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A Universal Structural Model for Human Hair to Understand the Physical Properties 1

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A universal structural model for human hair has been proposed in order to understand the physical properties of hair. The model consists of two structural parts, both of which have two states (Two-part/two-state model). The transition temperature (T_c) between the two states of one part is about 70 °C, and that of the other part is about 0 °C in a water medium. These transition temperatures depend highly upon the water content of the hair. A higher transition temperature is observed in hair having a lower water content. Above the transition temperatures, both parts of the hair are soft and plastic (a melted state); they are hard and elastic (a solid state) below the transition points. One part of hair which has a higher transition temperature (ca. 70 °C in water) is assigned to be macrofibril and exo-cuticle consisting of keratinous proteins; the other part with a lower T_c (ca. 0 °C) is inter-macrofibrillar materials, a cell-membrane complex (CMC), and the endo-cuticle of non-keratinous proteins and lipids. This structural model was derived from the results of thermal-setting and relaxation experiments as well as TEM observations after permeating a dye with a high electron density (Erythrosin B).

The physical properties of human hair, such as shape-control, permeation of chemical compounds and mechanical properties, are, of course, very important to develop various hair-care and/or hair-cosmetic products.[1] Hair properties, in principle, result from its structures. The relationship between the structure and properties of human hair, however, has been discussed and given as an individual matter. For example, the elastic and yield behaviors of hair in stress-strain curves are usually discussed from the viewpoints of α-helical structures and their transformation to the β-form of keratin;[2—4] permeation pathways are related to CMC structures;[5,6] permanent waving behaviors are always interpreted based on S–S bond rearrangements,[7] and so on. A universal structural model used to understand most of the physical properties of human hair must be significantly useful for hair science as well as for developing various kinds of hair-care and cosmetic products. The purpose of this series of papers is to provide such a universal model, and to explain the shape-control, dye permeation, and mechanical behaviors of human hair, utilizing the proposed universal model.

Experimental

Materials. Non-chemically treated (virgin), Japanese black and straight hair was obtained from a female teenager and a boy of 8 years old. The hair samples were washed with aqueous solutions of an anionic surfactant (alkyl poly(oxyethylene)sulfate type), rinsed thoroughly by deionized water, and finally air-dried. Reduced hair was prepared by being immersed for 10 min at 30 °C in a 6.0 wt% ammonium thioglycolate (mercaptoacetate) solution buffered at pH = 8.5 by NH_4HCO_3, then washed twice with deionized water for 30 s, and finally air-dried.

The dyes, Sulforhodamine B (or Acid Red 52) and Erythrosin B (sodium salt of tetraiodofluorescein), employed in the experiments for permeation and TEM observations were purchased from Kanto Chemical Co., Inc. and Tokyo Chemical Industry Co., respectively, and were used without further purification. The reducing agents, *N*-acetyl-L-cysteine (NAC) and sodium sulfite, and all of the solvents used in this work were obtained from Wako Pure Chemical Industries Ltd. or Tokyo Chemical Industry Co., and were of guaranteed reagent grade.

Hair-Setting and Relaxation Experiments. The experimental procedures for the thermal-setting and relaxation of hair are illustrated in Fig. 1. A single hair fiber was wound on a small Teflon® rod (3 mm ϕ), and set at a certain temperature for 1 h in water or a water/ethanol (1/1 in weight) mixture. The hair sample was then moved to a relaxation solvent (water/ethanol = 1/1), and left relaxed at −15 or 25 °C for 24 h. The curl diameter remaining after 24 h in the hair sample was measured, and the setting-ratio (%) was defined as $(D_0/D)\times 100$, where D_0 and D are the curl diameter of the original (3 mm) and relaxed states (after 24 h). *N*-acetyl-L-cysteine (NAC) or sodium sulfite (Na_2SO_3) was added at 30 mM ($1\ M = 1\ mol\ dm^{-3}$) into the setting solvent to examine the effects of S–S bonds on the setting transition. The pH value of the setting solvent was also changed in some cases.

Water-setting and relaxation experiments were performed by the procedures shown in Fig. 2. A hair fiber wound on a Teflon® rod was set at 25 or 60 °C in the same way as that of the thermal setting mentioned previously. The hair fiber was taken out of the setting solvent and dried in N_2 atmosphere in a dry-box being kept at 0% RH, and then released from the Teflon® rod. The hair sample maintained its spiral shape even after released (water-setting). The water-set hair fiber was left relaxed for 24 or 220 h at various temperatures in many kinds of solvents.

Permeation Experiments of Dyes into Hair. Hair fibers were immersed in aqueous solutions of 1 mM Sulforhodamine B at various temperatures for 20—120 min. Three of the hair fibers

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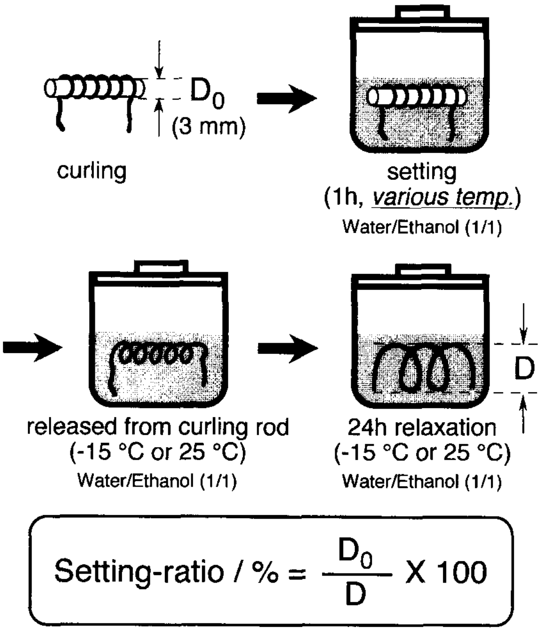

Fig. 1. Experimental procedures for thermal hair-setting. Hair is set for 1 h in a water/ethanol mixture (1/1 in weight) at various temperatures, and relaxed at −15 °C or 25 °C for 24 h.

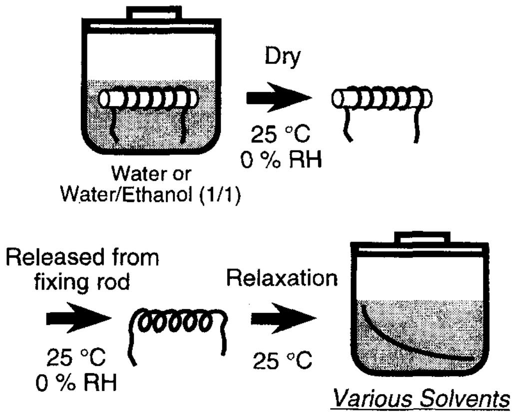

Fig. 2. Experimental procedures for water-setting of hair. Hair is put for 20—30 min in water or a water/ethanol mixture (1/1 in weight) at 25 or 60 °C, and dried in N_2 gas atmosphere in a dry-box being kept at 0% RH. Water-set hair is relaxed in various solvents at 25 °C for appropriate time.

were taken out of the dye solution at appropriate intervals, and the samples were washed twice with deionized water for 30 s, and air-dried. Sulforhodamine B-permeated hair fibers were embedded in a cellulose resin, and sliced by a microtome to obtain a thickness of 10 μm. The cross section of a sliced hair fiber was observed, and photographed by a fluorescence microscope (Nikon type XF-EFD2). The permeation distance of the dye from the surface of the hair was determined from the photographs, and the diffusion coefficient of the dye migration inside the hair fiber was calculated, assuming an infinite cylindrical shape of the hair fiber.[8] The detailed procedures to calculate the diffusion coefficient will be described in the next paper of this series.

Transmission Electron Microscopic (TEM) Observations. Erythrosin B, which is a dye with high electron density, is utilized to make the contrast clear. Three hair fibers were immersed in an aqueous solution of 0.1 M Erythrosin B at pH ≅ 8.5. Penetration of the dye was performed for 1 h at 100 °C (sample 1) and for 72 h at 60 °C (sample 3). The so-dyed hair fibers were washed twice with deionized water for 30 s, and air-dried. In order to prepare a hair sample dyed only in the high-T_c-part (sample 2), coloring and decoloring experiments were performed by the following procedures. A coloring experiment was conducted at 100 °C for 1 h in the same manner as that described previously. Decoloration was carried out at 25 °C, immersing the dyed hair fibers in deionized water (50 ml) for 24 h. The hair samples were finally air-dried.

So-obtained sample hair fibers were dipped in 99.5% ethanol for 15 min and in absolute ethanol for 15 min to remove any water in the samples, and dipped in propylene oxide for 30 min to give the hair surface an affinity with epoxy resin. The hair samples were embedded in an epoxy resin, and cut first by a glass knife to obtain their smooth end and then sliced precisely by a microtome with a diamond knife to be a thickness of 50—500 nm. Precise slicing was made under the following conditions so as to avoid any mechanical damages to the sample: a water surface was placed close to the knife edge and the sliced sample was floated on the water surface.[9] Aqueous solutions of ca. 2 M $MgCl_2$ were used instead of pure water to prevent the dye from dissolving out of the thin hair slices. Sample hair slices were put on a copper mesh covered with collodion membrane, washed with pure water for 10 s, and air-dried. TEM observations were performed with a Hitachi type H-7000 TEM apparatus. The acceleration voltage was 75 kV.

Temperature-dependence of –SH Group Content in Hair Fibers. The relative content of –SH group in a hair fiber was determined with an EPMA apparatus (Shimadzu ESCA Type-3000) by a modified method of silver staining for TEM.[10,11] A hair fiber was sliced to a thickness of 20 μm in the same manner as that in the dye-permeation experiments described previously. The sliced hair sample was immersed in an aqueous solution of 1.0 mM $AgNO_3$, 2.0 mM EDTA, and 100 mM Tris buffer (pH = 7.4) for 15 min at various temperatures. The –SH groups in the hair reacted with Ag^+ ions and were stained. The stained hair slices were washed with deionized water at the same temperatures as those in the staining process, further washed with a 0.1 M ammonium thioglycolate at pH = 4.0 to remove the adsorbed Ag^+ ions at the surface of the hair, and finally with deionized water for 15 min in each washing. An EPMA analysis was made for S and Ag atoms with no sensitivity correction, and the relative Ag contents were estimated from the intensity ratio of Ag/S.

Heat Capacity Measurements. The heat capacity of the hair sample was measured so as to clarify the sort of transition at high T_c. An adiabatic calorimeter equipped with a computer-controlled heat supplier and temperature reader was utilized. The temperature was determined with an accuracy of 10^{-7} K. Hair samples (0.95 g) cut in pieces of less than 2 mm length and 2.1 g of 30 mM NAC solution at pH = 8.5 were packed together in a Mylar [poly(ethylene telephthalate)] bag, and employed for heat-capacity measurements. In order to obtain the heat-capacity values of only the hair sample, those of the cell containing the bag and NAC solution were determined separately and subtracted from the above values.

Results

Thermal Hair-Setting. Figure 3 shows the results of the setting-ratio plotted against the setting temperature when the relaxation temperature was −15 °C. It can be

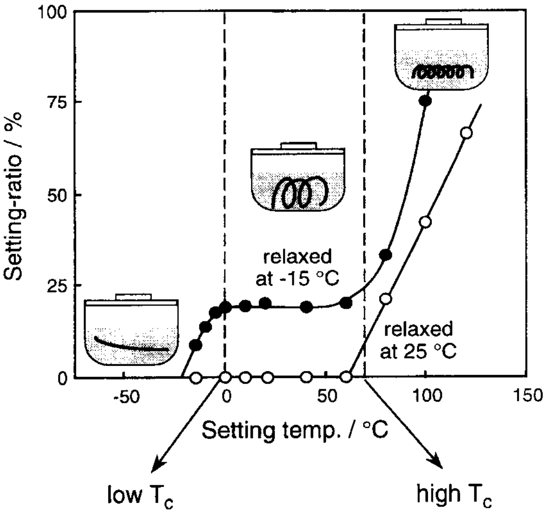

Fig. 3. Setting-ratio (%) of a hair fiber plotted against setting temperature when relaxed at −15 °C (●) or 25 °C (○) for 24 h.

clearly seen that there are two characteristic temperatures. One is about 70 °C (designated hereafter as high T_c), above which hair can be set very efficiently, and the other is about 0 °C (low T_c), below which hair cannot be set at all. The setting-ratio exhibits intermediate values between the two characteristic temperatures. The results of setting-ratio vs. setting temperature when relaxed at 25 °C are also shown in Fig. 3. In this case, only one characteristic temperature is observed at about 70 °C.

Similar curves measured in 30 mM NAC and Na_2SO_3 are illustrated in Fig. 4. The reducing agents depress the higher transition temperature remarkably. This result indicates that the S–S bonds play an important role in the transition phenomena at high T_c. Figure 5 shows the effect of the pH on the transition at high T_c. One can easily see that the transition temperature decreases with increasing pH value.

Water-Setting of Hair and Transition at Lower T_c. Water-setting and relaxation experiments of a hair fiber were conducted as shown in Fig. 2. The setting-ratios of hair fibers remained after 24 h of relaxation in iso-propanol containing 50, 5.0 and 0 wt% water are plotted against the relaxation temperatures in Fig. 6. The transition temperatures at about 0, 60, and 85 °C were observed in a solvent containing 50, 5.0, and 0 wt% water, respectively. It should be noticed that the transition point at ca. 0 °C is similar to that in Fig. 3. These results indicate that the low T_c highly depends upon the water content in the hair fiber.

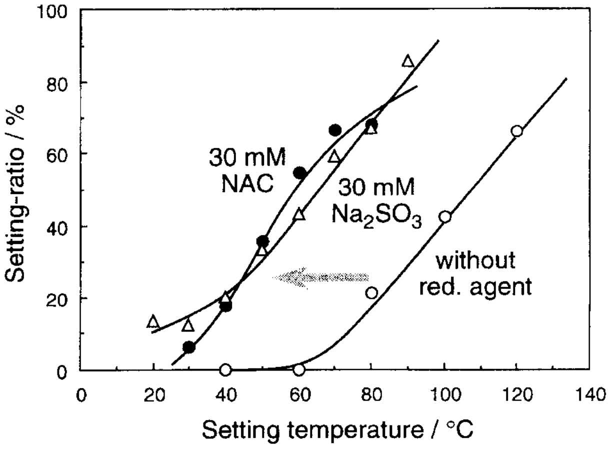

Fig. 4. Effect of reducing agents on the higher transition temperature of hair fiber. Relaxation temperature is 25 °C.

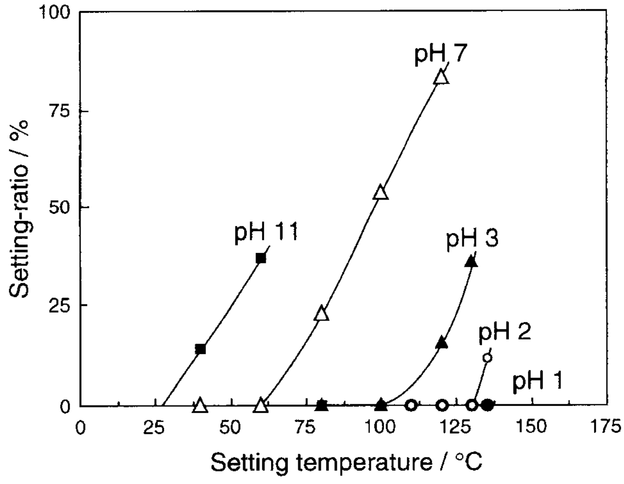

Fig. 5. Effect of pH on the higher transition temperature of hair fiber. Relaxation temperature is 25 °C.

Figure 7 shows the setting-ratio remaining after 220 h of relaxation of water-set hair in various kinds of solvents at 25 °C plotted against the dielectric constant of the solvent. One can see a beautiful relationship between the remaining setting-ratio and the dielectric constant of the solvents. The water-set hair fibers were completely relaxed in solvents having a dielectric constant greater than ca. 20, but not in those solvents having a smaller dielectric constant.

Permeation of Fluorescent Dye into Hair. Figure 8 shows fluorescence microscopic photographs of the cross

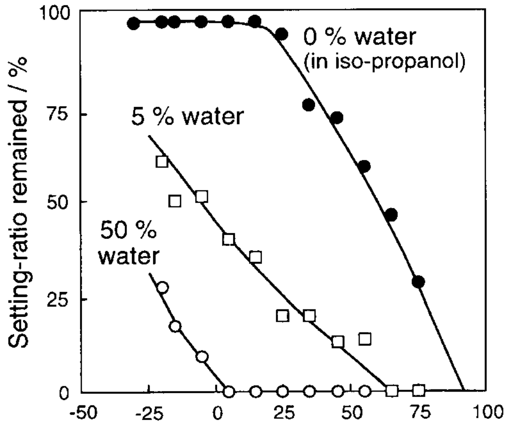

Fig. 6. Setting-ratio of water-set hair remained after 24 h relaxation in iso-propanol containing 0 (●), 5.0 (□) and 50 wt% (○) water plotted against relaxation temperatures. Water-setting was done at 60 °C for 30 min in a water/ethanol mixture (1/1 in weight), and the hair fiber was dried in N_2 gas atmosphere in a dry-box (0% RH).

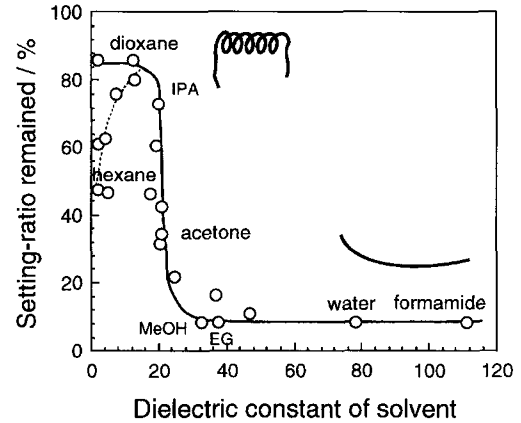

Fig. 7. Setting-ratio of water-set hair remained after 220 h relaxation at 25 °C in various kinds of solvents plotted against dielectric constant of the solvent. Water-setting was made at 25 °C for 20 min in water, and the hair fiber was dried in N_2 gas atmosphere in a dry-box (0% RH). Relaxation experiments in non-aqueous solvents were also performed in the dry-box. Solvents used are hexane, 1, 4-dioxane, benzene, diethyl ether, chloroform, tetrahydrofuran, *t*-butyl alcohol, benzyl alcohol, butyl alcohol, ethyl acetate, 2-propanol, 1-propanol, aceton, acetic anhydride, ethanol, methanol, *N*,*N*-dimethylformamide, ethylene glycol, dimethyl sulfoxide, water, and formamide in the order from small dielectric constant value.

sections of hair fiber into which a fluorescent dye, Sulforhodamine B, permeates from the surface. The moving rate of the front of the dye allowed us to calculate the diffusion coefficient. The calculated diffusion coefficients of Sulforhodamine B are plotted against the temperature in Fig. 9. It is quite interesting to note that the diffusion coefficient suddenly increases at a certain temperature, which is close to the high T_c in Fig. 3. The decrease in the transition temperature of the reduced hair also shows the same behavior as that in Fig. 4.

TEM Observations. As shown in Fig. 9, the permeation rate of dye into a hair fiber increases dramatically at the transition temperature. We can utilize this behavior to identify the high- and low-T_c-parts in real hair structures. When hair is dyed at higher temperatures than both transition points (Sample 1), all parts of the hair must be colored. A hair sample dyed only in the high-T_c-part (Sample 2) can be obtained by dying at a higher temperature than the high T_c, and decoloring at an intermediate temperature. Only the low-T_c-part must be dyed, on the other hand, upon penetration of the dye at temperatures between the two transition points (Sample 3).

Figure 10 shows TEM images of the cross section for Samples 1 (a), 2 (b), and 3 (c), for the case that Erythrosin B was used as a dye with a high electron density. All parts were dyed with very weak contrast in the Sample 1. It is particularly interesting to see that the contrasts in the TEM images are completely reversed to each other in Samples 2 and 3. One can easily recognize that the dyed parts in Sample 2 are the macrofibril and exo-cuticle parts, and the intermacrofibril, CMC and endo-cuticle regions in the Sample 3.

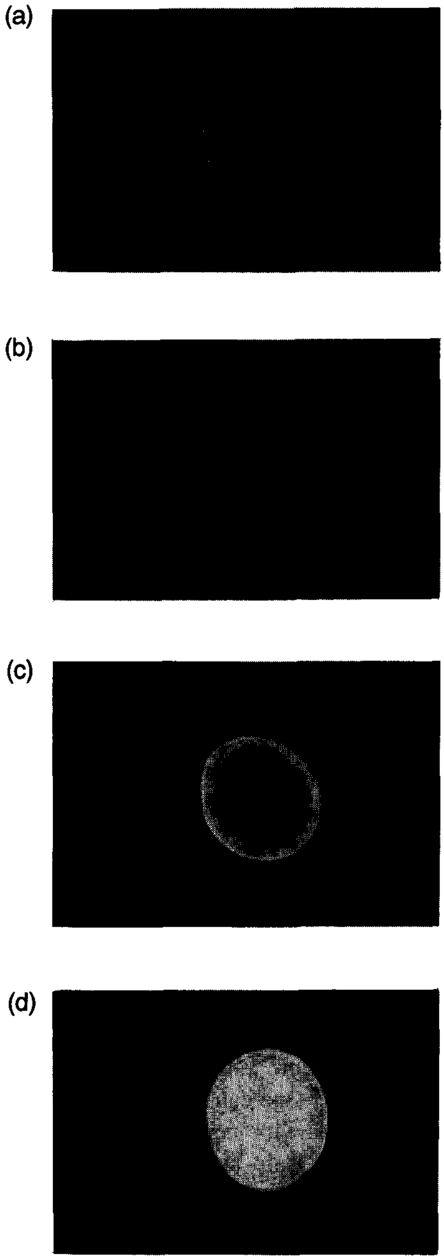

Fig. 8. Fluorescence microscopic photographs of cross sections of hair fiber into which a fluorescent dye, Sulforhodamine B, permeates from the hair surface for 60 min at 60 (a), 80 (b), 100 (c), and 120 °C (d).

Discussion

Two-Part/Two-State Model in Real Hair Structures. As already mentioned previously, TEM images of the cross section of the dyed hair fiber with Erythrosin B evidently show that the high-T_c-parts are the macrofibril and exo-cutuicle, and the low-T_c-parts are the inter-macrofibrillar materials, CMC and endo-cuticle. Macrofibril is composed of microfibrils and a matrix of keratinous proteins, and is known to contain S–S bonds in high density.[12] Highly cross-linked keratin with S–S bonds must show a high transition temperature. Exo-cuticle is an amorphous keratin having even more

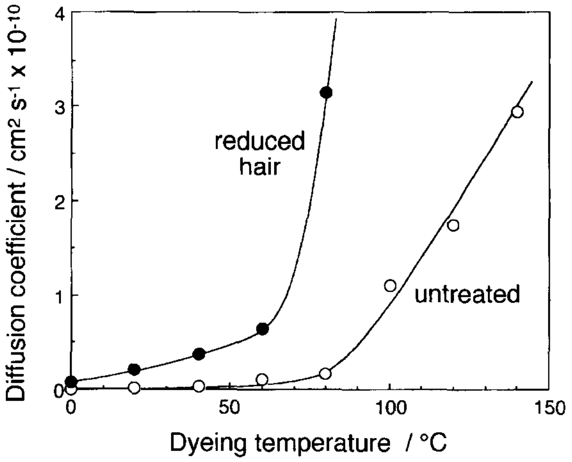

Fig. 9. Diffusion coefficients of Sulforhodamine B in a hair fiber plotted against temperature. Chemically non-treated hair (○), and reduced hair (●).

S-S bonds than the matrix of macrofibril.[12] Inter-macrofibrillar materials, CMC and endo-cuticle are non-keratinous proteins and some kinds of lipids. They have much less cross-linked S–S bonds than macrofibril and exo-cuticle,[12,13] and are reasonably assigned to be the low-T_c-part.

The TEM photographs in Fig. 10 show the structural image of human hair. Macrofibrils with high T_c are discretely present in the continuous structures of low-T_c materials (inter-macrofibril and CMC). This structural model is illustrated in Fig. 11. Feughelman has proposed a two-phase model to interpret the mechanical properties of keratin fibers.[3,14] His two-phase belongs to the high-T_c-part in our model; this relationship will be mentioned in our next paper.

Hair-Setting and Permeation Behaviors Interpreted by the Structural Model. The melted state above T_c is assumed to be soft and plastic, and thus can be easily deformed. When hair fibers are set at higher temperatures than the high T_c (ca. 70 °C in water) and are relaxed at −15 °C (lower temperature than low T_c), both the high- and low-T_c-parts must be converted to a new (wound or spiral) shape. If they are set below 0 °C, on the other hand, neither parts can be deformed. Strong and efficient setting of hair above 70 °C, and no setting below 0 °C in Fig. 3 can be clearly interpreted from this model. When hair is set at an intermediate temperature between the two, only the low-T_c-part can be deformed and the high-T_c-part maintains the original (straight) shape in memory. Thus, the obtained shape is a loose spiral. What happens when hair is relaxed at 25 °C ? At 25 °C the low-T_c-part is always in a melted state, and only the high-T_c-part is responsible for shape-control. This is the reason why only one characteristic temperature (high T_c) is observed when relaxed at 25 °C. Weigmann et al. observed the transition at ca. 70 °C for wool[15] and ca. 80 °C for human hair[16] in the turn-over point extensions of stress-strain curves. These are high T_c in our model, and will be discussed in more detail in our subsequent paper.

The water-setting and relaxation behaviors can also be explained by the two-part/two-state model. A typical water-

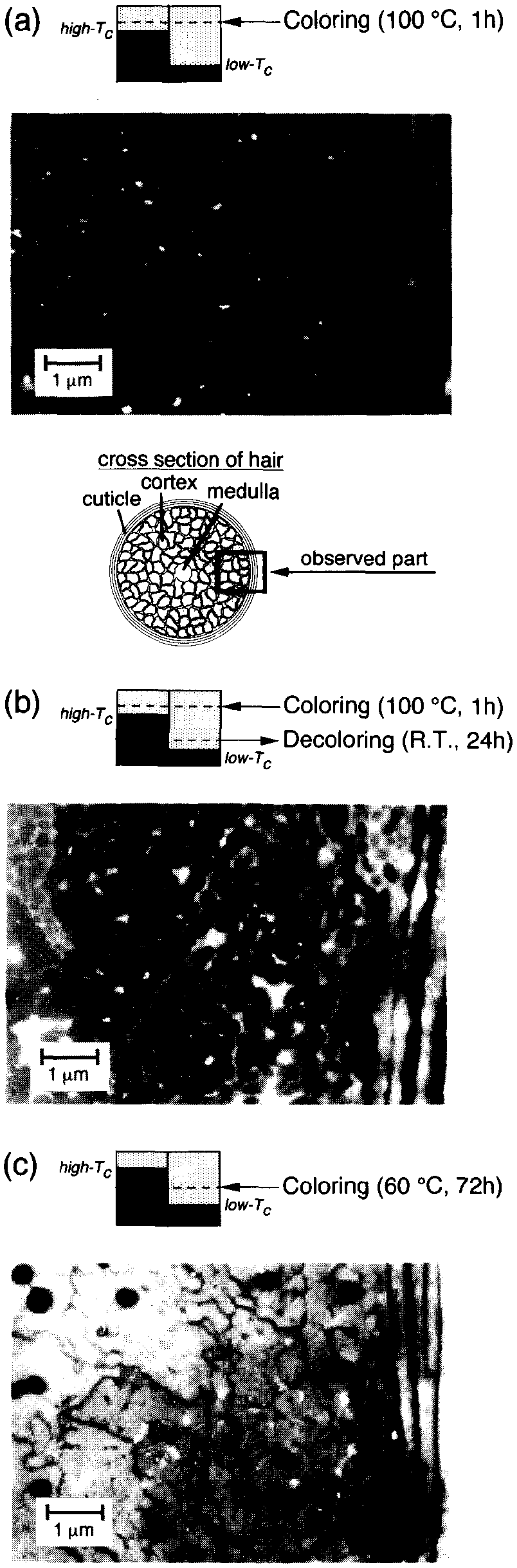

Fig. 10. TEM images of the cross section for hair samples 1 (a), 2 (b), and 3 (c). Sample 1: hair is dyed at higher temperatures (100 °C) than both transition points for 1 h, Sample 2: dyed at higher temperature (100 °C) than the high T_c for 1 h and decolored at an intermediate temperature (25 °C) for 24 h, Sample 3: dyed at the temperature (60 °C) between the two transition points for 72 h. Erythrosin B is used as a dye with high electron density.

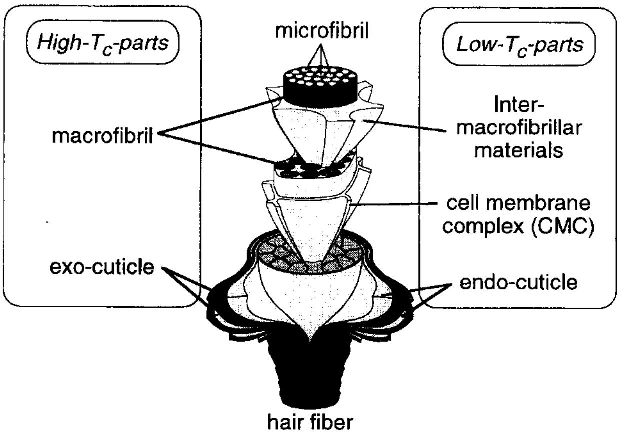

Fig. 11. Illustration of structural model of human hair. High-T_c-parts are darkly shaded, and are macrofibril and exo-cuticle. Low-T_c-parts are lightly shaded and are inter-macrofibrillar materials, cmc and endo-cuticle.

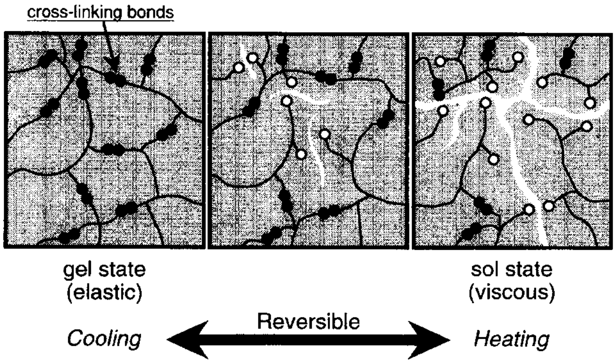

Fig. 12. Molecular image of the gel–sol transition at high and low T_c. Cross-linkers are S–S bonds for high T_c, and hydrogen and/or ionic bonds for low T_c. Bonded (-●●-) cross-linkings are cleaved (-O O-) with increasing temperatures. Percolation of bond networks is broken down at the transition temperatures.

setting phenomenon is as follows. When hair is fixed in some shape under a wet condition (say, after taking a bath) and dried (say, in the next morning), the shape is maintained even after being released from fixation. It is also characteristic that the shape-fixed hair easily recovers to the original shape when water is put on it. The value of T_c (low T_c in this case) decreases with increasing the water content in the hair, as shown in Fig. 6. Upon the wet condition, T_c is lower than room temperature, and the hair can be deformed to a new shape. When dried, T_c elevates above room temperature and the hair is fixed as a new shape. The new shape can be easily returned to the original one when the hair is wetted with water, since T_c decreases again below room temperature.

It is quite reasonable to assume that chemical compounds can more easily migrate in the soft and plastic melted state than in the solid state. A drastic increase in the diffusion coefficient of Sulforhodamine B shown in Fig. 9 is due to the transition of the high-T_c-part. It should be noticed that the temperature at which the diffusion coefficient starts to increase coincides well with the high T_c in hair-setting experiment in Fig. 3. More data and a quantitative analysis on the permeation behaviors of the dye will be presented in the next paper of this series.

Transitions at High and Low T_c. It is an interesting question what kind of transition takes place at high and low T_c. Honestly speaking, we have no decisive data to clarify the sort of transition. A gel–sol transition is, however, the most plausible candidate. Figure 12 illustrates the molecular image of this gel–sol transition. The cross-linkers are S–S bonds in the high-T_c transition, and hydrogen and/or ionic bonds in the low-T_c one. At low temperatures, cross-linking networks are fully formed, and make the part of hair in the gel state. Some of the cross-linkings are cleaved with increasing temperature, and finally the percolation of the bond networks is broken down at the transition point. When the bond percolation is broken, the polymer body can be easily deformed (soft and plastic) and some chemical compounds can migrate rapidly along the cleavages. Scission of S–S bonds at high-T_c region is substantiated from Fig. 13, in which the number of –SH groups is shown to markedly increase at 70—80 °C. This result also indicates that the scission of S–S bonds is a kind of reductive reaction, although the reducing agent cannot be identified.

Theoretical studies on a gel–sol transition in the systems of thermally reversible polymer association have been conducted by Tanaka,[17—19] and the transition should be of 3rd order.[20] If the transition is of 3rd order, the heat capacity should have an inflection at the transition temperature. Figure 14 shows the heat-capacity data of a hair sample in a 30 mM NAC solution which exhibits a break point at around 35 °C. This break point must be referred to the transition temperature shown in Fig. 4. The decrease in the high T_c upon adding reducing agents shown in Fig. 4 may also substantiate the above-mentioned transition model. Reducing agents promote S–S bond cleavage, and depress the transition temperature. The effect of the pH on the transition temperature (Fig. 5) can also be interpreted by the same bond-cleavage

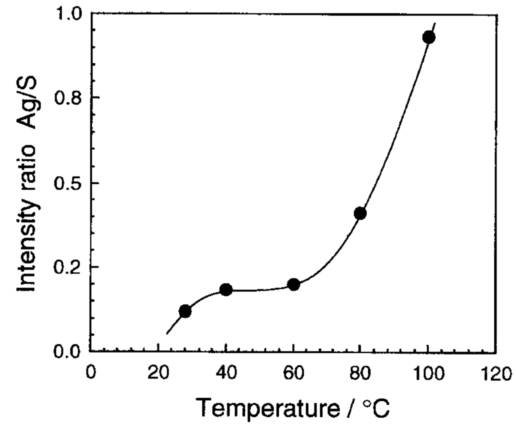

Fig. 13. Intensity ratio of EPMA signals for Ag/S in the hair samples treated with a silver nitrate solution plotted against the treating temperature. Aqueous solution of 1.0 mM $AgNO_3$, 2.0 mM EDTA, and 0.1 M Tris buffer at pH = 7.4 was used as a treating solution (1 M = 1 mol dm^{-3}).

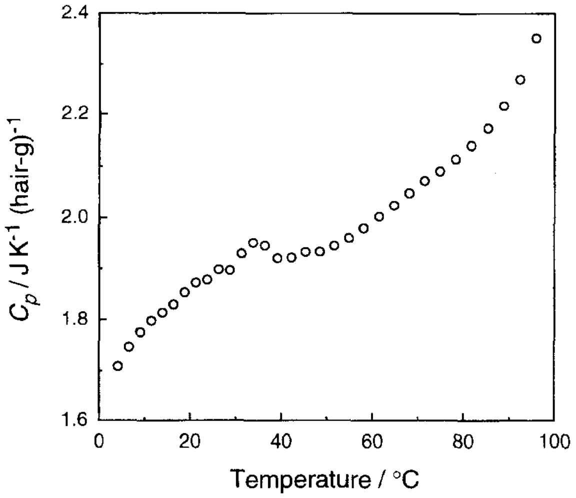

Fig. 14. Specific heat capacity of hair in 30 mM NAC in the temperature range close to high T_c. The sample was once cooled below 0 °C, and then heated to measure the heat capacity. Accurate data were obtained after the contained solution was fully melted at ca. 10 °C.

concept, since the reaction of the disulfide bond to –SH is accelerated at high pH.[21] Water-setting phenomena are reflections of the transition at low T_c. The results exhibited in Fig. 7 clearly indicate that those solvents having greater dielectric constant than ca. 20 depress the low T_c below room temperature, but those solvents with a smaller dielectric constant do not. Water is a very effective depressing agent of low T_c, as can be understood from Fig. 6. One can imagine that the governing factor of the transition at low T_c is hydrogen bonding and/or electrostatic ionic bonding. We will show some data in a successive paper of this series on mechanical properties which give evidence of the above.

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References

1 C. R. Robbins, in "Chemical and Physical Behavior of Human Hair," 3rd ed, Springer-Verlag, New York (1994).

2 H. P. Bader, in "Hair and Hair Diseases," ed by C. E. Orfanos and R. Happle, Springer-Verlag, New York (1990), pp. 60—61.

3 M. Feughelman, *J. Soc. Cosmet. Chem.*, **33**, 385 (1982).

4 A. Elliott, *Textile Res. J.*, **22**, 783 (1952).

5 J. D. Leeder, J. A. Rippon, F. E. Rothery, and I. W Stapleton, "Proc. of The 7th International Wool Textile Research Conference," Tokyo, (1985), Vol. 5, pp. 99—108.

6 J. D. Leeder, L. A. Holt, J. A. Rippon, and I. W. Stapleton, "Proc. of The 8th International Wool Textile Research Conference," Christchurch, New Zealand (1990), Vol. 4, pp. 227—238.

7 pp. 120—126 in Ref. 1.

8 J. Crank, in "The Mathematics of Diffusion," Oxford University Press, London (1956), Chap.5.

9 A. Suzuki, in "Preparation Methods of Biological Specimens for Electron Microscopy," 2nd ed, ed by Kanto Division of Japanese Society of Electron Microscopy, Maruzen, Tokyo (1986), pp. 1—166, (in Japanese).

10 L. P. S. Piper, *J. Text. Inst. Trans.*, **57**,185 (1966).

11 V. G. Kulkarni and J. H. Bradbury, *Aust. J. Biol. Sci.*, **27**, 383 (1974).

12 pp. 68—72 in Ref. 1.

13 H. Zahn, "Proc. of The 6th International Wool Textile Research Conference, Plenary Lecture," Pretoria, South Africa, (1980), pp. 1—45.

14 M. Feughelman, *Text. Res. J.*, **29**, 223 (1959).

15 H. D. Weigmann, L. Rebenfeld, and C. Dansizer, *Text. Res. J.*, **35**, 604 (1965).

16 L. Rebenfeld, H. D. Weigmann, and C. Dansizer, *J. Soc. Cosmet. Chem.*, **17**, 525 (1966).

17 F. Tanaka, *Macromolecules*, **22**, 1988 (1989).

18 F. Tanaka, *Macromolecules*, **23**, 3784 (1990).

19 F. Tanaka, *Macromolecules*, **23**, 3790 (1990).

20 F. Tanaka, *Butsuri* (in Japanese), **48**, 546 (1993).

21 pp. 98—100 in Ref. 1.