aqueous solution of sodium hydroxide. The preparation and irradiation of the solutions were performed under dark.

Poly(methyl methacrylate) (PMMA) was supplied by Wako Pure Chemical Industries, Ltd., polyvinyl alcohol (PVA) by Tokyo Kasei Kogyo Co., Ltd., poly(vinyl formal) (PVF) by Aldrich, poly(2-hydroxyethyl methacrylate) (P2HEMA) by Scientific Polymer Products, Inc.. PMMA was dissolved in THF, precipitated by adding a large amount of methanol, and dried by heating. Poly(vinyl acetal) (PVAc) and poly(vinyl cyclohexanal) (PVCH) were synthesized from PVA and aldehydes by acid catalyzed reactions (Sorenson et al. 2001). Acetaldehyde supplied by Junsei Chemical Co., Ltd. and cyclohexanecarboxaldehyde (97%) by Aldrich were used for the syntheses of PVAc and PVCH, respectively.

Polymer films containing the iodonium salt were prepared by solution casting. Polymers were dissolved in THF without stabilizers, and the iodonium salt was added in the solutions. The solutions were casted on petri dishes made of Teflon. The dishes were put on a vacuum oven, and the solvent was slowly evaporated at room temperature for 3-4 days. Films 0.1-0.3 mm thick were obtained. The films were evacuated with a vacuum line and sealed in glass ampoules. They were irradiated with γ -rays from the ^{60}Co source. The irradiated films were dissolved in THF, and the acid concentrations in the solutions were obtained by the titration. The preparation and irradiation of the films were performed under dark.

Ionization potentials of radicals were obtained by the difference of the total energies of the neutral radical and its cation. The total energies were computed on the respective optimized structures of the neutral and cation by density functional theory with B3LYP exchange and correlation functionals and with 6-31G (d) basis set. The calculations were performed with the PC GAMESS/Firefly QC package (Granovsky) under Windows, which is partially based on the GAMESS (US) (Schmidt et al. 1993) source code. The computers used were PCs with 3.06 GHz Celeron or 2.80 GHz Pentium 4 and 2.0 GB RAM. The computation times were from 0.5 h to 4 h.

3. Results

3.1 Acid formation in polyvinyl alcohol

The concentrations of acid in irradiated polyvinyl alcohol (PVA) films containing the iodonium salt are plotted in Fig. 1 as a function of the absorbed dose. The concentration increases with increasing dose. The G-value of the acid formation was obtained from the slope in Fig. 1.

The G-value is plotted in Fig. 2 as a function of the concentration of the iodonium salt. The G-value is more

than 50, shows a maximum of 270 at 0.06 mol kg⁻¹, and decreases at the higher concentrations. These results demonstrate that the chain reactions of the iodonium salt occur even in the solid polymer films.

The decrease of the G-value at the higher salt concentration will be caused by a reaction between phenyl radical and the iodonium salt (Koizumi et al. 2002). Phenyl radical may add to aromatic compounds, which results in the formation of cyclohexadienyl radical (Scaiano and Stewart 1983). The cyclohexadienyl type radical is more stable than phenyl radical. This radical cannot abstract a hydrogen from PVA. The chain reactions terminate through this reaction.

Fig.2 shows some scatter. This can be ascribed to residual air in the films. The yield of the chain reactions is very sensitive to oxygen. We degassed the films carefully. However, trace of oxygen remains and the amount of the residual oxygen will vary slightly depending on the film. This will cause the scatter.

3.2 Acid formation in poly(methyl methacrylate) containing alcohol

The G-value of acid formation in poly(methyl methacrylate) (PMMA) films containing the iodonium salt and hexadecanol are plotted in Fig.3 as a function of concentration of hexadecanol. Hexadecanol was added to the films, since alcohols or ethers are required in the chain reactions. The G-value is less than 1/5 of the G-value in polyvinyl alcohol. PMMA disturbs the chain reactions.

The inhibitive effect of PMMA on the chain reactions was also found in solution. The G-values of acid formation in diphenyl iodonium solutions in THF with and without addition of 10 wt% PMMA were 201 and 128, respectively. With the addition of 10 wt% PMMA, the G-value decreased by about 35 %.

3.3 Acid formation from acetal compounds in solutions

In order to find a chemical structure suitable for the chain reactions, the G-values of acid formation in various acetal compounds were measured. Since solubility of the iodonium salt is low in some of the compounds, 40 vol% solutions in acetone containing 0.02 mol dm⁻³ of the iodonium salt were used. The G-values of the acid formation are shown in table 1. The G-values for cyclic acetals, 1,3-dioxane, 4-methyl-1,3-dioxane, and 2,4-dimethyl-1,3-dioxane are high, more than 120, followed by formaldehyde diethyl acetal. The G-values for dimethoxymethane, dimethyl acetal, and acetone dimethyl acetal are low, less than 20.

3.4 Acid formation in polyvinyl acetals

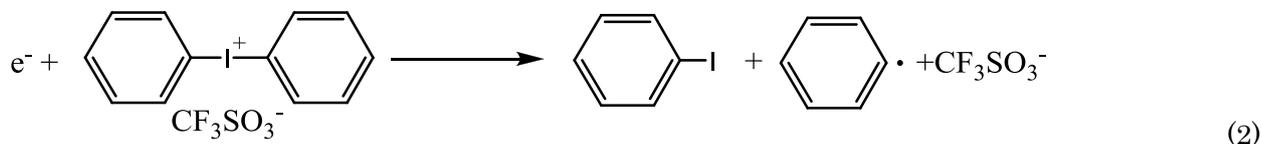
The G-values of the acid formation in the cyclic acetals are high, and hence the cyclic acetal structure will be suitable for the chain reactions. Acetal compounds can be converted to alcohol and ketone or aldehyde by acid catalysis, and thereby change their solubility. Hence polymers containing the acetal structure can be a candidate for the dually amplified resist. Therefore the acid formation in polyvinyl acetal films containing the iodonium salt was examined.

The G-values of acid formation in poly(vinyl formal), poly(vinyl acetal), and poly(vinyl cyclohexanal) films containing the iodonium salt are shown in table 2. The G-value for poly(2-hydroxyethyl methacrylate) containing the iodonium salt was also obtained, and shown in table 2, since the G-value for the iodonium solution in ethanol is high, 2.8×10^3 (Hayashi 1991; Ma et al. 1988). The G-values are from 18 to 44. The chain reactions occur in these films.

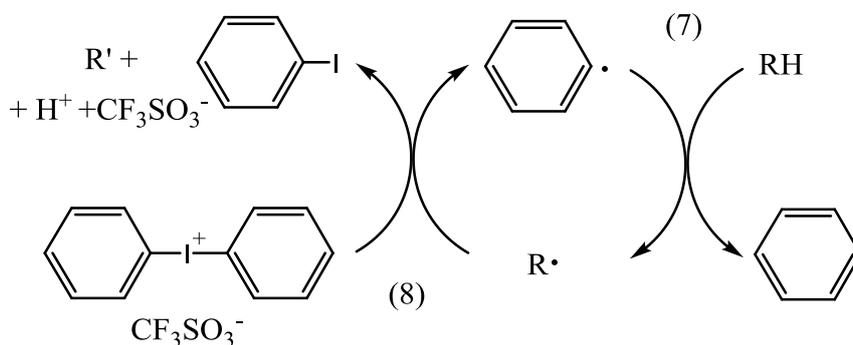
4. Discussion

4.1 Chemical structure suitable for the chain reactions

Reaction mechanisms of the radiolysis of alcohol or ether solutions of iodonium salt have been proposed by Ma et al. (Ma et al. 1988). The chain reactions are initiated by the following reactions:



Solvent molecules (RH) are ionized or excited by radiation (1). Phenyl radicals are generated through dissociative electron attachment to diphenyliodonium salt (2), while solvent radicals (R·) are generated by proton transfer from solvent cations to RH (3), dissociation of excited solvent molecules (5), and reaction between hydrogen atoms and RH (6). The radicals cause the following propagation reactions (Hennig et al. 2001; Ma et al. 1988):



A phenyl radical abstracts a hydrogen from RH, and results in R· (7) (Fang et al. 1995; Madhavan et al. 1978). R· causes electron transfer to the iodonium salt (8) (Crivello 1993; Ledwith 1978; Yagci et al. 1987). A phenyl radical and a protonic acid are generated in this reaction.

The termination reactions will be due to combination reactions of the radicals (Simic et al. 1969):



In order to proceed the propagation reactions efficiently, a solvent molecule, RH, should have the following

properties. First, RH has a hydrogen that can be abstracted by a phenyl radical. Second, the ionization potential of $R\cdot$ is low enough. The cation of $R\cdot$ can release a proton. The second and third requirements are necessary for the electron transfer from $R\cdot$ to a iodonium salt to proceed.

4.2 Inhibitive effect of PMMA

The G-value of the acid formation is low in PMMA compared in PVA. The addition of PMMA to THF solution decreased the G-value of the acid formation. These inhibitive effects will be explained by difficulty in the electron transfer from a radical of PMMA to iodonium salt.

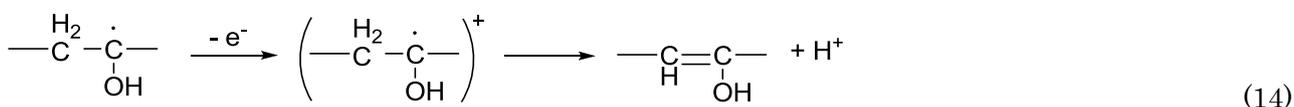
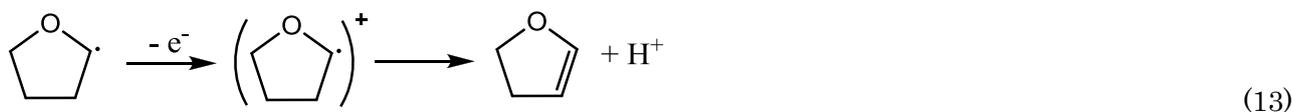
The ionization potentials of radicals generated from THF, and model compounds of PMMA and PVA are shown in Table 3. The ionization potentials were calculated by density functional theory with B3LYP exchange and correlation functionals and with 6-31G(d) basis set. The ionization potential of a radical of the PMMA model compound is more than 0.5 eV higher than those of THF and the PVA model compound, and hence the electron transfer from the radical of PMMA is more difficult than from those of THF and PVA.

If the ion produced by the electron transfer releases a proton, the proton and a deprotonated product are more stable than the ion, and the electron transfer occurs more easily. In condensed phase, an ion is stabilized by polarization of the medium. The polarization energy P_+ for a cation is negative. It is given by Born's equation (Born 1920; Koizumi et al. 1994)

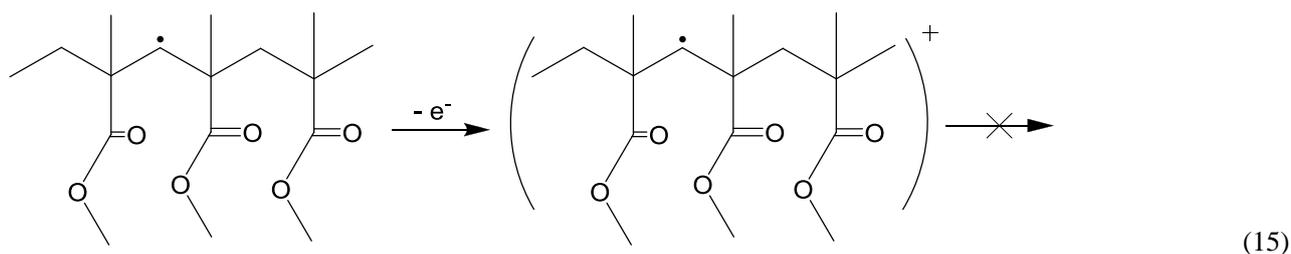
$$P_+ = \frac{-e^2}{8\pi\epsilon_0 R} \left(1 - \frac{1}{\epsilon_r} \right) \quad (12)$$

where R is the radius of the positive ion, e is the electron charge, ϵ_0 is the permittivity of the vacuum, and ϵ_r denotes the relative dielectric constant of the medium. $|P_+|$ increases with decreasing R , Hence the smaller the radius of an ion is, the more stable the ion is. Since proton is the smallest ion, the stabilization energy by the polarization is the largest. If the cation generated by the electron transfer releases a proton, the electron transfer proceeds efficiently, since the products are more stable than an ion not releasing a proton.

The cation generated from the radicals of THF and PVA can release a proton with forming a double bond:



However, the release of a proton is difficult from the cation generated from the radical of PMMA:

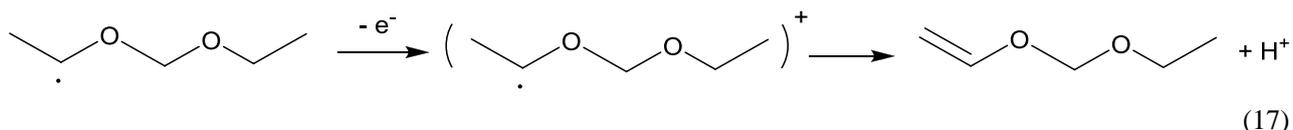
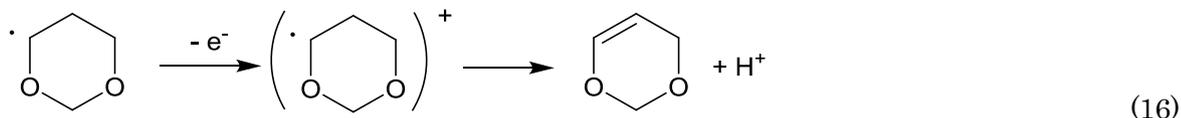


Phenyl radicals will abstract a hydrogen from PMMA, However, the electron transfer from the radical of PMMA

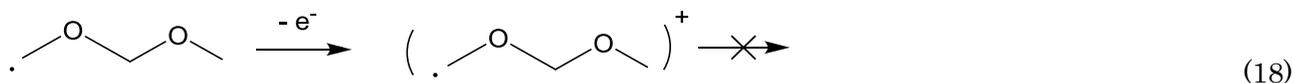
is difficult. The propagation reactions thereby terminate, and the acid formation is inhibited.

4.3 Difference in the G-values of acid formation in acetal compounds

The G-values of acid formation for the cyclic acetals are larger than those for the chain acetals. This difference can be explained by the difference in possibility of the proton release from the cation of the radicals. The cations generated from the radicals of the cyclic acetals and formaldehyde diethyl acetal can release a proton with forming a double bond.



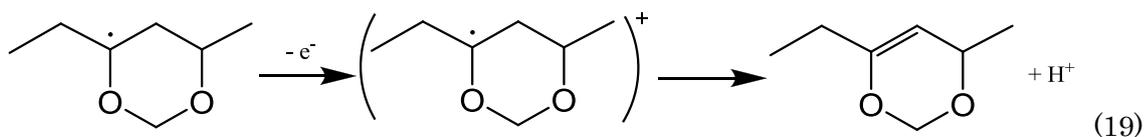
However, the release of a proton is difficult from the cation generated from dimethoxymethane and acetone dimethyl acetal.



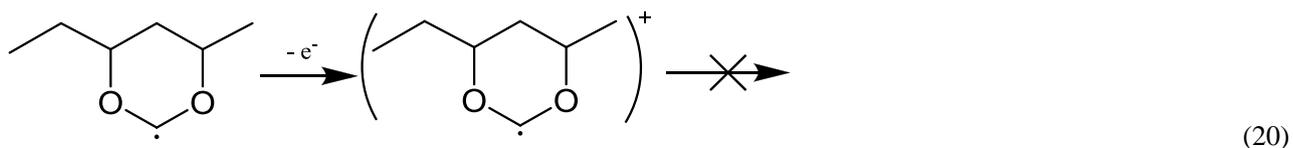
Hence the products by the electron transfer for the cyclic acetals and formaldehyde diethyl acetal are more stable than those for dimethoxymethane and acetone dimethyl acetal. The electron transfer occurs more efficiently in the cyclic acetals and formaldehyde diethyl acetal than the other chain acetals. It will cause the difference in the G-value of acid formation.

4.4 The G-values of acid formation in polyvinyl acetal films

Acid formation in polyvinyl acetal and poly(2-hydroxyethyl methacrylate) films occurs through the chain reactions. However, the G-values are lower than the value in PVA: 18-44. The lower G-values in polyvinyl acetals will be ascribed to difficulty in formation of tertiary radicals in solids (Ichikawa et al. 1999; Ichikawa et al. 2000). If a hydrogen bonded to the main chain is abstracted, the generated radical can release a proton:



However, this abstraction is difficult because a tertiary radical is generated by the abstraction. Hence, a hydrogen bonded to the carbon between the oxygen atoms will be abstracted. The cation of the radical generated by this reaction is difficult to release a proton, and the electron transfer is difficult:



The propagation reactions thereby terminate. The ionization potentials of the other radicals bonded to a carbon nonadjacent to an oxygen is high, and the electron transfer from the radicals is difficult.

In the case of poly(2-hydroxyethyl methacrylate), a radical generated by abstraction of a hydrogen bonded to a carbon of the 2-hydroxyethyl group can release a proton. The electron transfer from the radical will occur.

However, the abstraction of a hydrogen bonded to the main chain may occur. The ionization potential of the generated radical is high, and it is difficult for the cation of the radical to release a proton as for the radical of PMMA. The electron transfer from the radical is difficult. It reduces the G-value.

5. Conclusions

Acid formation in polymer films and solutions containing iodonium salt by γ -irradiation has been examined. Protonic acids are generated through chain reactions in the films and solutions. The difference in G-value of the acid formation is mainly determined by efficiency in the electron transfer to the iodonium salt from radicals of polymers and solvents generated by hydrogen abstraction by phenyl radicals. Compounds containing a cyclic acetal structure give a large G-value. Polyvinyl acetals will be a candidate for the dually amplified resist.

Acknowledgement

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References

- Born, M., 1920. Volumes and heats of hydration of ions. *Z. Phys.* 1, 45-48.
- Crivello, J.V., 1993. Latest developments in the chemistry of onium salts. In: J.P. Fouassier, J.F. Rabek (Eds.), *Radiation curing in polymer science and technology*. Elsevier Applied Science, London, pp. 435-471.
- Fang, X., Mertens, R., von Sonntag, C., 1995. Pulse radiolysis of aryl bromides in aqueous solutions: some properties of aryl and arylperoxyl radicals. *J. Chem. Soc. Perkin Trans. 2*, 1033-1036.
- Granovsky, A.A., PC GAMESS/Firefly version 7.1.F, www <http://classic.chem.msu.su/gran/gamess/index.html>.
- Hayashi, K., 1991. Radiation-induced polymerization and polymer reactions sensitized by onium salts. *Rep. Asahi Glass Found.* 58, 245-251.
- Hennig, H., Brede, O., Billing, R., Schonewerk, J., 2001. Photoinduced chain reactions of alcohols in the presence of diphenyliodonium ion pairs with cyanometallates - steady state UV/visible spectroscopic and pulse radiolysis studies. *Chem. Eur. J.* 7 (10), 2114-2121.
- Ichikawa, T., Kagei, K., Ishitani, Y., Tachikawa, H., Koizumi, H., 1999. Control factors for hydrogen-atom abstraction from organic molecules in cryogenic solids. *Radiat. Phys. Chem.* 55, 529-534.
- Ichikawa, T., Takeshi, T., Koizumi, H., Takada, T., 2000. Matrix effect on hydrogen atom tunneling: comparison between hydrogen addition and abstraction. *J. Phys. Chem. A* 104, 2581-2586.
- Ito, H., Willson, G.G., 1983. Chemical amplification in the design of dry developing resist materials. *Polym. Eng. Sci.* 23, 1012-1018.
- Koizumi, H., Lacmann, K., Schmidt, W.F., 1994. VUV light-induced electron emission from organic liquids. *J. Electron Spectrosc. Rel. Phenom.* 67, 417-427.
- Koizumi, H., Sasaki, T., Ichikawa, T., 2002. Radiation-induced chain reactions in alcohol solutions of diphenyliodonium salts: a high-sensitivity chemical dosimeter. *Radiat. Res.* 158, 241-246.
- Kozawa, T., Yoshida, Y., Uesaka, M., Tagawa, S., 1992. Radiation-induced acid generation reactions in chemically amplified resists for electron beam and X-ray lithography. *Jpn. J. Appl. Phys.* 31, 4301-4306.
- Ledwith, A., 1978. Possibilities for promoting cationic polymerization by common source of free radicals. *Polymer* 19, 1217-1219.
- Ma, X.-H., Yamamoto, Y., Hayashi, K., 1988. Radiolysis of solutions of diphenyliodonium and triphenylsulfonium hexafluorophosphates in various solvents. *J. Org. Chem.* 53, 5443-5445.
- Madhavan, V., Schuler, R.H., Fessenden, R.W., 1978. Absolute rate constants for reactions of phenyl radicals. *J. Am. Chem. Soc.* 100 (3), 888-893.
- Nagahara, S., Sakurai, Y., Wakita, M., Yamamoto, Y., Tagawa, S., Komuro, M., et al., 2000. Methods to improve radiation sensitivity of chemically amplified resists by using chain reactions of acid generation. *Proc. SPIE.* 3999, 386-394.
- Scaiano, J.C., Stewart, L.C., 1983. Phenyl radical kinetics. *J. Am. Chem. Soc.* 105, 3609-3614.
- Schmidt, M.W., Baldrige, K.K., Boatz, J.A., Elbert, S.T., Gordon, M.S., Jensen, J.H., et al., 1993. General atomic and molecular electronic structure system. *J. Comput. Chem.* 14, 1347-1363.
- Simic, M., Neta, P., Hayon, E., 1969. Pulse radiolysis of alcohols in aqueous solution. *J. Phys. Chem.* 73, 3794-3800.
- Sorenson, W.R., Sweeny, F., Campbell, T.W., 2001. *Preparative methods of polymer chemistry*, 3rd ed. John Wiley & Sons, New York.
- Yagci, Y., Pappas, S.P., Schnabel, W., 1987. On the reactions of diphenyliodonium and triphenylsulfonium salts with

hydroxyl and 2-hydroxy-2-propyl radicals. *Z. Naturforsch.* 42, 1425-1427.

Yamamoto, H., Kozawa, T., Nakano, A., Okamoto, K., Tagawa, S., Ando, T., et al., 2005. Study on acid generation from polymer. *J. Vac. Sci. Technol. B* 23, 2728-2732.

Figure Captions

Figure 1. Concentration of acid in γ -irradiated polyvinyl alcohol films containing diphenyliodonium trifluoromethanesulfonate as a function of absorbed dose.

Figure 2. The G-value of acid formation in polyvinyl alcohol films containing diphenyliodonium trifluoromethanesulfonate as a function of the concentration of the iodonium salt.

Figure 3. The G-value of acid formation in poly(methyl methacrylate) films containing 0.04 mol kg^{-1} diphenyliodonium trifluoromethanesulfonate and 2-hexadecanol as a function of the concentration of hexadecanol.

Tables

Table 1. G-values of acid formation in mixtures of acetal compounds (40 vol%) and acetone containing 0.02 mol dm^{-3} diphenyliodonium trifluoromethanesulfonate.

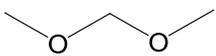
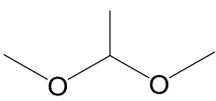
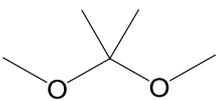
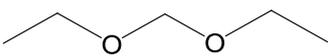
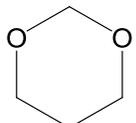
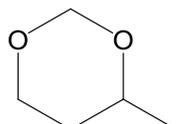
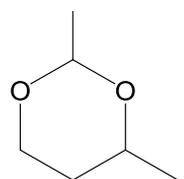
Acetal compound	G-value
dimethoxymethane 	18.1
acetaldehyde dimethyl acetal 	9.7
acetone dimethyl acetal 	7.9
formaldehyde diethyl acetal 	77.3
1,3-dioxane 	129
4-methyl-1,3-dioxane 	138
2,4-dimethyl-1,3-dioxane 	145

Table 2. G-values of acid formation in polymer films containing 0.04 mol kg⁻¹ diphenyliodonium trifluoromethanesulfonate.

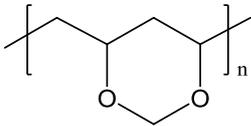
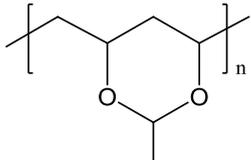
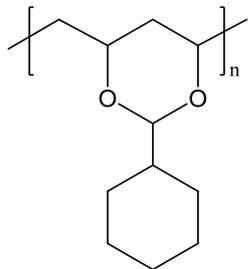
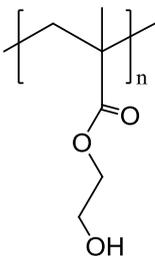
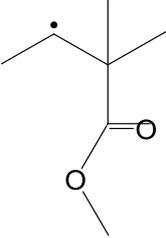
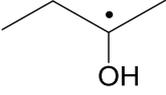
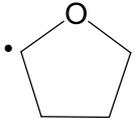
Polymer	G-value
Poly(vinyl formal) 	43.9
Poly(vinyl acetal) 	27.1
Poly(vinyl cyclohexanal) 	18.4
Poly(2-hydroxyethyl methacrylate) 	40.6

Table 3. Ionization potentials of radicals calculated using density functional theory with B3LYP exchange and correlation functionals and with 6-31G(d) basis set.

Radical	Ionization Potential / eV
	6.31
	5.74
	5.92

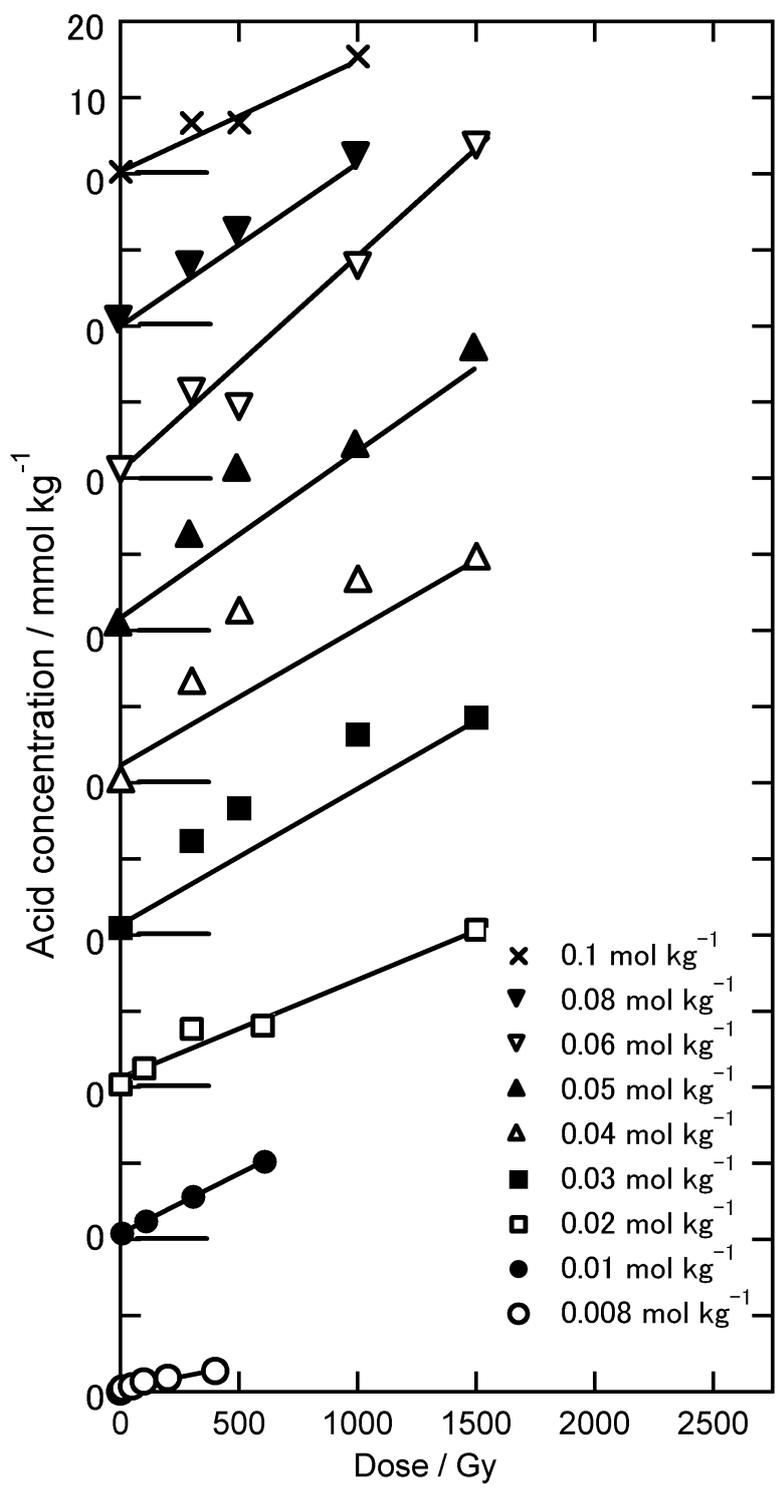


Figure 1. H. Koizumi et al.

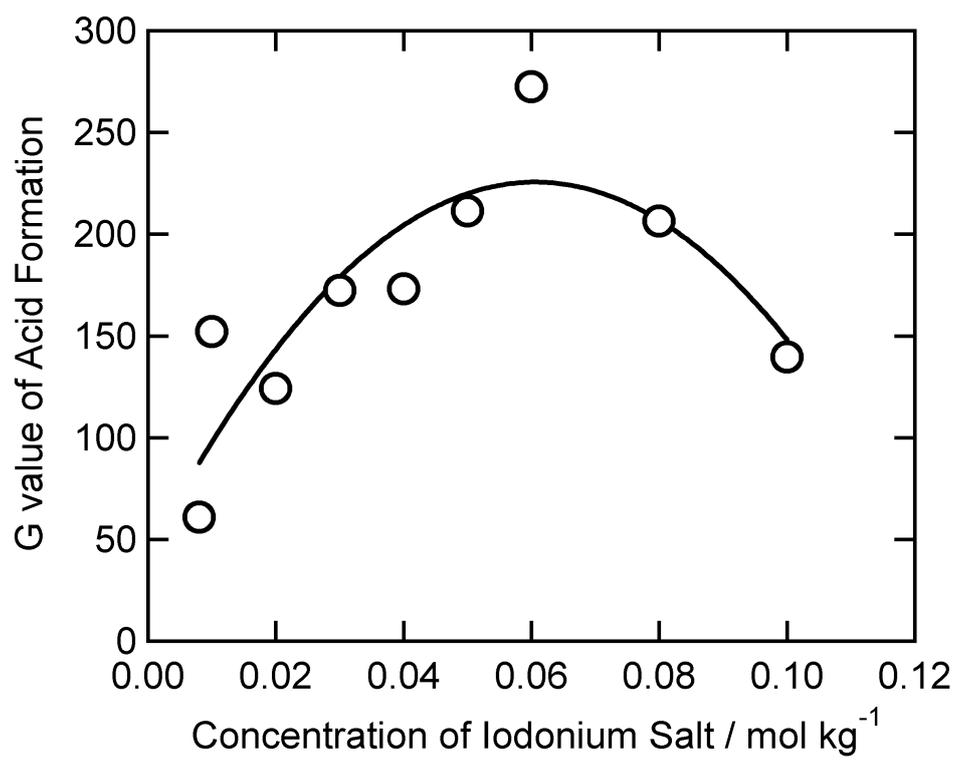


Figure 2. H. Koizumi et al.

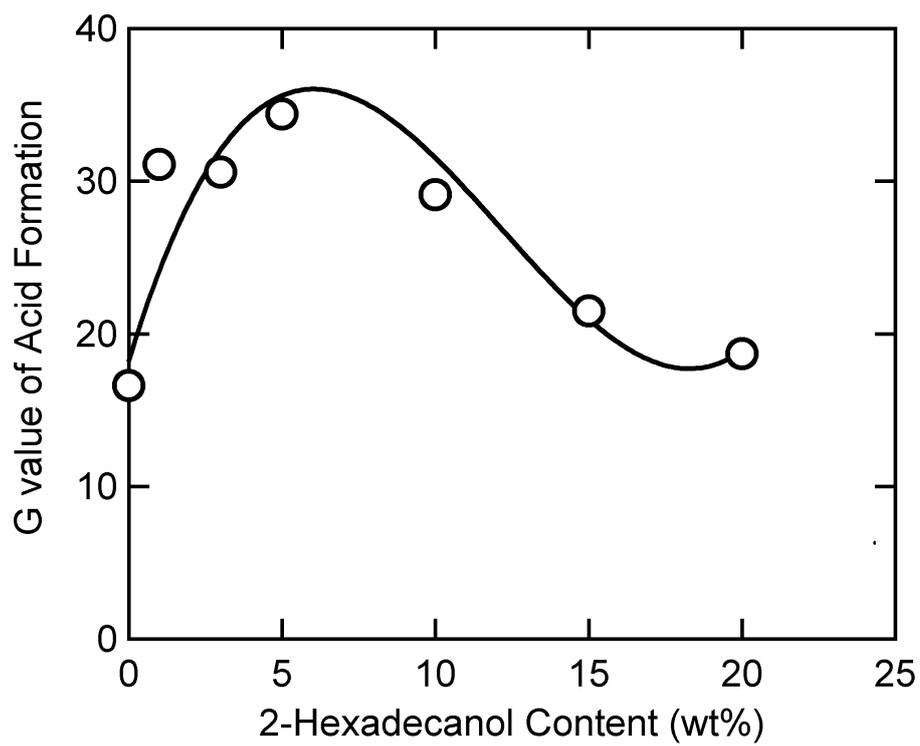


Figure 3. H. Koizumi et al.