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Author(s)	Okamoto, Kazumasa; Ishida, Takuya; Yamamoto, Hiroki; Kozawa, Takahiro; Fujiyoshi, Ryoko; Umegaki, Kikuo
Citation	Chemical physics letters, 657, 44-48 https://doi.org/10.1016/j.cplett.2016.05.058
Issue Date	2016-07-16
Doc URL	http://hdl.handle.net/2115/70977
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Type	article (author version)
File Information	Dynamics of the radical cations2.pdf

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Dynamics of radical cations of poly(4-hydroxystyrene) in the presence and absence of triphenylsulfonium triflate as determined by pulse radiolysis of its highly concentrated solution

Kazumasa Okamoto^{1*}, Takuya Ishida¹, Hiroki Yamamoto², Takahiro Kozawa², Ryoko Fujiyoshi¹, and Kikuo Umegaki¹

¹*Division of Quantum Science and Engineering, Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan*

²*The Institute of Scientific and Industrial Research (ISIR), Osaka University, Ibaraki, Osaka 567-0047, Japan*

*Corresponding author

Kita13 Nishi8, Kita-ku, Sapporo, Hokkaido, 060-8628

Tel: +81-0-11-706-6672

E-mail: kazu@eng.hokudai.ac.jp

Abstract

Pulse radiolysis of highly concentrated poly(4-hydroxystyrene) (PHS) solutions in cyclohexanone and *p*-dioxane was performed both with and without an onium-type photoacid generator (PAG). With increasing PHS concentration, the rate constant of deprotonation of PHS radical cations was found to decrease. In the presence of PAG, the yield of the multimer radical cation of PHS was shown to decrease. We found that pairing between the anions produced by the attachment of dissociative electrons of PAGs and the monomer PHS radical cations restrict local molecular motions, leading to the formation of the multimer PHS radical cations.

Keywords: poly(4-hydroxystyrene); deprotonation; pulse radiolysis; radiation chemistry; resist

1. Introduction

Chemically amplified resists (CARs) have been utilized as patterning materials for mass production of semiconductor devices using conventional photolithography (ArF, KrF, etc.) [1,2]. Patterning of typical CARs uses a polarity change induced by acid-catalyzed deprotection of nonpolar groups of polymers. CARs mainly consist of matrix polymers and photoacid generators (PAGs). Acid generation is induced by a thermal procedure, which is followed by energy deposition of photons onto the resist film. CARs remain one of the most important materials used in extreme-ultraviolet (EUV) and electron beam (EB) lithography [3], because of their ability to increase the sensitivity to the exposure dose. The mechanism of reactions on EUV and EB resists exposed to ionizing irradiation involves formation of short-lived intermediates such as ions, electrons, radicals, and excited states [4,5]. The acid generation mechanism in a CAR has been proposed to proceed as follows: Secondary electrons initially formed via the ionization step attach to PAG, producing counteranions of Brønsted acids. Highly acidic ionized matrices containing an OH group (radical cations) are then deprotonated. The protons thus generated then migrate through the matrix and encounter counteranions.

Pulse radiolysis, a time-resolved spectroscopic method used for ionized resist polymers such as novolaks [6,7], acrylates [8–10], and polyoxystyrenes [11–16], has been used to model base polymers of CARs. Pulse radiolysis studies of resist polymers have been conducted mainly in dilute solution. Radiation-induced intermediates are selectively produced by changing the solvent. In lithography, however, thin-film resists are used in the exposure process. Thus, bulky samples of amorphous polymers such as atactic polystyrene and acrylates are used to conduct radiolysis using an electron beam with MeV-order pulses. Poly(4-hydroxystyrene) (PHS), a typical constituent of EUV

and EB CARs, has been used in KrF (248 nm) lithography as a backbone polymer. However, the dynamics of radical cations of this compound in solid states are poorly understood. Pulse radiolysis of solid PHS samples having sub-centimeter thickness is difficult because of their low transparency, which is a result of their crystalline nature.

We have recently reported that a difference exists in the molecular dynamics of resist polymers with and without PAG in dilute solutions [16]. The dynamics of radical cations of PHS and poly(4-methoxystyrene) (PMOS) solutions with PAG are known: the yield of PMOS radical cations increases with the addition of PAG, whereas the yield of PHS radical cations only slightly increases with such addition. In the present study, we attempted pulse radiolysis of a highly concentrated solution containing PAG in order to clarify the acid-generation mechanism in a solid CAR film.

2. Experimental procedure

2.1 Apparatus

Pulse radiolysis was used to observe the time-resolved photoabsorption of short-lived intermediates produced after EB pulse irradiation. Pulse radiolysis experiments were performed at the Institute of Scientific and Industrial Research (ISIR), Osaka University. Samples were irradiated by an 8 ns EB pulse from a 27 MeV L-band linac. A Xe flash lamp producing white light was used as the light source. Light was finally passed through a sample in a monochromator (Ritsu MC-10N) and was detected by using Si (300–1000 nm) and InGaAs (950–1600 nm) photodiodes. Signals from the photodiode were sent to a digital oscilloscope (Tektronix TPO7254 or Iwatsu DS-5314).

2.2 Samples

PHS (11,000 g/mol, Sigma-Aldrich), anhydrous *p*-dioxane (Sigma-Aldrich), and

cyclohexanone (Sigma-Aldrich) were used without further purification. Triphenylsulfonium triflate (TPS-tf; Midori Kagaku) was used as received. Condensation of the sample was carried out in a vacuum oven at 60–90 °C. Highly concentrated sample solutions of PHS (>50 wt%) used for pulse radiolysis were orange to brown but remained transparent in the near-infrared region. Further deaeration procedures were not carried out, because primary process of radical cations is immune to O₂ [17]. Dosimetry was performed by using a KSCN dosimeter. The dose per shot of the EB was around 270 Gy. The solutions were irradiated at room temperature in a quartz cell with 1.0 cm optical path length. Viscosimetry was carried out with a Cannon–Fenske viscometer (Shibata).

3. Results and discussion

Previous studies have determined the primary process after ionization of PHS by using pulse radiolysis [11–16]. These studies mainly used samples of diluted PHS solutions. Solvents possessing ionization energies higher than that of PHS (< 8.34 eV), such as cyclohexanone, benzonitrile, and dioxane, have also been used in a similar study [18]. The reaction mechanism after the ionization in a concentrated PHS solution (> 10 wt%) is assumed to be as follows:

Ionization and excitation of solvent molecules (Solv) and PHS occurs via secondary electrons, as shown in Reactions (1) and (2). Radical cation of the solvent molecule ($\text{Solv}^+\bullet$) are then transferred to local phenyl rings (Ph-OH) and stacking sites $[(\text{Ph-OX})_2]$ (Reaction (3)). A monomer radical cation ($\text{Ph-OH}^+\bullet$) and an intramolecular dimer radical cation $[(\text{Ph-OH})_2^+\bullet]$ are also produced by molecular relaxation (Reaction (4)). The structures of ($\text{Ph-OH}^+\bullet$) and ($\text{Ph-OH})_2^+\bullet$ are shown in Fig. 1. Since the positive charge is localized on both the monomeric phenyl group ($n = 1$) and the stacking site of the phenyl group ($n > 1$), monomer and multimer radical cations respectively form [17,19,20]. The radical cations are neutralized by electrons through recombination (Reaction (5)); the electrons, however, may be scavenged by O_2 dissolved in the solution. Deprotonation mainly occurs at the hydroxyl group of the PHS radical cations, leading to the formation of phenoxyl radicals ($\text{Ph-O}\bullet$; Reactions (6) and (6')). Deprotonation has been hypothesized to occur through both static and dynamic mechanisms. Static deprotonation occurs immediately after ionization (within picoseconds), while dynamic deprotonation occurs via molecular motions. In phenol derivatives, the dynamic and static deprotonation ratio is 1:1 [21].

Figure 2 shows the transient absorption spectra obtained by pulse radiolysis of PHS solutions in *p*-dioxane and cyclohexanone. Broad bands in the near-infrared region may be ascribed to the charge resonance (CR) band of the multimer radical cation, as previously reported for PHS solutions [12–16]. Figure 3 shows kinetic traces of the CR band at 1150 nm. Fast and slow formations of the $(\text{Ph-OH})_2^+\bullet$ radicals were observed in the highly concentrated PHS solution ($[\text{PHS}] = \sim 50 \text{ wt\%}$) without PAG. Fast

formation of the $(\text{Ph-OH})_2^+\bullet$ radical within the EB pulse (8 ns) corresponds to Reactions (2) and (3); curves for slow formation depict Reaction (4). The decrease in absorption intensity of $(\text{Ph-OH})_2^+\bullet$ indicates the occurrence of deprotonation (Reaction (6')). We investigated the rate constant of dynamic deprotonation (k_D) in the region for concentrated PHS (> 40 wt%) to determine the relationship between k_D and the PHS concentration ([PHS]). The dependence of both k_D and the kinematic viscosity of both cyclohexanone and *p*-dioxane solutions on [PHS] is shown in Fig. 4. We found that k_D drastically decreased with [PHS] while the viscosity of the PHS solution increased. The viscosity of both solutions increased exponentially at [PHS] = 30 wt%. k_D also decreased as [PHS] increased, reaching a plateau in the region where [PHS] $< 45\%$. This result suggests that deprotonation is delayed as large molecular motions such as concerted main-chain motion are impeded by both molecular entanglement and an increase in steric hindrance [22]. The probability of intermolecular proton transfer, however, increases with increasing [PHS]. The rate of deprotonation of PHS radical cations increased because of conformation and/or orientation change of the PHS radicals in the solution. Because of a rapid increase in viscosity and the restriction of large molecular motion in the high-concentration region ([PHS] < 50 wt%), we assumed that k_D changes by a relatively small amount in this region. Values of k_D extrapolated to [PHS] of 100% in the cyclohexanone and dioxane solutions are assumed to be below 2×10^5 and $5 \times 10^4 \text{ s}^{-1}$, respectively. The large difference between these two k_D values may be explained by the differing states of PHS molecules in each solution. Cyclohexanone was shown to be a relatively poor solvent of PHS, as evaluated by dynamic light scattering experiments at room temperature. By contrast, interactions among polymer chains become enhanced in cyclohexanone, suggesting that the

deprotonation mechanism in cyclohexanone solution is similar to that in a solid PHS film.

Pulse radiolysis of concentrated PHS solutions using a typical PAG, TPS-tf, was also carried out. Figure 2 shows the transient absorption spectra obtained by pulse radiolysis of concentrated PHS solutions of cyclohexanone and *p*-dioxane using TPS-tf ([PHS] $\approx$ 50 wt%) after a 50 ns EB pulse irradiation. The broad bands in the near-infrared region appeared because of the CR band of the multimer radical cation. Figure 3 shows the kinetic traces of transient absorption in the presence of TPS-tf at 1150 nm. The addition of TPS-tf clearly caused a decrease in the intensity of the CR absorption band. In a recent study, we observed the effects of pulse radiolysis of dilute solutions of TPS-tf in PHS ([PHS] $\approx$ 2.3 wt%) [16]. In this study, the yield of the multimer radical cation increased slightly upon addition of TPS-tf, thus indicating that the reaction mechanism depends upon the solution concentration. Curves depicting formation of multimer radical cations in PHS solutions without TPS-tf (Fig. 3) were observed within 1 μ s after irradiation with the EB pulse. Formation curves for PHS solutions of TPS-tf were not observed because of changes in the molecular dynamics of the radical cation due to the addition of TPS-tf, the details of which are discussed below. The rate constant of decay of the CR band was determined for each solution. The formation and decay curves, which are represented by k_1 and k_D , respectively, can be fitted to a first-order exponential kinetic model, as shown in Table 1. The k_D value obtained in cyclohexanone decreased with increasing TPS-tf concentration. In the PHS solution with TPS-tf, the following reactions occur in addition to those mentioned above [16]:

Reaction (7) represents electron scavenging by TPS-tf leading to the conversion of TPS-tf into the triflate anion (X^-). Reaction (8) shows the subsequent formation of the ion pair between $(\text{Ph-OH})_n^+ \bullet$ and X^- $[(\text{Ph-OH})_n^+ \bullet \dots X^-]$. A previous study has proposed that the formation of the ion pairs occurs via a reaction between PMOS radical cations and X^- [16]. In dilute PHS solution formation of $(\text{Ph-OH})_n^+ \bullet \dots X^-$ was not apparent because of the fast contact between the constituting ions $[(\text{Ph-OH})_n^+ \bullet \dots X^-]$, leading to deprotonation. In highly viscous media, however, such approach is restricted, thus allowing formation of the ion pair. The high polarity of cyclohexanone (relative permittivity (ϵ) = 18.3, Reichardt parameter = 0.281 [23]) may contribute to stabilization of $(\text{Ph-OH})_n^+ \bullet \dots X^-$ via solvation. In contrast, the relatively low polarity of *p*-dioxane (ϵ = 2.2, Reichardt parameter = 0.164 [23]) results in relatively poor stabilization of the ion pair via solvation. The Reichardt parameter is an empirical measure of polarity of the solvent based on its photoabsorption. For water and tetramethylsilane, its values are assumed to be 1.000 and 0.000, respectively. Thus, this parameter is consistent with the dependence of k_D on the TPS-tf concentration.

The decrease in the intensity of the CR absorption band upon addition of TPS-tf is of interest, as it signifies an increase in ion yields due to the obstruction of ion recombination upon addition of an electron scavenger, which is typical of a radiation chemical reaction [24–26]. The decrease in the intensity of the CR absorption band coincides with the multimer radical cation yield. Similarly, the formation of benzene multimer radical cations has been reported to be suppressed in the presence of an electron scavenger in a viscous glassy matrix [17]. In a semisolid state, formation of

$(\text{Ph-OH})^+ \bullet \dots \text{X}^-$ is assumed to occur via a reaction between PHS radical cation and triflate anion, as depicted in Reaction (8). Formation of the ion pair leads to the restriction of the dynamic conformational change of the polymer chain; that is, it blocks formation of multimer radical cations from the monomer radical cation. In a previous study, we reported that the formation of the multimer radical cation reduces k_D by stabilization of the CR [12]. In this study, the probability of deprotonation of the multimer radical cation formed in the PHS film in the presence of a PAG was estimated to be 30–50% lower than a previous estimate for the diluted solution; the yield of the multimer radical cation decreased along with the TPS-tf concentration.

The acid generation mechanism in the PHS film may be explained on the basis of the phenomena described above (Fig. 5). Fast deprotonation of the PHS radical cation occurs immediately after ionization. In the absence of PAG, acids are not produced (Fig. 5 (a)). Electrons are recombined with radical cations and/or captured by impurities such as O_2 and radiation-induced products. However, in the absence of PAG, slow deprotonation observed via pulse radiolysis mainly occurs through pairing between radical cations and X^- . The probability of deprotonation of the PHS monomer radical cation increases with addition of PAG to a highly concentrated solution, which has a characteristic very similar to that of solid film. We previously reported that the deprotonation rate of the monomer radical cation of PHS is higher than that of the multimer radical cation [12]. Therefore, a reduction of the π -stacking interactions in the styrene units of a styrene-based CAR may explain the apparent increase in deprotonation efficiency. However, molecular relaxation, which occurs within a nanosecond after ionization, is not inhibited at room temperature in non-CARs. Along with acid generation, the deprotonation efficiency and efficiency of PAG sensitization

determine the resist performance in terms of properties such as sensitivity and line edge (width) roughness. We also found that rate of deprotonation depends on the viscosity and polarity of the medium. Hence, molecular designs that enhance static deprotonation via energetic destabilization of the radical cation are important in enhancing the efficiency of acid generation.

4. Conclusions

The mechanism of reactions on CARs in the presence of a PAG in a highly concentrated PHS solution was experimentally investigated. PHS solution was used as a model of a resist. The mechanism of radiolysis in the PHS solution has been discussed in terms of the dynamics of radical cations of the solution. Different reaction mechanisms in highly concentrated (~50 wt%) and diluted (~2.3 wt%) PHS solutions are proposed on the basis of pulse radiolysis experiments. Deprotonation of the PHS radical cation occurs immediately after ionization (fast deprotonation). Slow deprotonation, which has been observed by pulse radiolysis experiment, occurs mainly by pairing between X^- (anion obtained through the reaction of TPS-tf with e^-) and the radical cations of PHS monomer or multimers. A large conformational change in the polymer chain is restricted in the viscous matrix. This restriction implies that the yield of deprotonation of the multimer radical cations decreases in the solid film. Therefore, deprotonation of the monomer radical cation is more important than is deprotonation of the polymer cation in dilute solution because of the decrease in π -stacking interactions, as previously hypothesized. The increase in deprotonation efficiency may thus be a suitable strategy for enhancing the acid yield.

Acknowledgments

The authors wish to express their thanks to the members of the Research Laboratory for Quantum Beam Science, ISIR, Osaka University, for their assistance with the pulse radiolysis experiments. This work has been partly supported by the Cooperative Research Program of the Network Joint Research Center for Materials and Devices and by the Grant-in-Aid for Scientific Research (project nos. 24561037, 25630424, and 15K06662) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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Figure captions

Fig. 1.

Structures of $\text{Ph-OH}^+\bullet$ and $(\text{Ph-OH})_2^+\bullet$.

Fig. 2.

Transient absorption spectra obtained by EB pulse radiolysis at 50 ns after EB pulse irradiation of a PHS solution (~50 wt%) in cyclohexanone (a) and *p*-dioxane (b) with (the concentration of TPS-tf is 5 and 10 wt% with respect to PHS) and without TPS-tf.

Fig. 3.

Kinetic traces of the PHS (~50 wt%) solution in cyclohexanone (a) and *p*-dioxane (b) with (the concentration of TPS-tf is 5 and 10 wt% with respect to PHS) and without TPS-tf as obtained by pulse radiolysis at 1150 nm. Fit curves are also shown.

Fig. 4.

Dependence of PHS concentration in cyclohexanone (a) and *p*-dioxane (b) on the kinematic viscosity of the solution (dashed line) and kinetic constant of deprotonation (k_D) of the PHS radical cation (solid line).

Fig. 5.

Mechanism of radiation-induced acid generation in a PHS film without (a) and with PAG (b).

Table 1. Rate constants for the formation of the multimer radical cation (k_1) and deprotonation (k_D) in cyclohexanone and *p*-dioxane with and without TPS-tf, as obtained by pulse radiolysis at 1150 nm.

Solvents	[TPS-tf] /wt%	$k_1/10^6 \text{ s}^{-1}$	$k_D/10^6 \text{ s}^{-1}$
cyclohexanone	0	2.6	5.5
	5	-	4.1
	10	-	3.4
<i>p</i> -dioxane	0	7.2	6.4
	5	-	7.9
	10	-	7.0

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5