Pulse Radiolysis Study on a Highly Sensitive Chlorinated Resist ZEP520A

Yuji Hosaka¹, Tomoko Gowa Oyama², Akihiro Oshima¹,³, Satoshi Enomoto³, Masakazu Washio¹, and Seiichi Tagawa¹,³

¹: Research Institute of Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku, Tokyo 169-8555 Japan
²: Quantum Beam Science Directorate, Japan Atomic Energy Agency, 1233 Watanuki, Takasaki, Gunma 370-1292 Japan
³: The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047 Japan

ZEP520A is one of the most popular positive electron beam (EB) resists used in research and photomask fabrication owing to its good spatial resolution, high sensitivity, and high dry etching resistance. Herein, EB-induced early reactions of ZEP520A were investigated via pulse radiolysis. Dissociative electron attachment and formation of a charge transfer complex were definitive contributing factors to the efficient degradation of ZEP520A. Furthermore, products induced by direct ionization of ZEP520A were observed in a highly concentrated ZEP520A solution in tetrahydrofuran, suggesting that early reactions in the ZEP520A solid film that were induced only by direct ionization could be simulated during pulse radiolysis in specific solutions.

Keyword: electron beam resist, ZEP520A, pulse radiolysis, direct ionization

1. Introduction

Chlorinated polystyrene derivatives such as poly(chloromethylated styrene) (CMS) and poly(α-methyl chloromethylated styrene) have been studied as cross-linking type (negative) electron beam (EB) resists containing phenyl rings that improve the dry etching resistance of the resists [1,2]. On the other hand, the development of main-chain scission type (positive) EB resists exhibiting dry etching resistance is relatively difficult given that their high tendency towards degradation reduces the dry etching resistance [3]. ZEP520A (ZEON) is a relatively recently developed positive EB resist exhibiting high tendency towards degradation and dry etching resistance. ZEP520A is a 1:1 alternating copolymer of α-methylstyrene and α-chloromethacrylate. The α-methylstyrene units in ZEP520A contain phenyl rings that improve the dry etching resistance [4], and the α-chloromethacrylate units in ZEP520A contain reactive chlorine atoms. The chemical structure of ZEP520A is shown in Figure 1.

![Chemical structure of ZEP520A](image-url)
ZEP520A is practically applied in researches and photomask fabrication owing to its excellent properties. For example, the spatial resolution of ZEP520A is as high as 10 nm, its sensitivity is about 10 times higher than that of poly(methyl methacrylate) [5], and it exhibits high dry etching resistance. In spite of the excellent performance of ZEP520A, the mechanisms of EB-induced degradation of ZEP520A have not been fully clarified. In previous work, the mechanisms of degradation of ZEP520A were investigated based on analysis of the final products of degradation by means of X-ray photoelectron spectroscopy (XPS), gel permeation chromatography (GPC), Fourier transform IR spectroscopy (FT-IR), and nuclear magnetic resonance (NMR) spectroscopy. Efficient random chain scission with a G-value of approximately 8 was observed by means of GPC [7], and the decomposition of C−Cl bonds in irradiated ZEP520A was observed using XPS and FT-IR [6,7]. Moreover, NMR spectroscopy confirmed that terminal double bonds (−CH=CH₂) generated via main-chain scission were formed at both the α-chloromethacrylate unit and α-methyl-styrene unit [7]. Therefore, multi-channels of degradation were suggested, which were induced by dissociative electron attachment (DEA) and the after-mentioned formation of a charge transfer (CT) complex between the phenyl ring and chlorine atom.

The radiation-induced early reactions of polystyrene in chlorinated solvents have been studied by utilizing pulse radiolysis and laser flash photolysis [8-10]. The transient absorption band of the CT complex formed between the phenyl ring and chlorine atom is typically observed around 320 nm and 500 nm for polystyrene solution in chloroform (CHCl₃) [8-10], in carbon tetrachloride (CCl₄) [9,10], and in dichloromethane (CH₂Cl₂) [10]. The CT complex is also generated by irradiation of other polystyrene derivatives in the presence of a chlorine atom, and often induces cross-linking or decomposition in these polystyrene derivatives. For example, cross-linking of CMS film is induced by a side-chain benzyl type radical and main-chain α-radical, which are generated by the CT complex [11,12], and main-chain scission of poly-α-methylstyrene in chloroform and carbon tetrachloride is induced by main-chain β-radical that is generated by the CT complex [13,14]. Because ZEP520A contains a phenyl ring as well as chlorine atom, generation of the CT complex of ZEP520A is also conceivable, and the CT complex is plausibly involved in the EB-induced efficient degradation of ZEP520A. In the present study, the radiation-induced early reactions of ZEP520A, including DEA and generation of the CT complex, were investigated using pulse radiolysis.

2. Experimental

A solution of ZEP520A ($M_w = ~57,000$) in anisole (methoxybenzene) was purchased from ZEON, and was purified by the reprecipitation technique using isopropyl alcohol and toluene to generate a powder. Polystyrene ($M_w = 15000$) and poly-α-methylstyrene ($M_w = 8300$) were purchased from Sigma-Aldrich, and used without further purifications. Dichloromethane (DCM) and tetrahydrofuran (THF) were purchased from Kishida Chemical and Wako Pure Chemical, and used as solvents without purification.

The pulse radiolysis experiments based on optical absorption spectroscopy were performed at room temperature using the EB pulse (beam energy: 28 MeV; bunch length: 8 ns) which was obtained from the L-band linac in the Institute of Scientific and Industrial Research, Osaka University. The EB pulse and the white probe light emitted by the Xe lamp were injected to the quartz sample cell (light path length: 2.0 cm) coaxially. The time resolution of the pulse radiolysis system was about 10 ns. All of the samples were deoxidized by bubbling with Ar for 10 minutes and sealed in the quartz sample cell.

3. Results and Discussion

3.1. Pulse radiolysis in DCM

Figure 2 shows the normalized transient absorption spectra of 200 mM ZEP520A, 200 mM polystyrene, and 200 mM poly-α-methylstyrene solution in DCM obtained via pulse radiolysis immediately after the EB pulse ($t = 0$ ns). Broad absorption bands were observed at 500 nm for these solutions in DCM. Normalized kinetic traces of these solutions acquired at 500 nm are also shown in the insert in Figure 2. The absorption band that was observed for the polystyrene solution in DCM at 500 nm is derived primarily from the CT complex formed between the phenyl
ring and chlorine atom [10]. The CT complex is formed in DCM by EB irradiation as follows:

\[
\begin{align*} 
\text{DCM} & \rightarrow \text{DCM}^{\ast\ast} + e^{-} \quad (1) \\
\text{DCM}^{\ast\ast} + \text{Ph} & \rightarrow \text{DCM} + \text{Ph}^{\ast\ast} \quad (2) \\
\text{DCM} + e^{-} & \rightarrow \text{CH}_2\text{Cl}^{\ast} + \text{Cl}^{-} \quad (3) \\
\text{Ph}^{\ast\ast} + \text{Cl}^{-} & \rightarrow [\text{Ph}^{\ast\ast\delta}\text{Cl}^{-\delta}]^{\ast} \quad (4)
\end{align*}
\]

DCM is initially ionized by EB irradiation (Eq. (1)), the phenyl cation radical (Ph\(^{\ast\ast}\)) is generated by hole transfer from DCM to Ph (Eq. (2)), and the chlorine ion (Cl\(^{-}\)) is generated by electron scavenging caused by the solvent, which contains a chlorine atom (Eq. (3)). The CT complex is formed by the recombination of Ph\(^{\ast\ast}\) with Cl\(^{-}\) (Eq. (4)).

Given that the absorption band of the CT complex of poly-\(\alpha\)-methylstyrene solution in carbon tetrachloride was reported previously [14], which was similar to that of polystyrene solution in DCM, the absorption band observed at 500 nm for the poly-\(\alpha\)-methylstyrene solution in DCM (Figure 2) was attributed primarily to the CT complex. More precisely, these absorption bands observed at 500 nm are overlapping signals of the CT complex and Ph\(^{\ast\ast}\); however, the intensity of the absorption of Ph\(^{\ast\ast}\) at 500 nm is very low for polystyrene solution in DCM [10]. Generation of the CT complex is also conceivable for ZEP520A solution in DCM as shown in Figure 2 because of the similarity of the absorption band and the structure to those of poly-\(\alpha\)-methylstyrene. Given that the absorption of Ph\(^{\ast\ast}\) at 500 nm for the ZEP520A solution in DCM may not be negligible, the lifetime of the CT complex of ZEP520A is difficult to determine from the data in the insert in Figure 2.

The lifetime of the CT complex of the poly-\(\alpha\)-methylstyrene solution was longer than that of the polystyrene solution (insert of Figure 2). The CT complex may be dissociated by the abstraction of nearby hydrogen atoms [14]. The hydrogen atom is bonded to the \(\alpha\)-position of polystyrene, whereas the methyl group is bonded to the \(\alpha\)-position in poly-\(\alpha\)-methylstyrene. Consequently, hydrogen abstraction is inhibited and the \(\beta\)-radical is generated instead of the \(\alpha\)-radical in the case of poly-\(\alpha\)-methylstyrene. Because the \(\beta\)-radical is not able to interact with the conjugated system of the phenyl ring, in contrast to the \(\alpha\)-radical, the \(\beta\)-radical is relatively unstable, and thus efficient degradation of poly-\(\alpha\)-methylstyrene in halogenated solvents induced by the \(\beta\)-radical has been reported [13,14]. Given that the methyl group is bonded to the \(\alpha\)-position of the \(\alpha\)-methylstyrene units in ZEP520A (Figure 1), similar to the case of poly-\(\alpha\)-methylstyrene, it is concluded that formation of the CT complex is a precursor of degradation for the ZEP520A solution in chlorinated solvents.

3.2. DEA of ZEP520A in THF

The transient absorption spectrum that is obtained via pulse radiolysis immediately after the EB pulse \((t = 0\ ns)\) for pure THF is shown in Figure 3. The broad absorption band of the solvated electron is observed for pure THF in the IR and visible wavelength regions in response to EB irradiation. The wavelength of maximum absorption of the solvated electron in THF is 2.1 \(\mu m\) [15,16]. Thus, the broad absorption band observed for pure THF in Figure 3 is due to the solvated electron in THF. EB-induced fundamental reactions in THF are presented in Eqs. (5-7).

\[
\begin{align*} 
\text{THF} & \rightarrow \text{THF}^{\ast\ast} + e^{-} \quad (5) \\
e^{-} & \rightarrow e_{\text{solvated}}^{-} \quad (6) \\
\text{THF}^{\ast\ast} + \text{THF} & \rightarrow \text{THF}(-H)^{\ast} + \text{THF}(+H)^{\ast} \quad (7)
\end{align*}
\]

Equation (5) represents the generation of the cation radical of THF (THF\(^{\ast\ast}\)) by EB-induced ionization, Eq. (6) represents solvation of the electron, and Eq. (7) represents the reaction of THF\(^{\ast\ast}\) with solvent THF.
The transient absorption spectra that were obtained via pulse radiolysis immediately after the EB pulse ($t = 0$ ns) for 50 mM ZEP520A solution and 500 mM ZEP520A solution in THF are also shown in Figure 3. The intensity of the absorbance of the solvated electron decreased with increasing concentration of ZEP520A. It is conceivable that the lifetime of the solvated electron was shortened due to electron scavenging by ZEP520A, which contains a chlorine atom. Consequently, it was difficult to observe the short-lived solvated electron using the nanosecond pulse radiolysis system with 10 ns time resolution.

$$ZEP + e_{solvated}^{-} \rightarrow ZEP(-Cl)^{+} + Cl^{-}$$ (8)

Equation (8) represents electron scavenging by dissociative electron attachment (DEA) of ZEP520A. Because the chlorine atom in ZEP520A is bonded directly to the main-chain as shown in Figure 1, dissociation of the chlorine atom generates a main-chain radical at the $\alpha$-chloromethacrylate unit of ZEP520A. Main-chain scission ($\beta$-scission) may be induced by the radical to generate terminal double bonds at the $\alpha$-chloromethacrylate unit of ZEP520A, as has been observed by NMR analysis [7]. Hence, it is concluded that DEA is a precursor of the degradation of ZEP520A.

3.3. Direct ionization of ZEP520A in THF

A weak absorption band was also observed at 500 nm for the 500 mM ZEP520A solution in THF, as shown in Figure 3. It is conceivable that the absorptions of the CT complex and Ph$^{+}$ overlap in the band at 500 nm, in common with DCM solvent. However, Ph$^{+}$ is not generated via hole transfer from THF to Ph unlike in the case of DCM solvent, given that THF$^{+}$ is very quickly consumed by the THF solvent, as represented in Eq. (7). Therefore, Ph$^{+}$ and the CT complex are not generated in THF solvent via the same mechanism as in DCM solvent.

Figure 4 shows the transient absorption spectra obtained via pulse radiolysis of 500 mM ZEP520A solutions with 5 mM tri-n-octylamine, which is a cation scavenger, in THF. A tail of absorption band with relatively long lifetime was observed beyond 900 nm for 500 mM ZEP520A solution in THF in the absence of tri-n-octylamine; the absorption band beyond 900 nm was short-lived in the presence of tri-n-octylamine. It has been reported that the intramolecular dimer phenyl cation radical (Ph$_2^{++}$) of polystyrene exhibits a broad absorption band.
at 1200 nm in DCM due to charge resonance [10]. The absorption band observed beyond 900 nm for the ZEP520A solution in THF is plausibly attributable to Ph$_2$$^+$, but intramolecular Ph$_2$$^+$ is not generated in ZEP520A because intramolecular charge resonance of the phenyl rings occurs only when the number of carbons between the phenyl rings is 3 [17]. The number of carbons between the phenyl rings in ZEP520A is 5 because ZEP520A is an alternating copolymer as shown in Figure 1. Therefore, the absorption band observed beyond 900 nm is attributed to intermolecular Ph$_2$$^+$.

The insert in Figure 4 shows kinetic traces acquired at 500 nm for 500 mM ZEP520A solution in THF. The absorption at 500 nm was also short-lived in the presence of tri-n-octylamine; however a component with long lifetime persisted for more than 100 ns after the pulse. These results confirm that the absorption at 500 nm constitutes overlapped absorption of the CT complex, which is hardly affected by the cation scavenger, and of Ph$_2$$^+$, which is easily scavenged by the cation scavenger.

Observation of Ph$_2$$^+$, Ph$_2$$^+$, and the CT complex without hole transfer from THF solvent is plausibly because Ph$_2$$^+$ is generated by the direct ionization of ZEP520A. The mass percentage of ZEP520A in a 500 mM ZEP520A solution in THF is about 12%, and the percentage of direct ionization of ZEP520A may be roughly comparable to this value. The electron generated by direct ionization of ZEP520A was also scavenged by DEA in ZEP520A (Eq. (8)) and converted to Cl$^-$. Consequently, the formation of the CT complex by the geminate recombination of Ph$_2$$^+$ and Cl$^-$ occurs very rapidly for a 500 mM ZEP520A solution in THF, as shown in the insert in Figure 4.

The EB-induced reactions in the solid film of ZEP520A are due only to the direct ionization of ZEP520A. Because the CT complex generated by the direct ionization of ZEP520A was observed in THF, the CT complex should be also generated in the solid film of ZEP520A. Because the CT complex is a precursor of degradation in ZEP520A solution in chlorinated solvents as mentioned above, the CT complex of ZEP520A should also be a precursor of degradation in the solid film, and generate terminal double bonds at the α-methylstyrene unit of ZEP520A, as has been observed via NMR analysis [7]. These inferences suggest that the radiation-induced early reactions in the solid film can be simulated via pulse radiolysis of the concentrated solution in THF. It is a unique result obtained via pulse radiolysis.

4. Conclusion

Electron scavenging of ZEP520A by DEA was observed during the present pulse radiolysis experiment in THF solvent. The main-chain radical derived from DEA plausibly induces β-scission of ZEP520A. The CT complex formed between the phenyl ring and chlorine atom of ZEP520A was observed via pulse radiolysis of ZEP520A solutions in both DCM and THF, and the phenyl cation radical and the CT complex, which were generated by the direct ionization of ZEP520A, were observed in THF. The CT complex is proposed to be a precursor of degradation of ZEP520A, similar to the case of radiation-induced main-chain scission induced by the CT complex of poly-α-methylstyrene in halogenated solvents. These two reaction channels definitively contribute to the efficient degradation of ZEP520A. Furthermore, given that the products generated by the direct ionization of ZEP520A are observed in THF, we suggest that the radiation-induced early reactions in the solid film can be simulated via pulse radiolysis of a concentrated solution in THF.

Acknowledgements

The authors acknowledge Dr. Kazuyuki Enomoto, Dr. Shoji Suemine, and Prof. Takafumi Kondoh (Osaka University) for assistance with linac operation, and Dr. Kazuyuki Sakaue (Waseda University), Dr. Kazumasa Okamoto (Hokkaido University), and Dr. Toshitaka Oka (Tohoku University) for fruitful discussions. This work was supported by the RISE research project 11L01 (Waseda University) and by the Cooperative Research Program of “Network Joint Research Center for Materials and Devices” (2011246, 2012256).

References

(1979), 1628.