Electron-Beam-Induced Chromism Combined with Photo- or Thermal Reverse Reaction for Color Imaging

Kazuyuki Enomoto,^{a†} Yasunari Maekawa,^{a*} Sachiko Kono,^b Masakazu Iwasaki,^c and Tadashi Narita^c

^a High Performance Polymer Group, Environment and Industrial Materials Research Division,
Quantum Beam Science Directorate, Japan Atomic Energy Agency (JAEA)
1233 Watanuki, Takasaki, Gunma 370-1292, Japan

^b Department of Applied Chemistry, Faculty of Engineering, Saitama Institute of Technology,
1690 Fusaiji, Fukaya, Saitama 369-0293, Japan

^c Department of Applied Chemistry, Graduate School of Engineering,
Saitama Institute of Technology, 1690 Fusaiji, Fukaya, Saitama 369-0293, Japan

[†] Current address: The Institute of Science and Industrial Research, Osaka University
E-mail: maekawa.yasunari@jaea.go.jp

Reversible color imaging on polymer films with a spiropyran (**SP-NO₂**) or a diarylethene (**DE**) has been examined by electron-beam (EB) induced chromism combined with a photo- or thermal reverse reaction. Colorless **SP-NO₂** in a poly(methyl methacrylate) (PMMA) film transformed into red-colored zwitterionic merocyanine (**MC-NO₂**), which subsequently converted to the original **SP-NO₂** via thermal treatment. After six time repetition of the reaction cycle, the absorption intensity of **MC-NO₂** decreased to 56% of the initial level. The decrease was attributed to the formation of a protonated **MC**-form (**MC-H⁺**) via the reaction of **MC-NO₂** with an acid generated by EB-radiolysis of PMMA. Contrary to thermal treatment in the polymer films containing **SP-NO₂**, a photo reverse reaction could be applied for EB-induced color imaging using **DE** in the polymer films, where the thermally stable colored close-form of **DE** (**DE_{Cl}**) obtained by an EB-induced reaction can be converted to the original colorless open-form (**DE_{Op}**) via photoreaction. The matrix effect of poly(BFP-*alt*-DOX) was observed with good efficiency of color formation and higher fatigue resistance of **DE** than those in PSt and PMMA matrices. The color imaging of these films was performed by electron beam direct writing to form 100–1000 nm square and line/space (L/S) patterns. The color images of 5 μm square patterns were produced in the PMMA film containing **SP-NO₂** with a dose of 100 μC cm⁻²; the images could be faded upon the thermal treatment. The poly(BFP-*alt*-DOX) film containing **DE** yielded clear color imaging of 100 nm L/S patterns with a dose of 200 μC cm⁻². Subsequently, the patterns bleached upon the irradiation of visible light of > 430 nm. It is noted that these reactions are the first example for reversible transformation of color imaging induced by EB radiation together with heat or light treatment.

Keywords: Electron-beam; Chromic Dye; Color Imaging.

1. Introduction

Electron beam direct writing (EBDW) technique now enables a resolution limit down to sub-10 nm, which would not be achieved by light, and thus should be applicable to high-density recording devices.¹ The major requirement for EB recording devices is that EB-induced chemical changes provide optical or reflective-index differentiation between the exposed and unexposed regions. We previously reported that polymer films with acid-responsive chromic molecules and acid generators were well acted as an electron beam-induced color imaging system. The

EBDW on the acid-chromic polymer films yielded clear color imaging of 100–200 nm line/space (L/S) patterns with a dose of only 10 μC cm⁻².² Although design and search for highly EB-sensitive materials are required for realizing such devices, little is known of the EB radiolysis of potential materials.³

Photochromism is photo-induced reversible isomerization of chemical species between two forms having different absorption spectra. The fast change in properties arising from the chemical-bond reconstruction via photo-excitation has been attracting

much attention from the viewpoint of both fundamental phenomena and application to optoelectronic devices such as rewritable optical memory and switches.^{1f,4} The reversible transformation of typical photochromic compounds, such as azobenzene, spiropyran, spirooxazine, and diarylethene, takes place thermally and/or photochemically.⁵ A data recording and de-recording system in optical memory is consisted of an each chromic dye dispersed in the transparent matrix such as poly(methyl methacrylate) (PMMA) and polycarbonate (PC).⁶ If EBDW technique with a beam size of 10 nm is applied for data-recording of optoelectronic devices, the density of memory extremely increases by several orders of magnitude.⁷

Thus, herein we propose EB-induced color imaging systems that show reversible transformation of chemical species between two isomers with EB irradiation and heat (or light). Spiropyran (**SP-NO₂**) and diarylethene (**DE**) were employed here as photochromic dye molecules. One of the major problems to utilize the focused EB for the color imaging is low radiation resistance (mainly degradation) of matrix materials such as PMMA and PC.⁸ The fluorinated polymer prepared by radiation-induced polyaddition of bis(α -trifluoromethyl- β , β -difluorovinyl) terephthalate with 1,4-dioxane, poly(BFP-*alt*-DOX), has higher radiation resistance, compared with typical degradation polymers such as PMMA and polystyrene (PSt), as shown in Scheme 1.⁹ Thus, we also investigated the matrix effect of poly(BFP-*alt*-DOX) on the above color imaging system compared with that of conventional polymers such as PSt and PMMA.

Scheme 1

2. Experimental

Materials. 1',3',3'-Trimethyl-6-nitrospiro[1(2H)-benzopyran-2,2'-indoline] (**SP-NO₂**) was purchased from Aldrich and used as received. 1,2-Bis[2-methyl benzo[b]thiophen-3-yl]3,3,4,4,5,5-hexafluoro-1-cyclopentene (**DE**) was purchased from TCI and used as received. Poly(methyl methacrylate) (PMMA) (Aldrich; M_w 15000), and polystyrene (PSt) (Scientific Polymer Products, Inc.; M_w 45000) were purified by reprecipitation from dichloromethane solution (5 wt.-%) to a large excess amount of

methanol, and then dried *in vacuo*. Poly(BFP-*alt*-DOX) was prepared by the γ -rays-induced polyaddition of bis(α -trifluoromethyl- β , β -difluorovinyl) terephthalate (BFP) with 1,4-dioxane (DOX) and purified according to our previous article (M_n = 10600).⁹ Triphenylsulfonium trifluoromethanesulfonate (TPS-Tf) was purchased from Toyo Gosei Co., Ltd. and recrystallized from methanol and ethyl acetate. Cyclohexanone and 2-ethoxyethanol were supplied by Wako Pure Chemical Industries, Ltd. and used as received.

Instruments. UV-visible spectra were measured with a Hitachi U-3210 spectrophotometer. Film thickness was measured using a Mitsutoyo SURFTEST SV-600 surface profiler. Visible light illumination was conducted on an USHIO optical system with a high-pressure mercury lamp (SH-UI500XQ) as a light source. The light was filtered before injecting perpendicularly on a film surface. A water cylindrical glass container with 10 cm in length was used for cutting off the infrared to avoid heating of the film. Color glass filter, Y-43 (Asahi Technoglass), was used for controlling the illumination wavelengths.

Preparation of polymer films. Solutions containing matrix polymers, poly(BFP-*alt*-DOX), PSt, and PMMA, and 5 wt.-% of **SP-NO₂** or 8 wt.-% of **DE** (relative to polymer weight) in cyclohexanone/2-ethoxyethanol (2:1 (w/w)) were passed through a 0.20 μm filter. The solutions obtained were spin-coated onto quartz or silicon substrates followed by pre-bake at 90 °C for 3 min on an Iuchi P-DHP hot plate. The film thickness was controlled by changing solution concentration (15–30 wt.-%) and spinning speed (1800–3000 rpm) with a Mikasa Spincoater 1H-D7.

EB irradiation. The polymer films containing **SP-NO₂** or **DE**, which were covered with Kapton film (12 μm thickness) and placed on water-cooled copper metal plates, were irradiated with EB of 1 MeV and 0.5 mA in an atmosphere using a Cascade Type Electron Accelerator (Dynamitron) at JAEA, Takasaki. The changes in absorption spectra of exposed films were measured by UV-visible spectra.

EBDW. The nanoscopic color imaging of the polymer film containing **SP-NO₂** or **DE** was conducted with a raster scanning EB, using the JSM-5310W Tokyo Technology Beam Draw System. The accelerating voltage of the incident electron beam was kept at 20 keV. The beam diameter was 50 nm with a probe current of 200 pA. The probe current was calibrated by using a Faraday cup before and after experiments. Scanning color images were acquired using a KEYENCE VK-8500 digital microscope and using a Lasertec 1LM21H confocal scanning laser microscope.

3. Results and Discussion

3-1. EB-induced reactions of spiropyran

The progress of the EB-induced reaction of **SP-NO₂** in PMMA films on a quartz plate was monitored using UV-vis spectroscopy because the similar films exhibited a reversible phenomenon involving photo-induced changes in the visible absorption region. Figure 1 shows changes in the UV-vis spectra of the PMMA films containing **SP-NO₂** with 5 wt.-% of the polymer with irradiation doses in the range of 0–200 $\mu\text{C cm}^{-2}$. The unexposed film has the absorption in an UV region with absorption edge at around 400 nm (only UV region). Upon EB-irradiation, the PMMA film containing **SP-NO₂** showed an absorption band at $\lambda_{\text{max}} = 552$ nm, assigned to merocyanine (**MC-NO₂**), which has a red-colored zwitterionic open-form.¹⁰ The new band increased gradually with increasing an irradiation dose with isosbestic points at 287 nm and 356 nm during EB-irradiation in the spectrum. The maximum absorption intensity was 0.04 μm^{-1} with a dose of 200 $\mu\text{C cm}^{-2}$.

Figure 2 shows changes in UV-vis absorption spectra of the PMMA film containing **SP-NO₂** with 5 wt.-% of the polymer by EB irradiation with a dose of 100 $\mu\text{C cm}^{-2}$ and subsequent thermal treatment at 90 °C for 30 s; the chromic reaction between **SP-NO₂** and **MC-NO₂** isomers was depicted in Scheme 2. Upon EB-irradiation, the PMMA film containing **SP-NO₂** exhibited a new absorption peak at $\lambda_{\text{max}} = 552$ nm, corresponding to red color with a dose of 100 $\mu\text{C cm}^{-2}$; then, the newly generated absorption band (**MC-NO₂**) disappeared upon the thermal treatment. It is obvious that **SP-NO₂** molecules in the PMMA film reversibly transform between colorless **SP-NO₂** and colored **MC-NO₂** with EB and thermal reactions, respectively. The absorption intensity of irradiated and thermally treated films was plotted at an each chromic cycle in Figure 2, Inset. The absorbance of the colored **MC** form at 552 nm decreased with

Figure 1. UV-vis spectra of the PMMA films containing **SP-NO₂** with 5 wt.-% of the polymer with irradiation doses in the range of 0–200 $\mu\text{C cm}^{-2}$.

Figure 2. UV-vis spectral changes of the PMMA film containing **SP-NO₂** upon the chromic reactions with EB irradiation (100 $\mu\text{C cm}^{-2}$) and thermal treatment (90 °C, 30 s). Inset figure: the plot of absorption intensities of irradiated and thermally treated films monitored at 552 nm at an each coloration/ decoloration cycle.

Figure 3. UV-vis spectral changes of the PMMA film containing **SP-NO₂** upon the chromic cycles with (a) after EB irradiation (100 $\mu\text{C cm}^{-2}$) and (b) thermal treatment (90 °C, 30 s).

increasing cycle number: at six cycles, the absorbance decreased to 56% of the initial level. Figure 3 shows the UV-vis spectra of the PMMA film containing **SP-NO₂** after EB irradiation (Figure 3a) and thermal treatment (Figure 3b) at each EB/thermal chromic cycle. Both spectra were changed with isosbestic points at 501 nm and 372 nm. One possible explanation for both spectral changes to show the isosbestic points is that the EB/thermal chromic cycles transformed the initial **SP-NO₂** form into colored

MC-NO₂ with a slight amount of a single by-product due to a side reaction.

The by-product with absorption band at around 440 nm (Figure 3b) is probably attributed to the protonated form (**MC-H⁺**) of the zwitterionic MC open-form by comparing the absorption band with the photolytic product in acidic solutions.¹¹ In order to confirm the formation of **MC-H⁺**, PMMA films containing the same amount of **SP-NO₂** with extra TPS-Tf, which is a highly EB-sensitive material producing a strong acid (Scheme 3),¹² was irradiated. The acid generated in the film by EB induced reaction of TPS-Tf should bind with **MC-NO₂** to form the protonated **MC-H⁺** form.

Scheme 3

Figure 4 shows the UV-vis spectra of the PMMA film containing **SP-NO₂** and TPS-Tf as an acid generator with doses up to 300 $\mu\text{C cm}^{-2}$. The intensity of the absorption band around 440 nm gradually increased with increasing irradiation doses, as observed in Figure 3b. **MC-NO₂** is trapped with the acid (H^+) generated from TPS-Tf immediately to give **MC-H⁺**. The acid, therefore, acts as a trapping agent of **MC-NO₂** (Scheme 4). In order to examine the amounts of acid generated from PMMA upon EB irradiation, the PMMA film containing 3',6'-bis-

Scheme 4

Figure 4. UV-vis spectral changes of the PMMA film containing **SP-NO₂** and TPS-Tf as an acid generator with a dose in the range of 0–300 $\mu\text{C cm}^{-2}$.

(diethylamino)fluoran (rhodamine B base), which undergoes a γ -lactone ring opening reaction to give the protonated rhodamine with absorption band at $\lambda_{\text{max}} = 560 \text{ nm}$, was irradiated under the same conditions.^{2,13} The PMMA film containing rhodamine with 1 wt.-% of the polymer was irradiated with a dose of 100 $\mu\text{C cm}^{-2}$. The intense absorption at around 560 nm was observed, strongly indicating the acid generation from EB-radiolysis of the PMMA matrix. Furthermore, the acid generation from the radiolysis of ethyl acetate (AcOEt), which seems to be an analog of a PMMA monomer repeating unit, is well established.¹⁴ The initial products in the radiolysis of AcOEt are the AcOEt cation and the electron (e^-). The AcOEt cation subsequently converts to AcOEt radical and an acid (H^+), as shown in reactions 1 and 2, respectively.

According to the above results, **MC-H⁺** at $\lambda_{\text{max}} = 460 \text{ nm}$ generates in the protonation of zwitterionic **MC** (open-form) with the acid (H^+) resulting from EB-radiolysis of the PMMA matrix.

The EB-induced chromic reactions of **SP-NO₂** in the PMMA matrix can be formulated by a mechanism shown in Scheme 5. **SP-NO₂** primarily leads to upper or the lowest excited states of **SP-NO₂** by direct excitation or energy transfer from matrix polymers, followed by transformation into zwitterionic **MC-NO₂**; in the absence of acid, **MC-NO₂** reverts thermally to **SP-NO₂**. In the presence of acid, on the other hand, **MC-NO₂** reacts with the acid generated by EB-radiolysis of the PMMA matrix, giving the protonated **MC-H⁺** form.

Scheme 5

3-2. EB-induced reactions of diarylethene.

Contrary to thermal treatment for the reverse reaction in the polymer films containing **SP-NO₂**, a photo reverse reaction was applied for nanoscopic EB-induced color imaging using diarylethene (**DE**) in polymer films because it is well known that colorless open-form (**DE_{Op}**) and a thermally stable colored close-form (**DE_{Cl}**) can be converted to each other via

Figure 5. UV-vis spectral changes of the PSt films containing **DE_{Op}** with 8 wt.% of the polymer with a dose in the range of 0–600 $\mu\text{C cm}^{-2}$.

photoreactions with different wavelengths light.^{1f}

Figure 5 shows changes in UV-vis absorption spectra of the PSt film containing **DE_{Op}** with 8 wt.% of the polymer during irradiation doses up to 600 $\mu\text{C cm}^{-2}$. Upon EB-irradiation, the PSt film containing **DE_{Op}** showed a new absorption band at $\lambda_{\text{max}} = 525 \text{ nm}$, which assigned to **DE_{Cl}**.^{1f} The new band gradually increased with the increases of irradiation doses and then saturated at absorption intensity of $0.037 \mu\text{m}^{-1}$ with a dose of 300 $\mu\text{C cm}^{-2}$. Figure 6 shows changes in UV-vis absorption spectra of the PSt film containing **DE_{Op}** upon alternating irradiation with EB and $> 430 \text{ nm}$ light. Upon EB irradiation, the PSt film containing **DE_{Op}** exhibited a red color with a dose of 100 $\mu\text{C cm}^{-2}$; the film became colorless upon the subsequent irradiation of visible light of $> 430 \text{ nm}$ for 1 min. The EB/photo chromic cycle is repeated eight times. As shown in Figure 6, Inset, changes in absorption intensity of the colored **MC**-form after EB irradiation decreased with increasing cycle numbers: the absorption intensity at eight cycles was 59% of that observed at the first cycle. The low durability of **DE** doped in PSt film may accounts for the formation of by-product due to a side reaction induced by the EB-radiolysis of PSt as well as PMMA (vide ante).

Figure 7 shows UV-vis absorption spectra of the PSt film containing **DE_{Op}** at each alternating irradiation cycle with EB (100 $\mu\text{C cm}^{-2}$) and $> 430 \text{ nm}$ light for 1 min; (a) after EB irradiation and (b) after visible light irradiation. The absorption bands at $\lambda_{\text{max}} = 525 \text{ nm}$ and at around 370 nm, which were separated via an isosbestic point at 460 nm, decreased and increased with increasing cycle numbers, as shown in Figure 7a. The absorption band at around 370 nm in the film after visible light exposure also increased with increasing cycle numbers (Figure 7b). The presence of isosbestic points indicates that a slight amount of a single by-product gradually accumulated during the EB/photo chromic cycles even though, at this moment, the by-product possessing

Figure 6. UV-vis spectral changes of the PSt film containing **DE_{Op}** upon alternating irradiation with EB (100 $\mu\text{C cm}^{-2}$) and light ($> 430 \text{ nm}$, 1 min). Inset figure: the plot of absorption intensity of EB and photo irradiated films monitored at 525 nm at each coloration/decoloration cycle.

Figure 7. UV-vis absorption spectra of the PSt film containing **DE_{Op}** at each alternating irradiation cycle with EB (100 $\mu\text{C cm}^{-2}$) and $> 430 \text{ nm}$ light for 1 min; (a) after EB irradiation and (b) after visible light irradiation.

absorption maxima at around 370 nm cannot be assigned.

The polyaddition of BFP and DOX proceeds without remarkable cross-linking and the scission of the polymer main chains in the corresponding ether solution to give poly(BFP-*alt*-DOX) of $M_n = 5100$ with a dose of 3000 kGy though most polymers are subjected to some damage by γ -rays and EB irradiation at doses of over 100 kGy.⁹ This indicates

Figure 8. The plots of absorption intensity of the film containing DE_{Op} at 510 nm as a function of irradiation doses: (●) PSt, (▲) poly(BFP-*alt*-DOX), and (■) PMMA.

that poly(BFP-*alt*-DOX) has high radiation-resistance, and therefore it should work as a matrix polymer for EB-induced chromic systems. Upon EB-irradiation, the poly(BFP-*alt*-DOX) film containing colorless DE_{Op} exhibited red color with a dose of $100 \mu\text{C cm}^{-2}$. The new band at $\lambda_{\text{max}} = 510 \text{ nm}$ assigned to the red-colored DE_{Cl} , transformed from DE_{Op} via a cyclization reaction, by comparing the new band with that obtained by γ -rays and photo-induced reactions.^{1f,4c,15} The formation of DE_{Cl} , therefore, should be expressed by the cyclization reaction of DE_{Op} in the poly(BFP-*alt*-DOX) film in Scheme 6. The matrix effect of poly(BFP-*alt*-DOX) on the chromic reactions was compared with that of conventional polymers such as PSt and PMMA. Figure 8 shows plots of absorption intensity at 510 nm as a function of an irradiation dose. The absorbance attributing to the formation of DE_{Cl} was gradually increased with increasing irradiation doses and then saturated, except for PMMA. The EB-induced reaction in the poly(BFP-*alt*-DOX) film containing DE_{Op} exhibited a few times higher coloration efficiency than that in the PMMA film.

Figure 9 shows relative absorption intensity of the films containing DE_{Op} in poly(BFP-*alt*-DOX), PMMA, and PSt at 510 nm after EB-irradiation at each EB/photo cycle (up to 9). The relative intensity of the colored form in the poly(BFP-*alt*-DOX) matrix almost kept constant even after 5 cycles, then gradually declined to 81% ($0.015 \mu\text{m}^{-1}$) of the first cycle at 8 cycles. Although the PSt film containing DE_{Op} exhibited a high EB-induced coloration efficiency at the first cycle, the relative intensity of the PSt film containing DE_{Op} at 510 nm decreased linearly to 80% of the first cycle with 3 cycles. A similar result was obtained with the PMMA film. These results may account for the following two

Figure 9. Relative absorption intensity of the films containing DE_{Op} in poly(BFP-*alt*-DOX), PMMA, and PSt at 510 nm after EB-irradiation at each EB/photo cycle: (●) PSt, (▲) poly(BFP-*alt*-DOX), and (■) PMMA.

reasons: (1) the side reaction such as cross-linking and scission by EB-radiolysis was depressed by usage of high radiation-resistant poly(BFP-*alt*-DOX) as a matrix; (2) poly(BFP-*alt*-DOX) has higher electron density than PMMA does, and thereby showed higher generation efficiently of the activated (excited or ionized) species of DE_{Op} than that in PMMA.

3-3. EB-induced color imaging.

The color imaging of $5 \mu\text{m}$ square and L/S patterns on the PMMA film containing SP-NO_2 ($0.362 \mu\text{m}$ thickness) was performed using EBDW with a 50 nm diameter beam, and was then evaluated using optical and confocal laser microscopy. Figure 10a shows the optical microscopic image of $5 \mu\text{m}$ squares on the PMMA film containing SP-NO_2 drawn with a dose of $100 \mu\text{C cm}^{-2}$. Dark regions (blue color), $5 \mu\text{m}$ squares, correspond to the areas exposed with EB. Although the optical contrast was not high, the square patterns were observed with a dose of $100 \mu\text{C cm}^{-2}$; unfortunately, the L/S patterns with nanoscale resolution were blurred. The square patterns faded again upon the thermal treatment. It is indicated that the SP-NO_2 molecules doped in the PMMA film reversibly transform between the colorless SP-NO_2 and colored MC-NO_2 isomers with EB and thermal reactions, respectively. Figures 10b and 10c show the optical microscopic pictures of $5 \mu\text{m}$ square and L/S patterns on the PMMA film containing SP-NO_2 drawn with a dose of $400 \mu\text{C cm}^{-2}$, in which a clear blue color image was observed compared by that with a dose of $100 \mu\text{C cm}^{-2}$. These patterns, however, were thermally irreversible. This is due to the formation of MC-H^+ with increasing irradiation dose. We can observe the better imaging patterns of the same films with confocal scanning laser micrograph since it provides a monochrome image with high resolution.

Figure 10. *Top*: Optical microscopic image of 5 μm square patterns on the PMMA film containing **SP-NO₂** made with a dose of (a) 100 $\mu\text{C cm}^{-2}$ and (b) 400 $\mu\text{C cm}^{-2}$. *Bottom*: (c) Optical microscopic image of a L/S pattern with 100–1000 nm on the PMMA film containing **SP-NO₂** made with a dose of 400 $\mu\text{C cm}^{-2}$, and (d) Confocal scanning laser micrograph of the same film.

As shown in Figure 10d, Clear L/S (black and white) patterns with the resolution of 200 nm can be observed.

Next, color imaging of the poly(BFP-*alt*-DOX) film containing **DE_{Op}** (0.338 μm thickness) was examined using EBDW and observed using confocal scanning laser microscopy (Figure 11). The square and L/S patterns with optical differentiation between exposed (white) and unexposed (black) regions showed the clearest pattern of the film with a dose of 200 $\mu\text{C cm}^{-2}$ with the resolutions of 200 nm and 100 nm, respectively. Subsequently, the black and white patterns bleached upon the irradiation of visible light of > 430 nm. Thus, the nanoscale color imaging by

Figure 11. Confocal scanning laser micrograph of the poly(BFP-*alt*-DOX) film containing **DE_{Op}**, which was exposed using EBDW with a dose of 200 $\mu\text{C cm}^{-2}$.

reversibly transformation between colorless **DE_{Op}** and colored **DE_{Cl}** isomers can be achieved through EB and photochemical reactions, respectively.

4. Conclusion

The reversible color imaging on polymer films with a spiropyran (**SP-NO₂**) or a diarylethene (**DE**) has been examined by electron-beam (EB) induced chromism combined with photo or thermal reverse reactions. The colorless **SP-NO₂** in a poly(methyl methacrylate) (PMMA) film transformed into a red-colored zwitterionic merocyanine (**MC-NO₂**), which subsequently converted to the original **SP-NO₂** molecule via thermal treatment. Six time repetition of the reaction cycle made the absorption intensity of **MC-NO₂** decreased to 56% of the initial level. The decrease was attributed to the formation of the protonated **MC-form (MC-H⁺)** via a side reaction of **MC-NO₂** with an acid generated by EB-radiolysis of PMMA. Contrary to thermal treatment in the polymer films containing **SP-NO₂**, a photo reverse reaction could be applied for nanoscopic EB-induced color imaging using **DE** in the polymer films, where the thermally stable colored close-form of **DE (DE_{Cl})** obtained by an EB-induced reaction can be converted to the original colorless open-form (**DE_{Op}**) via photoreaction. The matrix effect of poly(BFP-*alt*-DOX) was observed with good efficiency of color formation and higher fatigue resistance of **DE** than that in PSt and PMMA matrices. The color imaging of these films was performed by electron beam direct writing (EBDW) with a 50 nm diameter beam to form 100–1000 nm square and line/space (L/S) patterns. The color images of 5 μm square patterns were produced in the PMMA film containing **SP-NO₂** with a dose of 100 $\mu\text{C cm}^{-2}$; the images could be faded upon thermal treatment. The poly(BFP-*alt*-DOX) film containing **DE** yielded clear color imaging of 100 nm L/S patterns with a dose of 200 $\mu\text{C cm}^{-2}$. Subsequently, the patterns bleached upon the irradiation of visible light of > 430 nm. It is noted that these reactions are the first example for reversible transformation of color imaging induced by EB radiation together with heat or light treatment.

Acknowledgments

The authors thank Mrs. S. Maniwa and H. Hanaya for making the facilities of the JAEA Electron Accelerator available to us. Technical support from Ms. K. Yuasa is also acknowledged.

References

- (1) (a) H.-P. Brack, C. Padeste, M. Slaski, S. Alkan, H. H. Solak, *J. Am. Chem. Soc.* **2004**, 126, 1004; (b) P. M. Mendes, S. Jacke, K. Critchley, J. Plaza, Y. Chen, K. Nikitin, R. E. Palmer, J. A. Preece, S. D. Evans, D.

- Fitzmaurice, *Langmuir* **2004**, *20*, 3766; (c) M. T. Russell, L. S. C. Pingree, M. C. Hersam, T. J. Marks, *Langmuir* **2006**, *22*, 6712; (d) Y. Wada, M. Katsumura, Y. Kojima, H. Kitahara, T. Iida, *Jpn. J. Appl. Phys.* **2001**, *40*, 1653; (e) S. Hosaka, H. Sano, K. Itoh, H. Sone, *Microelectron. Eng.* **2006**, *83*, 792; (f) M. Irie, *Chem. Rev.*, **2000**, *100*, 1685; (g) G. Berkovic, V. Krongauz, V. Weiss, *Chem. Rev.*, **2000**, *100*, 1741; (h) Y. Kaburagi, S. Tokita, M. Kaneko, *Chem. Lett.* **2003**, *32*, 888; (i) J. C. Scaiano, M. Laferriere, M. G. Ivan, G. N. Taylor, *Macromolecules*, **2003**, *36*, 6692.
- (2) Y. Maekawa, K. Yuasa, K. Enomoto, H. Matsushita, J. Kato, T. Yamashita, K. Ito, M. Yoshida, *Chem. Mater.*, **2008**, *20*, 5320.
- (3) (a) M. Farhataziz, A. J. Rodgers, *Radiation Chemistry, Principles and Applications*; VCH Publishers: New York, 1987; (b) Y. Tabata, Y. Ito, S. Tagawa, *Handbook of Radiation Chemistry*; Y. Tabata, Ed.; CRC Press: Boca Raton, 1991; (c) A. Hummel, In *Advances in Radiation Chemistry*; M. Burton, J. L. Magee, Eds.; John Wiley & Sons: New York, 1974, Vol. 4, 1-102.
- (4) (a) M. Irie, T. Fukaminato, T. Sasaki, N. Tamai, T. Kawai, *Nature*, **2002**, *420*, 759; (b) M. Irie, S. Kobatake, M. Horiuchi, *Science*, **2001**, *291*, 1769; (c) S. Kobatake, M. Irie, *Bull. Chem. Soc. Jpn.*, **2004**, *77*, 195; (d) K. Uchida, A. Takata, M. Saito, A. Murakami, S. Nakamura, *Adv. Funct. Mater.*, **2003**, *13*, 755; (e) C. Sanchez, B. Lebeau, F. Chaput, J. P. Boilot, *Adv. Mater.*, **2003**, *15*, 1969.
- (5) (a) K. Ichimura (Ed.); *Development of Chromic Materials*; CMC, Tokyo, 2000; (b) M. Irie (Ed.); *Application of Functional Dyes*; CMC, Tokyo, 2002.
- (6) S. Kawata, Y. Kawata, *Chem. Rev.*, **2000**, *100*, 1777.
- (7) (a) T. Imai, N. Shida, T. Higuchi, K. Suga, T. Iida, F. Yokogawa, *Jpn. J. Appl. Phys.*, **2001**, *40*, 1661; (b) M. Takeda, M. Furuki, T. Ishimoto, K. Kondo, M. Yamamoto, S. Kubota, *Jpn. J. Appl. Phys.*, **2000**, *39*, 797; (c) Y. Wada, M. Katsumura, Y. Kojima, H. Kitahara, T. Iida, *Jpn. J. Appl. Phys.*, **2001**, *40*, 1653.
- (8) V. S. Ivanov, *Radiation-chemistry of polymers*; VSP 1992, Chapter 4.
- (9) K. Enomoto, Y. Maekawa, Y. Katsumura, T. Miyazaki, M. Yoshida, H. Hamana, T. Narita, *Macromolecules*, **2005**, *38*, 9584.
- (10) (a) S. Kawata, Y. Kawata, *Chem. Rev.*, **2000**, *100*, 1777; (b) G. Berkovic, V. Krongauz, V. Weiss, *Chem. Rev.*, **2000**, *100*, 1741.
- (11) (a) K. Sumaru, M. Kameda, T. Kanamori, T. Shinbo, *Macromolecules*, **2004**, *37*, 4949; (b) I. Shimizu, H. Kokado, E. Inoue, *Bull. Chem. Soc. Jpn.*, **1969**, *42*, 1726; (c) K. Yoda, T. Ohzeki, T. Yuzawa, H. Takahashi, *Spectrochim. Acta.*, **1989**, *45A*, 855; (d) A. Fissi, O. Pieroni, N. Angelini, F. Lenci, *Macromolecules*, **1999**, *32*, 7116.
- (12) (a) S. Tagawa, S. Nagahara, T. Iwamoto, M. Wakita, T. Kozawa, Y. Yamamoto, D. Werst, A. D. Trifunac, *Proc. SPIE* **2000**, 3999, 204; (b) S-Y. Moon, Y. Maekawa, M. Yoshida, *Chem. Lett.* **2001**, 408; (c) K. Enomoto, Y. Maekawa, S-Y. Moon, J. Shimoyama, K. Goto, T. Narita, M. Yoshida, *J. Vac. Sci. Technol. B*, **2006**, *24*, 2337.
- (13) (a) M. Yanagita, I. Aoki, S. Tokita, *Bull. Chem. Soc. Jpn.*, **1997**, *70*, 2757; (b) S. Tokita, K. Nagahama, F. Watanabe, *J. Photopolym. Sci. Technol.*, **2000**, *13*, 187; (c) S. Tokita, F. Watanabe, K. Hashimoto, T. Tachikawa, *J. Photopolym. Sci. Technol.*, **2001**, *14*, 221; (d) M. Hojo, T. Ueda, M. Yamasaki, A. Inoue, S. Tokita, M. Yanagita, *Bull. Chem. Soc. Jpn.*, **2002**, *75*, 1569; (e) T. Tachikawa, M. Naito, *J. Photopolym. Sci. Technol.*, **2004**, *17*, 81.
- (14) (a) G. Ramanathan, *J. Phys. Chem.*, **1976**, *80*, 1553; (b) L. K. M. Kiminkinen, L. C. Zeller, H. I. Kenttamma, *J. Chem. Soc., Chem. Commun.*, **1992**, 466.
- (15) (a) S. Irie, M.-S. Kim, T. Kawai, M. Irie, *Bull. Chem. Soc. Jpn.*, **2004**, *77*, 1037; (b) S. Irie, M. Irie, *Bull. Chem. Soc. Jpn.*, **2002**, *75*, 2071; (c) S. Irie, M. Irie, *Bull. Chem. Soc. Jpn.*, **2000**, *73*, 2385; (d) S. Irie, M. Irie, *Mol. Cryst. and Liq. Cryst.*, **2000**, *345*, 179.