JOURNAL OF IMAGING SCIENCE AND TECHNOLOGY • Volume 41, Number 5, September/October 1997

Improvement in Durability Against the Repetition of Image Formation and Deletion by Crosslinking of the Polymer in Thermoreversible Recording Media

Yoshihiko Hotta and Tsuguo Yamaoka
Department of Image Science, Chiba University, 1-33, Yayoi-cho, Inage-ku, Chiba 263, Japan

Tetsuya Amano
Chemical Products Business Center, Ricoh Company, Ltd.,16-1, Honda-machi, Numazu, Shizuoka 410, Japan

We studied the durability against the repetition of image formation and deletion by crosslinking of the polymer in thermoreversible recording media composed of a polymeric film with dispersed long-chain molecules. These media have two different optical states, transparent or light scattering, depending on the thermal history. However, the media have the problem that the densities of the images change and the images become invisible as the number of repetitions of image formation and deletion increases. By observation of the internal structures in the recording layers, it was clarified that the deterioration of the image is caused by the particle growth of long-chain molecules in the recording layer; the particles grow by the heat and shear stress applied from the thermal printhead. Next, the properties of the recording layer crosslinked with electron beam irradiations were investigated, and it was clarified that the crosslinked recording layer did not soften very much at a high temperature. A high degree of crosslinking of the layer was obtained by applying multifunctional monomers, and the durability against the repetition was improved to 1000 times, at which the image contrast hardly changed from that before the repetitive experiment by the crosslinking.

Journal of Imaging Science and Technology 41: 542–549 (1997)

Introduction

Materials used as reversible recording media are now attracting attention from environmental as well as technological viewpoints because they would conserve plastic products, such as the cards and sheets used for an overhead projector. By offering superior functionality, they also would find new markets.

Ueno, Nakamura, and Tani showed that in a polymer having cholesteric liquid crystals as the pendant group, the pendant liquid crystals have two different alignments, depending on the rate at which the polymer is cooled to room temperature after being heated to 90–100°C. They also demonstrated that the polymers align in a planar conformation during slow cooling, whereas they align in a random conformation during rapid cooling.[1]

Two-component materials composed of some polymers and liquid crystals make up another group of candidates for thermoreversible materials. McIntyre and Soane reported on the thermoreversible behavior of a mixture of a polymer and a nematic-type liquid crystal, *N*-(4-ethoxybenzylidene)-4'-*n*-butylaniline,[2] and Takahashi and colleagues reported on the thermo-optical effects of a mixture of a polymer and 4-alkoxy-3-chlorobenzoic acid.[3] These polymeric films can assume either a transparent or a light-scattering state, depending on the method of heating and cooling. Although some promising thermoreversible materials have been reported, most of them require careful control of the cooling rate, which requires complicated devices for the recording and erasing.

A thermoreversible recording material composed of a polymer matrix with a dispersed low-molecular-weight compound may be promising for practical use[4] because the two optically different states (transparent and light-scattering) can be selected using only temperature; control of the cooling or heating rate is not necessary.

In a previous paper,[5] we proposed that the thermoreversible response of a recording material composed of a polymer matrix with a dispersed fatty acid is caused by the production of voids in the light-scattering state and the disappearance of voids in the transparent state. The assumption is explained in Fig. 1 as follows:

Figure 1(a) shows changes in transmittance in the heating–cooling cycle of the recording material, and Fig. 1(b) is a schematic illustration of the proposed internal structural changes of one particle of the fatty acid and the polymer matrix around the particle in the recording material. Consider what happens when a light-scattering film is heated to a temperature (T-temp) just below the melting point (T_m) of the fatty acid and cooled (A → B → D): The voids decrease and the transmittance increases above the glass transition temperature (T_g) of the polymer. At the T-temp, the fatty acid in the domain is still in a partially melted state; the melted fatty acid fills the voids, causing them to disappear, and the transmittance becomes near

---

Original manuscript received November 27th, 1996.

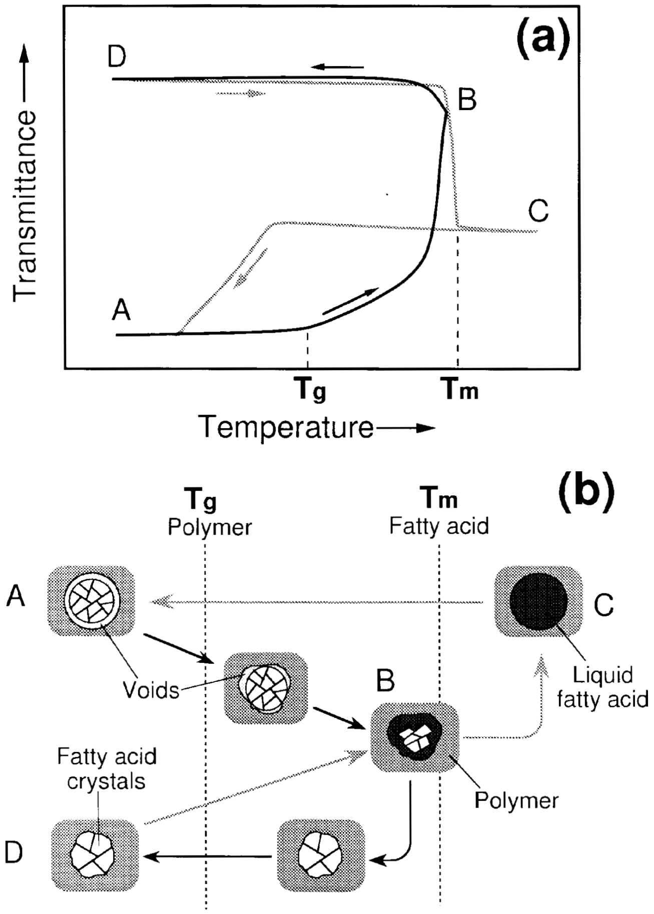

Figure 1. (a) Changes in transmittance and (b) schematic illustration of internal structural changes during heating–cooling cycles of thermoreversible recording media composed of a polymer with dispersed fatty acid.

maximum. When the film is cooled from this temperature, the fatty acid forms crystals without voids. The maximum transparent state is maintained at room temperature because at the temperature at which the fatty acid crystallizes, the matrix polymer is still soft and compensates for a volume shrinkage of the fatty acid by crystallization. On the other hand, when the transparent film is heated to a temperature (O-temp) higher than the T_m of the fatty acid (D → B → C), the fatty acid in the domains melts and the film becomes translucent. When the film is now cooled from O-temp to room temperature (C → A), the fatty acid crystallizes below the T_g by supercooling, forming a group of microcrystals together with many air-filled voids, and the film returns to the first light-scattering state. This is because the matrix polymer is rigid at the temperature at which the fatty acid finally crystallizes and thus cannot compensate for the volume shrinkage of the fatty acid.

The mechanistic study of this thermal response suggested the conditions required for such thermoreversible characteristics: that a glass transition temperature of the matrix is between two crystallizing temperatures of the fatty acid in the matrix. The two crystallizing temperatures of the fatty acid play a key role in the thermoreversibility. The fatty acid in the matrix crystallizes at a temperature just below the melting point of the fatty acid when it is cooled after being heated to a temperature slightly below the melting point, whereas the fatty acid crystallizes around 30°C lower than the melting point when it is cooled after being heated to a temperature higher than the melting point. Fatty acids themselves do not exhibit the supercooling phenomenon that the crystallizing temperatures are around 30°C lower than the melting points. The supercooling of fatty acids occurs only when the fatty acids formed particles dispersed in the polymer matrix. In a previous paper,[6] we presented the observation that proper immiscibility between the polymers and the fatty acids is required for forming the small-particle domains of the fatty acids in the polymeric films that is an essential requirement for the supercooling of the fatty acids. In another paper,[7] we presented the effects of the particle sizes of the long-chain molecules, the polarity of the molecules, and the dielectric constant of the polymer matrices on the supercooling phenomenon that is a key factor in thermoreversibility.

The light-scattering images usually are formed on the thermoreversible recording media by heating using a thermal printhead, and the images are deleted by heating using a hot stamp. The image formation and the deletion can be repeated from several times to several hundred times. However, there is a serious problem in that the densities of the images change, and the images become invisible as the number of repetitions of formation and deletion increases. Surprisingly few studies have been undertaken on the durability against the repetition of the image formation and deletion in the recording media.

This paper describes the changes in the internal structure of thermoreversible recording media composed of polymeric film with dispersed long-chain molecules and the effects of durability against the repetition of the image formation and deletion by crosslinking of the polymer in the media.

Experimental Section

Materials. Behenic acid (BA, 99% purity) was obtained from Sigma Chemical Co. Eicosanedioic acid (EDA, 99% purity) was purchased from Okamura Oil Mill, Ltd.

A copolymer of vinyl chloride and vinyl acetate (P(VC-VAc), M_n = 25,000, copolymerization ratio = 80/20) was obtained from Kaneka Corp. A vinyl chloride and vinyl acetate copolymer phosphate (P(VC-VAc-P), M_n = 20,000, copolymerization ratio = 84/15/1) was obtained from Denki Kagaku Kogyo Kabushiki Kaisha.

Dipentaerythritol hexaacrylate e-caprolacton adduct (DPHAC, M_W = 920, commercial product name DPCA-30) and trimethylolpropane triacrylate (TMPTA, M_W = 296) were purchased from Nippon Kayaku Co., Ltd. Neopentylglycol diacrylate (NPGDA, M_W = 212) was purchased from Shin-Nakamura Chemical Co., Ltd.

Dibutyltin bis-mercapto ester (DBTME, commercial product name JF-9B) was purchased from Sankyo Organic Chemicals Co., Ltd.

A mixture of acrylic monomers and free-radical initiator (commercial product name C7-157) was purchased from Dainippon Ink & Chemicals, Inc.

Tetrahydrofuran (THF) and toluene were purchased from Kanto Chemical Co., Inc.

Measurements. Recording films for analyses of the deterioration of light-scattering image density were prepared by dissolving P(VC-VAc) and BA in a mixture of THF and toluene and then coating it on polyester films using a wire bar. The coated films were dried at 130°C to form a layer about 10-µm thick.

We prepared recording films by dissolving P(VC-VAc), BA, EDA, DBTME, and various acrylic monomers in a mixture of THF and toluene and then coating the mixture on aluminized polyester films using a wire bar for dynamic thermal mechanical analysis. The coated films were dried at 130°C and then crosslinked by electron beam irradiation with various irradiation doses using a CURETRON EBC-200-100 area beam type electron beam processor from Nissin-High Voltage Co., Ltd., to form a recording layer about 10-μm thick. For comparison, the films without the acrylic monomer and the films not electron beam irradiated also were prepared in almost the same manner.

We prepared recording films by dissolving P(VC-VAc), BA, EDA, DBTME, and various acrylic monomers in a mixture of THF and toluene and then coating the mixture on aluminized polyester films on which P(VC-VAc-P) had been coated to form adhesive layers of about 0.5–1.0 μm using a wire bar, for experiments of image formation and deletion with a thermal printer. The coated films were dried and then cured in the manner previously described to form a recording layer about 10-μm thick. For comparison, the films without the acrylic monomer and the films not electron beam irradiated also were prepared in almost the same manner. The mixture of acrylic monomers and free-radical initiator was coated on the coated films to form a cured layer of about 2.5-μm thickness with ultraviolet irradiations using a high-pressure mercury-vapor lamp (80 W/cm, 2 s).

Polymeric films for gel fraction measurements were prepared by dissolving P(VC-VAc) and various acrylic monomers in a mixture of THF and toluene and then coating it on aluminized polyester films using a wire bar. The coated films were dried and then cured in the manner previously described to form a layer about 10-μm thick. For comparison, the films without the acrylic monomer and the films not electron beam irradiated were also prepared in almost the same manner.

Experiments of repetitive image formation and deletion were performed using an Okura thermal printer with a thermal printhead for the image formation and a hot stamp for the image deletion. The light-scattering image was formed by heating at 1.8 J/cm^2 using a Kyocera KBE-40-3MGKI thermal printhead having 320 dots in total, arranged at a density of 8 dots/mm, and deleted by heating at 120°C for 10 s using a brass hot stamp having a sheathed heater. The interval between the image formation and the deletion was 5–10 s.

Optical density measurements were performed using a Macbeth RD-914 reflection densitometer.

We observed the microscopic structure of the recording layer with a Hitachi H-500H TEM. The layer was stained by exposing it to OsO_4 vapor for 12 h, fixed with two-pack epoxy from Sony Chemicals Co. and sliced with an RMC MT6000-XL microtome to prepare a 1200–1300 Å thin film.

A recording layer and a polymeric layer prepared on substrates were peeled off and used for dynamic elastic properties and gel fraction measurements.

Gel fraction measurements were performed by measuring the weights of each layer and the remaining layer after soaking in THF for 24 h and then heating at 130°C for 3 h and by calculating the weight ratio of the remaining layer-to-layer before soaking.

Dynamic thermal mechanical analysis was performed with a Seiko Instruments TMA/SS150 in the pulling mode at a frequency of 0.02 Hz. The range of pulling stress was about 5–20 g/mm^2, and the temperature was continuously varied at the rate of 5°C/min.

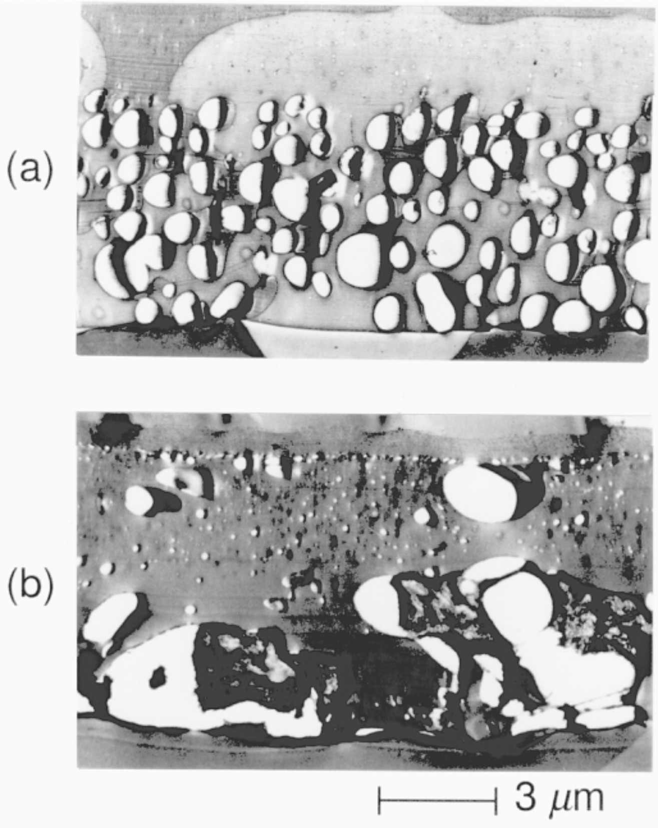

Figure 2. Cross-sectional TEM images of film composed of P(VC-VAc) with dispersed BA and EDA (a) before repetitive experiment and (b) after 400 cycles of image formation and deletion.

Results and Discussion

Analyses of Deterioration of Recording Layers by Repetition of Image Formation and Deletion. We studied the influences of the internal structures in the recording layers on the deterioration of the light-scattering image density in the thermoreversible recording media composed of P(VC-VAc) film with dispersed BA and EDA by the repetition of image formation and deletion with a thermal printer. Figure 2 shows TEM images of cross sections of the film (a) before the repetitive experiment and (b) after deterioration by 400 repetitions of image formation and deletion. The densities of the light-scattering image were 0.25 for the film before the repetitive experiment and 0.9 for the deteriorated film. The bright areas indicate voids in which BA and EDA existed before the recording layers were sliced with a microtome. The occurrence of voids seems to be the cause for the BA and EDA drop-off from the sliced films, because the recording films are still thinner than the diameters of the BA and EDA particles, and the BA and EDA are themselves brittle. However, a portion of BA and EDA, indicated by the uneven gray areas in Fig. 2(b), has remained in the voids. The dark areas around the bright areas and the uneven gray areas indicate the P(VC-VAc).

Figure 2(a) shows that BA and EDA are phase separated from the P(VC-VAc) to form small-particle domains (sizes 0.5–1.5 μm). However, in Fig. 2(b), although BA and EDA are also phase separated from the P(VC-VAc) matrix, the domains have grown large, and the very small domains (sizes 0.1–0.3 μm) also have increased. The deterioration of the light-scattering image by the repetition of

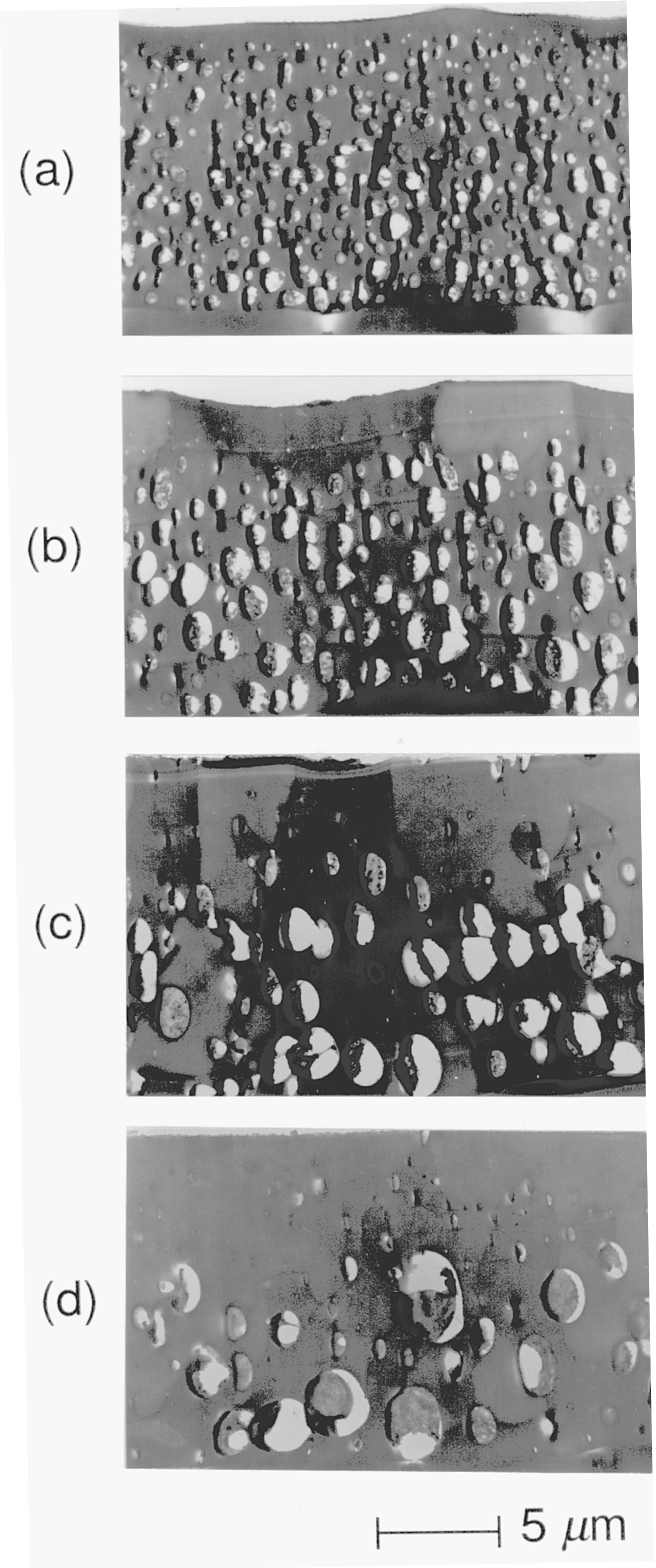

Figure 3. Cross-sectional TEM images of films composed of P(VC-VAc) with dispersed BA (a) before heating, and after heating at (b) 140, (c) 160, and (d) 170°C for 10 min.

image formation and deletion may have been caused by this particle growth. For example, it is possible that the crystallizing temperature of BA and EDA, after heating to a temperature higher than the melting point of EDA, approaches the glass transition temperature of P(VC-VAc) as the particles of the BA and EDA become larger,[7] and voids necessary in the recording layer for a sufficient light-scattering state do not occur. The detailed mechanism will be reported in a future paper.

We studied the effects of heat and pressure on the particle growth in the recording layer. In this experiment, BA alone was used as a long-chain molecule because the effects can be analyzed easily by decreasing the kinds of materials in the layer. Figure 3 shows TEM images of cross sections of polymeric films with dispersed BA (a) before heating, and after heating at (b) 140, (c) 160, and (d) 170°C for 10 min. The particle domains grow large as the heating temperature increases. This experimental result makes it clear that the particle growth in the recording layer also occurs by heating alone. This particle growth can be explained by Ostwald ripening,[8] the phenomenon that big droplets become bigger by absorbing small droplets because the small droplets are at a disadvantage in energy due to a larger interfacial area per unit volume. The particles grown by heating alone are smaller than the particles in the deteriorated film shown in Fig. 2(b); this indicates that the particle growth in the deteriorated layer is caused by another factor described below in addition to heating.

Figure 4 shows TEM images of cross sections of P(VC-VAc) films with dispersed BA after applying pressure and heat to them. Figure 4(a) shows a film after applying a normal stress of about 5 kg/cm^2 at 140°C for 1 h in an oven by placing a weight on a polyester film layered on top of the recording layer. The particle growth is not very much influenced by the normal stress; the particle sizes of BA shown in Fig. 4(a) are much the same as those shown in Fig. 3(b). This indicates that the heat and pressure by the hot stamp for image deletion is not the cause of the particle growth, because the hot stamp provides normal stress and heat. Figure 4(b) shows a film after applying a shear stress of about 440 g/cm^2 and a normal stress of about 5 kg/cm^2 at 140°C for 1 h in an oven by tilting the table on which the film and its weight were placed. The BA has become huge and occupies almost half the layer. The huge BA domains may be due to contact between adjacent BA particles in the layer. For example, it is possible that the thickness of the polymeric wall between adjacent particles becomes thin because of the shear stress and the heat, and the adjacent particles unite. This internal structure is very similar to that indicated in Fig. 2(b). Therefore, it is likely that the changes in the internal structure in the recording layer by the repetition of image formation and deletion with the thermal printer are due to the shear stress and heat applied by the thermal printhead, because the relative position of the printhead and the recording film changes with touching each other when the light-scattering image is formed.

Influences of Acrylic Monomers and Electron Beam Irradiation on Properties of Layers by Crosslinking of Polymer. We studied the properties of the recording layers at a high temperature by a crosslinking of the polymer in the recording layer with electron beam irradiation. The gel fractions of polymeric films for various irradiation doses of electron beam and various acrylic monomers were measured. Figure 5 shows

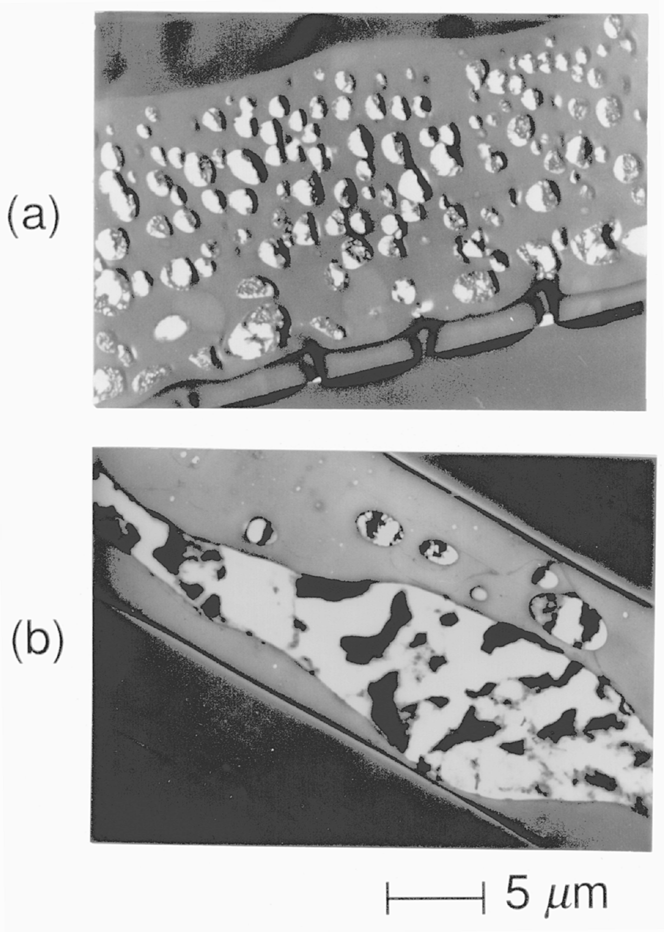

Figure 4. Cross-sectional TEM images of films composed of P(VC-VAc) with dispersed BA after applying (a) a normal stress of about 5 kg/cm^2 and (b) a shear stress of about 440 g/cm^2 and a normal stress of about 5 kg/cm^2, both at 140°C for 1 h.

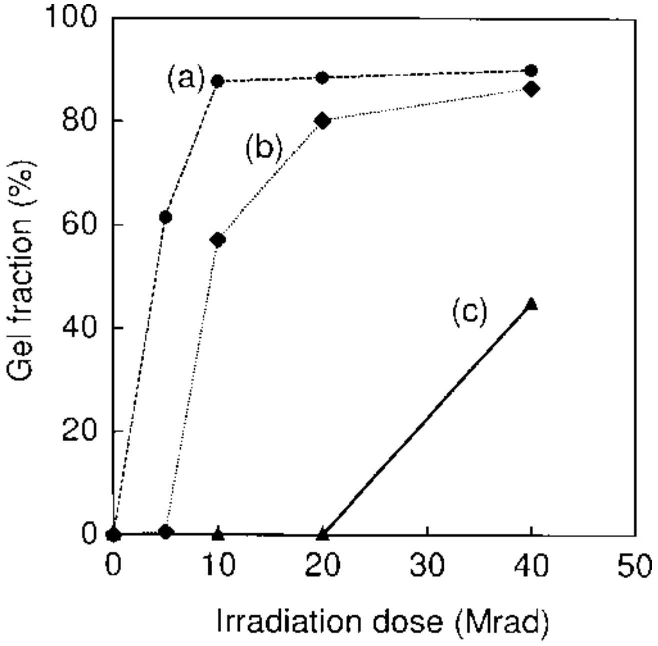

Figure 5. Gel fractions as a function of the irradiation dose of the electron beam for films composed of P(VC-VAc) with (a) DPHAC, (b) TMPTA, and (c) without acrylic monomer.

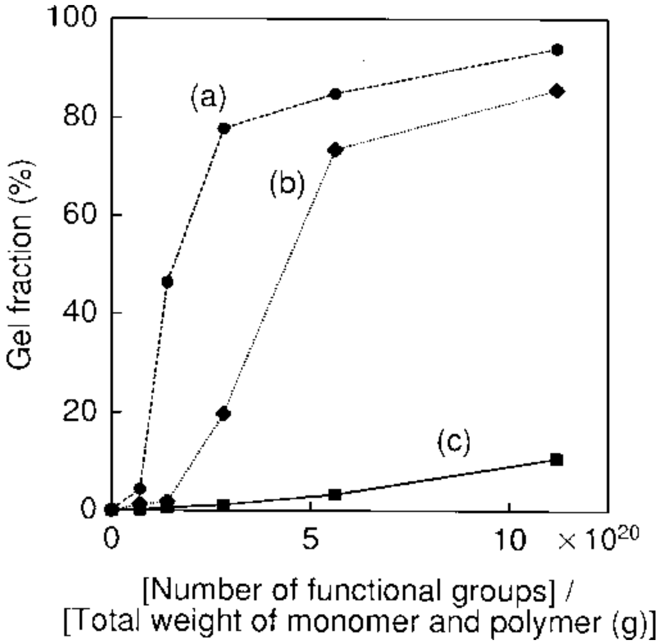

Figure 6. Gel fractions as a function of concentration of acrylic monomer groups, which is the number of functional groups per total weight of monomer and polymer, for films composed of P(VC-VAc) with (a) DPHAC, (b) TMPTA, and (c) NPGDA.

the gel fractions of P(VC-VAc) layers with (a) DPHAC, (b) TMPTA, and (c) without acrylic monomer for no or various irradiation doses of electrons. The concentration of acrylic functional groups, which is the number of acrylic functional groups per a total weight (g) of monomer and polymer, was 5.61×10^{20}. The gel fractions, that indicate the degree of crosslinking of the layers, become higher in the following order: films without acrylic monomer, films with TMPTA, and films with DPHAC. In the films with DPHAC, the values steeply rise at electron beam irradiations below 10 Mrad and then are steady at about 90% at irradiations above 10 Mrad.

Figure 6 shows gel fractions of P(VC-VAc) layers without acrylic monomer and with the addition of various quantities of (a) DPHAC, (b) TMPTA, and (c) NPGDA, applied by a 20-Mrad electron beam. The concentration of acrylic functional groups in the polymeric layers was varied from 0.7×10^{20} to 11.2×10^{20}. The gel fractions become higher in the following order: the films with NPGDA, TMPTA, and DPHAC as the concentration of acrylic functional groups increase. In the films with DPHAC, the values grow sharply at concentrations of acrylic functional groups below 2.8×10^{20} and then gradually increase to around 80% to 95% or more at concentrations above 2.8×10^{20}. From Figs. 5 and 6, it is apparent that the gel fractions for the films with DPHAC at a concentration of 5.6×10^{20} or more applied with a beam larger than 20 Mrad become 70% or greater.

The difference in the gel fraction among the various kinds of acrylic monomers in spite of the same concentration of acrylic functional groups seems to be caused by the difference in the crosslinking rate between the polymer and the acrylic monomers due to the molecular structure of each acrylic monomer. The crosslinking rate of the polymer and the acrylic monomers having long molecular chains may become high because of the flexibility of the molecular chains. The crosslinking rate between the polymer and DPHAC especially, may become

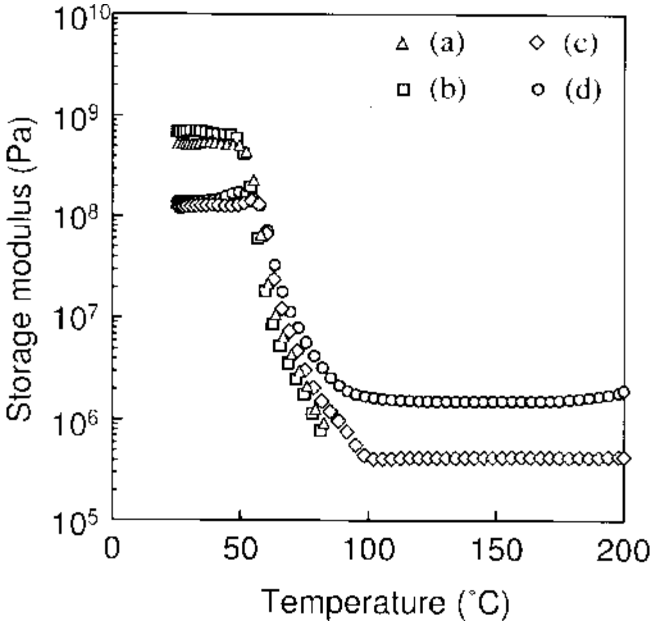

Figure 7. Dynamic storage modulus as a function of temperature for the recording layers (a) without acrylic monomer, and with (b) NPGDA, (c) TMPTA, and (d) DPHAC, irradiated with 20 Mrad of electrons.

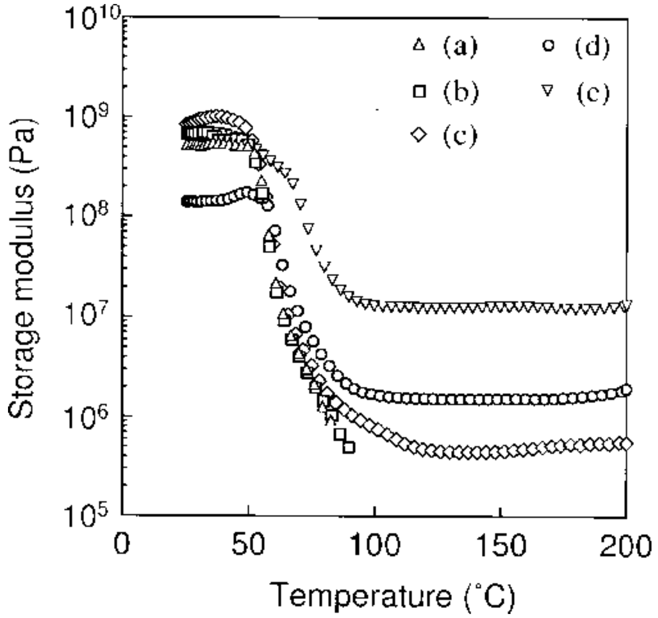

Figure 8. Dynamic storage modulus as a function of temperature for the recording layers (a) without acrylic monomer, and with various concentrations of acrylic functional groups, irradiated with 20 Mrad of electrons. Concentrations: (b) 1.4×10^{20}, (c) 2.8×10^{20}, (d) 5.6×10^{20}, and (e) 11.2×10^{20}.

still higher, because the flexibility of the molecular chain becomes even stronger due to the addition of ε-caprolacton.[9]

We studied the viscoelastic properties of crosslinked recording layers that had been electron beam irradiated. Figure 7 shows the dynamic storage modulus as a function of temperature for the recording layers (a) without acrylic monomer, and (b) with NPGDA, (c) TMPTA, and (d) DPHAC, irradiated with 20 Mrad of electrons. The curves for the layers without acrylic monomer and with NPGDA are not indicated at temperatures above about 80°C because the layers expand as the temperature rises and snap at about that temperature due to their low degree of crosslinking. The curves for the layers with TMPTA and DPHAC fall in the same curve as the previous two layers at temperatures below 80°C, but at temperatures above 100°C they level out until 200°C. This occurs because the layers expand as the temperature rises but do not snap above 80°C due to their high degree of crosslinking. This difference seems to be related to the degree of crosslinking indicated in Figs. 5 and 6.

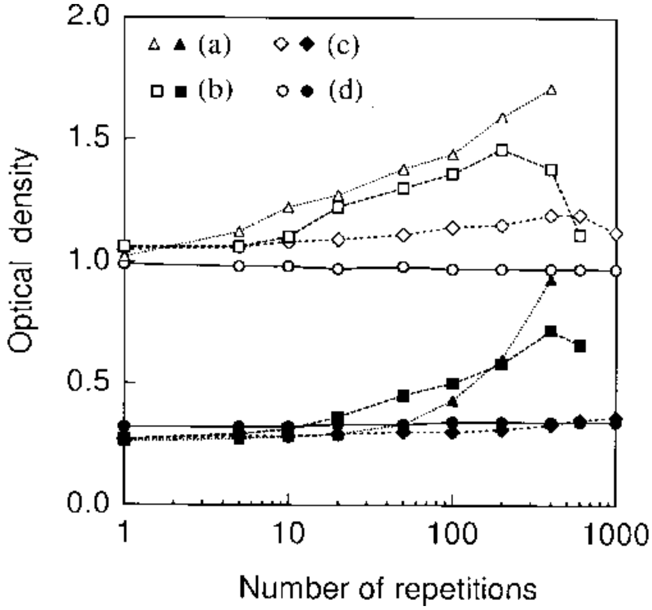

Figure 9. Optical density of the light-scattering (closed symbols) and transparent (open symbols) states versus the number of repetitions of image formation and deletion for recording films (a) without acrylic monomer, and with (b) NPGDA, (c) TMPTA, and (d) DPHAC, irradiated with 20 Mrad of electrons.

Figure 8 shows the dynamic storage modulus as a function of temperature for the recording layers without acrylic monomer and with the addition of various quantities of DPHAC irradiated with 20 Mrad of electrons. The curves for the layers (a) without acrylic monomer and (b) with a concentration of acrylic functional groups of 1.4×10^{20} are not indicated at temperatures above about 90°C because the layers expand as the temperature rises and snap at about that temperature due to their low degree of crosslinking. The curves of the layers with concentrations of (c) 2.8×10^{20}, (d) 5.6×10^{20}, and (e) 11.2×10^{20} fall in the same curve as the previous two layers at temperatures below 90°C, but at temperatures above 100°C, they level out until 200°C. This occurs because the layers expand as the temperature rises but do not snap at temperatures above 90°C due to their high degree of crosslinking. This difference seems to be related to the degree of crosslinking indicated in Fig. 6.

Repetition of Image Formation and Deletion for Crosslinked Recording Films. We investigated the durability against repetition of image formation and deletion for the crosslinked recording films. Figure 9 shows the optical densities (ODs) of the light-scattering and transparent states as a function of the number of repetitions for the

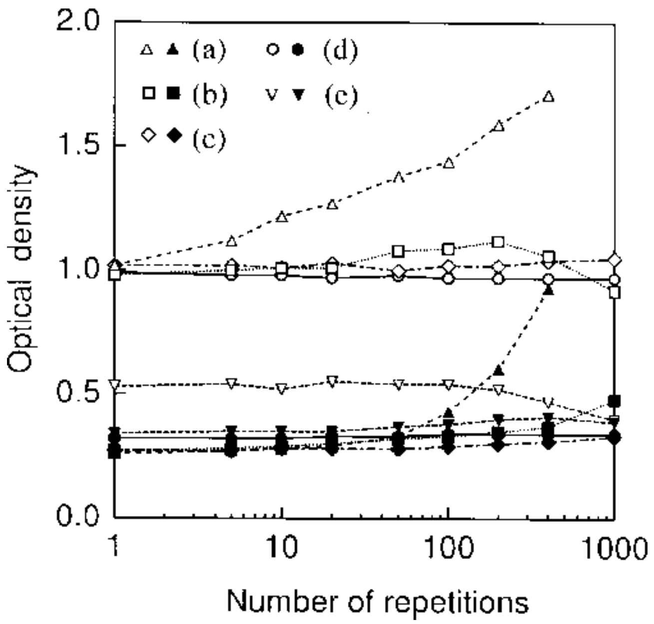

Figure 10. Optical density of the light-scattering (closed symbols) and transparent (open symbols) states versus the number of repetitions of image formation and deletion for recording films (a) without acrylic monomer, and with various concentrations of acrylic functional groups, irradiated with 20 Mrad of electrons. Concentrations: (b) 1.4×10^{20}, (c) 2.8×10^{20}, (d) 5.6×10^{20}, and (e) 11.2×10^{20}.

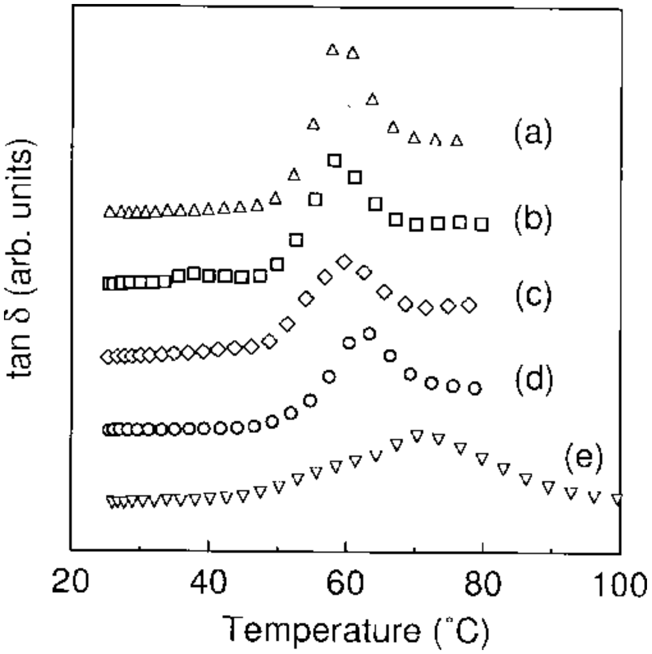

Figure 11. Loss tangent as a function of temperature for the recording layers (a) without acrylic monomer, and with various concentrations of acrylic functional groups, irradiated with 20 Mrad of electrons. Concentrations: (b) 1.4×10^{20}, (c) 2.8×10^{20}, (d) 5.6×10^{20}, and (e) 11.2×10^{20}.

recording films (a) without acrylic monomer, and with (b) NPGDA, (c) TMPTA, and (d) DPHAC, irradiated with 20 Mrad of electrons (these are the same films indicated in Fig. 7). The light-scattering states were obtained by heating using a thermal printhead, and the transparent states were obtained by heating the film on which the light-scattering states were formed using a hot stamp. The repetitive cycle was defined as each formation and deletion of a light-scattering image.

In Figs. 9 and 10, the closed symbols indicate the light-scattering images, and the open symbols indicate the transparent portions deleted the light-scattering images. The reason the OD values of the transparent portions are greater than those of the light-scattering images is as follows: When the OD of the transparent portion is measured, the incident light irradiated from a light source in the reflection densitometer does not reach a photosensor in the densitometer due to the regular reflection of the incident light by an aluminum layer under the recording layer because the light is irradiated from an angle of 45° and the photosensor is placed in a position vertical to the recording film. On the other hand, when the OD of the light-scattering portion is measured, the incident light is scattered in the recording layer, and a part of the scattered light reaches the photosensor.

As shown in Figs. 9(a) and 9(b), the ODs of the light-scattering images for no or slightly crosslinked films become high at 20 cycles or more with an increase in the number of repetitions. On the other hand, as shown in Figs. 9(c) and 9(d), those for highly crosslinked films remain steady. The changes in the OD of the transparent portions also decrease as the degree of crosslinking becomes greater.

Figure 10 shows the ODs of the light-scattering and transparent states as a function of the number of repetitions for the recording films without acrylic monomer and with the addition of various quantities of DPHAC, irradiated with 20 Mrad of electrons, (these are the same films indicated in Fig. 8). The ODs of the light-scattering images for the film without DPHAC become greater at 20 cycles or more with an increase in the number of repetitions, but those for the films with DPHAC do not change much until 1000 repetitions.

The ODs of the transparent portions for the film without DPHAC become higher with an increase in the number of the repetitions, whereas those for the films with concentrations of acrylic functional groups of (c) 2.8×10^{20} and (d) 5.6×10^{20} level out at a density of around 1.0. Those for the films with concentrations of (b) 1.4×10^{20} and (e) 11.2×10^{20} do not change until 200 repitítions but then gradually fall. Furthermore, the values for the film with a concentration of 11.2×10^{20} are lower than those for the other films.

As shown in Figs. 9 and 10, the changes in the densities of the light-scattering images and the transparent portions with an increase in the number of repetitions decrease as the degree of crosslinking becomes higher. A possible mechanism to explain this phenomenon is that as the degree of crosslinking becomes higher, the particles composed of BA and EDA in the recording layer become hard to grow by the repetitions of image formation and deletion because the polymer in the recording layer becomes harder at temperatures higher than T_g with an increase in the degree of crosslinking, as shown in Figs. 7 and 8.

The decreases in the density of the transparent portions at more than 200 repitítions shown in Figs. 9(b), 9(c), 10(b), and 10(e) with an increase in the number of repetitions may be due to increases in the roughness of the surfaces of the recording films. For example, it is possible that the surfaces of the films slightly crosslinked, as shown in the first three of these figures, becomes rough due to the softness of the recording layer at temperatures higher than

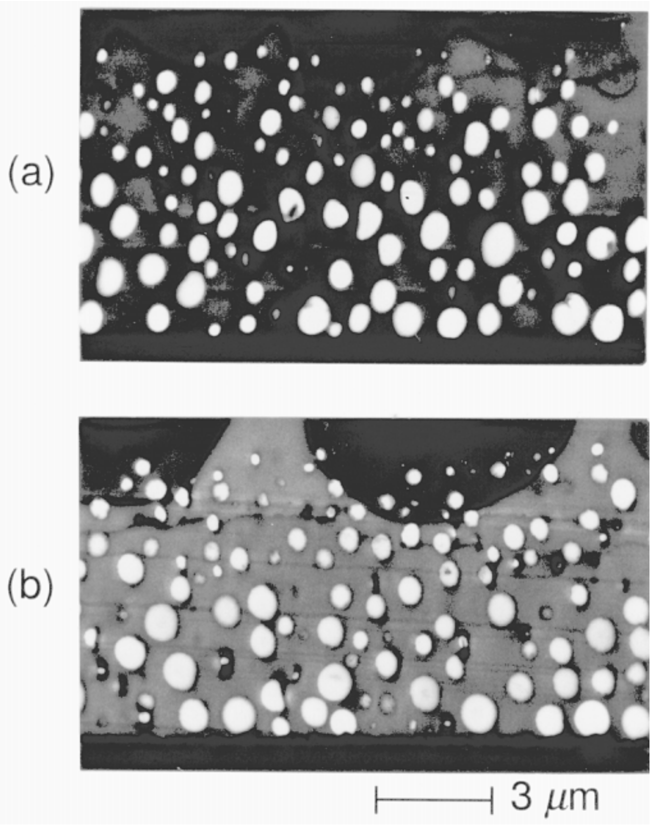

Figure 12. Cross-sectional TEM images of films composed of P(VC-VAc) with dispersed BA and EDA and added DPHAC irradiated with 20 Mrad of electrons (a) before repetitive experiment and (b) after 1000 cycles of image formation and deletion.

T_g, and in contrast, the surface of the film scarcely crosslinked, as shown in the final figure, is cracked due to the hardness of the recording layer.

The deterioration in the density in this latter case has two possible explanations: One is that the polymer cannot compensate for the volume shrinkage of BA and EDA due to the hardness of the recording layer at 100–200°C, shown in Fig. 8. Another is that the polymer is still rigid at the crystallizing temperature of BA and EDA after being heated to T-temp and cannot compensate for the volume shrinkage because the T_g became high. Figure 11 shows the loss tangent as a function of temperature for the films without acrylic monomer and with the addition of various quantities of DPHAC, irradiated with 20 Mrad of electrons (the same films indicated in Figs. 8 and 10). The T_g determined by the maximum of the loss tangent peaks suddenly rises from Figs. 11(d) to 11(e). This experimental result supports the second interpretation. However, further study is needed to clarify the cause of the deterioration in density shown in Fig. 10(e).

Figure 12 shows TEM images of the cross sections of the recording films with DPHAC at a concentration of 5.6 $\times 10^{20}$ irradiated with 20 Mrad of electrons (a) before the repetitive experiment and (b) after 1000 cycles of image formation and deletion. The shapes of the particles of BA and EDA in the recording layers for the film after 1000 cycles remained almost unchanged.

Conclusions

We have demonstrated that the durability of the thermoreversible recording media against the repetition of image formation and deletion improves by the crosslinking of the polymer matrix in the recording layer. At first, by observation of the internal structures in the recording layers, it was clarified that the deterioration of the image is caused by the particle growth of long-chain molecules in the recording layer, and the particles grow because of the heat and the shear stress applied from the thermal printhead. Next, the properties of the recording layer crosslinked with electron beam irradiations were investigated, and it was clarified that the crosslinked recording layer did not soften very much at a high temperature. The degree of crosslinking of the layer became high by applying multifunctional monomers, and the durability of the repetition could be improved by the crosslinking to 1000 times, at which the image contrast had hardly changed from that before the repetitive experiment.

References

1. T. Ueno, T. Nakamura, and C. Tani, *Proc. Jpn. Display,* **290** (1986).
2. W. D. McIntyre and D. S. Soane, *Appl. Opt.* **29,** 1658 (1990).
3. Y. Takahashi, N. Tamaoki, Y. Komiya, Y. Hieda, K. Koseki, and T. Yamaoka, *J. Appl. Phys.* **74,** 4158 (1993).
4. W. Dabisch, P. Kuhn, S. Muller, and K. Narayanan, DP 2907352, 1980.
5. Y. Hotta, T. Yamaoka, K. Morohoshi, T. Amano, and K. Tsutsui, *Chem. Mater.* **7**, 1793 (1995).
6. Y. Hotta, T. Yamaoka, and K. Morohoshi, *Chem. Mater.* **9**, 91 (1997).
7. Y. Hotta, R. Hiraoka, and T. Yamaoka, *High Perform. Polym.* in press.
8. The Editorial Committee of Dictionary for Physics, Ed.; *Butsurigakujiten*; Dictionary for Physics, 2nd ed., Baifukan, Tokyo, 1992, p. 233.
9. J. Seto, T. Noguchi, T. Nagai, and S. Arai, *Jpn. J. Polym. Sci. Tech.* **40,** 9 (1983).