Formation of Stable Molecular Glasses of Yttrium(III) Acyl-DL-Alaninate Complexes

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Yttrium(III) acylalaninate complexes such as tris(*N*-hexanoyl-DL-alaninato)yttrium(III) (=Y(hex-DL-ala)$_3$) and tris(*N*-octanoyl-DL-alaninato)yttrium(III) (=Y(oct-DL-ala)$_3$) form stable glassy states by an evaporation of solvent from the methanol solution. The trend of formation of the stable glassy state is sensitive to a difference in the acylalaninate ligands.

A creation of stable glassy state for low molecular-weight compounds (i.e., molecular glasses) is one of important subjects to constitute a new class of functional materials, since the low molecular glasses can be more easily designed and characterized in comparison with macromolecular glasses. Such kinds of compounds, however, are almost limited to a series of organic π-electron compounds.[1] Although metal complexes have high and extensive functionalities, most of them are easily crystallized. Thus their stable glassy states at room temperature are reported only for a few compounds.[2–7] Among metal soaps, long-chained tris(octadecanoato)lanthanides take more stable vitreous states than shorter-chained lanthanide soaps do.[7–10] Most of the lanthanide soaps actually tend to form mixed crystalline-glassy states or thermotropic liquid crystals and thus their glassy states have not been well characterized.[9,10]

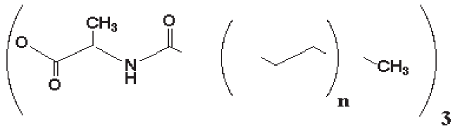

Figure 1. Tris(acylalaninato)yttrium(III) complex. $n = 2$, 3, and 5.

In the present study, we have newly prepared the Y(hex-DL-ala)$_3$, Y(oct-DL-ala)$_3$, (or Y(oct-L-ala)$_3$,) and Y(dod-DL-ala)$_3$ complexes (in Figure 1, $n = 2$, 3, and 5, respectively) and found that Y(hex-DL-ala)$_3$ and Y(oct-DL-ala)$_3$ easily form transparent and uniform glassy states despite the shorter alkyl chains. We focus on the fact that in the metal complex surfactants the geometrical mode of the ligand around the central metal sometimes causes a significant effect on the trend of taking either isotropic or anisotropic state.[11] The characteristics of the glassy states were estimated by using differential scanning calorimeter (DSC), X-ray diffraction (XRD), and polarizing microscope (PM).

All the *N*-acylalaninatoyttrium(III) complexes were prepared as follows. *N*-acylalanine (3.2×10^{-3} mole) in methanol was neutralized to pH 7–8 with an addition of methanol solution of potassium hydroxide. A methanol solution of yttrium chloride hexahydrate (1.0×10^{-3} mole) was then gradually added. In the reactions, small amounts of white precipitates (main component is yttrium octanoate[12]) formed were filtered out. After a complete evaporation of methanol, the glassy solid obtained was washed with distilled water and then with acetone, and dried in vacuo at room temperature. The purities of the complexes thus obtained were confirmed by CHN elemental analyses, Karl–Fisher titration, and ^{13}C NMR spectra.

The solubilities of Y(hex-ala)$_3$ and Y(oct-ala)$_3$ complexes were more than 10 wt % in methanol, ethanol, chloroform, and benzene. For Y(hex-DL-ala)$_3$ and Y(oct-DL-ala)$_3$, the vitreous solids were isolated by the solvent evaporation from the methanol solutions; these complexes were very hard to be crystallized out from solutions. On the other hand, for the Y(oct-L-ala)$_3$ and Y(dod-DL-ala)$_3$ complexes, the solids were usually isolated as crystalline states from methanol and could be recrystallized. These crystalline powders thus obtained contain 2.5 water per yttrium. It is characteristic that the crystalline Y(oct-L-ala)$_3$•2.5H$_2$O and Y(dod-DL-ala)$_3$•2.5H$_2$O complexes[13] could be transformed to the glassy states by dehydration treatments at 110 °C for one day, whereas 0.5 water per yttrium was still contained. The ^{13}C NMR spectra and CHN elemental analysis also gave a confidence that any chemical change does not occur by heating at 110 °C for one day.[14] All the glasses obtained were not hygroscopic on exposure to air.

In order to compare the properties of Y(oct-DL-ala)$_3$ and Y(oct-L-ala)$_3$ complexes with those of metal soaps, we isolated tris(octanoato)yttrium(III) (=Y(octnt)$_3$) according to the method for tris(dodecanoato)lanthanide(III).[9] The PM observation showed that the Y(octnt)$_3$ salt is anisotropic both in the solid state and in concentrated (e.g., toluene) solutions as observed for common surfactants. In contrast to the Y(oct-DL-ala)$_3$ and Y(oct-L-ala)$_3$ complexes, Y(octnt)$_3$ was immediately devitrified by melting and then by cooling, which is also a usual phenomenon for common surfactants. The glassy acylalaninatoyttrium(III) complexes are completely isotropic and transparent and the isotropy is confirmed both in the gel states containing methanol and in the concentrated methanol solutions of the Y(hex-DL-ala)$_3$ and Y(oct-DL-ala)$_3$ complexes.

DSC Curves: The glassy state was characterized by DSC in the temperature range of 0–250 °C (with a Shimadzu DSC-50 or a Rigaku Thermo plus 2 at a constant rate of 10 K min^{-1}). The DSC curve was largely affected by the presence of water. Although both PM image and X-ray scattering showed a formation of glassy state, if 2–2.5 waters are included per molecule, a broad endothermic peak appeared over 130–180 °C. The reproducibility of the area and position of this broad peak is somewhat worse. However, for the less-hydrated sample (still contains 0.5–1.0 water per yttrium) prepared by the annealing as described above, the broad endothermic peaks were almost disappeared and glass transitions were observed as shown in Figure 2 ($T_g = 59$ and 45 °C). Above T_g, the hard glassy solid was changed to a rubberlike state.

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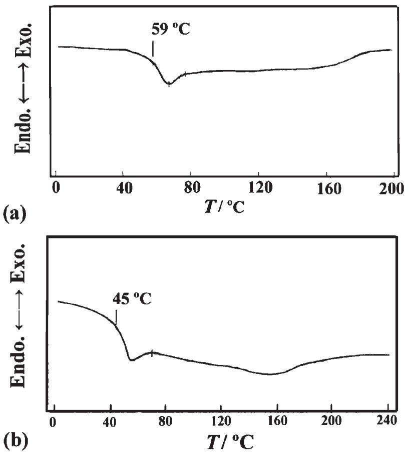

Figure 2. Typical DSC curves for the glassy states of (a) Y(oct-DL-ala)$_3\cdot0.5\mathrm{H_2O}$, (b) Y(hex-DL-ala)$_3\cdot\mathrm{H_2O}$.

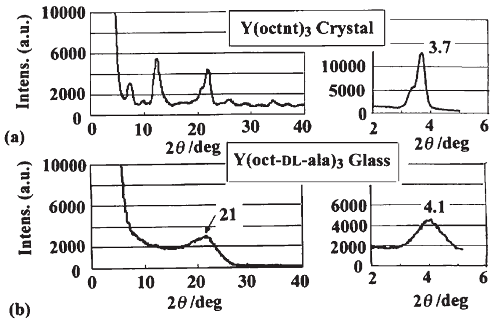

Figure 3. WAXD and SAXS profiles for the (a) Y(octnt)$_3\cdot2\mathrm{H_2O}$ crystal and (b) Y(oct-DL-ala)$_3\cdot0.5\mathrm{H_2O}$ glass.

Molecular Weights: We determined the molecular weights for the glasses obtained by the above heating treatment. The vapor pressure depressions for the methanol solutions of the Y(hex-DL-ala)$_3\cdot1.0\mathrm{H_2O}$, Y(oct-DL-ala)$_3\cdot0.5\mathrm{H_2O}$, and Y(dod-DL-ala)$_3\cdot0.5\mathrm{H_2O}$ complexes were measured with a Knauer Vapor Pressure Osmometer at 37 °C up to 0.4 mol kg^{-1}. This result indicates that these complexes are present almost as monomers in methanol solutions and the possibility of the formation of polymerized glassy state by the annealing is excluded.

WAXD and SAXS Profiles: The measurements of wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) were carried out at room temperature to compare the extent of the amorphous structure[15] between the Y(octnt)$_3\cdot2.0\mathrm{H_2O}$ crystal and the Y(oct-DL-ala)$_3\cdot0.5\mathrm{H_2O}$ glass (Figures 3a and 3b, respectively) as well as those between the Y(oct-L-ala)$_3\cdot2.5\mathrm{H_2O}$ crystal and the Y(oct-L-ala)$_3\cdot0.5\mathrm{H_2O}$ glass. Both the WAXD and SAXS curves indicate that these two crystalline states give many sharp diffraction peaks, while the two glassy states provide only two broad peaks at $2\theta = 4.1°$ and 21°. The peaks in the small-angle region correspond to the bilayer thickness ($d =$ 2.2, 2.4, and 1.9 nm for the Y(oct-DL-ala)$_3$ (or Y(oct-L-ala)$_3$) glasses, for the Y(octnt)$_3$ crystal, and for the Y(oct-L-ala)$_3$ crystal, respectively) in the aggregation due to the alkyl chains while the broad peak in the wide-angle region for the glassy sample is specific to the disordered alkyl chains.

The broad peak at $2\theta = 4.1°$ was shifted to a larger position ($2\theta = 4.7°$, $d = 1.9$ nm) for the Y(hex-DL-ala)$_3\cdot\mathrm{H_2O}$ glass and to a smaller position ($2\theta = 3.3°$, $d = 2.7$ nm) for the Y(dod-DL-ala)$_3\cdot0.5\mathrm{H_2O}$ glass depending on the chain length. On the other hand, the peak at around $2\theta = 21°$ was nearly constant for all these glassy complexes. The d spacing is shorter for the Y(oct-DL-ala)$_3$ complex (Figure 3b) than for the Y(octnt)$_3$ complex (Figure 3a) in spite of the larger size of the head group. This will be due to a closer packing structure in the former system.

In conclusion, the yttrium complexes studied here can be grouped into the following three classes in view of the easiness of the glass formation. 1) Y(hex-DL-ala)$_3$; Y(oct-DL-ala)$_3$ 2) Y(oct-L-ala)$_3$; (dod-DL-ala)$_3$ 3) Y(octnt)$_3$.[16] The class 1 cannot easily take a state containing crystals, whereas the class 3 cannot easily take a purely glassy state. The easier trend for the glass formation of the hexanoyl and octanoyl complexes is in contrast with a trend for rare-earth metal soaps where the stable glassy state has been reported for the long-chained tris(octadecanoato)-lanthanides by supercooling.[10] The more easiness of the glass formation for the complex having the DL-ligands than that for the L-ligands would be due to the larger randomness of the geometry around the yttrium atom in the DL-complex.

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11 S. R. Collinson and D. W. Bruce, "Transition Metals in Supramolecular Chemistry," ed. by J. P. Sauvage, Wiley, New York (1999), Chap. 7.
12 It was confirmed by the FTIR spectrum.
13 The melting points of the $2.5\mathrm{H_2O}$ crystals were around 90 °C.
14 Calc. for Y(oct-DL-ala)$_3\cdot0.5\mathrm{H_2O}$: C, 53.51; H 8.30, N, 5.67. Found: C, 53.28; H, 8.55; N, 5.71%. Calcd. for Y(oct-L-ala)$_3\cdot0.5\mathrm{H_2O}$: C, 53.51; H 8.30, N, 5.67. Found: C, 53.53; H, 8.27; N, 5.70%. Calcd. for Y(hex-DL-ala)$_3\cdot\mathrm{H_2O}$: C, 48.72; H 7.57, N, 6.31. Found: C, 48.98; H, 7.43; N, 6.39%. Calcd. for Y(dod-DL-ala)$_3\cdot0.5\mathrm{H_2O}$: C, 59.45; H 9.42, N, 4.62. Found: C, 59.43; H, 9.45; N, 4.63%.
15 The WAXD ($2\theta = 5$–40°) and SAXS ($2\theta = 0.5$–5 °) experiments were performed with a 12 kW rotating-anode X-ray generator (Rigaku RDA operated at 150 mA at 40 kV) at room temperature. The Cu Kα X-ray source ($\lambda = 1.54$ Å) was monochromatized with a plate-like graphite monochrometer. The small-angle X-ray scattering (SAXS) intensity distribution was measured with a position sensitive proportional counter (PSPC).
16 It is notable that we have also isolated tris(DL-alaninato)yttrium(III) complex and confirmed that it is very hard to take a glassy state.

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