

Mechanistic Study of Thermoreversible Recording Media Composed of Polymeric Films with Dispersed Fatty Acids

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Polymeric films containing fatty acids or analogous compounds were studied, and it was found that they exhibit thermoreversibility in optical transmittance. Clear films are converted into light-scattering films by cooling to room temperature after heating to temperatures higher than the melting point of the fatty acid. These light-scattering films return to the original transparent state, if they are heated again to a specific temperature just below the melting point of the fatty acid and then cooled again to room temperature. This phenomenon of films can be potentially used for thermal recording. A mechanistic study of the films revealed that the essential requirements for this reversible behavior are the formation of small-particle domains of the fatty acid, and a particular relationship between the crystallizing temperature of the fatty acid and the softening temperature of the polymeric films. The crystallizing temperature of the fatty acid is not constant in polymeric films but is variable depending on the thermal history of the film. DSC measurements indicate that the exothermic peaks of the films due to crystallization of the fatty acid are closely related not to the molecular structure of the polymeric material used for the matrix but to the temperature to which the film is heated. In addition, the softening temperature of the polymer host is another factor that determines the utility of the film as a thermoreversible material. This paper describes the detailed mechanism of the recording and erasing.

1. Introduction

Materials used as reversible recording media are now attracting attention from environmental as well as technological viewpoints. Soref reported in 1970 that a mixture of nematic and cholesteric liquid crystals shows two different transparencies when it is cooled or heated gradually.¹ In addition Kahn demonstrated in 1973 that when a smectic liquid crystal is sandwiched between two substrates and first heated then cooled to room temperature, it exhibits dual optical states: a transparent state or a light-scattering state, depending on the cooling rate.²

Although liquid crystals are attractive for use as reversible recording material, special devices with cells, electrodes, or polarizing films are required in most cases. Research has therefore been focused on eliminating the need for these complicated peripherals. Ueno et al. showed that a polymer having cholesteric liquid crystals as the pendant group has two different alignments when it is heated to 90–100 °C and then cooled to room temperature. They also demonstrated that the polymers align in a planar conformation during slow cooling, whereas they align in a random conformation during rapid cooling.³

Two-component materials composed of some polymers and liquid crystals make up another group of candidates for thermoreversible materials. McIntyre et al. reported on the thermoreversible property of a mixture of a polymer and the nematic-type liquid crystal *N*-(4-ethoxybenzylidene)-4'-*n*-butylaniline,⁴ and Takahashi et al. reported on thermo-optical effects for a mixture of a polymer and 4-alkoxy-3-chlorobenzoic acid.⁵ These polymeric films can assume either a transparent or 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, as mentioned above, requires complicated devices for the recording and erasing.

The thermoreversible recording material composed of a polymer matrix with a dispersed low molecular weight compound may be promising for practical use,⁶ because the two optically different states (transparent and light-scattering states) can be selected using only temperature; control of the cooling or heating rate is not necessary.

(3) Ueno, T.; Nakamura, T.; Tani, C. *Proc. Jpn. Display* **1986**, 290.

(4) McIntyre, W. D.; Soane, D. S. *Appl. Opt.* **1990**, 29, 1658.

(5) Takahashi, Y.; Tamaoki, N.; Komiya, Y.; Hieda, Y.; Koseki, K.; Yamaoka, T. *J. Appl. Phys.* **1993**, 74, 4158.

(6) Dabisch, W.; Kuhn, P.; Muller, S.; Narayanan, K. DP 2907352, 1980.

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(1) Soref, R. A. *J. Appl. Phys.* **1970**, 41, 3022.

(2) Kahn, F. J. *J. Appl. Phys. Lett.* **1973**, 22, 111.

Several papers have reported a mechanistic study of similar materials. For example, Hotta⁷ and Matsuda⁸ proposed that thermoreversibility is due to the crystal size or the crystal form of the low molecular weight compound. However, the detailed mechanism is still a matter of controversy. This paper describes a thermoreversible recording material composed of polymeric materials with a dispersed fatty acid as the low molecular weight compound and discusses a plausible thermoreversibility mechanism.

2. Experimental Section

2.1. Materials. Poly(vinyl chloride), polystyrene (PS, $M_w = 96\,000$), poly(ethyl methacrylate), poly(propylene chlorinated), polybutadiene, and poly(vinyl isobutyl ether) were obtained from Aldrich Co., Ltd. A copolymer of vinyl chloride and vinyl acetate (PVC-VAc), $M_n = 20\,000$, copolymerization ratio = 86/14 and phenoxy resin were purchased from Union Carbide Chemicals and Plastics Co., Ltd. Chlorinated poly(vinyl chloride) and poly(vinyl butyral) were purchased from Sekisui Chemical Co., Ltd. Cellulose acetate and cellulose acetate butylate were purchased from Eastman Kodak Co. Polysulfone was purchased from Nissan Chemical Industries, Ltd. Polycarbonate (PC) was purchased from Teijin Ltd. Polyamide was purchased from Toray Industries, Inc. Epoxy resin was purchased from Yuka Shell Epoxy Co., Ltd. Polyester was purchased from Toyobo Co., Ltd. A copolymer of vinylidene chloride and acrylonitrile was purchased from Asahi Chemical Industry Co., Ltd. Polyurethane was purchased from Mitsubishi Heavy Industries, Ltd.

Behenic acid (BA) was available from Sigma Chemical Co. and was 99% pure. Tetrahydrofuran and toluene were purchased from Kanto Chemical Co., Inc. Sodium bromide and distilled water (chromatograph grade) were obtained from Wako Pure Chemical Industries, Ltd.

2.2. Measurement. A series of recording layers were prepared by various combinations of the matrix polymer and BA as the low molecular weight material. The polymer and BA were dissolved in a mixture of tetrahydrofuran and toluene. The solution was coated onto a transparent poly(ethylene terephthalate) (PET) support using a wire bar. The coated films were dried at 110 °C to form a recording layer about 10 μm thick.

The transparency of the film at various temperatures was measured with the Thermo-system (FP80HT/FP82HT) from Mettler-Toledo AG and a Nikon Optiphot2 microscope. The temperature was varied continuously at the rate of 2 °C/min.

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

A recording layer prepared on a substrate was peeled off and used for X-ray diffraction, differential scanning calorimetry (DSC), thermomechanical analyzer (TMA), and sample density measurements.

X-ray-diffraction experiments were performed using a Rigaku RINT 1100, with a $\text{Cu K}\alpha$ X-ray source.

DSC measurements were performed on samples of about 5 mg by using the DSC 3100, a Mac Science DSC. The scanning rate was 2 °C/min. The elongation ratio was measured with the TMA/SS150 from Seiko Instruments. Pulling stress was about 7 g/mm², and the temperature was varied continuously at the rate of 5 °C/min.

The density of the recording layer was measured by a flotation method. The recording layer was put in a solution of sodium bromide and distilled water, and the recording layer density was determined by measuring the density of the

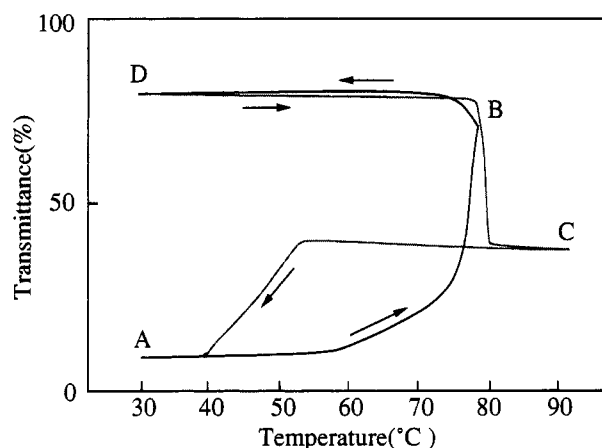


Figure 1. Changes in transmittance during heating and cooling of a film composed of P(VC-VAc) with dispersed BA.

solution, then adjusted to a mixture ratio of the solution so that the layer floated in the solution. The solution density was measured by using a Lipkin-Davison pycnometer.

3. Results and Discussion

3.1. Thermal Characteristics of Polymeric Film with Dispersed Fatty Acid. The thermal behavior of a recording film composed of P(VC-VAc) with dispersed BA (BA-P(VC-VAc)) was studied. The optical transmittance change of the film is shown in Figure 1 as function of temperature. When the recording film in the light-scattering state is heated to a temperature just below the melting point of BA (80.7 °C), it becomes transparent (A → B). This transparency is maintained after the film is cooled to room temperature (B → D). On the other hand, when the transparent film is heated to a temperature above the melting point of BA, it becomes translucent (D → B → C) and then reaches the light-scattering state after being cooled to room temperature (C → A). This thermal response can be repeated for almost 1000 cycles. Temperatures corresponding to points B and C will be denoted hereafter as T-temp and O-temp, respectively.

The transmittance in the transparent state (D) and the light-scattering state (A) is unrelated to the rate of cooling from T-temp or O-temp to room temperature. For instance, even if the films heated to T-temp or O-temp are cooled rapidly by dipping them into water, the transmittance of the films is not different from that produced by slower cooling.

3.2. Relation between Thermoreversibility and Morphological Structures of the Polymeric Films.

The thermoreversible response was studied in terms of combinations of BA and polymer matrices. Recording films sliced thin and stained with OsO_4 were studied by TEM. Typical examples of the TEM images of cross sections of the BA and P(VC-VAc), polycarbonate, cellulose acetate, and poly(vinyl isobutyl ether) recording films are shown in Figure 2. The bright and dark areas indicate BA and matrix, respectively. Figure 2a,b clearly show that BA is phase separated from the matrix polymer to form small particle domains. However, in Figure 2c, although BA is also phase separated from cellulose acetate matrix, the domains are larger and some of them are fused to each other. In Figure 2d, the domains are not observed and the cross section shows a homogeneous morphology. This indicates that

(7) Hotta, Y.; Kubo, K. *Proc. 4th Symp. NIP. Tech., Tokyo* **1987**, 57.

(8) Matsuda, G.; Tanji, S.; Tanaka, A.; Hayashi, Y. *Proc. 8th IS&T's Int. Cong. NIP. Tech., Virginia* **1992**, 442.

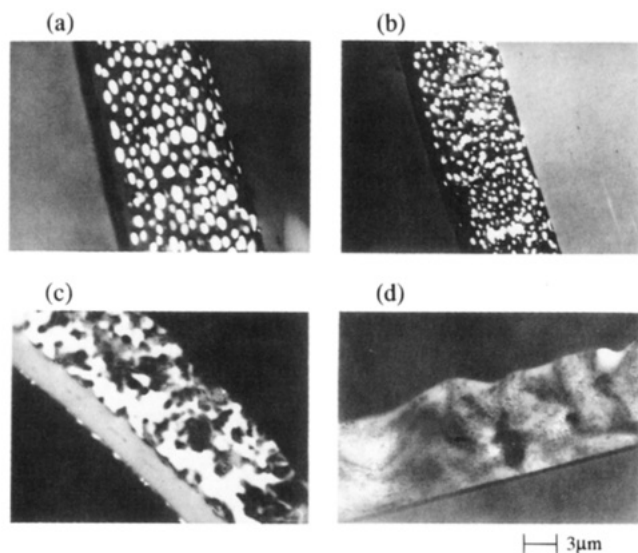


Figure 2. Cross-sectional TEM pictures of films composed of polymer matrices and BA. Matrix = (a) P(VC-VAc), (b) polycarbonate, (c) cellulose acetate, and (d) poly(vinyl isobutyl ether).

BA is uniformly mixed with the poly(vinyl isobutyl ether) matrix.

In Table 1, the relationship between thermoreversibility and the morphological structures are summarized for 19 matrix polymers used as the matrix. Glass transition temperatures (T_g) of each polymer were measured by the DSC method and are also reported in Table 1. The morphological structures of the recording films, which are making particles, blooming, compatible, separation, and the size of particle domains, seem to depend on the compatibility of BA and the polymer matrix. The relationship between the internal structure and compatibility will be reported in detail in a future paper.

The data in Table 1 indicate that formation of particle domains is a prerequisite for recording films exhibiting thermoreversibility. Some recording films, however, satisfy this condition but do not exhibit a thermal response. Here, three types of recording films, i.e., BA-P(VC-VAc), a film composed of PS with dispersed BA (BA-PS), and a film composed of PC with dispersed BA

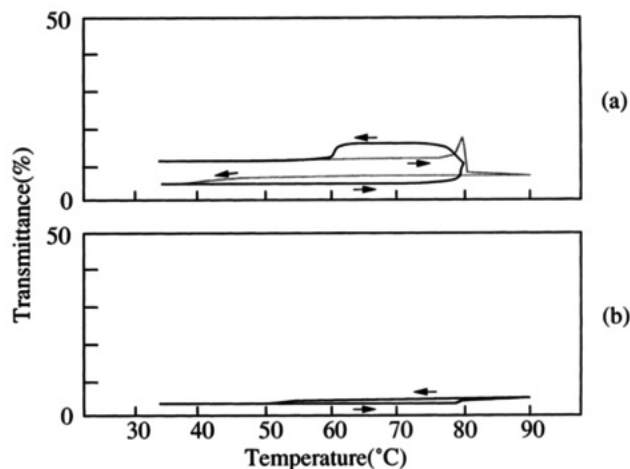


Figure 3. Changes in transmittance during heating and cooling of films composed of (a) PS and (b) PC containing dispersed BA.

(BA-PC) were selected from the 19 film samples shown in Table 1. As mentioned above, BA-PC and BA-PS films show no or very slight thermoresponse, respectively, and the initial appearance of light-scattering is almost unchanged as shown in Figure 3, while the BA-P(VC-VAc) films has the thermoreversible characteristics as shown in Figure 1.

3.3. Particle Domains of BA in Transparent and Light-Scattering States. The internal structures of the recording films in both the transparent and light-scattering states were investigated by TEM. The cross-sectional TEM pictures of the BA-P(VC-VAc) film in Figure 4 clearly show the BA particle domains. Comparing the pictures of the recording films in the transparent and light-scattering states reveals no significant difference. Thus, the transparent and light-scattering characteristics of BA-P(VC-VAc) film seem not to be caused by changes in size or the state of dispersion of the particle domains. The cross-sectional observation of BA-PS and BA-PC films also offered no clues to the optical behavior of these recording films.

3.4. Crystalline Structures of BA in the Polymers. Figure 5a shows X-ray diffraction patterns of BA-P(VC-VAc) films in both the transparent and light-scattering states. The states were obtained by cooling

Table 1. Internal Structure and Thermal-Optical Responses for Various Matrix Polymers Containing BA

| polymer | internal structure | thermal response | glass transition temp (°C) |
|--|--------------------|---------------------------------------|----------------------------|
| poly(vinyl chloride) | making particles | thermoreversible | 81 |
| P(VC-VAc) | making particles | thermoreversible | 72 |
| chlorinated poly(vinyl chloride) | making particles | thermoreversible | 83 |
| phenoxy resin | making particles | thermoreversible | 84 |
| epoxy resin | making particles | thermoreversible | 79 |
| polyester | making particles | thermoreversible | 62 |
| poly(vinylidene chloride-co-acrylonitrile) | making particles | thermoreversible | 15 |
| polyurethane | making particles | thermoreversible | 36 |
| polystyrene | making particles | thermoirreversible (light-scattering) | 107 |
| polycarbonate | making particles | thermoirreversible (light-scattering) | 155 |
| poly(propylene chlorinated) | making particles | thermoirreversible (light-scattering) | 139 |
| poly(vinyl butyral) | blooming | thermoirreversible (transparent) | 89 |
| cellulose acetate butylate | blooming | thermoirreversible (transparent) | 99 |
| polyamide | compatible | thermoirreversible (transparent) | 22 ^a |
| poly(ethyl methacrylate) | compatible | thermoirreversible (transparent) | 68 |
| polybutadiene | comptible | thermoirreversible (transparent) | -95 ^a |
| poly(vinyl isobutyl ether) | compatible | thermoirreversible (transparent) | -19 |
| cellulose acetate | separation | thermoirreversible (light-scattering) | 30-55 ^b |
| polysulfone | separation | thermoirreversible (light-scattering) | 189 ^b |

^a Data supplied from manufactures. ^b The Society of Polymer Science, Japan Ed.; *Koubunshizairyoubinran*; Handbook for High Polymer Materials; Corona Publishing Co. Ltd.: Tokyo, 1973; p 1275.

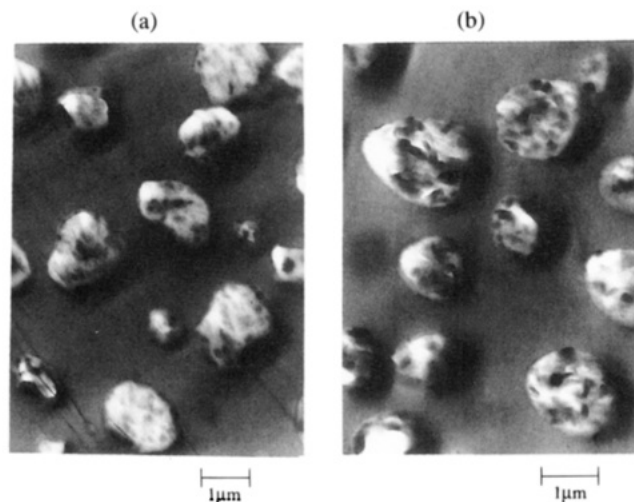


Figure 4. Cross-sectional TEM pictures of (a) transparent and (b) light-scattering films composed of P(VC-VAc) with dispersed BA.

the films to room temperature after heating them to either T-temp (77 °C) or O-temp (90 °C), respectively. These patterns imply that BA is forming C-form microcrystals⁹ in both states, which are identifiable by the characteristic of X-ray diffraction peaks,¹⁰ and that the peak intensities are stronger in the transparent state than in the light-scattering state.

Figure 6 shows high-magnification TEM images of a single domain and reveals the internal structure of a particle of BA in both the transparent and light-scattering states. A banded structure seen in each particle seems to be a crystalline lamellar structure of BA. In the transparent state, long lamellar structures are observed, whereas these structures are relatively short in the light-scattering state. This indicates that the domain is filled with relatively large crystals in the transparent state and with small crystallites in the light-scattering state. This in turn indicates that the difference in the peak intensities of the X-ray diffraction patterns depend on the size of the BA crystals in the composites.

X-ray diffraction patterns of BA-PS and BA-PC films that were cooled to room temperature after being heated to T-temp (77 °C) or O-temp (90 °C) were measured. The patterns shown in Figure 5b,c indicate that the films heated to T-temp exhibit stronger peak intensities than those heated to O-temp. In other words, the peak X-ray diffraction intensities of these films depends on the maximum temperature to which the films are heated before measurement. The fact that both films exhibit no or very slight thermoresponsive optical changes means that the peak intensity of X-ray diffraction patterns is not related to the reversible response.

3.5. Crystallization of BA in the Cooling Process. Figure 7a shows DSC curves of BA-P(VC-VAc) measured after cooling to room temperature from near T-temp or O-temp. The exothermic peaks appearing upon cooling were due to crystallization of BA in the polymer matrix. The number of the peaks for each sample appearing depends primarily on the starting

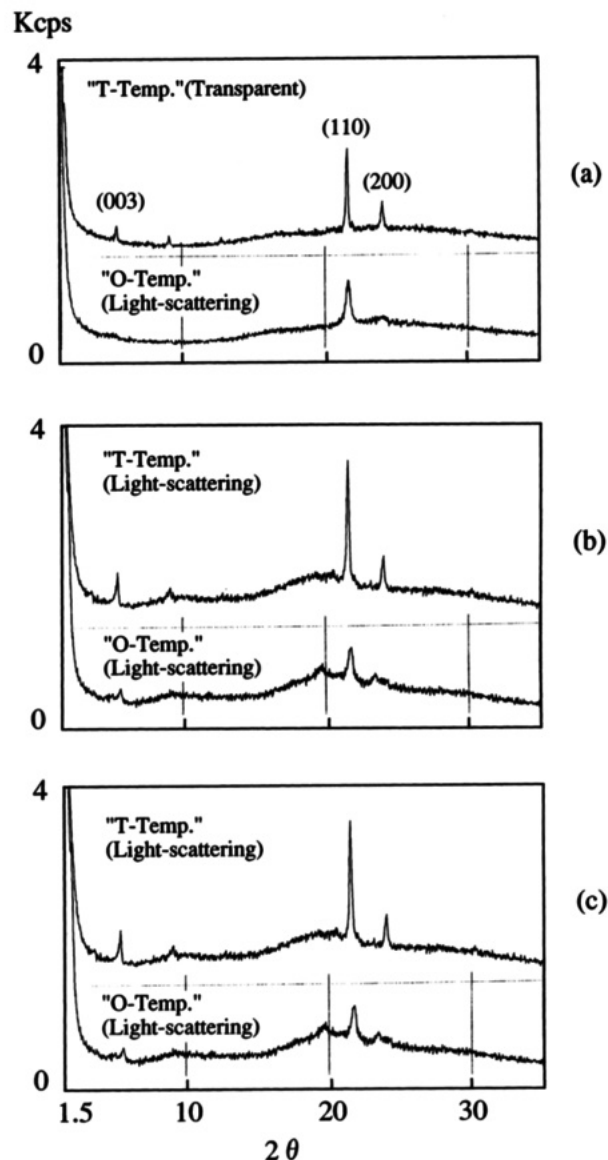


Figure 5. X-ray diffraction patterns of films composed of (a) P(VC-VAc), (b) PS, and (c) PC with dispersed BA obtained by cooling to room temperature after heating to either "T-temp" or "O-temp".

temperature. When the film is cooled from 76.4 °C, a strong peak appears at about 75 °C and a weak peak appears at about 60 °C. As the temperature was increased from 76.8 to 90.0 °C, the number of the peaks first increased and then decreased to a single broad peak.

Upon cooling from 76.4 and 76.8 °C (T-temp), temperatures at which BA partially melts, the exothermic peaks appeared just below the melting point of BA. The intensity of another peak appearing at about 60 °C increased as the heating temperature was increased and then almost disappeared at 78.4 °C (O-temp). A broad peak appeared at about 37–55 °C, which is apparently due to supercooling of the BA.

Figure 7b,c shows DSC curves of BA-PS and BA-PC measured upon cooling to room temperature from near T-temp or O-temp. Comparing DSC curves for the three types of films, the temperature at which the exothermic peaks appeared and the number of the exothermic peaks differ. However, the characteristic whereby the exothermic peaks appear just below the melting point of

(9) Hernqvist, L. *Crystallization and Polymorphism of Fats and Fatty Acids*; Garti, N., Sato, K., Eds.; Marcel Dekkers: New York, 1988; p 97.

(10) Goto, M. *Jpn. Oil Chem. Soc.* **1970**, *19*, 583.

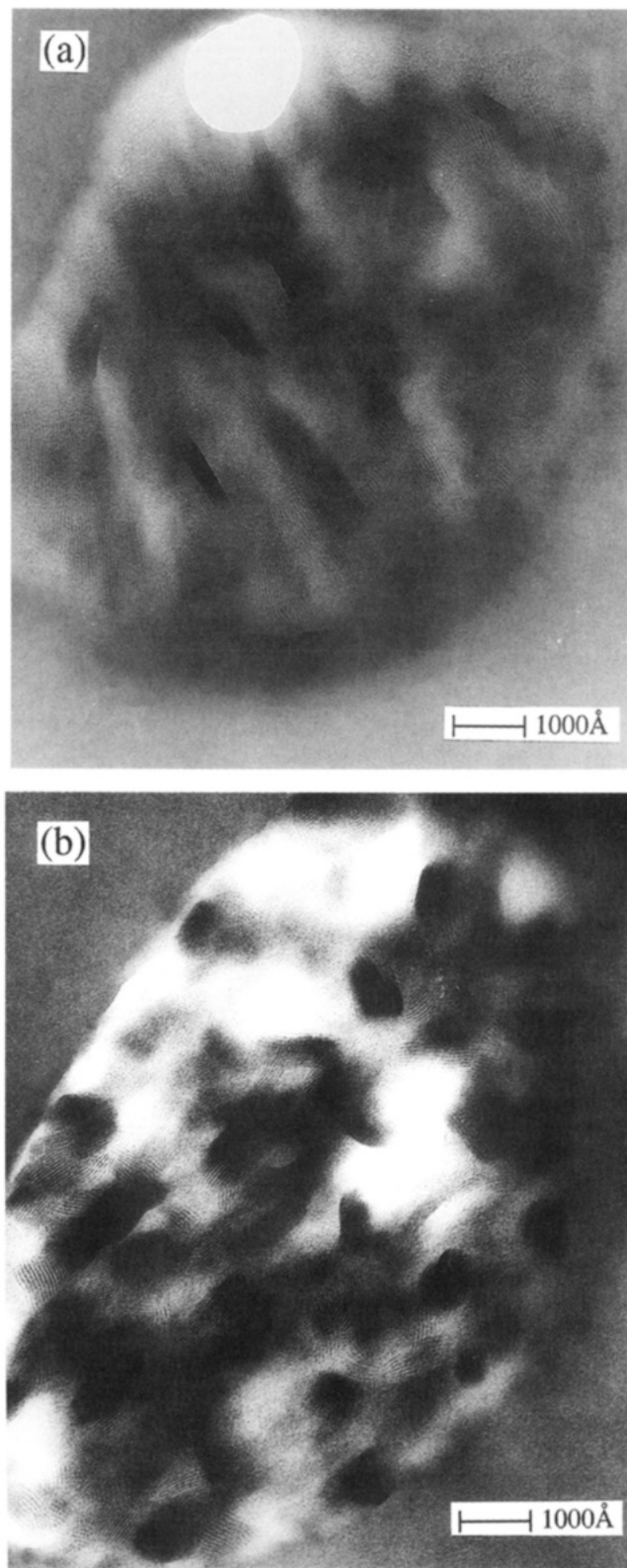


Figure 6. Cross-sectional TEM images showing a magnified view of the inside of a BA particle in (a) transparent and (b) light-scattering films composed of P(VC-VAc) with dispersed BA.

BA when the heating temperatures are lowered and shift to at lower temperatures when the initial heating temperature is increased agrees for the three types of films.

Figure 8 shows DSC curves of BA itself measured upon cooling to room temperature from near T-temp or O-temp, in the same way as in Figure 7. As shown in

this figure, BA itself did not show the supercooling phenomenon. The supercooling of BA observed occurred only when BA formed particle domains dispersed in the polymer matrix.

The crystallization of BA at multiple temperatures may be due to interaction between BA and the polymers. For instance, it is possible that the crystallization temperature of BA at the particle core differs from that near the interface between the particle and polymer, although this is still speculative.

The size difference of BA crystals indicated in Figure 6 may be affected by the crystallizing process. In the transparent state, crystals do not melt completely, and the crystals will grow to surroundings of remaining crystals and will become larger, whereas in the light-scattering state, the crystals will grow rapidly because of supercooling and therefore form many small crystalline units.

3.6. Thermomechanical Characteristics. The thermomechanical characteristics of these recording films were measured. Figure 9 shows the elongation ratio as a function of heating temperature under a constant pulling-stress of around 7 g/mm^2 . This figure shows that only BA-P(VC-VAc) film is softened at a temperature below the melting point of BA, whereas the softening points for BA-PS and BA-PC films are higher than the melting point of BA. The matrix polymers for BA-PS and BA-PC films are still glassy at the temperature where BA starts to crystallize. The polymer of the BA-P(VC-VAc) film is glassy only when BA crystallizes during cooling from O-temp, however, the polymer of BA-P(VC-VAc) film is softened when BA crystallizes during cooling from T-temp.

It may be reasonable to assume, on the basis of these experimental data, that the softening point of the matrix polymer plays a key role in the thermomechanical response of BA-P(VC-VAc). The thermomechanical characteristics of these three films were almost the same as those of each pure polymer. This seems to indicate that BA does not mix with the polymers.

3.7. Thermoreversible Response Mechanism. A proposed thermoreversible response mechanism is illustrated in Figure 10, which shows the crystallized BA in the particle domains for both transparent and light-scattering states. In the transparent state, BA in the domain forms relatively large crystals with no voids, and the incident light is not scattered by the domain because the refractive indexes of BA and the matrix polymer are very similar. In the light-scattering state, on the other hand, BA apparently forms many small microcrystals and some voids. The incident light might be scattered by the BA in the domain because the difference in the refractive index between the air in the voids and the matrix polymer is very large. The optically transparent or light-scattering state of the films may thus be governed by the existence of voids in the domain.

Figure 11 can be used to explain the thermoreversible response mechanism for BA-P(VC-VAc) film. Consider what happens when light-scattering film is heated to a temperature just below the melting point of BA (T-temp) and cooled (A \rightarrow B \rightarrow D): The voids decrease above the softening temperature (T_s) of P(VC-VAc). At T-temp, BA in the domain is still in a partially melted state where BA molecules can diffuse about the domain. The volume expansion of BA fills the voids, causing

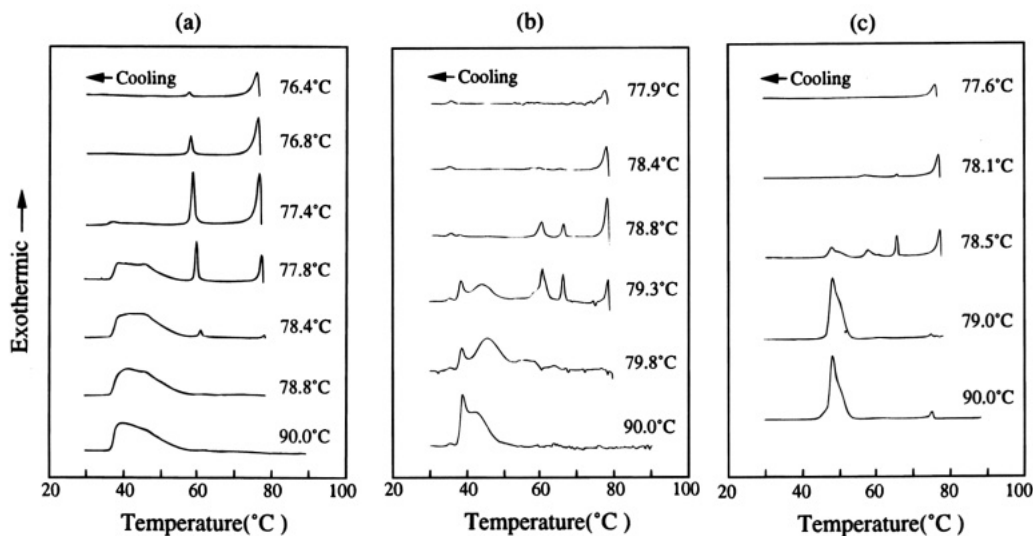


Figure 7. DSC curves of films composed of (a) P(VC-VAc), (b) PS, and (c) PC with dispersed BA obtained by cooling from various temperatures.

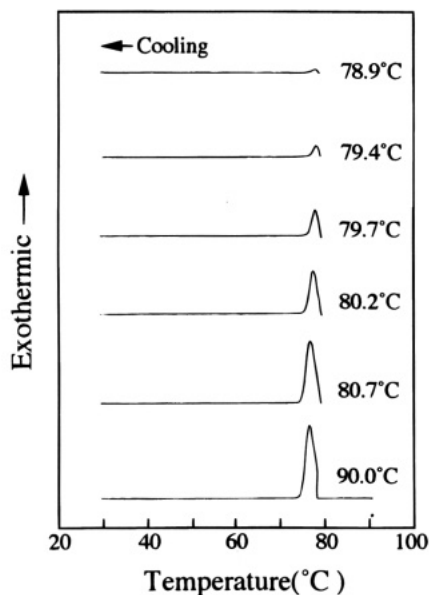


Figure 8. DSC curves of pure BA obtained by cooling from various temperatures.

them to disappear. If the film is cooled from this temperature, BA forms a single crystal or relatively large crystals without voids. This is because at the temperature where BA is solidified, the matrix polymer is still soft and can compensate for the volume shrinkage of BA.

If transparent film is heated to a temperature higher than melting point of BA (O-Temp) (D \rightarrow B \rightarrow C), BA in the domain melts. If the film is now cooled from this temperature to room temperature (C \rightarrow A), the melted BA in the domain is also cooled. As indicated by the DSC in Figure 4a, however, BA in the domain remain a liquid in a supercooled phase until 53 °C and solidifies at about 40–50 °C to form a group of microcrystals together with many air-filled voids, because the matrix polymer is rigid at the temperature where BA finally crystallize and cannot compensate for the volume shrinkage of BA. The domains thus formed should scatter the incident light.

The density of BA-P(VC-VAc) film in both light-scattering and transparent states was measured by the

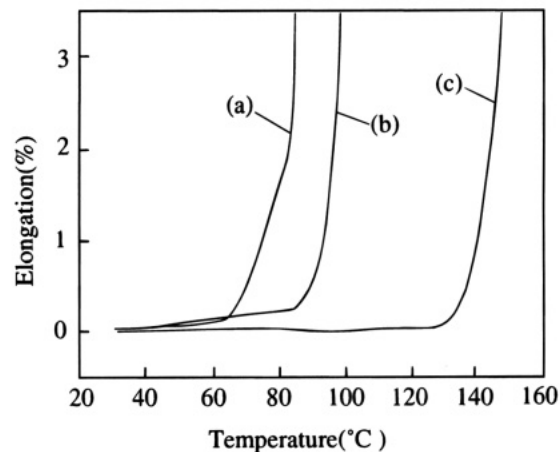


Figure 9. Elongation of three films composed of (a) P(VC-VAc), (b) PS, and (c) PC with dispersed BA as a function of temperature.

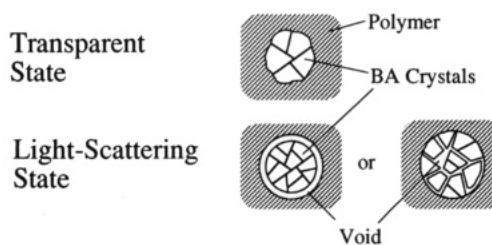


Figure 10. Difference in the dispersed phase between transparent and light-scattering states.

flotation method. The density of the transparent film was 1.237 g/cm³, while that of the light-scattering film was only 1.181 g/cm³. The difference in density between these two films closely agrees with the density calculated with a voluminal change between the solid and liquid fatty acid.¹¹ The result of this experiment supports our assumption. The existence of voids was also directly observed with a supersonic magnifier and will be reported later.

(11) The Japan Oil Chemists' Society, Ed.; *Yushikagakuinran*; Handbook on Fats and Fatty Oils, 2nd ed.; Maruzen: Tokyo, 1971; p 157.

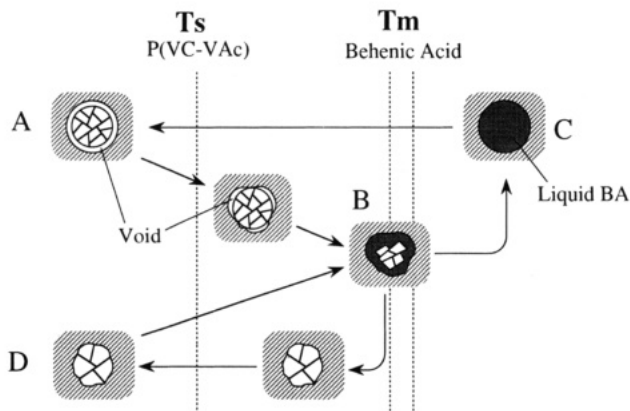


Figure 11. Schematic illustration of the proposed internal structural changes in the heating-cooling cycle.

4. Conclusion

It was found that some polymeric films containing behenic acid have two different optical states, transparent or light-scattering, depending on the thermal history. These states can be selected repeatedly by controlling the heating temperature and can be recycled repeatedly. If the film is heated to a temperature that is slightly below the melting point of BA and then cooled to room temperature, the film is transparent. On the other hand, if the same film is heated to a temperature higher than the melting point of BA, followed by cooling to room temperature, the film is light-scattering. A

mechanistic study of this thermal response suggested the conditions required for such thermoreversible characteristics. The essential requirement is that small domains of BA are formed and uniformly distributed in the polymeric layer by phase separation of the polymer matrix and BA. This means that the incompatibility of BA and matrix polymers is necessary. In addition, the softening temperature of the matrix polymer should be below the melting point of BA. In summary, a transparent film is obtainable when the sample is heated to a temperature range where BA is partially melted and subsequently cooled to room temperature. If the film is heated above the melting point of BA, it becomes light-scattering under these conditions.

BA in the phase-separated domains crystallize around 30 °C lower than the melting point of pure BA to produce microcrystals and domain voids. Due to the large difference in the refractive index of the polymer matrix and air, the incident light is scattered. In the case where the film is heated to the partially melted state and cooled, BA crystallizes just below the melting point of BA to form relatively large crystals, resulting in no void in the domains. In this case, the difference in the refractive index between BA and the matrix polymer is apparently not so large and the film is transparent.

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